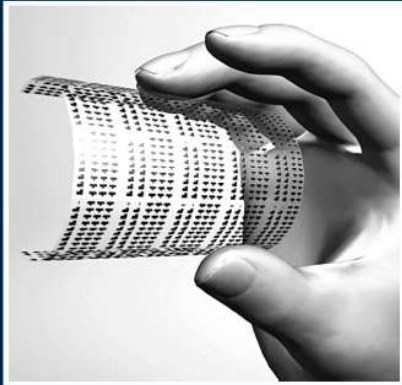


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Alastair Buckley



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Synthesis of electroluminescent conjugated polymers for OLEDs

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Abstract: This chapter discusses the most important synthetic routes to the main classes of electroluminescent π -conjugated polymers, highlighting advantages and limitations of the different methods in terms of versatility, stereo- and regioselectivity and efficiency. The discussion not only covers the synthesis of basic classes of polymers such as polyarylenes, poly(arylenevinylene)s and poly(aryleneethynylene)s, but also describes routes to systems with more complex structures, including multifunctional copolymers and coordination polymers.

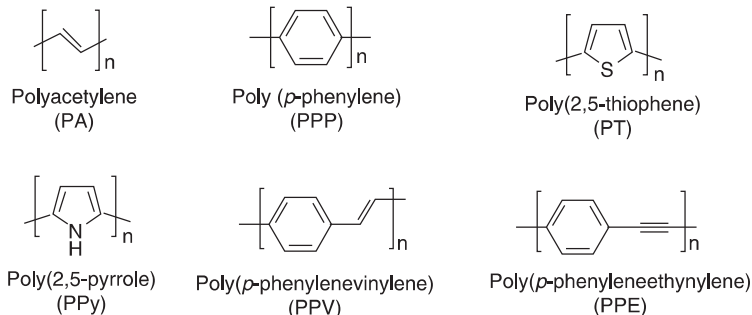
Key words: semiconducting polymers, conjugated polymers, light-emitting polymers, electroluminescent polymers, organic coordination polymers, organic synthesis, electroluminescence, OLEDs.

1.1 Introduction

Although the most common uses of organic polymers in electronics have been traditionally associated with their insulating properties, the fundamental discovery by Shirakawa and co-workers (Shirakawa *et al.*, 1977) of the relatively high electrical conductivity in doped thin films of polyacetylene paved the way for the development of a wide range of organic polyconjugated materials as semiconductors for several technological applications. The basic structures and acronyms of some of the main classes of these conjugated polymers are summarized in Fig. 1.1.

The applications of poly(*p*-phenylene) (PPP), polythiophene (PT), poly(*p*-phenylenevinylene) (PPV) and poly(phenyleneethynylene) (PPE) polymers in organic electronic devices include organic light-emitting diodes (OLEDs) (Kraft *et al.*, 1998), organic field effect transistors (Operamolla and Farinola, 2011), plastic lasers (Hide *et al.*, 1997) and polymer solar cells (Günes *et al.*, 2007).

Conjugated polymers with more complex architectures, such as multifunctional copolymers, metal coordination polymers (i.e. organic polyconjugated blocks wired by metal coordination bonds) have been continuously developed over the last few decades, aiming to achieve improved performances in electrical and electrooptical devices and to disclose new functions.



1.1 Structures and acronyms of the main classes of organic conjugated polymers.

The synthetic methods set up for these materials are characterized not only by high efficiency and selectivity, but especially by flexibility in creating different multifunctional structures tailored for the specific target application. These synthetic methods deeply affect stereochemistry, average molecular weights, photophysical and electrical properties of the resulting materials, and eventually determine their performances in devices.

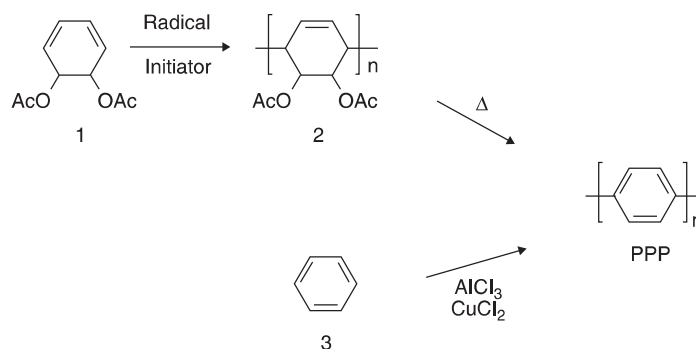
An overview of the most important synthetic routes to the main classes of polyconjugated compounds will be given in this chapter, highlighting advantages and limitations of alternative methods in terms of versatility, efficiency, stereo- and regioselectivity. The chapter is organized in the following sections:

- 1.2 Polyarylenes
- 1.3 Poly(arylenevinylene)s
- 1.4 Poly(aryleneethynylene)s
- 1.5 Conjugated copolymers
- 1.6 Coordination polymers

Section 1.7 reports concluding remarks and Section 1.8 is a list of some specialized books and reviews on this topic.

1.2 Polyarylenes

This class of rigid-rod electroluminescent polymers includes several families of different conjugated structures, such as polyphenylenes, polyfluorenes, polythiophenes. Unsubstituted polyarylenes, as most conjugated polymers, are insoluble in common organic solvents and thin films can only be obtained from soluble precursors which are subsequently converted into the conjugated polymer after their deposition. In the case of poly(*p*-phenylene) (PPP), a non-conjugated soluble precursor **2**, polymerized from **1** in the absence of solvent with radical initiator, can be converted into the corresponding conjugated polymer PPP by a

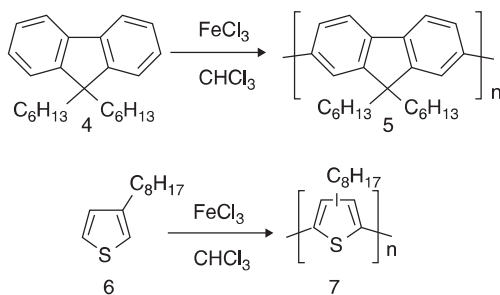


1.2 Synthesis of PPP by the soluble precursor method and the Kovacic reaction.

thermal aromatization process, as shown in Fig. 1.2 (Ballard *et al.*, 1988). PPP can also be synthesized by Kovacic's route, consisting of the dehydro coupling of aromatic nuclei **3** by oxidant catalyst (Kovacic and Jones, 1987), but the reaction conditions are rather harsh for the introduction of many substituents.

Unsubstituted or alkyl substituted polyfluorenes (PFs) and polythiophenes (PTs) can be obtained by electrochemical polymerization (Rault-Berthelot and Simonet, 1985) or by chemical oxidation with FeCl_3 in chloroform (Österholm *et al.*, 1989; Fukuda *et al.*, 1993) (Fig. 1.3). These approaches produce polymers with low regioregularity and, in some cases, a certain degree of branching. Moreover, PFs obtained by chemical oxidation methods can hardly achieve average molecular weights higher than $\approx 5.0\text{--}6.0\text{ kDa}$.

In most cases, introduction of substituents in the main conjugated backbone demands for mild C–C bond forming reactions that must tolerate the side functionalities which also introduce regioselectivity issues. Approaches based on



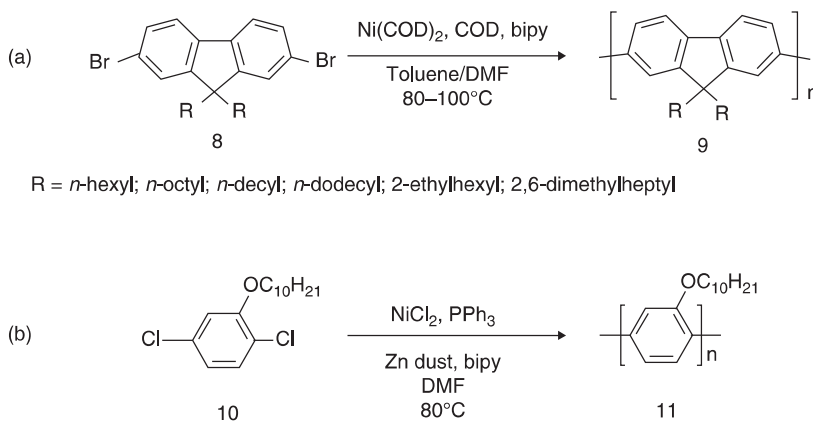
1.3 Synthesis of poly(9,9-dialkylfluorene) and poly(3-alkylthiophene) by electrochemical polymerization or chemical oxidation.

transition metal-catalyzed coupling reactions enable good structural control and tolerance of a wide range of substituents on the polymer backbone (Babudri *et al.*, 2004).

The Yamamoto procedure (Yamamoto, 1992), consisting of a nickel-activated reductive homocoupling of aryl dihalides, can afford high molecular weight polyarylenes. The polymerization is performed by reduction of the reaction monomer with a stoichiometric amount of bis(1,5-cyclooctadiene)nickel(II) complex $[\text{Ni}(\text{COD})_2]$, in the presence of 2,2'-bipyridine ligand. Poly(9,9-dialkylfluorene)s **9** for OLED application with Mw higher than 200.0kDa were obtained in toluene/DMF solvent mixture by this approach (Fig. 1.4a) (Nothofer *et al.*, 2000).

Instead of using the expensive $\text{Ni}(\text{COD})_2$ complex in stoichiometric amount, a Ni(II) salt can be adopted as the catalyst in combination with zinc powder as the reductant. Poly(*p*-phenylene) **11** bearing decyloxy substituents was synthesized by this protocol (Fig. 1.4b) and employed as emissive material in the active film of a blue OLED with an ITO/PVK/PPP/Ca double layer configuration (PVK: polyvinylcarbazole), 3% external quantum efficiency and brightness of $490 \text{ cd}\cdot\text{m}^{-2}$ at 30 V (Yang *et al.*, 1996).

Polyfluorenes usually exhibit blue but relatively broad emission in combination with good processability and charge carrier mobility (Scherf and List, 2002). The achievement of pure blue emission from these polymers is still an issue because of the formation of fluorenone defects in the polymer chain induced by photo- or chemical oxidation at the 9 position of the fluorene rings. Such defects mainly originate on 9-monoalkylated fluorene units in the polymer backbone, thus careful purification of the monomers to remove traces of monoalkylated species can avoid this drawback. Introduction of bulky substituents, i.e. branched alkyl chains



1.4 (a, b) Synthesis of polyarylenes via the Yamamoto reaction.

in the 9 position, and capping the end of chains with sterically hindering units can reduce aggregation leading to increased luminescence efficiencies.

Reducing homocoupling processes can be used to end-cap growing polymeric chains with monofunctional co-monomers. For example, end-capping with *N,N*-bis(4-methylphenyl)-*N*-(4-bromophenyl)amine **13** (Fig. 1.5) generates polymer **14** endowed with improved holes mobility due to the triaryl amino functionalities (Miteva *et al.*, 2001).

The main problem of the Yamamoto route is the difficult removal of metal impurities from the final product, which negatively affects the electrical properties of materials in devices. Alternative methods adopting palladium complexes as catalysts are preferred in many cases for the synthesis of polyfluorenes, as reported below in this chapter.

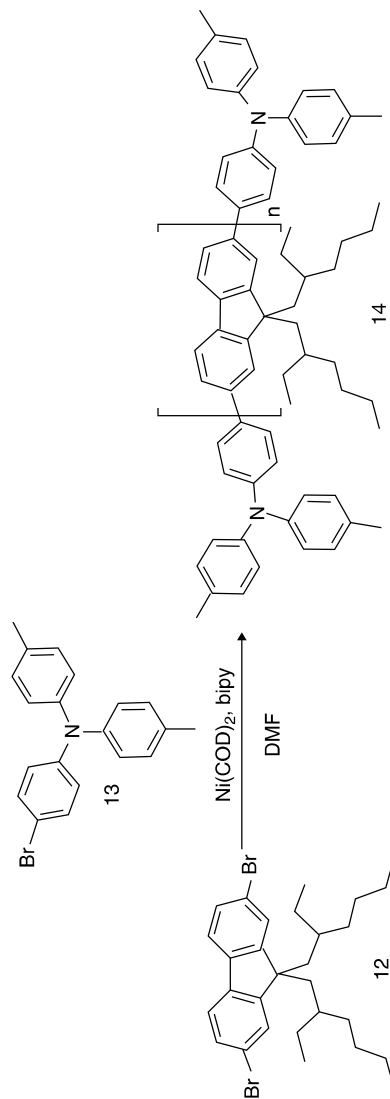
Poly(3-alkylthiophene)s (P3ATs) can be prepared by the Yamamoto route as well (Yamamoto *et al.*, 1992), but other organometallic procedures are more convenient to control regioregularity. Possible configurations originated by the coupling of two 3-substituted thiophene rings are shown in Fig. 1.6. The regioregularity degree, i.e. the percentage of head to tail (HT) connections between two consecutive 3-alkylthiophene units, affects electroluminescence properties. In fact, head-to-head (HH) connections induce out of plane twisting between two consecutive thiophene rings and reduce the polymer conjugation length. This increases the bandgap with subsequent blue-shift of the emitted light, but also limits the formation of solid state aggregates, that are responsible for solid state photoluminescence (PL) quenching. However, reduced aggregation in polythiophenes may also negatively affect the charge transport properties of the material.

Thus, fine control of the regioregularity degree and/or introduction of bulky substituents in the 3- or both 3- and 4-positions enable modulation of polythiophene bandgap (and emission color) by steric effects and prevent PL quenching in the solid state induced by aggregation. Indeed, it was demonstrated for the series of alkyl-substituted polythiophenes **15–18** (Fig. 1.7) that increasing the distance between HH linkages red-shifts the emission maxima from 460 nm for **15** to 550 nm for **18** (Gill *et al.*, 1994).

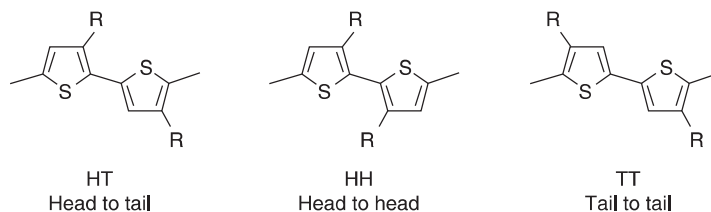
The regioregular poly(3-arylthiophene) **20** (Fig. 1.8) shows PL efficiency in solution comparable to that of P3ATs, but much higher solid-state value which is attributed to the bulky aryl groups ensuring greater interchain separation (Andersson *et al.*, 1999). Polymer **20** represents an example of regioregular polymer (HT ~94%) produced by oxidation of the starting monomer **19** with FeCl₃ (Fig. 1.8): the regioselectivity of the reaction is likely due to the high steric hindrance of the aryl substituent.

In contrast to oxidative protocols, the Rieke (Chen *et al.*, 1995) and the Grignard metathesis (Loewe *et al.*, 1999) methods are among the most reliable synthetic procedures leading to high molecular weight regioregular P3ATs.

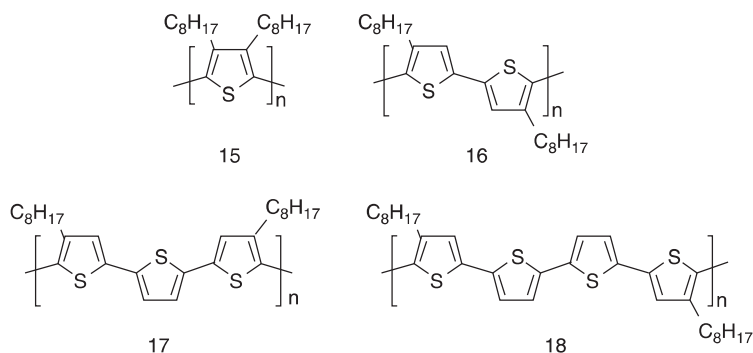
The Rieke protocol is based on the Negishi coupling of organo-zinc reagents, as summarized in Fig. 1.9. The 2,5-dibromo-3-alkyl substituted thiophene **21** is a



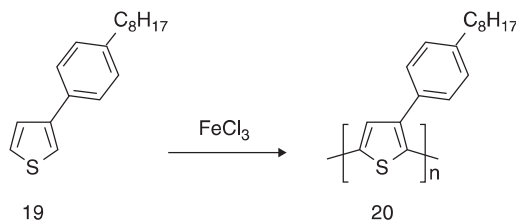
1.5 Synthesis of polyfluorene **14** via the Yamamoto route.



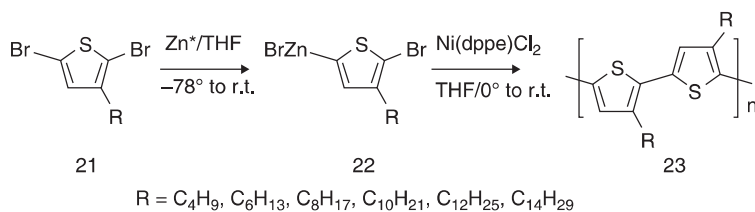
1.6 Possible configurations of poly(3-alkylthiophene)s.



1.7 Structures of polythiophenes **15–18**.



1.8 Regioselective synthesis of poly(3-arylthiophene) **20** by chemical oxidation method.



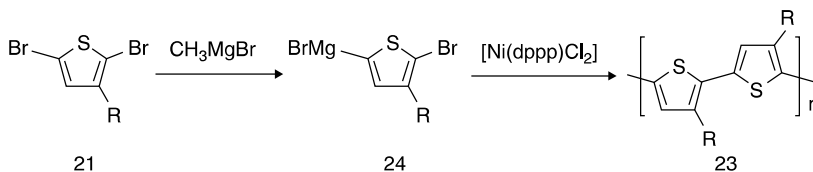
1.9 Synthesis of poly(3-alkylthiophene)s via Rieke protocol.

suitable starting material that is easily prepared in high yield and purity. Activated Rieke zinc (Zn^*) (Chen *et al.*, 1993) undergoes oxidative addition to the C-Br bond of **21** predominantly at the 5 position. Regioselectivity can be controlled by the reaction temperature and values as high as $\approx 97\text{--}98\%$ were achieved with several alkyl substituents operating at -78°C . The polymerization is performed in a one-pot procedure, introducing the catalyst $\text{Ni}(\text{dppe})\text{Cl}_2$ (dppe: 1,2-bis(diphenylphosphino)ethane) in the reaction mixture at 0°C .

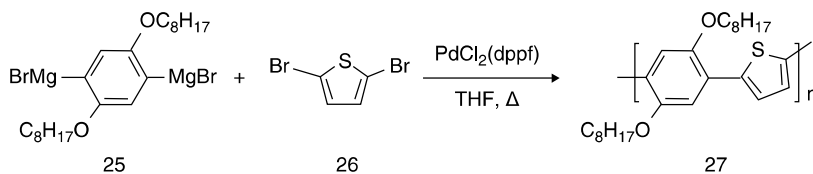
Synthetic protocols for P3ATs based on the nickel catalyzed cross-coupling of thiophene organomagnesium reagents (Kumada cross-coupling) (Fig. 1.10) were introduced by McCullough *et al.* in 1992 and 1999 (McCullough and Lowe, 1992; Loewe *et al.*, 1999). This protocol, also known as Grignard metathesis (GRIM), is based on the regioselective metalation at the 5 position of **21** with methylmagnesium bromide. Subsequent polymerization with $\text{Ni}(\text{dppp})\text{Cl}_2$ (dppp: 1,3-bis(diphenylphosphino)propane) produces the regioregular polymer in good yields (around 60% after purification) with high molecular weight (typically in the range 25–45 kDa).

An analogous one-pot method developed by Yamamoto, i.e. a self-coupling of aryl dihalides in the presence of stoichiometric amounts of Mg with mild Ni catalysis, was applied to the synthesis of poly(phenylene)s (Yamamoto *et al.*, 1978). However, this methodology has been seldom used to prepare polyarylenes, compared with the more straightforward reductive homocoupling procedure.

Coupling of bis-organomagnesium derivatives with aryl dihalides has been applied to the synthesis of alternating copolyarylenes. Cross-coupling of the Grignard reagent **25** with 2,5-dibromothiophene **26**, in the presence of $\text{PdCl}_2(\text{dppf})$ (dppf: 1,1'-bis(diphenylphosphino)ferrocene) as the catalyst, yielded the alternating poly[1,4-(2,5-dioctyloxyphenylene)-2,5-thiophene] **27** (Babudri *et al.*, 2002), which was studied for a number of optoelectronic applications (Fig. 1.11) (Naso *et al.*, 2003; Tanese *et al.*, 2006; Giancane *et al.*, 2010).



1.10 Synthesis of poly(3-alkylthiophene)s via Grignard metathesis.



1.11 Synthesis of copolymer **27**.

Polyarylenes can be conveniently prepared by the Pd-catalyzed Suzuki–Miyaura cross-coupling reaction of aromatic diboron derivatives with aryl dihalides in the presence of a base (Miyaura, 2004). The Suzuki–Miyaura protocol can afford a wide variety of polyarylenes, owing to the compatibility of the reaction conditions with a number of functional groups. However, a careful choice of the reaction parameters, such as the palladium complex ligand, the base/solvent system and the nature of boron derivative is required to achieve high molecular weight and good yield. The advantage of this organometallic approach lies in the stability of the organoboron derivative that can be purified and stored under ambient conditions, as well as in the low catalyst amount required for polymerization (typically between 1–3 mol% and for some protocols the catalyst loading is lower than 0.3 mol%) (Sakamoto *et al.*, 2009). In addition, this method offers the opportunity to achieve regular alternating copolymers by use of proper monomers, rather than statistical copolymers as in the case of the Yamamoto approach.

For example, 2,7-fluorene diboronic esters or acids can be synthesized from the corresponding dihalides by treatment with *n*-butyllithium followed by quenching with a trialkoxyborane (Fig. 1.12). The diboronic ester **29** was coupled with dibromofluorene **30** bearing dendron substituents on the 9,9-positions to generate the alternating copolymer **31** which emits blue light in the solid state by suppression of the green spectral band typically produced by aggregates formation in poly(9,9-dialkylfluorene)s (Chou and Shu, 2002).

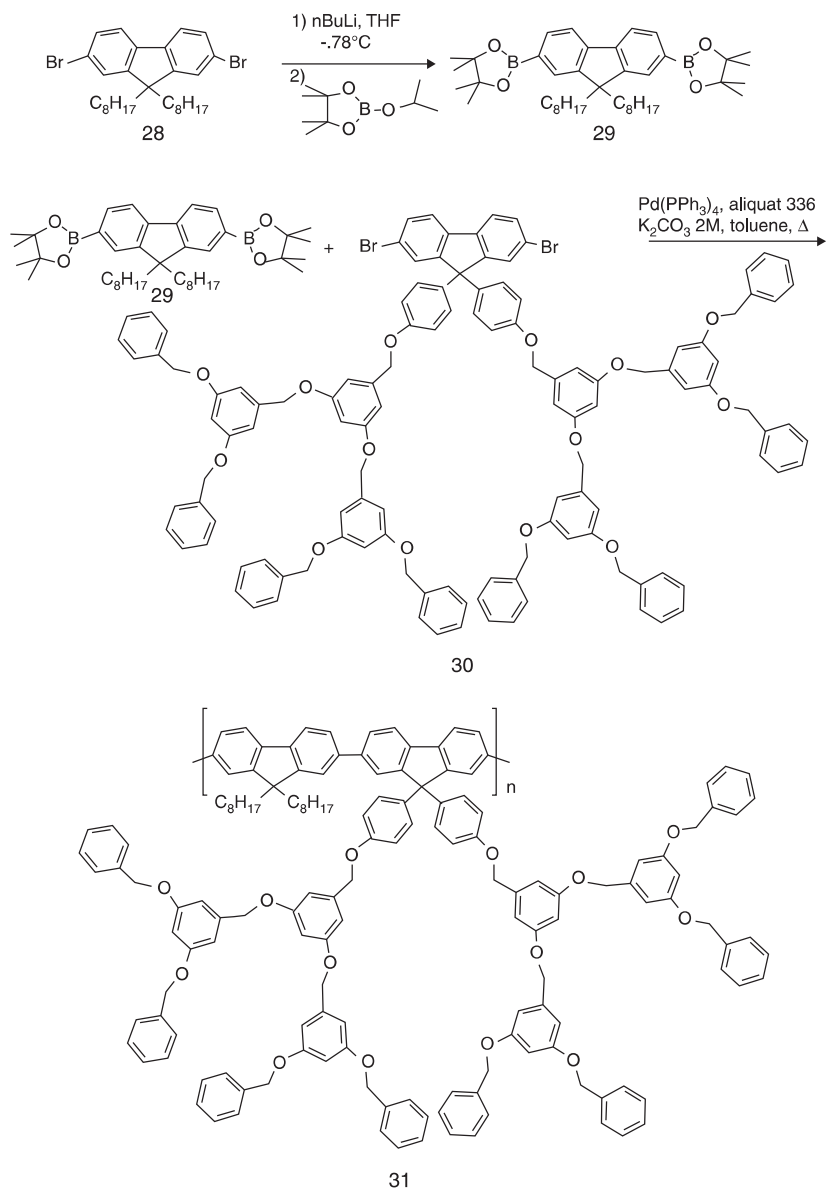
An excellent example showing the versatility of the Suzuki polycondensation is the synthesis of methylene-bridged ladder-type polymer **36** (Scherf, 1999) reported in Fig. 1.13: a precursor polymer **34** is prepared via AA–BB Suzuki polycondensation; the precursor polymer then undergoes reaction with CH_3Li followed by ring closure with BF_3 and produces polymer **36** with bridging methylaryl methylene units.

Extensive application of Suzuki-based methods to the synthesis of regioregular P3ATs (Guillerez and Bidan, 1998) has been prevented by easy deboronation processes that limit polymer molecular weight (Jayakannan *et al.*, 2001). The use of $\text{Pd}(\text{OAc})_2$ without ligands was proposed as a possible way to face this issue (Guillerez and Bidan, 1998), but polymers with a low degree of regioregularity were produced.

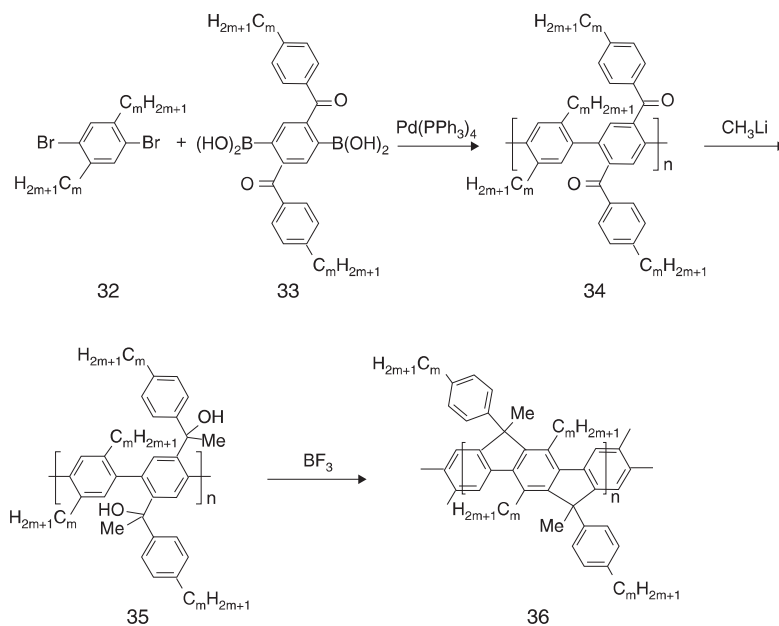
Recent studies (Liversedge *et al.*, 2006) have highlighted the benefits of the catalyst formed *in situ* by $\text{Pd}(\text{OAc})_2$ and the Buchwald's ligand S-Phos (Barder *et al.*, 2005) in the Suzuki polymerization of **37**. This catalyst can give remarkable results when used in the Suzuki polymerization of α -thiophene pinacolboronates (Operamolla *et al.*, 2011) (Fig. 1.14).

The use of the Pd-catalyzed Stille cross-coupling reaction of aryl organostannanes with aryl halides represents an alternative to the Suzuki–Miyaura coupling for building polyarylene skeletons. Figure 1.15 shows the synthesis of the blue emitting polymer **40** by coupling of 2,5-bis(tributylstannyl)thiophene **38** with the

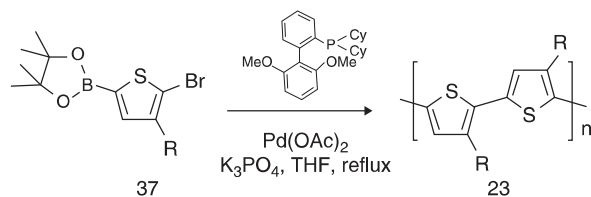
12 Organic light-emitting diodes (OLEDs)



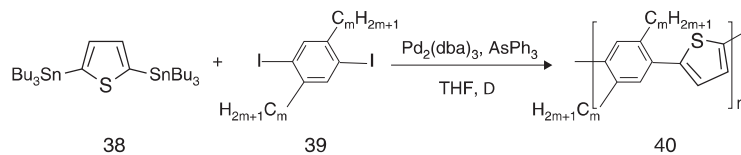
1.12 Synthesis of copolymer **31** via Suzuki cross-coupling reaction.



1.13 Synthesis of the ladder-type polymer **36**.



1.14 Synthesis of poly(3-alkylthiophene)s via Suzuki cross-coupling reaction.



1.15 Synthesis of polymer **40** via Stille cross-coupling reaction.

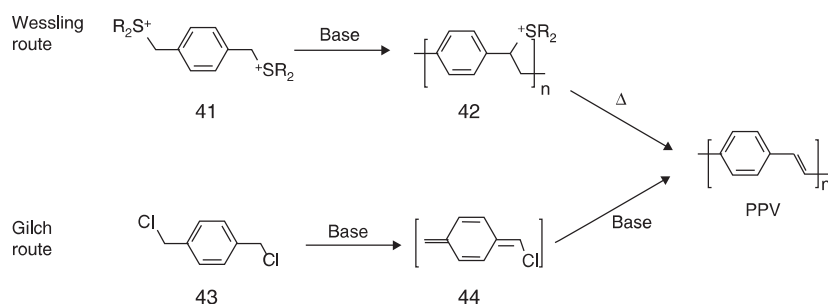
diiododerivative **39** (Bao *et al.*, 1995): in this case, the $\text{Pd}(\text{AsPh}_3)_4$ catalyst, generated *in situ* by mixing the weakly coordinated $\text{Pd}_2(\text{dba})_3$ with triphenylarsine, showed high stability and efficiency, allowing the synthesis of relatively high molecular weight polymers ($M_n \sim 22 \text{ kDa}$; $M_w \sim 56 \text{ kDa}$). The high reactivity of bis(tributylstannyl)thiophene monomers makes the Stille coupling a very useful polymerization route for polymers containing 2,5-thienylene units.

1.3 Poly(arylenevinylene)s

Electroluminescence in poly(*p*-phenylenevinylene) (PPV), the simplest poly(arylenevinylene), was first reported by Burroughes *et al.*, (1990) and, since then, the interest in this class of materials has been continuously growing (Dai *et al.*, 2001).

PPVs, as well as poly(*p*-phenylene)s, can be prepared by precursor routes in which a non-conjugated soluble precursor polymer undergoes a thermal or chemical elimination reaction to afford the corresponding conjugated material. Two most important protocols are based on this approach (Fig. 1.16): in the Wessling route a processable sulfonium precursor **42** is converted into PPV by thermal treatment (Wessling, 1985); the Gilch route proceeds via a base-promoted condensation of *p*-quinodimethane **44** generated *in situ* from benzyl dihalides (Gilch and Wheelwright, 1966). The precursor methods are amenable (particularly the Gilch process) to scale up to kilogram production (Becker *et al.*, 2001), but in many cases they lead to conjugated materials with structural defects due to the non-complete efficiency, regioregularity and stereospecificity of the elimination processes. Nevertheless, the Gilch route is still applied to obtain PPVs with high molecular weights (Schwalm *et al.*, 2009).

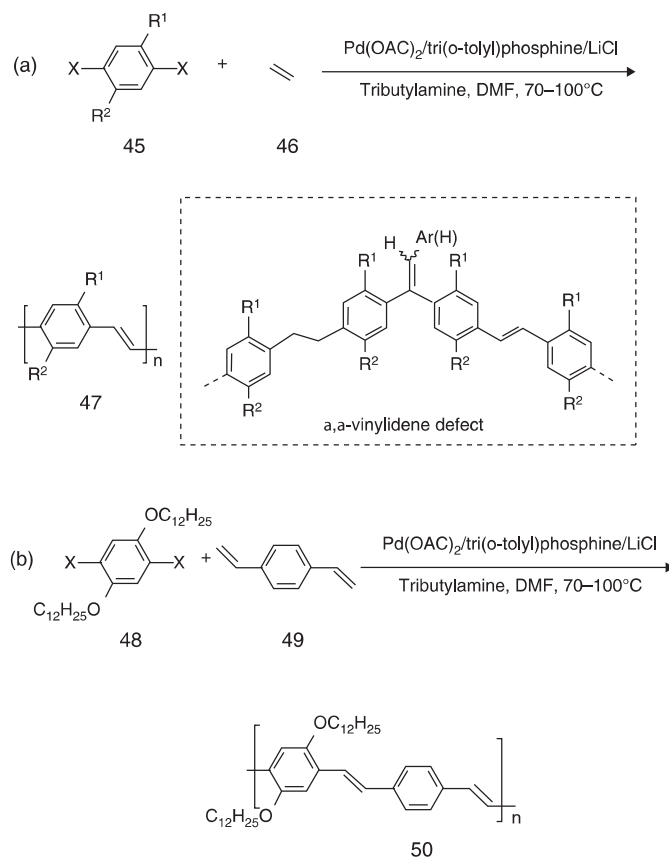
PPVs containing *cis* double bonds were also prepared by the Wittig and related condensation reactions (Gourley *et al.*, 1984; Chen *et al.*, 1999; Ahn *et al.*, 2000). A subsequent *cis*–*trans* isomerization step is required to obtain stereodefined polymers with all-*trans* configuration of the vinylene units.



1.16 Synthesis of PPV by soluble precursor methods.

On the other hand, better control over the vinylene units stereochemistry can be achieved using Pd-catalyzed C-C bond forming reactions of vinyl monomers with aryl dihalides that also enable preparation of variously substituted PPVs thanks to mild experimental conditions and tolerance of a wide variety of functional groups.

The Pd-catalyzed Heck coupling reaction of aryl dihalides with alkenes in the presence of a base can be applied to the synthesis of arylenevinylene polymers (Bräse and de Meijere, 1998). Although structural defects are less frequent in polymers generated by this method than in the case of materials obtained via the precursor approaches, some α,α -vinylidene defects can be present especially when the Heck coupling is carried out using ethylene **46** as the vinyl monomer (Fig. 1.17a) (Wetzel and Müllen, 1990; Martelock *et al.*, 1991; Klingelhöfer *et al.*, 1997). The presence of such defects is negligible in polymer **50** generated from the divinylbenzene **49** (Bao *et al.*, 1993), as it generally occurs when bulky



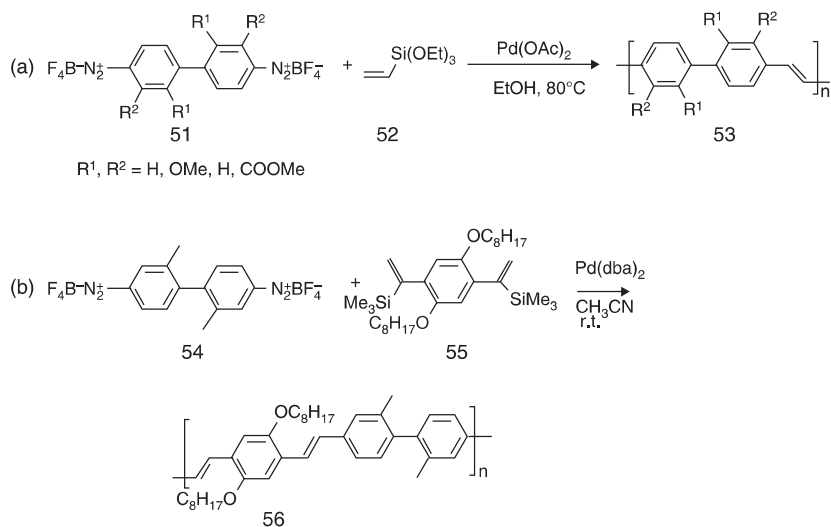
1.17 (a, b) Synthesis of PPVs via Heck coupling reaction.

substituents are present on the reaction monomers (Fig. 1.17b). Both polymers, analyzed by means of FTIR spectroscopy, show the vinylene units predominantly in the *trans* configuration.

Arenediazonium tetrafluoroborate salts are compounds of facile synthesis and they can react either with trialkoxysilylene **52** or with bis(α -trimethylsilylvinyl) arene **55** yielding PPV polymers. Two selected examples of such reaction are reported in Fig. 1.18a,b. Pd-catalyzed arylation and aryldesilylation processes occur in the reaction of **52** with arenebis(diazonium) tetrafluoroborates **51**, yielding polymers **53** in the presence of phosphine free Pd(OAc)₂ as the catalyst (Sengupta *et al.*, 1998; Sengupta and Sandhukhan, 1999).

A phosphine free palladium catalyst, the weakly coordinated Pd(dba)₂ complex, is also adopted for the arylation reaction of trimethylsilyl arylalkenes: this reaction proceeds regio- and stereoselectively when a 1-trimethylsilyl-1-arylalkene is coupled with arenediazonium tetrafluoroborates in acetonitrile as the solvent, while poorer regio- and stereoselectivity are achieved when 2-trimethylsilyl-1-arylalkenes are employed (Kikukawa *et al.*, 1981; 1983; Ikenaga *et al.*, 1986; 1988; Sengupta and Bhattacharyya, 1993). Thus, a double aryldesilylation process on the α,α' -bis(trimethylsilyl) derivative **55** with arenebis(diazonium) tetrafluoroborate **54** was applied to the synthesis of **56** (Ancora *et al.*, 2002; Babudri *et al.*, 2001b).

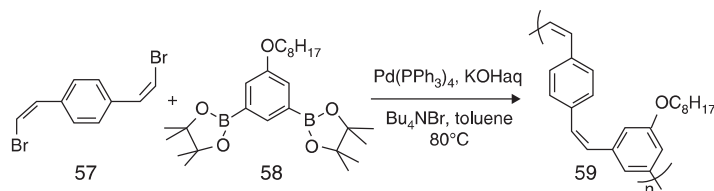
The Suzuki–Miyaura cross-coupling of organoboron derivatives with aryl halides has been only seldom applied to the synthesis of stereodefined PPVs



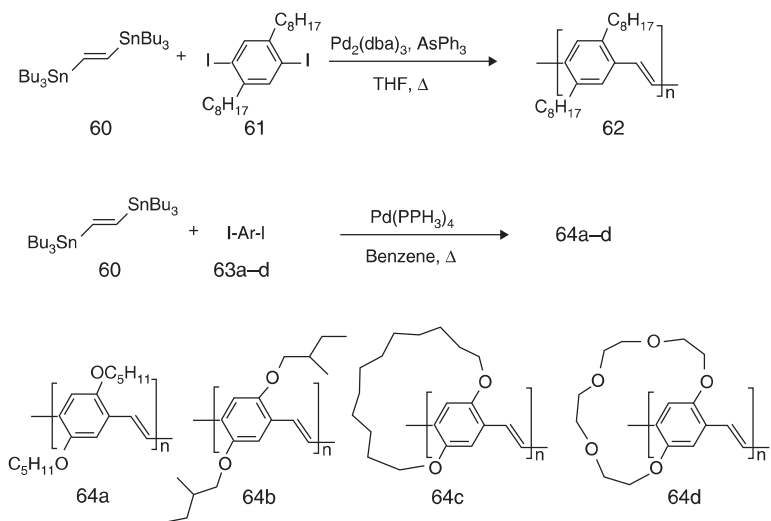
1.18 Synthesis of poly(arylenevinylene)s **53** (a) and **56** (b).

(Koch and Heitz, 1997; Katayama *et al.*, 2006; Wakioka *et al.*, 2010; Babudri *et al.*, 2008b). A highly stereocontrolled synthesis of *cis*-poly[(arylenevinylene)-*alt*-(2,5-dioctyloxy-1,4-phenylenevinylene)] **59** was accomplished by the Suzuki–Miyaura type polycondensation of (*Z,Z*)-bis(2-bromoethenyl)benzene **57** with 5-octyloxy-1,3-benzenediboronic acid pinacolate **58** in the presence of $\text{Pd}(\text{PPh}_3)_4$ catalyst, aqueous KOH base and Bu_4NBr phase-transfer catalyst (Fig. 1.19) (Wakioka *et al.*, 2010).

Arylenevinylene type polymers can also be prepared by the Stille cross-coupling reaction of 1,2-bis(tributylstannyl)ethene **60** with aryl dihalides (Fig. 1.20). Though early studies on the Stille polymerization (Bao *et al.*, 1995) pointed out the low reactivity of **60** in the presence of the $\text{Pd}(\text{AsPh}_3)_4$ catalyst if compared to the 2,5-bis(tributylstannyl)thiophene **38**, several



1.19 Stereoselective synthesis of PPV **59** via Suzuki cross-coupling reaction.

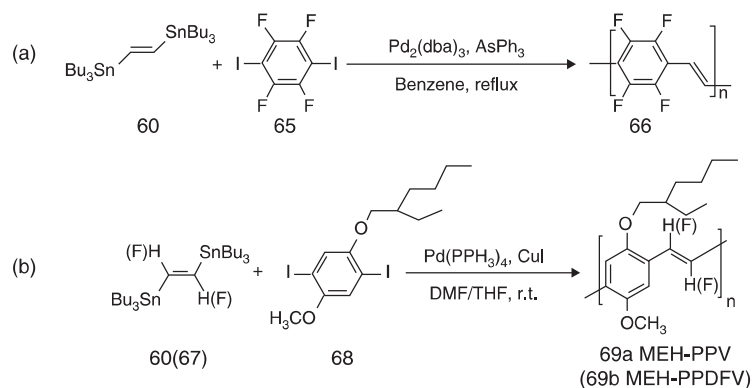


1.20 Synthesis of PPVs via Stille cross-coupling reaction.

poly(*p*-phenylenevinylene)s with linear, branched or bridged alkoxy and/or polyetheral chains **64a–d** were prepared by coupling **60** with diiodobenzenes **63a–d** in the presence of $\text{Pd}(\text{PPh}_3)_4$ as the catalyst (Babudri *et al.*, 1996; 2000; Bolognesi *et al.*, 1999; Chiavarone *et al.*, 1999).

Theoretical calculations have shown that the introduction of electron withdrawing substituents on PPV can be used to decrease the LUMO energy, enabling better electron injection at the cathode of electroluminescent devices (Bredas and Heeger, 1994). Fluorine functionalization generally shows this effect (Babudri *et al.*, 2007). Substitution of C-H bonds with C-F bonds may be useful to lower the HOMO and LUMO levels of PPV polymers: this eventually improves their stability against photooxidation and agevolates electron injection at the cathode with respect to unfluorinated PPVs (Kang *et al.*, 1997). The soluble precursor route was applied to the synthesis of PPVs with different degree of fluorination of the phenylene ring (McCoy *et al.*, 1991; Kang *et al.*, 1994; Gurge *et al.*, 1997; Gan *et al.*, 2001). However, some difficulties were encountered in the synthesis of polymers with fully fluorinated aromatic rings (Brooke and Mawson, 1990; Benjamin *et al.*, 1996). The Stille polymerization turned out to be a versatile approach to the synthesis of selectively fluorinated PPV polymers. PPV **66** with fluorinated aromatic rings was obtained by coupling 1,2-bis(tributylstannyl) ethene **60** with tetrafluoro-1,4-diiodobenzene **65** (Fig. 1.21a) (Babudri *et al.*, 2001a, 2003a). Thin films of **66** were obtained by thermal evaporation and green emission was achieved in OLED devices. Green electroluminescence represents a considerable blue shift with respect to the red–orange emission of alkoxy-substituted PPVs.

The Stille cross-coupling of either **60** or the fluorinated bis(tributylstannyl) ethene **67** with aryl diiodide **68** was also used to synthesize MEH-PPV **69a** and the fluorinated MEH-PPDFV **69b**, respectively (Fig. 1.21b) (Babudri *et al.*, 2008a;

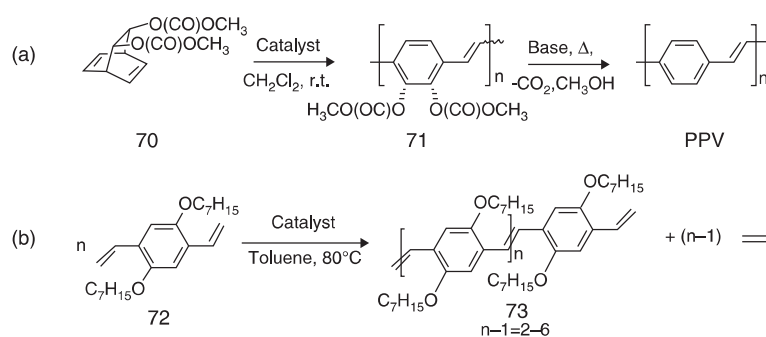


1.21 (a, b) Synthesis of fluorinated PPVs via Stille cross-coupling reaction.

Cardone *et al.*, 2010). Solid state properties of the two materials differing only for the presence of fluorine atoms on the double bonds were systematically compared (Losurdo *et al.*, 2008). MEH-PPDFV shows a large blue shift of the emission wavelength with respect to MEH-PPV, as a consequence of the presence of fluorine atoms on the vinylene units which determines a twisted conformation. In fact, steric repulsion between fluorine atoms on the double bonds and alkoxy substituents on the aromatic rings induces torsion between the vinylene units and the substituted benzene units (Piacenza *et al.*, 2008). An OLED made with MEH-PPDFV **69b** as the emitting layer showed stable blue emission and increased stability compared to the non-fluorinated material **69a** (Losurdo *et al.*, 2009).

Metathesis reactions of dienes or alkenes, most commonly catalyzed by Schrock type molybdenum alkylidene complexes, can be used for the synthesis of arylenevinylene polymers. The main advantage of this method consists in its living polymerization character, which originates high molecular weight materials with low polydispersity. For instance, the ROMP (Ring Opening Metathesis Polymerization) process was exploited to produce the soluble precursor polymer **71** starting from bicyclo[2.2.2]octadiene **70**, which was then converted into unsubstituted PPV by thermal treatment in the presence of acid or base catalyst (Fig. 1.22a) (Conticello *et al.*, 1992). The thermal conversion, which is also responsible for the isomerization of all-*cis* double bonds to their *trans* configuration, occurs efficiently. However, the poor processability of **71** limits the application of this method to the preparation of ordered thin films for optoelectronics.

Divinylbenzenes can be polymerized via ADMET (Acyclic Diene METathesis), according to Fig. 1.22b. In this case, only oligomers with 2–6 repeating units are formed because of the poor reactivity of the dialkoxy-substituted monomer **72** (Thorn-Csany and Kraxner, 1997; Thorn-Csany *et al.*, 1998).



Catalyst $\text{Mo}(=\text{NAr})(=\text{CHCMe}_2\text{Ph})[\text{OCMe}(\text{CF}_3)_2]_2$ Ar = 2,6-dimethylphenyl

1.22 (a, b) Synthesis of PPVs via metathesis reactions.

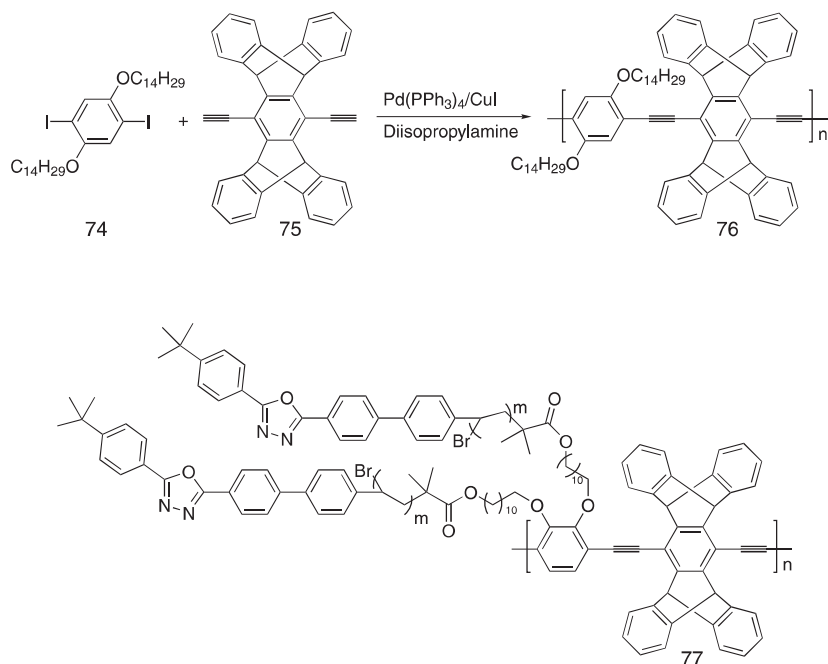
1.4 Poly(aryleneethynylene)s

Poly(aryleneethynylene)s (PAEs) exhibit remarkable luminescence properties both in solution and in the solid state and can display better photostability in comparison to other classes of luminescent polymers, such as poly(arylenevinylene)s (PAVs) (Bunz, 2009; Holzer *et al.*, 1999). Due to their rigid rod structure, they usually display stronger solid state intermolecular interactions than poly(arylenevinylene)s, and this causes a larger red shift of light emission from solution to the solid state than that observed in PAVs (Müllen and Scherf, 2006). Moreover, an undesirable emission tail at the highest wavelengths can appear in the presence of structural defects such as high polydispersivity (Grimsdale *et al.*, 2009). These issues mainly explain why PAEs have been generally less used than PPVs in electroluminescence applications. The two main approaches used to synthesize PAEs are based on: (a) the Pd-catalyzed Csp-Csp² bond forming reactions (Bunz, 2000), namely the Cassar-Heck-Sonogashira (Marsden and Haley, 2004) and related cross-coupling processes; (b) the metathesis reaction (Bunz, 2001).

The Cassar-Heck-Sonogashira cross-coupling has been widely employed to build structurally complex or multifunctional polymers with the aryleneethynylene backbone, opening the access to an impressive number of structurally different materials. The reaction consists in the arylation of terminal ethynyl moieties by coupling with the Csp² of aryl or heteroaryl halides in the presence of a palladium catalyst, a copper (I) co-catalyst and a base. The reaction can be carried out following different experimental protocols depending on the specific structure and substituents of the coupling partners and it can be easily applied to the synthesis of regular alternating copolymers.

As shown in Fig. 1.23, the blue emitting poly(*p*-aryleneethynylene) **76** alternating alkoxy-substituted benzene rings with bulky pentiptycene units was synthesized by this approach, using the bis-ethynyl derivative **75** and the aryl dihalide **74** as the monomers in the presence of Pd(PPh₃)₄ and CuI as the catalysts and diisopropylamine as the base (Yang and Swager, 1998). Polymer **76** maintains the blue emission in the solid state as in solution since solid state intermolecular interactions are inhibited by the bulky pentiptycene groups. Single layer blue OLEDs could be fabricated using the analogous polymer **77**, bearing appended oligoarylene branches with oxadiazole rings grafted via ester linkages to the polymer backbone (Breen *et al.*, 2005). Oxadiazole-containing oligoarylene side groups improve negative charge transport properties in the solid state, allowing efficient electron transport from the electrode into the polymer film. In fact, OLED device showed a peak efficiency of 0.29% and a luminance efficiency of 0.34 cd A⁻¹. In addition, polymer **77** maintains higher operational efficiency over a larger range of current densities compared to the dialkoxy-substituted PPE **76**.

The formation of butadiyne defects in the polymer chain of PAEs due to the oxidative homocoupling of ethynyl monomers is the major drawback of the

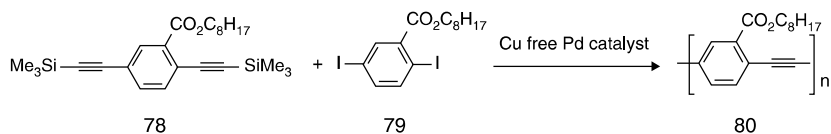


1.23 Synthesis of PPEs via Cassar-Heck-Sonogashira cross-coupling reaction.

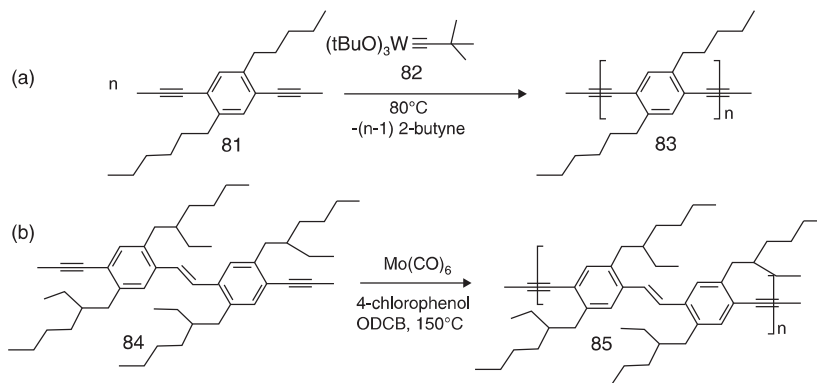
Cassar-Heck-Sonogashira cross-coupling-based polymerization. It is caused by the occurrence of the so-called Glaser coupling activated by copper-salts (Kotora and Takahashi, 2002). Oxidative homocoupling represents a considerable issue in the polymerization reactions since it causes imbalance of the monomers ratio which, in turn, strongly limits the molecular weight. In addition, the presence of structural butadiyne defects lowers performances of PAEs in electroluminescent devices. Finally, the presence of butadiyne defects can determine cross-linking processes in the solid state.

The occurrence of the undesired homocoupling reaction can be reduced or completely suppressed by coupling aromatic halides with trimethylsilyl alkynes instead of the corresponding terminal alkynes, in the presence of a palladium complex and silver oxide as the activator (Mori *et al.*, 2001). This protocol has been applied to the synthesis of several PAEs (Häger and Heitz, 1998; Babudri *et al.*, 2003b; 2006) and one example of application of such procedure to the preparation of the functionalized PPE **80** (Häger and Heitz, 1998) is shown in Fig. 1.24.

The metathesis reaction (ADIMET=Acyclic Diyne METathesis) has been extensively used for the preparation of poly(*p*-aryleneethynylene)s (Bunz, 2001). Contrary to the Cassar-Heck-Sonogashira cross-coupling, this method affords

1.24 Synthesis of PPE **80**.

polymers free of butadiyne defects, but it cannot be easily used for the synthesis of alternating copolymers. Typically the ADIMET protocol is based on the reaction of a dipropynyl arene in the presence of the catalyst. Earlier procedures used the Schrock tungsten carbene $(\text{tBuO})_3\text{W}=\text{C}(\text{tBu})$ complex **82** as the catalyst (Fig. 1.25a). The method was successfully applied to the polymerization of the dialkynyl benzene **81** affording defect-free PPE polymer **83** in high yield, with a degree of polymerization reaching almost 100 repeating units (Fig. 1.25a) (Weiss *et al.*, 1997). However, the Schrock catalyst **82** is rather difficult to prepare and it is air and moisture sensitive. Molybdenum based complexes obtained by mixing molybdenum hexacarbonyl with 4-chlorophenol or 4-trifluoromethylphenol can be advantageously adopted as an alternative to **82** since they are inexpensive, air stable and active in non-dried solvents (most typically *o*-dichlorobenzene). Several polymers, including the PPV-PPE alternating copolymer **85**, were prepared using these Mo complexes (Fig. 1.25b) (Brizius *et al.*, 2000).



1.25 (a, b) Synthesis of PPEs via metathesis reactions.

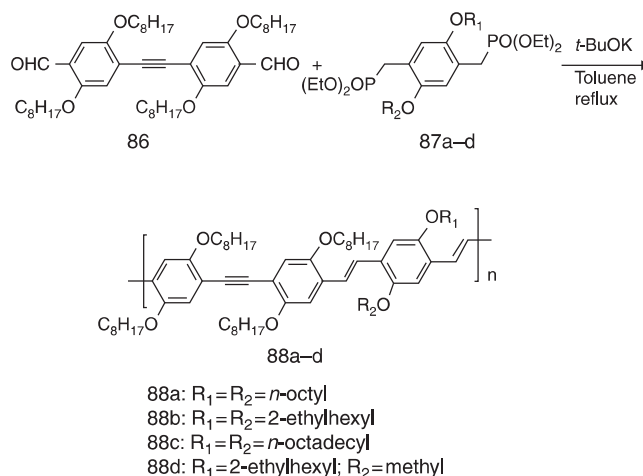
1.5 Conjugated copolymers

Conjugated copolymers combine in a single macromolecular structure two or more types of repeating units. Their structural diversity enables fine tailoring of properties, including charge transport and light emission color.

The opportunity to optimize several properties in one single molecular structure makes copolymers particularly suitable for the fabrication of devices based on a single active polymer layer performing different functions, such as different emission colors and charge transport. Reducing the number of layers in devices is highly desirable in OLEDs fabrication to lower costs and simplify processing, as well as to circumvent the drawbacks of phase separation and differential aging that affect performances and stability of devices based on multiple active layers or on blends of different active molecules.

Poly(phenyleneethynylene)-*alt*-poly(phenylenevinylene)s (PPE-PPVs), like polymer **85** briefly introduced in the previous section, combine PPE and PPV repeating units in a single polymeric backbone. Compared to PPEs, they exhibit bathochromically shifted absorption and emission spectra and enhanced solid state fluorescence quantum yield due to reduced solid state π - π interchain interactions, thanks to the presence of the phenylenevinylene moieties. Compared to PPVs, they are characterized by higher electron affinity, which is reflected by low turn on voltages of light emitting diodes fabricated with these materials (Egbe *et al.*, 2011).

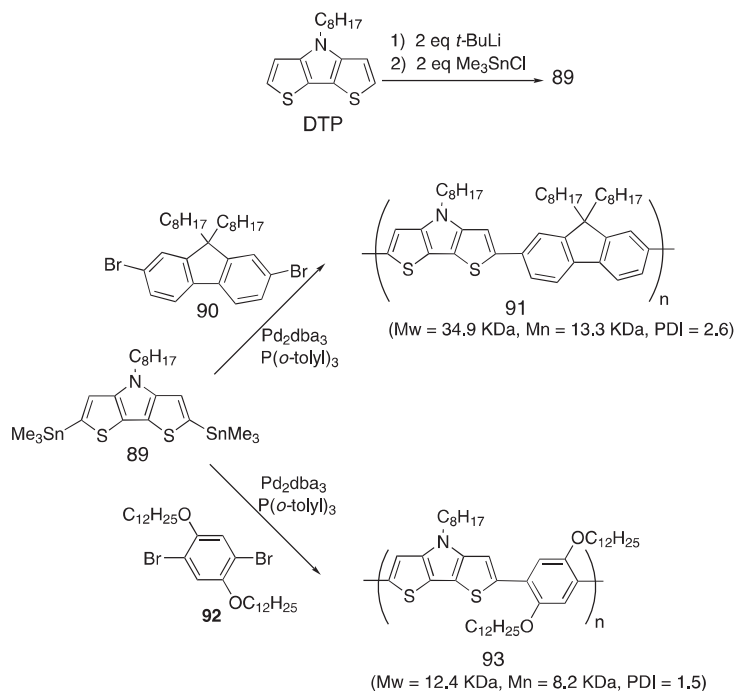
Alkoxy substituted and π -bridged PPE-PPVs **88a-d** reported in Fig. 1.26 could be synthesized either by the Cassar-Heck-Sonogashira cross-coupling or by polycondensation reactions. However, the Horner-Wadsworth-Emmons polycondensation of dialdehydes with bisphosphonate esters was preferred since it yielded polymers without butadiyne defects, with higher molecular weight and more than 98% double bonds in *trans* configuration (Egbe *et al.*, 2001).



1.26 Synthesis of copolymers **88a-d** via Horner-Wadsworth-Emmons polycondensation reaction.

The PPE-PPV polymers are thermally stable up to temperatures of at least 300°C and their solid state photophysical properties (absorption, emission, photoluminescence quantum yield, fluorescence kinetics, photoconductivity) depend on size, geometry (linear or branched), number and position of grafted alkoxy side groups. Polymers bearing long linear octadecyloxy or branched 2-ethylhexyloxy side groups exhibit improved OLED performances thanks to their enhanced solubility, film-forming capability and optimized film morphology. The long linear or branched side chains also inhibit the interchain interactions, thereby enhancing exciton confinement and electroluminescence efficiency. Best performances were obtained in a green emitting device based on polymer **88c** with glass substrate/ITO/PEDOT:PSS/polymer/Ca/Al configuration [PEDOT:PSS=poly(3,4-ethylenedioxythiophene) poly(styrenesulfonate)] with an external quantum efficiency of 2.15%, a turn on voltage of 5V and a luminance of 3.6 cd·A⁻¹ (Egbe *et al.*, 2004).

The Stille cross-coupling reaction was used for the synthesis of dithieno[3,2-*b*:2',3'-*d*]pyrrole-arylene copolymers **91** and **93** (Fig. 1.27), designed as green and



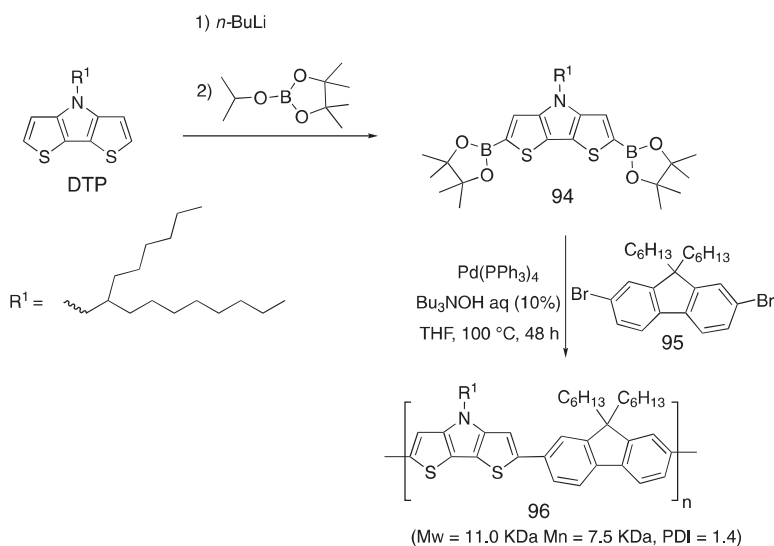
1.27 Synthesis of copolymers **91** and **93** via Stille cross-coupling reaction.

red emitting thiophene based materials with better performances in OLEDs with respect to classic polythiophenes (Evenson *et al.*, 2011).

In fact, as mentioned in Section 1.2, the main drawback limiting the application of polythiophenes as emitting homopolymers in OLEDs is related to the strong interactions occurring between the polymer chains in the solid state, which significantly reduce the emission efficiency by promoting non-radiative decay via interchain processes, as well as allowing intersystem crossing caused by the heavy atom effect of sulphur (Perepichka *et al.*, 2009; Ding *et al.*, 2001).

This issue can be overcome by: (a) introduction of arylene units in the polymer backbone, such as alkyl substituted fluorene or dialkoxybenzene, that contribute to reduce intermolecular interactions; and (b) conversion of the single thiophene moieties into fused heteroaryl units, such as the *N*-functionalized dithieno[3,2-*b*:2',3'-*d*]pyrrole (DTP), which confers higher carrier mobilities with respect to the single thiophene counterparts. Copolymers **91** and **93** were obtained by the Stille coupling of the highly pure distannane **89** with the aryl dibromides **90** and **92** (Fig. 1.27).

An analogous copolymer **96**, which differs from **91** only in the DTP and fluorene side chains (2-hexyldecyl in place of *n*-octyl for DTP, *n*-hexyl in place of *n*-octyl for fluorene) was previously synthesized via the Suzuki cross coupling of the diboronic ester **94** with 2,7-dibromo-9,9-dihexylfluorene **95** (Fig. 1.28) (Zhang *et al.*, 2008).



1.28 Synthesis of copolymer **96** via Suzuki cross-coupling reaction.

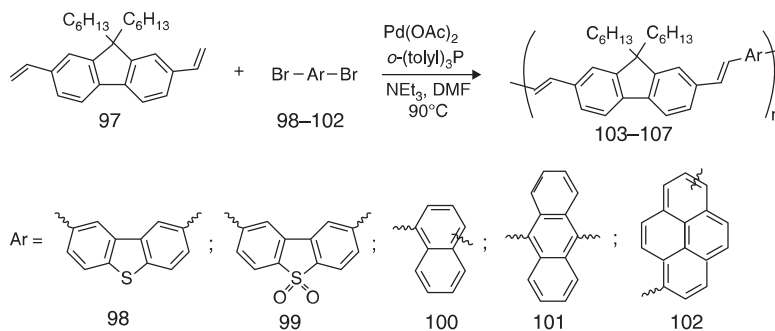
Compared to the synthesis based on the Stille coupling, the Suzuki copolymerization reaction resulted in a significantly lower molecular weight ($M_n = 7.5$ KDa, PDI = 1.4), likely caused by the lower purity degree of the precursor **94** which negatively affects the polymerization stoichiometry.

The device with configuration ITO/PEDOT:PSS/**91**/Alq₃/LiF/Al gives luminance ~1.6 times higher (197 vs 125 cd·m⁻²) than that observed for devices made with analogous dithienylfluorene copolymers (Donat-Bouillud *et al.*, 2000), showing the advantage of DTP over typical thiophene-based systems.

Alternating copoly(arylenevinylene)s **103–107** were synthesized by the Heck coupling of 9,9-dihexyl-2,7-divinylfluorene **97** with a series of polynuclear aromatic dibromides **98–102** containing units such as anthracene, perylene, naphthalene, dibenzothiophene and dibenzothiophene-5,5-dioxide (Fig. 1.29) (Mikroyannidis *et al.*, 2006; 2007).

Devices made with copolymers **103–107** with configuration ITO/PEDOT:PSS/copolymer/Mg:Ag/Ag showed green-blue electroluminescence with low quantum efficiencies caused by various factors including π - π interactions in the solid state between polynuclear aromatic rings which favour charge carrier trapping and exciton annihilation.

The most significant technological interest in electroluminescent copolymers is related to their application as single white light emitting materials in large area and easy processable OLED devices for lighting (Farinola and Ragni, 2011). White electroluminescence can, in fact, be achieved by copolymers composed of different conjugated units covalently bound in proper arrangement and ratio, simultaneously emitting light of two complementary (e.g. orange and blue) or the three fundamental (i.e. red, green and blue) colors. Very careful control of the relative amount and connection of the single conjugated units is necessary to manage energy transfer processes (Laquai *et al.*, 2009) that are fundamental for white light production as a result of simultaneous emission from blocks of different colors.

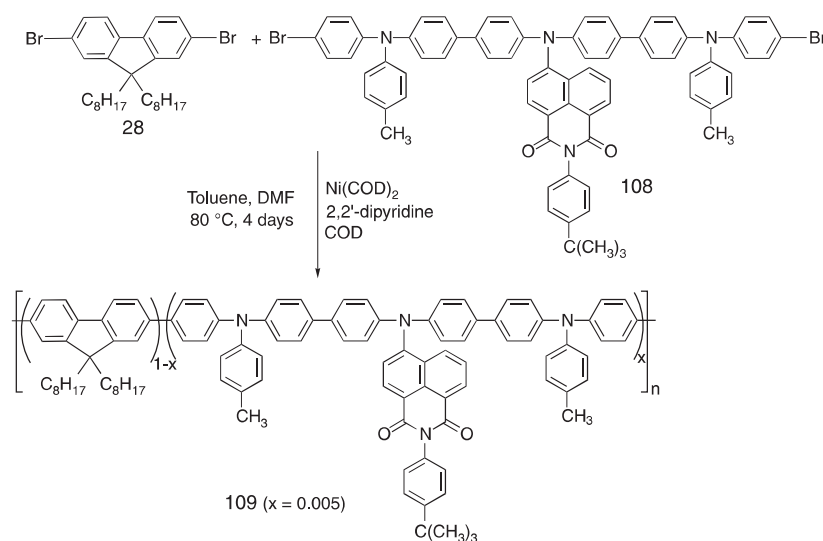


1.29 Synthesis of copolymers **103–107** via Heck coupling reaction.

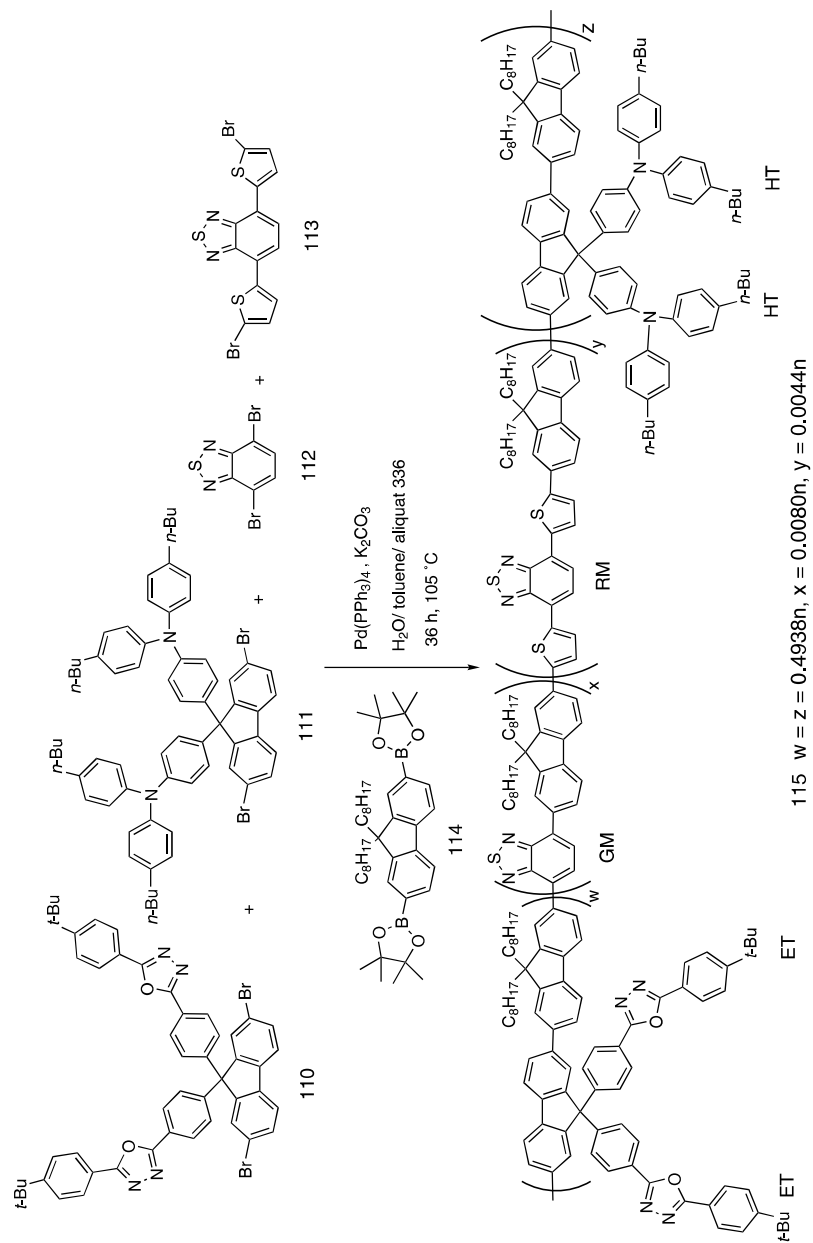
Many synthetic approaches to white electroluminescent conjugated copolymers bearing blue, green and red or blue and orange emitting moieties in the main chain or as side groups have been reported thus far (Raja *et al.*, 2008). The Yamamoto Ni(0) catalyzed polycondensation reaction of aryl dibromides was used for the synthesis of copolymer **109** consisting of polyfluorene blocks as the blue emitting component and 1,8-naphthalimide units as the orange emitters combined with the hole transporting triarylamine moieties (Fig. 1.30) (Tu *et al.*, 2006).

The amount of unit **108** bearing the 1,8-naphthalimide moiety has to be small (0.005 molar ratio) to prevent complete energy transfer from the blue polyfluorene units to the orange emitting units, thus obtaining highly pure white light with CIE coordinates (0.32, 0.36). 2.0 lm W^{-1} . Power efficiency devices were easily fabricated by spin-coating the single copolymer **109** active layer from solution.

The Suzuki cross-coupling reaction has also been widely used for the synthesis of white light emitting copolymers, such as the multifunctional polymer **115** reported in Fig. 1.31 (Chuang *et al.*, 2007). **115** is composed of green emitting (GM) blocks containing the benzothiadiazole ring and red emitting (RM) blocks containing bis(thienyl)benzothiadiazole moieties covalently incorporated into the backbone of a bipolar blue emitting polyfluorene functionalized with both electron (ET) and hole transporting (HT) pendant groups (Fig. 1.31).



1.30 Synthesis of copolymer **109** via Yamamoto polycondensation reaction.



1.31 Synthesis of copolymer **115** via Suzuki cross-coupling reaction.

This multifunctional polymer was synthesized by cross-coupling the fluorenyl diboronate **114** with four different aryl dibromides **110–113** combined in proper ratio to carefully control the concentrations of the low-energy-emitting species **GM** and **RM** in the copolymer. OLED devices fabricated using a single emitting layer of the copolymer **115** showed luminance efficiency of $4.87 \text{ cd} \cdot \text{A}^{-1}$ with external quantum efficiency 2.22% and color coordinates (0.37, 0.36) very close to the ideal CIE chromaticity coordinates for pure white light (0.33, 0.33).

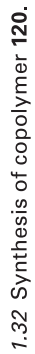
Another representative example of the Suzuki cross-coupling as a copolymerization method affording white electroluminescent polymers is the synthesis of **120** which exhibits a broad emission covering the entire visible region from 400 to 700 nm (Li *et al.*, 2009). The complex structure of **120** consists of blue emitting oligofluorenes (**OPF**), red emitting porphyrins (**Por**) and green emitting oligo(phenylenevinylene)s (**OPV**) combined with hole transporting triphenylamine pendant groups (Fig. 1.32). The device made using a single emitting layer of copolymer **120** showed good color stability and CIE coordinates (0.29, 0.30).

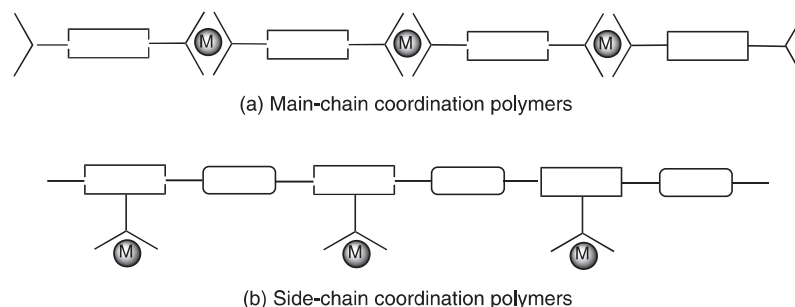
1.6 Coordination polymers

The term coordination polymer is widely used in materials chemistry current literature, although its meaning is quite different if the viewpoints of inorganic and organic chemist communities are considered. According to the inorganic chemists' definition, a coordination polymer is a one-, two- or three-dimensional solid state network in which molecular building blocks are held together by metal coordination interactions which commonly are not strong enough to survive in solution (Dobrawa and Würthner, 2005; Janiak, 2003; Kitagawa *et al.*, 2004). According to the definition of organic chemists, coordination polymers, also known as metallo-supramolecular conjugated polymers, are macromolecules having stable polymeric structures, both in solution and in the solid state, which contain organometallic complexes in the polymer main chain (Fig. 1.33a) or covalently attached to the polymeric backbone as side groups (Fig. 1.33b) (Brunsveld *et al.*, 2001; Burnworth *et al.*, 2007; Weck, 2007).

Coordination polymers have the main advantage of combining in a single material the easy solution processability of soluble conjugated polymers with the properties typical of some luminescent organometallic complexes such as high thermal stability, good charge transport ability, and high photo- and electroluminescence efficiencies.

The synthetic routes to coordination polymers can be classified in two main categories. The first approach consists of metal ion complexation of organic building blocks bearing two terminal coordinating units as the polymerization reaction (Fig. 1.34a). This synthetic approach is suitable for the preparation of 'main-chain' coordination polymers (Fig. 1.33a) in which both the organometallic complexes formed during the polymerization and the organic building blocks are in the polymeric backbone.

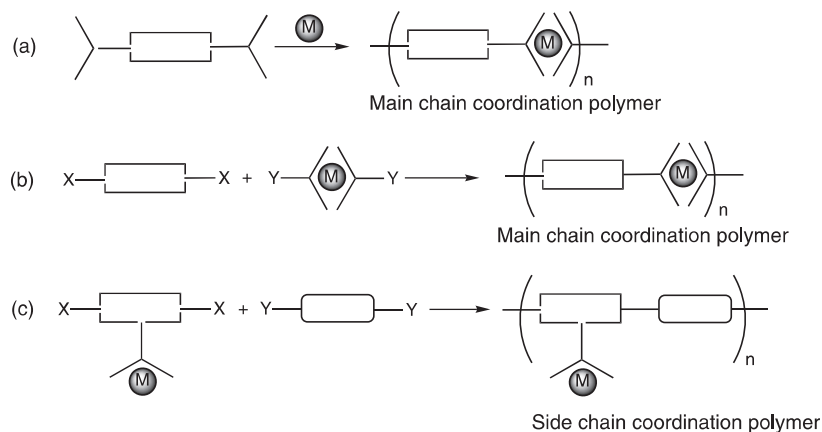




1.33 (a, b) Schematic drawing of coordination polymers structures.

The second kind of polymerization method is based on condensation or cross-coupling processes between two (or more) monomers, one of which (at least) contains a pre-formed organometallic complex in the main monomer structure (Fig. 1.34b) or covalently grafted as pendant group (Fig. 1.34c). Hence, this strategy can be applied to the preparation of both ‘main-chain’ and ‘side-chain’ coordination polymers depending on the structure of the monomer bearing the organometallic complex.

The main advantage of the synthetic routes reported in Fig. 1.34a is that polymerization based on metal-ligand complexation occurs in high yields and does not require the use of catalysts. On the other hand, protocols based on cross-coupling or polycondensation reactions (Fig. 1.34b,c) can afford alternating, block- or random copolymers from monomers with different characteristics. This allows the synthesis of multifunctional conjugated sequences with high structural complexity and tailored properties by controlling the content of the organometallic moieties in the polymeric chain.

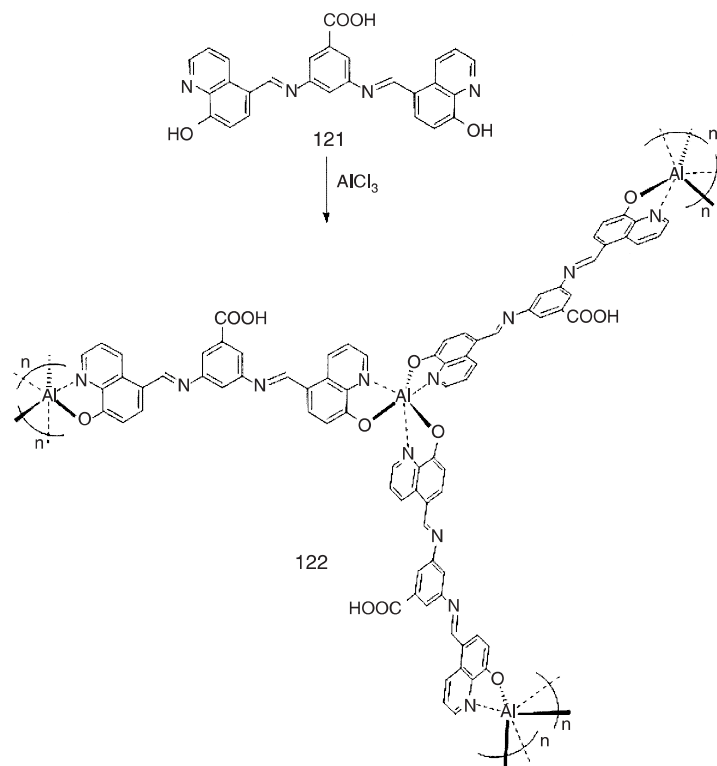


1.34 (a-c) Main synthetic approaches to coordination polymers.

Although only a limited number of OLED devices based on coordination polymers as light emitting materials has been reported in the literature so far, the great interest of academic and industrial communities in supramolecular polymer chemistry is confirmed by many reports dealing with the synthesis, characterization and properties of these promising materials (Brunsveld *et al.*, 2001; Burnworth *et al.*, 2007; Weck, 2007; Han *et al.*, 2007; Knapton *et al.*, 2006; Bernhard *et al.*, 2003; Dobrawa *et al.*, 2005).

Coordination polymers bearing aluminium-hydroxyquinoline type complexes in the main chain have been synthesized and used as electroluminescent and/or charge transporting materials in light emitting diodes. In fact, tris(8-hydroxyquinoline) aluminium complex AlQ₃ is one of the most common electron transporting molecules used in OLEDs even though its thin layer processability in devices requires vapor thermal deposition techniques (Jonda *et al.*, 2000).

Polymer **122** was obtained by the complexation reaction of AlCl₃ with 3,5-bis(8-hydroxyquinoline Schiff base)-benzoic acid **121** (Fig. 1.35). **122** was used as



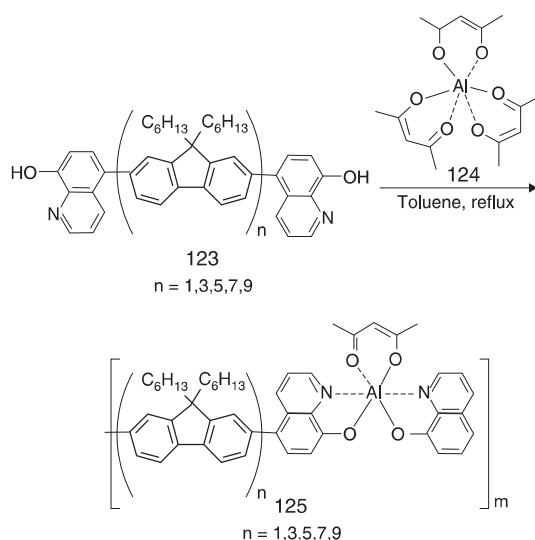
1.35 Synthesis of polymer **122**.

the electron transporting layer in a device with configuration ITO/PEDOT/MEH-PPV/**122**/LiF/Al demonstrating its higher performance and easier processability by spin-coating with respect to the simple AlQ_3 complex (Jiang *et al.*, 2008, 2009).

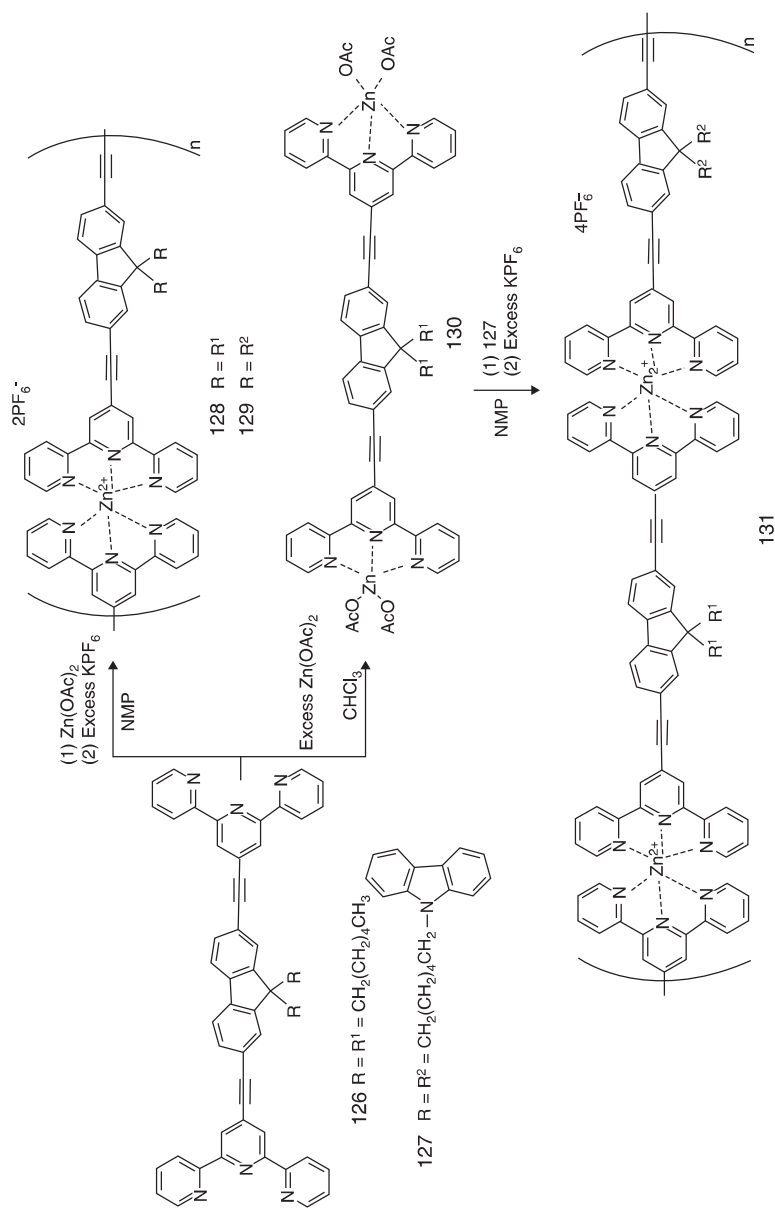
The main-chain coordination polymers **125** were synthesized in the same period using the ligand exchange of the complex tris(acetylacetonate)aluminium **124** with oligofluorenes **123** functionalized with two hydroxyquinoline terminal units (Fig. 1.36) (Montes *et al.*, 2009). Preliminary experiments with devices fabricated by a spin-coated emitting layer of **125** led to maximum external quantum efficiency up to 1.2%.

Several luminescent zinc-terpyridine type main-chain coordination polymers have been synthesized using the complexation reaction of equimolar amounts of zinc acetate and ditopic ligands composed of a central oligomer connected to two terminal terpyridine units (Winter *et al.*, 2008; Chen *et al.*, 2006; Yu *et al.*, 2003). The emission color of these materials can be widely tuned in the whole visible range by properly selecting the structure of the central spacer. After the polymerization, an excess of KPF_6 salt is always added to the reaction mixtures to substitute acetate anions which balance the positive charges of Zn^{2+} containing polymers.

A representative example of this synthetic method is shown in Fig. 1.37 which demonstrates the possibility to adapt such polymerization protocol to obtain either coordination homopolymers (**128** and **129**) or an *alternating*-copolymer **131**



1.36 Synthesis of polymers **125**.



1.37 Synthesis of polymers **128**, **129** and **131**.

(Chen *et al.*, 2006). The latter material represents the first example of coordination *alt*-copolymer reported in the literature and its synthesis was carried out by adding dropwisely the ditopic ligand **126** to a solution of an excess of zinc acetate in order to favor the formation of intermediate **130** instead of homopolymer **128**. Then, an equimolar amount of the ditopic ligand **127** was added to the reaction mixture to build the main chain of the *alt*-copolymer **131**.

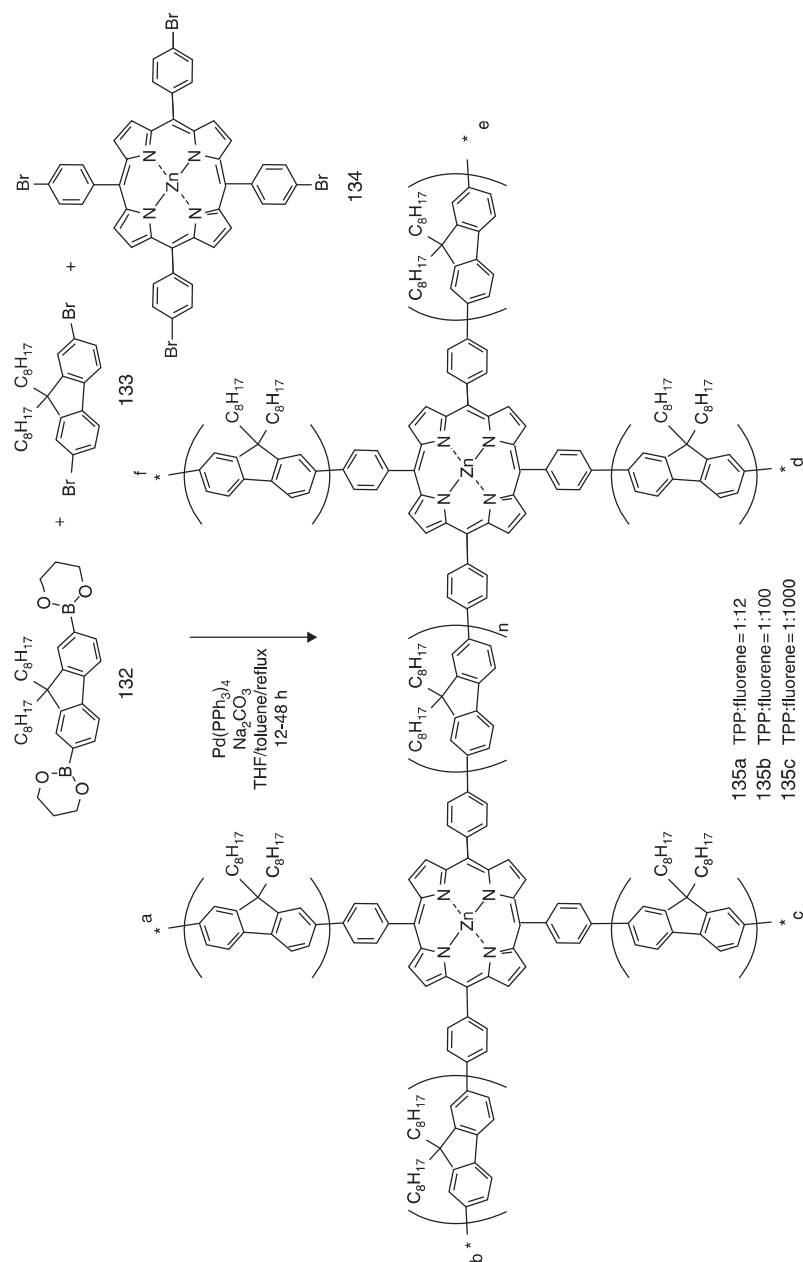
Coordination polymers bearing zinc-salen (Peng *et al.*, 2005) and zinc-porphyrin (Wang *et al.*, 2010) complexes in the main chain have also been prepared and used as emitting materials in OLEDs. In particular, according to the general approach reported in Fig. 1.34b, branched electroluminescent zinc tetraphenylporphyrin (ZnTPP)-fluorene copolymers **135a–c** were obtained by a one-pot Suzuki cross-coupling reaction of the diboronate **132** with the halides **133** and **134**, demonstrating that this strategy makes it possible to tune from pink (for **135c**) to pure red (for **135a**) the emission color of the resulting materials by properly adjusting the molar ratio of porphyrin monomers versus fluorene monomers (Fig. 1.38) (Wang *et al.*, 2010). Compared to linear polymers, these branched systems are less prone to self-aggregation and emission quenching in the solid state.

Coordination polymers based on d^6 phosphorescent transition metal (e.g. Ir, Pt, Ru, Os) complexes (Evans *et al.*, 2006) have attracted attention as emitting materials for PHOLED applications since they combine the good processability of organic polymers with the high electroluminescence efficiency of organometallic triplet emitters. Platinum (Brooks *et al.*, 2002) and iridium (Lamansky *et al.*, 2001; Ragni *et al.*, 2006; 2009) complexes are also most frequently used in consideration of their color tunability by appropriate design of molecular structures.

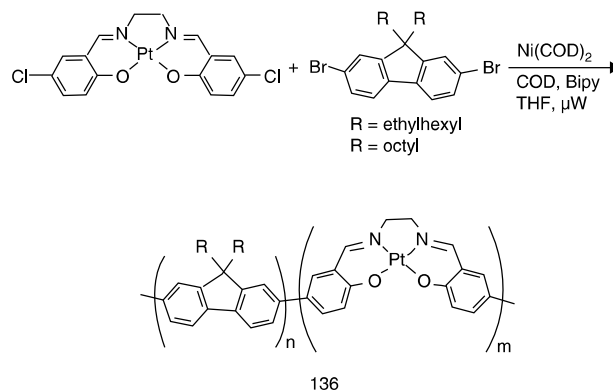
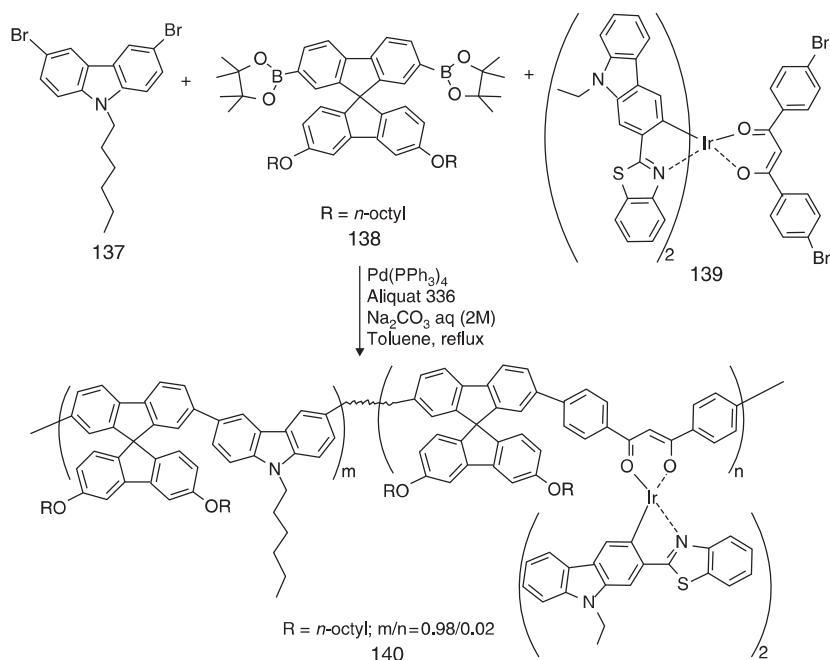
A very fast microwave promoted Yamamoto polycondensation reaction was used for the synthesis of polyfluorenes with electrophosphorescent main-chain platinum-salen chromophores **136** (Fig. 1.39) (Galbrecht *et al.*, 2005). OLED devices based on these novel copolymers reached efficiencies as high as $6 \text{ cd} \cdot \text{A}^{-1}$.

A variety of electroluminescent main- and side-chain iridium coordination polymers has also been synthesized thus far, according to the general synthetic route reported in Fig. 1.34b,c. The palladium catalyzed Suzuki cross-coupling represents the most commonly used polymerization reaction for the synthesis of these materials (Park *et al.*, 2010; Zhang *et al.*, 2006; Ying *et al.*, 2009) even though ruthenium-catalyzed ring opening metathesis (Kimyonok *et al.*, 2007) and rhodium catalyzed polycondensation (Vicente *et al.*, 2010) reactions have been reported as well.

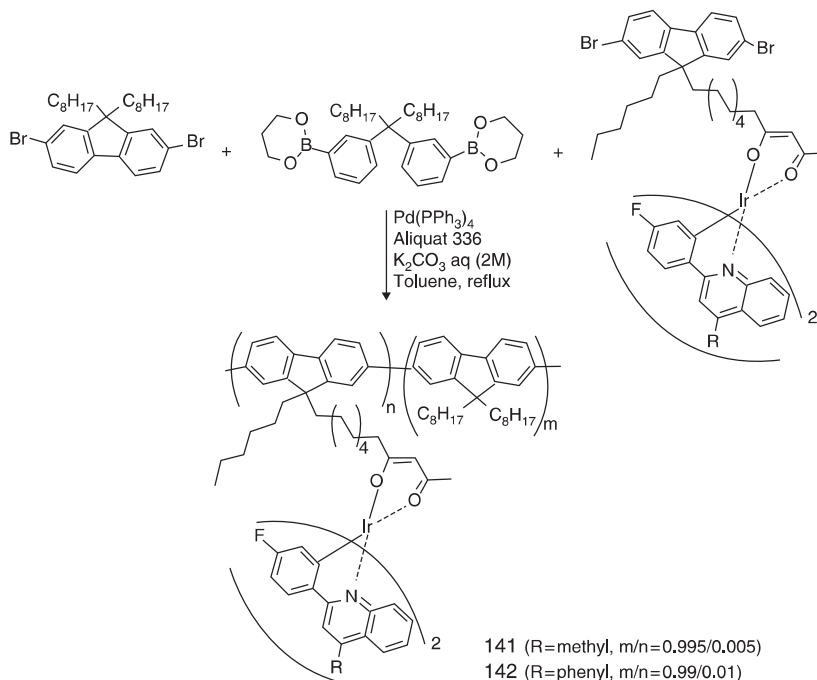
The white electroluminescent copolymer **140** with a red emitting iridium complex coordinated in the main backbone was synthesized by coupling, in proper feed ratios, the diboronic ester **138** with 3,6-dibromo-*N*-hexylcarbazole **137** and the dibromo functionalized heteroleptic complex **139**, as reported in Fig. 1.40 (Park *et al.*, 2010).



1.38 Synthesis of polymers **135a-c**.


 1.39 Synthesis of polymers **136**.

 1.40 Synthesis of polymer **140**.

A similar polymerization protocol was also used for the synthesis of the blue emitting polyfluorene copolymers **141** and **142** bearing small amounts of grafted orange phosphorescent iridium complex pendant groups (Fig. 1.41), which led to white light emitting diodes with power efficiency up to $2.35 \text{ lm} \cdot \text{W}^{-1}$ (Mei *et al.*, 2007).

1.41 Synthesis of polymers **141** and **142**.

1.7 Conclusion and future trends

The survey presented in this chapter has covered the main synthetic tools for a great variety of electroluminescent conjugated polymers with tailored properties for application in OLEDs. Various transition metal catalyzed cross-coupling and metathesis reactions are suitable for the synthesis of these materials usually showing advantages with respect to polycondensation reactions such as stereo- and regioselectivity as well as tolerance of many functional groups. Research efforts for the development of synthetic protocols leading to stereodefined, highly pure and efficient polyconjugated materials are continuing. Particular attention is currently focused on molecular design, synthesis and application of novel multifunctional materials with quite complex architecture, such as copolymers and coordination polymers, which combine in a single molecular structure various repeating organic or organometallic units with specific functions such as charge transport, different emission color and high electroluminescence efficiency. These materials nowadays represent the most promising candidates for highly efficient white light emitting devices for lighting applications.

Easy synthetic access to efficient, stable, multifunctional emitters represents a cornerstone in the development and wide technological impact of organic electroluminescence.

1.8 Sources of further information

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Transparent conducting thin films for OLEDs

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Abstract: In an organic light-emitting diode, at least one of the electrodes has to be transparent or semitransparent. Transparent conducting thin films for organic light-emitting diodes (OLEDs) are of great importance for designing high performance OLEDs. In this chapter, three major transparent/semitransparent thin films, i.e. transparent conducting oxide thin films, metal thin films and carbon based conductive thin films, as transparent electrodes in OLEDs will be discussed. In particular, the focus will be on the optimization of desired work function of these thin films.

Key words: transparent conducting oxides (TCOs), metal thin films, graphene, work function, energy level alignment.

2.1 Introduction

The first electroluminescence (EL) in organic materials was reported in 1965 by Helfrich and Schneider (Helfrich and Schneider, 1965). This phenomenon was not thought to be useful until 1987 when Tang and co-workers demonstrated the first efficient organic electroluminescent diode using an organic heterostructure, i.e. an organic light-emitting diode (OLED) (Tang and VanSlyke, 1987). This discovery has been generally recognized as a milestone in the development of organic optoelectronics. In the last two decades, significant effort has been devoted to maximizing device efficiency by designing new organic materials (Baldo *et al.*, 1998; Su *et al.*, 2008, 2009; Mi *et al.*, 2009; Gao *et al.*, 2009) and device structures (Choudhury *et al.*, 2009; Helander *et al.*, 2010b; Liu *et al.*, 2009). For example, fluorescent (Tang *et al.*, 1989) and phosphorescent (Baldo *et al.*, 1999) organic dopants have been used as in a guest-host system. In terms of device structure, different functional layers, such as hole (electron) injection layer, hole (electron) blocking layer and exciton blocking layer, have been proposed to enhance the device efficiency (Ikai *et al.*, 2001; Adamovich *et al.*, 2003; O'Brien *et al.*, 1999). Some other device structures such as double emission zones and *n*-type and *p*-type chemical doping have also been proposed to improve the efficiency (He *et al.*, 2004). The device performance and working mechanism of all these designs have been discussed at length by other authors in this book. In this chapter, our purpose is to focus on some elementary aspects of the transparent conducting thin films commonly used as electrodes in OLEDs. In particular,

engineering the work function of the transparent conducting electrodes in order to optimize the device performance will be discussed in detail.

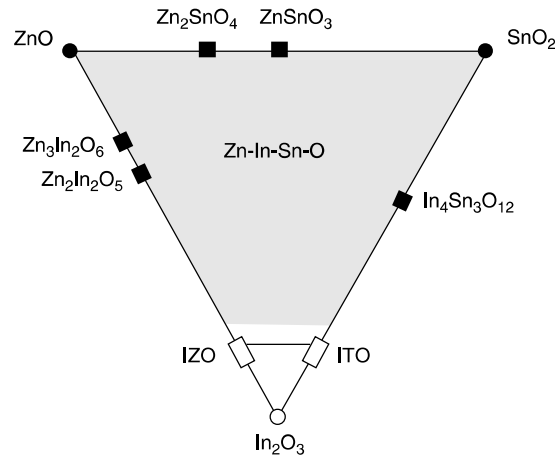
The simplest form of an OLED is composed of one or more organic layers, where at least one of the layers is electroluminescent, sandwiched between an anode and a cathode. Generally, at least one of the electrodes has to be transparent or semitransparent to allow light to escape the device. Transparent conducting oxide (TCO) thin films have commonly been employed as electrodes in OLEDs due to their high transparency and low electrical resistivity. For example, tin-doped indium oxide (ITO) is the *defacto* standard anode used in both research and production. Another major type of electrode is semitransparent metal thin films. Although light will be absorbed as it exits the device through the metal thin film, high efficiencies are still possible with proper optical design of the device. Semitransparent metal thin films are also commonly used as semitransparent cathodes in various top emission OLEDs (Smith *et al.*, 2004; Lu *et al.*, 2002). Noble metals are typically the most commonly used metals due to their high conductivity, good environmental stability, and ease of patterning and deposition. Recently, carbon based thin films have emerged as another promising candidate for low-cost transparent electrodes. For example, graphene has been demonstrated as an efficient anode in OLEDs due to its high transparency, conductivity and chemical stability (Han *et al.*, 2012). In the remainder of this chapter, the applications of these three types of transparent/semitransparent thin film electrodes (i.e., TCO thin films, metal thin films and carbon based conductive thin films), will be discussed in detail in sections 2.2, 2.3 and 2.4 respectively. Section 2.5 is the summary and the discussion of future trends.

2.2 Thin film electrodes (TCOs)

2.2.1 Major TCOs

The general requirements of a TCO thin film for practical use are a resistivity of $<10^{-3} \Omega \cdot \text{cm}$ and a transmittance of $>80\%$ in visible range. To achieve these requirements, the TCO should have a band gap of at least 3 eV and a carrier density of more than 10^{20} cm^{-3} (Hamberg and Granqvist, 1986; Tadatsugu, 2005). TCOs are therefore usually degenerate *p*-type or *n*-type semiconductors that are transparent in the visible range. Although *p*-type conductive oxide was discovered in 1993 (Sato *et al.*, 1993), most of the TCOs that are suitable for practical use are still *n*-type semiconductors. Figure 2.1 summarizes the most commonly used practical TCOs for transparent thin film electrodes, i.e. the $\text{ZnO-In}_2\text{O}_3\text{-SnO}_2$ system that is composed of (i) impurity doped ZnO , In_2O_3 and SnO_2 , such as $\text{In}_2\text{O}_3\text{:Sn}$ (ITO), $\text{SnO}_2\text{:F}$ (FTO) and ZnO:Al (AZO); and (ii) multicomponent oxides based on the ternary zinc indium tin oxide (ZITO) system, such as $\text{In}_4\text{Sn}_3\text{O}_{12}$ (Minami, 2008b).

Among all of the TCOs, ITO is the most mature and has been most commonly used in all kinds of optoelectronic devices, such as liquid crystal displays (LCDs)

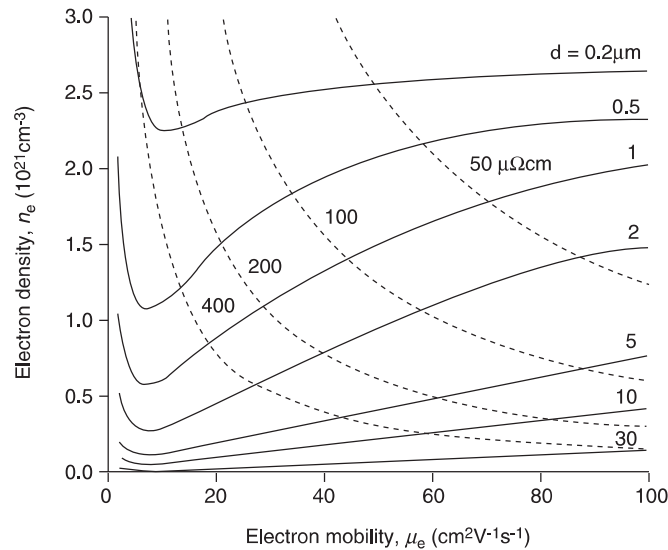


2.1 Practical TCO thin-film materials. Reprinted with permission from Minami, 2008b.

and thin film solar cells. ITO uses the majority of the world production of indium, which unfortunately is a scarce and expensive metal. There have therefore been intense development efforts to find alternative TCOs that require less indium usage, such as Zn-In-Sn-O, or indium-free TCOs such as AZO and ZnO:Ga (GZO) (Liu *et al.*, 2010; Minami, 2008a; Hoel *et al.*, 2010).

One major focus of TCO development is to achieve low resistivities. It is believed that the only way to achieve a resistivity in the range of $10^{-5} \Omega \cdot \text{cm}$ is by impurity doping, regardless of the exact fabrication method (Tadatsugu, 2005). A resistivity of $10^{-5} \Omega \cdot \text{cm}$ in ITO thin films has been frequently reported since the 1990s (Tadatsugu, 2005). While AZO thin films with similarly low resistivity in the range of $10^{-5} \Omega \cdot \text{cm}$ were first reported in 2003 (Agura *et al.*, 2003). Although AZO and GZO are believed to be the best candidates to replace ITO, there still remains a lot of significant challenges to be overcome (Minami, 2008a). For example, it is still difficult to achieve a resistivity of better than $10^{-4} \Omega \cdot \text{cm}$ in thin films with a thickness of only $\sim 50 \text{ nm}$. Moreover, the stability of thin films with a thickness $< 100 \text{ nm}$ has to be improved before they become practical alternatives to ITO. The electrical properties, fabrication methods and existing problems associated with the major TCO candidates to replace ITO have been thoroughly discussed in references (Tadatsugu, 2005; Minami, 2008a,b; Hoel *et al.*, 2010).

In terms of OLED research, there have been a lot of comparative studies between indium-free TCOs and ITO (Chen *et al.*, 2011; Berry *et al.*, 2008; Tomita *et al.*, 2007; Nam *et al.*, 2010; Wang *et al.*, 2010a). However, the report of high performance OLEDs using indium-free TCOs still remains rare. Usually, when optimizing OLED device performance, the transmittance and sheet resistance of



2.2 Contours of skin depth (solid lines) and resistivity (dashed lines) as a function of electron density and mobility. Reprinted with permission from Edwards *et al.*, 2004.

the transparent electrode are two major competing factors, i.e. the thicker the TCO film, the lower the sheet resistance but the worse the transmittance. To achieve a reasonably high performance in OLEDs, a compromise between these two competing factors has to be made. Figure 2.2 shows a calculated electromagnetic skin depth contour (solid lines), which determines the transparency of TCO thin films, and resistivity (dashed lines) of an ITO film at an incident wavelength of 800 nm as a function of both the carrier mobility and carrier density (Edwards *et al.*, 2004). When the carrier density is increased, the low transmittance region of the spectrum in the near-infrared will shift towards the visible due to the plasma resonance of the free electron gas in the conduction band (Hamberg and Granqvist, 1986; Edwards *et al.*, 2004). It is noted that the resistivity is also closely related to the carrier concentration. Different strategies such as tuning the deposition/annealing conditions have been shown to achieve low resistivity and high transparency concurrently for high performance OLEDs in indium-free TCO thin films (Wang *et al.*, 2010a).

2.2.2 Work function of TCOs

Other than low resistivity and high transmittance, the work function of TCO thin films also plays a significant role in OLED performance. Different work functions are needed depending on whether the TCOs are used as anode or cathode. As for

anodes, a high work function (>5.0 eV) is required to match the highest occupied molecular orbital (HOMO) of the hole transport layer (HTL) to sufficiently inject holes. While as for cathodes, a low work (<4.0 eV) function is required to match the lowest unoccupied molecular orbital (LUMO) of the electron transport layer (ETL) to sufficiently inject electrons.

ITO typically has a work function of 4.7–5.0 eV depending on the cleaning process and the surface treatment used. For example, ultraviolet ozone (UV-ozone) treatment can increase the work function to 5.0 eV. Therefore, ITO is usually used as a transparent anode, although there have been some reports of using ITO as a cathode in top emission OLEDs (Smith *et al.*, 2004) and inverted OLEDs where *n*-type doping of the ETL was used to enable electron injection from the relatively high (>4.0 eV) work function of the ITO cathode (Meyer *et al.*, 2008; Xiong *et al.*, 2008). In the rest of this section, different strategies to modify the work function of ITO, and other TCOs, will be discussed.

Work function and its measurement

Before we begin the discussion about how to achieve the desired work function of TCOs we have to first review the basic concepts about work function as well as its measurement.

The work function of a uniform surface is defined as the difference between the electrochemical potential $\bar{\mu}$ of electrons in the bulk and the electrostatic potential energy $-e\Phi_{vac}$ of an electron in the vacuum just outside the surface (Herring and Nichols, 1949),

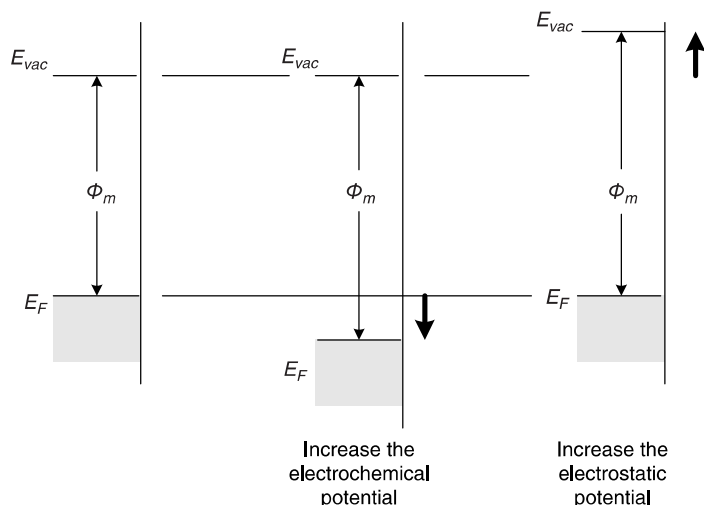
$$e\phi_m = -e\Phi_{vac} - \bar{\mu}. \quad [2.1]$$

Equivalently, the work function is the difference between the local vacuum level E_{vac} and the Fermi level,

$$e\phi_m = E_{vac} - E_F. \quad [2.2]$$

According to Eqs 2.1 and 2.2, by either changing the Fermi level (electrochemical potential) or the local vacuum level (electrostatic potential) of the thin film, the work function of a surface can be altered (see Fig. 2.3). However, since TCOs are semiconductors, changing their electrochemical potential may also alter other properties of the material, such as the conductivity and transmittance (Sze, 1981). Alternatively, the electrostatic potential can be altered, for example, by adding a layer of dipole moments to the surface without altering other material properties. Species with high electronegativity, such as halogen atoms, have been used to functionalize the surface of TCOs to change their work function.

Work function was first described in 1887 by Heinrich Hertz and Wilhelm Hallwachs (Hertz, 1887; Hallwachs, 1888) as part of the photoelectric effect – the



2.3 Schematic energy diagrams showing two ways to increase the work function.

observation that electrons (called photoelectrons) can be removed from the surface of a solid when irradiated with light above a certain threshold frequency (known today as the work function). In 1905 Albert Einstein explained the photoelectric effect in one of his now famous *annus mirabilis* papers (Einstein, 1905), as arising from the absorption of light quanta (i.e., photons). This discovery played a major role in the development of quantum theory and earned Einstein the Nobel Prize in Physics in 1921.

From Einstein's explanation of the photoelectric effect the maximum kinetic energy of a photoelectron is given by,

$$E_{k,\max} = h\nu - e\phi_m, \quad [2.3]$$

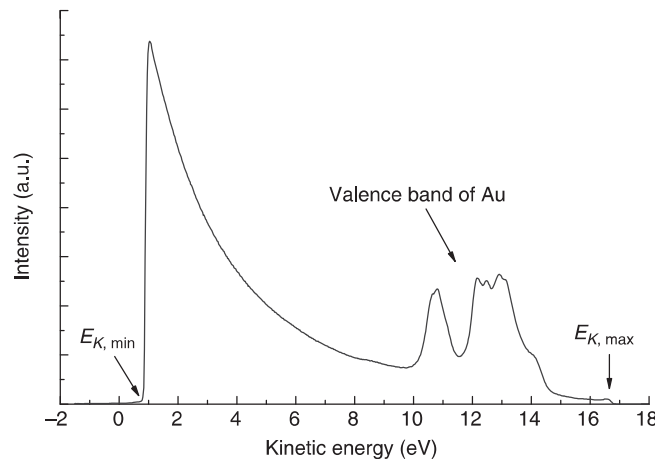
where $h\nu$ is the photon energy. This maximum kinetic energy occurs for a photoelectron emitted from the Fermi level. In principle, work function can be measured by varying the photon energy and determining the threshold photon energy required for the onset of photoemission. This method was in fact one of the original techniques used to measure work function (Herring and Nichols, 1949). However, more recently photoelectron spectroscopy (PES), which uses a single fixed photon energy, has become the most commonly used and reliable technique to measure the work function of a surface (Michaelson, 1977; Helander *et al.*, 2010a).

In PES the work function of a surface is given by,

$$e\phi_m = h\nu - (E_{K,\max} - E_{K,\min}), \quad [2.4]$$

where $E_{K,\min}$ is the minimum measured kinetic energy in the photoelectron spectrum as shown in Fig. 2.4. Note that $E_{K,\min}$ is usually not equal to zero due to a contact potential difference between the sample and the spectrometer used for the PES measurements. For a detailed discussion of this effect see Helander *et al.* (2010a). For semiconductors the Fermi level typically falls in the band gap, which means that $E_{K,\max}$ must be determined from a metal sample in electrical contact (i.e., the Fermi levels are aligned) with the semiconductor sample.

The point of minimum kinetic energy in a photoelectron spectrum $E_{K,\min}$ occurs in the region of the spectrum typically referred to as the secondary-electron cut-off (SEC) since (i) the majority of the signal is comprised of low kinetic energy secondary electrons, and (ii) in this region the spectrum is suddenly ‘cut-off’ due to the local vacuum level. In other words, an electron leaving the sample with energy less than E_{vac} has insufficient kinetic energy to escape, and hence does not contribute to the photoelectron spectrum. This implies that the electrons of interest leave the sample with zero kinetic energy. However, it is extremely difficult, if not impossible, to measure electrons leaving the sample with zero kinetic energy. Even electrons with near zero kinetic energy may have insufficient kinetic energy to make it into the spectrometer. Therefore, a small negative bias is typically applied to the sample when measuring the SEC region of the spectrum. This bias helps accelerate the lowest kinetic energy



2.4 He I α ($h\nu=21.22\text{ eV}$) valence band spectrum of an Ar+ sputter cleaned Au thin film. The maximum and minimum measured kinetic energies are indicated in the figure, where $E_{K,\max}$ corresponds to the Fermi level. Adapted with permission from Helander *et al.*, 2010a.

electrons into the spectrometer (and also helps to overcome the contact potential difference).

Engineering work function

Most of the research on modifying the work function of TCOs is to increase the work function for use as anodes. In the case of OLEDs, many common HTLs such as N,N'-diphenyl-N,N'-bis-(1-naphthyl)-1-1'-biphenyl-4,4'-diamine (α -NPD) have a HOMO level of >5.0 eV. Therefore a high work function is desired to reduce the facility for the injection of holes. Moreover, most of the host materials for phosphorescent OLEDs such as 4,4'-bis(carbazol-9-yl)biphenyl (CBP) have an even deeper HOMO level of >6.0 eV. Therefore, there is a significant energy mismatch between the work function of most TCO electrodes and the deep HOMO level of the host materials. A 'step-wise' design has been commonly used to overcome the energy level mismatch problem, i.e. a number of intermediate organic layers with subsequently deeper HOMO level may be used to let holes pass through several smaller barriers rather than a single large barrier between the TCO electrode and host material. It was recently found that the 'step-wise' design is not optimal as the additional energy barriers introduced by the intermediate layers can contribute to exciton quenching, which will be discussed in greater detail in Section 2.3. Moreover, each additional layer increases the fabrication complexity of the device. A higher work function TCO electrode is thus necessary to match the HOMO level of the host material, to enable OLEDs with a simple structure and high performance.

One common way to increase the work function of a TCO substrate is to clean the surface of the substrate to remove contaminants. Typically, as mentioned before, the surface of the TCO substrate may be cleaned using UV-ozone or O_2 plasma treatment (Wu *et al.*, 1997; Mason *et al.*, 1999). Such treatments are effective in removing organic contaminants and may leave electronegative oxygen species on the surface of the TCO substrate. It is worth noting that the UV-ozone and O_2 plasma cleaning treatments are reversible (Brumbach *et al.*, 2007). For example, the surface of the cleaned TCO substrate may be re-contaminated and/or electronegative oxygen species on the surface of the TCO may desorb over time (see Fig. 2.6).

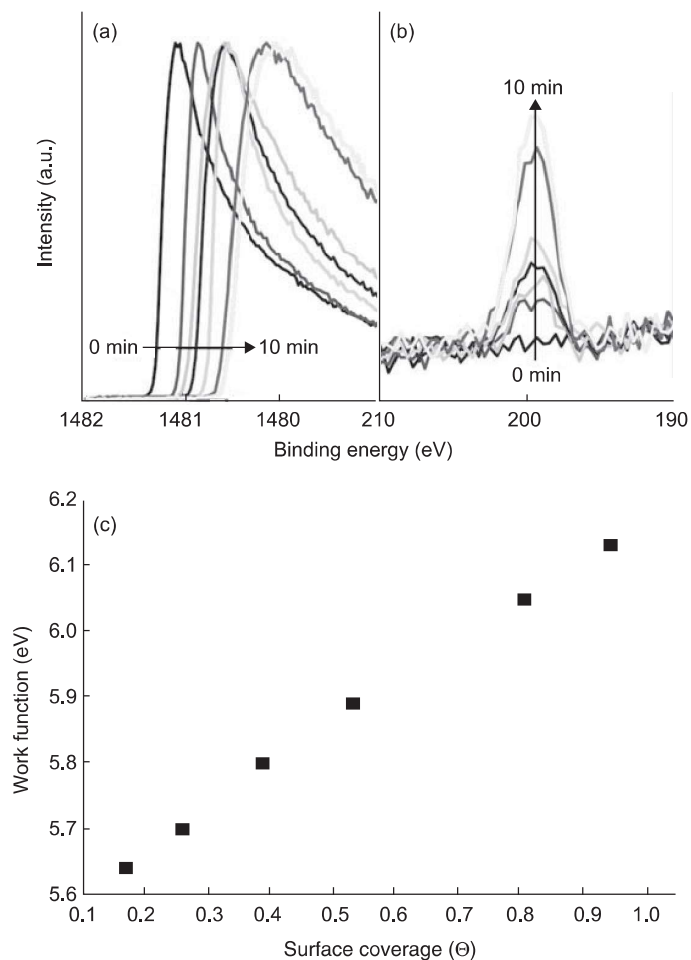
Another way to increase the work function of TCO electrodes is to chemically treat the substrate with an electronegative halogen (e.g. fluorine) or a halogen-containing acid (e.g. hydrochloric acid) (Li *et al.*, 1997, 2005; Sun *et al.*, 2003). Due to the electronegativity of the halogen, the work function of TCO substrate can be increased. However, these processes are difficult to control. The surface of the substrate may be etched leaving very little halogen functionalized to the surface of the substrate. Hence, the increase of work function may not be significant. Furthermore, the roughness, conductivity and transparency of the substrate may become worse using these processes.

The work function of a TCO substrate may also be increased using a halogen-containing plasma. For example, a fluorocarbon plasma such as CFH_3 , an inorganic fluorine containing plasma such as SF_6 , or a pure halogen plasma such as F_2 have been used to increase the work function (Hung *et al.*, 2001; Ikagawa *et al.*, 2008; Jo *et al.*, 2007). It is noted that halogen-containing plasmas are typically used as standard reactive ion etching (RIE) industrial processes to dry etch TCO substrates. Therefore, such treatment to increase the work function will etch the surface of the substrate, which may decrease the conductivity and contaminate the surface with halocarbons reducing the work function.

Recently, a new method was developed to increase the work function of TCO electrodes by reacting the surface with electronegative species that are obtained from a halogen-containing organic precursor (e.g., dichlorobenzene) under ultraviolet radiation (Helander *et al.*, 2011). The work function of the electrode can be tuned by controlling the surface coverage of halogen atoms (i.e., by precise control of the treatment time) (see Fig. 2.5). In particular, a chlorinated ITO (Cl-ITO) with a work function up to 6.1 eV has been demonstrated with approximately one monolayer of Cl atoms covered on the ITO surface. More importantly, the surface roughness, conductivity and transmittance of the Cl-ITO barely change as compared to regular ITO. Also, the high work function was found to be stable with time (see Fig. 2.6).

Another common method of increasing the work function of TCO electrodes is to coat the surface with a layer of another high work function material such as a polymer, for example poly(3,4-ethylenedioxythiophene:poly(styrenesulfonate) (PEDOT:PSS) (Carter *et al.*, 1997), or a transition metal oxide (e.g. WO_3 , MoO_3 and V_2O_5) (Wang *et al.*, 2009a, 2010c). However, introducing additional injection layers complicates the device structure and can often introduce additional problems with device stability. For example, the high acidity of PEDOT:PSS tends to erode the surface of ITO resulting in poor interfacial stability (de Jong *et al.*, 2000).

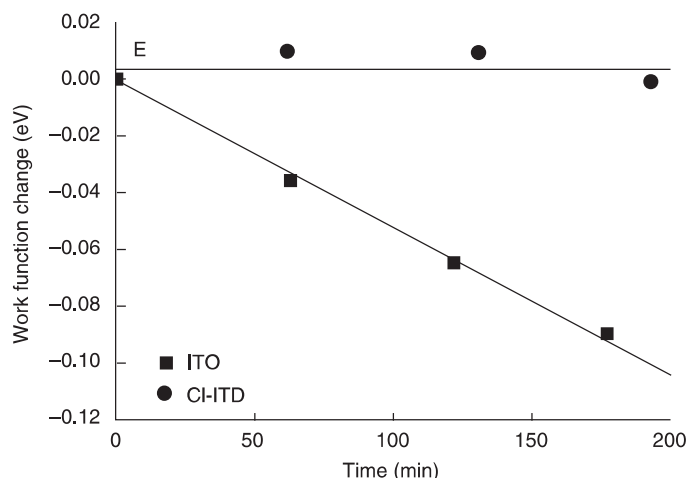
Although the majority of work function engineering has focused on increasing the work function, it is still of great importance to obtain a low work function transparent electrode from a stable electrode such as ITO. Low work function ITO can be achieved by surface treatment with an organic base such as tetrabutylammonium hydroxide $\text{N}(\text{C}_4\text{H}_9)\text{OH}$ (Nuesch *et al.*, 1999). Another commonly used strategy to lower the work function of an electrode is to coat the surface with an additional layer of low work function small molecules such as tetrakis(dimethylamino) ethylene (TDAE) (Osikowicz *et al.*, 2004) or inorganic materials such as Cs_2CO_3 (Huang *et al.*, 2007). However, low work function materials are usually reactive and unstable. Recently, a work function lower than 3.6 eV was demonstrated for ITO by coating a thin layer of polyethylenimine ethoxylated (PEIE) or branched polyethylenimine (PEI) on the surface (Zhou *et al.*, 2012). It was also found that the PEIE-coated ITO electrodes are fairly stable in ambient air. Moreover, this method was found to be universal to reduce the work function of a lot of other electrodes, such as ITO, ZnO, FTO, Au, Ag, Al and graphene.



2.5 Work function and Cl surface coverage. (a) Secondary electron cut-off and (b) Cl 2p peak as a function of increasing UV treatment time. (c) Work function as a function of Cl surface coverage (Θ); $\Theta = 1.0$ corresponds to one monolayer. Reprinted with permission from Helander *et al.*, 2011.

2.2.3 Application of high work function TCOs in OLEDs

In the previous subsection, different strategies of engineering the work function of TCOs have been introduced. Now we move on to discuss the application of high work function electrodes in simplified high efficiency OLEDs.

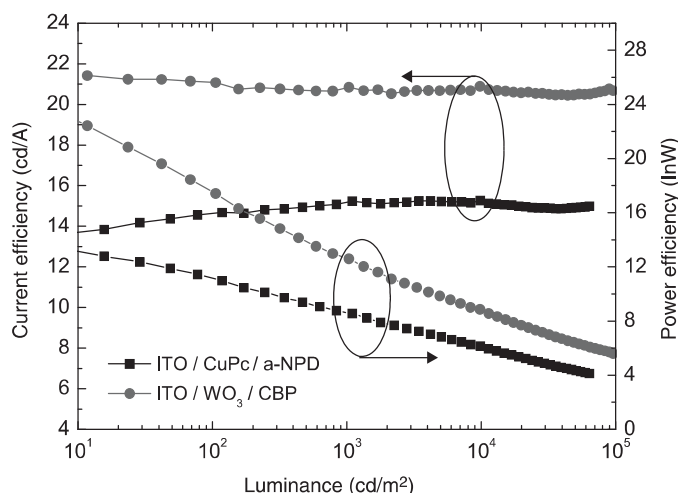


2.6 Stability of work function of Cl-ITO and UV-ozone cleaned ITO over time. Reprinted with permission from Helander *et al.*, 2011.

It was recently discovered that in simple α -NPD/Alq₃ heterjunction OLEDs [where Alq₃ is tris(8-hydroxy-quinolinato)aluminum], accumulated radical cations at the the α -NPD/Alq₃ interface negatively impact the device performance (Wang *et al.*, 2010c). To prevent the accumulation of radical cations, a hole transport material with very deep HOMO such as CBP may be used as HTL to replace α -NPD. Therefore, the challenge with using a molecule like CBP with a HOMO of 6.0 eV (Wang *et al.*, 2010b) as HTL is the high injection barrier from an ITO electrode with a work function of less than 5.0 eV.

Of course, a step-wise device design as mentioned before with a structure of ITO/HIL/ α -NPD/CBP/Alq₃ can be used to overcome this challenge, where the HIL is a hole injection layer such as copper phthalocyanine (CuPc). The device efficiency was indeed found to be about ~ 20% increased by using this structure (Wang *et al.*, 2010b). However, it is apparent that this is not an optimal device design strategy as the structure is significantly more complicated. More recently, direct hole injection into CBP was demonstrated using an ITO/WO₃ (1 nm) anode, where WO₃ served as a surface modification layer to increase the work function (Wang *et al.*, 2010c). The drop-in replacement of the α -NPD HTL with CBP enhanced the device efficiency >40% in fluorescent OLEDs doped with 2,3,6,7-tetrahydro-1,1,7,7-tetramethyl-1H,5H,11H-10-(2-benzothiazolyl) uinolizino-[9,9a,1gh] coumarin (C545T) as compared with traditional device designs (see Fig. 2.7).

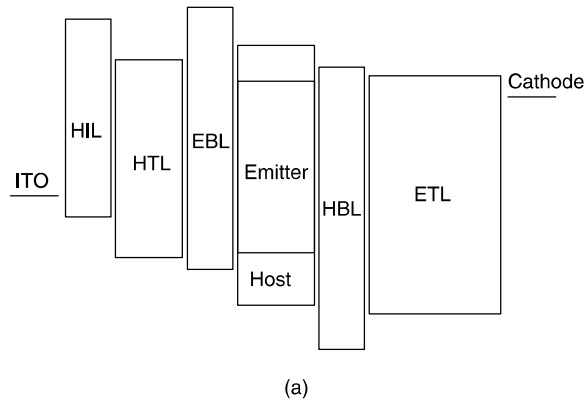
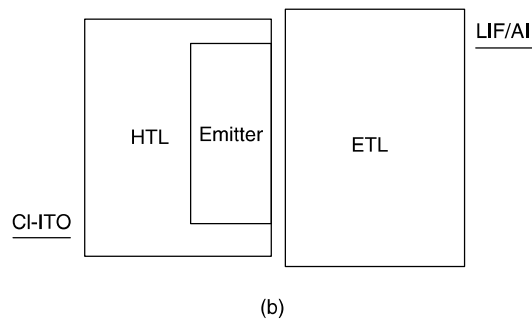
One may argue that using the design of ITO/WO₃/CBP does not really simplify the device structure that much as compared to the step-wise design,



2.7 Current efficiency and power efficiency as a function of luminance of using α -NPD and CBP as HTL. Adapted with permission from Wang *et al.*, 2010c.

because the use of WO_3 (or any other high work function transition metal oxide to functionalize the surface) also adds an additional layer to the device, i.e. a high work function HIL. However, this layer can be completely eliminated if a high work function Cl-ITO electrode is used instead. More importantly, this device design concept, i.e. using a deep HOMO HTL that is enabled by a high work function anode, has even more advantages in phosphorescent OLEDs.

It is generally believed that a nearly 100% internal quantum efficiency may be achieved in a phosphorescent OLED. Due to the much longer lifetime of the triplet excited states in phosphorescent OLEDs than the singlet states in fluorescent OLEDs, a lot of other functional layers, i.e. hole blocking layers, electron blocking layers and exciton blocking layers, have been used to confine the excitons in the emission zone to enhance the device performance (Ikai *et al.*, 2001; Adamovich *et al.*, 2003; O'Brien *et al.*, 1999). Other device designs such as double emission zones have also been shown to improve the performance of phosphorescent OLEDs (He *et al.*, 2004). Therefore, a high performance phosphorescent OLED is usually a lot more complicated (see Fig. 2.8a) than a fluorescent OLED. Extending the deep HOMO HTL design introduced above, Helander *et al.* (2011) demonstrated a highly simplified phosphorescent green OLED using high work function Cl-ITO. In the device, CBP was used as both HTL and host for the phosphorescent emitter, bis(2-phenylpyridine) (acetylacetonate) iridium(III) $[\text{Ir}(\text{ppy})_2(\text{acac})]$ (see Fig. 2.8b). Not only did this design tremendously simplify the device structure, it also reached a record high device efficiency (see Fig. 2.9).

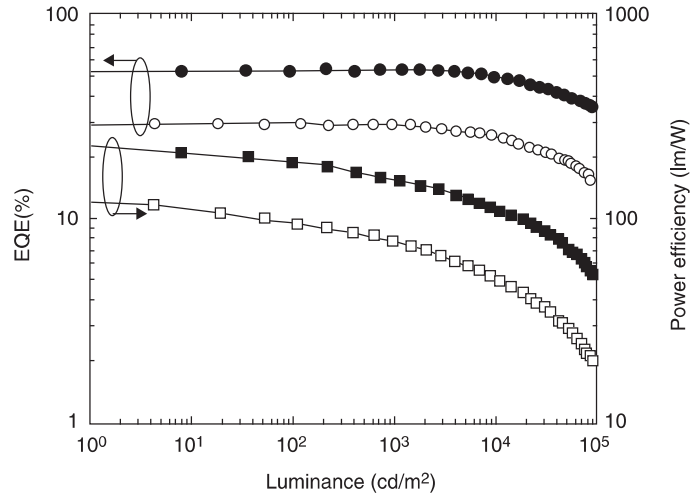


2.8 Schematic energy-level diagram of: (a) complex multi-layer OLED structure with different functional layers; (b) simple bi-layer OLED structure using CI-ITO (Helander *et al.*, 2011).

2.3 Semitransparent metal thin film electrodes

2.3.1 Optical properties of metal thin films

As mentioned above, ITO is the *de facto* standard anode in OLEDs due to its high conductivity, transparency and relatively high work function. However, ITO also has some problems that may limit the potential applications of OLEDs. For example, to achieve low resistivity, ITO usually requires a high annealing temperature, which is not compatible to most plastic substrates. One of the major advantage of OLEDs is that they can be fabricated on lightweight flexible plastic substrates with low manufacturing cost using roll-to-roll processing (Forrest, 2004). Using semitransparent metal thin films as a direct drop-in replacement for



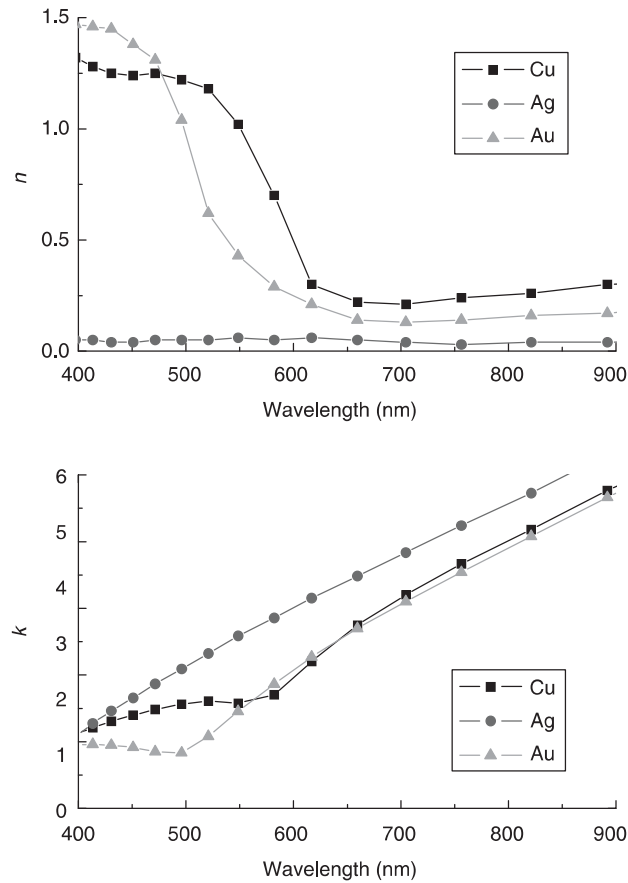
2.9 Extremely high efficiency of phosphorescent OLED achieved using a CI-ITO anode. Solid points correspond to the result with optical out-coupling. Reprinted with permission from Helander *et al.*, 2011.

ITO may solve this problem due to their ease of patterning and deposition. Moreover, metal thin films, in particular noble metals, have an even lower resistivity than ITO of $10^{-6} \Omega\cdot\text{cm}$. A lower resistivity is of great significance to large area OLEDs for lighting applications to achieve uniform luminance. Metal thin film electrodes also have advantages in top emission OLEDs used in flat panel display applications; top emission OLEDs are more suitable than traditional bottom emission OLEDs in high resolution active matrix OLED displays as the aperture ratio can be higher (Lu *et al.*, 2002).

Although metal thin films may have some superior properties to ITO electrodes, according to Maxwell equations that describe the propagation of light in a medium, metals damp the intensity of light in a relatively short distance, i.e. metal thin films used as electrodes in OLEDs will absorb the emitted light. Figure 2.10 summarizes the refractive index of the noble metals Cu, Ag and Au. The imaginary part of the refractive index k is also called the damping constant or absorption constant as it is proportional to the absorption coefficient α ,

$$\rho(\epsilon) = \frac{1}{\sqrt{2\pi\sigma}} \exp\left(-\frac{\epsilon}{2\sigma^2}\right). \quad [2.5]$$

Figure 2.11 shows the transmission of Au thin films with different thickness as compared to ITO in the visible range. Clearly, the transmission of Au is a lot lower

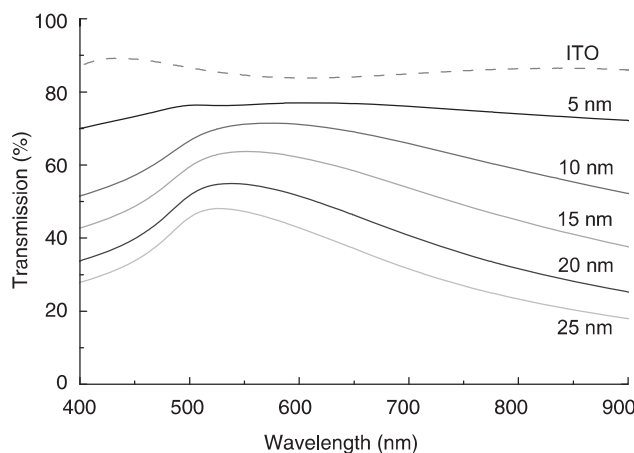


2.10 Refractive index of Cu, Ag and Au thin films in the visible range. Data were obtained from Johnson and Christy, 1972.

(semitransparent) than ITO when the thickness is >10 nm. However, this does not mean that Au thin films are not suitable for OLED electrodes. Although the absorption coefficient of gold is large, the high reflectivity of the metal can be taken advantage of to design a micro-cavity in OLEDs to enhance the optical out-coupling of light (Helander *et al.*, 2010b; Smith *et al.*, 2004; Thomschke *et al.*, 2009; Wang *et al.*, 2011; Chen *et al.*, 2010).

2.3.2 Electrical properties of metal thin films

As discussed above, the thickness of metal thin films should be as thin as possible to reduce the absorption. However, the conductivity of metal thin films is also

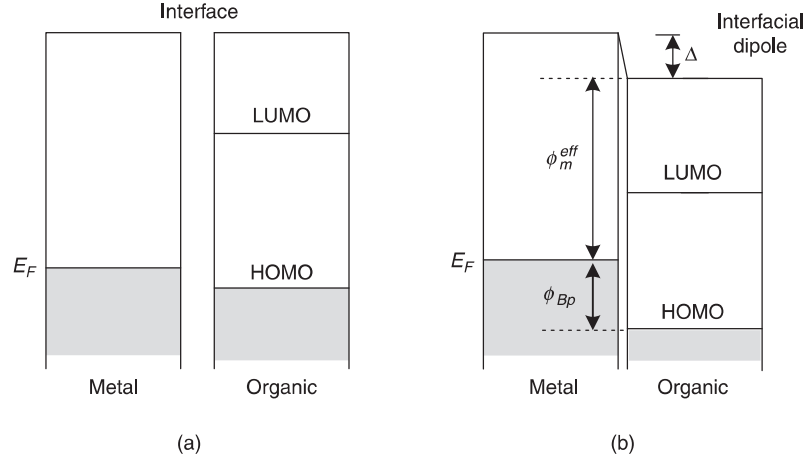


2.11 Transmission of Au thin films with different thickness as compared to ITO. Adapted with permission from Helander *et al.*, 2010b.

highly dependent on the thickness and morphology of the films. For example, there have been extensive studies about the influence of grain boundaries on the conductivity of nano-crystalline Au thin films at different thicknesses (van Attekum *et al.*, 1984; Zhang *et al.*, 2006b; Vries, 1987). Generally, the smaller the thickness the lower the conductivity becomes. Although the overall conductivity of metal thin films is lower than the corresponding bulk materials, it is still high enough to outperform ITO.

However, there may be another important factor that hinders metal thin films from replacing ITO anodes. It is well known that there exist strong interfacial dipoles at metal/organic interfaces (Ishii *et al.*, 1999) which may eventually change the energy level alignment and thus change the injection barrier (Helander *et al.*, 2008b). For example, Au has high work function of up to 5.3 eV. However, the hole injection barrier between Au and α -NPD (with a HOMO of 5.4 eV) is >1.0 eV, i.e. much larger than the difference between work function of Au and the HOMO of α -NPD. The cause of such a big difference is the interfacial dipole formed at the Au/ α -NPD interface. Figure 2.12 illustrates the formation of an interfacial dipole at a metal/organic interface, i.e. schematic energy diagrams of a metal and an organic material (a) before and (b) after making contacts.

In traditional semiconductor physics, the band alignment for Schottky contacts formed at metal/semiconductor interfaces can be described by the interface dipole theory (Robertson, 2002; Mönch, 1994; Yeo *et al.*, 2002). The formation of an interfacial dipole was explained by the charge neutrality level, i.e. the point at which the interface is equally donor- and acceptor-like, of the semiconductor, which tends to align with the Fermi level of the metal. It was argued that this



2.12 Schematic energy diagram at metal/organic interface (a) before and (b) after making contact.

theory can also be used to describe metal/organic interfaces (Mönch, 2006; Helander *et al.*, 2008b).

According to this theory, the effective work function ϕ_m^{eff} of the metal, which is defined as the difference between the work function of the metal and the interfacial dipole, i.e. $\gamma\phi_m^{\text{eff}} = \phi_m - \Delta$ (see Fig. 2.12b), can be described as (Cowley and Sze, 1965):

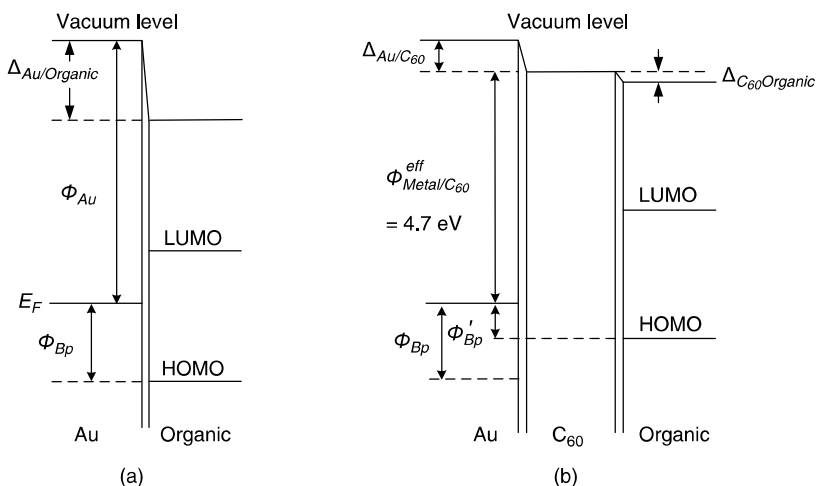
$$\phi_m^{\text{eff}} = \phi_{\text{CNL}} + S_\phi (\phi_m - \phi_{\text{CNL}}). \quad [2.6]$$

In Eq. 2.6, S_ϕ is the interface slope parameter that describes how much the Fermi level of the metal can be pinned to the charge neutrality level of semiconductor. Empirically, it was found that for weakly interacting interfaces, this parameter can be described as a function of the optical dielectric constant ϵ_∞ as (Mönch, 1987):

$$S_\phi = \frac{1}{1 + 0.1(\epsilon_\infty - 1)^2}. \quad [2.7]$$

2.3.3 Applications of semitransparent metal thin films as electrode in OLEDs

A lot of work has been done to disrupt the strong interfacial dipole at metal/organic interfaces to enable metals as efficient anodes. For example, a thin layer of C_{60} (3 nm) was shown to improve the charge injection from Au to CuPc (Han *et al.*, 2006). The injection improvement of using Au/ C_{60} anode was ascribed to the Fermi level pinning to the charge neutrality level of C_{60} of 4.7 eV (see Fig. 2.13)



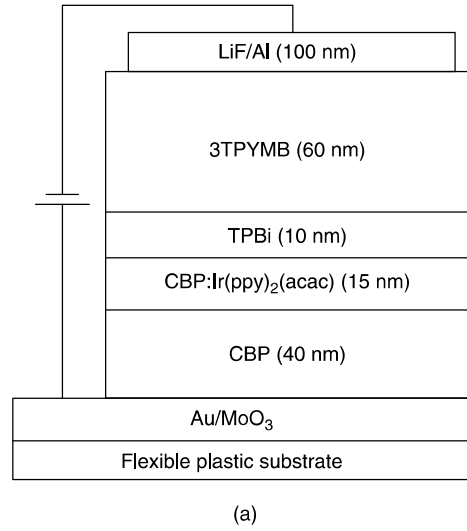
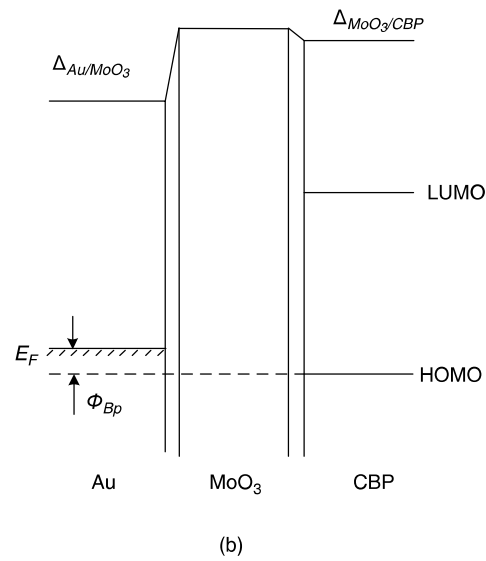
2.13 Energy level alignment at the (a) Au/organic interface and (b) Au/C₆₀/organic interface. Adapted from Wang *et al.*, 2009b.

(Wang *et al.*, 2009b). It was also found that C₆₀ can also increase the charge injection for other metals such as Cu, Ag and Mg due to Fermi level pinning (Helander *et al.*, 2008a).

Although C₆₀ can enable Au as anode, a HIL such as CuPc is still needed, i.e. the effective work function of Au/C₆₀ is only ~4.7 eV, which is not sufficiently high. To take advantage of the better device design strategy of using deep HOMO HTL as discussed in the previous section, a much higher work function is still needed.

Another commonly used method to improve the effective work function of metals is to add an additional thin layer of metal oxides, such as the high work function transition metal oxides that have been successfully employed to enhance the work function of ITO (Cao *et al.*, 2006; Wang *et al.*, 2011; Jiang *et al.*, 2007). This strategy can easily improve the effective work function to more than 6.0 eV. Alternatively, metal oxides formed by oxidation using UV-ozone or O₂ plasma from pure metal films have also been shown to improve the hole injection. For example, Ag/AgO (Choi *et al.*, 2005), Cu/CuO (Murdoch *et al.*, 2008) and Au/AuO_x (Helander *et al.*, 2010b) have been demonstrated as anodes in OLEDs.

Figure 2.14a provides an example of using MoO₃ (1 nm) modified Au as a semitransparent anode in phosphorescent OLEDs. Figure 2.14b is the corresponding schematic energy diagram at the Au/MoO₃/CBP interface explaining how a thin layer of MoO₃ disrupts the strong interface dipole and thus improves the hole injection from Au into CBP with deep HOMO level.



2.14 (a) Device structure of using Au/MoO₃ as anode on flexible substrate (Wang *et al.*, 2011). (b) Schematic energy diagram at Au/MoO₃/CBP interface.

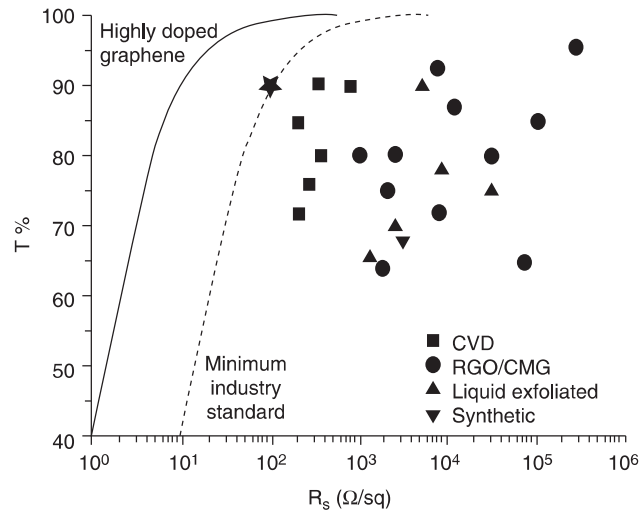
2.4 Carbon-based thin film electrodes

Another important group of transparent conductive thin films is the carbon-based thin films, such as conductive polymers, carbon nanotubes (CNTs) and graphene. Driven by the development of flexible electronics, there has been extensive research on these carbon-based thin film electrodes for ITO replacement.

Poly(3,4-ethylene):poly(styrene sulfonate) (PEDOT:PSS) is one of the most thoroughly studied conductive polymers and has been developed as a transparent conductive electrode for various optoelectronic devices (Na *et al.*, 2008, Cai *et al.*, 2011; Zhou *et al.*, 2012). More detail about the synthesis and conduction mechanism in PEDOT:PSS can be found in Hecht *et al.* (2011) and Ouyang *et al.* (2004). Higher conductivity and transparency is still the major challenge for any practical use of conducting polymers as a replacement for ITO in OLED applications. Instead, conductive polymers have been more commonly used as HILs to increase the power efficiency of the OLED due to its relatively high conductivity (as compared to other regular hole transport materials) and high work function (5.0–5.2 eV). (Helander *et al.*, 2009). Another major challenge for conductive polymers is their stability. For example, the conductivity may decrease with exposure to high temperatures and humidity. (Nardes *et al.*, 2008; Vitoratos *et al.*, 2009, Yue *et al.*, 1991).

CNTs are also one of the promising candidates for ITO replacement in flexible optoelectronics due to their high transparency in the visible range (Wu *et al.*, 2004; Zhang *et al.*, 2005, 2006a). However, there are still two major challenges for CNT electrodes in OLED applications. Reports of high performance OLEDs achieved on CNT electrodes still remain rare. First of all, although the conductivity of an individual CNT is very high, the junction resistance between two CNTs is very high. Therefore, a high density of CNTs above the percolation threshold is needed and the typical sheet resistance is only in the range of 100–200 Ω/sq (Liangbing *et al.*, 2010). The other challenge is the high surface roughness which will make the light emission in OLEDs very ‘patchy’, i.e. non-uniform emission. Moreover, it was found that the protruding tubes may easily short the OLED device (Liangbing *et al.*, 2010), which is not desirable in large area OLEDs. Usually, an additional layer of conductive polymer such as PEDOT:PSS will be coated on top of the CNTs to smooth the surface.

Graphene is so far the most promising carbon-based thin film electrode as a replacement for ITO due to its very high transparency and conductivity. Figure 2.15 summarizes the transmittance and sheet resistance data of graphene thin films fabricated with different methods reported in the literature up until 2010 (De and Coleman, 2010). More recently, a sheet resistance of as low as 30 Ω/sq has been achieved in a four-layer graphene film doped with HNO_3 (Han *et al.*, 2012; Bae *et al.*, 2010). The properties and fabrication methods of graphene have been nicely summarized in other review papers (Pang *et al.*, 2011; Hecht *et al.*, 2011).



2.15 Transmittance and sheet resistance data reported in the literature. Reprinted with permission from De and Coleman, 2010.

The relatively low work function of graphene of $\sim 4.4\text{ eV}$ is one of the major limits for OLED applications. The most commonly used method to solve this problem is adding additional layers of high work function conductive polymers, such as PEDOT:PSS to tune the work function. For example, high performance flexible OLEDs have been recently demonstrated using graphene anode modified with a gradient hole injection layer comprised of PEDOT:PSS and a tetrafluoroethylene-perfluoro-3,6-dioxo-4-methyl-7-octenesulfonic acid copolymer (Han *et al.*, 2012).

2.5 Conclusion

In summary, three major types of transparent/semitransparent conductive thin films, i.e. transparent conducting oxide thin films, semitransparent metal thin films and carbon-based transparent conductive thin films, as electrodes in OLED applications have been discussed. The discussion has focused on the mis-match of the pristine work function of these thin films and the energy levels of the organic materials. Different approaches and related science about how to tune the work function have been presented as well. Particularly, the design of a highly simplified phosphorescent OLED with exceptionally high efficiency by using the high work function Cl-ITO of $>6.0\text{ eV}$ has also been shown, i.e. an example to show the importance of achieving high work function transparent conductive electrode.

Finally, despite recent advances in the development of alternative transparent conducting thin film electrodes, there are still several remaining challenges in order to unseat ITO as the *de facto* standard in OLEDs. The long term stability and device lifetime of new transparent conducting thin films needs to be examined on packaged devices operating under real conditions to ensure that the electrodes are stable for the lifetime of any commercial product they may be used in.

From a practical point of view, it is still not clear if scale-up of alternative transparent conducting thin film materials are truly viable. For example, state-of-the-art flat panel displays are manufactured on Generation 8.5 sized substrates ($2.2 \times 2.5 \text{ m}^2$). To date, only ITO is compatible with such large substrates with adequate uniformity, yield and processing time. Nonetheless, with the strong growing momentum behind OLEDs and other organic optoelectronics the present barriers to alternative low-cost transparent conducting thin film electrodes are poised to be overcome in the near future.

2.6 Sources of further information

Further reading materials for the TCO technology such as the fabrications and thin film properties can be found in Hoel *et al.* (2010), Minami (2008a,b) and Hamberg and Granqvist (1986). Further information about work function measurement and energy level alignment can be found in Herring and Nichols (1949) and Helander *et al.* (2010a).

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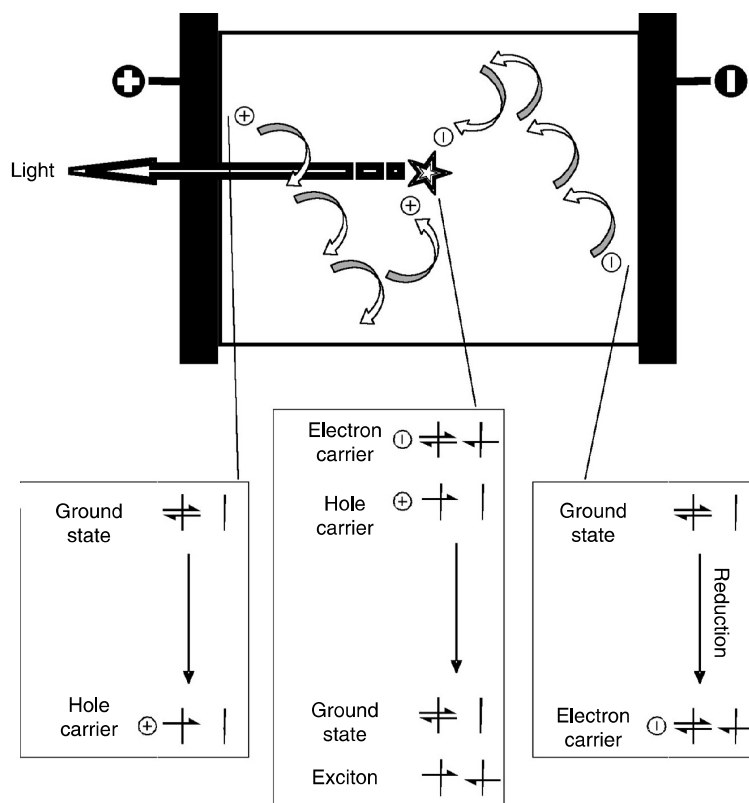
Abstract: The excited states generated in an organic light-emitting diode (OLED) by recombination of opposite charges may be singlet or triplet states, the latter being formed in ratios as high as 3 : 1 over the singlets. Such triplet states are normally non-emissive in a purely organic device, due to the spin selection rule. This chapter describes how phosphorescent complexes of heavy metal ions, particularly iridium(III) and platinum(II), can be used as dopants to induce emission from the triplet states, exploiting the high spin-orbit coupling constants of these elements. Design strategies for preparing highly luminescent metal complexes are discussed, together with methods for tuning the emission colour through rational structural modification. Examples of some representative blue, red and white-emitting systems are presented.

Key words: cyclometallated complexes, platinum, iridium, luminescence, OLED.

3.1 Introduction to triplet-emitting metal complexes in OLEDs

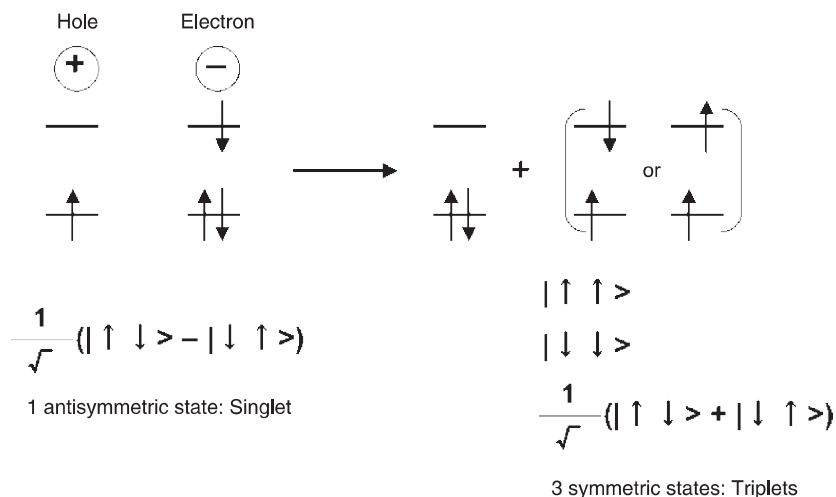
3.1.1 Electroluminescence versus photoluminescence: formation of the triplet state

The emission of light from organic light-emitting diodes (OLEDs) arises from excited states that are formed from the combination of electrons and holes, injected into a conjugated material by the application of an electric potential. In its simplest form, an OLED consists of an organic material sandwiched between two electrodes. The material becomes partially reduced at the cathode and partially oxidised at the anode, and the resulting electrons and holes migrate under the electric field towards the opposite electrode, transiently reducing and oxidising the organic molecules as they do so (Hung and Chen, 2002). The combination of two oppositely-charged species leads to the generation of one molecule in an excited state and the second in the ground state, as summarised in Fig. 3.1. The emission of light from the electrically-generated excited state is called electroluminescence (EL), similar to the better-known process of fluorescence (or photoluminescence, PL), where the source of energy used to access the excited-state molecule is light. There is an important difference between the two, however,



3.1 Schematic representation of electroluminescence in organic materials. The exciton formed as a result of charge recombination is, in this case, shown as a singlet state, but note that it may also be a triplet state – see Fig. 3.2.

which is at the heart of this chapter's topic. When the charge carriers combine in EL, they may do so to give either singlet or triplet states, according to whether the spins of the highest-energy electrons are parallel or antiparallel. Quantum mechanics shows that, statistically, there are three symmetric states (triplet states) formed for every antisymmetric (singlet) state (Fig. 3.2). In contrast, in the case of PL, normally only singlet states are populated by absorption of light, owing to the spin-selection rule $\Delta S=0$. Access to triplet states in PL normally occurs only by intersystem crossing (ISC) from the singlet states, and this process may be very inefficient in strongly fluorescent molecules. As a result, whilst a molecule may have a fluorescence quantum yield Φ_F as high as 1 in PL, the same molecule in EL will be limited to $\Phi_F=0.25$.



3.2 The excitons produced in the process shown in Fig. 3.1 may be singlets or triplets. Statistically, there are three triplet states formed for every singlet state.

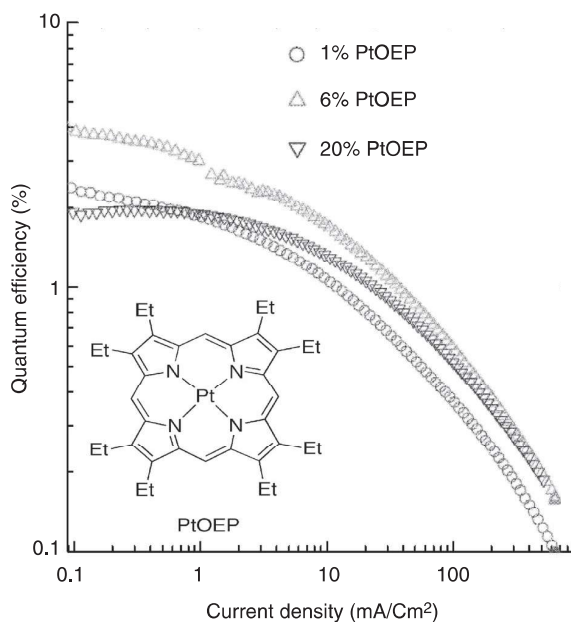
3.1.2 The role of heavy metal ions in facilitating emission from triplet states

The problem with the triplet states that are formed in EL is that the $T_1 \rightarrow S_0$ emission, termed phosphorescence, is spin-forbidden, owing to the same $\Delta S=0$ selection rule mentioned above. Phosphorescence from organic molecules is rarely observable under ambient conditions, because the rate constant of emission is too low compared to that of non-radiative processes (e.g. energy transfer into vibrations; reaction with quenchers such as molecular oxygen). In order to accelerate the triplet radiative rate constant and allow phosphorescence to be observed, spin-orbit coupling (SOC) is required, to break down the $\Delta S=0$ selection rule. Discussed in more detail in Section 3.3, SOC essentially mixes singlet and triplet character of excited states. The magnitude of the spin-orbit coupling constants, ζ , of atoms is proportional to Z^4 , and is hence most effective for heavy elements. It is for this reason that complexes of heavy metal ions, iridium(III) and platinum(II) in particular, have such interesting potential as OLED emitters (Yersin, 2007). The high ζ values of these metal ions, coupled with a judicious choice of ligands having appropriately positioned energy levels to mix well with atomic orbitals of the metals, have allowed materials to be developed over the past 15 years that emit with very high efficiency from triplet states.

By doping such phosphorescent compounds into the emissive layer of an OLED, emission from triplet states can be induced. The presence of the metal ion

also ensures that the $S_1 \rightarrow T_1$ process is accelerated, such that potentially all excitons – singlets and triplets – emit, and the internal quantum efficiency of the OLED can be increased up to 100%.

Platinum(II) octaethylporphyrin (Fig. 3.3) was the first metallophosphorescent dopant to be tested successfully for this purpose (Baldo *et al.*, 1998). When doped into the widely used EL emissive material Alq₃ {tris(8-hydroxyquinolino) aluminium}, a device with an internal EL quantum efficiency of 23% was obtained, and 90% of the energy from the Alq₃ host was transferred to the complex. Further optimisation of the device using a different host led to an internal efficiency of 32% (O'Brien *et al.*, 1999). However, at the higher currents necessary for high brightness devices, the efficiency was found to fall off dramatically (Fig. 3.3). This effect is due to severe triplet–triplet annihilation (equation 3.1): the triplet excited states of the platinum porphyrin molecules are so long (~60 μ s or more) that as their concentration increases, they have time to encounter one another and undergo this detrimental process.



3.3 The quantum efficiency of PtOEP emission as a function of current density for OLED devices comprising PtOEP doped into Alq₃ as the emitting layer, at the three concentrations shown (% by mass), revealing the steep roll-off in efficiency as the current is increased. Reproduced with permission from Baldo *et al.* (1998). Copyright 1998, Nature Publishing Group. The structure of PtOEP is shown in the inset.

In order to overcome this problem, it is clearly necessary to design and synthesise new molecular materials that have shorter triplet excited state lifetimes. Obviously, the lifetime should be made shorter by increasing the rate constant of radiative decay k_r , and not the rate constants of the non-radiative decay processes Σk_{nr} , in order not to compromise the efficiency of the system. An increase in k_r requires the SOC influence of the metal ion to be enhanced, and the ways in which this has been achieved are discussed in the sections that follow, with representative examples of molecular materials.

3.1.3 Desirable features of metal complexes for use as OLED emitters

The best classes of materials for the purpose are likely to satisfy the following criteria:

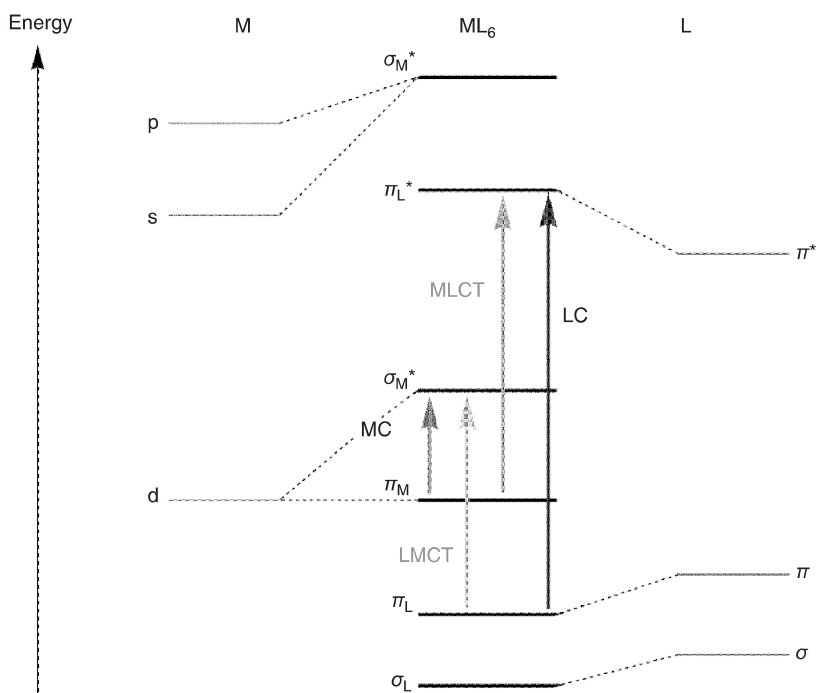
- They should be highly emissive, with phosphorescence quantum yields Φ_p ideally approaching unity at ambient temperature.
- The emission lifetime should be around 1 μ s or less, to avoid competition from triplet–triplet annihilation at high currents.
- Ideally, it should be possible to obtain efficient red, blue and green emitters by making small changes to the structure of the complexes, without fundamentally altering their chemistry or other properties.
- The compounds should be charge-neutral, in order to avoid migration under the influence of the applied electric field.
- They should have low molecular weight and either be sublimable (for incorporation into vacuum-processed devices) or readily soluble in organic solvents (for solution-processed devices).
- Complexes which have reversible oxidation and reduction processes at accessible potentials are attractive in that they can act as charge carriers and sites for exciton formation, rather than serving simply as acceptors of excited-state energy from excitons localised on the host molecules.
- They should normally not be susceptible to aggregation or segregation within the host material, as this frequently leads to self-quenching of the emission. Note, however, that in some cases, particularly for planar platinum complexes, the aggregate species may themselves be emissive, and this feature may then be deliberately exploited for the generation of NIR and white-light OLEDs – see sections 3.6 and 3.7 respectively.

3.2 Excited states of metal complexes

3.2.1 Overview

In order to appreciate the design strategies employed in the development of metal complexes as phosphors for OLEDs, it is useful to first provide an overview of the

main classes of excited states that are commonly encountered in d-block metal complexes. In the case of conjugated organic molecules, the excited states involved in fluorescence are usually either those associated with excitation of electrons from filled bonding π orbitals to empty π^* orbitals ($\pi-\pi^*$), or from non-bonding orbitals to π^* orbitals ($n-\pi^*$). The coordination of a transition metal ion to such a conjugated organic unit, acting as a ligand, introduces a greater variety of excited states that are typically best considered in terms of a molecular orbital (MO) description. Figure 3.4 represents a simplified MO diagram for a 6-coordinate metal complex. The d, s and p orbitals of the metal are able to bond to combinations of ligand orbitals offering appropriate symmetry. Although delocalised over all atoms in the molecule, the resulting MOs can frequently be classified as ‘ligand-based orbitals’ or ‘metal-based orbitals’ according to their positions, energetically, relative to the orbitals of the metal and ligands before complexation, and reflecting the distribution of electron density within them.



3.4 Simplified molecular orbital diagram for a typical octahedral metal complex, showing how the molecular orbitals have predominant metal or ligand character, allowing classification of electronic transitions as metal-centred (MC), ligand-centred (LC), metal-to-ligand charge-transfer (MLCT) or ligand-to-metal charge-transfer (LMCT).

Using such a description, it is easy to represent the four principal classes of transitions giving rise to electronic excited states as metal-centred $d-d^*$ (those involving metal-based orbitals only, labelled MC in Fig. 3.4), ligand-centred $\pi-\pi^*$ (similar to those for the isolated organic ligands, labelled LC), metal-to-ligand charge transfer $d-\pi^*$ (MLCT), and ligand-to-metal charge transfer $\pi-d^*$ (LMCT) (Balzani *et al.*, 2007). The order of energies of these transitions will be determined by the relative energies of the constituent ligand and metal orbitals. It should also be noted that there are both singlet and triplet states in each case, and their order may be different, since the effects of electron–electron correlation are more significant for more localised states (e.g. $d-d$ and $\pi-\pi^*$ rather than CT states).

Absorption bands corresponding to the excitation of the molecule from the ground state to the singlet states of each of these different types of excited states can, in principle, be observed for a given metal complex. In practice, the oscillator strengths of the CT and LC transitions tend to be much higher than those of the Laporte forbidden $d-d$ transitions, so that the latter may be concealed by the former. For small complexes of second- and third-row transition metals, of the type that will be discussed in subsequent sections, ISC is normally so efficient, being promoted by the SOC of the metal ion, that the singlet states convert to the lowest-energy triplet state on a timescale that is much faster than that of fluorescence. ISC rate constants $>10^{12} \text{ s}^{-1}$ have been measured for some of the archetypal complexes (Hedley *et al.*, 2009, 2011). Thus, it is the lowest-energy triplet state that is central to emission: its energy determines the colour of light emitted in PL and EL. Nevertheless, knowledge of higher-lying states – both singlet and triplet – can be very informative in understanding the efficiency and lifetime of the triplet state emission, as discussed in Section 3.3.

3.2.2 Complementary techniques: electrochemistry and theory

Since the pertinent excited states can often be rationalised in terms of the above MO description, knowledge of the oxidation and reduction potentials of the material can be useful in interpreting the excited-state energies. These are typically obtained using techniques such as cyclic voltammetry in solution. The oxidation potential provides an indication of the energy of the highest occupied MO (HOMO), whilst the reduction potential should be related to the energy level of the lowest-unoccupied MO (LUMO). The link between electrochemical and optical data has to be approached with some caution, not least because the excited-state molecule is a different chemical species from the ground-state molecule. Nevertheless, for CT states in particular, *trends* in excited-state energies of metal complexes of the types used in OLEDs frequently correlate well with $|E_{\text{ox}}^0 - E_{\text{red}}^0|$.

Meanwhile, time-dependent density-functional theory is becoming widely used to explore the distribution of electron density in the MOs and to identify those orbitals involved in the important excited states and their energies and oscillator

strengths (Hay, 2002; Williams *et al.*, 2008). Some examples of this approach appear in the later sections.

3.2.3 The quantum yield of emission

Aside from the energy of the lowest-lying triplet state, which determines the colour of the light emitted, the crucial parameter is the efficiency of emission, quantified as the quantum yield Φ . Assuming that the emitting state is formed with unitary efficiency, Φ is determined by the relative magnitudes of the rate constants of radiative (k_r) and non-radiative (Σk_{nr}) deactivation of the excited state, according to equation 3.2.

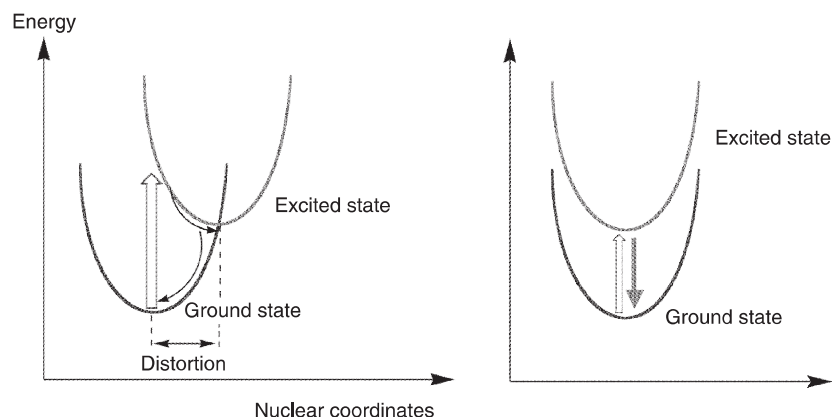
$$\Phi = k_r / (k_r + k_{nr}). \quad [3.2]$$

Evidently, to obtain an efficient emitter, it is necessary to maximise k_r and minimise k_{nr} , and the design of metal complexes for OLEDs revolves around these two objectives.

3.3 The pre-eminence of cyclometallated iridium(III) and platinum(II) complexes for OLEDs

3.3.1 The desirability of $^3\text{MLCT}$ states

Of the four classes of excited states described in Section 3.1.1, the most appropriate for the purpose of generating intense triplet emission, and hence use in OLEDs, is the metal-to-ligand charge transfer (MLCT). All the best contenders for use have lowest-lying triplet excited states that can be classified as MLCT or at least have significant MLCT character. A purely ligand-centred state is not suitable, because metal character is required to introduce the SOC that will promote the formally forbidden triplet-to-singlet emission. Ligand-centred states in metal complexes will tend to have low k_r values and hence long luminescence lifetimes, often around 100 μs or more and, in the extreme case, not much shorter than the corresponding uncoordinated proligand. It is precisely this effect that renders platinum porphyrins rather unsuitable for OLEDs, as mentioned in Section 3.1.2: the lowest-energy excited state is essentially $\pi-\pi^*$. At first sight, a metal-centred d-d state might sound attractive to ensure a high k_r . However, the formation of a metal-centred excited state typically involves population of an antibonding orbital (e.g. $t_{2g} \rightarrow e_g$ transition in an octahedral d^6 complex). This leads to longer bonds and hence substantial distortion in the excited state compared to the ground state. As a useful rule of thumb, excited state distortion is detrimental to emission, as it can lead to efficient pathways of non-radiative decay and hence to large k_{nr} values (Williams, 2007; Fig. 3.5). An MLCT state, on the other hand, ensures the participation of the metal required to facilitate triplet emission, but potentially without excessive distortion.

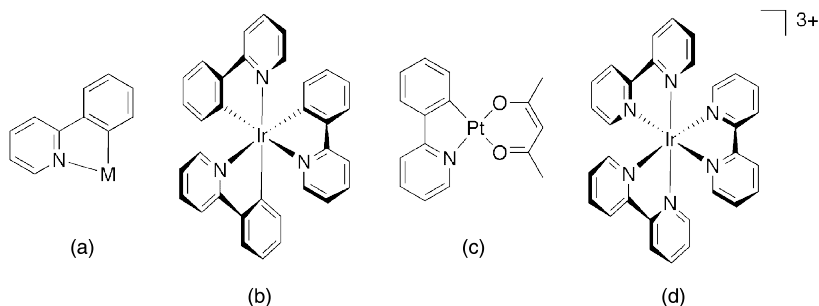


3.5 Simplified potential energy surfaces representing cases with and without significant distortion accompanying formation of the excited state (left and right respectively). A large distortion in the excited state compared to the ground state leads to non-radiative decay back down to the ground state (left), whereas rigidity favours emission (right).

3.3.2 Cyclometallated Ir(III) and Pt(II) complexes

Although rather simplistic, the above considerations are very useful in the design of efficient phosphorescent emitters, and account for the success of the large class of cyclometallated compounds that have been explored for use as OLED phosphors. The archetypal structural unit comprises an aryl heterocycle, frequently a 2-phenylpyridine unit, that is bound to the metal through the heteroatom of the heterocycle and through a metallated carbon atom *ortho* to the interannular bond (Fig. 3.6a). Cyclometallated compounds have been known for decades. Formally organometallic compounds in the sense that they contain M–C bonds, they are often particularly stable, due in part to the chelate effect.

The high degree of covalency in Ir–C and Pt–C bonds and, frequently, a good match between the energies of the highest filled metal and ligand-based orbitals, together with the presence of a low-energy π^* orbital associated with heterocycles such as pyridine, typically leads to the lowest-energy excited state being one of MLCT character or, at least, having a significant MLCT component (in some cases, the excited state may be better described as mixed $d/\pi \rightarrow \pi^*$ MLCT/LC) (Flamigni *et al.*, 2007). The most well-known example is *fac*-Ir(ppy)₃ (Fig. 3.6b) comprising three phenylpyridine ligands bound to iridium(III) and oriented in a facial arrangement, with each pyridyl group *trans* to a phenyl group (King *et al.*, 1985). This complex emits in the green region of the spectrum ($\lambda_{\text{max}} = 510 \text{ nm}$ in solution) with a quantum yield Φ of 0.97 [recently revised upwards from the value of 0.40 originally reported, which was probably underestimated due to the high

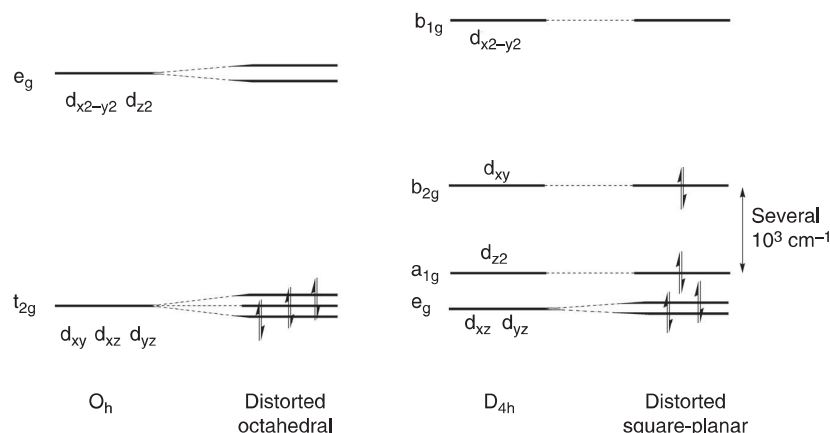


3.6 The structures of (a) the metallated phenylpyridine unit common to many of the most brightly luminescent metal-based emitters, (b) Ir(ppy)₃, (c) Pt(ppy)(acac) and (d) [Ir(bpy)₃]³⁺ (ppyH=phenylpyridine, acac=the anion of 2,4-pentanedione, bpy=2,2'-bipyridine).

sensitivity to quenching by O₂] (Sajoto *et al.*, 2009). The tris-cyclometallation also ensures that the complex carries no overall charge, as desired (Section 3.1.3). Similarly, the complex Pt(ppy)(acac), incorporating an analogous platinum-bound phenylpyridine unit (Fig. 3.6c), is phosphorescent in a similar region of the spectrum ($\lambda_{\text{max}}=486$ nm in solution in 2-methyltetrahydrofuran) with $\Phi=0.15$ (Brooks *et al.*, 2002). The lifetimes of these complexes, 1.9 and 2.6 μs respectively, are short enough to ensure that the triplet–triplet annihilation mechanism of deactivation will be insignificant when doped into a host material in an OLED. Corresponding coordination complexes of Ir(III) and Pt(II) that do not incorporate cyclometallated units typically have smaller k_r values, due to the lower participation of the metal and hence less efficient SOC. For example, for [Ir(bpy)₃]³⁺ (Fig. 3.6d), k_r is around 2×10^4 s⁻¹ compared to a value of 4×10^5 s⁻¹, around 20 times higher, for *fac*-Ir(ppy)₃ (Williams *et al.*, 2008).

3.3.3 SOC pathways

Although a useful guideline, the notion that all that is required to promote k_r for triplet emission is a lowest-lying triplet excited state of MLCT character is overly simplistic. The ³MLCT excited state must couple, through SOC, to ¹MLCT states, for which the transition to the singlet ground state is spin-allowed (Rausch *et al.*, 2007; Yersin *et al.*, 2011). The three substates of the triplet state may couple with different efficiencies to such higher singlet states. At very low temperatures the radiative rate constants of the substates may be very different from one another, but at room temperature there is equilibration between them, and the rate constant is determined by the most allowed transition. There is an inverse dependence between the radiative rate constant of a triplet substate i and $|E(T_1) - E(S_n)|$, the gap between the triplet state energy and that of the pertinent higher-lying singlet MLCT state. The best emitters are therefore likely to have low-lying ¹MLCT states. Moreover,

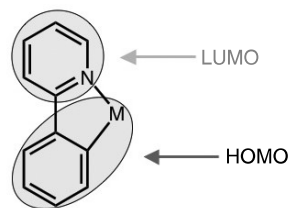


3.7 Splitting of the d orbitals in an octahedral (O_h) and distorted octahedral complex and in a square-planar (D_{4h}) and distorted square-planar complex. Note that, for an octahedral-based d^6 complex (e.g. iridium(III) complexes), there are filled d orbitals having similar energies, whereas for square-planar-based d^8 complexes (e.g. platinum(II) complexes), there is a large difference in energy between the highest filled d orbitals. Diagram based on that of Yersin *et al.*, 2011.

these $^1\text{MLCT}$ states with which the $^3\text{MLCT}$ state should couple must involve different filled d orbitals. Upon consideration of the ligand-field splitting diagrams for distorted octahedral and square-planar complexes (Fig. 3.7), it becomes immediately apparent that there are more likely to be energetically close-lying $^1\text{MLCT}$ states in the former than the latter, and it is probably for this reason that radiative rate constants tend to be higher for iridium complexes than for platinum analogues with the same types of ligands (Rausch *et al.*, 2007). Nevertheless, the quantum yields of the brightest Pt(II) complexes can be competitive with the best Ir(III) complexes, possibly because of lower non-radiative decay processes through fewer ligands being present (Rausch *et al.*, 2009a).

3.4 Colour-tuning strategies in cyclometallated complexes

Aside from the strong ligand field associated with cyclometallating ligands, which favours high emission efficiency, complexes of such ligands are also attractive because they offer control over the excited state energy, and hence emission colour, through rational substitution of the ligand in either of the two rings. Calculations based on time-dependent density functional theory typically reveal that, to a first approximation, the HOMO in such complexes is based primarily on the metal and metallated aryl ring, whilst the LUMO is largely associated with the



3.8 In complexes of cyclometallated arylpyridines, the HOMO is typically based largely on the metal and metallated aryl ring, whereas the LUMO is based on the pyridine ring.

heterocycle (e.g. the pyridyl ring in the case of ppy complexes; Fig. 3.8) (Hay, 2002). As a result, substituents introduced into the metallated aryl ring tend to affect the HOMO energy much more than the LUMO, whilst the reverse is true for the heterocyclic ring. Obviously, the effects will depend on the position of substitution within the rings, and caution must be applied particularly for substituents in the 5-position which are conjugated through to the other ring, and which may therefore have a significant effect on both frontier orbitals (Dixon *et al.*, 2000). Nevertheless, the simple picture is a very useful one. Since electron-withdrawing substituents normally stabilise molecular orbitals, be they filled or empty, while electron-donating substituents destabilise orbitals, it becomes quickly apparent how to tune the emission from the 'parent' complex {e.g. the green emitter *fac*-Ir(ppy)₃} either towards the blue or the red:

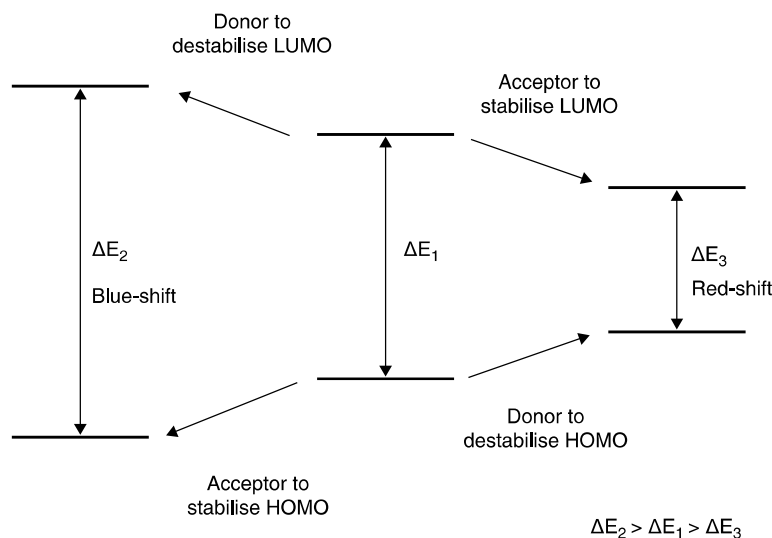
Blue-shift: should be achieved by introducing electron-withdrawing substituents into the metallated aryl ring to decrease the HOMO level and/or electron-donating substituents into the heterocyclic ring (the pyridyl ring in the case of ppy complexes) to increase the LUMO level; i.e. HOMO–LUMO gap increased.

Red-shift: should be achieved by introducing electron-donating substituents into the metallated aryl ring to increase the HOMO level and/or electron-withdrawing substituents into the heterocyclic ring to decrease the LUMO level, i.e. HOMO–LUMO gap decreased.

These strategies are summarised schematically in Fig. 3.9.

It should also be noted that the use of metallated aryl rings with more extended conjugation (e.g. fused polyaromatic hydrocarbons and related electron-rich heterocycles frequently containing sulfur), will also typically lead to a narrowing of the HOMO–LUMO gap, just as in organic molecules.

In the sections that follow, we shall present selected examples of blue- and red-emitting complexes that have been successfully designed and tested in OLEDs using these design principles. There are already excellent green emitters available, represented by the parent structures such as *fac*-Ir(ppy)₃; research is therefore targeted mostly at the blue and red. The coverage is by no means comprehensive,



3.9 The effect of electron-donating and withdrawing groups on the energies of orbitals allows control over the energy gap between the frontier orbitals and hence the colour of emission.

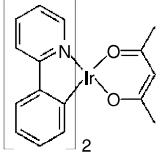
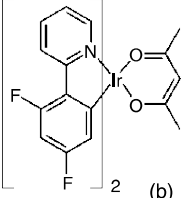
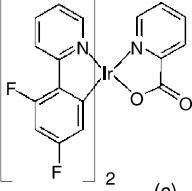
a vast range of elegant systems having been reported over the past decade. Rather, our objective is to present a flavour of some of the types of compounds investigated and the rationale behind them.

3.5 Blue-emitting complexes

Blue emitters have proved to be particularly challenging, due to the need for high energy emission from a large HOMO–LUMO gap in the phosphor. Blue-emitting complexes tend to exhibit poorer colour purity and lower efficiency than red and green phosphors (Fu *et al.*, 2011). A further complication is the long-term chemical stability of blue emitters, which remain less robust than lower energy emitters.

3.5.1 The influence of fluorine substituents in the aryl ring

The design of many of the blue emitters investigated can be understood using the guidelines presented in Section 3.4. The introduction of inductively electron-withdrawing fluorine atoms into the phenyl rings of $\text{Ir(ppy)}_2(\text{acac})$ (at the 3 and 5 positions, where position-1 is the metallated carbon), to give $\text{Ir(F}_2\text{ppy)}_2(\text{acac})$, leads to a lowering of the HOMO with little effect on the LUMO, and hence to a blue-shift in the emission (Fig. 3.10) (Rausch *et al.*, 2009b). Electrochemical data confirms this interpretation: the oxidation potential is anodically shifted by around

			
	(a)	(b)	(c)
$\lambda_{\text{max}}/\text{nm}$	516	486	471
E_{OX}/V	0.87	1.22	1.37

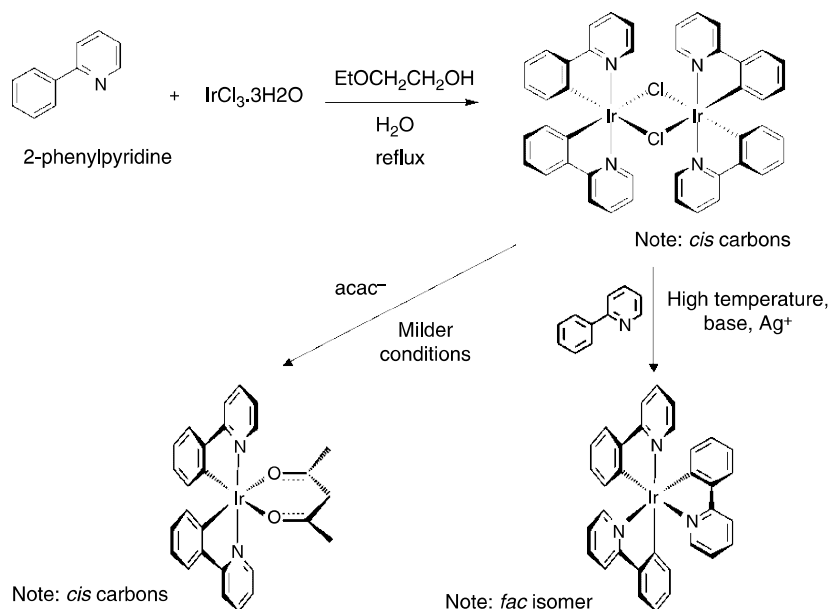
3.10 Strategies for shifting the colour of complexes based on $\text{Ir}(\text{ppy})_2(\text{acac})$ (a) towards the blue. The F atoms in the phenyl ring of (b) stabilise the HOMO, leading to an anodic shift of the oxidation wave and a shift of the emission to the blue. Replacement of the acac ligand by picolinate in (c) leads to a further stabilisation of the HOMO.

0.35 V, indicative of the stabilisation of the HOMO. A further blue shift is achieved upon replacement of the O[^]O-coordinated acac co-ligand by the N[^]O-coordinating picolinate ligand (pic) to give $\text{Ir}(\text{F}_2\text{ppy})_2(\text{pic})$ frequently known as FIrpic. This effect can be understood in terms of a further lowering of the HOMO, seen also in the anodic shift of the oxidation potential (Fig. 3.10), due to the more electron-deficient nature of pic compared to acac.

FIrpic was introduced as a blue emitter into OLED technology by Adachi *et al.* (2001) and has since been employed frequently both in blue and white devices (see also Section 3.7). For example, an external efficiency, η_{ext} , of $10.1 \pm 0.5\%$ has been achieved in a multi-layer device with Commission Internationale d'Eclairage (CIE) coordinates of (0.16, 0.29) (Lee *et al.*, 2008).

It is perhaps pertinent to mention at this point that the use of these heteroleptic $\text{Ir}(\text{N}^{\wedge}\text{C})_2(\text{L}^{\wedge}\text{X})$ complexes, comprising *two* cyclometallating aryl ligands in combination with one other bidentate $\text{L}^{\wedge}\text{X}$ ligand coordinated via heteroatoms, is driven partly by the ease of synthesis of the $\text{Ir}(\text{N}^{\wedge}\text{C})(\text{L}^{\wedge}\text{X})$ class compared to *fac*- $\text{Ir}(\text{N}^{\wedge}\text{C})_3$ systems. In the latter case, high temperatures are typically required to introduce the third $\text{N}^{\wedge}\text{C}$ ligand and to rearrange from the *mer* to more emissive *fac* geometry (Fig. 3.11). In contrast, $\text{L}^{\wedge}\text{X}$ ligands such as acac and pic can be introduced under mild conditions. In some cases, the $\text{L}^{\wedge}\text{X}$ ligand does not behave simply as an ancillary ligand influencing the metal d orbitals only: the localisation of the excited state can be displaced to this ligand if low-energy orbitals are available on it (e.g. Yoo and Park, 2005; Baranoff *et al.*, 2011).

The $\text{Ir}(\text{F}_2\text{ppy})_2$ unit has also been incorporated into dendrimeric OLED phosphors: Lo *et al.* (2005) reported an external efficiency of 10.4% measured at 100 cd m^{-2} and 6.4 V for such a system, which emitted blue light akin to that of FIrpic. Inductively electron-withdrawing trifluoromethyl groups on phenylpyridine

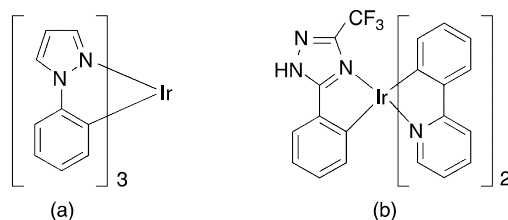


3.11 The synthesis of iridium complexes containing cyclometallated phenylpyridine rings typically proceeds via the chlorobridged dinuclear compounds. Cleavage of such dimers with a third cyclometallating ring usually requires high temperatures, leading to the facial isomers of the $\text{Ir}(\text{C}^{\wedge}\text{N})_3$ compounds. In contrast, reaction with $\text{O}^{\wedge}\text{O}$ or $\text{N}^{\wedge}\text{O}$ ligands (such as *acac* and *pic* respectively) occurs under milder conditions.

have also been shown to shift light towards the blue region of the spectrum in iridium complexes. For example, Tokito *et al.* (2003) achieved an external efficiency of 11% at a current density of 0.01 mA cm^{-2} for a green-blue device incorporating $(3,5\text{-CF}_3\text{-ppy})_2\text{Ir(pic)}$.

3.5.2 Electron-rich heterocycles

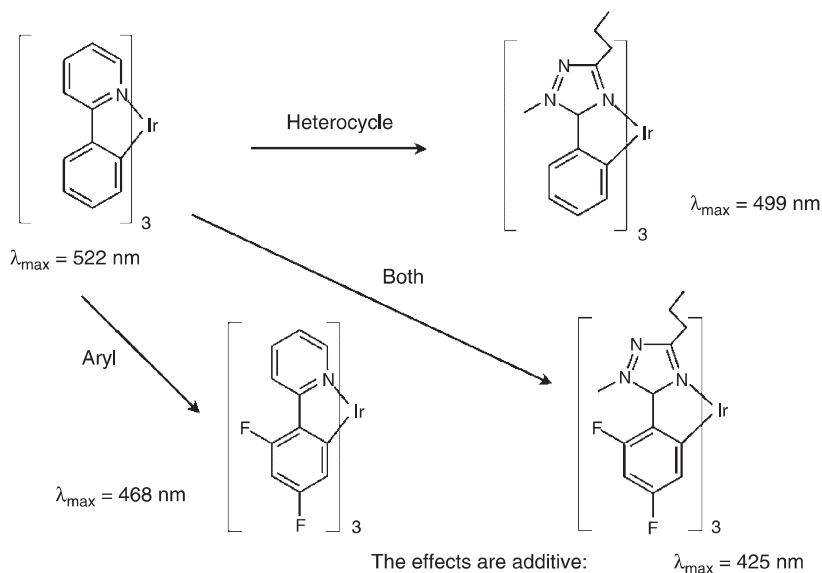
As described in Section 3.4, apart from lowering the HOMO, which is the predominant effect of the F atom in Section 3.5.1, the other way to blue-shift the emission should be to raise the energy of the LUMO. This can be achieved by introducing electron-donating substituents into the pyridine ring of ppy (*vide infra*) or replacing the pyridyl ring altogether by a more electron-rich azaheterocycle with a higher π^* orbital. The MLCT energy will then necessarily be increased. An early example of the latter case was the observation that *fac*- $\text{Ir}(\text{ppz})_3$, where ppz is phenyl-1-pyrazole (Fig. 3.12a), emits deeply in the blue ($\lambda_{\text{max}} = 414 \text{ nm}$ at 77 K).



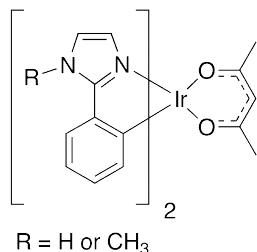
3.12 (a) Structure of $\text{Ir}(\text{ppz})_3$. (b) Heteroleptic iridium complexes incorporating a 5-aryl-1H-1,2,3-triazole ligand.

However, its emission at room temperature is too weak to be useful, $\Phi < 10^{-3}$ (Tamayo *et al.*, 2003).

By using a C-linked triazole unit in place of the N-linked pyrazole of ppz, Lo *et al.* (2006) were able to obtain complexes which, though less shifted to the blue, were more strongly luminescent at ambient temperature. Moreover, the LUMO-raising effect can be combined with the HOMO-lowering effect of F substituents in the phenyl ring, in an essentially additive manner, as summarised in Fig. 3.13. CIE coordinates of (0.16, 0.20) and (0.16, 0.12) were obtained for OLEDs



3.13 Strategies for blue-shifting the emission of $\text{Ir}(\text{ppy})_3$ -based complexes through replacement of the pyridyl ring by a more electron-rich triazole unit. The effect can be combined with the HOMO-lowering effect of phenyl F substituents. Data from Lo *et al.*, 2006.



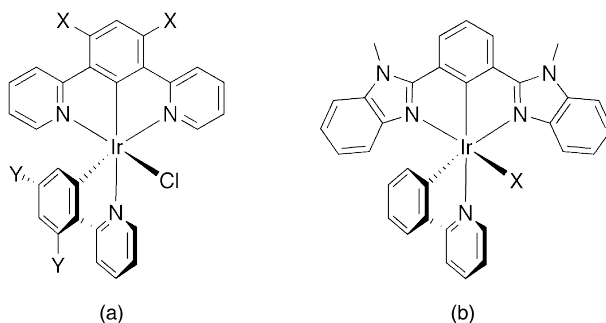
3.14 Blue-emitting iridium complexes with phenylpyrazole and phenylimidazole ligands.

prepared using each of the non-fluorinated and difluorinated triazolate complexes, respectively, although the efficiency drops off markedly for the latter. 5-Aryltriazole ligands have also been incorporated into heteroleptic complexes with two F₂ppy ligands. For example, for complexes based on the structure in Fig. 3.12b with differently substituted ppy ligands, λ_{max} values range from 530 to 455 nm and quantum yields from 0.70 to 0.38 (Mak *et al.*, 2005); the corresponding CIE coordinates span a large area of the blue region from (0.12, 0.15) to (0.40, 0.57).

Like pyrazoles and triazoles, imidazoles are also more electron-rich than pyridines and can likewise be used to blue-shift emission. Blue-emitting devices have been prepared using complexes that incorporate C-linked 2-phenylimidazole ligands, such as that shown in Fig. 3.14 (Kim *et al.*, 2007).

3.5.3 Examples incorporating tridentate ligands

The vast majority of iridium complexes tested for OLEDs incorporate bidentate cyclometallating ligands. However, tridentate ligands may also be used, and indeed, there may be advantages in doing so owing to the extra rigidity which they confer on complexes (this point is discussed further in Section 3.5.4). Iridium complexes based on the structure Ir(N[^]C[^]N)(N[^]C)Cl have been investigated by Williams and co-workers (Fig. 3.15a; Wilkinson *et al.*, 2006; Brulatti *et al.*, 2012). Here N[^]C[^]N represents a ligand based on 1,3-dipyridylbenzene and N[^]C a bidentate ligand such as 2-phenylpyridine. The parent complex, (X=CH₃, Y=H), emits brightly in the green region, much like Ir(ppy)₃, with a high quantum yield of 0.76 in solution. As for the bidentate systems, the introduction of appropriately placed F substituents leads to blue-shifting of the emission, the effect being larger for substituents in the tridentate ligand, which plays a more prominent role than the bidentate ligand in the excited state according to TD-DFT calculations. Thus, EL emission maxima shift from 503 nm (X=CH₃, Y=H) to 487 nm (X=F, Y=H) and then to 476 nm (X=Y=F), corresponding to CIE coordinates of (0.26, 0.64), (0.20, 0.50) and (0.17, 0.34) respectively, albeit accompanied by a modest decrease in the quantum efficiency (Brulatti *et al.*, 2012).



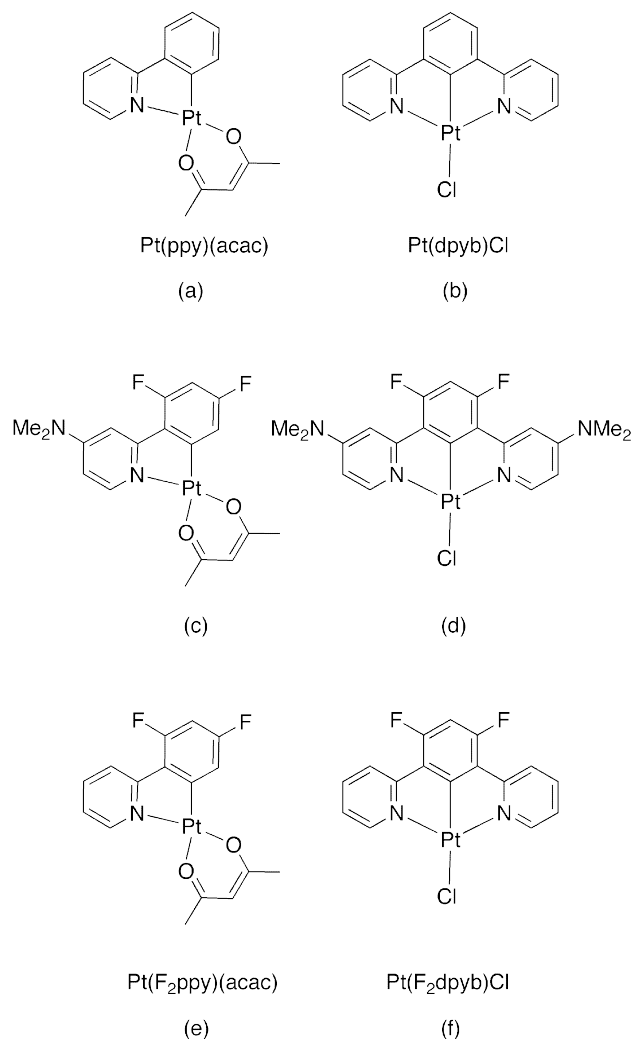
3.15 (a, b) The structures of two representative iridium(III) complexes with tridentate cyclometallating ligands, as discussed in the text.

Another group to eschew bidentate ligands in favour of tridentate ligands is that of Haga, who also synthesised iridium complexes of the form $\text{Ir}(\text{N}^{\wedge}\text{C}^{\wedge}\text{N})(\text{ppy})\text{X}$ where $\text{N}^{\wedge}\text{C}^{\wedge}\text{N}$ in this case is bis(*N*-methylbenzimidazol-2-yl)benzene or bis(*N*-methylpyrazolyl)benzene (Fig. 3.15b; Yang *et al.*, 2008; Ashizawa *et al.*, 2009). The most efficient device was that prepared using bis(2-methyl-8-quinolinolato) phenolatealuminium(III) (BALq_2) as a host material, which gave an external efficiency of 14.0% with blue-green CIE co-ordinates of (0.55, 0.44) (Kuwabara *et al.*, 2012).

3.5.4 Blue-emitting devices based on platinum complexes

The distribution of the frontier orbitals illustrated in Fig. 3.8 applies equally to Pt complexes of arylpyridine ligands. In a landmark paper, Brooks *et al.* (2002) showed how substituents introduced into the phenyl and pyridyl rings of green-emitting $\text{Pt}(\text{ppy})(\text{acac})$ (Fig. 3.16a) can be used to tune the emission towards the blue or red. For the blue, electron-withdrawing groups in the aryl ring and donating groups in the pyridyl ring are again the required combination. For example, by inserting electron-withdrawing F atoms into the phenyl ring and the strongly-donating $\text{Me}_2\text{N}-$ group into the pyridine ring, a complex (Fig. 3.16c) that emits deep into the blue was obtained, at least at low temperature ($\lambda_{\text{max}} = 440\text{ nm}$ at 77 K). However, the blue-shift is accompanied by a dramatic drop in the room-temperature quantum yield to $<10^{-3}$. Such a decline in efficiency is typically observed for blue emitters, possibly due to the higher-lying d-d states becoming thermally accessible from the high-energy emitting states (Barigelletti *et al.*, 1988; Sajoto *et al.*, 2009), and/or to molecular distortion in the excited state (Section 3.3.1).

The use of tridentate ligands can help to combat the problem of distortion. In contrast to bis-bidentate complexes, where the two $\text{Pt}(\text{L}^{\wedge}\text{L})$ planes can twist relative to one another, analogues with tridentate ligands are necessarily more



3.16 The structures of Pt(ppy)(acac) (a) and the related complex Pt(dpyb)Cl (b) incorporating a tridentate cyclometallating ligand. Corresponding complexes (c–f) incorporating substituents to blue-shift the emission. Complex (d) emits strongly at room temperature whereas (c) does not.

rigid. A family of complexes based on Pt(dpyb)Cl (Fig. 3.16b), has proved to be particularly successful in giving brightly emissive complexes that are suitable for use in OLEDs (Williams, 2009). Pt(dpyb)Cl itself is a green emitter with a high quantum yield of 0.6 in solution. By using the same strategy described above of

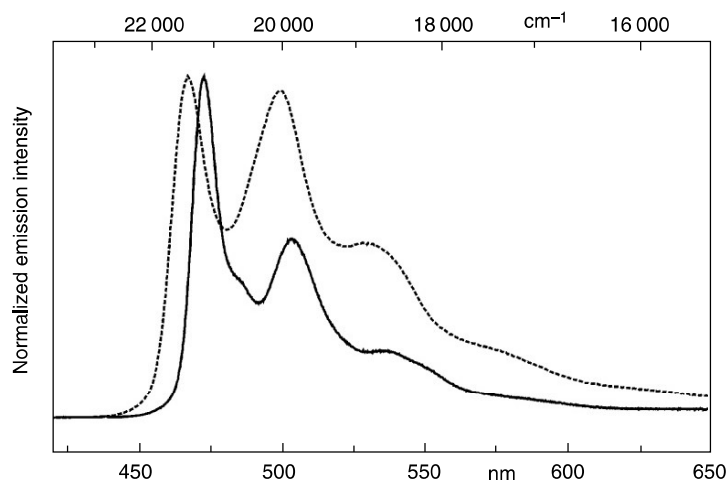


3.17 Frontier orbital plots of Pt(dpyb)Cl from TD-DFT calculations.

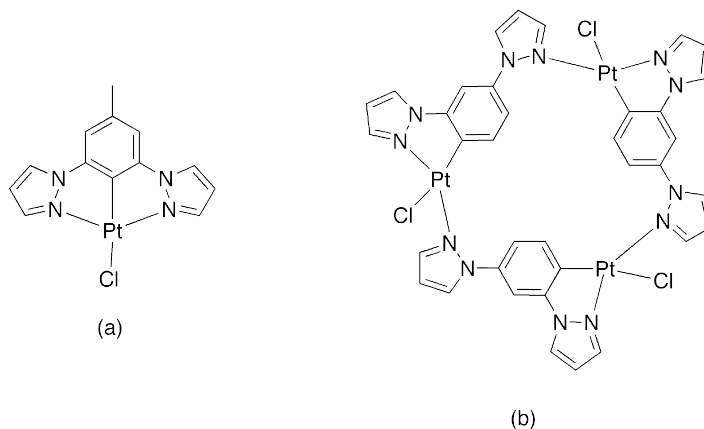
donating and withdrawing groups in pyridyl and aryl rings respectively (Fig. 3.16d), its emission can be shifted into the blue. The optimal positions of substitution to achieve this purpose are clear upon inspection of the frontier orbitals generated by TD-DFT calculations (Fig. 3.17; Rochester *et al.*, 2009). The 4-position of the pyridyl rings plays a role in the LUMO but lies on a node in the HOMO, so that electron-donating amino groups at these positions should destabilise the former without affecting the latter. In contrast, the positions in the central aryl ring *meta* to the metal make a major contribution to the HOMO but not to the LUMO, and so electron-withdrawing F atoms at these positions should independently allow the HOMO to be lowered without affecting the LUMO. The net effect is a large increase in the HOMO–LUMO gap and a shift to $\lambda_{\text{max}} = 453 \text{ nm}$. Importantly, in contrast to the bidentate complex, the high quantum yield is retained even at ambient temperature (Murphy *et al.*, 2012). In a multilayer OLED, colour coordinates of (0.20, 0.30) have been obtained using the complex doped into TCTA at 3% by weight. Higher concentrations lead to increasing contribution from excimer-like emission and to efficient generation of white light (see Section 3.7.2).

In an attempt to probe the origin of the superior performance of the tridentate complexes, a detailed comparison between Pt(F₂ppy)(acac) and Pt(F₂dpyb)Cl (Fig. 3.16e and f) has been made by a cryogenic spectroscopic study, to examine the electronic and vibronic structures behind their emissive properties. The key difference between the two is a greater degree of molecular rigidity for the tridentate complex, which leads to a lesser distortion on moving from the ground state to the excited state. Consequently, the Huang-Rhys parameter, quantifying the distortion, is smaller by a factor of two for the tridentate complex. Not only is the emission of the tridentate complex brighter, therefore, but it also gives a purer colour, because of the lower contribution of the higher vibrational modes (0–1, 0–2 etc.) to the emission spectrum (Fig. 3.18; Rausch *et al.*, 2012).

As described for iridium in Section 3.5.2, replacing the pyridyl rings by more electron-rich heterocycles should provide an alternative strategy for shifting to the blue. Indeed, the platinum complex of 1,3-bis(1-pyrazolyl)-5-methylbenzene (Fig. 3.19a) does emit in the blue region ($\lambda_{\text{max}} = 453 \text{ nm}$; Develay *et al.*, 2008). However, in this case, there is a sharp fall in the quantum yield ($\Phi = 0.02$ in solution at room temperature), as encountered in the bidentate complexes. It is likely that the 5-membered heterocycles, when incorporated into a tridentate



3.18 Emission spectra of $\text{Pt}(\text{F}_2\text{ppy})(\text{acac})$ (dashed line) and $\text{Pt}(\text{F}_2\text{dpyb})\text{Cl}$ (solid line) (the complexes shown in Fig. 3.16e and f) in CH_2Cl_2 at 300K, showing the more pronounced contribution of the 0–1 and 0–2 vibrational bands for the bidentate complex. Reprinted with permission from Rausch *et al.*, 2012. Copyright 2012, American Chemical Society.



3.19 Platinum complexes of 1,3-bis(1-pyrazolyl)benzene ligands, featuring tridentate (a) and bidentate (b) coordination, as discussed in the text.

ligand, are not able to offer the optimal bite angle for strong binding, and that there is greater distortion in the excited state, as suggested by the pronounced blue-shift observed at 77 K. It is notable that the corresponding ligand lacking the 5-methyl substituent shows a propensity to bind as a bidentate rather than tridentate ligand, producing the trinuclear system shown in Fig. 3.19b (Willison

et al., 2008). This observation tends to support the notion that the ligand is not well suited to tridentate binding of the platinum ion.

3.6 Red- and near infra-red-emitting complexes

3.6.1 Introduction

As conjugation in a molecule increases, the HOMO–LUMO gap decreases, thus causing a bathochromic shift to the red. As in organic molecules, such a strategy can be used to obtain red-emitting transition metal complexes, by incorporating ligands with increasingly extended conjugation. Meanwhile, based on the discussion in Section 3.4, the addition of electron-withdrawing substituents into the parts of the molecule on which the LUMO is predominantly localised – typically the azaheterocycle – should red-shift ³MLCT emission.

Both of these strategies are successfully used to prepare red emitters. However, with regard to the first strategy, it should be noted that as the conjugation increases, and the ligand-based HOMO rises in energy, it is likely that the metal will make a lesser and lesser contribution to the lowest-lying excited states, and the triplet state will become more like an organic triplet, with a low radiative rate constant. Simply adding additional conjugating groups does not lead to efficient emitters, as illustrated by a series of complexes with cyclometallated oligothiopyridine ligands (Kozhevnikov *et al.*, 2011). Moreover, the shift to the near infra-red (NIR) is especially challenging, because luminescence quantum yields tend to decrease with decreasing excited state energy. This trend reflects the combined effects of increasingly rapid non-radiative decay through vibrations (i.e. k_{nr} increased; Caspar and Meyer, 1982; Meyer, 1986; Cummings and Eisenberg, 1996), compounded by the fact that the coefficient of spontaneous emission varies with ν^3 , such that k_r declines for longer wavelength emission.

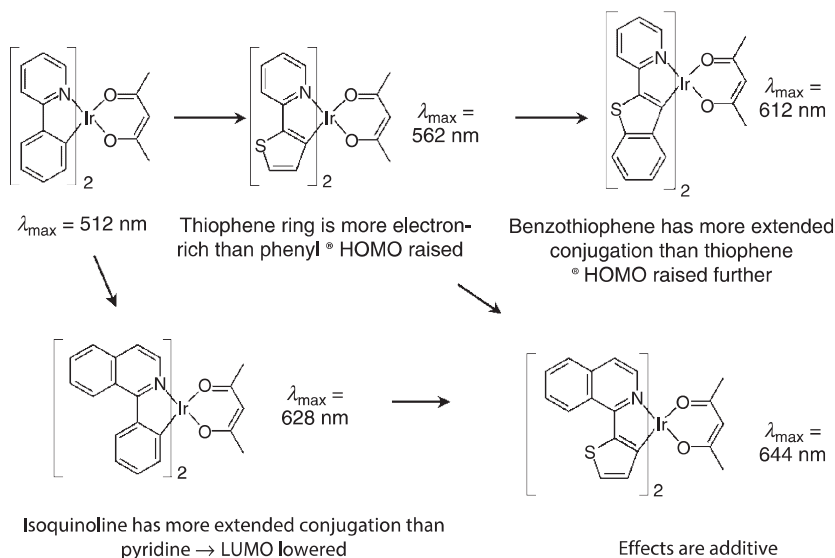
3.6.2 Metalloporphyrins

As noted in Section 3.1.2, a platinum porphyrin was the first phosphorescent metal complex to be explored as a doped phosphor for OLEDs (Baldo *et al.*, 1998). The highly conjugated nature of the porphyrin macrocycle leads to deep red emission, but the lifetime was undesirably long leading to self-quenching of emission. Nevertheless, some researchers have continued to explore such systems. An improvement in OLED external quantum efficiency was observed for more substituted platinum(II) porphyrin structures (Graham *et al.*, 2011), with an increase from 8.0 to 9.2% recorded for compounds containing four *tert*-butylphenyl groups over simple phenyl groups. Fluorenyl-substituted porphyrins led to a red-shift compared to phenyl substituted compounds, as well as reduced roll-off at high currents (Drouet *et al.*, 2010). Red devices containing platinum

porphyrins incorporated into dendrimers (Li *et al.*, 2006), triads (Montes *et al.*, 2006) and polymers (Hou *et al.*, 2005) have also been fabricated.

3.6.3 Iridium complexes with bidentate ligands

The group of Thompson and Forrest reported on a large series of complexes containing two bidentate C^N-coordinating ligands with β -diketonate ancillaries (Lamansky *et al.*, 2001b), of which several displayed red emission. The strategy for red-shifting follows the guidelines presented in section 3.6.1 above, and some key examples are summarised in Fig. 3.20. Thus, changing the phenyl of ppy to the more electron-rich thiophene ring in Ir(thpy)₂(acac) leads to a red-shift (from 512 to 562 nm in solution), due to the increase in HOMO energy, whilst further extension of the conjugation in the benzothiophene complex Ir(btp)₂(acac) further shifts the emission to 612 nm. Alternatively, changing the pyridine unit to isoquinoline in Ir(piq)₂(acac) stabilises the LUMO and also red-shifts the emission to 628 nm. Again, the effects are additive, such that Ir(thiq)₂(acac) emits deep into the red at 644 nm. A device comprising Ir(btp)₂(acac) in the emissive layer produced saturated red emission with CIE coordinates (0.68, 0.32) at a maximum external quantum efficiency of $7.0 \pm 0.5\%$ and power efficiency of $4.6 \pm 0.5 \text{ lm W}^{-1}$, measured at a current density of 0.01 mA cm^{-2} .



3.20 Strategies for red-shifting the emission of iridium complexes: raising the HOMO level and/or lowering the LUMO.

Meanwhile, the homoleptic complex of the phenylisoquinoline ligand, $\text{Ir}(\text{piq})_3$, emits with $\lambda_{\text{max}} = 620 \text{ nm}$, and incorporation into a layered device generated pure-red emission with CIE coordinates of (0.69, 0.32) at an external quantum efficiency of 10.3% (Tsuboyama *et al.*, 2003). Okada *et al.* (2005) showed that substituents in the piq ligand can have a significant influence on the excited state, with λ_{max} in the range 598–635 nm and luminescent quantum yields from 0.17 to 0.32. An OLED containing the iridium complex of (4-fluoro-5-methylphenyl)isoquinoline gave very high efficiency red light at an η_{ex} value of 15.5%, corresponding to a power efficiency of 12.4 lm W^{-1} , with CIE coordinates (0.66, 0.34).

Heteroleptic complexes containing a combination of piq and ppy ligands, both $\text{N}^{\wedge}\text{C}$ -cyclometallated, emit primarily from excited states based upon the piq, which have lower π^* orbitals associated with them compared to those based upon ppy (Deaton *et al.*, 2010) and undergo dissipation of energy more quickly (Hedley *et al.*, 2009). Emission maxima are 627 and 631 nm for $\text{Ir}(\text{piq})_2(\text{ppy})$ and $\text{Ir}(\text{piq})(\text{ppy})_2$, respectively, with high quantum yields of 0.37 and 0.40, and devices with efficiencies of 11.4% and 10.8% were prepared using these compounds (Deaton *et al.*, 2010).

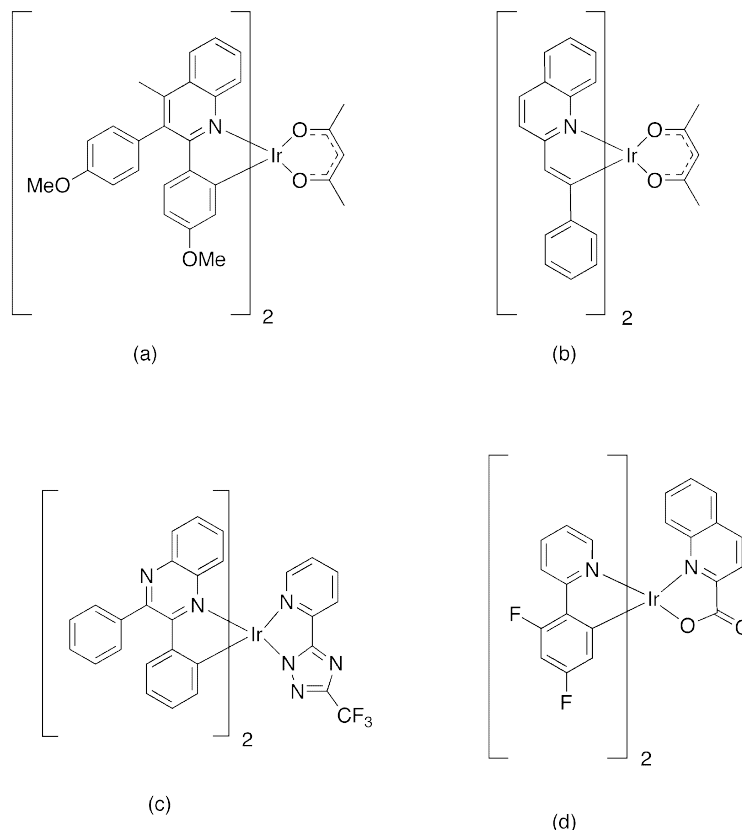
Iridium complexes comprising quinolines, quinoxalines and other polyarenes are related systems from which efficient red emission has been achieved. An OLED comprising the quinolyl complex in Fig. 3.21a as the emitter gave a luminous efficiency of 9.81 cd A^{-1} with CIE coordinates of (0.64, 0.38) and (0.62, 0.38) (Park and Ha, 2008). Rayabarapu *et al.* (2005) increased conjugation further using an unusual metallated alkenyl group (Fig. 3.21b) to produce red light-emitting diodes with η_{ext} values up to 7.23%. Meanwhile, as part of a pioneering rational study of red emitters, the groups of Chi and Chou (Hwang *et al.*, 2005) investigated a set of quinoxaline complexes, such as that shown in Fig. 3.21c, which emit efficiently in the red ($\lambda_{\text{max}} = 642 \text{ nm}$ in solution). A device incorporating this complex doped into PVK gave a maximum η_{ext} of 3.15 at a brightness of 1751 cd m^{-2} . Colour coordinates at maximum brightness (7750 cd m^{-2}) were (0.64, 0.31).

Use of the ‘ancillary’ ligand

As noted in Section 3.5.1, the so-called ‘ancillary’ ligand in heteroleptic complexes, e.g. the acac in $\text{Ir}(\text{ppy})_2(\text{acac})$, is not necessarily an ‘innocent’ ligand. If this ligand has lower-lying π^* orbitals associated with it, then it may play a major role in the excited state. For example, use of a quinoxaline carboxylate as the third ligand (Fig. 3.21d) caused emission to shift well into the red region, with $\lambda_{\text{max}} = 666 \text{ nm}$ (Yoo and Park, 2005).

3.6.4 Platinum complexes

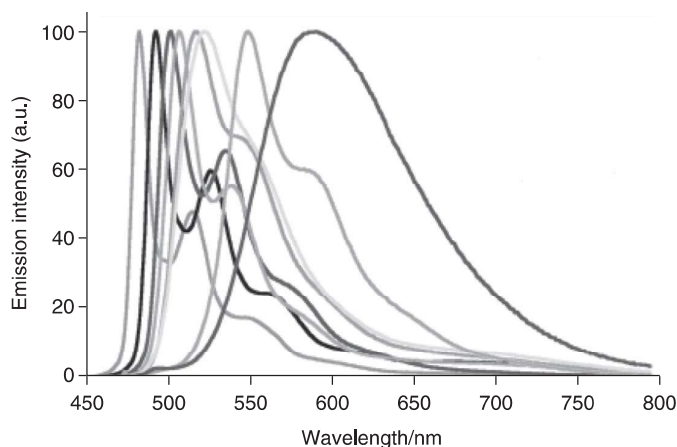
Similar strategies of raising the HOMO and/or lowering the LUMO can be used for $\text{Pt}(\text{II})$ complexes. For example, incorporation of increasingly electron-rich



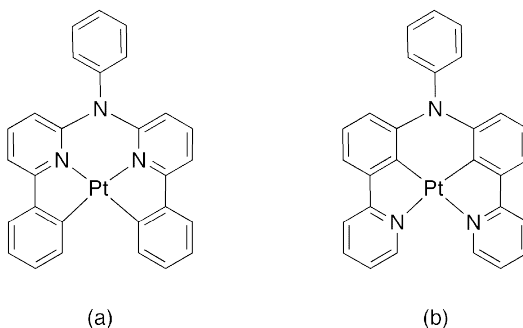
3.21 (a–d) Structures of some representative red-emitting iridium(III) complexes incorporating cyclometallating bidentate ligands.

aryl substituents into the 4-position of the central aryl ring of Pt(dpyb)Cl (Fig. 3.16b) leads to a rise in the HOMO energy without significantly affecting the LUMO, which can be immediately rationalised in terms of the contribution of this position to the frontier orbitals in Fig. 3.17. The emission can be tuned from the green through orange almost to the red (Fig. 3.22). Closer inspection of the spectra shown in Fig. 3.22 reveals that the spectrum for the most red-shifted complex, with a $p\text{-Me}_2\text{N-C}_6\text{H}_4$ -substituent, has a rather different form, lacking any vibrational structure, and indeed a combined theoretical and spectroscopic analysis shows that there is a switch to an intraligand charge-transfer state in this complex, reminiscent of the well-known dual fluorescence of 4-(dimethylamino) benzonitrile (Farley *et al.*, 2005; Rochester *et al.*, 2009).

The increasing non-radiative decay rates that typically compromise the efficiency of red emitters can be attenuated by increasing the rigidity of the



3.22 Tuning the colour of Pt(dpyb)Cl-based complexes towards the red through incorporation of increasingly electron-donating substituents at the 4-position of the central ring.



3.23 (a, b) Platinum complexes with tetradentate ligands developed by Huo and co-workers (Vezzu *et al.*, 2010).

system. As seen above for the platinum porphyrins, however, this should not be done at the expense of significant metal participation in the excited state. Elegant work by Huo and colleagues (Vezzu *et al.*, 2010) has made use of platinum complexes of tetradentate ligands, comprised of two cyclometallating N^C units linked via a bridging nitrogen atom (Fig. 3.23). Compared to analogous bis-bidentate complexes, the emission efficiencies are greatly increased, probably owing to the greater rigidity. The distortion that can occur through rotation of the two $Pt(N^C)$ planes relative to one another in the bis-bidentate complexes is inhibited for the tetradentate complex. Moreover, the synthesis is also facilitated:

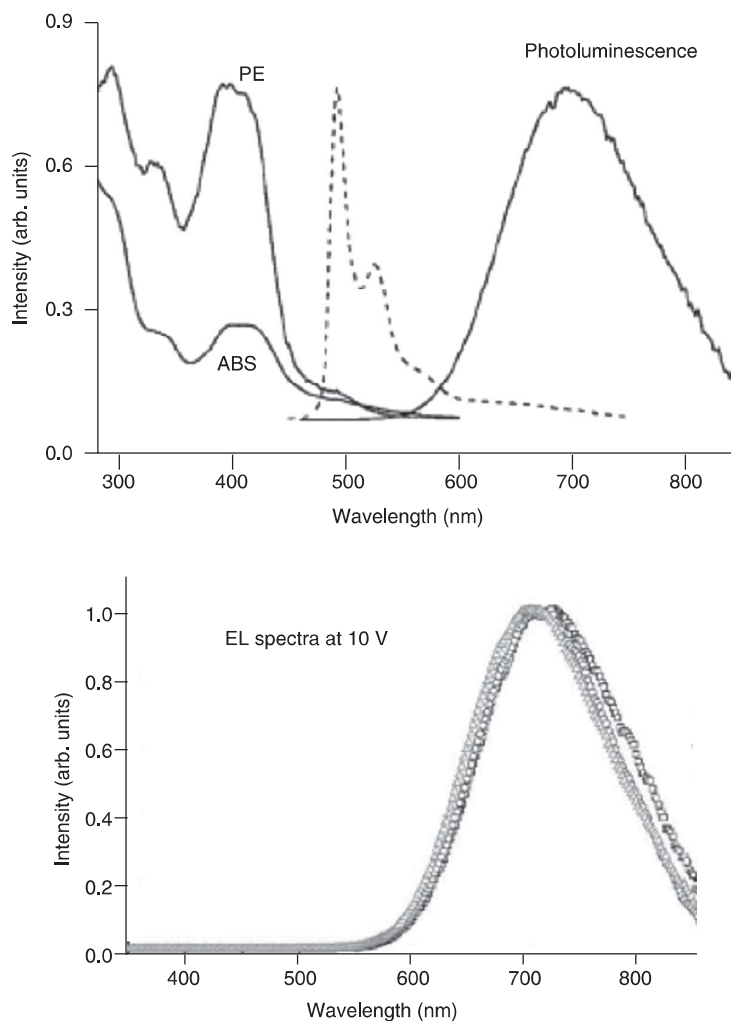
the complexation step proceeds under much milder conditions and does not require the use of lithiated ligands. Of the two shown in Fig. 3.23, the redder-emitting complex is the N[^]C[^]C[^]N-coordinated system (b), for which $\lambda_{\text{max}} = 613 \text{ nm}$ compared to 512 nm for its isomer (a). The difference can readily be understood in terms of the influence of the electron-donating bridging aryl amine, which will raise the HOMO in the case of (b), but raise the LUMO in (a), with the accompanying shift to red and blue respectively.

Excimers and aggregates

Strong intermolecular interactions are a feature of many platinum(II) complexes due to the square-planar geometric preference of d⁸ metal ions, which enables axial interactions. These may involve Pt–Pt interactions (d_{z²}–p_z overlap), π – π stacking between aromatic ligands, or a combination of both. Such interactions may occur in the ground state, described as an *aggregate*, or they may become attractive only when one of the two molecules involved is first promoted to its excited state, in which case the new excited-state species formed is an *excimer*. In both cases, the resulting species have lower energy excited states than the isolated molecules, and so, if they are emissive – which is by no means always the case – the emission is red-shifted.

This effect has been exploited in some studies for the preparation of red and NIR OLEDs. By using neat films of the materials as emitting layers, it can be possible to obtain exclusively excimer/aggregate emission, leading to devices that emit in the red and/or NIR. It should be noted that this feature is essentially unique to platinum: in contrast, iridium complexes at high concentrations in films tend to undergo self-quenching through triplet-triplet annihilation processes, and emission efficiency decreases dramatically. As an example, Cocchi *et al.* (2007) made use of derivatives of Pt(dpyb)Cl (Fig. 3.16b). As noted in Section 3.5.4 and earlier in the current section, these complexes are highly efficient phosphors when doped into emitting layers, and they can be tuned from green to blue or to orange/red. However, they also form excimers readily in solution, which are unusually highly emissive, centred at around 700 nm in the case of Pt(dpyb)Cl and its derivatives carrying substituents in the 4-position of the phenyl ring (Farley *et al.*, 2005). A device incorporating a neat film of such a complex displays uniquely excimer-like emission in electroluminescence, essentially identical to the photoluminescence spectrum of a neat, vacuum-deposited film (Fig. 3.24; Cocchi *et al.*, 2007). Further optimisation of the device architecture gave devices offering unusually high forward-viewing external quantum efficiencies of up to 14.5% and a power efficiency of up to 6% at a forward output of 25 mW/cm² (Cocchi *et al.*, 2008).

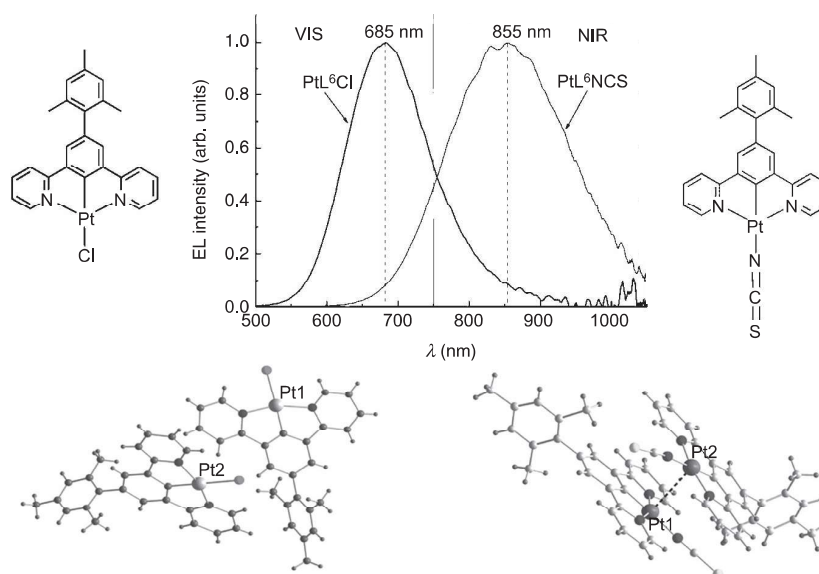
Whether such emission is best described as arising from an excimer or aggregate is not always clear-cut. Some motion of the molecules relative to one another, following formation of the monomeric excited state, is required to form an



3.24 Top: the photoluminescence spectrum of Pt(dpyb)Cl in a neat film, together with the corresponding absorption (ABS) and excitation (PE) spectra. The contrasting emission spectrum of the same complex in a doped film is also shown (dashed line). Bottom: electroluminescence spectra of neat films of Pt(dpyb)Cl and two 4-substituted derivatives, showing the exclusively excimer-like red emission. Adapted from Cocchi *et al.*, 2007.

excimer, whereas an aggregate involves a pre-existing ground-state intermolecular interaction. A detailed study by Kalinowski *et al.* (2010) suggests that both types of interaction may be involved. It is also noteworthy that microcrystalline samples of Pt(dpyb)Cl that display uniquely red emission at room temperature give rise to additional monomer bands in the green on cooling to 77 K, which would be consistent with some thermally activated molecular motion being required to induce the formation of the red species (Rochester, 2007).

A recent example from Rossi *et al.* (2012) demonstrates how excimer-like or aggregate emission can give rise to distinctly different emission bands. The complex Pt(4-mes-dpyb)Cl (where mes = 2,4,6-trimethyl benzene) behaves much like Pt(dpyb)Cl when used neat as the emitting layer in an OLED, displaying an emission band centred at 685 nm, similar to that of the excimer formed in solution (Fig. 3.25). In contrast, an analogous device prepared from the thiocyanate derivative Pt(4-mes-dpyb)NCS shows a greatly red-shifted emission, $\lambda_{\text{max}} = 855$ nm, even though its excimer in solution appears at the same position as Pt(4-mes-dpyb)Cl. The origin of this difference may arise from the different packing of the molecules, and indeed X-ray diffraction analysis of crystals of the NCS complex reveal short Pt–Pt interactions, so that the lower-energy emission observed might reasonably be attributed to aggregates.



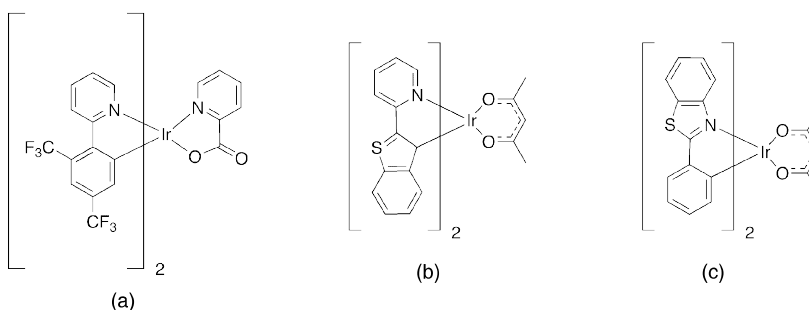
3.25 The emission spectra of OLEDs prepared using neat films of the two complexes shown. The red-shifted emission of the thiocyanate derivative compared to the chloro complex may reflect the presence of Pt–Pt interactions, as observed in the crystal structure shown.

3.7 Complexes for white-light-emitting OLEDs (WOLEDs)

Strategies for generation of white light are discussed in more detail in other chapters of this volume and so, in the present chapter, we shall limit our coverage to a few examples involving Ir(III) and Pt(II) complexes.

3.7.1 Multiple emitters

Most approaches to white light work on the principle of balancing the light output from a combination of two or more emitting organic materials to produce light spanning the visible spectrum. The combination of a blue phosphor and a red-orange phosphor (Fig. 3.26a and b respectively) in adjacent layers of a multi-layered WOLED led to external quantum efficiencies of up to 12% and a maximum luminance efficiency of 18 cd A^{-1} (Tokito *et al.*, 2003). A bilayer device containing the same red phosphor in conjunction with the blue FIrpic complex previously discussed had CIE coordinates of (0.37, 0.40) and an external efficiency of $5.2 \pm 0.5\%$; coordinates were improved to (0.35, 0.36) upon addition of the related yellow complex (Fig. 3.26c) although η_{ext} dropped to $3.8 \pm 0.4\%$ (D'Andrade *et al.*, 2002b). Combining ppy derivatives of iridium into one layer was limited by the efficiency of the blue-emitting FIrpic derivative (Lamansky *et al.*, 2001a), though an external quantum efficiency of 12% was later obtained for an optimised device with CIE coordinates of (0.43, 0.45) (D'Andrade *et al.*, 2004). Use of two different host layers with iridium compounds, FIrpic doped into *N,N'*-dicarbazolyl-1,4-dimethene-benzene (DCB) and Ir(piq)₂(acac) doped into CBP, removed the need for an exciton blocking layer due to the large energy gap of the host materials, making device fabrication simpler (Lei *et al.*, 2006). External efficiency, η_{ext} , was dependent on layer thickness as well as dopant concentration, with maximum efficiency of 5.8% and a power efficiency of 9.8 cd A^{-1} . Yook *et al.* (2010) prepared



3.26 (a–c) Iridium complexes used in the preparation of white-light-emitting OLEDs comprising two or more phosphors of different colours.

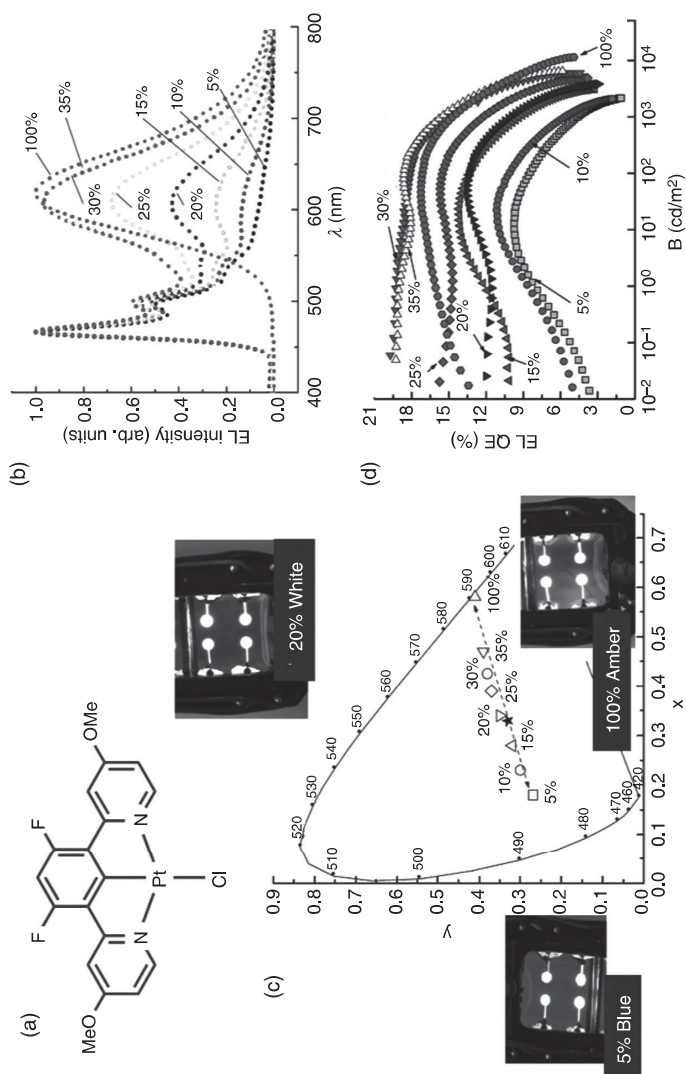
a multilayer device with excellent white characteristics – CIE coordinates (0.29, 0.33) – through the use of red-, green- and blue-emitting iridium complexes in a phosphine oxide host, in conjunction with a variety of hole and electron transport materials, to enhance efficiency up to 27.2 cd A^{-1} .

In some cases, a blue emitting *fluorescent* compound has been used in conjunction with green- and red-emitting phosphorescent metal complexes. For example, Sun *et al.* (2006) prepared a bilayer device containing red and green emitters, $\text{Ir}(\text{piq})_2(\text{acac})$ and $\text{Ir}(\text{ppy})_3$, respectively, doped into a region of the host spatially separated from that of the fluorescent blue emitter 4,4'-bis(9-ethyl-3-carbazovinylen)-1,1'-biphenyl. The resulting device exhibited an excellent external quantum efficiency of $18.7 \pm 0.5\%$, corresponding to a power efficiency of $37.6 \pm 0.6 \text{ lm W}^{-1}$ with CIE coordinates of approximately (0.40, 0.40). Wang *et al.* (2008) used the same two phosphorescent iridium compounds in a device with three emissive layers containing the perylene derivative, 2,5,8,11-tetra-*tert*-butylperylene, as the fluorescent blue source, obtaining an efficiency up to 14.2 cd A^{-1} at a brightness of nearly 600 cd m^{-2} . Yook *et al.* (2009a) used a fluorescent blue fluorene derivative alongside $\text{Ir}(\text{ppy})_3$ and the red emitter $\text{Ir}(\text{pq})_2(\text{acac})$ to achieve a high efficiency of 12.3%. Removal of the green phosphor and optimisation of the host and interlayers led to suppressed roll-off at high currents (Yook *et al.*, 2009b), influencing the colour stability but not the device lifetime (Yook and Lee, 2011).

3.7.2 WOLEDs based on monomer and excimer/aggregate emission of a single complex

The tendency of square-planar platinum complexes to form low-energy-emitting excimers and aggregates, discussed in Section 3.6.4, can be exploited for the generation of white light using just one triplet-emitting species. The combination of blue-green emission from isolated phosphors and red emission from the excimers/aggregates can lead to good coverage across the visible region, and hence to white light, if an appropriate concentration of the complex is used within the host. Adamovich *et al.* (2002) demonstrated the concept with $\text{Pt}(\text{F}_2\text{ppy})(\text{acac})$. A doping concentration in *N,N'*-dicarbazolyl-3,5-benzene (mCP) at which the monomer and excimer bands have approximately equal intensity gave light close to that of standard white light. Use of $\text{Ir}(\text{ppz})_3$ as an electron/exciton blocking layer (EBL), to achieve a good photon-to-electron ratio by confining excitons to the emissive layer, gave a peak efficiency of 6.4% at 17.0 cd A^{-1} , CIE coordinates of (0.36, 0.44) and a CRI of 67 at 1 cd m^{-2} (Adamovich *et al.*, 2002).

Complexes based on $\text{Pt}(\text{dpyb})\text{Cl}$ have proved to be particularly successful for this purpose, owing to the exceptionally bright excimers they form. Much of the work in this area has been discussed in detail in a recent review (Kalinowski *et al.*, 2011). One of the limitations of $\text{Pt}(\text{dpyb})\text{Cl}$ itself is that the excimer band is a little



3.27 Data for OLEDs with emitters of varying concentrations of the platinum complex shown (a), which incorporates electron-donating methoxy substituents to destabilise the excimer: EL spectra (b), CIE coordinates (c), and efficiency versus brightness plots (d). At low phosphor concentrations, the LEDs are blue-biased but become red-biased at higher concentrations, as the emission becomes dominated by the excimers. The device with a 20 wt% content of the phosphor approaches closely to white light with CIE coordinates (0.33, 0.33).

too low in energy, much of it lying in the NIR region, and leaving rather poor coverage in the 550–650 nm region. The incorporation of electron-donating substituents into the pyridyl rings has been found to blue-shift the excimer band, such that this zone of the spectrum is covered more efficiently and little energy is wasted in the NIR (Fig. 3.27; Cocchi *et al.*, 2010). Highly efficient single-dopant white-light OLEDs are accessible in this way.

3.8 References

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Chemical and photophysical properties of materials for OLEDs

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Abstract: In the past three decades, organic light-emitting diodes (OLEDs) have made a huge breakthrough in both research and industry. At present, OLED technology is used in commercial applications such as displays for mobile phones and portable digital media players, car radios and digital cameras. The high light output of OLEDs means they are favoured in portable applications for readability in sunlight and their low power drain. These achievements show us the great charm of flexible electronics based on organic materials. All of these developments not only depend on the improvement of processing technology, but also on the in-depth understanding of the device physics and synthesis of new organic materials. The physical and chemical properties of the major material constituent of the OLED largely determine the final device performance. In the first half of this chapter, we consider the energy level of the molecule as a clue to the characteristics of organic semiconductors, including energy level alignment for OLEDs and tuning of molecular energy level. In the second part, we discuss the photophysical behavior and thermal stability of materials for OLEDs.

Key words: OLEDs, energy level, photophysics, energy transfer, thermal stability.

4.1 Introduction

Comprehending the chemical and photophysical properties of electroluminescent (EL) materials is helpful in gaining an in-depth grasp of organic light-emitting mechanisms. In organic light-emitting diodes (OLEDs), three major physical processes exist: (i) charge injection and transport, (ii) charge recombination and excitons energy transfer, and (iii) light emission. Each of these processes plays an important role in such factors as the turn-on voltage, external quantum efficiency and luminance of OLEDs. The intrinsic properties of light-emitting materials such as energy level, mobility and thermal properties have a significant effect on the aforementioned three processes.

In OLEDs, the conductivity of the active layers dramatically affects the charge transfer and turn-on voltage. Unlike inorganic semiconductors, organic semiconductors used in OLED are mainly amorphous π -conjugated systems. The mechanism of conductivity is therefore different to the conventional valence band theory. In terms of the molecule itself, the conductivity of organic semiconductors

depends on the conjugation. Energy levels constitute another important characteristic of organic semiconductors that play an important role in the OLED. The energy band gap of the emitting materials determines the wavelength of the light emitted, so different kinds of emitter are therefore used to meet different requirements. Secondly, a suitable energy level alignment must be achieved in order to maintain efficient charge transfer and carriers balance, which can have a huge impact upon the quantum efficiency and luminance of OLEDs. Before light is emitted, the carriers are injected with opposite charges, statistically independent of one another, and tend to form electron-hole pairs. The photophysical behaviors of organic semiconductors form the core of an OLED. We need to know the yield of excitons, the ratio of single to triplet and the mechanisms of energy loss.

This chapter reviews the photophysical, chemical, and thermal properties of polymer and small organic light-emitting materials. Section 4.2 focuses on energy levels, including the energy level alignment for charge injection and the main experimental techniques (cyclic voltammetry (CV) and ultraviolet photoelectron spectroscopy (UPS)) used to evaluate the energy levels. Section 4.3 briefly describes the major physical fundamentals of the materials; including the mechanism of exciton energy transfer and the photophysical behaviors of light emission. In terms of applied research, the thermal stability of OLEDs will need to be improved if they are to become suitable for large-scale industrialization. Section 4.4 looks into the thermal stability of light-emitting materials.

4.2 Organic semiconductors

Inorganic semiconductors, such as Si, Ge, and GaAs, are more familiar than organic ones due to their relatively mature role in computer-integrated circuits, telecommunications, and other consumer electronic devices. They are often highly crystalline, with strong covalent bonds (bond energy: $\sim$ eV); are hard and brittle and have high melting points.^{1,2} By contrast, the organic semiconductors used in OLEDs are usually in the form of amorphous structures. The organic small molecules or polymers interact with one another through Van der Waals forces, which are much weaker than covalent bonds (bond energy: $\sim$ meV) (Table 4.1). As a result, organic semiconductors are flexible and melt at relatively low temperatures.^{3,4} These characteristics illustrate some of the advantages of plastic electronics.

4.2.1 π -Conjugated organic semiconductor

Organic semiconductors are mainly π -conjugated systems, which are classified into two groups based on the weight, namely π -conjugated polymers and small molecules. Organic compounds are almost endless in number and range in size from small molecules to macromolecules. This greatly increases the range of

Table 4.1 Physical and electronic properties of Si and anthracene crystals

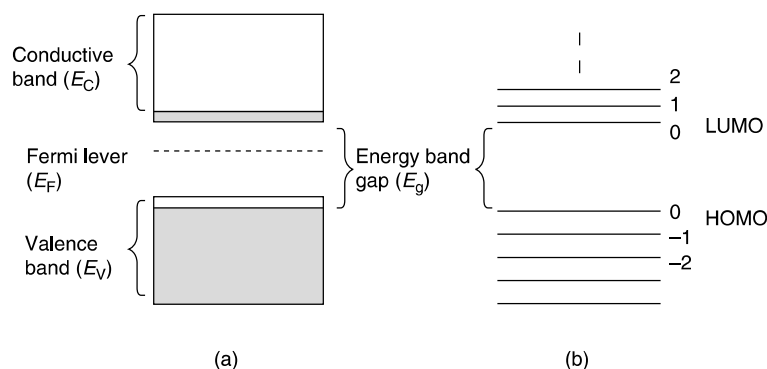
Property	Si	Anthracene
Density (g/cm ³)	2.33	1.28
Atomic or molecular weight (g/mol)	28.09	178.2
Crystal structure	Diamond	Monoclinic
Lattice constant (nm)	0.543	0.604–1.116
Melting point (K)	1685	490
Thermal conductivity [w/(cm K)]	1.412	10 ⁻³
Electron mobility at 300 K [cm ² /(Vs)]	1420	1.06
Hole mobility at 300 K [cm ² /(Vs)]	470	1.31
Intrinsic carrier concentration at 300 K [cm ² /(Vs)]	1.45*10 ¹⁰	~10 ⁻⁴
Ionization potential (eV)	5.2	5.8

Source: Data from Ref. 2 and Ref. 3.

screening and design possibilities for organic semiconductors and provides an advantage over inorganic semiconductors.

In addition to the richness of organic materials, inorganic and organic semiconductors behave differently in terms of their architectural approach. Ideally, in inorganic semiconductors, atoms are connected by covalent bonds and obey the typical band theory. A semiconductor consists of an almost-filled valence band and an almost-empty conduction band; the transfer of electrons from the valence band to the conduction band determines the behavior of a semiconductor (Fig. 4.1a). In organic semiconductors, the sp² hybrid configuration is the most relevant because of the remaining p-orbital, which is capable of participating in a π -bond to increase the delocalization of electrons. When these conjugated molecules are bound into a solid, the overlap of their delocalized π -electron systems gives rise to conductivity.³⁻⁵ The conductivity of an OLED dramatically affects the charge transfer, especially in hole and electron transfer layers. The morphology of organic films also plays an important role in conductivity; however, that is outside the scope of this chapter.

In contrast to inorganic semiconductors, occupied and unoccupied molecular orbitals (MOs) in organic semiconductors are not closely packed. A correct representation of the energy level diagram is shown in Fig. 4.1b. In charge transfers in organic semiconductors, hole transport takes place in the highest occupied molecular orbit (HOMO), which is formed by overlapping molecular π -orbitals. Similarly, electron transport results from overlap between anti-bonding π -orbitals (π^*) and occurs in the lowest occupied molecular orbit (LUMO). The energy required to pump an electron from the HOMO to the LUMO is referred to as the HOMO-LUMO, E_g , and is analogous to the valence-conduction band gap in an inorganic semiconductor.⁶ There is ongoing debate about whether to characterize the electronic structure of conjugated polymers as semiconductors or molecules.



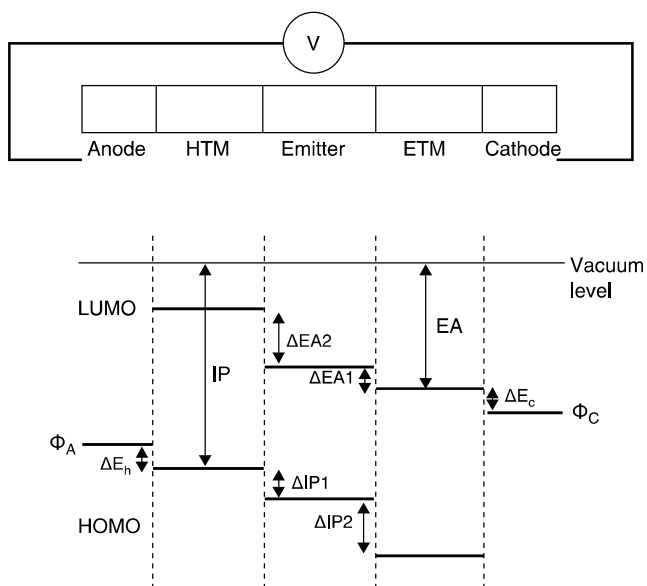
4.1 (a) Energy band diagram of the inorganic semiconductor showing the valence band E_v , conduction band E_c , energy bandgap E_g , and Fermi energy E_F ; (b) energy level diagram of the organic semiconductor showing the highest occupied molecular orbitals (HOMO) and the lowest unoccupied molecular orbitals (LUMO).

4.2.2 Energy level for EL materials

The light-emitting wavelength for emitting materials is mainly determined by E_g , but is also affected by the associations of molecules, self-absorption and microcavity effects. In addition, the alignment of energy levels would affect the charge transfer and consequently the efficiency of an OLED. In this sense, the energy levels, especially the HOMO and LUMO energy levels, are key parameters of materials for OLEDs. Several issues concerning energy levels will be discussed as follows.

Energy level alignment

Three main types of material are used in OLEDs: hole-transfer materials (HTM), electron-transfer materials (ETM) and light-emitting materials (ELM). Simultaneous injection of both electrons and holes from ETM and HTM respectively induces the electroluminescence of the emitting materials. For efficient OLEDs with a single-layer configuration, the organic ELM is required to have a high luminescence quantum yield and to be able to facilitate injection and transport of electrons and holes to maintain the carrier balance. Organic layers in OLEDs with efficient light emission and good electron- and hole-injection and transport properties significantly improve the device performance.^{9,10} Unfortunately, there is not one single material among those currently in use that is able to meet all these functional requirements at once.^{7,8} In Fig. 4.2, the energy-level diagrams define some of the electronic structure parameters relevant in designing organic materials for OLEDs. The electron affinity (EA) or HOMO



4.2 Energy level diagram of an organic light-emitting diode with a hole-transport material (HTM), an electron-transport material (ETM), the electron affinity (EA), the ionization potential (IP), cathode work function (Φ_C), and the anode work function (Φ_A).

level and the ionization potential (IP) or HOMO level relative to the cathode work function (Φ_C) and the anode work function (Φ_A) respectively, determine the charge injection into the diode. Large mismatches lead to substantial barriers to hole injection at the anode ($\Delta E_h = \Phi_A - \text{IP}$) and electron injection at the cathode ($\Delta E_c = \Phi_C - \text{EA}$), resulting in poor OLED performance. In a previous study, poly(p-phenylenevinylene) (PPV) with IP and EA of 5.1 and 2.7 eV respectively was used to fabricate the first polymer OLED (single-layer configuration: ITO/PPV/Al). This OLED had a very low external quantum efficiency (EQE), because the Φ_C of Al is about 4.3 eV, creating a large electron-injection barrier.¹⁰ Using calcium as the cathode ($\Phi_C \sim 2.9$ eV) resulted in significant improvements in EQE and brightness, which confirmed the significant effect of charge injection barriers on OLED performance. However, calcium is not stable, so there is more research to be done on this field to develop stable electron transfer materials.¹¹ For efficient injection, a limited energy barrier needs to be ensured for ΔE_c , ΔE_h , ΔIP1 , and ΔEA1 . Meanwhile, ΔIP2 and ΔEA2 should be appropriate for HTM and ETM to block the transfer of electrons and holes, respectively.¹² If the cathode (anode) is given, the suitable energy level of electron (hole) injection and transfer materials is important for optimizing the performance of the OLED.

Energy levels and molecular structures

As above, the energy levels of organic semiconductors constitute a key parameter. Consequently, the design of materials for OLEDs should include tuning of the energy levels. The optoelectronic properties of conjugated polymer materials could be easily improved and adjusted via simple chemical modifications (i.e. the introduction of specific functional groups). Therefore, device performance could be controlled through chemical modification of the materials. Molecules with a rigid structure result in a weaker non-radiative relaxation, higher quantum yield and stronger light intensity of corresponding devices. Widely studied and commonly used polymer electroluminescent materials can be categorized as follows: PPVs, polyfluorenes (PFs), poly(p-phenylenes) (PPPs) and polythiophene, as well as trapezoidal, comb, and hyperbranched conjugated polymers. In this chapter, PPV and PF are selected as examples to investigate the relationship between the molecular structure of a polymer and the regulation of its energy levels.

The polymer electroluminescent material PPV and its derivatives are currently the most widely studied electroluminescent materials and are considered to be the most promising materials in terms of industrial application. PPV is a type of conjugated polymer with an insoluble and infusible rigid molecular structure. Unmodified PPV, therefore, does not meet the requirements for the fabrication of light-emitting devices. However, flexible long side groups could be introduced to modify the molecular structure of PPV, which would solve this problem. The introduction of different substituents to the PPV skeleton can improve the solubility of PPV and adjust the E_g of the polymer as well, thus changing the light color. In 1991, Heeger *et al.*¹¹ synthesized the soluble PPV derivatives poly[2-methoxy-5-(2'-ethyl-hexyloxy)-1,1-phenylene vinylene], which resulted in an orange-red fluorescent with a wavelength red shift to 590 nm. Friend *et al.*¹³ introduced the cyano (CN) substituent to PPV skeleton and obtained the soluble PPV derivative CN-PPV. The introduction of nitrile not only improves the electron affinity of the polymer, but also reduces the E_g necessary to achieve an efficient red light. Devices requiring green light materials, on the other hand, obviously have an advantage in terms of the available brightness and efficiency because of the superiority of the band-gap position. Modifying PPV with benzene or two benzenes can inhibit the migration of excitons but can also change the molecular structure, thereby either enhancing the efficiency of the device or causing blue shift.

PF is the most representative blue light-emitting polymer with E_g between approximately 2.7 eV and 3.0 eV. The HOMO and LUMO energy levels of PF do not match with the electrodes, which results in a large barrier for the injection of electrons and holes. This causes a reduction in the light-emitting efficiency and brightness of PF-based OLEDs. Moreover, in the preparation process of PF-based polymer light-emitting diodes, exciplex formation and fluorenone defects may

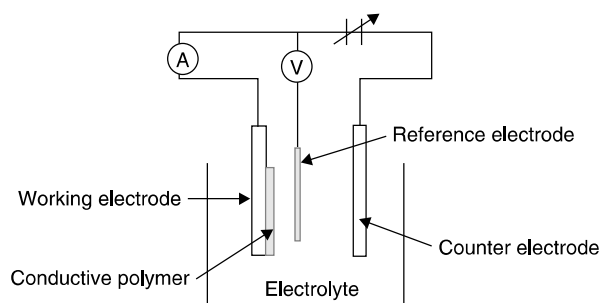
reduce the efficiency and color purity, hence limiting its practical applications. Several efforts have been made to inhibit the formation of exciplexes, such as substituting 9-C with silicon atoms or introducing polybenzenes and polyspirobifluorenes. Holmes *et al.*¹⁴ replaced the 9-C of fluorene with silicon atoms, which significantly improved the spectral stability of the polymer compared to poly(alkylfluorene); in addition, the electron affinity was also improved because of the conjugation effect. Carter *et al.*¹⁵ synthesized a fluorene derivative whose 9-C position is surrounded by Fréchet-type dendritic PF molecules that completely inhibit aggregation by the spatial isolation effect of the molecular branches, thereby achieving pure blue materials. In addition, the introduction of hole transport or electronic transport groups into the 9, 9'-site of fluorene could not only inhibit the exciplex formation, but also increase the charge transport capability and reduce the injection barrier of polymer light-emitting devices, leading to enhanced efficiency. Copolymers have been created using fluorene and other chromophore groups whose emitting spectrum covers the entire visible region. Combining wide band-gap with narrow-gap functional groups in one polymer is one way to achieve red emission through intermolecular energy transfer. For example, the copolymer of fluorene and thiophene is a red light-emitting material with an emissive peak of 666 nm, demonstrating the energy transmission from blue to red light-emitting groups.¹⁶

4.2.3 Methods for energy level measurement

The corrected energy band structure of polymers should also be considered, according to the band gap theory of inorganic semiconductors (Fig. 4.1b). The band gap of semiconductor materials (E_g) can be defined as the energy difference between the top of the conduction band and the valence band. Chemically, the band gap is the energy (E_g). Therefore, E_g can be calculated if the electron affinity and ionization energy are known. Determining the ionization energy and electron affinity of a material is significant in understanding the capability of the material to lose electrons (oxidation) and obtain electrons (reduction). It is difficult to experimentally determine the absolute electronic energy levels (EA and IP values relative to vacuum level) of an organic material. However, various experimental methods have been used to estimate the energy levels, including CV^{17,18} and UPS.^{19,20}

CV

CV is an electrochemical method that can accurately illuminate the process by which an organic molecule receives or loses electrons, based on the relationship between potential (V) and current (I). The experimental device is a simple electrochemical system (Fig. 4.3). The experimental process is as follows: voltage is applied at a certain rate from one potential (E_s) to another potential (E_p) using a



4.3 Schematic diagram of cyclic voltammetry.

standard reference electrode as the reference. The scans are then repeated, and finally a coordination of the current with the potential changes is selected.

Doping, especially electrochemical doping, is one of the most effective means to improve the conductivity of a polymer. The relationship between I and V can be obtained through electrochemical doping and de-doping, in order to determine electron affinity and ionization energy. There are two kinds of doping processes. In the first type of process, electrons are transferred from the doping agent to the conduction band of the material; that is, the conductive polymer is used as the anode and acceptor. The bottom of the conduction band of the polymer continues to ascend as the doping process continues. The reduction potential V_{red} can be determined according to the U-V curve. In the second, alternative process, the doping agent captures electrons from the valence band of the conductive polymer; that is, the polymer material is used as cathode and donor. The top of the valence band of the polymer continues to descend as the doping process continues. Similarly, the oxidation potential V_{ox} can be determined based on the results. Given that V_{red} and V_{ox} are the values relative to the reference electrode, when the potential of the reference electrode is E_o , then

$$E_{\text{HOMO}} (E_{\text{LUMO}}) = E_o + eV_{\text{ox}} (eE_{\text{red}}) \quad [4.1]$$

At this stage, the CV method cannot be used to accurately determine the specific bandwidth of the conduction band and valence band. In addition, when the conductive polymer material is not highly porous, trace impurities could decrease V_{red} and V_{ox} , directly resulting in a lower value of the measured E_g than the actual E_g . The error will increase in correlation to the impurity content. Such results do not reflect the actual situation. Meanwhile, the use of different scaling factors for relating the redox potentials (vs. SCE or internal standards, such as ferrocene) to the vacuum level has led to significant ambiguity over the reported energy levels. Therefore, this method requires a high level of purity in the materials, dopants and electrolytes used, and an anaerobic environment.

UPS

In UPS, ultraviolet light occurs on a thin film sample, which ejects electrons from its surface. The kinetic energy of the electron varies according to its MO, and the sum of the absolute value of the electron kinetic energy and its orbital potential energy is equal to the photon energy. An electron from the HOMO has the highest kinetic energy:

$$E_k = h\nu - E_{\text{HOMO}} \quad [4.2]$$

where E_k is the highest kinetic energy and $h\nu$ is the energy of the ultraviolet photon. E_k can be derived from the UPS spectrum. In general, the HOMO levels estimated from UPS are higher than those estimated by CV. However, solution-based CV experiments determine the relative molecular oxidation potentials that are indirectly related to E_{HOMO} . Therefore, UPS is appropriate for use in determining E_{HOMO} . The high cost and complexity of UPS systems, however, favor the use of CV in many laboratories.¹⁹

4.3 Photophysical properties of OLED materials

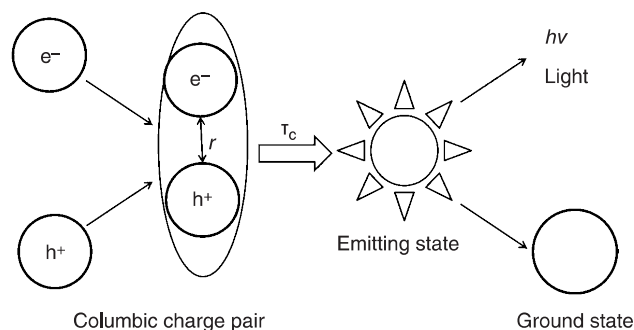
The double injection of electrons and holes simultaneously from ETM and HTM can induce electroluminescence in the emitting materials. Although the charge transfer is also important, this section mainly focuses on the photophysical properties of emitting materials.

4.3.1 Recombination

Before light emission, the oppositely charged carriers, injected statistically separately, tend to form electron-hole pairs. In order that a bond can form, the electron-hole pair requires coulombic attraction to be greater than the thermal energy, as shown in the following:

$$\frac{q^2}{4\pi\epsilon r} > kT \quad [4.3]$$

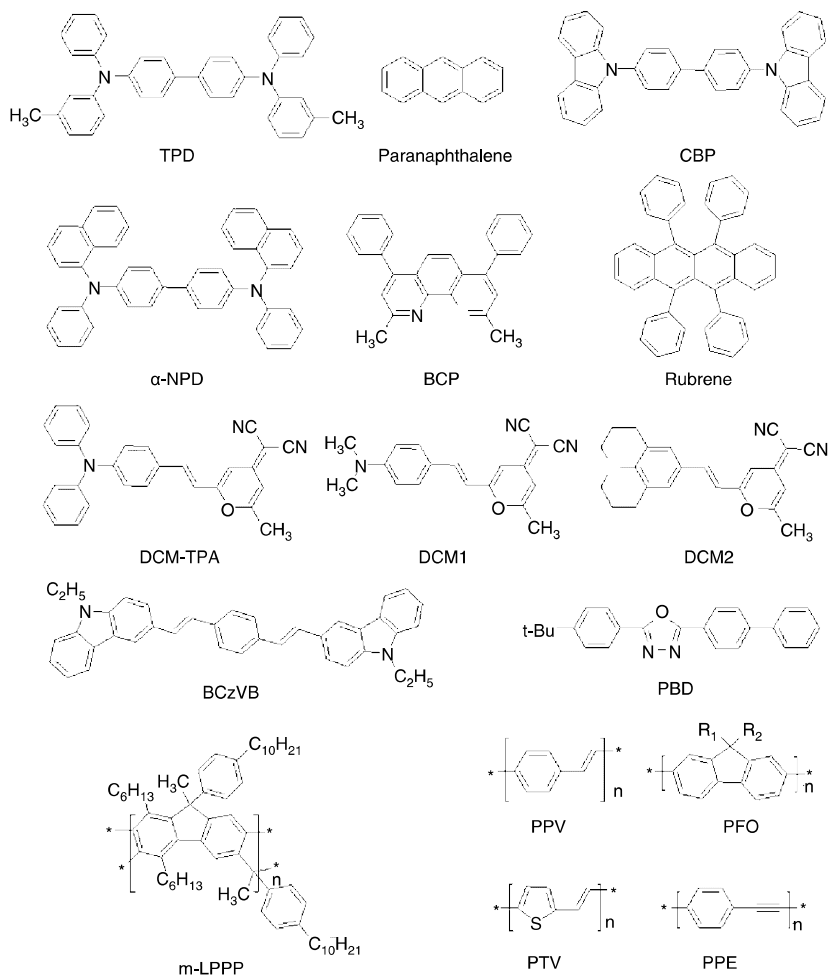
Coulombic capture radius r_c ($r_c = q^2/4\pi\epsilon k$) is the maximum separation for electron-hole capture. Electron-hole recombination is thought to follow the Langevin²¹ or Thompson²² bimolecular recombination models. In these models, the recombination process is typically treated in relation to the carrier motion time (τ_m), which is the time required to get the carriers within r_c , the elementary capture time (τ_c), which is the time taken to reach the emitting state, and the average mean free path (λ) or hopping distance of the carriers (Fig. 4.4). The ultimate recombination time (τ_{rec}), which is the time that the charges take to annihilate each other, is inversely related to the motion time and the capture time ($1/\tau_{\text{rec}} = 1/\tau_m + 1/\tau_c$). The Langevin model holds when the capture time is much smaller than the motion time ($\tau_c \ll \tau_m$) and the hopping distance is



4.4 Electron-hole recombination process.

much smaller than the coulomb capture radius ($\lambda \ll r_c$). The Thompson model holds when the capture time is much larger than the motion time ($\tau_c \gg \tau_m$) and the hopping distance is much larger than the coulomb capture radius ($\lambda \gg r_c$). These models are generally valid in the case of small molecules or polymer materials with low carrier mobility. However, the Langevin model is generally valid when working with organic materials such as conjugated polymers and small molecules, where the mean free path or hopping distance (of order 1 nm) is much less than the coulomb capture radius (of order 17 nm at room temperature).

As implied by the Langevin model, the capture process is spin-independent. In other words, the probability of triplet excitons forming is the same as that of singlet excitons forming from the charge transfer state in singlet configuration. Consequently, the ratio of triplet to singlet is 3 to 1, which limits the maximum internal efficiency of fluorescent OLEDs to 25%. In early studies, the 25% limit was the maximum reached. In 1999, Baldo, *et al.*²³ adopted the phosphorescent dye (2,3,7,8,12,13,17,18-octaethyl-21*H*,23*H*-porphine platinum(II), PtOEP) and the fluorescent dye, 2-methyl-6-[2-(2,3,6,7-tetrahydro-1*H*,5*H*-benzo[*ij*]quinolizin-9-yl)ethenyl]-4*H*-pyran-4-ylidene]propane-dinitrile (DCM2) (Fig. 4.5) as indicators to study the singlet formation fraction of tris(8-hydroxyquinoline) (Alq₃). They found that the singlet fraction of excitons in Alq₃ was $22 \pm 3\%$, which was spin-independent. However, Wohlgenannt and coworkers²⁴ found that this fraction is over 25% in some conjugated polymers (Table 4.2). In the same year, Friend and coworkers²⁵ determined the absolute fraction of singlet states generated in a platinum-containing conjugated polymer (PtBPQn) and its corresponding monomer (PtBPQ). They found an average singlet generation fraction of $22 \pm 1\%$ for the monomer, but $57 \pm 4\%$ for the polymer. These results indicate that spin-dependence in exciton formation does exist in polymers. However, it was still necessary to determine how the length of conjugation affects the singlet fraction. In 2002, Janssen and coworkers²⁶ measured the ratio of singlet (σ_s) and triplet (σ_t)



4.5 Molecular structure of small molecules and polymers.

excitons in conjugated oligomer and polymer (Pth) films, using a spectroscopic technique. They demonstrated a universal relation between r and the conjugation length (CL): r^{-1} depends linearly on CL^{-1} , irrespective of the chain structure. These results indicate that polymers have an advantage over small molecules in OLED applications. It is generally acknowledged that a major potential difference between polymer and small molecule OLEDs is the possibility of spin-dependent charge recombination in the latter. In this case, the singlet exciton formation yield, which is one of the key parameters determining device efficiencies, deviates from

Table 4.2 The singlet generation fraction of some small molecules and polymers

Emitting materials	Singlet generation fraction (%)	Ref.
Alq ₃	22 ± 3	22
PtBPQ	22 ± 1	24
PtBPQn	57 ± 4	24
Pth	~63.6–80.1%	25
PPV	~67.7%	23
PFO	~80.1%	23
PTV	~83.3%	23
PPE	~63.6%	23

the 25% prediction of simple quantum mechanical spin statistics. For polymers, the departure from this limit has been demonstrated on several occasions, yielding a wide range of values from 25% up to 95%. However, the theory of spin-dependence is still under debate.^{27,28}

4.3.2 The light emission process

The principle of photophysics

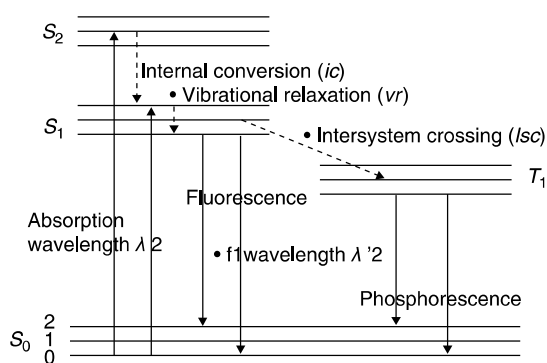
Electrons move around the nucleus in different orbitals and create different electronic energy levels. After electron excitation, an electron moves from a low-energy orbital to a high-energy orbital. This is known as the electronic transition process. The electronic energy levels and electronic transitions of organic materials can be shown using a Jablonsky graph. The ground state is a singlet state, S_0 ; S_1 is the first excited singlet state; S_2 is the second excited singlet state and T_1 is the lowest triplet state. Once the molecule has absorbed the photons, the transition occurs in 10^{-13} s to 10^{-15} s. For most molecules, the transition will not be $0 \rightarrow 0$, but will occur between other levels. As shown in Fig. 4.6, the electron transfers to the second vibrational level and causes excited molecules to collide with surrounding molecules. The electron then degrades to the lowest vibrational level of the same electronic energy, due to vibration energy loss. This process is known as vibrational relaxation (V_r). Further degradation to the lowest vibrational level of a lower electronic energy level is called internal conversion (IC). V_r and IC are both types of V_r process and are conducted very quickly, in c. 10^{-13} s to 10^{-14} s. This is so fast that after the molecules have absorbed photons, they almost all instantly jump down to the lowest vibrational level of S_1 . Subsequently, the following processes can occur:

1. Return to the S_0 via luminescence, shown as f1 in Fig. 4.6. The luminous process of S_1 to S_0 is known as fluorescence, and the process takes 10^{-5} s to 10^{-9} s.
2. Return to the S_0 via collisions between molecules, losing energy. This process is called IC.
3. Transition to the triplet state T_1 . The transition from S_1 to T_1 contains multiple state changes; therefore, this transition is called intersystem crossing (ISC). This process is slower (about 10^{-6} s) than IC because the direction of spin needs to be changed. Two main processes occur after T_1 :
4. Return to the S_0 after ISC from T_1 to S_0 .
5. Return to S_0 through luminescence. The $T_1 \rightarrow S_0$ luminant phenomenon is known as phosphorescence, denoted by phos. Both processes necessitate a change in spin direction. They are therefore quite slow – about 10^{-4} s to 10 s.

The two processes IC and ISC, which involve energy loss but not light radiation, are called non-radiative deactivation processes. In addition to radiation and non-radiative transition processes, the inactivation of organic molecules from the excited state back to the S_0 could also take place through energy transfer, electron transfer, chemical reactions and other channels.

Frank–Condon principle

Organic semiconductors (small molecules and polymers) are typically comprised of at least hundreds of atoms, necessitating complicated quantum analysis. Therefore, the analysis of molecular transitions relies on the Born–Oppenheimer (B–O) approximation, which allows the wave function of a molecule to be broken into its nuclear and electronic components. Electronic transitions take place vertically between potential energy surfaces and they occur more rapidly than the



4.6 Jablonski energy level diagram.

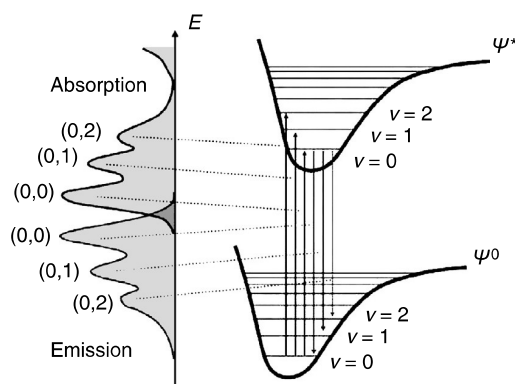
nuclei can respond, because of their large mass difference. Electronic transitions such as photon absorption and emission occur in 10^{-15} s, and molecule relaxation happens in 10^{-13} s, which further validates this approximation.

Electrons that are photo- or electro-excited to the vibrational levels of higher electronic states vertically within the nuclear configuration are unchanged. The electrons then relax to the lowest excited state with a new nuclear equilibrium position. When a photon is vertically emitted, the spectrum is red-shifted, which is called the Frank–Condon shift. This may be as large as 1 eV in some molecules, making them transparent to their own emission. Emission spectra therefore ‘mirror’ absorption but are displaced toward lower energy (Fig. 4.7). However, for the same polymer, non-mirror image symmetry between absorption and fluorescence is an interesting phenomenon. Conformational disorder in the polymer backbone is of utmost importance as it directly dictates the electronic properties of the polymer by disruption of the intrinsic π -conjugation.^{29,30}

Effect of heavy metals

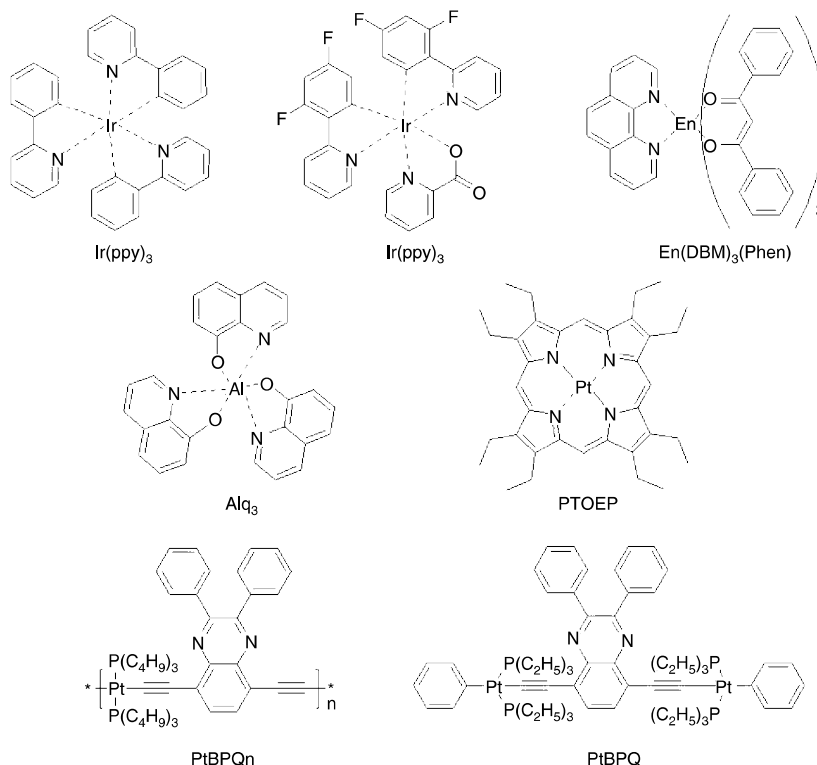
Some coordination compounds with heavy metals have strong spin–orbit coupling interactions, which can mix singlet and triplet excited states to increase the probability of generation of triplet excitons. This effect is also known as the heavy metal effect. Most heavy metal complexes, especially those with 4d and 5d electronic structures, show significant heavy metal effect. In this case, the process of dropping excited electrons back to S_0 is no longer subject to the spin-forbidden excited triplet state. These materials have a high luminous efficiency and a shorter phosphorescent lifetime.

Compared with fluorescence, phosphorescence emission is a long-life process. In the radiative transition process, the inactivation process is prone to occur due to triplet exciton collisions. In addition, this process competes with



4.7 Frank–Condon principle.

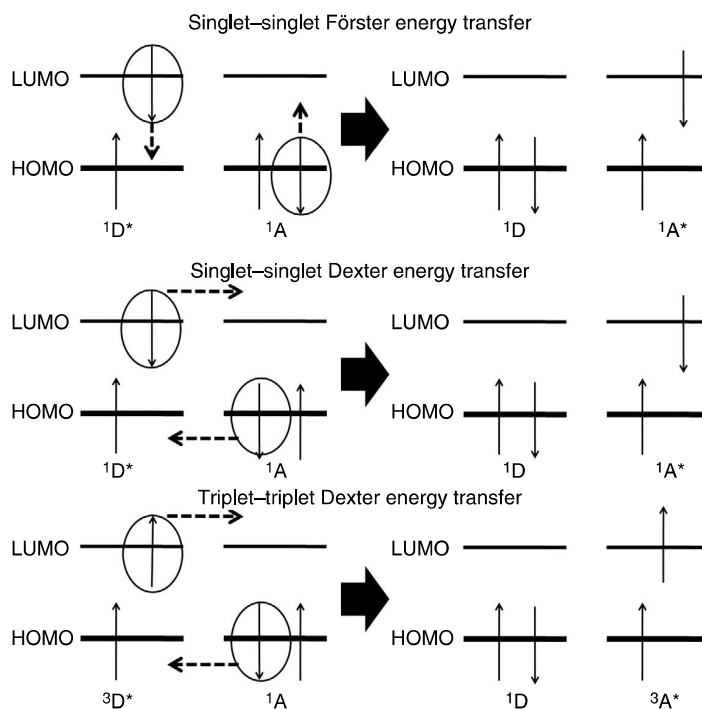
phosphorescence emission. The collisions between two excited triplet states lead to the generation of one excited singlet state and one ground singlet state, with the loss of at least one triplet exciton. This is known as the 'triplet annihilation' effect and is more obvious at high current density, leading directly to the reduced efficiency of light-emitting devices. To avoid this phenomenon, the host-guest system is usually used as the emitting layer of the phosphorescent light-emitting device. Host materials are fluorescent small molecules or polymers and guest materials are doped phosphorescent molecules covalently linked to the host materials. A certain energy match should exist between the host and guest. Therefore, electroluminescent phosphorescence emission could be achieved through energy transfer from the host to the guest. The coordination complexes of Ru, Re, Os, Ir, Pt (Fig. 4.8) and other metals are widely used in the field of electroluminescent phosphors, in particular Ir cyclopentadienyl organometallic complexes, which have a high quantum efficiency and a short triplet state lifetime. During the past few years, research in this area has been conducted around the world.^{31,32}



4.8 Metal complexes for OLED.

4.3.3 Exciton energy transfer

After electrons and holes are transported to the emitting layer, opposite charges recombine to generate excitons. Charge recombination process between an injected electron and an injected hole usually occur in two stages.³³ In the first step, the initially fully separated charges coalesce into loosely bound singlet or triplet polaron pairs, which are also referred to as charge-transfer excitons. In the second step, these intermediate states decay into lower singlet or triplet neutral exciton states. For excited states, the transfer of energy from one site to another requires (i) some electronic coupling, (ii) sufficient (thermal) energy to overcome possible differences between the initial and final energy site that may arise due to energetic disorder in the amorphous film, and (iii) configuration change of the molecular backbone at the initial and final sites. The electronic coupling between spin-singlet electrons is dominated by dipole-dipole interactions (Förster-type transfer).³⁴ However, an orbital overlap mechanism, such as exchange coupling (Dexter-type transfer)³⁵ is required to provide an electronic coupling for triplet transfer and singlet transfer³⁶ (Fig. 4.9).



4.9 Schematic diagram for Förster and Dexter energy transfers.

Förster-type transfer

Förster created a model to prove that the energy released from an excited donor (D) could simultaneously excite the ground-state acceptor (A), based on the coulombic interaction between these two chemical groups. At the lowest order, the electrostatic interaction between neutral molecules takes place between the dipolar components of their charge distributions. Given that there are transition dipole moments of randomly oriented D and A molecules, the transfer rate is³⁵

$$\Gamma_{\text{d-d}} = \frac{1}{\tau_{\text{D}}} \left(\frac{R_0}{R} \right)^6 R_0^6 = \frac{3\Phi_{\text{em}}}{4\pi} \int \left(\frac{\hbar c}{nE} \right)^4 F_{\text{D}}(E) \sigma_{\text{A}}(E) dE \quad [4.4]$$

where $F_{\text{D}}(E)$ is the normalized fluorescence emission spectrum and $\sigma_{\text{A}}(E)$ is the acceptor absorption cross-section. The natural lifetime of the donor is, τ_{D} , its emission quantum yield is Φ_{em} and n signifies the refractive index of its surroundings. According to Eq. 4.4, the competing rates of transfer and natural decay on the donor become equal when $R = R_0$, the Förster radius. Consequently, R_0 depends upon the overlap between donor emission and acceptor absorption. The operating distance of a Förster-type transfer is up to several nanometers, because of the long range of the coulombic interaction.

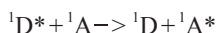
Dexter-type transfer

However, when the wave functions of donor and acceptor are spatially overlapped, the electron–electron repulsion exchange becomes significant. In 1953, Dexter considered the phenomenon of transfer by higher order multipoles, as well as previously neglected exchange effects. In the Dexter energy transfer process, two molecules (intermolecular) or two parts of a molecule (intramolecular) bilaterally exchange their electrons. The Dexter transfer rate can be described as follows^{35,37,38}.

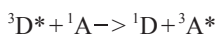
$$\Gamma_{\text{exch}} = \frac{2\pi}{\hbar} |V_{\text{exch}}|^2 \int F_{\text{D}}(E) F_{\text{A}}(E) dE \quad [4.5]$$

where the overlap between the normalized donor emission [$F_{\text{D}}(E)$] and the acceptor absorption [$F_{\text{A}}(E)$] reflects the joint density of states for the transition. Unfortunately, Eq. 4.5 rarely gives quantitative predictions because matrix elements (V_{exch}) are difficult to evaluate. Another problem that can occur is that the donor phosphorescence and the acceptor singlet→triplet absorption may be too weak to measure. However, the Dexter mechanism qualitatively relies on wave function overlap that is only significant when D and A are neighbors. As a result, excitons can only move among the nearest neighbor molecules via Dexter exchange. This exchange mechanism typically occurs within 10 Å and can also be referred to as the short-range energy transfer. The exchange mechanism is based on the Wigner spin conservation rule; thus, the spin-allow process could be one of the following:

Singlet–singlet energy transfer:



Triplet–triplet energy transfer:



According to the above energy transfer mechanisms, this host–guest strategy could be adopted to improve the efficiency and expand the spectrum of the luminance to achieve colorful luminance.^{23,31,32,39} Alq₃ is a widely used fluorophore in OLED, however it has a major shortcoming in its low fluorescence yield (~8%). To overcome this issue, Tang *et al.* improved the EL efficiency by a factor of 2 by doping the Alq₃ layer with highly efficient fluorescent molecules (DCM1 and DCM2).⁹ The energy transfer of excited states is singlet–singlet Förster-type transfer. As mentioned above, the maximum internal quantum efficiency in the EL process is usually only 25%, which originates from the ratio (1 : 3) of singlet and triplet for small molecules. However, this strategy still does not overcome the limitation of 25% for singlet generation. Thus, utilizing the energy of the triplet is significant in improving the luminous efficiency of OLEDs. A reasonable approach would be to extract triplet excitons from a semiconducting host material using a phosphorescent dye dopant. In 1998, Forrest and coworkers³⁹ reported high-efficiency (>90%) energy transfer from both singlet and triplet states (Dexter energy transfer), in a host material (Alq₃) doped with the phosphorescent dye (PtOEP). These doped electroluminescent devices generate saturated red emission with peak external and internal quantum efficiencies of 4% and 23%, respectively. PtOEP possesses superior quantum and power efficiencies by at least one order of magnitude compared to some Eu complexes.⁴⁰ Then, external quantum efficiencies of up to 5.6±0.1% at low brightness and 2.2±0.1% at 100 cd/m² were further obtained by using BCP as the host material.⁴¹ Phosphorescent dyes with these properties have demonstrated very high-efficiency luminescence. However, triplet–triplet annihilation in phosphorescence degrades phosphorescent emission efficiency at high excitation density.⁴² Fluorescent materials are therefore suited to many electroluminescent applications. In 2000, Forrest and coworkers⁴³ demonstrated that triplet states can be used to achieve fluorescence in OLEDs by using a phosphorescent sensitizer to excite a fluorescent dye. The mechanism for energetic coupling between phosphorescent and fluorescent molecular species is a long-range, non-radiative energy transfer: the internal efficiency of fluorescence can be as high as 100%. Table 4.3 summarizes some important energy transfers used in highly efficient OLEDs.

4.3.4 Annihilation

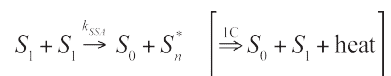
Energy transfer may also occur between one excited state and another. Such events are termed ‘annihilation’ reactions, because the product is in both a ground

Table 4.3 Energy transfer mechanisms for high efficient OLED

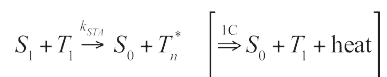
Host	Donor	Acceptor	Type	Mechanisms	Ref.
Alq ₃	Alq ₃	DCM2	S-S	Förster	37
	Alq ₃	PtoEP	T-T	Dexter	
BCP	BCP	Ir(ppy) ₃	S-S	Förster	41
	BCP	DCM2	S-S	Förster	
	BCP	Ir(ppy) ₃	S-T	Dexter	
	Ir(ppy) ₃	DCM2	S-S	Förster	
	Ir(ppy) ₃	DCM2	T-S	Förster	

state and a highly excited state, resulting in the net loss of one exciton. Annihilation reactions involve either two excitons, or an exciton and a free (or trapped) polaron. These processes play a critical role in the operation of OLEDs, which affects the quantum efficiency and disturbs the estimation of the singlet generation fraction.

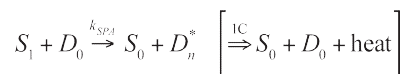
There are four broad categories of annihilation reaction. Singlet excitons may annihilate with other singlets (SSA):



or with triplets (STA):



or with polarons (D) (SPA):



Singlet annihilations tend to use the Förster-based theory of energy transfer, which is a long-range interaction. However, triplet–triplet annihilation (TTA) proceeds purely via Dexter exchange and has two spin conserving outcomes:

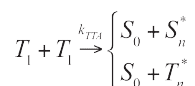


Table 4.4 gives some annihilation rate constants for small molecules and polymers. In general, the TTA rate is obviously lower than that of singlet annihilation. However, triplet annihilation plays a more central role compared to singlet, since a large fraction of electron-hole recombination events in an OLED result in the formation of triplet states. In the case of polymers, the TTA of PFO derivatives has been extensively researched. Recently, Hoffmann *et al.*⁴⁴ found that when using short oligomers instead of polymers and aiming for flexible rather than rigid backbones, the TTA rate is lower. Meanwhile, it is noted that singlets produced by TTA are responsible for delayed fluorescence. As a consequence the apparent

Table 4.4 Annihilation rate constants for several small-molecule and polymeric organic semiconductors

Materials	K_{SSA}	K_{STA}	K_{SPA}	K_{TTA}	Ref.
Anthracene	1×10^{-8}	5×10^{-9}	1×10^{-9}	2×10^{-11}	42
Alq3	1×10^{-10}		5×10^{-10}		40
Alq3:DCM		2×10^{-10}			43
BCP				2×10^{-14}	44
BCP:BCzVBi		8×10^{-10}			43
PFO	5×10^{-8}	5×10^{-10}			45, 46
m-LPPP		6×10^{-10}	9×10^{-8}		46, 47

Unit: $\text{cm}^3 \text{s}^{-1}$

fluorescent lifetime is much longer than the natural fluorescent lifetime since it derives from long-lived triplet states. This nonlinear loss mechanism for triplet excitons is in fact the reason why many previous studies drastically underestimated the number of triplet excitons generated, and thereby obtained excitation dependent (interpreted as electric field-dependent) singlet exciton generation rates as high as 95%.^{45,46} The results must therefore be studied and taken into account all together, in order to facilitate understanding.

4.4 Thermal stability

4.4.1 Glass transition temperature

Glass transition is the inherent nature of amorphous polymer materials, and dramatically affects the usefulness and processability of organic materials. Glass transition occurs between the high-elastic and glassy states. In view of the molecular structure, the glass transition temperature T_g reflects the relaxation of the polymer amorphous component from the frozen state to the thaw state. Below the T_g , the polymer is in a glass state, in which the molecular chain and the chain segment cannot move. Atoms and groups only vibrate in their equilibrium position, however the chain segment starts to exercise when the temperature increases, demonstrating high elastic properties. When the temperature is elevated sequentially, the entire molecular chain exhibits a viscous flow property. T_g is usually determined by differential thermal analysis (DTA) and differential scanning calorimetry (DSC).

4.4.2 Thermal decomposition temperature

The thermal decomposition temperature T_d , at which the molecule starts to break up and decompose, can be determined via thermogravimetry. T_d is related to the molecular structure, the activation energy of decomposition, the aggregated state and the crosslink density of organic materials.

4.4.3 Relationship between thermal stability and molecular structures

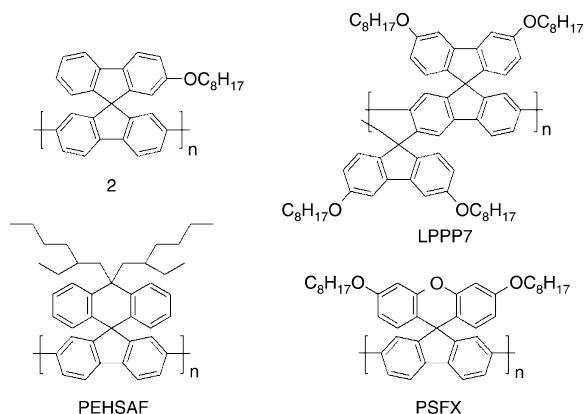
The effective tuning of material phase behavior is a key issue in materials science and practical application. The phases of a material can dramatically affect its optical and electronic properties. Compared to crystalline materials, liquid crystal in its isotropic amorphous state is widely studied because it has good processability and transparency.

The relationships between the molecular structure, glass formation, T_g and the stability of the glassy state indicate that the molecular design of amorphous materials needs to obey the following basic principles⁴⁷:

1. nonplanar molecular spatial configuration;
2. a variety of molecular conformations;
3. the introduction of bulky and rigid substituents in promoting the formation of the glassy state and enhancing the stability of the glassy state; and
4. large molecular size to improve T_g .

Polymers

A polymer material with weak crystallization and excellent process ability is necessary for large-area displays. At present, homopolymerization of fluorene and its derivatives is mainly carried out by the introduction of large steric aromatic groups. Bo and coworkers⁴⁸ synthesized a homopolymer of spirobifluorene, **2**, with a long-chain alkoxy group (Fig. 4.10). This polymer has a good solubility in tetrahydrofuran (THF) and high thermal stability ($T_g \sim 121^\circ\text{C}$, no green emission annealed at 200°C for 3 h). They also synthesized spirobifluorene derivatives and



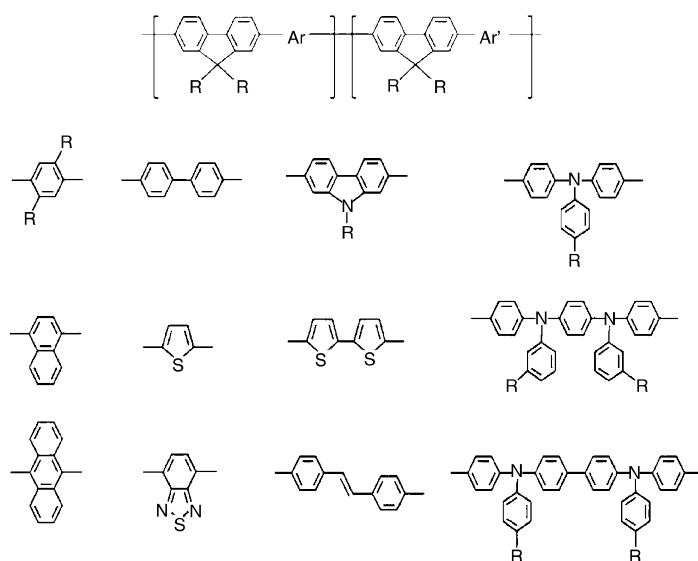
4.10 Molecular structures of **2**, LPPP7, PEHSAF and PSFX.

screwed the bridge ladder poly(p-phenylene) (LPPP7).⁴⁹ The polymer was annealed at 110°C for 24 h without green emission. Meanwhile, the EL of the device ITO/PEDOT/ladder-polymer/LiF/Al with color coordinates (0.17, 0.22) was the same as the photoluminescence of this molecule.

Based on the spiro fluorene structure, other researchers have introduced a six-membered ring spiro structure on the 9-position of the fluorene. Kim *et al.*⁵⁰ synthesized the polymer (PEHSAF) (Fig. 4.10). T_g is above the decomposition temperature 367°C because of the rigid structure of spiral anthracene fluorene. Based on the ITO/PEDOT (60 nm)/PEHSAF (70 nm)/LiF (5 nm)/Ca (10 nm)/Ag (150 nm) device, its brightness, maximum current efficiency and EQE were 1600 cd/m², 0.19 cd/A, and 0.20% respectively.

In 2005, Shu *et al.*⁵¹ synthesized 9-xanthene-substituted PF poly[2',7'-di-n-octyloxyspiro(fluorene-9,9'-xanthene)-2,7-diyl] (PSFX) (Fig. 4.10) using spiro (fluorene-xanthene) as monomers. Because of the presence of long-chain alkoxy, the T_g (149°C) of the polymer is lower than PEHSAF, but higher than poly(9,9-dialkylfluorene) because of the presence of long-chain alkoxy. The maximum EQE, brightness, and current efficiency of ITO/PEDOT/PSFX/TPBI/Mg:Ag/Ag device were 1.74%, 1000 cd/m², and 0.82 cd/A respectively.

However, the hot issue in current research is that of copolymers. Device performance is easily improved through the copolymerization of different monomers. Dow has developed a variety of high-performance PF-like copolymers⁵² (Fig. 4.11) for efficient blue, green, and red emission. In this study,



4.11 Molecular structures of the copolymers and the monomers.

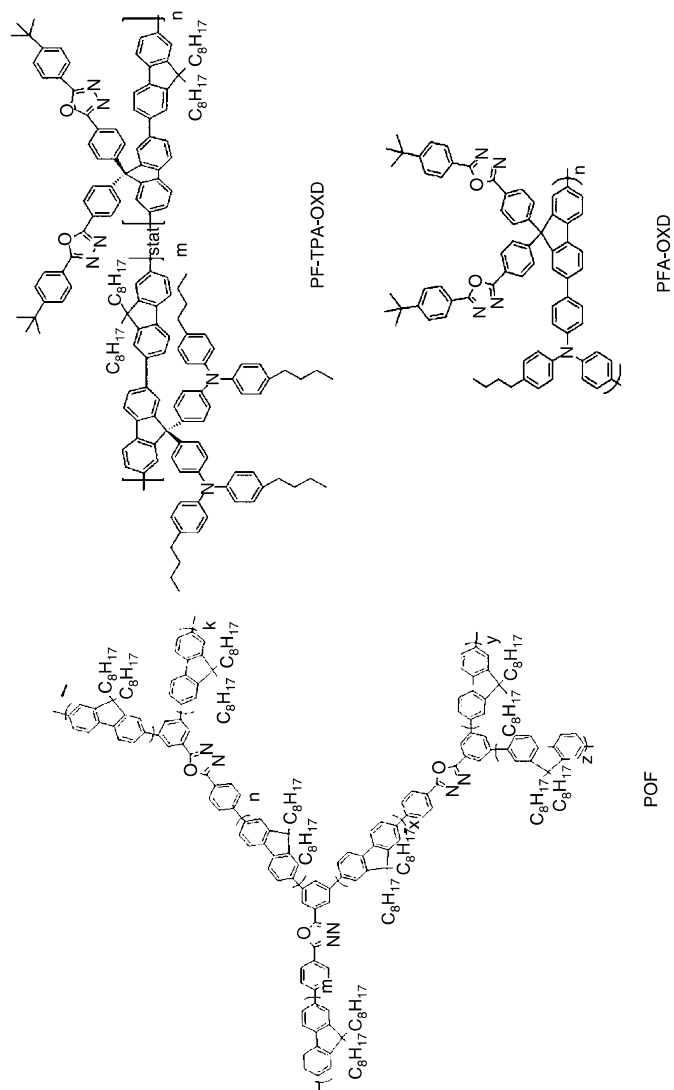
a series of copolymers with weight of 220 000 to 430 000 and T_g of 100 °C was synthesized via a modified Suzuki coupling reaction. The inorganic impurity content of these materials is below 50 ppm. Among these, poly(3,4-ethylenedioxythiophene) (PEDOT) served as the hole transport layer and Ca as the cathode. The color coordinates were (0.16, 0.19) and the maximum current efficiency was 2.82 cd/A (190 cd/m²). When the brightness was 4000 cd/m², the maximum efficiency was 2.0 cd/A.

Shu *et al.*^{53,54} copolymerized fluorene with a monomer that had good charge transport ability, to improve its performance. By introducing the hole transport group triphenylamine (TPA) and the electron transport group oxadiazole (OXD), they synthesized the bipolar fluorene derivative PF-TPA-OXD (Fig. 4.12). This polymer has a high T_g (166 °C), and the EL of the film remains unchanged after heat treatment at 150 °C. Device ITO/PEDOT:PSS/PF-TPA-OXD/Ca/Ag showed a sky blue emission, color coordinates of (0.191, 0.141), a maximum EQE of 1.21%, and a maximum brightness of 4080 cd/m². They also synthesized a PF copolymer containing the electronic transport group of the OXD-based monomers and the hole transport group of TPA (Fig. 4.12).⁵⁵ The bipolar PF derivative PFA-OXD can also improve the balance of the electron and hole injection, with its T_g up to 306 °C. Green emission was not detected when the polymer was annealed in an argon atmosphere at 150 °C for 20 h. The ITO/PEDOT:PSS/PFA-OXD/TPBI/Mg:Ag device resulted in good blue emission, of which the maximum current efficiency and EQE, maximum brightness, and color coordinates were 2.07 cd/A, 1.59%, 7128 cd/m² and (0.14, 0.15) respectively.

Hyperbranched polymers with a three-dimensional (3D) molecular structure, high solubility and good processability can help to reduce intermolecular interactions in enhancing luminance efficiency.^{56,57} Huang *et al.*⁵⁸ introduced an OXD unit into hyperbranched PF to synthesize poly(9,9-dioctylfluorene) (Fig. 4.12). The electronic transport of PF can be increased by introducing the OXD-branched unit with electron acceptor properties, whereas the aggregation and generation of a base-excited association complex would be inhibited. Only a slight change in the PL spectrum was observed after heat treatment, which showed good thermal stability. The EQE and maximum brightness of device ITO/PEDOT/PVK/polymer/Ba/Al were 1.5% and 1150 cd/m²; its EL and PL spectra were very similar.

Amorphous molecules

Small organic molecule materials usually have relatively low glass transition temperatures. Joule heat is generated when the device works. Heat re-crystallizes small organic molecules, damages the homogeneity of the material and reduces the lifetime of the device. In recent years, research has been carried out into the development of amorphous molecular materials⁵⁹ with the following features: controlled structure, uniform molecular weight, fewer defects, simple purification and good processability via vapor deposition or spin coating to form a stable



4.12 Molecular structures of hyperbranched polymers.

amorphous film. This category of materials includes small molecule materials and amorphous oligomers.

Obviously, the molecular structure of the amorphous material significantly affects stability. Currently, the spatial structure of molecules can be divided into spiro-shaped, star-shaped, dendritic, tetrahedral, and other configurations based on a 3D π -conjugated electron system:

1. *Spiro material*: the most typical spiral-shaped molecules are spiro-bifluorenes, in which sp^3 hybridization of the central atom bridges the two fluorene monomers together. Spiro-bifluorene with an orthogonal three-dimensional structure can reduce the aggregations or excimer formations to improve quantum efficiency. In addition, it can increase the material T_g and reduce the tendency of molecular crystallization to form a stable glassy material.⁶⁰ Kim *et al.* connected fluorene to 9,10-bi[(2',7'-di-*t*-butyl)-9',9'-spirobifluorene] anthracene, whose T_g is up to 207°C and the current efficiency of which is 3 cd/A.⁶¹ Shen *et al.* synthesized a series of 2',7'-di-*tert*-butyl-9',9'-spirobifluorene derivatives with aromatic amines, with a T_g of 215°C and an EQE of 4.2%.⁶² Recently, Xie *et al.* have synthesized an H-shaped double-spiral structure of the fluorene derivatives, in which T_g is as high as 320°C.⁶³
2. *Star-shaped material*: Pei *et al.*⁶⁴ synthesized a series of star-shaped materials using a core of truxene and an arm of aryl oligomers. These materials show blue-violet light in THF; T_g is 196°C, and EQE in solution is up to 98%.
3. *Dendritic materials*: Yang *et al.*⁶⁵ synthesized multibranched compounds of tricarbazolyl benzene, which can produce strong fluorescence emissions. Zhao *et al.* synthesized anthracene-based molecules using diphenyl benzene as the dendrimer branch, whose EQE is 0.82%, but a T_g of only 59°C.⁶⁶
4. *Tetrahedral materials*: Liu *et al.* synthesized a tetrahedral molecule using silicon atoms as the center and fluorene and carbazole derivatives as the arms. The maximum emission peak of this film is 399 nm, with a quantum efficiency of up to 80%. However, it has a T_g of only 78°C.⁶⁷

4.5 Conclusion and future trends

OLEDs are mainly used for two purposes: flat panel displays and lighting. Excellent device performance and outstanding stability are two essential elements for the future large-scale application of OLEDs. In order to achieve improvements in these areas, efficient materials and excellent processing are necessary. In the past few decades, materials for OLEDs have made remarkable progress, achieving high electrical conductivity of the charge transport materials and high quantum efficiency of fluorescent and phosphorescent materials. These advances have allowed OLEDs to graduate from laboratorial to industrial functions. However, there are still some issues that need to be explored and resolved. There is still a need for development of more efficient materials, especially for highly efficient

blue-light phosphorescent materials. In addition, the relationship between the molecules, or between the materials (organic films) formed by these molecules, and the conductivity or photophysical properties of the OLED requires further study. In terms of device physics, the following challenges need to be overcome: (i) the mechanism of exciton annihilation, which affects the control of the triplet and singlet; (ii) the mechanism of OLED degradation, which significantly affects device stability and the design of processing technology. From this review, it can be posited that developments in their constituent materials will allow further developments in the field of OLEDs.

4.6 References

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Phosphorescent OLEDs for solid-state lighting

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Abstract: Several properties of phosphorescent emitters and various device architectures enable high-efficacy white phosphorescent organic light-emitting diodes (OLEDs). For example, white OLEDs (WOLED) can avail of phosphorescent exciplex states that efficiently produce very broad emission. The level of efficacy suggests that WOLEDs could be used for solid-state lighting applications, so tools and methods have been developed to screen new materials and to model electro-optical characteristics for the optimization of device efficiency. After two decades of research on WOLEDs, commercialization of devices is close to widespread adoption because of many advances in the technology, and the next decade may clarify the success of phosphorescent OLEDs for solid-state lighting.

Key words: phosphorescent, white, illumination, organic light-emitting diode (OLED), efficiency.

5.1 Introduction

Fluorescent materials were the first type of emitters that were investigated for use in white organic light emitting diodes (WOLED) (Kido *et al.*, 1994), but phosphorescent materials opened the opportunity for widespread applications of WOLEDs in solid-state lighting. Phosphorescent materials harness all available molecular energetic states created from the injection of electrons and holes into a device and efficiently create light. Initial researchers, however, avoided phosphorescent materials because phosphors were generally assumed to be inefficient emitters at room temperature, and their long radiative lifetimes stymied any potential usefulness. The chemical, photophysical, synthetic production, purification, packaging, decomposition, method of incorporation into devices, and other details of phosphorescent materials however have been studied since 1998 when results on red emission from 2,3,7,8,12,13,17,18-octaethyl-21H, 23H-porphine platinum(II) (PtOEP) were published (Baldo *et al.*, 1998).

The seminal discovery of Baldo *et al.* was soon followed by other reports on phosphorescent material phenomena and properties that influence every aspect of WOLEDs (Adachi *et al.*, 2001; Anthopoulos *et al.*, 2003; Baldo *et al.*, 1999, 2000; D'Andrade *et al.*, 2002). Device efficiency climbed (D'Andrade *et al.*, 2008a; Su *et al.*, 2009), reliability improved (Xia *et al.*, 2007a), and a range of colors suitable for high quality illumination sources (Brown *et al.*, 2004) were achieved within a decade after the demonstration of phosphorescent emitters in

organic light-emitting diodes (OLED), but low-cost manufacturing and competitive technologies have made for an arduous effort to attain large scale availability of WOLED luminaires. For example, blue light-emitting diodes (LED) were successfully commercialized in 1993; thereafter, white LEDs were used in hundreds of illumination products, and there are reports on the power efficacy of white LEDs exceeding 200 lm/W (Sun, 2012).

The total power efficacy of a WOLED is a measure of the total optical power emitted in all directions divided by the total electrical power, and the total power efficacy of small laboratory devices has steadily increased to 150 lm/W (Reineke *et al.*, 2009) between 2000 and 2009. Table 5.1 lists a sample of laboratory devices and their associated performance characteristics including WOLED architectures, the maximum reported efficacy, Commission Internationale de l'Eclairage (CIE), and color rendering indices (CRI) (Tokito *et al.*, 2003; Sun *et al.*, 2006; Sun and Forrest, 2007; Su *et al.*, 2008; Reineke *et al.*, 2009; D'Andrade *et al.*, 2002, 2004; Adamovich *et al.*, 2002; Liu *et al.*, 2000; Ko and Tao, 2001; Kido *et al.*, 1994; Jordan *et al.*, 1996; Jiang *et al.*, 2000; Hide *et al.*, 1997; Deshpande *et al.*, 1999; Komoda *et al.*, 2011).

WOLED architectures, including those listed in Table 5.1, have tremendous variety compared to monochromatic OLEDs because multiple emitters have to be incorporated and unique interactions between emitters are often utilized to create novel devices. For example, fluorescent blue emitters have been combined with green and red phosphorescent emitters to enable an internal quantum efficiency (ratio of photons formed to electrons injected) of 100% (Sun *et al.*, 2006); or a single phosphorescent emitter material can produce white emission from a combination of monomer and excimer states (D'Andrade *et al.*, 2002); or multiple devices can be vertically stacked and electrically connected in series (Forrest *et al.*, 1997; Hatwar *et al.*, 2010; Komoda *et al.*, 2011). One key goal of all device architectures is to enable high efficacy, because there is a constant demand for novel high efficacy illumination sources.

Lighting accounted for 8.3% and 7% of all the energy consumed in the United States in 2001 and 2010, respectively. The notable decrease from 765 Tera-watt-hours to 700 Tera-watt-hours of electricity usage for illumination from 2001 to 2010 may be partially attributed to an increase in the average efficacy, based on energy use and lumen production in the United States, from 45 lm/W to 58 lm/W. Sixty-five Tera-watt-hours is equivalent to the energy produced by about twenty-one 500-MW coal burning plants and the total energy consumed by about 3.7 million homes in 2010 (United States Department of Energy, 2001, 2012).

The United States Department of Energy (U.S. DOE) and other funding agencies are cognizant of those energy consumption statistics and of WOLED efficacy improvements; hence, the U.S. DOE has been a steadfast financial supporter of propelling laboratory WOLED results towards commercial lamps with lumen output comparable to traditional bulbs. Also, the European Commission supported the OLED100.eu project with several objectives including enabling

Table 5.1 Selected WOLED architectures with their corresponding performance characteristics

Architecture	η_p (lm/W) ^a	CIE ^b	CRI	Label	References
Phosphorescent with three emissive sub-layers	49, 150	(0.41, 0.49)	69	i	(Reineke <i>et al.</i> , 2009)
Phosphorescent with multiple emissive sub-layers	58, 98.6	(0.34, 0.40)	68	ii	(Su <i>et al.</i> , 2008)
Phosphorescent with three emissive layers	32, 54	(0.37, 0.41)	81	iii	(Sun and Forrest, 2007)
Phosphorescent and fluorescent hybrid	22.1, 37.6	(0.40, 0.41)	85	iv	(Sun <i>et al.</i> , 2006)
Phosphorescent triple-doped emissive layer	26, 42	(0.43, 0.45)	80	v	(D'Andrade <i>et al.</i> , 2004)
Multilayer phosphorescent	10, 17	(0.35, 0.36)	≤60	vi	(Tokito <i>et al.</i> , 2003)
Phosphorescent excimer	12.2, 21	(0.36, 0.44)	67	vii	(Adamovich <i>et al.</i> , 2002)
Multi-emissive phosphor doped layers	6.4, 11	(0.37, 0.40)	83	viii	(D'Andrade <i>et al.</i> , 2002)
Two doped and one neat emissive layers	1.93, 3.3	(0.35, 0.34)	≤80	ix	(Ko and Tao, 2001)
Doped blocking layers	1.39, 2.4	–	–	x	(Jiang <i>et al.</i> , 2000)
Multiple quantum wells	1.1, 1.9	(0.32, 0.38)	≤80	xi	(Liu <i>et al.</i> , 2000)
Interlayer sequential energy transfer	0.35, 0.6	(0.33, 0.33)	≤70	xii	(Deshpande <i>et al.</i> , 1999)
Hybrid polymer/inorganic	0.63, 1.1	(0.34, 0.29)	≤70	xiii	(Hide <i>et al.</i> , 1997)
Three neat emissive layers	0.5, 0.9	(0.31, 0.41)	≤80	xiv	(Jordan <i>et al.</i> , 1996)
Triple doped polymer with vacuum deposited transport layers	0.83, 1.4	–	–	xv	(Kido <i>et al.</i> , 1994)

Notes: Where the color rendering index (CRI) is not reported, a maximum value is estimated from spectral data.

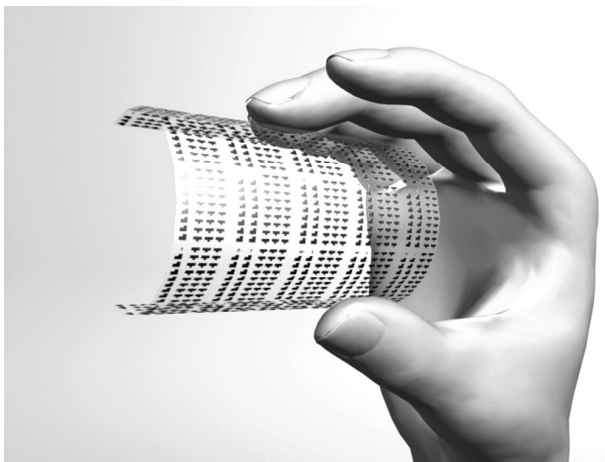
^a Maximum reported forward viewing external power efficiency is the first number. The second is the maximum total external power efficiency. Where not reported, it is the maximum forward viewing external power efficiency multiplied by 1.7.

^b Commission Internationale de l'Eclairage coordinates at 100 cd/m².

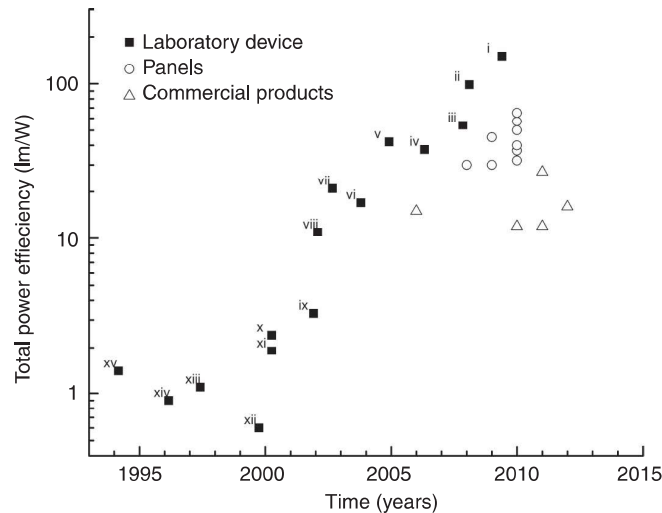
WOLEDs with low-cost 100 Euro/m², high power efficacy (100 lm/W), long lifetime of 100 000 hours, and large area form factor of about 100 × 100 cm². In Japan, the New Energy and Industrial Technology Development Organization has funded WOLED projects.

WOLED manufacturing costs, however, remain a formidable challenge. Inorganic LED costs have decreased from US\$20/lm to US\$0.01/lm over the last four decades, and the cost of an incandescent lamp is less than \$0.03/lm; whereas, an estimate for WOLED costs is about \$10/lm (So *et al.*, 2008). WOLEDs in 55-inch flat-panel displays have been produced using vacuum sublimation and under very strict quality requirements that exceed those necessary for illumination products, so there are numerous lessons that may be learned from display manufacturers and applied to development costs for organic solid-state lighting. The potential solution, however, to reducing WOLED costs may be in new manufacturing technologies such as roll-to-roll processes (So *et al.*, 2008). Organic electronic circuits are capable of being formed on flexible plastic as shown in Fig. 5.1; hence, the ability to have a roll-to-roll process has the potential to be commercially realized.

The efficacy of WOLED panels, which are typically several square centimeters and are capable of producing several lumens, and the efficacy of commercial products have also increased, but the panel and product efficacies are low compared to state-of-the-art laboratory results. Fig. 5.2 is a plot of device (square), panel (circle), and commercial product (triangle) efficacies versus the time the efficacy value was publicly released. The difference between the efficacy of



5.1 Organic electronics fabricated on a flexible substrate have the potential for commercial applications and to enable roll-to-roll manufacturing methods.

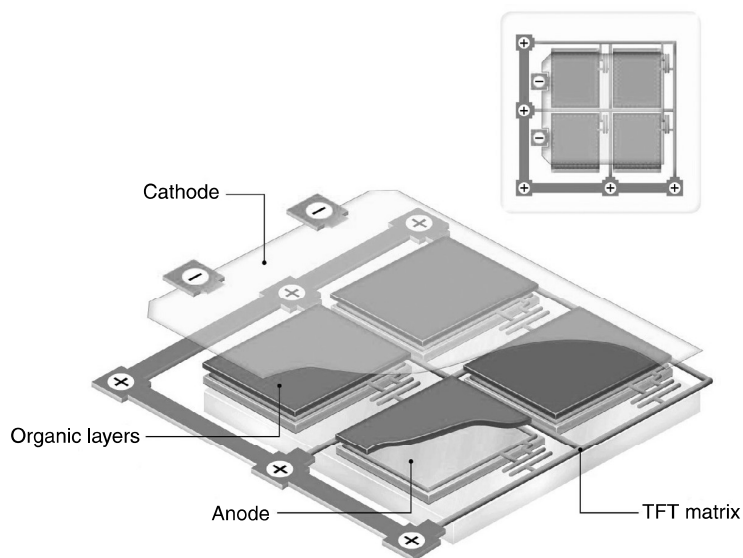


5.2 Plot of device (■), panel (○) and commercial product (△) efficacies versus the approximate time when the efficacy value was publicly released.

laboratory devices and products or panels is due to multiple issues such as electrical losses in indium-tin-oxide (ITO) (Cester *et al.*, 2010; Pinato *et al.*, 2009a), efficiency roll-off with increasing light output (Setoguchi and Adachi, 2010), outcoupling efficiency (Meerheim *et al.*, 2010), thermal stability, availability of advanced materials, and architectural complexity of high-efficacy devices.

It may require months or years for new advanced generation materials to be scaled up to sufficient quantities for mass production and to be fully qualified for a myriad of manufacturing specifications that are not necessary for laboratory demonstrations. Furthermore, research tools typically are highly reconfigurable to allow for novel device architectures, but production tools do not have the same ease of tool modification.

For WOLED products to successfully compete with incumbent fluorescent lighting technologies and to gain significant market penetration, commercial product efficacies have to improve beyond the values plotted in Fig. 5.2. For example, the commercial and institutional lighting market segments present a promising opportunity for WOLEDs because those segments account for 40% of the entire lighting market and 75% of all fluorescent luminaires are sold into those segments (Ngai, 2010). For WOLED technology to effectively displace fluorescent luminaires, its efficacy may have to be above 70 lm/W at a luminance value above 2000 cd/m² and product lifetimes may have to exceed 50 000 hours (Ngai, 2010). Interestingly, manufacturers of active matrix OLEDs (see Fig. 5.3) are



5.3 Active matrix organic light emitting diode pictorialized pixel circuit and layout. Image courtesy of © Exponent, Inc. 2008.

currently producing WOLED products with about 53 lm/W, and a luminaire manufacturer, Acuity Brands, has demonstrated concept luminaires with 53 lm/W that produce 6400 lm.

This chapter examines several properties of phosphorescent emitters that enable high efficacy WOLEDs. Methods and materials used to enable device operation at low voltage, another key requirement for high efficacy, are important topics discussed elsewhere (Meerheim *et al.*, 2009). Properties and phenomena of phosphorescent materials such as triplet-singlet energy transfer are discussed in Section 5.2, and Section 5.3 contains references to reports on novel WOLED architectures that utilize the properties and phenomena of phosphorescent emitters. Finally, Section 5.4 is a general outlook, including a discussion on what needs to be accomplished, and a brief comparison of the progress of inorganic white LEDs with WOLEDs.

5.2 Phosphorescent materials

5.2.1 Properties

Phosphorescent materials have been used as hosts, transport layers, injection layers, and blocking layers. Here, the focus is on phosphorescent emitters. There are many phosphorescent emitter properties that assist in understanding the

physical and chemical nature of the phosphors and that assist in screening new materials for incorporation into a device.

For example, these four groups of data provide very useful measurements to developers and manufacturers of WOLEDs: optical properties (photoluminescence efficiency [PLQE], photoluminescence emission and absorption spectra, excited state lifetime, complex refractive index); transport properties (highest occupied molecular orbital [HOMO] energy, lowest unoccupied molecular orbital [LUMO] energy, mobility); thermal properties (glass transition temperature, sublimation temperature, thermal decomposition); and chemical properties (purity, steric hindrance, synthesis).

The design of a new emitter involves a significant amount of heuristics. If a potentially suitable emitter is discovered, it can be thoroughly qualified by the above measurements and commercially fail because it is unsuitable for a specific manufacturing process. Fortunately, there are hundreds of different chemical groups and many different positions on an emitter molecule; therefore, a commercially viable solution is often found by adding or removing functional groups from various positions on a core molecular structure.

Optical properties provide immediate and easily obtained feedback for the WOLED design process. Spectral analytical tools have been developed, sometimes specifically for OLED materials, that enable quick, reproducible results that allow effective comparisons of many molecules. After a library of data is created from these tools, molecules may be screened without device fabrication.

For example, time correlated single photon counting (TCSPC) is a low cost alternative to a streak camera that provides excited state lifetime data. Short excited state lifetimes are potentially more desirable because the emission will less likely be quenched and devices may have long operational lifetimes (Kawamura *et al.*, 2006; Xia *et al.*, 2010). Hamamatsu (Hamamatsu, 2011; Endo *et al.*, 2008) offers a small form factor system that effectively determines the absolute PLQE, which is used to investigate the performance of combinations of hosts and emitters (Kawamura *et al.*, 2005). Ideally, hosts doped with emitters should have a PLQE of 100%, but typical high-efficiency host-emitter combinations are at about 95% when the emitter concentration is optimized for devices.

J.A. Woollam Co. Inc. has a table top product, alpha-SE® ellipsometer, that can quickly determine the complex refractive index data over the visible spectrum, and that data is input for WOLED optical cavity design using software such as SETFOS® or simOLED®.

Both the HOMO and LUMO energy levels are helpful in designing or understanding device functionality, but they are costly data to obtain for every molecule using ultraviolet photoemission spectroscopy and inverse photoemission spectroscopy (Hill *et al.*, 2000). A correlation between the HOMO energy and the oxidation potential of a molecule was experimentally determined to be $E_{\text{HOMO}} = -(1.4 \pm 0.1) \times (qV_{\text{CV}}) - (4.6 \pm 0.08) \text{ eV}$ (D'Andrade *et al.*, 2005a), where

E_{HOMO} is the energy of the highest occupied molecular orbital in the solid state and qV_{CV} is the oxidation potential versus ferrocene/ferrocenium.

The LUMO energy can be estimated using knowledge of the HOMO energy and the energy at the onset of optical absorption, which can often be learned from knowledge of the imaginary component of the complex refractive index. Given these two energy levels, one can understand how charge flows get trapped and blocked in various WOLED architectures; therefore, one can improve device efficiencies and lifetimes with the appropriate selection of materials based on their HOMO and LUMO energy levels (Xia *et al.*, 2007b). These data together with electron and hole mobility values of each WOLED layer may be used in device simulation software to design WOLEDs.

The thermal properties listed above are more pertinent for device operational stability and commercial manufacturability. A low glass transition temperature may be indicative of short operational lifetimes (D'Andrade *et al.*, 2003). The sublimation temperature and thermal decomposition are also important because new materials have to be sublimed at temperatures comparable to other materials, so they do not decompose in the source boat and do not poison vacuum evaporation systems by migrating or unintentionally subliming during other process steps (Kwong *et al.*, 2006; MacKenzie *et al.*, 2008).

Finally, the list of chemical properties is extensive including, for example, purity, steric hindrance and synthesis. Chemists can make almost any molecule, but purification is significantly difficult, so material purity is about 99.7% instead of at or above 99.999%. Purity is particularly important for a device's operational stability and for reproducing results (Higashi *et al.*, 2003; Tipnis *et al.*, 2008). Molecular steric hindrance is manipulated to prevent aggregation and impurity quenching, which at least affects device efficiency, lifetime, and color (Baldo *et al.*, 2001; Markham *et al.*, 2002; Anthopoulos *et al.*, 2003; Lin *et al.*, 2006).

Various synthetic routes at the least can affect the material cost, material purity and device performance. Advances in device performance, such as operational lifetimes, may be related to the introduction of new materials and to advances in how the materials are synthesized, because it is possible there are differences in the impurities present in the final product depending on the synthetic process steps. Over time and with significant effort, chemists get better at making and purifying the materials that are used to enable long device lifetimes (Xia *et al.*, 2007b).

5.2.2 Energetics

Molecular phosphorescence can be understood by reviewing several references (Pope and Swenberg, 1999; Turro, 1991; Barltrop and Coyle, 1978; Birks, 1970; Silinsh and Capek, 1994). Using the Born-Oppenheimer approximation (Born and Oppenheimer, 1927), the nuclear motion, electronic motion, and

spin contributions to the molecular wave function are treated as independent functions. The ‘true’ molecular wave function, Ψ , is therefore approximated as follows:

$$\Psi \propto \psi_0 \chi \zeta \quad [5.1]$$

Here, ψ_0 , χ , ζ represent the approximate wave functions for the electronic wave function, for nuclear position, and for spin, respectively.

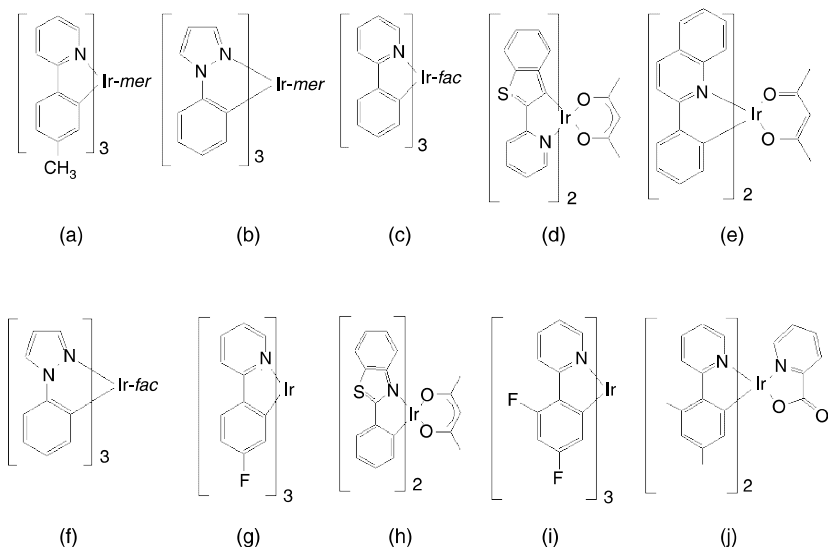
A singlet state is formed when a molecular configuration has no net spin ($\zeta=0$), i.e. for every electron that has spin $\frac{1}{2}$ (up), there is an electron that has spin $-\frac{1}{2}$ (down). Therefore, most molecules have a ground state singlet (oxygen is a notable exception that has a triplet ground state), since the electrons are placed in the lowest energy levels.

An excited state of a molecule however may possess two electrons whose spins are parallel and hence has $\zeta=1$. A non-zero spin occurs because the electrons are unpaired and exist in two different orbitals; hence, the Pauli Exclusion Principle is obeyed. Due to the different spin of triplets and singlets, transitions between triplet and singlet states of a molecule are disallowed unless they proceed due to spin–orbit coupling perturbations that increase with heavy atoms such as iridium and platinum (Myers and Xue, 2012). Said differently, a molecule in an excited triplet state will not efficiently return to the ground singlet state and emit light unless it contains a heavy atom.

Phosphorescent emitting materials therefore are not surprisingly comprised of iridium or platinum metal centers to which multiple organic ligands are attached. Figure 5.4 shows examples of an organometallic phosphorescent emitter including the archetype, fac-tris(2-phenylpyridine) iridium or Ir(ppy)₃. Manipulation of the various aromatic groups on each ligand changes all of the emission characteristics such as color, color saturation, and emission efficiency. Furthermore, the addition of different organic chemical species, such as a methyl group, at different positions on the ligands has significant effects on device properties such as operational stability.

Manipulation of energy transfer paths is a typical method used to control the efficiency and emission from phosphorescent WOLEDs. Three means by which energy is transferred from one molecule to another are radiative, Förster (Förster, 1959), and Dexter energy transfer mechanisms (Dexter, 1953). The radiative mechanism of energy transfer is a trivial case, which consists of the emission of a quantum of light by one molecule and the subsequent absorption of the emitted photon by a second molecule (Birks, 1970). This transfer is maximized when the quantum yield of emission by the first molecule is close to unity, when the second molecule has a high extinction coefficient, and when there is spectral overlap between the emission of the first molecule and the absorption of the second molecule.

Förster energy transfer is a resonant energy transfer mechanism where electronic dipoles of two molecules are coupled via a dipole–dipole interaction (Barttrop



5.4 (a–j) Organic ligands are attached to a metal atom to enable efficient phosphorescence. These are examples of organometallic emitters that efficiently emit from singlets and triplets. Fac-tris(2-phenylpyridine) iridium or Ir(ppy)₃, labeled (c), is the archetype molecule that is famously known.

and Coyle, 1978; Förster, 1959; Förster, 1965). The transition rate of energy from the donor to the acceptor molecule, K_{DA} , is as follows:

$$K_{DA}(R) = \left(\frac{1}{\tau_D} \right) \left(\frac{R_0}{R} \right)^6 \quad [5.2]$$

Here, R_0 is the Förster radius, and τ_D is the average donor lifetime for recombination in the absence of energy transfer. The critical Förster radius is given by the following integral over all frequencies, ν :

$$R_0^6 = 1.25 \times 10^{17} \frac{\eta_D}{n^4} \int F_D(\nu) \alpha_A(\nu) \frac{d\nu}{\nu^4} \quad [5.3]$$

where η_D is the donor quantum emission efficiency, n is the refractive index of the host, F_D is the area normalized emission spectrum of the donor, and α_A is the molar extinction coefficient of the acceptor. Typical values of R_0 for systems are a few nanometers. Förster energy transfer is also used to explain phosphor sensitized fluorescence where spin is not conserved in this sensitization energy transfer, so triplets transfer energy from one molecule to singlet states in a distinct molecule.

Förster energy transfer is a long range coulombic interaction that can exceed 10 nm and resembles a transmitter-antenna mechanism. It is unlike Dexter energy

transfer (Barltrop and Coyle, 1978; Dexter, 1953), which is a short-range (~ 1 nm) exchange interaction that requires diffusive collisions between molecules. The rate constant of energy transfer in this case is given by:

$$K_{DA} = AJ \exp(-2R_{DA}/L) \quad [5.4]$$

where A is related to the orbital interactions, J is the spectral overlap integral normalized for the extinction coefficient of the acceptor, and R_{DA} is the donor–acceptor separation relative to their van der Waals radii, L (Turro, 1991). The exponential term limits the range of the interaction in this mechanism.

Dexter energy transfer can be envisaged as two electrons that are physically and coherently switched between two molecules, i.e. an electron is removed from the donor molecule and inserted into the acceptor molecule, while simultaneously an electron is removed from the acceptor molecule and inserted into the donor molecule. When a molecule is part of an extended solid, such as an organic crystal or solid film, there are important differences that exist between excited state properties of the single molecule and that of the extended system. Many photophysical processes of small aggregates of molecules and crystals are directly understood in terms of individual molecules due to their weak van der Waals interactions. The interaction energy between the molecules, however, imposes a collective response embodied in a quasi-particle called an exciton (Pope and Swenberg, 1999).

Two types of excitons are the Frenkel (Frenkel, 1931) and charge-transfer exciton (Silinsh and Capek, 1994). The Frenkel exciton is a correlated electron-hole pair localized on a single molecule, with a radius comparable to the size of the molecule. A charge-transfer exciton is an un-relaxed polaron pair with the positive and negative polarons located on discrete, neighboring molecules. A linear combination of these two types of excitons describes exciplexes or excimers, which are uniquely able to enable white emission using a single emitter material.

5.3 Device design and fabrication

5.3.1 Efficiency

Niche applications such as flexible thin lighting luminaires pictorialized in Fig. 5.5 or vehicular applications as exemplified by headrest displays shown in Fig. 5.6 are foreseeable in the near future. For solid state lighting applications, research has focused on improving device efficiency, because WOLED efficacies may have to exceed 70 lm/W at luminance values over 2000 cd/m² to gain widespread acceptance. An OLED device power efficacy consists of radiative decay efficiency, charge carrier balance efficiency, exciton spin factor efficiency, outcoupling efficiency, and voltage efficiency (Meerheim *et al.*, 2009). The internal quantum efficiency (IQE) consists of the first three and external quantum efficiency (EQE) consists of the first four efficiencies.



5.5 Thin and flexible form factors are attractive features of future OLED solid-state illumination systems. The image shows thin white OLEDs on curved surfaces. Image courtesy of © Exponent, Inc. 2008.



5.6 There is potential to apply OLEDs in vehicular applications such as accent lighting or displays in headrests.

The radiative decay efficiency is closely related to the PLQE that was previously discussed, but the radiative decay efficiency is affected by other energy transfer and loss mechanisms that may play significant roles in WOLEDs. Excitons diffuse and can interact with other entities by transferring energy through Dexter or Förster mechanisms, so the efficiency of energy transfer between emitters and between emitters and hosts are important.

The control of energy transfer is necessary to balance the spectral components to obtain white light. For example, a triple-doped emissive layer in a WOLED will contain a high concentration of blue phosphors and a low concentration of red and green phosphors because energy is transferred from the blue phosphor to the green and red phosphors (D'Andrade *et al.*, 2004). Other WOLED architectures may manage energy transfer by separating the emitters into different layers, or by stacking OLEDs. For example, a yellow phosphorescent OLED can be fabricated on top of and serially connected to a blue fluorescent OLED (Komoda *et al.*, 2011).

Charge carrier balance relates to the number of electrons and holes that bind and form an exciton to the number of electrons injected into a device (Erickson and Holmes, 2011). Various device architectures are employed to improve the charge carrier balance such as blocking layers, which constrain the recombination location of holes or electrons and prevent them from traversing from one electrode to the opposite electrode (Kanno *et al.*, 2006). The carrier mobility in various layers that comprise an OLED may also be manipulated to enable unity charge carrier balance (Meerheim *et al.*, 2009). Charge carrier balance is also critical for long operational lifetime which is discussed in the next section.

There are a number of challenges to optimizing the charge balance in a WOLED including: simultaneously optimizing the charge recombination location with the location of optical antinodes, creating multiple recombination locations, charge injection efficiency, trapping of charge on emitters, and controlling dopant concentrations. WOLED architectures that minimize the complexities of charge balance include using a blue phosphorescent OLED with down-conversion films (Lee and So, 2010), using red-green-blue stripes with a diffuser (D'Andrade *et al.*, 2005b), using a single broad emission from exciplexes (Williams *et al.*, 2007, D'Andrade *et al.*, 2002), and reducing the number of device layers (D'Andrade and Esler, 2008).

OLEDs for solid-state lighting must have at least one phosphorescent emitter to ensure that 100% of excitons formed can be used to create light. Simple spin statistics sets 25% and 75% of excitons formed by electron injection into an OLED to be singlets and triplets, respectively, and the goal is to have all excitons be converted to photons. Hence, the single greatest ability of phosphorescent emitters is to utilize 100% of all the excitons. Typically, only singlets radiatively emit from fluorescent emitters while both singlets and triplets radiatively emit from phosphorescent materials. Hence, phosphorescent devices are considered to

have a unity exciton spin factor; however, OLEDs with fluorescent emitters are not necessarily limited to 25% exciton spin factor efficiency.

It has been reported that a triplet state can produce singlets through triplet-triplet annihilation (Kondakov *et al.*, 2009). Also, triplet to singlet energy transfer (Baldo *et al.*, 2000) and partitioning of excitons between fluorophors and phosphors (Sun *et al.*, 2006) can enable devices with near unity exciton spin factor.

The outcoupling efficiency is the ratio of the number of photons that escape an OLED structure to the number of photons formed by excitons. Outcoupling efficiency has remained the lowest efficiency in OLEDs and represents a significant hurdle to the power efficacy of WOLEDs for solid-state lighting. Some solutions may achieve 40%–50% outcoupling efficiency (D'Andrade and Brown, 2006; Reineke *et al.*, 2009; Yoo *et al.*, 2010), but 80%–90% efficiencies need to be achieved in the future by, for example, reducing surface plasmon losses (Meerheim *et al.*, 2010).

Furthermore, the optical antinode location in an OLED is different for each wavelength of light; hence, a single emissive layer where all wavelengths are emitted from the same region (D'Andrade *et al.*, 2002, 2004) cannot maximize the OLED optical cavity influence on efficiency. OLED modeling software (Schober *et al.*, 2011), therefore, is vital for design, and multiple recombination locations can be employed to ensure that blue excitons and red excitons are at different positions within a device or within a stacked OLED architecture (Kanno *et al.*, 2006; Reineke *et al.*, 2009).

Minimizing the operating voltage of an OLED is another key requirement. Device structures that employ p-type and n-type doped organic transport layers have operating voltages that approach the fundamental thermodynamic limits of operation where the operating voltage limit quantitatively corresponds to the average energy, in electron-volts, of photons (Meerheim *et al.*, 2006, 2009).

Although OLEDs have been shown to operate at voltages at the thermodynamic limit (Pfeiffer *et al.*, 2002; Meerheim *et al.*, 2006), the light output at those low operating voltages is not sufficient for lighting applications. The operating voltage of a WOLED inherently is numerically higher than the average energy of an emitted photon. An electron must be biased with about 3.0 V to create a blue photon with 3.0 eV of energy; however, the average energy of photons emitted for a warm white color is closer to red photon energies (2.0 eV). One method to avoid this voltage loss is to use stripes of red, green and blue OLEDs and then diffuse the light from the individual colored OLEDs to produce a white color (D'Andrade *et al.*, 2005b).

A WOLED is very complex and the broad spectral emission necessary for white does not easily afford the simultaneous maximization of all device efficiency parameters. Many device architectures (D'Andrade and Forrest, 2004) have been reported due to the large number of variables that may be optimized, and each set of materials often enables unique characteristics and properties that promote new WOLED architectural designs (Gather *et al.*, 2011; Sasabe and Kido, 2011; Xiao *et al.*, 2011; Zhou *et al.*, 2010).

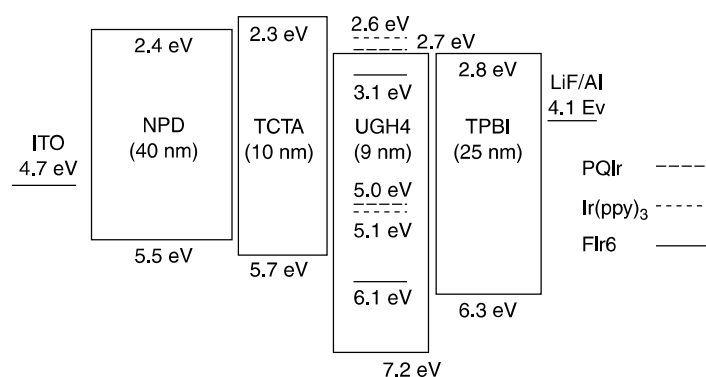
5.3.2 Exemplar phosphorescent white OLEDs (WOLEDs)

Triple doped

One instructional example of energy transfer optimized for high efficiency is a triple-doped device (D'Andrade *et al.*, 2004). The triple-doped WOLED was optimized by minimizing voltage operation, efficiently confining charge and excitons, and by effectively using Förster and Dexter transfer mechanisms. The emissive layer (EML) in this example consisted of 2 wt.% iridium(III) bis(2-phenyl quinolyl-N,C2') acetylacetonate (PQIr), 0.5 wt.% fac-tris(2-phenylpyridine) iridium ($\text{Ir}(\text{ppy})_3$) and 20 wt.% bis(4',6'-difluorophenylpyridinato) tetrakis(1-pyrazolyl)borate (Flr6) co-doped into a wide energy gap p-bis(triphenylsilyl)benzene (UGH2) host.

Provided the quantum efficiency remains constant, thin layers reduce the voltage drop across an EML and electron transport layer (ETL), thereby improving power efficacy. The approximate magnitude of electric fields across the ETL and EML are $6.0 \times 10^5 \text{ V/cm}$ and $1.5 \times 10^6 \text{ V/cm}$, respectively, obtained by measuring the applied voltage at 10 mA/cm^2 for various EML and ETL thicknesses. Therefore, a thin emissive layer reduces voltage losses in a WOLED and multiple phosphors must be doped into a single layer to take advantage of the low voltage losses enabled by thin layers. Many other WOLEDs have multiple EMLs with different emitters in each layer, so reducing voltage losses by using thin layers is not possible.

EQE is also significantly affected by the thicknesses of the EML and ETL. Inefficient charge and exciton confinement severely reduce EQE of devices having an EML thickness $< 5 \text{ nm}$, and additional reductions in quantum efficiency are incurred when the ETL thickness is $< 25 \text{ nm}$ due to exciton quenching at the metal cathode. The optimized device (Fig. 5.7) effectively balanced the competing effects of low operating voltage and reduced quantum efficiency of thin devices.



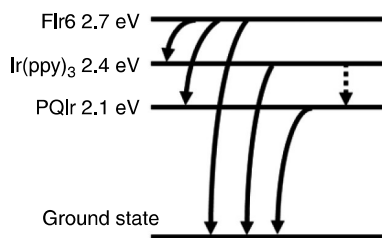
5.7 Energy level diagram of a triple doped WOLED.

The effectiveness of charge confinement relies on differences in the LUMO and HOMO potential energy levels between the EML and the adjacent layers, and the efficiency of trapping charge on the emitters. Preferably holes are trapped on a particular emitter to also enable high device operational reliability. As shown in Fig. 5.7, the LUMO of 4,4',4''-tri(N-carbazolyl)triphenylamine (TCTA) is at least 0.3 eV above that of the dopants and host, thus preventing electron leakage from the EML. At 20 wt.% doping FIr6 in UGH2, FIr6 efficiently transports charge in the EML. The 0.2 eV energy barrier between the HOMO of FIr6 at 6.1 eV, and 1,3,5-tris(N-phenylbenzimidazol-2-yl)benzene (TPBI) at 6.3 eV, therefore acts as an efficient barrier to hole transport across the EML/ETL interface. These two barriers improve the recombination efficiency within the 9-nm-thick EML, leading to improvement in EQE.

Exciton diffusion (by Dexter energy transfer between FIr6 emitters) out of the EML towards the ETL or towards the hole transport layer is prevented by employing materials with energy gaps greater than that of the blue dopant. TCTA and TPBI have energy gaps of 3.4 and 3.5 eV, respectively, which are >0.3 eV of that of FIr6. Energy transfer therefore is not favorable since the energy gaps of TCTA and TPBI are non-resonant with those of the phosphorescent emitters.

The majority of excitons are generated by trapping on FIr6, and then subsequently efficiently transferred by Förster mechanisms to the green and red dopants. Hence, the quantum efficiency of the blue dopant limits that of the entire device. The energy transfer mechanisms between the EML emitters was elucidated by photoluminescence transient responses of two thin-films of (1) UGH2 doped at 20 wt.% with FIr6, and of (2) the triple-doped EML.

The time rate of decay of FIr6, Ir(ppy)₃ and PQIr in the triple doped film showed that the lifetime of FIr6 decreased because FIr6 was being quenched by additional non-radiative pathways. In this case, those pathways are energy transfer processes to the green and red dopants. Radiative energy transfer from Ir(ppy)₃ to PQIr is possible (dashed line Fig. 5.8) but the low concentration of both species makes



5.8 Energy transfer paths from blue phosphorescent emitter to green and red emitters for the device shown in Fig. 5.7. Both Dexter and Förster energy transfer mechanisms are used to balance the emission color and device efficiency.

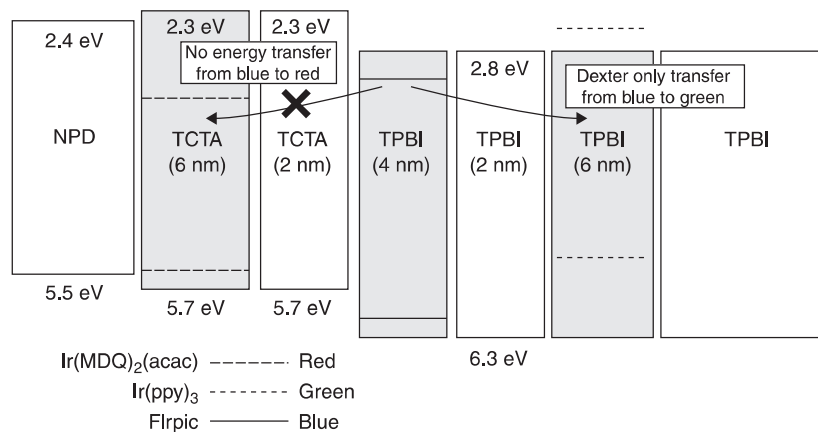
this process unfavorable. The transfer processes may be schematically depicted as in Fig. 5.8.

The triple-doped WOLED is not commercially practical because very thin layers are problematic to implement in manufacturing due to thickness uniformity issues. Additionally, there are probably no full-scale production tools that can thermally evaporate four materials simultaneously, because there are complexities associated with controlling material deposition rates. The operational lifetime of the device is also questionable; hence there was no corresponding commercial panel that used similar materials to achieve high power efficacy, and the gap in commercial and laboratory device efficacy remained as shown in Fig. 5.2.

WOLED with three emissive sub-layers

An alternative design for WOLEDs has each emitter in a separate layer which allows finer manipulation of energy transfer between various emitters. The WOLED reported by Reineke *et al.* (2009) is among the most efficient ever reported at that time. Multiple parameters including novel outcoupling structures enabled their WOLED efficiency, but the structure of the WOLED EML sub-layers is interesting to recite here.

Figure 5.9 shows the HOMO and LUMO and the materials in the EML in this device. Holes and electrons enter the emission region from NPD to the red



5.9 The WOLED reported by Reineke *et al.* (2009) is among the most efficient and the energy levels of the emissive region are shown in this diagram. The flow of excitons was finely tuned to produce white emission by separating red, green and blue phosphorescent emitters into separate sub-layers.

emissive layer TCTA:Ir(MDQ)₂(acac) (iridium[III]bis[2-methyldibenzo[f,h]quinoxaline][acetylacetonate]) and from TPBi to TPBi:Ir(ppy)₃, respectively. Carriers accumulate at the TCTA/TPBi interface and excitons are created within about 3 nm of the interface. Therefore excitons form in both the Ir(MDQ)₂(acac) doped TCTA layer and the TPBi:FIrpic (iridium-bis-(4,6,-difluorophenyl-pyridinato-N,C2)-picolinate) blue layer.

Neat host materials separate sub-layers doped with a particular emitter to decouple the sub-layers from unwanted energy transfer. Here, 2 nm was sufficient to suppress Förster energy transfer from blue to red and from blue to green emitters according to the authors. Dexter energy transfer from a blue to a red emitter is also strongly reduced with the introduction of the high-triplet-energy TCTA interlayer. Excitons however diffuse by a Dexter mechanism from blue to green emitters. This architecture convincingly was optimized to balance the various energy transfer mechanisms.

Unfortunately, this is another laboratory WOLED example that is not likely to be commercially manufactured due to the likely operational instability of WOLEDs containing the materials shown in Fig. 5.9. Additionally, the outcoupling methods employed to achieve the outstanding results are not cost-effective.

5.3.3 Operational lifetime

Two other important considerations for viable solid-state lighting are device area and device lifetime. These two considerations are often considered separately from the development of high-efficiency devices. Large areas of white OLED devices are necessary to produce sufficient lumens, but thickness uniformity and low conductivity of transparent electrodes are two limitations to the manufacture of large-area devices. Those engineering limitations are not specific to phosphorescent OLEDs and they include effects on color homogeneity, luminance uniformity, resistive losses, thermal degradation, and outcoupling efficiencies (Neyts *et al.*, 2006; Cester *et al.*, 2010; Pinato *et al.*, 2009b). Additionally, one must assume that solutions to large area are available given the production of 55 inch OLED televisions by Samsung and LG. Although these engineering challenges require attention, phosphorescent OLED lifetime is more pertinent to the focus of this chapter because product lifetimes may have to exceed 50 000 hours (Ngai, 2010), and there are no obvious solutions or theoretical limitations.

Operational degradation refers to the increase in drive voltage and simultaneous decrease in luminance when an OLED is driven at constant current over time. The operational lifetime is typically limited by the emitter with the shortest lifetime. For example, blue phosphorescent OLEDs have the shortest reported lifetimes; therefore, a WOLED employing a blue phosphor will have a lifetime closer to the lifetime of a blue phosphorescent OLED if all other colored emitters have much longer lifetimes than the blue emitter.

The lifetime of phosphorescent OLEDs has been extensively studied (Giebink *et al.*, 2008, 2009; Kondakov *et al.*, 2007), but many results are confidential or published in patents instead of academic journals. Typically, WOLED lifetimes are not deeply studied because WOLEDs are too complicated to make, so fundamental research focuses on a single colored OLED, which is typically a blue phosphorescent OLED. Novel materials have often produced the largest improvements in lifetime compared to other developments such as material synthesis and purification, device architecture, and device processing conditions.

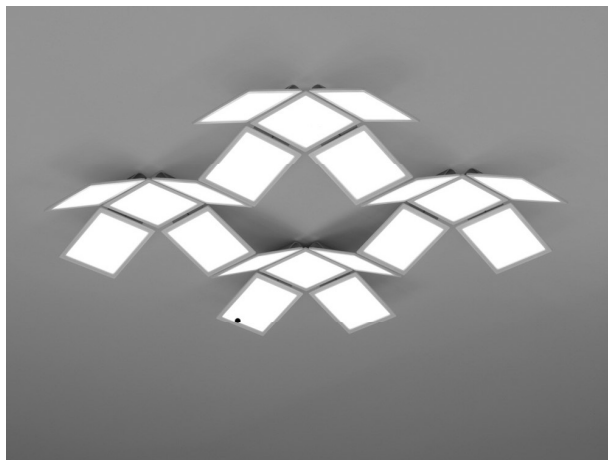
A key goal for the efforts to attain long lifetime is to maintain a high level of purity throughout all aspects of OLED device and material creation because a very small number of impurities may lead to significant luminance loss (Giebink *et al.*, 2008). Many of the material properties that are manipulated to enable long lifetimes have been discussed in Section 5.2.1, but there are also strict processing conditions that enable long operational lifetime.

One step towards improving the lifetime of devices is to search for clues on degradation pathways. For example, an examination of glass transition temperatures by using readily observed physical changes in devices led to an understanding of how doping may be used to increase the glass transition temperature of a device layer, or an examination of ITO revealed that indium be diffusing into OLEDs (Popovic and Aziz, 2002).

A difficult question to answer is how are phosphorescent molecules changing if they are the source of degradation (i.e. are molecular bonds being broken such that undesirable molecular fragments are being formed). The question has been extremely difficult to answer because the amount of emitter material and any undesirable quenching fragments are miniscule. There is ample evidence, however, that organic materials used as hosts and transport layers are being broken into fragments and those fragments may cause device degradation (Kondakov *et al.*, 2007; Adamovich *et al.*, 2007).

Device architecture affects lifetime in multiple ways. One feature of device architecture that affects device degradation is charge balance. Blocking layers, for example, provide efficient means to confine charge and boost efficiency; however, high concentrations of holes or electrons at blocking layer interfaces may be undesirable because the charged molecules may be more likely to be unstable. In general, there are trials and errors with many unexpected results obtained along the path to discovering very stable device structures (Adamovich *et al.*, 2007).

Device processing also affects device lifetime. From the treatment of ITO substrates through to OLED encapsulation, care is exercised to prevent intrusion of impurities such as water and oxygen. For example, reduction in the water content of a phosphorescent OLED processed under ultra-high vacuum (6.5×10^{-7} Pa) conditions enabled a 25% increase in lifetime over a similar OLED processed under high vacuum (7.6×10^{-6} Pa) conditions (Yamamoto *et al.*, 2011). Therefore, standard practices for using high vacuum processing, such as



5.10 Revel™ by Acuity Brands' Winona Lighting, 2011 LIGHTFAIR® International 'Most Innovative Product of the Year'. Image courtesy of © John Sutton Photography 2011.

conditioning of all sources, are necessary, and routine calibration of material properties assists in maintaining consistent results.

Phosphorescent emissive materials are particularly sensitive to quenching by oxygen. Oxygen has a triplet ground state, so energy transfer between a ground state oxygen molecule and the excited state of an emitter is efficient. Oxygen quenching of emission is another reason devices are handled in glove-boxes with less than 2.0 ppm of water and less than 2.0 ppm of oxygen; however, oxygen and water are still concerns even under those conditions because there is evidence that 50 ppm can cause a change in the photoluminescence spectral power distribution (D'Andrade *et al.*, 2008b).

There are many lifetime challenges, as briefly discussed above, that await breakthroughs. Based on previous trends, the largest improvements may be delivered by development of novel materials. The progress towards highly efficient and long-lifetime OLED continues due to the persistent efforts of several companies; therefore, it is reasonable to assume that phosphorescent OLEDs for solid-state lighting will be readily available in the future. An example WOLED product that is already available is the Revel™ by Acuity Brands and it is shown in Fig. 5.10.

5.4 Conclusion and future trends

The future of phosphorescent OLEDs for solid-state lighting looks excellent. The U.S. DOE solid-state lighting annual workshop is a good resource for more

Table 5.2 The performance of blue, green and red phosphorescent OLEDs used in a stripe WOLED produced by Universal Display Corporation and presented at a workshop for the U.S. Department of Energy solid-state lighting program

Color	Luminance (cd/m ²)	Voltage (V)	Efficacy (lm/W)	Lifetime LT70 (hrs)
Red	2900	3.3	26	32 000
Green	2750	3.0	87	100 000
Blue	550	5.1	32	27 000

information about phosphorescent OLEDs and LED technology. One state of the art for phosphorescent materials incorporated in a striped WOLED was provided at the 2012 workshop and some reported results are shown in Table 5.2 (Weaver *et al.*, 2012). Furthermore, the 2020 target for phosphorescent WOLEDs is 168 lm/W with 100 000 hours of lifetime and emitting 10 000 lm/m² (or about 3000 cd/m²), and this target seems feasible given a current state-of-the-art efficacy of 128 lm/W (Komoda *et al.*, 2011).

The most significant challenge is the outcoupling efficiency of OLED, because the practical limit for OLED outcoupling efficiency was reported to be 60% (Weaver *et al.*, 2012) and the current outcoupling efficiency is about 40%; whereas, LED outcoupling efficiencies have exceeded those limits. LEDs are capable of maximizing outcoupling efficiency, for example, by using current spreading so emission does not occur between metallic electrodes, by using thick transport layers that reduce surface plasmon losses, by surface roughening, and by using narrow spectral distribution emission from within a die. There are obvious advantages beyond efficacy improvements that may be obtained by independently doubling the outcoupling efficiency from 40% to 80%. For example, one may estimate at least a doubling in the lifetime of a WOLED if the outcoupling efficiency may be independently doubled.

Research and development efforts are expected to continue because of interest by major manufacturers such as LG Chem, Philips, Osram, Konica Minolta, Idemitsu Kosan, Samsung, Acuity Brands Lighting, and Panasonic. There are frequent updates at SPIE and SID meetings occurring across the globe and daily updates on LinkedIn.com groups and oled-info.com. The results and products of the next decade should clarify the successfulness of phosphorescent OLEDs for solid-state lighting.

5.5 References

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Abstract: The basics of highly efficient organic light-emitting diodes (OLEDs) based on small molecules are discussed. All factors influencing OLED efficiency are explained and the benefits of pin-type OLEDs are given. It is shown how the pin concept can be used to realize highly efficient monochrome and white OLEDs. Finally, a short overview on the different microscopic mechanisms of OLED degradation and techniques to study these mechanisms is given.

Key words: highly efficient organic light emitting diodes, basics of OLEDs, pin OLEDs, white OLEDs, degradation of OLEDs.

6.1 Introduction

Ever since the invention of organic light-emitting diodes (OLEDs) by Tang and VanSlyke in 1987,¹ the field has developed rapidly. The efficiency of OLEDs has increased steadily, making OLEDs a promising alternative to many of today's display and lighting technologies.

Tang and VanSlyke were not the first to observe electroluminescence of organic materials. In an early study in the 1950s, Bernarose studied light emission from a single crystal of an organic compound.^{2,3} These early devices suffered from a high driving voltage and consequently a low power efficiency.^{4,5} The use of thin amorphous films led to thinner active layers and lower driving voltages,^{6,7} but it was not until Tang and VanSlyke used an organic hetero-structure that the power efficiency of OLEDs reached reasonable levels of above 1 lm/W.

In recent years, two key developments drove OLED research. The discovery of highly efficient phosphorescent emitters led to a quadruplication of the achievable quantum efficiency, and internal quantum efficiencies of nearly 100%^{8,9} were reached. Furthermore, the use of electrically doped layers reduced the driving voltage and thus increased the power efficiency.^{10,11} Nowadays, monochrome OLEDs with more than 50% external quantum efficiency and white OLEDs reaching the luminous efficacy of fluorescent tubes have been reported.^{12,13}

The success of OLEDs has triggered significant interest from industry. Currently, two main applications are envisaged: OLED displays and OLED lighting. Today, several companies such as Samsung, Sony, and LG are selling OLED displays for handheld devices or even small TV sets. The strengths of OLED displays compared to the established LCD technology are high contrast

ratios, wide viewing angles, extremely thin displays, and lower power consumption. However, despite their advantages, OLED manufacturing turned out to be challenging, and the production technology is still much in its infancy and limited to rather small substrates.

For OLED lighting, OLEDs can profit even more from their high power efficiency. Currently, commercially produced OLEDs are more efficient than a normal incandescent lamp by a factor of 2–3, and the efficiency is still increasing. For example, OSRAM (ORBEOS lighting panels) and Philips (Philips lumiblade) are selling white OLEDs as demonstrator kits. Besides their high power efficiency, OLEDs are truly flat area devices generating soft high-quality light without further light distribution, can be made transparent, and can be produced on flexible substrates, which enables many novel and exciting design opportunities.

In this chapter, the advances of pin-type OLEDs are described. Starting with a short introduction to the OLED technology (Section 6.2) and the pin concept (Section 6.3), highly efficient monochrome OLEDs are described (Section 6.3). Emphasis is put on the optimization of the optical microcavity of the OLED and the improvement of the outcoupling efficiency, which has the highest potential to improve OLED efficiency. In Section 6.4, the design principles used for monochrome OLEDs will be applied to white OLEDs and one approach – the triplet harvesting OLED – is discussed in detail. The chapter closes with a short discussion of OLED degradation (Section 6.5).

6.1.1 Basics of OLEDs

In its simplest form, an OLED consists of a single layer of organic material, contacted by a reflecting (metal) contact – the cathode – and a transparent anode, which often consists of indium doped tin oxide (ITO). Upon application of a positive voltage, electrons and holes are injected at the cathode and anode, respectively. The charge carriers drift towards the center of the device, recombine and form excitons, i.e. bound electron-hole pairs. Usually, excitons in organic materials are of the Frenkel-type, i.e. due to the strong coulomb interaction both electron and hole are located on the same molecule. The exciton can relax towards the ground-state of the molecule and can emit a photon during this process.

To quantify the efficiency of all these processes involved in light generation, several definitions have been proposed in the past. The most commonly used ones are the external quantum efficiency (EQE or η_q) and the power efficiency or luminous efficacy (η_p). The EQE is defined as the ratio of the number of emitted photons to the number of injected charge carriers. It can be expressed as a product of the so-called electrical efficiency γ , the exciton spin factor χ , the efficiency of radiative decay η_r , and the outcoupling efficiency ξ .^{14,15}

$$\eta_q = \gamma \chi \int_{\lambda} \eta_r(\lambda) \xi(\lambda) s_{PL}(\lambda) d\lambda \quad [6.1]$$

where $S_{PL}(\lambda)$ denotes the normalized photoluminescence spectrum of the emitter.

$$\int_{\lambda} S_{PL}(\lambda) d\lambda = 1$$

The electrical efficiency γ is defined as the ratio of injected charge carriers to the number of formed excitons, i.e. γ includes all electrical losses. A significant parameter determining the electrical efficiency is the charge carrier balance, which is the ratio of injected electrons to injected holes. If there is an imbalance between electron and hole injection, not all charge carriers will recombine with a charge carrier of opposite polarity and the energy is lost. Thus, for highly efficient devices, the injection of holes and electrons has to be balanced.

The exciton spin factor χ is defined as the ratio of radiative excitons to the total number of excitons. Due to spin statistics, three out of four excitons formed in the device are triplets and only one exciton is a singlet. In fluorescent emitters, only singlets can radiatively relax to the ground state and thus χ equals 0.25. However, if phosphorescent molecules are used, all excitons can decay radiatively, and an exciton spin factor of unity can be reached.⁸

η_r is the efficiency of radiative decay or photoluminescence (PL) efficiency. It depends on the radiative (Γ_{rad}) and non-radiative (Γ_{nrad}) decay rates of the emitter as follows:

$$\eta_r = \frac{\Gamma_{rad}}{\Gamma_{rad} + \Gamma_{nrad}} \quad [6.2]$$

As the flat OLED structure forms an optical micro-cavity, the radiative decay rate Γ_{rad} depends strongly on the optical environment and, according to Fermi's golden rule, on the optical mode density at the position of the emitter.¹⁶

$$\Gamma_{rad,ij} \propto |M_{ij}|^2 \rho(\nu_{ij}) \quad [6.3]$$

where $\Gamma_{rad,ij}$ is transition rate from state i to j , M_{ij} is the matrix element connecting state i and j , and $\rho(\nu_{ij})$ is the photonic mode density at the transition frequency ν_{ij} .

The photonic mode density can be influenced by the cavity length and the position of the emitter. If the cavity is in resonance at the peak wavelength of the emission and if the emitter is placed into the antinode of the optical field, the photonic density is large, resulting in an increase of radiative rate (cf. Eq. 6.3) and radiative efficiency (cf. Eq. 6.2). On the contrary, if the cavity is detuned or if the emitter is placed in a node of the optical field, the emission is inhibited.

This effect, known as the Purcell effect,¹⁷ can be described by the Purcell factor F , which is the ratio of the power radiated at the wavelength λ by the dipole in the cavity to the power radiated by the same emitter in infinite space. It can be expressed as

$$F(\lambda) = \int_0^\infty K(\lambda, u) du^2 = 2 \int_0^\infty u K(\lambda, u) du \quad [6.4]$$

where $uK(\lambda, u)$ is the spectral power density, i.e. the power the emitter radiates in the cavity at a given wavelength, and u is the in-plane wave vector, i.e. the photon wave vector k is split into an in-plane component u and an out-of-plane component v . If normalized to the full wave vector $k = \frac{2\pi}{\lambda} n(\lambda)$, with n index of the material where photon generation occurs, the following relation holds for u and v :

$$1 = u^2 + v^2 \quad [6.5]$$

Once the Purcell factor has been calculated, the radiative rate of the emitter inside the cavity Γ_{rad} can be determined by

$$\Gamma_{rad} = F(\lambda) \Gamma_{rad,inf} \quad [6.6]$$

i.e. the radiative rate of the emitter in infinite space (outside the cavity) $\Gamma_{rad,inf}$ is multiplied by the Purcell factor. If the Purcell factor F is high – corresponding to a high photonic mode density (cf. Eq. 6.3) – the radiative rate increases. Thus, the radiative efficiency η_r of the emitter depends strongly on the optical microcavity and the photonic mode density at the position of the emitter (cf. Eq. 6.2).

Finally, ξ is the outcoupling efficiency, i.e. the ratio of photons emitted to outer space to the total number of photons generated within the OLED cavity. In the general OLED stack, there are two interfaces with significantly differing refractive indices: the interface between the organic layers including the anode made of indium tin oxide ITO ($n \sim 1.7$ – 1.8) and the glass substrate ($n \sim 1.5$) and the interface between glass and air. A large share of photons is trapped in the cavity due to total reflection at these interfaces. The critical angle for total reflection at these interfaces can be expressed in terms of the in-plane wave vector $u_{crit}(\lambda)$. Rewriting Snell's law yields

$$u_{crit}(\lambda) = \frac{n_0(\lambda)}{n_e(\lambda)} \quad [6.7]$$

i.e. only the part of the power spectrum with an in-plane wave-vector smaller than $u_{crit}(\lambda)$ can be transmitted from the emitter material (refractive index $n_e(\lambda)$) into the layer with refractive index $n_0(\lambda)$. Light reflected at the interface organic layers/glass substrate feeds so-called organic modes, and light reflected at the interface glass substrate/air is lost in substrate modes.

Therefore, only a fraction of the power emitted by the molecule escapes the OLED cavity. If $U(\lambda)$ denotes the outcoupled power (normalized to the power emitted by the molecule in infinite space), the outcoupling efficiency can be written as

$$\xi(\lambda) = \frac{U(\lambda)}{F(\lambda)} \quad [6.8]$$

Simple calculations show that only approximately 20% of all light is extracted from the cavity, if no special measures are taken.¹⁸

The external quantum efficiency is only a photon generation probability, i.e. the ratio between the flux of injected charge carriers and the flux of generated photons, and does not account for the power conversion efficiency of the device. To obtain the power efficiency or luminous efficacy, the external quantum efficiency has to be multiplied by the photon energy $h\nu$ and divided by the energy of an injected electron eV :

$$\eta_p = K \int_{\lambda} V(\lambda) \gamma \chi \eta_r(\lambda) \xi(\lambda) \frac{h\nu}{eV} d\lambda \quad [6.9]$$

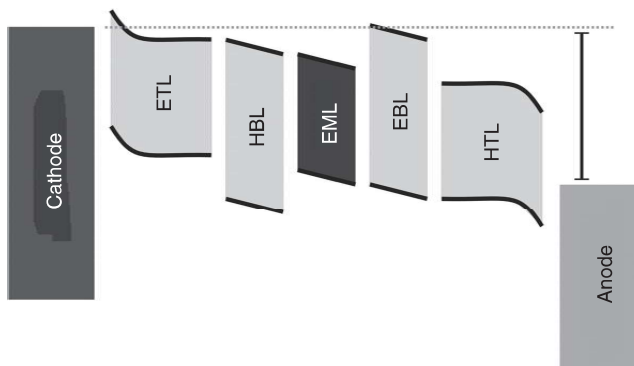
As the luminous efficacy is a photometric quantity, the efficiency is weighted by the sensitivity of the human eye $V(\lambda)$. K is a constant and amounts to 683 lm/W.

According to Eq. 6.9, OLEDs should be driven at the lowest possible operating voltage to optimize not only the quantum efficiency, but also the power efficiency of OLEDs. One concept that ensures both low driving voltage and high quantum efficiency is the pin concept consisting of p- and n-doped charge carrier transport layers and intrinsic emission layers.

6.1.2 Pin OLEDs

To reach higher efficiency, an OLED usually needs more than one layer as described in the preceding section. The reason is that one layer cannot usually serve all functions involved in the light generation process, i.e. charge injection and transport, charge recombination, and optimized outcoupling. In the pin concept discussed here, the OLED consists of at least five organic layers (cf. Fig. 6.1), i.e. a p- and n-doped hole and an electron transport layer (HTL (p) and ETL (n)), an emission layer (EML (i)) and two blocking layers (hole blocking layer, HBL, and electron blocking layer, EBL). The charge transport layers ensure a good injection and transport of charge carriers towards the emission layer, where the excitons are formed and decay. To optimize the charge carrier balance, the EML is enclosed by two charge blocking layers, which confine the charges inside the EML and thus ensure that all charges recombine with a charge of opposite polarity.

p- and n-type doping of the HTL and the ETL leads to optimized charge carrier injection and transport.^{14,15} Doping increases the number of free charges in the organic layers so that the conductivity rises by several orders of magnitude.¹⁰ This minimizes the voltage drop across the transport layers and makes it possible to drive the OLEDs close to the thermodynamic limit.¹¹ Furthermore, the use of doped transport layers significantly improves injection at the contacts.¹⁹ A space charge region is formed at the interface, which leads to strong level bending and thin injection barriers, which can easily be tunneled through by the charge carriers.¹⁹ Thus, a quasi-ohmic contact is formed and charge carriers can be injected into the device without additional voltage loss.



6.1 General setup of a pin OLED consisting of electron and p- and n-doped charge transport layers (ETL and HTL), electron and hole blocking layer (EBL and HBL) and the emission layer (EML).

Doped organic transport layers have a further advantage since they can be used to optimize the OLED cavity. As the doped transport layers have a much higher conductivity compared to the intrinsic emission and blocking layers, a very small voltage drops across the doped layers and the thickness of the doped layers can be adjusted to optimize the OLED cavity and to shift the emitter position into the antinode (i.e. maximum) of the optical field with no influence on the electrical characteristics. Hence, the radiative rate of the emitter increases (cf. Eq. 6.6) and, as will be shown in the next section on monochrome OLEDs, the outcoupling efficiency increases as well.

6.2 Highly efficient monochrome OLEDs

The strength of organic electronics is based on the near endless number of different organic compounds. In particular, organic emitters span the whole visible spectrum and monochrome OLEDs in all colors are available.

For monochrome devices, external quantum efficiencies beyond 20% are well established.^{20–23} He *et al.*²³ reached an EQE of close to 20% by using two different host materials – one electron and one hole conductive host. Tanaka *et al.*²⁰ even reached 29% external quantum efficiency for a green OLED at a brightness of 100 cd/m² or 26% at 1000 cd/m². Tanaka *et al.* also reached 21% EQE for a phosphorescent blue device²⁴ using matrix materials with a high triplet level. Chopra *et al.*²² reported on an increase in EQE of blue OLEDs to 23% if the excitons are well confined in the EML by blocking layers with a high triplet energy.

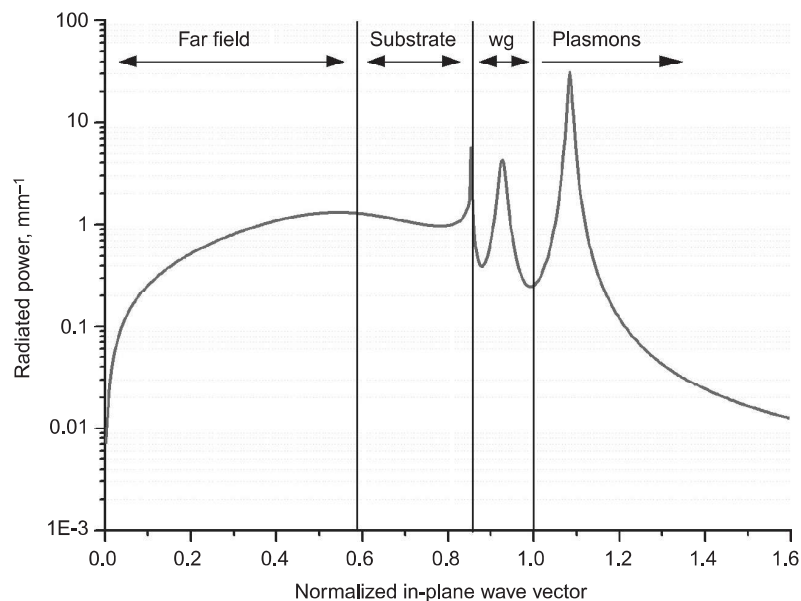
Considering that only approximately one-fifth of all generated photons are extracted from the device,¹⁸ these results show that a nearly perfect charge to

photon conversion or internal efficiency has been reached in monochrome devices, but that still a large amount of photons are trapped in the OLED microcavity.

Thus, the largest improvement in OLED efficiency can be reached by increasing the outcoupling efficiency ξ for which a detailed understanding of the optical properties of the OLED cavity is essential. Several reports on modeling of the different loss-channels in OLEDs have been published in the past,^{25–27} which quantify the different loss mechanisms in OLEDs. The results of such studies as published by Meerheim *et al.*¹² are discussed in the following.

The simulation results for a monochrome red OLED, i.e. the different modes excited in the microcavity, are shown in Fig. 6.2. The pin-OLED consists of an ITO anode, 60 nm of NHT-5 doped with 4 wt% NDP-2 (Novaled AG) as HTL, 10 nm of 2,2',7,7'-tetrakis-(N,N-diphenylamino)-9,9'-spirobifluorene (Spiro-TAD) as EBL, 20 nm of N,N'-di(naphtalen-2-yl)-N,N'-diphenyl-benzidine (NPB) doped with the red phosphorescent emitter iridium(III)bis(2-methyldibenzo-[f,h]quinoxaline)(acetylacetonate) ($\text{Ir}(\text{MDQ})_2(\text{acac})$) (10 wt%) as EML, 10 nm of bis-(2-methyl-8-quinolinolato)-4-(phenyl-phenolato)aluminium(III) (BALq) as HBL, and finally BPhen doped with Cs as ETL. To study interference effects and the effect of the cavity on the efficiency of the devices, the thickness of the ETL has been varied between 30 nm and 260 nm.

The simulations are based on an optical model treating the emitting molecule as forced damped harmonic oscillator. In Fig. 6.2 the normalized radiated power, i.e.



6.2 Spectral power density of a red pin OLED.

$uK(\lambda, u)$ (cf. Eq. 6.4) of a dipole in the cavity at a wavelength of 610 nm for an ETL thickness of 70 nm is plotted vs. the normalized in-plane wave vector.

The normalized radiated power peaks at several in-plane wave vectors, which correspond to the various resonant modes of the cavity.¹⁶ For normalized in-plane wave vectors u in the EML larger than 1, the out-of-plane wave vector v is imaginary ($v = \sqrt{1 - u^2}$), which means that the waves are evanescent. In particular, there is one dominating mode at $u \sim 1.1$, which is the surface plasmon polariton localized at the cathode surface.

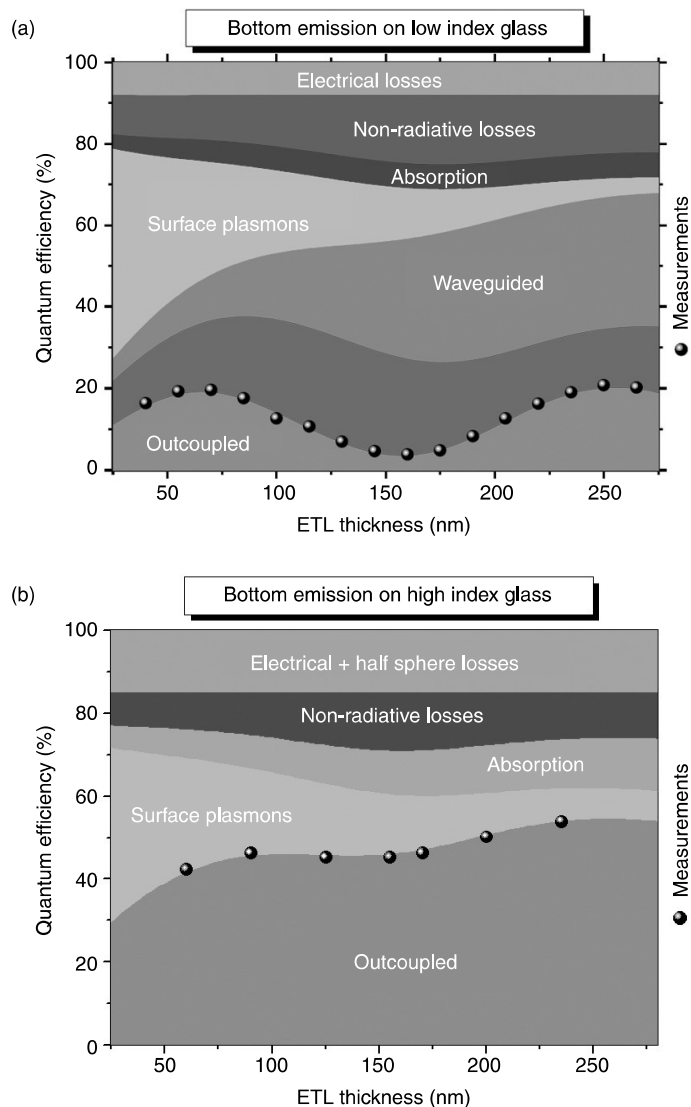
For in-plane wave vectors below 1, the out-of-plane wave vector is real and the corresponding waves are plane waves. However, as discussed in Section 6.2, due to total reflection at the interface organic layers/glass substrate (at $u_{\text{crit}} \sim 0.88$) and at the interface glass substrate/air (at $u_{\text{crit}} \sim 0.6$), not the whole wavelength range from 0 to 1 couples to external modes. Only emission at wave vectors below the critical angle for total reflection at the interface glass/air (cf. Eq. 6.7) can eventually be extracted from the device. In particular, there is one waveguided mode in the organic layers which limits the efficiency of the devices.

In conclusion, Fig. 6.2 shows that only a small fraction of the emitted power is coupled into the far field. In particular, coupling to the plasmonic mode is strong and thus much power is lost at the cathode. However, coupling to these evanescent modes is a near-field effect, i.e. an effect occurring only at relatively short distances from the emitter. If the distance between the emitter and the cathode is increased, coupling is strongly reduced.

This effect is shown in Fig. 6.3. The optical simulation is repeated for varying ETL thickness, i.e. the distance between the emitter and the cathode is varied. In Fig. 6.3, the strength of the different loss modes (plasmons, waveguided and substrate), losses due to a radiative efficiency η_r below 1 (non-radiative losses, Eq. 6.2), and electrical losses are summarized.¹²

Figure 6.3a shows that the number of outcoupled photons oscillates with ETL thickness, which is due to the different resonances of the OLED cavity. At the peaks of the plot of the fraction of outcoupled photons vs. the ETL thickness, the cavity is in resonance and the emitter is positioned at the antinode of the optical field of the cavity ensuring efficient light outcoupling. Furthermore, coupling to the plasmonic mode is strongly reduced if the thickness of the ETL is increased. However, due to the thicker cavity, coupling to waveguided modes increases and, overall, the outcoupling efficiency is only slightly increased.

To couple out waveguided modes, OLEDs can be processed on index-matched glass, i.e. glass with a refractive index matching the refractive index of the organic layers ($n \sim 1.7$ – 1.8 , cf. Eq. 6.7). Index matching ensures that no interface where total reflection can occur is present in the device and, as a consequence, virtually all internally generated photons can reach the outer surface of the substrate. Furthermore, to avoid reflections at the interface to air, a large outcoupling lens can be applied, so that all light can exit the substrate. The corresponding distribution of loss channels is shown in Fig. 6.3b. As the substrate is index-



6.3 Different loss channels for the red OLED on low index glass (a) and on high index glass (b) measured with an outcoupling lens.¹² Reprinted with permission from Meerheim *et al.*, *Applied Physics Letters* **97**, 253305 (2010). Copyright 2010, American Institute of Physics.

matched, all waveguide modes are suppressed and the outcoupling efficiency increases significantly. In particular, the thickness of the ETL can be increased without increasing losses due to waveguided modes. Thus, the outcoupling efficiency becomes larger for thicker ETLs, where coupling to plasmon modes is weaker.

The comparison of these numerical results with measured EQE data is shown as black dots in Fig. 6.3. For both, OLEDs on low-index (Fig. 6.3a) and high-index glass (Fig. 6.3b), the correspondence between experiment and calculations is excellent. For OLEDs on low index glass, the highest EQE is reached at 250 nm ETL thickness (second order cavity) and reaches 21%. For the high-index glass the EQE is significantly increased to 54%, i.e. more than half of the injected electrons generate a photon which is coupled out from the cavity.

In summary, highly efficient monochrome OLEDs can be designed if the optical structure of the OLED is optimized. However, although devices with an EQE beyond 50% are reached, these results are laboratory results as the application of a large outcoupling lens to extract all substrate modes is not practicable for commercial applications. Therefore, great efforts are made to find other outcoupling enhancement solutions that avoid waveguided and substrate modes and will increase OLED efficiency further. Concepts discussed in the literature are textured substrates,²⁸ microlens foils attached to the substrate,²⁹ layers in the OLED that scatter waveguided modes,³⁰ OLEDs on photonic crystals, or the use of horizontally aligned emitters.^{31,32} For more details, the reader is referred to the recent review article of Saxena *et al.*³³

Finally, the same concepts as discussed for monochrome OLEDs can be applied for the generation of white light. However, to generate white light with a good color quality, emission from red, green and blue emitters has to be well balanced, as is described in the next section.

6.3 Highly efficient white OLEDs

The first white OLEDs have been published by Kido *et al.*^{34,35} In these fluorescent materials were used, limiting the overall efficiency of these devices, but the use of phosphorescent emitters significantly increased the efficiency.^{36–38} In particular, the highest efficiency can be obtained by using triplet emitters for all colors. Using this so called all-phosphorescent setup, Sun and coworkers were able to reach an efficiency of 68 lm/W by using a low index grid to enhance the outcoupling efficiency.³⁹ However, at a lighting relevant brightness (500 cd/m²) the power efficiency dropped to 38 lm/W, but in 2006, Konica-Minolta announced an efficiency of 64 lm/W at a brightness of 1000 cd/m². In 2009, Reineke *et al.*¹³ used high index glass substrates and a high index outcoupling structure to increase the efficiency of white OLEDs. An efficiency of 90 lm/W at 1000 cd/m² (70 lm/W at 5000 cd/m²) was reached. Recently, Sasabe *et al.*⁴⁰ reported on a white OLED using a blue iridium carbene complex, which reaches (without outcoupling

enhancement methods) approximately 60 lm/W at low brightness and 43.4 lm/W at 1000 cd/m².

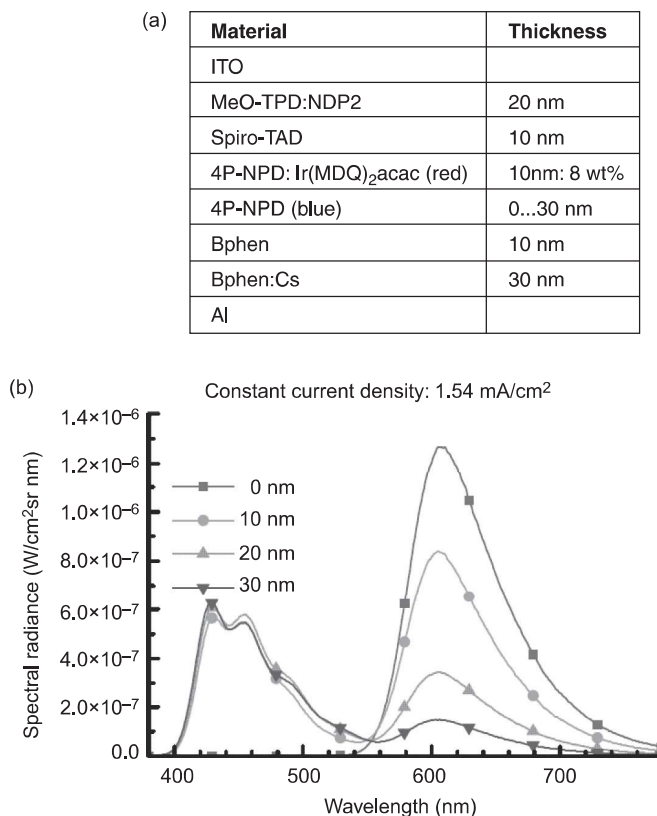
However, although stable phosphorescent red and green emitters are disclosed in the literature, there is a lack of stable phosphorescent blue emitters. In particular, the lifetime of the phosphorescent blue emitter FIrpic (iridium(III)-bis(4,6-di-*uorophenyl*-pyridinato-N,C2)-picolinate) is rather short (1–2 hours). Therefore, there is a great need to find alternative approaches, which avoid the use of unstable phosphorescent emitters.

One of these approaches are so called hybrid white stacks combining fluorescent blue with phosphorescent red and green emission.⁴¹ Using an ambipolar interlayer between the fluorescent blue and the phosphorescent green emitter to avoid quenching of triplets, Schwartz *et al.*⁴² were able to reach high efficiencies (14.4 lm/W at 1000 cd/m² without outcoupling enhancement). However, these approaches are always limited in efficiency since three out of four excitons formed on the blue emitter decay non-radiatively and are therefore lost.

To avoid these losses of excitons on the fluorescent blue emitter, the triplet harvesting concept has been proposed.^{43–47} This concept is based on the idea that an internal quantum efficiency of 100% is still possible in hybrid white OLEDs if the triplets formed on the blue emitter are transferred to the phosphorescent red or green emitter (i.e. the triplets are ‘harvested’). To transfer the triplets from the blue emitter to a phosphorescent emitter, the triplet energy of the blue emitter has to be larger than the triplet energy of the phosphorescent emitter. A candidate for triplet harvesting is 4P-NPD (N,N′-di-1-naphthalenyl-N,N′-diphenyl-[1,1′:4′,1″:4″,1″′-Quaterphenyl]-4,4″′-diamine). It has a triplet level of 2.30 eV⁴³ and thus allows harvesting on yellow or red emitters.

A triplet harvesting OLED as proposed by Schwartz *et al.*⁴⁴ and Rosenow *et al.*⁴⁶ is shown in Fig. 6.4. The OLED is a normal pin OLED. The emission layer consists of a neat layer of the blue emitter 4P-NPD with varying thickness (0–30 nm) and a layer of 4P-NPD doped with the red emitter Ir(MDQ)₂. 4P-NPD has a higher hole than electron conductivity, so that excitons are mainly formed at the interface between the undoped 4P-NPD and the hole blocking layer BPhen. Starting from this interface, the triplets diffuse towards the 4P-NPD layer doped with the red emitter, where the triplets can be harvested and can recombine radiatively. By plotting the spectrum in dependence of the undoped 4P-NPD layer thickness (Fig. 6.4b), triplet harvesting can be proven. For increasing undoped 4P-NPD layer thickness, the red emission decreases as fewer triplets reach the doped layer, but the emission in the blue spectral region remains constant.

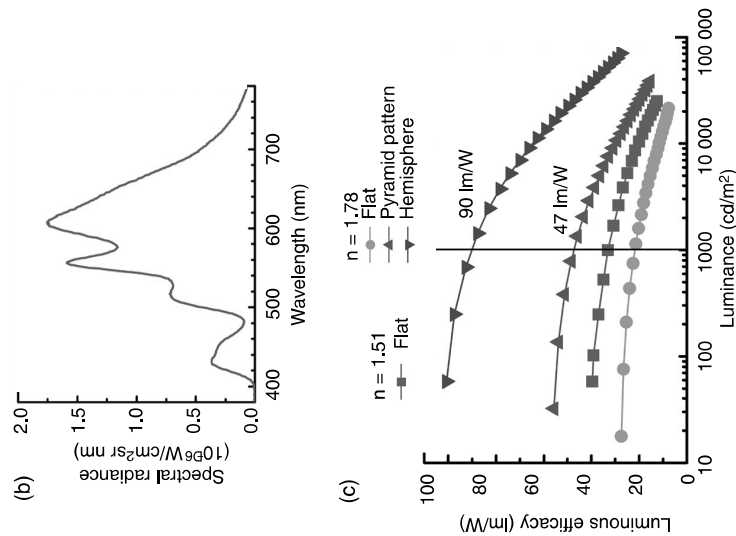
In the device shown in Fig. 6.4, the green part of the visible spectrum is missing and the emission is not white. As the molecule 4P-NPD does not allow harvesting onto green phosphorescent emitters directly, it is challenging to include a green emitter in the stack. However, it is possible to stack two OLEDs, one triplet harvesting blue-green and one green/yellow OLED as shown in Fig. 6.5.



6.4 (a) Red/blue triplet harvesting OLED (MeO-TPD: N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine). The excitons are formed at the interface between the undoped 4P-NPD layer and the hole blocker (BPhen). Starting from this interface, triplets diffuse towards the 4P-NPD layer doped with the red emitter Ir(MDQ)₂, where they are harvested.⁴⁶ (b) Spectrum of the triplet harvesting OLED for varying thickness of the intrinsic 4P-NPD layer. At a constant current density, the emission of the red emitter decreases, whereas the emission of the blue emitter remains constant. Reprinted with permission from Rosenow *et al.*, *Journal of Applied Physics* **108**, 113113 (2010). Copyright 2010, American Institute of Physics.

The stack is shown in Fig. 6.5a. The two individual OLED units are connected by a p–n junction consisting of p-doped HTL (MeO-TPD:NDP2), a thin layer of Al and n-doped ETL (BPhen:Cs). Operated in the reverse direction, electrons and holes are generated in the ETL and HTL, respectively, by Zener-Tunneling from the HOMO of the HTL to the LUMO of the ETL.⁴⁸ The complete stack can thus be seen as a simple series connection of the two individual OLEDs.

Material	Thickness
ITO	90
MeO-TPD:NDP2	40: 2 wt%
Spiro-TAD	10
4P-NPD: Ir(MDQ) ₂ acac (red)	5: 5 wt%
4P-NPD (blue)	5
Bphen	10
Bphen:Cs	90
Al	0.5
MeO-TPD:NDP2	65: 2 wt%
Spiro-TAD	10
TCTA: Ir(ppy) ₃ : (yellow)	10: 8 WT%
Ir(dhfp) ₂ acac (yellow)	1 WT%
TPBI	10
Bphen:Cs	75
Al	100



6.5 Stacked white triplet-harvesting OLEDs (TCTA: 4,4'-tris(N-carbazolyl)-triphenylamine, TPBI: 2,2'-[1,3,5-benzenetriyl)-tris[1-phenyl-1H-benzimidazole], Ir(dhfp)₂acac: bis(2-(9,9-dihexylfluorenyl)-1-pyridine) (acetylacetonate). Two OLEDs – a yellow one and a blue/red triplet harvesting OLED – are stacked (a), so that a white spectrum is reached (b). On high-index glass, 90lm/W are reached with a large outcoupling lens (c).⁴⁶ Reprinted with permission from Rosenow *et al.*, *Journal of Applied Physics* **108**, 113113 (2010). Copyright 2010, American Institute of Physics.

The spectrum shown in Fig. 6.5b consists of the emission of both OLED units and spans the whole visible range. 90 lm/W are reached at a luminance of 1000 cd/m², if the sample is prepared on high-index glass and measured with an outcoupling lens (see Fig. 6.5c). If a scalable outcoupling solution consisting of a sheet of high index glass with small pyramid-structures on top is used, 47 lm/W are reached.⁴⁶

In conclusion, it is possible to very efficiently generate white light using OLEDs. The use of unstable phosphorescent blue emitters can be avoided by replacing them with fluorescent emitters. However, it is still challenging to harvest on a phosphorescent green emitter, so that complex stacked OLEDs have to be used to reach a white spectrum. Therefore, further development has to be focused either on the development of stable phosphorescent blue emitters or on the development of fluorescent blue emitters with a low singlet/triplet splitting that makes it possible to harvest on a green emitter.

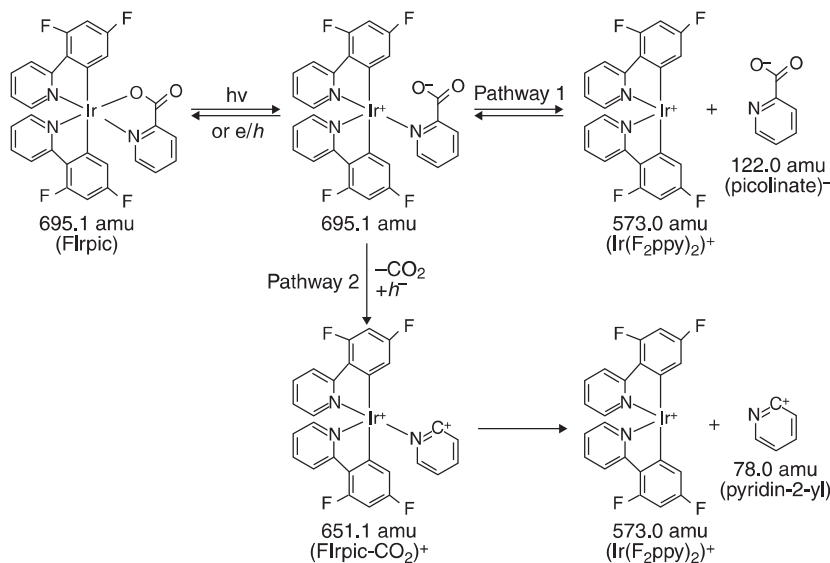
However, even the triplet harvesting OLEDs discussed in this section have lifetimes too short for commercial applications. Although white OLEDs with 100 000 h of lifetime have already been reported,⁴⁹ these high lifetimes have only been reached for hybrid white approaches without triplet harvesting. Therefore, some mechanisms that lead to the low lifetimes of OLEDs are discussed in the following section and it will be shown how long-living OLEDs can be realized.

6.4 Degradation of OLEDs

Although much progress has been made and the lifetime of OLEDs has significantly increased over the years, little is known about the precise degradation mechanism. There are many possible mechanisms of OLED degradation, related to intrinsic (such as degradation of emitter molecules) and extrinsic (such as contact delamination due to water vapor intake). Of particular interest are the intrinsic decay processes, for instance those related to chemical reactions occurring in the devices. Techniques which provide microscopic information about these reactions are especially useful since they allow optimization of devices based on a detailed understanding of the degradation processes.

One technique, which has been shown to be highly valuable in determining degradation pathways and reaction products in OLEDs, is MALDI-TOF-MS.^{50,51} Using this technique it is possible to deduce a common pathway for OLED degradation based on the dissociation of the Ir-emitter and the formation of complexes of the individual fragments with the hole blocking layer.^{21,50} For example, the proposed reaction pathway of the degradation of the phosphorescent blue emitter FIrp is shown in Fig. 6.6. Two dissociation reactions are postulated – a reversible (pathway 1) and an irreversible (pathway 2). The fragments can interact with the blocking materials, i.e. either with TPBi or with the charged complex BPhen + Cs, and build the final degradation product.⁵¹

In red OLEDs, the strength of the complexation was shown to correlate with the lifetime,⁵⁰ opening the possibility of finding optimized materials without



6.6 Proposed mechanism of the dissociation of the phosphorescent blue emitter Flrpic.⁵¹ Reprinted from Moraes *et al.*, *Organic Electronics* **12**, 341–347 (2011), with permission from Elsevier.

processing full OLED structures for test. Furthermore, it was shown that the lifetime of OLEDs can be increased significantly, if blocking materials are used which do not form complexes with the Ir-emitter. For example, the use of an alternative hole blocking layer, BAQ (bis-(2-methyl-8-quinolinolato)-4-(phenylphenolato) aluminum-(III)), instead of BPhen was shown to yield extremely long-living red OLEDs.²¹ Extrapolated lifetimes of more than 10^6 at an initial brightness of 100 cd/m^2 were reached.

In conclusion, OLEDs can be made long-living. However, the lifetime of highly efficient white OLEDs is still limited by the blue emitter. Further development has to take place to overcome these limitations.

6.5 Conclusion and future trends

The development of OLEDs has been impressive in all respects and both efficiency and lifetime has significantly improved over time. Currently, several companies are preparing for the mass-production of OLEDs for lighting or display applications or are already producing OLED devices. However, there are still challenges to be solved before OLEDs can reach their full potential.

One challenge is the improvement of outcoupling efficiency. Still, the majority of light generated inside the device is trapped in the OLED cavity. Although the use of high-index glass combined with an outcoupling lens

improves the outcoupling efficiency significantly, this approach is less suitable for commercial applications. Scalable and cost-effective solutions have to be found, which avoid total reflection or scatter light inside the cavity to surpass the efficiency limit.

A second limitation of OLED research is the lack of a stable and efficient blue phosphorescent emitter. Although the triplet harvesting approach can avoid the use of a phosphorescent emitter, the available triplet harvesting molecules are also limited in their lifetime. Further materials development is thus necessary and novel emitters have to be designed.

Finally, a predictive simulation of all physical processes of the OLED is still lacking. Up to now, all progress in device optimization was purely driven by experimental efforts, slowing down the development and hampering a deeper physical understanding of the OLED. The reasons for the lack of predictive modeling are manifold. The main reason is arguably the hopping transport occurring in the devices, which can only be described by mobility models depending on several unknown materials parameters. Combined with the large number of materials used in OLED research, the uncertainty in any simulation is large and forecloses a predictive simulation.

Nevertheless, research has reached a level where OLEDs can compete with conventional technologies in both fields of application, display and lighting. In particular for lighting applications, OLEDs have some distinctive features such as a slim form factor, flexible substrates and the possibility to be produced by roll-to-roll manufacturing that will lead to market success.

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Charge carrier mobility in amorphous organic semiconductors

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Abstract: An understanding of the mechanisms that control the mobility of charge carriers is central to the operation of organic semiconductor devices such as organic light-emitting diodes, field-effect transistors and solar cells. As an introduction into this research area, we present first a critical overview on experimental techniques available to measure charge carrier mobilities under various conditions. This is followed by a description of the pertinent theoretical concepts, illustrated by using representative experimental results. Finally we discuss current approaches taken to improve charge carrier mobility by controlling thin film morphologies.

Key words: charge carrier mobility, organic semiconductors, light-emitting diodes, field-effect transistors, Gaussian disorder model.

7.1 Introduction

The interest of physicists and chemists in the mobility that a charge may obtain in a disordered solid of π -conjugated molecules or polymers dates back more than half a century. It was originally stimulated by research into charge transport layers consisting of molecularly doped polymers. Such systems were needed for applications in photocopiers and laser printers that are omnipresent today. Conceptually, this field was drawing on models that were developed to describe charge transport by hopping between localized sites in inorganic disordered materials such as selenium, Se_2As_3 , and other chalcogenides (Anderson *et al.*, 1980). Today, the scientific interest in understanding charge transport is still driven by the potential organic semiconductors have for application. Present-day perspectives focus on opto-electronic devices such as organic field-effect transistors (OFETs), organic solar cells and organic light-emitting diodes (OLEDs), to be used for printable e-books, smart tags and displays, or for flexible solar panels and lighting panels. This strong interest is reflected by the large number of researchers that engage in this expanding field. To those that are new to this particular research area, maybe because they are graduates just starting research or because they are established researchers moving in from adjacent fields, the large number of publications on available experimental approaches and on the underlying models may be dazzling. In this chapter we therefore aim not to

attempt a comprehensive survey on current research but rather to provide a succinct introduction to the field of charge transport.

We start in Section 7.2 by presenting and discussing the methods that are available to experimentally determine the mobility of a charge carrier in an organic semiconductor. In particular, we try to clarify the limits and prerequisites for the applicability of any particular method, and what ‘kind’ of mobility the measurement yields. This is followed in Section 7.3 by an overview on the theoretical models that underlie our understanding of charge transport. We were aiming for a description that is short yet that still highlights all of the essential effects that need to be considered for an accurate understanding. This is backed up by a brief Section 7.4 where reference is given to a few key experimental results. For a more comprehensive survey and discussion on past and current experimental work, we refer the reader to a related book chapter (Bässler and Köhler, 2011). Section 7.5 on ongoing developments summarizes the field’s present knowledge on what controls charge mobility, and the approaches that are taken to advance this further. For those wishing to engage more with this fascinating and fruitful field of research, we give some guidance to available literature in Section 7.6.

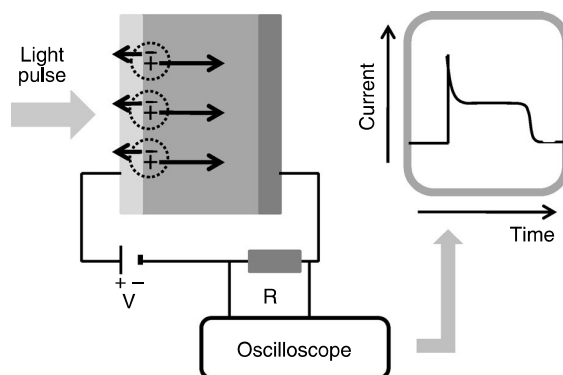
7.2 Experimental approaches

7.2.1 The time of flight (ToF) technique

The classic experiment to measure the mobility μ of charge carriers in a semiconductor is the time of flight (ToF) technique (Fig. 7.1) (Hertel and Bässler, 2008). One creates a spatially narrow sheet of charge carriers by photoexcitation next to the semitransparent top electrode in a sandwich-type sample by a short laser pulse and one records the mean arrival time of the charge carriers (transit time) $t_{tr} = \mu/dF$ at the exit contact, d being the sample thickness and F being the electric field. To observe ideal ToF signals requires that:

- (i) the sample is free of charges without photoexcitation, implying that the dielectric relaxation time $\epsilon_r \epsilon_0 / \kappa$ is large compared to the transit time t_{tr} , where κ is the conductivity;
- (ii) the RC-time constant is small compared to the transit time t_{tr} ;
- (iii) the thickness of the spatial spread of the packet of charge carriers is small compared to the film thickness d ;
- (iv) the concentration of charges is low enough that the charges do not interact;
- (v) there is no deep trapping; and that
- (vi) the mobility is time independent.

Under intrinsic optical charge generation, condition (iii) requires that the sample thickness is much larger than the penetration depth of light which is at least 100 nm or even larger. This implies a sample thickness of several μm . The problem



7.1 Schematic illustration of the time-of-flight method (ToF). An excitation pulse creates electron-hole pairs close to the front electrode. While electrons leave the device immediately by the front electrode, holes move through the semiconductor film to the back electrode, thus inducing a displacement current that is monitored using an oscilloscope. By changing the polarity of the applied electrical field, electron mobility can also be measured.

can be circumvented if charges are photoinjected from a thin sensitizing dye layer (Markham *et al.*, 2002). This method has been applied to samples as thin as 300 nm (Gambino *et al.*, 2008). Regarding condition (iv) one usually assumes that it is fulfilled if the number of transported charges is less than 5% of the capacitor charge in order to prevent distortion of the ToF signal. To satisfy this condition, one typically estimates that the concentration of mobile charges inside the sample should be smaller than 10^{15} cm^{-3} for a field of $10^5 \frac{\text{V}}{\text{cm}}$, a dielectric constant ϵ_r of 3 and a film thickness of $d = 2 \mu\text{m}$. A film thickness of 100 nm leads to a maximum carrier concentration of about $2 \times 10^{15} \text{ cm}^{-3}$.

7.2.2 Space-charge-limited currents (SCLC)

If an organic material is contacted with an 'ohmic' electrode, the measured current at a given applied voltage is only limited by the bulk mobility. The condition is that the electrode can inject enough charge carriers that the electric field at this electrode is zero. This is realized if the energy barrier for charge injection is $< 0.3 \text{ eV}$ (Davids *et al.*, 1997; Wolf *et al.*, 1999). In this case the current is space charge limited (SCL) and can be described by Child's law

$$j_{SCL} = \frac{9}{8} \frac{\epsilon_0 \epsilon_r \mu V^2}{d^3} \quad [7.1]$$

The measurement of the current-voltage characteristic thus allows the determination of the injected mobility of the charge carrier. One has to take care that the quadratic dependence of the current on voltage is indeed due to SCL and not accidental, as is often observed. Thus, in order to avoid misinterpretation of the data, one has to assure that the thickness scaling according to Eq. 7.1 is obeyed. The SCL formalism has been applied successfully to molecular crystals, (Mark and Helfrich, 1962), molecularly doped polymers (Abkowitz and Pai, 1986) and conjugated polymers (Blom *et al.*, 1996; Martens *et al.*, 2001; Hertel and Meerholz, 2007).

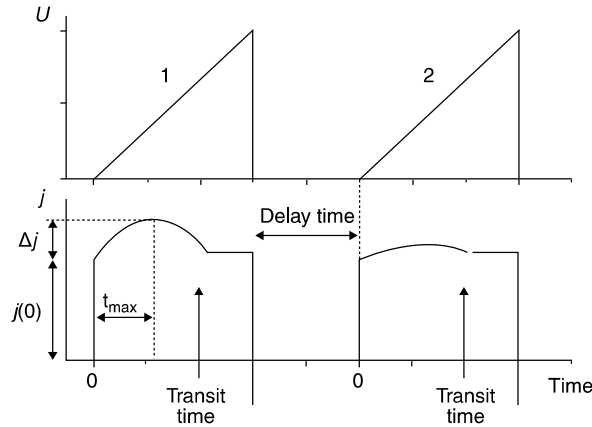
Another possibility to obtain the mobility from SCL currents is the use of a transient voltage instead of steady-state conditions (dark injection, DI-SCLC). The measured transient current upon applying a rectangular voltage pulse is increasing with time as the moving carriers experience an increasing electric field, which is redistributed by its own space charge. It can be shown (Many and Rakavy, 1962) that the transient current reaches a maximum at time $t_{max}=0.78 t_{tr}$, where t_{tr} is the charge carrier transit time for the device considered. After the current has reached its maximum, it decays to a constant value if trapping is absent. Transport studies in molecularly doped polymers and conjugated polymers have shown that the mobility inferred from an SCL experiment is equivalent to the ToF mobility (Poplavskyy and Nelson, 2003). Very often SCL currents are affected by trapping. In this case, the voltage dependence of the steady-state current becomes much steeper. In the case of an exponential distribution of trap levels the SCL current becomes

$$j_{SCL}(V) \propto \frac{V^{l+1}}{d^{2l+1}} = \frac{F^{l+1}}{d^l} \quad [7.2]$$

where $l = \frac{T}{T_0}$ is the slope parameter of the exponential distribution. For a trap free system $l=1$ (Pope and Swenberg, 1999; Mark and Helfrich, 1962). Later on the theory was extended to a Gaussian trap DOS distribution (Nespurek and Silinsh, 1976; Bonham, 1973). Again, the thickness dependence of $j_{SCL}(F)$ can be used as a test whether a current is indeed space charge limited or, rather injection limited.

7.2.3 Carrier extraction by linearly increasing voltage (CELIV)

The restriction of the ToF method to determine the mobility in systems with low dark conductivity can be circumvented by the recently developed CELIV technique (Fig. 7.2) (Juska *et al.*, 2000b). It is applicable to materials where the dielectric relaxation time is shorter than the transit time of a carrier and to materials that are intentionally or accidentally doped by electron donors or acceptors. One applies sequentially triangular voltage pulses to a sample in a sandwich-type diode with non-injecting contacts. The current rise following



7.2 Schematic illustration of the CELIV method. Adapted after Juska *et al.* (2000).

the first voltage pulse needs to be ignored since it is due to the capacitance of the sample, that is, the charging of the electrodes. The initial slope of the current in any of the following voltage pulse is related to the bulk conductivity (Juska *et al.*, 2000b):

$$\sigma_c = \epsilon_0 \epsilon_r \left. \frac{d(j/j(0))}{dt} \right|_{t=0}. \quad [7.3]$$

The time t_{max} at which the current reaches the maximum allows the calculation of the mobility according to Eq. 7.4:

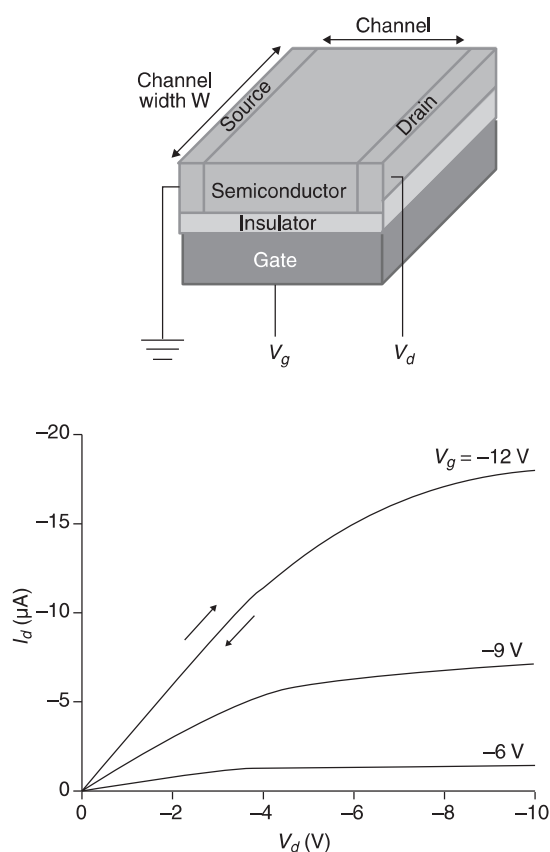
$$\mu = \frac{2d^2}{3At_{max}^2 [1 + 0.36\Delta j/j(0)]} \quad [7.4]$$

In Eq. 7.4, A is the velocity of the voltage of the triangular voltage pulse and Δj is the difference between the maximum current (at time t_{max}) and current at $t=0$. The derivation of Eq. 7.4 takes into account the electric field redistribution inside the sample upon charge flow. The mobility obtained is related to intrinsic carriers. This is different from the ToF technique, where optically excited excess charges are monitored. While the relaxation of charge carriers inside the density of states upon migration through the sample is important for ToF measurements, the CELIV technique monitors the transport of charge carriers in thermal equilibrium. The method can also be applied to photogenerated charge carriers (Bange *et al.*, 2010), though whether the carriers are then still in thermal equilibrium depends on the experimental conditions. The analysis of CELIV

experiments has to be modified if the charge carrier mobility is field dependent and if bimolecular charge recombination becomes important (Pivrikas *et al.*, 2007).

7.2.4 Field-effect transistor (FET) characteristics

The methods considered so far yield a mobility that is a bulk property of the material. In an organic FET the coplanar arrangement of the source and drain electrodes enables the source-drain current I_D to be measured as a function of the gate voltage V_g applied perpendicularly to a source-drain voltage V_d (Fig. 7.3) (Veres *et al.*, 2003). The organic layer is insulated from the gate by a dielectric



7.3 Schematic illustration of an organic field-effect transistor (OFET) and a typical output characteristics of an OFET measurement. Adapted after Sakanoue and Sirringhaus (2010).

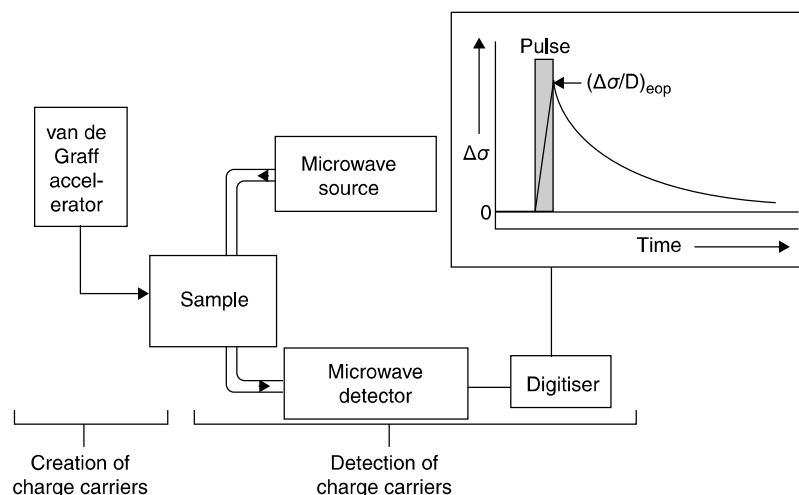
layer conventionally consisting of SiO_2 , or Al_2O_3 . The gate voltage gives rise to a unipolar capacitor charge at the interface between the insulator and organic layer. Applying a voltage V_d between source and drain results in a current increasing with V_d and V_g . It can be shown (Horowitz, 2007) that the mobility can be calculated from the drain current in the regime where it depends linearly on V_d according to Eq. 7.5:

$$\mu = \frac{L}{WC(V_g - V_T)V_d} I_d \quad [7.5]$$

The geometric dimensions of the FET are the channel length L and the channel width W . C is the capacitance and V_T the threshold voltage (Horowitz, 2007). Alternatively, the mobility can be evaluated from the saturation regime of the FET characteristics as well. The determination of the mobility is not unambiguous, since contact resistance effects influence the transfer characteristics (drain current) and hence, mobility. One has to stress that the mobility inferred from a FET experiment is an operationally defined value and not a material constant because charge carriers move in a thickness of a few monolayers at the organic–dielectric interface. Therefore, it is influenced not only by the morphology of that interface, but by the properties of the dielectric as well (Veres *et al.*, 2003; Dimitrakopoulos *et al.*, 1999). This is why μ_{FET} is dependent on the dielectric and sample geometry used for the FET (Horowitz, 2007). For instance, at the interface to SiO_2 , that is often used as an insulator between the polymer and the Si gate-electrode, there is a large concentration of hydroxyl groups that can act as traps for electrons (Ho *et al.*, 2005). A useful technique to study the density of states distribution of the organic layer deposited on top of the electrodes is the Kelvin probe force microscopy (Tal *et al.*, 2005; Celebi *et al.*, 2008; Lange *et al.*, 2011). Usually the FET mobility exceeds the value determined by the ToF technique because the gate-induced charges fill up tail states of the DOS distribution that lead to a reduction of activation energy for transport and a concomitant increase in mobility (Tanase *et al.*, 2003).

7.2.5 Time resolved microwave conductivity (TRMC)

The TRMC technique was pioneered by the Delft group (Gelinck and Warman, 1996). It is profitably used to monitor charge transport on short length and short time scales. This is relevant for conjugated polymers in which intra-chain transport can be much faster than inter-chain transport. TRMC is an electrode-less technique. Charge carriers are generated homogeneously inside the sample by irradiation with 5–20 ns pulses of 3 MeV electrons from a van der Graaff electron accelerator (Fig. 7.4). One probes their oscillatory motion by a microwave field on a short length scale yet within a ns to μs time scale, i.e. long compared to the inverse probing microwave frequency. Typical frequencies are either 10 GHz or 34 GHz. The peak amplitude of the microwave field is of the order of 100 V/cm, i.e. low as

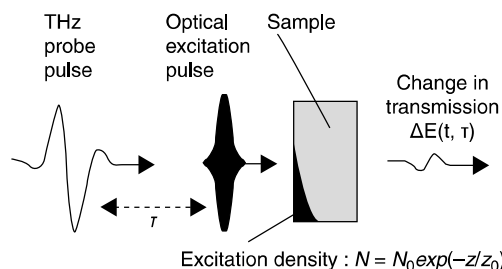


7.4 A simplified schematic representation of the pulse-radiolysis time-resolved microwave conductivity experiment. $[\Delta\sigma/D]_{\text{eop}}$ is the dose-normalized end-of-pulse conductivity. Adapted after Warman *et al.* (2004).

compared to the field strengths commonly used in ToF experiments. The radiation-induced conductivity is inferred from the decrease of the microwave power transmitted through the cell. It is given by the product of the charge carrier concentration and their mobility. The charge concentration can be estimated from the irradiation dose and the known ionization efficiency. In order to probe charge motion on isolated polymer chains, the polymer is dissolved in benzene solution, though the technique can also be used to study solid state effects in bulk samples. Monitoring the motion of electrons on the polymer chain requires thorough degassing and doping with a strong hole scavenger such as tetramethyl-p-phenylenediamine (TMPD). In order to selectively study the motion of holes, the solution can be saturated by oxygen that is an efficient scavenger for excess electrons.

7.2.6 Terahertz spectroscopy

The advancement of ultra-fast spectroscopy enables the direct probing of charge carrier motion on short timescales by THz pulses (Hegmann *et al.*, 2006; Hendry *et al.*, 2004, 2005) allowing for the probing of carrier transport in the ps time range. The measurement is a conventional time-resolved pump-probe experiment (Fig. 7.5). Typically, 100 fs pulses of a Ti-sapphire laser are used as excitation sources for the organic material. The THz probe pulse is produced from fs-excitation of either inorganic semiconductors which emit THz pulses upon



7.5 Schematic of the femtosecond-pump-terahertz-probe-experiment. Adapted after Hendry *et al.* (2005).

acceleration of the photo-induced carriers in an electric field or by excitation of non-linear crystals such as ZnTe. The emitted pulse is usually a few THz wide with an even lower electric field strength in comparison to microwave radiation. The detection is done by gating the THz probe pulse with an fs pulse of variable delay and with photoconductive or electro-optical sampling – basically the reverse of the methods used to generate THz pulses. The Fourier transformation of the pulses is used to calculate the refractive index and absorption. The complex dielectric functions can be used to obtain the complex conductivity. Again, as in TRMC, the charge generation efficiency of the organic material has to be known to obtain mobility in a time window of 1–40 ps. For a detailed description of THz spectroscopy the reader is referred to Hegmann *et al.* (2006).

7.2.7 Optical probing

At first glance transient electroluminescence may appear to be a useful technique to monitor charge transport. However, the difficulty of this experiment is to disentangle charge transport from time dependent injection, charge accumulation at internal interfaces, and bimolecular charge recombination (Pinner *et al.*, 2005). A way to overcome such problems is to confine charge recombination to a structurally well-defined thin layer next to the exit electrode. An example is the successful determination of the electron mobility in a spirofluorene based copolymer (Bange *et al.*, 2007).

An independent and complementary method to measure the charge carrier mobility on ultra-fast time scales has recently been introduced by Devižis *et al.* (2009), based on time resolved electric field-induced second harmonic generation (SHG). This method is commonly used to determine molecular hyperpolarizabilities. Any process that changes the electric field distribution in the material will affect the temporal SHG signal. In turn, the SHG intensity can be taken as a probe of changes of the electric field due to charge motion. Upon generating charge carriers in a charged capacitor by a short laser flash, the moving charge partially

shields the electric field and the SHG efficiency decreases. Measuring the decrease of the SHG signal as a function of time after the laser pulse yields the time dependence of the carrier motion.

7.3 Concepts

7.3.1 The Gill equation

The concepts for explaining charge transport in non-crystalline organic solids were stimulated by the development of xerography. The first generation of photoreceptors were amorphous chalcogenides. Meanwhile they have been replaced by electrically inert polymers doped with organic molecules that act as transport moieties for optically generated charge carriers (usually holes). Early on it has been recognized that charge transport is electric field assisted and temperature activated with an activation energy of about 0.5 eV. Gill cast the temperature and field dependence of the mobility into his famous empirical equation (Gill, 1972):

$$\mu(F, T) = \mu_0 \exp \left\{ -\frac{E_{act} - \beta \sqrt{F}}{kT_{eff}} \right\}, \quad \frac{1}{T_{eff}} = \frac{1}{T} - \frac{1}{T^*} \quad [7.6]$$

where E_{act} is the zero-field activation energy, β is a constant and T^* is the so-called Gill-temperature at which extrapolated $\ln \mu(F, T)$ vs. T^{-1} lines taken at different field strength F intersect.

The Gill equation is a modification of the Poole-Frenkel equation that has been used in trap-limited transport in which traps are considered to be charged when empty. It has also been applied to describe thermionic charge injection from a metallic electrode. In the latter case, the sibling charge is the image charge inside the metal. Gill found that the field dependence of the mobility can often be fitted with the Poole-Frenkel equation provided that the temperature is replaced by the effective temperature T_{eff} . However, there are serious shortcomings of this approach:

- (i) The classic Poole-Frenkel type field dependence rests upon the notion of trap-limited transport where the traps are charged when empty. For a broad range of materials used in xerography this an unrealistic assumption.
- (ii) Extrapolating to $\mu(F, T)$ to $T \rightarrow \infty$ yields intercept values that are far above the mobilities values measured for molecular crystals.
- (iii) At lower temperatures charge transport becomes dispersive, i.e. in a ToF experiment the photocurrent decays with time and the kink that usually marks the arrival of the charge carrier front at the exit electrode disappears. This is an unambiguous signature of a disorder phenomenon that is not taken into account in Eq. 7.6.

7.3.2 The disorder concept for charge transport in statistical DOS distribution

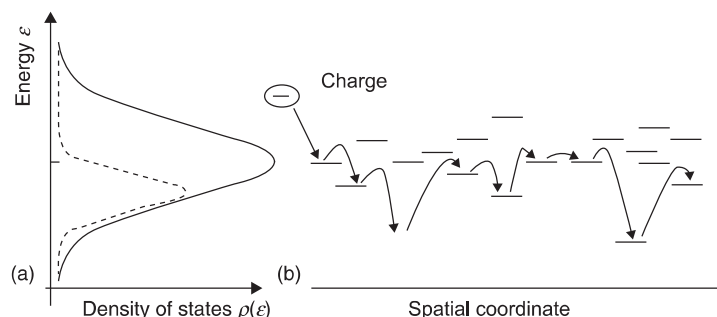
A breakthrough towards including disorder effects in random organic photoconductors was the continuous time random walk (CTRW) approach by Scher and co-workers (Scher and Montroll, 1975). They postulated that the probability of a charge carrier to leave an occupied lattice site is not an exponential function of time but that it is rather controlled by a broad waiting time distribution $\Psi(t)$ introduced in a heuristic manner. Under this condition a ToF signal features a time dependence of the photocurrent of the form

$$j(t) \propto \begin{cases} t^{-(1-\alpha)}, & t \leq t_{tr} \\ t^{-(1+\alpha)}, & t > t_{tr} \end{cases} \quad [7.7]$$

in which t_{tr} is the effective transit time defined by the kink in the $\ln j(t)$ vs $\ln t$ dependence, and α is a dispersion parameter, $\alpha = T/T_0$, where T_0 is the characteristic temperature of the exponential DOS of the tail states. We point out that α and the parameter l used in Section 7.2.2 refer to the same quantity but these different symbols are conventionally used in different contexts.

It turned out that the particular waiting time distribution $\Psi(t)$ chosen by Scher and co-workers, and the resulting dispersive photocurrent, is only realized in systems in which charge transport takes place via carrier jumps from an exponential distribution of localized states either to a well defined conduction band edge or to a so-called mobility edge within a distribution of hopping states (Rudenko and Arkhipov, 1979). The latter case is referred to as multiple trapping transport, the former is termed hopping transport. The multiple trapping concept and the hopping concept are functionally indistinguishable (Hartenstein *et al.*, 1996). The characteristic feature of transport within an exponential DOS is that a transient photocurrent remains dispersive within the entire time regime, i.e. a ToF signal never attains a plateau because quasi-equilibrium is never attained. This is at variance with the majority of random organic semiconductors. Obviously the tail of DOS distribution of organic systems decays faster than an exponential. This calls for choosing a Gaussian as a prototypical DOS distribution for random organic materials (Kador, 1991).

A basic concept to analyze the charge carrier mobility in a disordered organic solid is the Gaussian disorder model (GDM) (Arkhipov *et al.*, 2007; Bässler, 1993) that describes hopping in a manifold of sites with a Gaussian DOS distribution (Fig. 7.6). The DOS is characterized by the disorder potential σ to which inter-site as well as intra-site effects contribute, i.e. the van der Waals and the dipole/multipole coupling with the neighbor sites as well as intra-molecular conformational changes that affect the site energy. For conjugated polymers there is an additional contribution due to the variation of the energies of the conjugated segments of the chain in accordance with the ‘particle in the box’ concept.



7.6 Charge carrier hopping in a Gaussian density of states (DOS). (a) The solid line indicates an empty DOS, the dotted line denotes an occupied DOS. (b) The sequence of arrows indicates an arbitrary pathway for an electron through the molecular ensemble with energy levels of the individual molecules as indicated by the horizontal lines. Hopping to a higher energy site requires activation energy and thus is less likely than hopping to a lower energy site. Adapted after O'Neill and Kelly (2011).

In its original version, the system is considered as an array of structureless point-like hopping sites with cubic symmetry whose energies feature a Gaussian-type density of energetically uncorrelated states distribution (DOS) with variance σ . The simplest ansatz for the hopping rate is that of Miller and Abrahams (MA) (Miller and Abrahams, 1960):

$$v_{ij} = v_0 \exp\left(-2\gamma a \frac{\tau_{ij}}{\alpha}\right) \times \begin{cases} \exp\left(\frac{\epsilon_j - \epsilon_i}{kT}\right), & \epsilon_j > \epsilon_i \\ 1, & \epsilon_j \leq \epsilon_i \end{cases} \quad [7.8]$$

where $\frac{\tau_{ij}}{a}$ is the relative jump distance between i and j , α is the lattice constant and γ is the inverse localization radius related to the electronic coupling matrix element between adjacent sites, and v_0 is a frequency factor. Equation 7.8 implies that the hopping sites are point sites, neglecting that the dielectric coupling can depend on the mutual orientation of the transport molecules. The MA model assumes that the Boltzmann factor is equal to 1 for a downward jump regardless of electric field and that there is always an energy accepting phonon mode available to dissipate the excess energy. In a conventional ToF experiment or in Monte Carlo simulations, one generates independent charge carriers at energetically arbitrary sites and one follows their motion under the action of an applied electric field. This implies that the charges execute a random walk. In its course they tend to relax energetically towards quasi equilibrium. Asymptotically, an occupational density of states distribution (ODOS) with the same variance yet displaced from the center of the original DOS by σ^2/kT is approached. Subsequent charge transport occurs by

thermally activated jumps from the ODOS to a so-called transport energy somewhat below the center of the DOS (Arkhipov *et al.*, 2001). This process is terminated when the charges arrive at the exit electrode. During the relaxation process the mean hopping rate, and thus the velocity of the packet of charges, decreases. This implies that the mobility decreases with time until a steady state condition is approached. Depending on the experimental parameters this relaxation process may not be completed before the charge carriers arrive at the exit contact. In a ToF experiment this results in a dispersive signal (Fig. 7.7). In this case the ToF signal shows a featureless decay if plotted in a linear current versus time diagram. Only when displayed using logarithmic scales does a kink mark the arrival of the fastest carriers. Note that in this case of dispersive transport, the inferred ‘mobility’ is no longer a material parameter. Rather it depends on experimental parameters such as sample thickness. However, even if the energetic relaxation of the charge carriers is completed before they reach the exit contact, the tail of the ToF signal is broader than expected for a hopping system devoid of disorder. The reason is that disorder gives rise to an anomalous spatial spreading of the packet of charges that increases with electric field and degree of disorder (Pautmeier *et al.*, 1991; Richert *et al.*, 1989; Roichman and Tessler, 2002; Tal *et al.*, 2008; Tessler *et al.*, 2009). It turns out that this spread of the tail, defined as

$$w = \frac{(t_{1/2} - t_w)}{t_{1/2}} \quad \text{where } t_{1/2} \text{ is the time at which the current has decayed to half of the}$$

plateau value, is more or less universal, yielding $w=0.4\text{--}0.5$ for a system in which σ is about 0.1 eV (Borsenberger *et al.*, 1993).

In an extended version of the hopping concept, positional (‘off-diagonal’) disorder in addition to energetic (‘diagonal’) disorder has been introduced (Bässler, 1993; Fishchuk *et al.*, 2004). The simplest ansatz was to incorporate this by allowing the electronic overlap parameter $2\gamma a$ to vary statistically. Operationally, one splits this parameter into two site contributions, each taken from a Gaussian probability density, and defines a positional disorder parameter Σ , in addition to the energetic disorder parameter σ .

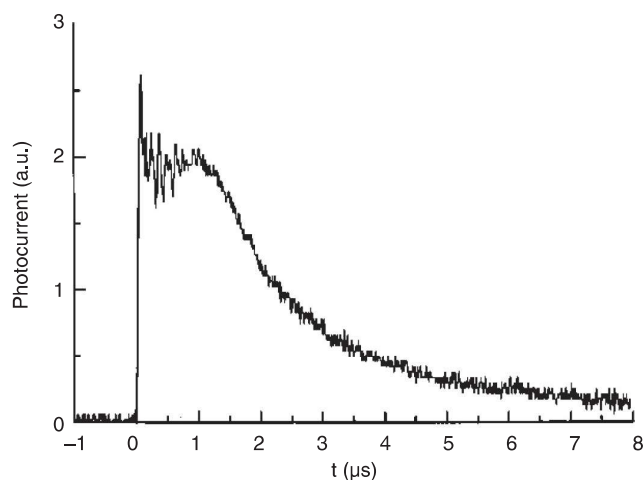
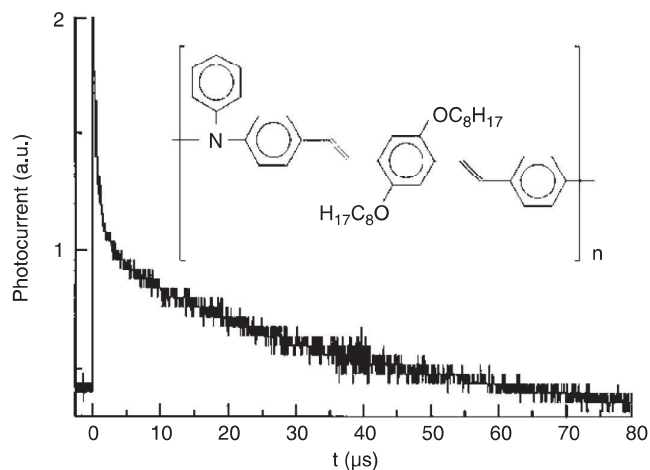
In a hopping system in which the $2\gamma a$ parameter is distributed, a charge carrier can find a larger number of favorable percolation paths to overcome a high energy barrier. Since such detours can involve carrier jumps against the field direction they are blocked at high fields. As a consequence, the mobility can decrease with field, if off-diagonal disorder dominates.

For a system with diagonal as well as off-diagonal disorder, Monte Carlo simulations (Bässler, 1993), analytical effective medium theory (Movaghar *et al.*, 1986) and stochastic hopping theory (Arkhipov *et al.*, 2007) predict a dependence of the charge carrier mobility as a function of temperature and electric field given in Eq. 7.9.

$$\mu(\hat{\sigma}, F) = \mu_0 \exp\left(-\frac{4\hat{\sigma}^2}{9}\right) \exp\left\{C'(\hat{\sigma}^2 - \Sigma^2)\sqrt{F}\right\} \quad \text{for } \Sigma \geq 1.5 \quad [7.9a]$$

$$\mu(\hat{\sigma}, F) = \mu_0 \exp\left(-\frac{4\hat{\sigma}^2}{9}\right) \exp\left\{C'(\hat{\sigma}^2 - 2.25)\sqrt{F}\right\} \quad \text{for } \Sigma \leq 1.5 \quad [7.9b]$$

where $\hat{\sigma} = \sigma/kT$ and C' is a numerical constant that depends on the site separation. If the lattice constant $a = 0.6$ nm, C is $2.9 \times 10^{-4} \text{ cmV}^{1/2}$. Equation 7.9 predicts a Poole-Frenkel-like field dependence. It is important to note, though, that the Poole-Frenkel-like field dependence is experimentally obeyed within a



7.7 ToF signals non-dispersive (top, $T = 313 \text{ K}$) and dispersive (bottom, $T = 153 \text{ K}$) transport regime for the PPV-copolymer shown as inset. Adapted after Hertel *et al.*, (1999).

significantly larger field range than predicted by simple simulation. The reason is that the energies of the hopping sites are essentially determined by the van der Waals interaction between a charged site and its polarizable neighbor sites which may carry an additional static dipole moment. This implies that the site energies are correlated (Gartstein and Conwell, 1994). Dunlap *et al.* (1996) pursued the idea further and proposed the following empirical relation for $\mu(\sigma_d, F)$:

$$\mu(\sigma_d, F) = \mu_0 \exp\left(-\frac{9\sigma_d^2}{25}\right) \exp\left\{C_0(\sigma_d^{1.5} - \Gamma) \sqrt{\frac{eaF}{\sigma_d}}\right\} \quad [7.10]$$

where $C_0=0.78$, Γ describes the positional disorder and σ_d is the width of the DOS caused by the electrostatic coupling of a charged site to neighboring dipoles. This correlated Gaussian disorder model (CDM) explains the observed range of the $\ln\mu(F) \propto \sqrt{F}$ dependence and reproduces the $\ln\mu(F) \propto 1/F^2$ type of the temperature dependence. Values for σ calculated by using Eq. 7.10 instead of using Eq. 7.9 turn out to be about 10% larger. Recently, Toney and co-workers (Toney and Freire, 2010) extended the Dunlap *et al.* (1996) treatment and included the coupling between a charge carrier and induced dipoles in the environment of a charge which, by the way, contributes essentially to the DOS distribution. When modeling a ToF experiment using a linear master equation the ubiquitously measured Poole-Frenkel-type of the field dependence of the mobility is recovered.

The concept described in the preceding paragraph rests upon the notion that the DOS distribution of the hopping sites is static on the time scale of the elementary charge transfer event. This condition is violated in polymers close to the glass transition temperature and in liquid crystalline systems. However, in two cases opposite effects have been observed. The work of Borsenberger *et al.* (1991) shows that shortly above T_g of a molecular glass the hole mobility decreases as compared to what is expected for a rigid hopping system. This is explained by broadening of the DOS distribution due to slow fluctuations. In the case of a liquid crystal the mobility can increase by two orders of magnitude relative to that of a static system because the onset of rapid motion allows for self-repairing of conformations that could otherwise act as deep hopping sites (Olivier *et al.*, 2009).

7.3.3 The influence of polaronic effects

So far we have disregarded polaronic effects. However, upon ionizing a molecule or a polymer chain by adding an extra electron there is a readjustment of bond lengths because the electron distribution changes. In optical transitions this effect is revealed by the coupling of the excitation to molecular vibrations. The interaction between the electronic excitation and the molecular lattice is also referred to as dynamic disorder. It reduces the energy of the excitation by the

polaron binding energy E_p and it can change the transfer integral between adjacent sites. The electron–phonon coupling can be quantified in terms of the Huang–Rhys factor. It determines the geometric relaxation energy, λ , between the initially generated vertical Franck–Condon transition and relaxed electronic state and thus the polaron binding energy $E_p = \lambda/2$. (Bredas *et al.*, 2004). When transferring a charge between a pair of chromophores the concomitant relaxation energy has to be transferred as well, and this implies that transport is polaronic. Unfortunately, the relaxation energy associated with placing a charge on a chromophore is not amenable to direct probing and needs to be calculated by quantum chemicals methods (Coropceanu *et al.*, 2007). Based upon computer simulations Parris *et al.* (2001) developed a theory for treating polaron transport in an energetically disordered and correlated hopping system. They introduced symmetric Marcus jump rates instead of Miller Abrahams rates. The predicted temperature dependence of the mobility is

$$\mu = \mu_0 \exp\left(-\frac{E_a}{kT} - C\left(\frac{\sigma}{kT}\right)^2\right) \exp\left(0.78(\delta^{1.5} - 1.75) \sqrt{\frac{e\alpha E}{\sigma}}\right) \quad [7.11]$$

with $C=0.31$. Fishchuk and colleagues tackled the same problem employing the effective medium approach (Fishchuk *et al.*, 2003). Their result is consistent with the treatment of Parris *et al.* except that the scaling parameter C is 0.125 instead of 0.31. Equation 7.11 defines the critical ratio of the parameters for which transport would predominantly be controlled by the molecular reorganization energy rather than by disorder, i.e. $\frac{E_a}{\sigma^2} > \frac{C}{kT}$. For $T=295$ K and $C=0.31$, we find the polaronic contribution dominates only if $\frac{E_a}{\sigma^2} > 12$. Since for charge transport σ is usually around 100 meV, E_a needs to be in excess of 120 meV for molecular reorganization to dominate. Because estimated values are almost an order of magnitude smaller (Meisel *et al.*, 2005), it is obvious that charge transport is almost entirely disorder controlled.

A related, though somewhat different concept for charge transport in a conjugated polymer, such MEH-PPV, has been introduced by the Alamos group (Tretiak *et al.*, 2002; Yu *et al.*, 2000). It assumes that the dynamics of thermally induced fluctuations in molecular geometry, specifically ring torsions, modify the energy levels of localized electronic states (polarons) and, by doing so, they temporally eliminate the activation energy needed for charge transfer. The underlying idea is self-trapping of a chromophore upon charging. It predicts an Arrhenius-type of temperature dependence of μ (see also Kreouzis *et al.*, 2006).

7.3.4 Effects due to charge trapping

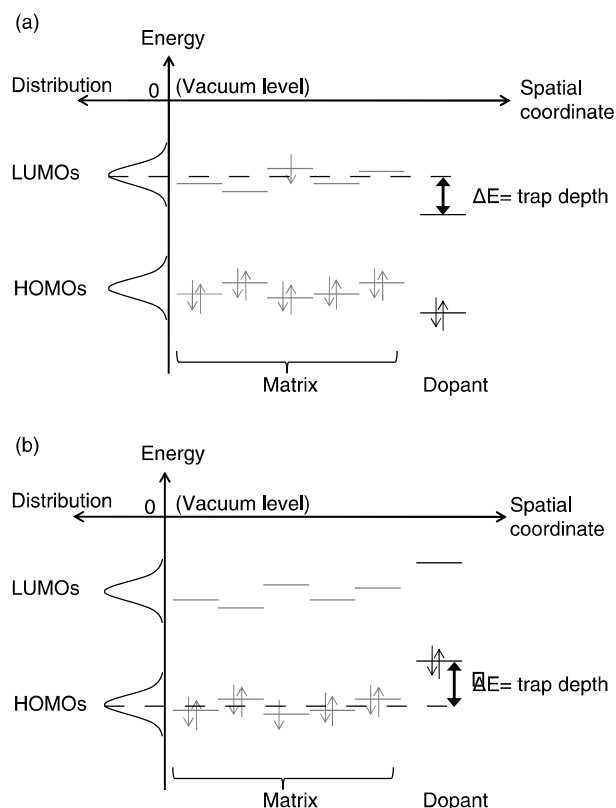
Charge transport in molecular systems is often hampered by trapping at chemical or physical defects. This was an ubiquitous problem in molecular crystal work,

and it is still of importance for the operation of today's devices, notably OFETs. In the molecular crystal case, the verification of band motion at temperature as low as 30 K was only possible after excessive material purification (Warta and Karl, 1985). Early on it was recognized that impurities with lower ionization energies (higher electron affinities) relative to the valence (conduction bands) of the crystal act as hole (electron) traps. A quantitative assessment of trapping effects was provided by the Hoesterey-Letson formalism (Hoesterey and Letson, 1963). It describes the charge carrier mobility in terms of the mobility in the absence of traps, μ_0 , the trap depth E_t , and the relative concentration, c , of traps,

$$\mu(T, c) = \frac{\mu_0}{1 + c \cdot \exp \frac{E_t}{kT}} \quad [7.12]$$

Note that at 295 K traps with a depth of 40 meV present at a concentration as low as 10^{-7} mole/mole are already sufficient to reduce the mobility in crystals by a factor of 2. Apart from chemical impurities, physical defects associated with crystallographic faults can also act as traps with continuous energy. This is the reason why charge transport under SCL conditions deviates from what Child's law would predict. Steady state SCL current studies as described in Section 7.2.2 therefore allow studying trapping in addition to thermally stimulated current (TSC) measurements (Simmons and Taylor, 1972).

In the case of polymers or molecular glasses one has to define what a trap is because, on average, all transport sites are localized and feature an intrinsic distribution of usually Gaussian shape. In the following we shall consider chemical impurities or deliberately added dopants as being external traps for holes or electrons if their HOMOs are energetically above the HOMO of the host material or if their LUMOs are below those of the LUMO of the host (Fig. 7.8). Otherwise an impurity would have no effect on charge transport. Observing trap-free hole (electron) transport in a conjugated polymer or a molecular doped polymer can therefore only be expected with a material with high lying HOMO (low lying LUMO), i.e. with low oxidation potential (high electron affinity). This was a guiding principle for molecularly doped polymers used in electrophotography. Other sources of trapping are structural faults, such as quasi-crystalline domains, in which tight molecular packing leads to the formation of low-energy sites or unintentional doping by coulombic centers. Such centers can generate deep tail states that often feature an exponential DOS distribution (Martens *et al.*, 2003, Silver *et al.*, 1989; Arkhipov *et al.*, 2005; Lewis and Movaghar, 1990). An example of the former case are crystalline domains dispersed in an amorphous phase of P3HT. Within the π -stacked domains the electronic coupling is increased. This generates tail states for holes and electrons. Note that states localized at grain boundaries of polycrystalline materials do not necessarily act as traps because at the internal interface the electronic coupling may be reduced (Kaake *et al.*, 2010).



7.8 Illustration of traps in an amorphous matrix material for (a) electrons, as indicated by an additional arrow in a LUMO, and (b) holes, as indicated by a missing arrow in a HOMO. For electrons (holes), the trap depth ΔE is given by the energy difference between the LUMO (HOMO) level of the dopant and the centre of the Gaussian distribution for the LUMO (HOMO) levels of the matrix.

When developing a formalism for trap controlled transport in a random organic semiconductor one has to take into account that the trap levels are also distributed in energy. In a first order treatment Wolf *et al.* (1997) used the Hoesterey-Letson approach given by Eq. 7.12 and replaced the trap-free mobility μ_0 by

$$\mu'_0 = \mu_0 \exp \left\{ - \left(\frac{2}{3} \frac{\sigma}{kT} \right)^2 \right\}. \text{ The trap depth } E_t \text{ was taken from the difference between}$$

the redox potentials of host and trap. Wolf *et al.* further demonstrated that under the realistic assumption that $\exp E_t/kT \gg 1$ one can adopt the conventional hopping formalism (Eq. 7.9) if σ in Eq. 9 is replaced by an effective disorder potential σ_{eff} given by

$$\left(\frac{\sigma_{eff}}{\sigma}\right)^2 = 1 + \left(\frac{2}{3} \frac{\sigma}{kT}\right)^{-2} \left(\frac{E_t}{kT} + \ln c\right) \quad [7.13]$$

provided that the trap depth is smaller than 3σ . This has been confirmed by Monte Carlo simulations (Wolf *et al.*, 1997). If the relative trap concentration exceeds 0.1 the trap controlled mobility increases. This is a signature of the onset of percolation among the network of trap levels (Pai *et al.*, 1984).

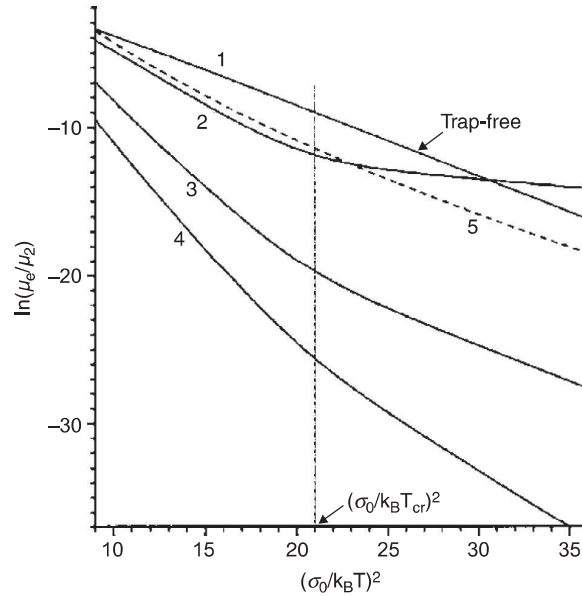
A more elaborate model has been introduced by Fishchuk *et al.* (2002) employing the effective medium approach. It is applicable to arbitrary trap depths, trap concentrations and different widths of the DOS distribution of host and trap states. This theory confirms that for moderate trap depths and temperatures, and for identical widths of the DOS distributions for host and trap, Eq. 7.13 provides a useful approximation. However, at lower temperatures the $\mu(T)$ dependence can deviate considerably from Eq. 7.13. The reason is that the effective transport energy depends on temperature as well as on the shape of the DOS distribution because introducing a trap distribution modifies the tail portion of the DOS distribution. This has two effects: it affects both the relaxation of charge carriers towards the tail states and, concomitantly, their occupancy and the effective transport energy. If the trap distribution is narrower than that of the host material, the relaxation of charge carriers upon sample cooling is diminished. At the same time the transport energy decreases. For this reason the temperature dependence of μ can become even weaker than that of the trap free system, notably at temperatures where transport is dominated by trap-to-trap hopping (Fig. 7.9). Ignoring this effect in a temperature dependent trapping study would result in erroneous values for the trap depth as well as on the prefactor mobility when extrapolating μ to $T \rightarrow \infty$. An alternative model uses the Mott-type variable range hopping concept for arbitrary DOS distributions with special emphasis on transport in a conjugated polymer doped with FeCl_3 . FeCl_3 creates positively charged PPV chains and FeCl_4^- -anions (Martens *et al.*, 2003). Coehoorn (2007) extended this treatment to the case of a finite space charge.

7.3.5 Transport in the presence of space charge

The transport models discussed above are premised on the condition that the interaction of the charge carriers is negligible. This is no longer granted if:

- (i) a trapped space charge distorts the distribution of the electric field inside the dielectric;
- (ii) ionized dopant molecules modify the DOS; or
- (iii) the current flowing through the dielectric is sufficiently large so that a non-negligible fraction of tail states of the DOS is already occupied.

The latter case is realized when either the current in the device is space-charge-limited (SCL) or when the current is confined to a thin layer of the

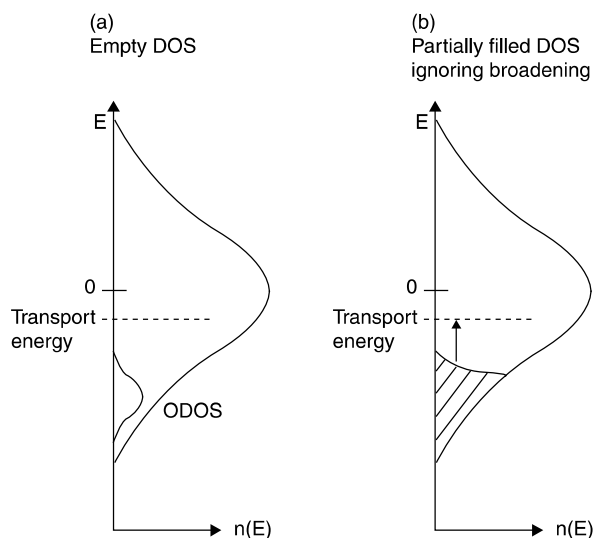


7.9 Theoretical dependence of charge transport in a hopping system characterized by a disorder parameter σ_0 in the absence of hopping (1) and in the presence of a trap concentration of $c=10^{-5}$ mole/mole at a normalized trap depth $E_t/\sigma_0=5$ with a trap distribution of $\sigma_t/\sigma_0=0.5$ (2), $\sigma_t/\sigma_0=1$ (3) and $\sigma_t/\sigma_0=1.25$ (4). The dashed line (5) denotes the $\mu(T)$ dependence calculated using the Hoesterey-Letson formalism. T_{cr} is the critical temperature below which direct trap-to-trap transport prevails. Adapted after Fishchuk *et al.* (2002).

dielectric, for instance in a field-effect transistor. It is conceptionally easy to understand that the temperature dependence of the charge carrier mobility must change when charge carriers fill up tail states of the DOS beyond the critical level defined by the condition of quasi-equilibrium. In this case the carrier statistic becomes Fermi-Dirac-like whereas it is Boltzmann-like if state filling is negligible. At low carrier density, a charge carrier in thermal equilibrium will relax to an

energy $\varepsilon_\infty = \frac{\sigma^2}{kT}$ below the centre of the DOS, provided it is given enough time to

complete the relaxation process. Charge transport, however, requires a certain minimum energy to ensure there are enough neighboring sites that are energetically accessible (Bässler, 1993). To reach this so-called transport energy from the thermal equilibrium energy, ε_∞ , an activation energy is needed. If, at higher carrier density, a quasi-Fermi level will be established above ε_∞ , the activation energy needed for a charge carrier to reach the transport level decreases and, concomitantly, the mobility increases (Fig. 7.10). This is associated not only with a weaker



7.10 Schematic view of the effect of state filling in the Gaussian distribution of the hopping stats. (a) In the low carrier limit, charge carrier transport requires thermally activated transitions of a charge carrier from the occupational DOS (ODOS) to the transport Energy E_{tr} . (b) In the high carrier limit, charge transport obeys Fermi-Dirac statistics.

temperature dependence of μ but also with a gradual change from the $\ln \mu \propto T^{-2}$ dependence to an Arrhenius-type $\ln \mu \propto T^{-1}$ dependence. This is because upward jumps of charge carriers no longer start from a temperature-dependent occupational DOS but from the Fermi level set by the applied voltage. The straightforward verification of this effect is the observation that the carrier mobilities measured under FET conditions can be up to 3 orders of magnitude larger than the values inferred from ToF experiments (Tanase *et al.*, 2005). Further, one observes a steeper increase of space-charge-limited current mobility with electric field than predicted by Child's law (Martens *et al.*, 2000). It is meanwhile recognized that this steeper increase is not due to a field dependence of the mobility under the premise of negligible concentration. Rather, as illustrated by Fig. 7.10, it is mostly an effect of the filling up of the DOS due to the increase of the charge carrier concentration (van Mensfoort *et al.*, 2008). Ignoring this effect in a data analysis would yield numerically incorrect results.

Among the first theoretical treatments of transport in the presence of a space charge is that of Arkhipov *et al.* (2002). These authors pointed out that in chemically doped materials and in the conduction channel of a FET, the number of charge carriers occupying deep tail states of the Gaussian DOS can be significant relative to the total density of states. They developed a stochastic hopping theory

based upon the variable range concept and incorporated the Fermi-Dirac distribution to describe the temperature dependence of the mobility. Currently the most frequently used formalism is that of Pasveer *et al.* (2005). It is based upon a numerical solution of the master equation representing charge carrier hopping in a lattice. Considering that only a fraction of sites are already occupied, charge transport is considered as a thermally assisted tunneling process with Miller-Abrahams rates in a Gaussian manifold of states with variance, σ , tacitly assuming that formation of a bipolaron, i.e. a pair of like charges on a given site, is prevented by coulomb repulsion. The results can be condensed into an analytical solution in factorized form,

$$\mu(T, F, n) = \mu_0(T) g_1(F, T) g_2(n) \quad [7.14]$$

where $\mu_0(T)$ is the temperature dependent mobility in the limit of $F=0$, $g_1(F, T)$ is the mobility enhancement due to the electric field and $g_2(n)$ is the enhancement factor due to state filling. Meanwhile the Pasveer *et al.* (2005) formalism has been termed as an ‘extended Gaussian disorder model (EGDM)’ and an ‘extended correlated disorder model (ECDM)’ depending on whether the correlation of sites is included or not (Bouhassoune *et al.*, 2009). A more comprehensive theoretical treatment has been developed by Coehoorn and co-workers (Coehoorn *et al.*, 2005; Coehoorn, 2007) in which the various approaches for charge carrier hopping in random organic systems have been compared.

A complementary formalism by Fishchuk *et al.* (2007) is based upon the effective medium approach of charge transport as a function of the charge carrier concentration within the DOS. In contrast to the work by Pasveer and colleagues they included polaron effects. It is obvious that the mode of how charges are transported, i.e. the trade-off between disorder and polaron effects, should have a major impact on the result. In the extreme case of vanishing disorder yet with strong polaronic coupling, filling tail states of DOS by charge carriers should not have an effect on the transport except at very large charge concentrations when coulomb repulsion becomes important. Filling-up tail states of the DOS will, however, become progressively important as the disorder contribution to charge transport increases. To incorporate polaron effects, Fishchuk *et al.* (2007) replaced the Miller-Abrahams-type of hopping rate by a Marcus rate. Note, however, that the magnitude of the effect of DOS filling is solely determined by the ratio between the disorder energy σ and the polaron energy E_p and not by the analytical form of the hopping rate.

Recently, Fishchuk and colleagues extended their effective medium approach to include a discussion of the so-called Meyer Neldel rule (Fishchuk *et al.*, 2010). The Meyer Neldel rule is an empirical relation, originally derived from chemical kinetics. It describes the fact that enthalpy and entropy of a chemical reaction are functionally related to each other. More generally, it states that in a thermally activated rate process an increase in the activation energy needed is partially compensated by an increase in the prefactor. There are numerous examples, notably in semiconductor physics, that this rule is fulfilled for various reasons.

Recently Emin advanced an adiabatic polaron hopping model that considers carrier-induced softening of the vibrations promoting charge carrier motion (Emin, 2008). Fishchuk and colleagues were able to show that in a disordered system with a partially filled density of states distribution, the Meyer Nedel rule is indeed fulfilled but it is not related to polaronic transport. Instead, it is a genuine signature of hopping transport in a random system with Gaussian DOS distribution upon varying the charge carrier concentration as realized, for example, in a field effect transistor at variable gate voltage. Interestingly, it turns out that the functional dependence of the charge carrier mobility in a field effect transistor is analogous to the Gill equation (see Eq. 7.6).

7.4 Representative experimental results

The key prediction of the disorder based transport models applied to random organic semiconductors are:

- (i) The temperature dependence of the charge carrier mobility is largely determined by hopping in a distribution of localized sites. This distribution is usually of a Gaussian shape and it is mostly due to the electrostatic interaction between a charged transport unit and spatially disordered induced and permanent dipoles. The hopping process leads to a temperature dependence of the mobility of the form $\mu(T) = \mu_0 \exp\left(-C\left(\frac{\sigma}{kT}\right)^2\right)$, provided that $\sigma/kT < 4$.
- (ii) For electric fields $> 10^4$ V/cm the field dependence of μ obeys an $\exp - \beta\sqrt{F}$ law, reminiscent of a Poole-Frenkel (PF) law. This is a signature of hopping within a Gaussian DOS distribution in the absence of traps that are charged when empty (which was the original premise of the PF model).
- (iii) The mobility extrapolated to $T \rightarrow \infty$ is a measure of the electronic overlap between the transport units.
- (iv) At lower temperatures, i.e. $\sigma/kT > 4$, charge transport becomes dispersive because the relaxation time of the charge carriers migrating within the DOS distribution exceeds their transit time. However, even under the condition of quasi-equilibrium there is anomalous spreading of the tail of a ToF signal.
- (v) The presence of a space charge modifies the temperature and the field dependence of μ because of filling of tail states of the DOS distribution and, concomitantly, the establishment of a Fermi level that controls thermally activated hopping.

7.4.1 Probes of the disorder model

The development of disorder models was stimulated by the need to understand and improve charge transport in molecularly doped polymers as photoreceptors

in photocopier machines. Since the majority of the work has been reviewed by the book of Borsenberger and Weiss (1998) a very brief summary of salient results will suffice. They show that the concept of temperature and field-assisted charge carrier hopping within a Gaussian DOS distribution is able to explain the majority of experimental facts including the transition from non-dispersive to dispersive transport. From the $\ln\mu$ versus T^2 dependence the disorder parameter σ has been derived. Depending on the polarity of matrix and dopant, σ ranges between 70 to 140 meV. It turned out that in some of the materials in which the dopant carries a large dipole moment, the σ parameter is almost independent of the concentration of the dopant. This is at first glance counterintuitive and led to the suggestion that σ is rather of intramolecular origin. Recently Tyutnev *et al.* (in press) resolved that paradox by considering that σ is the sum of the root mean square contributions of the van der Waals and the dipolar coupling of both the dopant and the matrix.

The disorder model was successfully applied also to conjugated polymers and oligomers (Markham *et al.*, 2002; Hertel *et al.*, 1999; Laquai *et al.*, 2006a, 2006b; Gambino *et al.*, 2008; Mozer *et al.*, 2005). Since the focus of the more recent work is on morphological aspects and issues related to transport in the presence of a space charge and to trapping it will be discussed in separate sections.

7.4.2 Polaron versus disorder effects

The most comprehensive study pertaining to the discrimination of polaron and disorder effects is that of Khan *et al.* (2007). They describe ToF experiments on sandwich-type samples with films of poly(9,9-dioctyl-fluorene) (PFO), and a series of fluorene-triarylamine copolymers with different triarylamine content covering a broad temperature and field range. In all cases, the field dependence of the hole mobility follows a $\ln\mu \propto \sqrt{F}$ dependence and a super-Arrhenius-type of temperature dependence. At lower temperatures the ToF signals are dispersive. When analyzing the experimental data the authors first checked whether or not the uncorrelated Gaussian disorder model (GDM) is appropriate.

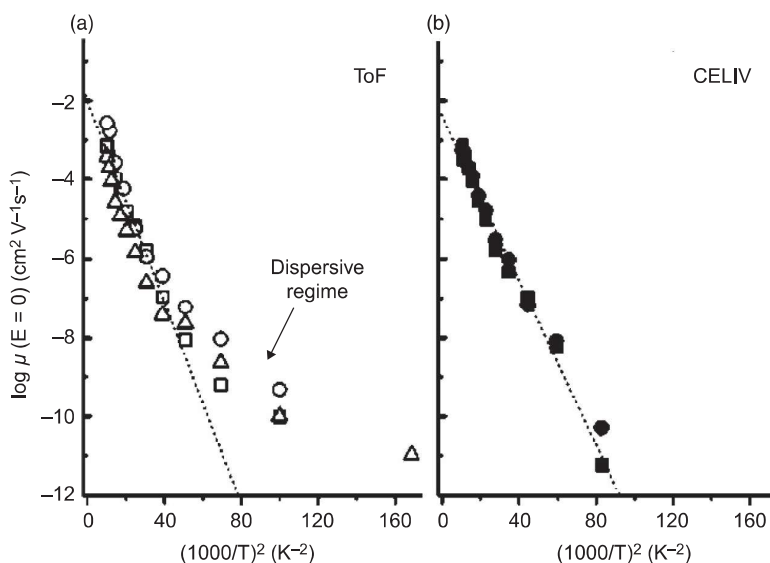
There are indeed reasonably good fits to the temperature and field dependence based upon Eq. 7.9. Recognizing, however, that experimentally observed $\ln\mu$ versus $\sqrt{F}$ dependence extends to lower fields than the GDM predicts, they went one step further and tested the correlated disorder model (CDM) in the empirical form of Eq. 7.10. Here the site separation enters as an explicit parameter. This analysis confirms the validity of the $\ln\mu \propto T^{-2}$ law. The positional disorder parameters are comparable and the values for the site separation are realistic, yet this approach does not consider any polaronic contributions. To also take into account polaron effects, the authors finally used the empirical expression Eq. 7.11. The difficulty is how to separate the polaron and disorder contributions to the T -dependence of μ . This can be done via an analysis of the field dependence

of μ . Once σ is known the factor $\exp\left(-\frac{E_a}{kT}\right)$, that accounts for the polaron contribution, can be determined. The parameters inferred from the data fits are then compared by Khan and coworkers (Khan *et al.*, 2007). They find that by taking into account polaronic contributions, the σ value decreases while the prefactor to the mobilities increases by roughly one order of magnitude. The polaron binding energy $2E_a$ is significant and ranges between 25 meV and 40 meV in agreement with the estimate based upon Eq. 7.11. It is larger in the copolymers as compared to the homopolymer PFO. A similar analysis has been carried out by Kreouzis and colleagues for hole transport in pristine and annealed polyfluorene films (Kreouzis *et al.*, 2006).

Note that when assessing polaronic effects, one should be cautious about overinterpreting the field and temperature dependence of the mobility obtained from ToF measurements. For instance, in the analyses of the data in Khan *et al.* (2007) and Kreouzis *et al.* (2006), ToF signals have been considered that are dispersive. It is well known that data collected under dispersive transport conditions carry a weaker temperature dependence because the charge carriers have not yet reached quasi-equilibrium. This contributes to an apparent Arrhenius-type temperature dependence of μ that might erroneously be accounted for by polaron effects. In fact in their recent work, van Mensfoort *et al.* (2008) conclude that in polyfluorene copolymers hole transport is entirely dominated by disorder. This is supported by a strictly linear $\ln\mu \propto T^{-2}$ dependence covering a dynamic range of 15 decades with a temperature range from 150 K to 315 K. Based upon stationary space-charge-limited current measurement, where the charge carriers are in quasi equilibrium so that dispersion effects are absent, the authors determine a width σ of the DOS for holes as large as 130 meV with negligible polaron contribution.

In this context it is appropriate to recall the work of Mozer *et al.* (2005) on hole transport in regio(3-hexylthiophene). These authors compared the field and temperature dependencies of the hole mobility measured via the ToF and CELIV methods. Quite remarkably, the temperature dependence deduced from ToF signals plotted on a $\ln\mu$ versus T^2 scale deviate significantly from linearity while the CELIV data follow a $\ln\mu \propto T^2$ law down to lowest temperatures (180 K) (Fig. 7.11). The reason is that in a ToF experiment the charge carriers are generated randomly within the DOS and relax to quasi-equilibrium in their hopping motion while in a CELIV experiment relaxation is already completed.

The conclusion that polaron effects contribute only weakly to the temperature dependence of the charge carrier mobility is supported by a theoretical study of polarons in several conjugated polymers. Meisel *et al.* (2005) considered the electron–phonon interaction and calculated polaron formation in polythiophene, polyphenylenevinylene and polyphenylene within an extended Holstein model. Minimization of the energy of the electronic state with respect to lattice degrees of freedom yields the polaron ground state. Input parameters of the Hamiltonian



7.11 Comparison of the temperature dependence of hole mobilities in regioregular P3HT measured (a) using the ToF method and (b) using the CELIV method. Different symbols refer to different samples. Adapted after Mozer *et al.* (2005).

are obtained from *ab initio* calculations based on density-functional theory (DFT). The authors determined the size and the binding energies of the polarons as well as the lattice deformation as a function of the conjugation length. The binding energies decrease significantly with increasing conjugation length because the fractional changes of bond lengths and angles decrease as the charges are more delocalized. The polaron extents are in the range of 6–11 nm for polythiophenes and polyphenylenevinyls, and the associated polaron binding energies are 3 meV for holes and 7 meV for electrons. For polyphenylenes, the polaron size is of about 2–2.5 nm and the binding energy is 30 meV for the hole and 60 meV for the electron. Although the calculations document that charge carriers are self-trapped they indicate that polaron binding energies are much smaller than the typical width of the DOS of representative π -bonded conjugated polymers.

7.4.3 Trapping effects

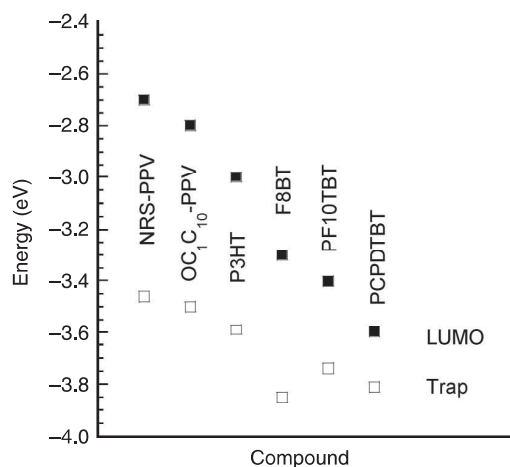
Systematic studies of hole trapping in a molecularly doped polymer were performed by Wolf *et al.* (1997) and Borsenberger *et al.* (1998) on tri-*p*-tolylamine doped polystyrene containing variable concentrations of tri-*p*-tolylamines carrying different anisyl-substituents. The results prove that for a trapping system

with traps having a trap energy of 0.25 eV, Eq. 7.13 provides a good fit to the data. The work of Mandoc *et al.* (2007) confirms the notion that in a disordered dielectric containing well identified traps the activation energy of μ can be less than what one expects based upon the difference of the redox potential of host and trap. The host materials were conjugated polymers of the PPV-family and the distribution of trap levels was approximated by a sum of symmetric exponentials centered at a mean trap energy. This simplifies the analytic treatment. It confirms that charge transport is thermally activated from the trap level to a transport level that decreases upon decreasing temperature. As a consequence, the apparent activation energy decreases and the temperature dependence of μ becomes weaker.

A similar concept has been used to rationalize electron transport in a copolymer consisting of fluorene and triarylamine units using the SCL technique (van Mensfoort *et al.*, 2009). A data analysis yields a disorder parameter of 70 meV and a concentration of the intrinsic hopping site of 10^{21} cm. The prefactor mobility for electron motion – obtained by extrapolating the temperature to infinity and thus corresponding to the trap free case – turns out to be $0.03 \text{ cm}^2/\text{Vs}$, comparable to trap-free hole transport. This confirms the notion that in a given material the electron and hole mobilities are comparable unless extrinsic traps are present. By the same token, a material with low lying LUMO should feature trap-free electron motion. A recent example is a novel electron transporting polymer based on a naphthalene diimide core ('Polyera ActivINK N2200') (Neher *et al.*, 2010). The room temperature electron mobility, inferred from dispersive ToF signals, is $6 \times 10^{-3} \text{ cm}^2/\text{Vs}$.

While the presence of ionized dopants and impurities is known to create deep states not featuring a Gaussian tail in the DOS distribution, there is no reason why the effect of neutral traps should be described by an exponential DOS distribution except that the analytic modeling becomes easier. To overcome this problem Nicolai *et al.* (2011) implemented a Gaussian distribution function in a numerical drift-diffusion model using an approximation of the Gauss-Fermi integral (Paasch and Scheinert, 2009). They showed that the Gaussian model can, indeed, be used to describe the temperature dependence of electron transport in three PPV derivatives that had previously been analyzed using an exponential distribution (Markov *et al.*, 2005). The σ parameter of the trap distribution is found to be 0.1 eV, the trap concentration is about 10^{17} cm^{-3} . The bulk σ parameters for electron transport are 0.13 eV for OC₁C₁₀-PPV, 0.12 eV for MEH-PPV and 0.14 eV for NRS-PPV, in good agreement with previous data analysis.

Subsequently, Nicolai *et al.* (2012) studied unipolar electron SCL-currents in 9 different polymers with LUMO energies ranging from -2.7 eV (NRS-PPV) to -3.6 eV (PCPDTBT). They observed that in all polymers there is a universal Gaussian distribution of trap levels located at a DOS center at -3.6 eV below vacuum with a width of 100 meV and a concentration of $3 \times 10^{17} \text{ cm}^{-3}$. Therefore trap-free electron transport can only be expected in polymers with LUMO levels



7.12 Schematic representation of the LUMO energies (■) and the centre of the trap distribution (□) for a range of polymers as detailed and adapted from Nicolai *et al.* (2012).

as deep as at least -3.6 eV, i.e. deeper than the -3.0 eV estimate proposed earlier (Fig. 7.12) (de Leeuw *et al.*, 1997). Materials that fulfill this requirement are PCBM and poly(ND12OD-T2). This work clearly indicates that electron trapping in conjugated polymers and related materials has a common origin and is most probably associated with water or oxygen incorporated in the course of device fabrication.

A complementary method to delineate the effect of traps is the thermally stimulated current (TSC) technique. The idea is to optically excite charge carriers in a biased sample, cool down the sample – preferentially to 5K – and measure the current upon warming up. The TSC system is a reflection of the distribution of trapped charges (Heil *et al.*, 2003).

7.5 Future trends

The study of charge transport in organic materials is driven by their potential use in modern opto-electronic devices such as OLEDs, solar cells and FETs. For application as photoreceptors in photocopiers or laser printers, mobilities as low as 10^{-5} cm²/Vs are acceptable. However, more control on charge mobility is needed for state-of-the-art opto-electronic devices.

For OLED applications in displays and lighting, high mobilities are not essential. For the operation of OLEDs it is rather central that the currents of electrons and holes balance. This is needed to maximize charge recombination, to minimize leakage currents and to ensure that the recombination zone is at the

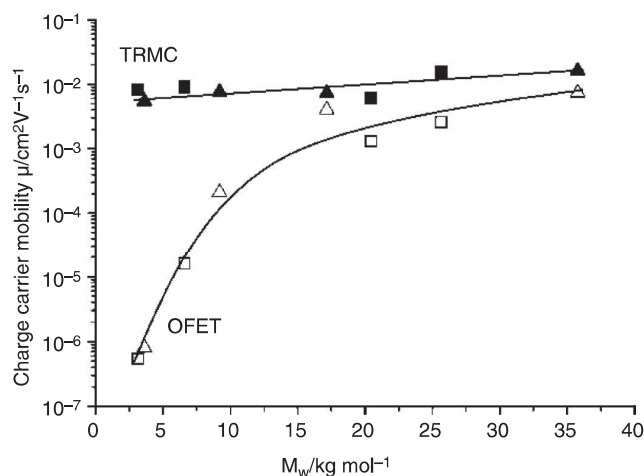
centre of the device and away from the electrodes. Mobilities up to 10^{-4} are usually sufficient. Differences in electron and hole mobilities are ideally compensated by adjusting injection barriers and by introducing suitable blocking layers in multi-layer devices (Greenham *et al.*, 1993; Campbell *et al.*, 2007). The role of charge carrier mobility in solar cell devices is currently attracting much attention (Howard *et al.*, 2010; Deibel *et al.*, 2009). In a solar cell, a photogenerated coulomb-bound electron hole pair dissociates by transferring a charge to a neighboring accepting molecule at an internal molecular interface. It appears that, immediately after the transfer, a high charge carrier mobility away from the interface is critical to ensure efficient charge separation and to avoid recombination. The mobility on longer timescales, when charges move towards the collecting electrodes, is not reported to have a significant influence on the performance of the solar cell. However, high charge carrier mobilities are required on all timescales for the operation of OFETs because they are frequently used in circuits requiring short switching times.

Unfortunately, the mobility depends on a variety of parameters that cannot all be optimized simultaneously. As outlined in Section 7.3, charge carrier mobility depends on polaronic effects, i.e. the molecular distortion associated with a charge state, on energetic and spatial disorder, on trapping effects and on the electronic coupling between adjacent sites. We shall briefly consider four factors in current approaches made to optimize each of these parameters.

The first, and most significant, factor to control mobility is the size of the electronic coupling between adjacent units (Bredas *et al.*, 2004). A prototype material to illustrate this is poly(3-hexylthiophene) (P3HT). Early on it was observed that the OFET mobility of P3HT increases by orders of magnitudes with increasing molecular weight of the polymer chain or with increasing degree of regioregularity of the chain (Sirringhaus *et al.*, 1999b; Kline *et al.*, 2003). Subsequent studies revealed that P3HT tends to form aggregates, and this tendency increases with molecular weight and side-chain ordering (Chang *et al.*, 2006). These aggregates have been identified by X-ray measurements, AFM measurements and also through their absorption spectra (Kline *et al.*, 2003; Sirringhaus *et al.*, 1999b; Clark *et al.*, 2007; Salleo *et al.*, 2010). Spano has derived a theoretical approach to treat the absorption and emission spectra of weakly interacting linear and circular H and J aggregates (Spano, 2005, 2006). P3HT forms such linear H-aggregates, and using Spano's approach, parameters such as the size of the electronic coupling for excitons and the correlation length can be derived from the absorption and emission spectra (Clark *et al.*, 2007, 2009; Spano *et al.*, 2009; Scharsich *et al.*, 2011; Turner *et al.*, 2011). While the excitonic coupling is based on a dipole interaction, the electronic coupling for charges requires wavefunction overlap. Due to the difference in the underlying coupling mechanism, a high excitonic coupling does not linearly imply a high transfer integral for charges. Nevertheless, it is reasonable to expect a larger wavefunction overlap in well-ordered aggregates than in an amorphous

film. In fact, charge carrier mobilities as high as $10^{-2} \text{ V/cm}^2 \text{ s}^{-1}$ have been observed in films containing a high fraction of well-ordered aggregates (Pingel *et al.*, 2010; Kline *et al.*, 2003; Scharsich *et al.*, 2011). This value is equal to the on-chain mobilities measured for hole transport in P3HT, independent of molecular weight, using the time-resolved microwave conductivity (TRMC) method (Pingel *et al.*, 2010) (Fig. 7.13). It indicates that lower values measured in FETs are due to a lack of connectivity between aggregated domains (Zen *et al.*, 2004; Pingel *et al.*, 2010; Lan and Huang, 2009) or due to grain boundary effects (Kline *et al.*, 2003; Jimison *et al.*, 2009). The amount to which these crystalline domains are formed can be controlled by processing conditions such as thermal treatment (Zen *et al.*, 2004) and choice of solvents (Clark *et al.*, 2009) as well as by materials parameters such as molecular weight, degree of regioregularity, and, for short chains, the synthesis route (Scharsich *et al.*, 2011). Similar effects of chain ordering and aggregate formation have also been observed for other conjugated polymers. Examples include selenium analogs of poly(thiophene) (PSSS), (Chen *et al.*, 2010) thiophene-based polymers bearing thiazolothiazole units and other thiophene derivatives (Osaka *et al.*, 2009).

The second factor of particular importance to improving mobility is the avoidance of deep trap states or, equivalently, their passivation by filling them. For example, in early-day-OFETs, electron mobility used to be significantly lower than hole mobility. This was recognized as resulting from electron traps at the



7.13 Comparison of mobilities determined by TRMC and by OFET measurements for non-deuterated P3HT (■, □) and deuterated P3HT (▲, △) as a function of molecular weight. Adapted after Pingel *et al.* (2010).

interface to the dielectric. By covering the surface with a buffer dielectric layer, either spin-coated or applied as self-assembled monolayers, these trap states could be passivated. As a result, high electron mobilities and ambipolar charge transport in OFETs could be demonstrated (Ho *et al.*, 2005). To date the record regarding the FET-electron mobility in a non-crystalline organic semiconductor that is either spin-coated or printed from solution is $0.45\text{--}0.85\text{ cm}^2/\text{Vs}$ under ambient conditions. This is close to the mobilities of anthracene-type of molecular crystals at room temperature. The material is poly((N,N'-bis(2-octyldodecyl)-naphthalene-1,4,5,8-bis(dicarboximide)-2,6-diyl)-alt-5,5'-(2,2'-bithiophene)) (PND12OD-T2) (Yan *et al.*, 2009). Since it is stable in air and processable using standard techniques it may be profitably used for fabricating low cost organic FETs with low power dissipation and acceptable circuit speed.

In a similar way, in solar cells and OLEDs, aggregates, dimers and excimers have been identified to act as trap states. They can be avoided by substituting the molecular unit with bulky side groups. While this removes the trap states, it also increases the jump length of charge carrier hopping and thus reduces the prefactor mobility (Laquai *et al.*, 2006a). Typical examples include the introduction of bulky spiro-linkages in conjugated polymers (Salbeck *et al.*, 1997). The problem of dimer or excimer formation has also recently been discussed for carbazole derivatives that are frequently used as hole transporting materials in OLEDs (Hoffmann *et al.*, 2011; Jankus and Monkman, 2011).

The third factor to consider is that energetic disorder limits charge carrier mobility in an OFET only to a moderate extent, while it has a more profound influence on solar cells. In contrast to solar cells, OFETs are operated at high charge carrier densities, so that a significant part of the DOS is filled and a Fermi-level is formed, thus reducing the activation energy needed to reach the transport level. Energetic disorder is reduced when the morphology of the film is smooth and when polymer chains are planarized to yield long conjugation length. Typically, attempts to optimize film morphology and chain conformation have a greater influence on mobility by improving the size of the electronic coupling between units.

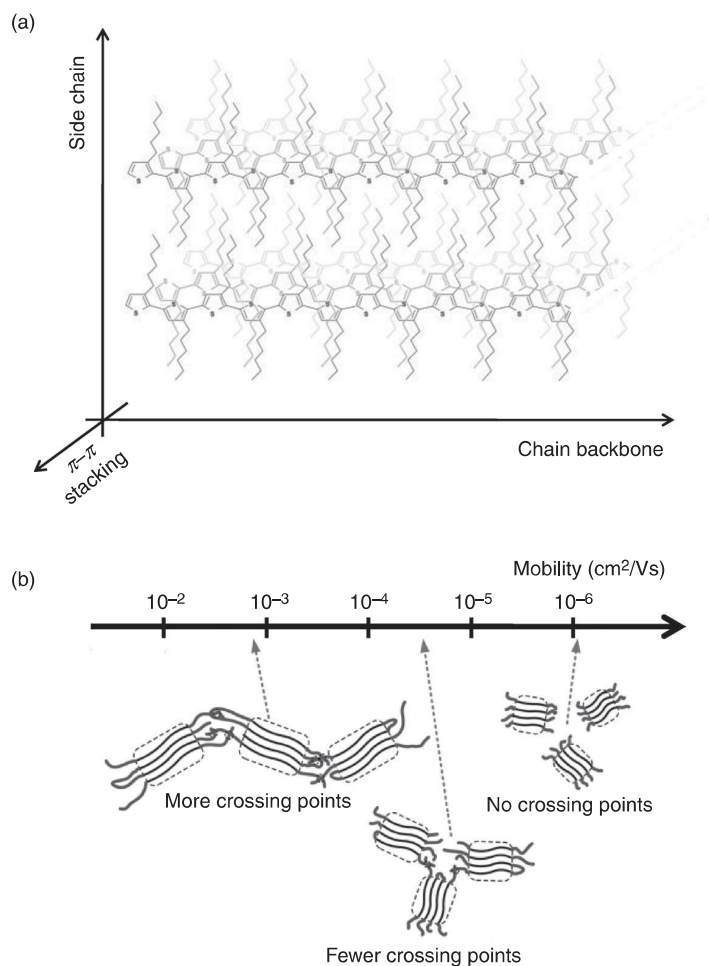
The fourth factor to consider is that the geometric distortion associated with a charged molecule has only a minor effect on charge carrier mobility in OFETs. In general, polaronic effects can be reduced by using polymers in place of short oligomers and rigid materials in place of molecules that allow for ring torsions or significant bond relaxations (Meisel *et al.*, 2005). The extent to which the approach of reducing polaronic effects may be exploited for charge separation in solar cells, for example by improving the charge carrier mobility immediately after photoexcitation, has not been addressed so far.

Since electronic coupling has been identified as the most significant factor that enables high charge carrier mobility, much research is concerned with the molecular assembly needed to obtain high coupling between adjacent units. A straightforward strategy is to enhance aggregation and crystallization in polymers

and molecular assemblies (Fig. 7.14). For the model compound P3HT, the formation of aggregates is driven by the long alkyl sidechains. The role of interdigitization of the sidechains for optimizing charge transport in thiophene-based polymers has been discussed by Kline *et al.* (2007). It turned out that in poly(5,5'-bis(3-dodecyl-2-thienyl)-2,2'-bithiophene) (PQT) and in poly(2,5-bis(3-alkylthiophene-2-yl)thieno(3,2-b)thiophenes (pBTTTs) the mobility is higher than in P3HT. The likely reason is that in the former materials there is, indeed, strong interdigitization that leads to lateral ordering because the closely packed sidechains help to establish a three-dimensional network by interlocking adjacent layers. This gives rise to a greatly increased domain size (from about 10 nm to micrometers) and improved charge transport leading to FET mobilities ranging from 0.1 to 0.5 cm²/Vs. In P3HT this layer registry is reduced because of the tilt angle of the side chains and leads to non-optimized charge transport. Similar phenomena of side-chain induced aggregate formation has also been observed for the polyfluorene backbone, when long octyl sidechains are used (Scherf and List, 2002; Bright *et al.*, 2009), or for polyphenylenevinylene (PPV) oligomers and polymer with alkoxy sidechains, where some electrostatic oxygen–hydrogen interactions seem to assist the planarization of the chain backbone (Hoffmann *et al.*, 2010). It thus seems that aggregate formation may take place for a large range of π -conjugated backbones, and that this is largely controlled by side-chain ordering in addition to the stabilizing effect of a delocalized π -system in a planar structure. Future research directions might consider the peculiarity the extended π -system adds to the models on polymer crystallization known from non-conjugated polymers such as polystyrene. Current approaches to understand aggregate formation mainly use methods and knowledge established in material sciences such as to start by measuring phase diagrams (Müller *et al.*, 2008). They are motivated by the need to control polymer crystallization in blends used for solar cell applications, where the solar cell efficiency is highly sensitive to the underlying film morphology.

For applications in OFETS, an important parameter is not only the amount and quality of aggregates formed, but also their orientation relative to the substrate. This was demonstrated in 1999 by Sirringhaus and colleagues who compared OFET mobilities obtained with P3HT aggregates oriented with their backbone either parallel or perpendicular to the dielectric interface (Sirringhaus *et al.*, 1999a). A perpendicular backbone orientation to the dielectric implies a coplanar orientation to source and drain electrode, and thus ensures higher mobilities.

Instead of inducing aggregation in polymers, a high electronic coupling in solution-processed films can also be obtained when molecules are used that self-assemble. A typical example are discotic liquid crystals (LC) (Warman *et al.*, 2004). Electronic coupling between extended π -systems can be strong, and by suitable processing conditions the orientation of the discotic LC stack with respect to the dielectric can be optimized. This has been demonstrated for derivatives of hexabenzocorene by van de Craats *et al.* (2003). Similar to



7.14 Schematic illustrating the effect of molecular packing. (a) Sketch detailing the molecular arrangement of chain backbone and the sidechains in an ordered segment of a P3HT aggregate, adapted after Pingel *et al.* (2010). (b) Typical region of the calculated charge mobility and the associated molecular conformation of P3HT in ordered and disordered domains. Areas with ordered P3HT segments are indicated by the dashed circumference. Adapted after Lan and Huang (2009).

polymer aggregates, high intra-stack mobilities have been measured using TRMC (Warman *et al.*, 2004), yet FET mobilities are limited by the inter-stack hopping rate.

When solution-processing is not required, high electronic coupling can be achieved by careful evaporation of molecules to form a thin crystalline layer. Since the pioneering days of this approach with α -sexithiophene (Hajlaoui *et al.*, 1997), high mobilities have been achieved for compounds such as pentacene and rubrene. Both materials have comparatively high hole mobilities of $10 \text{ cm}^2/\text{Vs}$ or higher at room temperature if measured in FET configuration (see Hasegawa and Takeya, 2009). Podzorov *et al.* (2004) measured a value of $30 \text{ cm}^2/\text{Vs}$ at 200 K. In a later work, Zeis *et al.* (2006) reported a maximal mobility of $13 \text{ cm}^2/\text{Vs}$ with strong anisotropy. A decrease of μ at lower temperatures is a signature of charge carrier trapping. Applying a hot wall deposition method, a hole mobility of only $2.4 \text{ cm}^2/\text{Vs}$ in rubrene has been measured. Obviously sample preparation and purification have a profound effect on the crystal properties, particularly if the sample is polycrystalline instead of single crystalline (Wang *et al.*, 2007). This is illustrated by the work of Minari *et al.* (2006). These authors measured the hole mobility in a single-grain pentacene FET within a temperature range between 300 K and 5.8 K and found a room temperature mobility of about $1 \text{ cm}^2/\text{Vs}$ and weakly activated transport below with an activation energy of 4.6 meV. In a polycrystalline sample the room temperature mobility is about $0.3 \text{ cm}^2/\text{Vs}$ and the activation energy is 55 meV. Obviously, grain boundaries act as charge carrier traps (Hamadani *et al.*, 2007; Hallam *et al.*, 2009).

In summary, it appears that future trends to control and improve charge carrier mobility will focus on the avoidance and passivation of traps and on controlling thin film morphology. Experimentally, this calls for techniques on surface treatments and material purification to avoid deep electron traps, clever chemical substitution schemes to reduce excimer formation while maintaining short hopping distances for charges, and a more detailed, profound understanding of the polymer crystallization process in π -conjugated materials.

7.6 Sources of further information and advice

In this chapter we have aimed to give an overview on current experimental and theoretical approaches to charge transport in organic opto-electronic devices. For those who are looking for more information on the operation and the current state of the art of such devices, we can recommend the book *Semiconducting Polymers* edited by Hadzioannou and Malliaras (2007). Notably chapters 10, 11 and 12 are suited to get an introduction to OLEDs, solar cells and OFETs, respectively (Campbell *et al.*, 2007; Dennler *et al.*, 2007; Horowitz, 2007). Regarding the experimental techniques presented in this chapter, a good and succinct description of TOF and SCLC is given in Chapter 8 of Schworer and Wolf (2007), while both processes are described in detail throughout the book by

Pope and Swenberg (1999). Details on the more recently developed techniques of CELIV (Juska *et al.*, 2000a), TRMC (Warman *et al.*, 2004; Grozema *et al.*, 2005) and THz-conductivity (Hegmann *et al.*, 2006) are given in the original articles and book chapters.

A good and concise introduction to charge transport in conjugated polymers can be found in Chapter 9 of *Semiconducting Polymers* (Blom *et al.*, 2007). In order to get a thorough overview on the concepts employed to describe charge transport, we refer the reader to a tutorial review by Tessler (Tessler *et al.*, 2009) and to a book chapter by Bässler and Köhler (2011). For those interested in the theoretical approaches and methodology, we recommend the following literature. The review article by Brédas *et al.* (2004) deals, among other topics, with the quantum chemical description of charge transfer in organic semiconductors, including ordered or crystalline compounds. A comparison of analytical approaches to hopping theory is given in the article by Coehoorn (2007), while Chapter 8 of *Semiconducting Polymers* covers the theoretical methods employed in the effective-medium approximation and stochastic hopping theory (Arkhipov *et al.*, 2007). We believe that both experimental methods and theoretical concepts are well covered by these sources of further information. In addition, edited books that also touch on the topic of charge transport include Baranovskii (2006) and Brütting (2005).

We hope that our brief introduction to this broad yet ubiquitous topic has stimulated the interest of our reader and that it may serve as a good starting point for further exploration, be it by experiment, theory or reading.

7.7 References

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Nanostructuring OLEDs to increase efficiency

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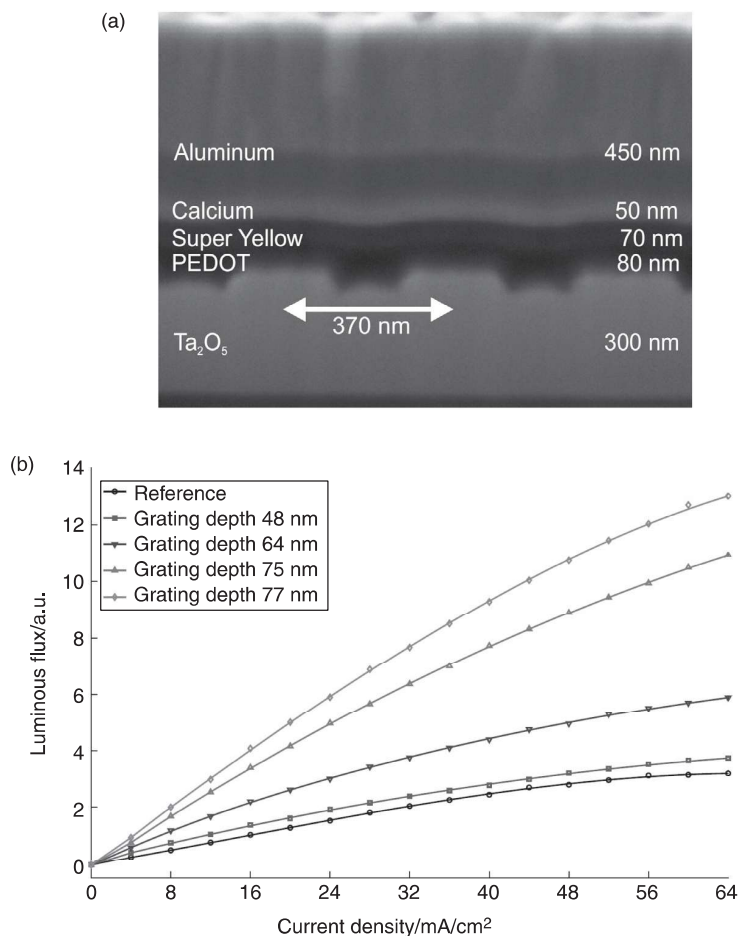
Abstract: A significant fraction of the photons emitted in an organic light-emitting diode (OLED) is trapped in the OLED layer stack as waveguide modes or surface plasmon polaritons (SPPs). This chapter discusses the use of nanostructures inside or close to the OLED stack for increasing the OLED efficiency. Three different routes are introduced for enhancing the efficiency with nanostructures in OLEDs – coupling guided modes to leaky modes, changing the spontaneous emission properties and inducing local electric fields. Fabrication methods for OLEDs with periodic (photonic crystal) and non-periodic nanostructures are presented.

Key words: scattering of guided modes in organic light emitting diodes, periodic photonic crystal nanostructures, non-periodic colloidal nanostructures, spontaneous emission properties in nanostructured materials.

8.1 Introduction

While the internal quantum efficiency of organic light-emitting diodes (OLEDs) is approaching 100%, the external quantum efficiency is much lower. Only about 20% of the generated photons leave the OLED as useful light for a standard OLED stack on a flat glass substrate. Modification of the glass/air interface has been employed to extract photons emitted into substrate modes, i.e. modes experiencing total internal reflection for a flat glass/air interface. However, about 50% of the photons are trapped in the OLED layer stack as waveguide modes or surface plasmon polaritons (SPPs). These photons are typically absorbed within short propagation distances in the micrometer range due to the strong absorption of the electrodes. In this chapter the use of nanostructures inside or close to the OLED stack is discussed for increasing the OLED efficiency by redistribution of energy into leaky modes, i.e. modes leaving the OLED as useful light. An example of a nanostructured OLED is shown in Fig. 8.1. The periodic grating structure in the vicinity of the emission layer causes an efficiency enhancement of up to 300% for deep gratings demonstrating the large potential of this method.

In Section 8.2 three different routes are introduced for enhancing the efficiency with nanostructures in OLEDs – coupling guided modes to leaky modes, changing the spontaneous emission properties and inducing local electric fields. These three routes are discussed in detail in sections 8.3 to 8.5. In Section 8.6, fabrication methods for OLEDs with periodic and non-periodic nanostructures are presented. The chapter concludes with a summary and a commentary on likely future trends.



8.1 (a) Scanning electron microscopy image of the cross-section of an ITO-free OLED on a periodically nanostructured Ta₂O₅ layer. The grating period is 370 nm and the grating depth is 50 nm. (b) Luminous flux over current density for different grating depths measured with an integrating sphere. Reprinted with permission from Riedel (2010a). Copyright 2010, American Institute of Physics.

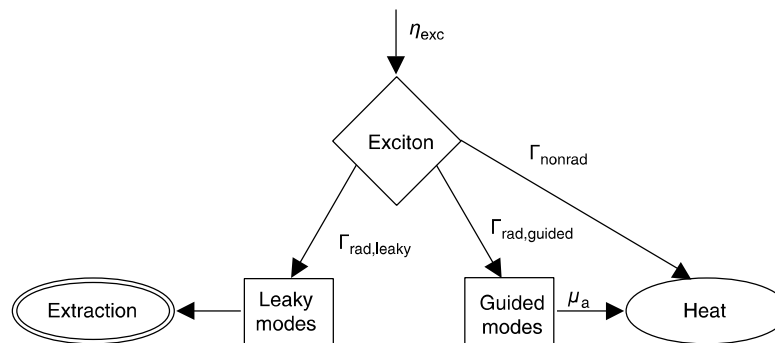
8.2 Routes for enhancing OLED efficiency with nanostructures

The external quantum efficiency of an OLED, i.e. the number of photons emitted by the OLED per injected electron, is determined by several factors. These factors include the charge carrier injection and exciton formation efficiency, the radiative

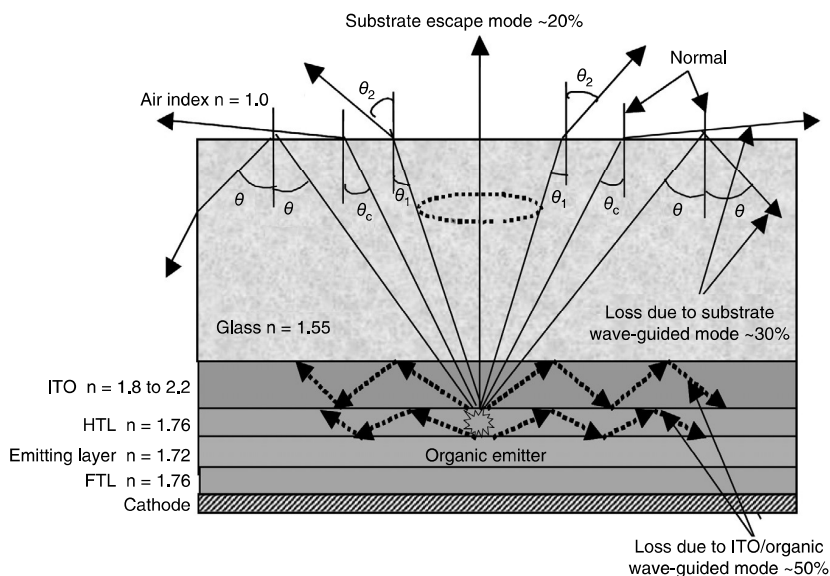
decay efficiency and the extraction efficiency. In this section it is discussed that nanostructures may be used to influence and improve all of these factors.

Figure 8.2 shows schematically the decay processes of an exciton in a standard OLED stack on a flat glass substrate. The exciton formation efficiency η_{exc} depends on the carrier injection, transport and recombination (Patel *et al.*, 2002). Excitons decay radiatively into leaky modes with a decay rate $\Gamma_{\text{rad,leaky}}$ or radiatively into guided modes with $\Gamma_{\text{rad,guided}}$ or non-radiatively with Γ_{nonrad} . Leaky modes are those modes that couple to the far field. They correspond to photons extracted from the OLED. Guided modes on the other hand correspond to photons emitted into waveguide modes in the substrate or in the OLED stack or to surface plasmon polaritons. These modes are damped by the losses in the structure with a mode-dependent absorption coefficient μ_a . In state of the art devices based on electrophosphorescence, the conversion of injected electron-hole pairs to radiative emission can approach 100% (Forrest, 2003; Reineke *et al.*, 2009). However, for a standard OLED stack on a flat glass substrate only 20% of the photons are emitted into leaky modes and extracted to the far field. As depicted in Fig. 8.3, typically 30% of the photons are emitted into waveguide modes in the substrate and 50% are emitted into waveguide modes in the OLED stack or into surface plasmon polaritons (Greenham *et al.*, 1994; Lu and Sturm, 2002; Saxena *et al.*, 2009). Thus, the emission into guided modes reduces the external quantum efficiency to only around 20%. Furthermore, the guided modes are absorbed in the device limiting the current density in the device due to heating. For efficient and high-power OLEDs it is therefore highly desirable to direct photon emission to leaky modes.

Several successful approaches have been established to extract guided modes from the substrate by modification of the substrate–air interface using microlenses,



8.2 Schematic of exciton decay processes in a standard OLED stack on a flat glass substrate. Only radiative decay to leaky modes leads to photons leaving the OLED. Photons emitted into guided modes are absorbed due to losses in the conductive electrodes.



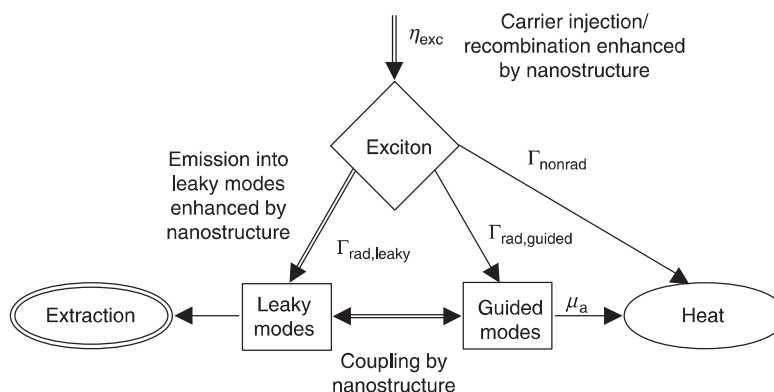
8.3 Schematic of multi-layer OLED stack on a flat glass substrate and optical ray diagram of light propagation in various modes, i.e. substrate escape, substrate wave-guided, and ITO/organic wave-guided modes. Approximately 20% of the photons are emitted into substrate escape modes. Fifty per cent of the photons are trapped and subsequently absorbed in guided modes in the ITO/organic layers and 30% are trapped in the substrate. Reprinted with permission from Saxena *et al.* (2009). Copyright 2009, Elsevier.

micropyramids or scattering layers (Greiner, 2007; Saxena *et al.*, 2009; and references herein). The extraction of modes guided within the OLED stack is more challenging, since any extraction structure has to be placed in the vicinity of these layers to allow an interaction of the guided mode with the extraction structure. Nakamura *et al.* (2005) and Reineke *et al.* (2009) demonstrated the use of high refractive index substrates to significantly redistribute light from OLED stack modes into substrate modes. This allows for using the standard concepts for substrate mode extraction in order to achieve higher external quantum efficiencies. Another method for decreasing the fraction of emission into the OLED stack is the use of thin OLED stacks as suggested by Lu and Sturm (2002), which support few or no guided modes. Both the use of high index substrates as well as the use of thin OLED stacks contradict today's OLED designs for cost-effective and at the same time highly efficient OLEDs. Thus, other methods are needed that allow for an extraction of photons guided in the organic/ITO stack. Nanostructuring of the organic/ITO stack has been demonstrated to be a promising route for increasing the OLED efficiency as detailed in the following.

As depicted in Fig. 8.4 nanostructures may be employed to influence the OLED efficiency by three different processes. Firstly, the nanostructure may couple guided modes to leaky modes allowing for the extraction of part of the light emitted into guided modes and modes guided in the OLED stack as well as modes guided in the substrate may be coupled to leaky modes by the nanostructure. Secondly, the nanostructure may influence the spontaneous emission properties of the emitter increasing the radiative emission rate into leaky modes $\Gamma_{\text{rad,leaky}}$ compared to the emission rate into guided modes $\Gamma_{\text{rad,guided}}$ and the non-radiative decay rate Γ_{nonrad} . This results in energy redistribution from guided modes to leaky modes. Thirdly, nanostructuring the OLED stack may enhance carrier injection and thus improve the exciton formation efficiency η_{exc} . In practice, a combination of all three effects of the nanostructure on the external quantum efficiency is observed. Which effect dominates depends on the design of the nanostructure. These three routes to enhancing OLED efficiency with nanostructures are now explained in more detail.

8.3 Coupling guided modes to leaky modes with nanostructures

Today, the most commonly employed route for increasing the efficiency of OLEDs with nanostructures is the coupling of guided modes to leaky modes. An OLED can be considered as a waveguide consisting of the substrate and a number of organic and electrode layers in the OLED stack. Optical waveguide modes are typically classified by their in-plane wavevector component k_x or the corresponding



8.4 Schematic of exciton decay processes in nanostructured OLED stack. The nanostructure may couple guided modes to leaky modes, it may enhance the emission into leaky modes by changing the spontaneous emission properties and it may influence the carrier injection by local electric field modification.

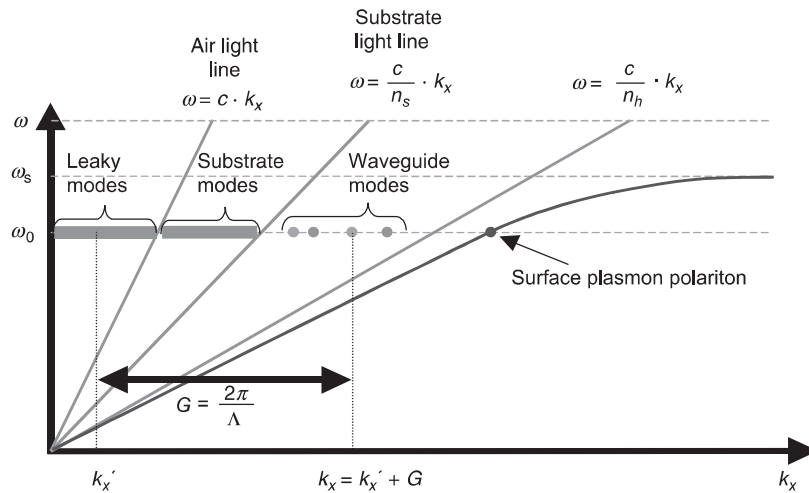
effective refractive index n_{eff} . Both are related by Eq. 8.1, where λ_0 is the wavelength in vacuum, k_0 is the absolute value of the total wavevector in vacuum, ω is the frequency and c_0 is the speed of light in vacuum.

$$k_x = \frac{2\pi n_{eff}}{\lambda_0} = k_0 n_{eff} = \frac{\omega}{c_0} n_{eff} \quad [8.1]$$

A useful tool for depicting the properties of different modes is the dispersion diagram plotting $\omega(k_x)$. Typically, the refractive index of the substrate is smaller than the highest refractive index in the OLED stack, such that Eq. 8.2 is true with n_s being the substrate refractive index and n_h the highest refractive index in the OLED stack.

$$1 < n_s < n_h \quad [8.2]$$

Figure 8.5 shows an example of a dispersion diagram for the case that Eq. 8.2 is fulfilled. Leaky modes, i.e. modes being able to leave the OLED to the far field, are found above the so called air light line. Their effective refractive index is smaller than one ($n_{eff} \leq 1$). A continuum of leaky modes exists. Modes with $1 < n_{eff}$



8.5 Dispersion diagram for modes with a frequency ω_0 in an OLED. n_s is the substrate refractive index and n_h the highest refractive index in the OLED stack. The continuum of leaky modes propagating to the far field lies above the air light line. Modes propagating in the substrate are found between the air light line and the substrate light line. To the right of the substrate light line discrete waveguide modes and surface plasmon polariton modes are located. A periodic nanostructure with period Λ couples modes that are separated in wavevector by G . As an example the coupling of a particular waveguide mode to a leaky mode is depicted.

$\leq n_s$ may propagate in the substrate. Due to the typically large thickness of the substrate compared to the wavelength of light, the substrate modes also may be considered as a mode continuum. For $n_{eff} = n_s$ the substrate light line is reached. As the thickness of the OLED stack is typically in the order of the wavelength of light, a discrete set of waveguide modes in the OLED stack with $n_s < n_{eff} \leq n_h$ needs to be considered. Finally, discrete surface plasmon polariton modes may exist. They only exist in TM-polarization. While OLEDs with emitters oriented in the plane of the organic layer are little affected by absorption due to surface plasmon polariton modes, these modes play an important role in OLEDs with randomly oriented emitters (Hobson *et al.*, 2002a, 2002b). The coupling of radiation to surface plasmon polariton modes is particularly high for states with a frequency ω that is just slightly smaller than the frequency ω_s given in Eq. 8.3. ω_s is asymptotically approached in the dispersion curve for the medium and exhibits a particularly high density of states (Raether, 1988; Okamoto *et al.*, 2004). In Eq. 8.3 ω_p is the plasma frequency in vacuum and ϵ_r is the relative dielectric constant of the medium.

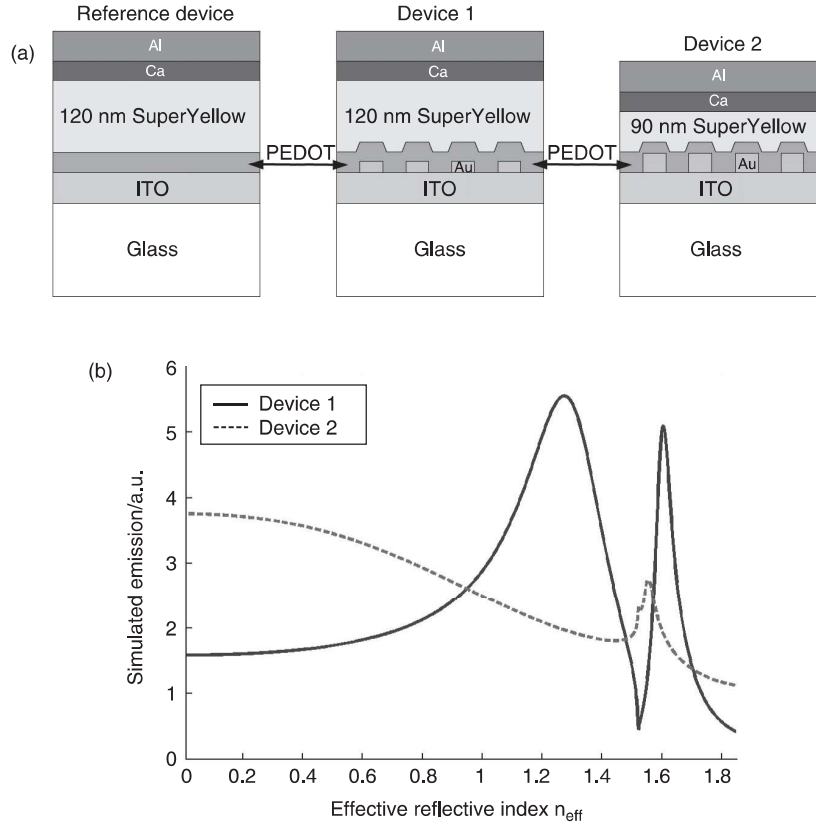
$$\omega_s = \frac{\omega_p}{\sqrt{1 + \epsilon_r}} \quad [8.3]$$

The purpose in introducing a nanostructure is to couple modes such that a redistribution of energy takes place between the modes and more energy is extracted from the OLED. This may be achieved both with periodic as well as with non-periodic nanostructures.

As an example we will discuss the coupling of modes achieved with an anode-side periodic grating structure (Bragg grating) of grating period $\Lambda = 375$ nm in the OLED devices depicted in Fig. 8.6a. The devices both consist of an ITO anode, a PEDOT:PSS hole-transport layer, a phenylene substituted poly(paraphenylenevinylene) (Ph-PPV; ‘SuperYellow’) emission layer, and a calcium (Ca)–aluminium (Al) cathode (Hauss *et al.*, 2011a). Device 1 has a 15-nm deep gold grating on the ITO-anode and device 2 has a 30-nm deep gold grating on the ITO-anode. The emission layer in device 1 has a thickness of 120 nm and that of device 2 is 50 nm. Even though the structure of these devices is rather similar, their emission properties differ significantly as seen in Plate I (see colour section between pages 414 and 415). Spectrally integrated measurements in an Ulbricht sphere reveal that device 1 exhibits about 25% enhanced power efficiency compared to the reference device, whereas device 2 only reaches 70–75% of the power efficiency of the reference device.

The introduction of the periodic nanostructure couples modes with different in-plane wavevectors k_x and k'_x by Bragg scattering following Eq. 8.4. Here $G = 2\pi/\Lambda$ is the reciprocal lattice constant of the grating with period Λ . The value of the integer m determines the scattering order.

$$k'_x = k_x \pm mG = k_x \pm m \frac{2\pi}{\Lambda}; \quad m = \pm 1, \pm 2, \dots \quad [8.4]$$



8.6 (a) Schematic of a reference OLED device and two different devices with anode-side gold gratings of grating period $\Lambda = 375$ nm. The grating depth of device 1 is 15 nm and that of device 2 is 30 nm. Furthermore, the thickness of the polymer layer in the two grating devices is different. (b) Simulated dipole emission as a function of the effective refractive index at a wavelength of 550 nm. Adapted from colour to grey-scale. Reprinted with permission from Hauss *et al.* (2011a). Copyright 2011, Optical Society of America.

Considering now first order coupling ($m=1$) of a guided mode with wavevector k_x to a leaky mode with a smaller wavevector $k'_x = k_x - G$, additional emission intensity is expected at the extraction angle to air θ corresponding to k'_x . This extraction angle θ is calculated from Eq. 8.5.

$$k'_x = k_0 \sin \theta = k_x \pm \frac{2\pi}{\Lambda} \quad [8.5]$$

Combining Eqs 8.1 and 8.5 results in Eq. 8.6.

$$\theta = \arcsin\left(\frac{k_x}{k_0} + \frac{2\pi}{\Lambda k_0}\right) = \arcsin\left(n_{eff} + \frac{\lambda_0}{\Lambda}\right) \quad [8.6]$$

Examining Eq. 8.6 it is seen that the grating of period Λ should result in enhanced emission at a particular angle θ for a given emission wavelength in vacuum λ_0 and effective refractive index n_{eff} of the waveguide mode. This explains the additional emission peaks observed in Plate I for device 1. On top of the broadband emission of leaky modes also observed for the reference device, a waveguide mode is coupled out. This additional energy coupled from a guided mode to a leaky mode results in the power efficiency enhancement of 25%.

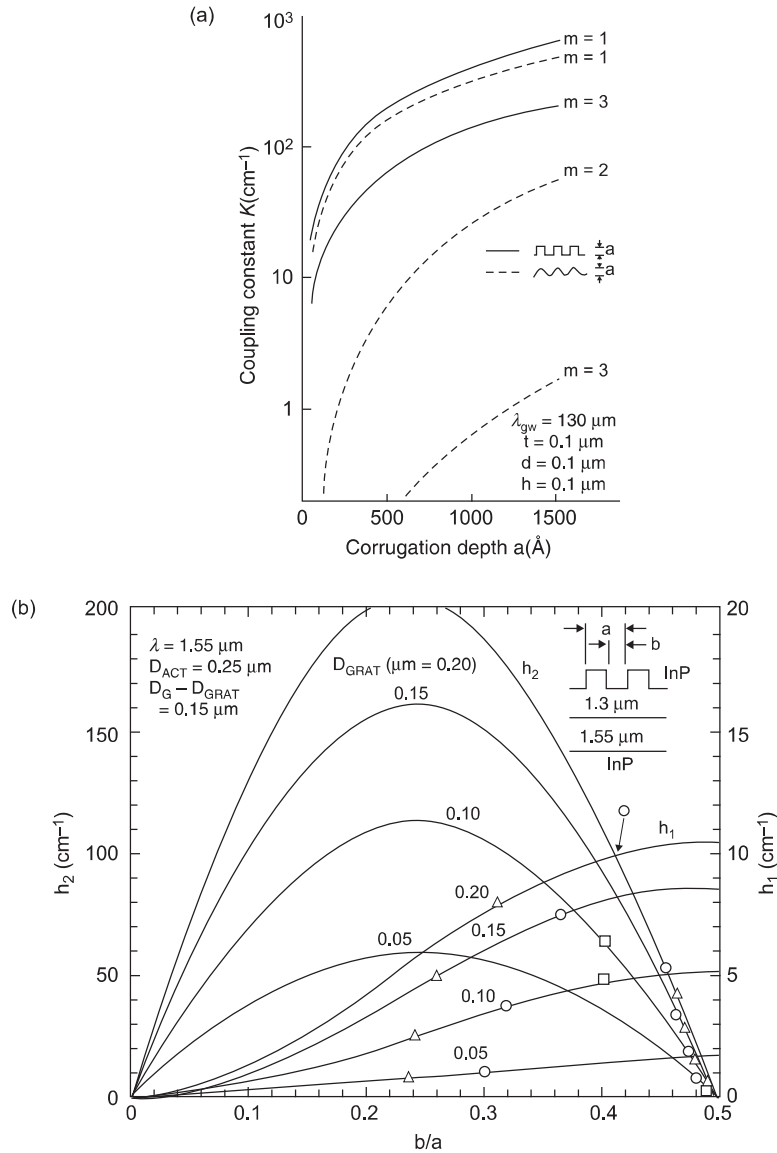
Considering now the performance of device 2 in Plate I, we note that the broadband emission is shifted compared to the reference device. This can be attributed to microcavity effects in the changed cavity thickness. Furthermore, dips are observed at distinct emission angles θ . In order to understand this behaviour it has to be considered that a nanostructure couples modes, but it does not determine the energy transfer direction. Energy transferred from the guided mode to the leaky mode or vice versa depends on the ratio of the population of two modes by the emitter as well as on the damping of the modes due to absorption or radiation to the far field. A strongly damped waveguide mode may show a lower population than a leaky mode. Thus, energy is transferred from the leaky mode to the waveguide mode after insertion of a nanostructure for mode coupling. This actually reduces the power efficiency of the device. Calculating the dipole emission for the two modes as described in Hauss *et al.* (2011a), the emission as a function of effective refractive index n_{eff} plotted in Fig. 8.6b is obtained. It is observed that for device 1 the waveguide mode at $n_{eff} \approx 1.6$ is highly populated compared to the leaky modes at $n_{eff} < 1$. For device 2 the situation is opposite, explaining the measured dips in the emission spectrum.

Besides the consideration of the state population, the second important aspect in designing nanostructures for coupling guided modes to leaky modes is the absorption coefficient of the guided modes. Due to the conductive electrodes the guided modes are damped with an absorption coefficient μ_a . The absorption coefficient μ_a differs for the different guided modes depending on the overlap of each mode with absorbing materials in the OLED device (Asada, 1991; Ngaffo *et al.*, 2005; Agrawal *et al.*, 2007). Typical mean free paths before absorption $d_a = 1/\mu_a$ for guided modes in the OLED stack are in the order of tens of microns. In order to achieve efficient energy transfer to leaky modes, $\mu_s \gg \mu_a$ needs to be fulfilled, i.e., the scattering coefficient μ_s has to be significantly larger than the absorption coefficient μ_a . Otherwise, the photon is absorbed before it is coupled to a leaky mode. This is valid not only for nanostructured OLEDs, but also needs to be fulfilled for microstructured OLEDs as discussed by Sun and Forrest (2008) as well as Koh *et al.* (2010) for the case of low-index grids embedded in the OLED stack. Because of the short mean free paths before absorption of guided modes in the OLED stack, macroscopic structuring has little influence on the guided mode

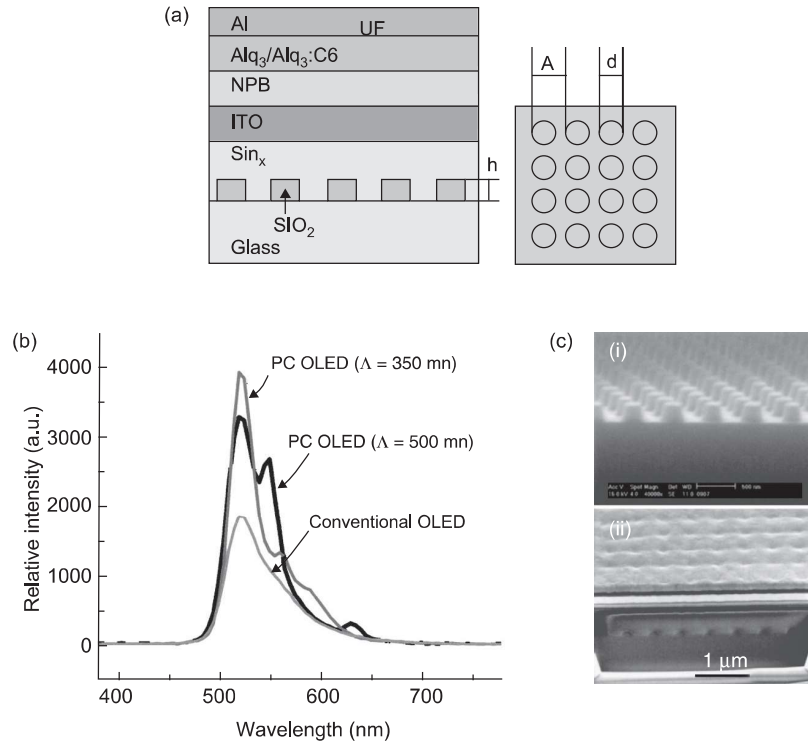
extraction. Only light from the immediate vicinity of edges is affected by these edges. This is different for substrate modes, as they typically exhibit a much longer mean free path before absorption.

The scattering coefficient μ_s refers to the mean free path before a scattering event occurs for the given guided mode into any other mode. The coupling of one mode to another mode is described by the coupling coefficient. The higher the coupling coefficient, the more efficient is the coupling between the two modes. Much knowledge exists on the integration of efficient gratings into waveguide structures from the design of distributed feedback lasers (Streifer *et al.*, 1975, 1976; Peng *et al.*, 1975; Yamamoto *et al.*, 1978) and waveguide grating couplers (Avrutsky *et al.*, 1990; Parriaux *et al.*, 1996). The design rules developed for those applications may be transferred to the design of periodic grating structures for OLED efficiency enhancement. The efficiency of a periodic nanostructure is determined by the overlap of the nanostructure with the guided mode of interest, the refractive index contrast, the grating shape, as well as the grating depth. Furthermore, the efficiency is different for a corrugation in a single layer compared to a corrugation that is transferred to several layers as it is typically the case for evaporated OLEDs. Figure 8.7 presents examples for the values of coupling coefficients as a function of the corrugation depth, the corrugation shape and the duty cycle of the corrugation for InGaAsP-waveguide structures. The higher grating efficiency for deeper gratings also is observable in Fig. 8.1. As more light is coupled to leaky modes before absorption, the OLED efficiency is increased. Studying the details of the experimental results in Riedel *et al.* (2010a) it is found that the grating couples both substrate modes and guided modes to leaky modes. It is a typical situation that a grating couples a variety of modes to each other, as all modes are coupled, whose wavevectors differ by mG as given in Eq. 8.4.

Besides one-dimensional Bragg gratings, two-dimensional photonic crystal structures or scattering non-periodic nanostructures may be used to couple guided modes to leaky modes. A discussion of coupling of guided modes to leaky modes using a two-dimensional photonic crystal slab is given by Turnbull *et al.* (2003). Figure 8.8 shows an example of an OLED with a square two-dimensional photonic crystal layer integrated below the ITO-anode (Do *et al.*, 2004). A 50% power efficiency enhancement is obtained for the nanostructured OLED compared to a conventional device without a change of the electrical properties. A quasi periodic buckling structure integrated in an OLED for efficiency enhancement is demonstrated by Koo *et al.* (2010). Possible non-periodic nanostructures for coupling guided modes to leaky modes include the integration of scattering nanospheres into the organic layers (Riedel *et al.*, 2011) and rough internal interfaces (Riedel *et al.*, 2010c). In principle two-dimensional grating structures and non-periodic scattering structures couple more guided modes to leaky modes as they influence all propagation directions. On the other hand, the efficiency of the grating structure and the population of the guided modes play an important role as discussed above. If there are many unpopulated guided modes, which are



8.7 (a) Coupling coefficient for different coupling orders m as a function of corrugation shape and depth for an InGaAsP-waveguide structure. For a square grating the 2-order coupling coefficient ($m=2$) vanishes for a 50% duty cycle (Reprinted with permission from Sakai *et al.* (1982). Copyright 1982, IEEE.) (b) 1-order coupling coefficient (h_1) and 2-order coupling coefficient (h_2) as a function of the grating duty cycle b/a and the corrugation depth D_{GRAT} (Reprinted with permission from Kazarinov and Henry (1985). Copyright 1985, IEEE.)



8.8 (a) Schematic of an OLED with a square two-dimensional photonic crystal (2D PC) layer integrated below the ITO-anode. (b) Experimental emission spectra of OLEDs without nanostructuring, with a 2D PC layer with a period of 350 nm and a 2D PC layer with a period of 500 nm. (c) Scanning electron micrograph of the 2D PC layer in SiO_2 (i) and cross-sectional view of nanostructured OLED (ii). Reprinted with permission from Do *et al.* (2004). Copyright 2004, American Institute of Physics.

not fed by the emitter, it is not helpful to couple these guided modes to leaky modes. This coupling will decrease the device efficiency.

In summary, the following important conditions need to be fulfilled in order to achieve an OLED efficiency enhancement, when integrating scattering periodic or non-periodic nanostructures into the OLED stack that couple guided modes to leaky modes:

- The guided mode has to exhibit a significantly higher photon population than the leaky mode.
- The scattering coefficient of the nanostructure needs to be larger than the absorption coefficient of the guided mode.

8.4 Spontaneous emission engineering with nanostructures

The spontaneous emission properties of an emitter in a structured environment are not an inherent property of the emitter. Depending on the position $\mathbf{r}_0$ of the emitter in the structure, the orientation described by the dipole moment $\mu = \mu \mathbf{n}_\mu$ with $\mathbf{n}_\mu$ being the unit vector in the direction of μ and the emission frequency ω_0 , the total radiative decay rate $\Gamma_{rad,tot}$ and the directional emission profile are changed. As described in detail by Novotny and Hecht (2006) the total radiative decay rate $\Gamma_{rad,tot}$ in the weak light-matter coupling regime is obtained using Fermi's Golden Rule to be:

$$\Gamma_{rad,tot} = \frac{2\omega}{2\hbar\epsilon_0} |\mu|^2 \rho(\mathbf{r}_0, \omega_0) \quad [8.7]$$

In Eq. 8.7 $\hbar$ is the Planck constant and ϵ_0 the dielectric constant. In terms of normal modes $\mathbf{u}_k$ with ω_k denoting the frequency of the mode k , the partial local radiative density of states $\rho(\mathbf{r}_0, \omega_0)$ in Eq. 8.7 is calculated as:

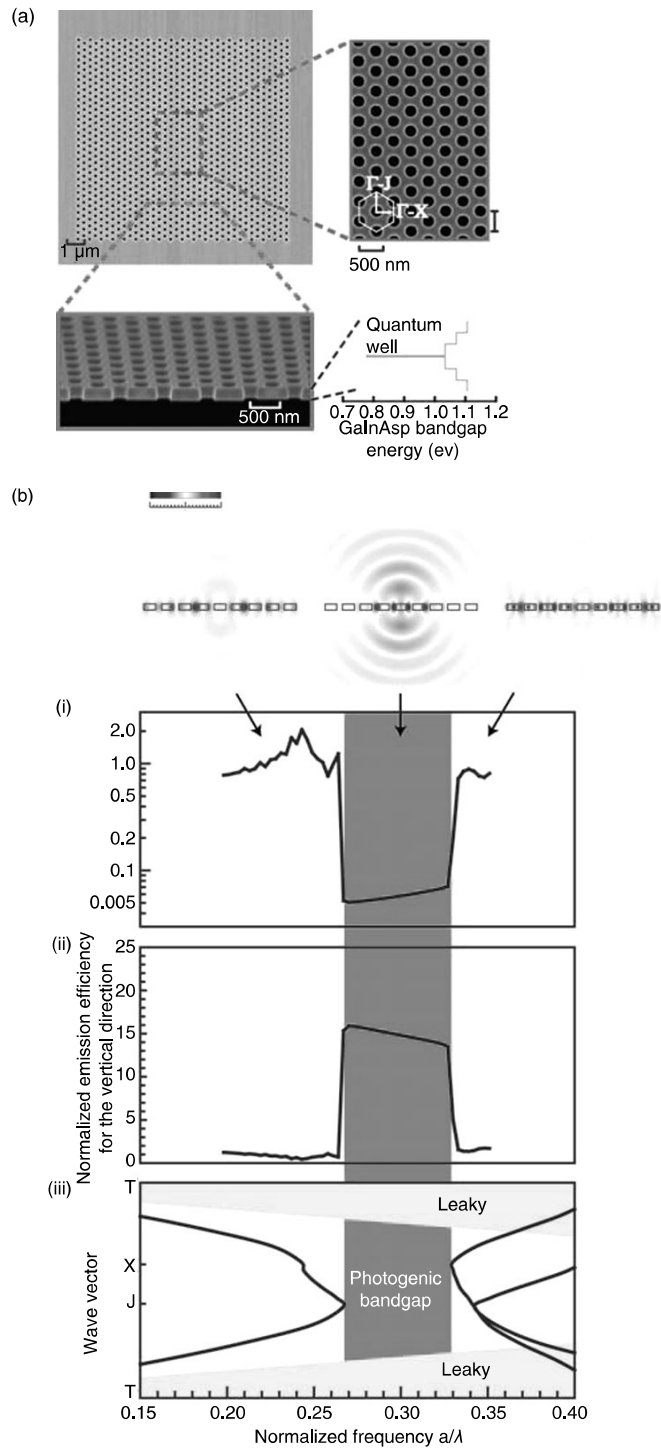
$$\rho(\mathbf{r}_0, \omega_0) = 3 \sum_k \left[\mathbf{n}_\mu \cdot \left(\mathbf{u}_k \mathbf{u}_k^* \right) \cdot \mathbf{n}_\mu \right] \delta(\omega_k - \omega_0) \quad [8.8]$$

As seen from Eq. 8.8, the partial local radiative density of states $\rho(\mathbf{r}_0, \omega_0)$ scales with the number of optical modes available at the emission frequency ω_0 of the emitter. For the case that no optical modes with frequency ω_0 of the emitter are available or the modes are aligned such that the emitter cannot couple to the modes, $\rho(\mathbf{r}_0, \omega_0)$ would vanish and the emitter would decay non-radiatively. Engineering the OLED structure such that a large number of optical modes is available at the emission frequency, enhances the spontaneous emission rate compared to the emitter in vacuum. Furthermore, by designing the available modes, the directional emission properties of the OLED may be engineered.

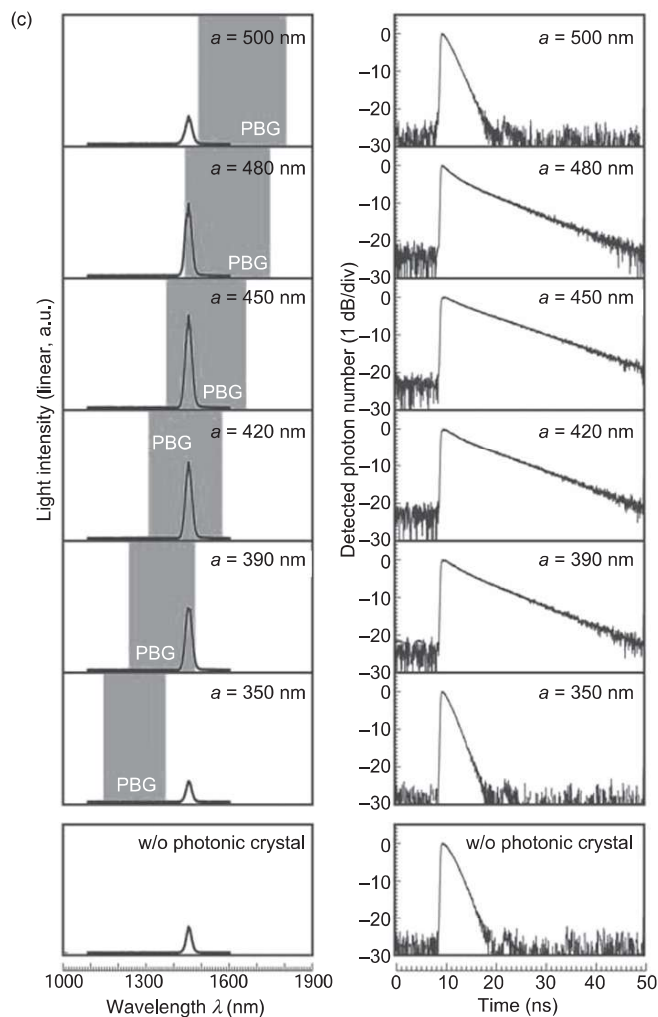
The decay time τ of the emitter is calculated from the total radiative decay rate $\Gamma_{rad,tot}$ and the non-radiative decay rate Γ_{nonrad} using Eq. 8.9. Dividing the total radiative decay rate $\Gamma_{rad,tot}$ into the radiative decay rate $\Gamma_{rad,leaky}$ into leaky modes and the radiative decay rate $\Gamma_{rad,guided}$ into guided modes the second equality of Eq. 8.9 is obtained. This corresponds to splitting the sum in Eq. 8.8.

$$\tau = \frac{1}{\Gamma_{rad,tot} + \Gamma_{nonrad}} = \frac{1}{\Gamma_{rad,leaky} + \Gamma_{rad,guided} + \Gamma_{nonrad}} \quad [8.9]$$

For efficient nanostructured OLEDs based on the modification of the spontaneous emission properties, the nanostructure should be designed such that the radiative decay rate $\Gamma_{rad,leaky}$ is large compared to $\Gamma_{rad,guided}$ and Γ_{nonrad} . Fujita *et al.* (2005a) demonstrated a fourfold enhancement of the emission intensity of a GaInAsP quantum well in a photonic crystal membrane. Scanning electron micrographs of the structure are shown in Fig. 8.9a. If the emission wavelength of the emitter lies



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8.9 (a) Scanning electron micrographs of a semiconductor (GaInAsP) two-dimensional photonic-crystal slab with a 5-nm-wide single quantum well at the centre. (b) Theoretical predictions for the spontaneous emission rate and the emission efficiency in the vertical direction as a function of normalized frequency. (c) Experimental results of time-integrated emission spectra and time-resolved photoluminescence measurements for fabricated photonic crystal slabs with lattice constants between 350 nm and 500 nm. When the spontaneous-emission spectrum lies within the photonic bandgap region, a significantly increased light emission into the vertical direction and a fivefold increase in the emission lifetime are observed. Both are caused by a suppression of spontaneous emission into guided slab modes due to the nanostructuring. Reprinted with permission from Fujita *et al.* (2005a). Copyright 2005, American Association for the Advancement of Science.

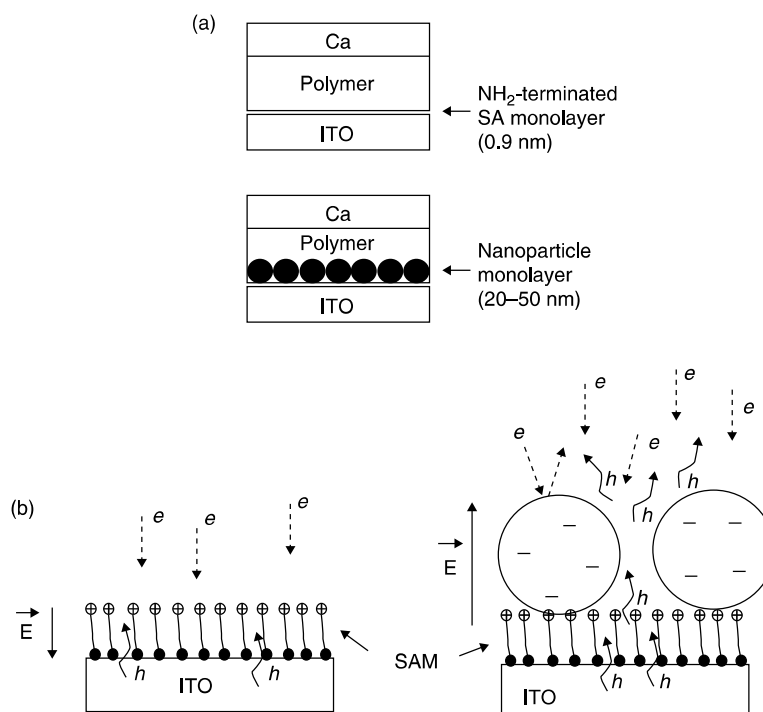
within the photonic bandgap of the photonic crystal membrane, no optical modes are available in the plane of the photonic crystal membrane (lateral direction). Thus, $\Gamma_{rad,guided}$ is significantly reduced leading to a reduced $\Gamma_{rad,tot}$ and a longer decay time τ of the emitter. This is observed both in theory and in experiment as shown in Fig. 8.9b and c. For a negligible Γ_{nonrad} the emission energy would be redistributed completely into the leaky modes, i.e. if the emitter cannot decay into guided modes due to the nanostructuring, it will decay into the leaky modes that are extracted from the structure. Depending on the ratio of $\Gamma_{rad,leaky}$ to Γ_{nonrad} the emission energy is redistributed from the guided modes partly to leaky modes and partly to non-radiative decay. The experimental results in Fig. 8.9c reveal a fourfold increase in the emission intensity in the vertical direction for a fivefold reduction in the decay time τ of the emitter.

An even larger effect of the nanostructured environment on the spontaneous emission properties is possible if the emitters are not distributed randomly in the structure, but placed at specific positions and with specific orientations. For randomly oriented emitters, Eq. 8.7 has to be integrated over all orientations of the dipole moment. Furthermore, for emitters placed randomly in a specific layer of the OLED, Eq. 8.7 also needs to be integrated over the local coordinate $\mathbf{r}$. This causes an averaging of large and small enhancements (or even inhibitions) of spontaneous emission into leaky modes. As seen in Koenderink *et al.* (2005) increases in the partial local radiative density of states $\rho(\mathbf{r}_0, \omega_0)$ at specific positions and wavelengths are accompanied by decreases at other positions and wavelengths. Placing emitters only in specific orientations at specific locations with particularly high enhancements promises the largest increase in efficiency.

The informed reader now may be wondering why spontaneous emission engineering using two-dimensional photonic crystals slabs is not even commonplace in research OLEDs yet, even though it holds such great potential for efficiency enhancements. There are several reasons why spontaneous emission engineering in OLEDs is difficult to achieve. The first is that a high refractive index contrast is needed in the nanostructuring for large effects. Fujita *et al.* (2005a) use a freestanding membrane with refractive indices of the substrate and air being 3.13 and 1.0. Refractive indices typically found in OLEDs range from 1.4 to 2.1. The smaller the refractive index contrast, the smaller is also the photonic bandgap. At the same time emitters in OLEDs typically have a rather broad spectrum. This results in an averaging of effects over different wavelengths. Finally, emitters are typically placed randomly in an emission layer (orientation may be given in polymers), leading to further averaging. In summary, for spontaneous emission engineering a high refractive index contrast, narrowband and specifically placed emitters, and a low non-radiative decay rate are desirable. While here periodic nanostructures were discussed, changes in the local radiative density of states are also observed in the vicinity of non-periodic nanostructures.

8.5 Local electric field effects due to nanostructures

Nanostructures in the OLED stack may induce local electric field effects, which cause a carrier blocking or an improved injection. Bliznyuk *et al.* (1999), e.g., showed that a nanoparticle monolayer in combination with a self-assembled monolayer of NH_2 -terminated alkoxy silane molecules causes an OLED efficiency enhancement. This enhancement is attributed to a reversal of the local electric field at the interface by the negatively charged nanoparticles as depicted in Fig. 8.10. This results either in improved hole injection or in a blocking layer for



8.10 (a) Schematic of OLED structure without and with a nanoparticle monolayer. The OLEDs consist of a calcium (Ca) cathode, a polymer emission layer, an indium tin oxide (ITO) anode and a self-assembled monolayer (SAM) of NH_2 -terminated alkoxy silane molecules. The device without the nanoparticles has a reduced efficiency compared to a reference device while the device with nanoparticles has an improved efficiency. (b) Schematic diagram of the local electric fields without and with the nanoparticles. The negatively charged nanoparticles cause a reversal of the local electric field at the interface either improving hole injection or serving as an electron blocking layer. Reprinted with permission from Bliznyuk *et al.* (1999). Copyright 1999, John Wiley and Sons.

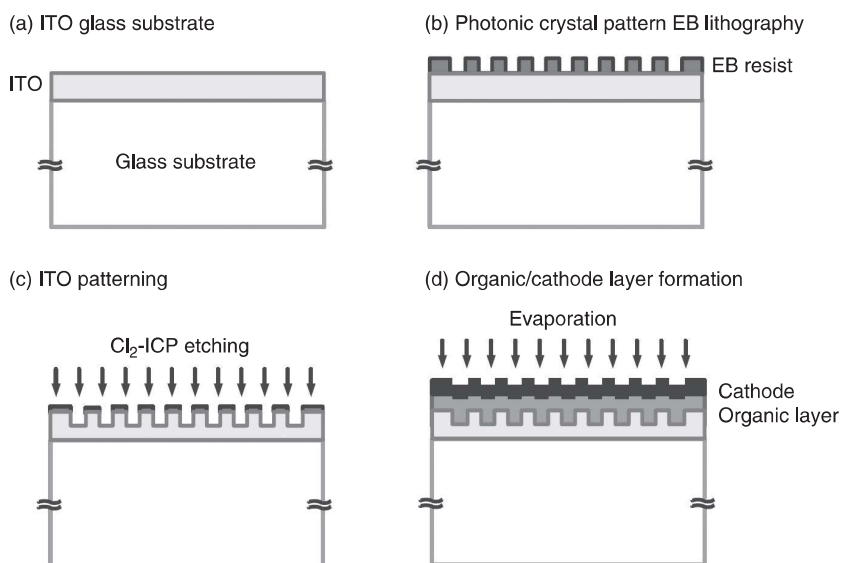
electrons. Riedel *et al.* (2010b) demonstrated an improved OLED efficiency and lower turn-on voltages with dielectric nanoparticle clusters between the organic layers and the cathode attributed to locally enhanced electric fields at the interface. As the internal quantum efficiency, i.e. the conversion of carriers to photons, already reaches 100% using other methods, currently this is not the main motivation for nanostructuring OLEDs. However, this may be a promising alternative to additional polymer layers for control of the carrier injection and the turn-on voltage in solution processed devices. The integration of nanoparticles into solutions is simple and low cost.

8.6 Fabrication of nanostructured OLEDs

This section discusses fabrication methods for nanostructured OLEDs. First the integration of periodic nanostructures into the OLED is considered, followed by a discussion of how non-periodic nanostructuring can be achieved.

8.6.1 Fabrication of OLEDs with periodic nanostructures

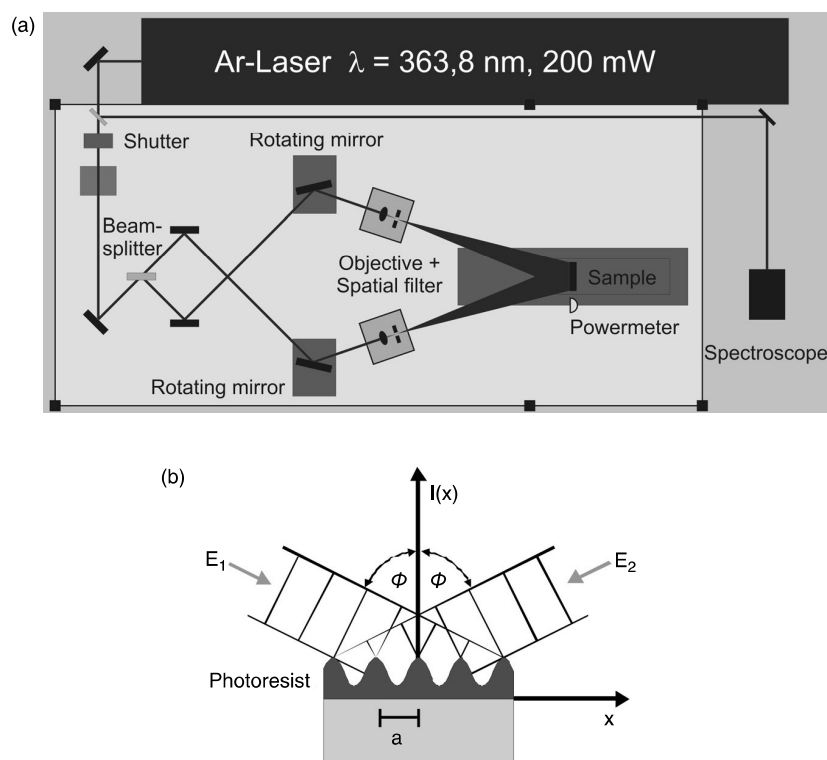
A common method for fabricating nanostructured OLEDs is the fabrication of a nanostructured substrate, onto which subsequently the OLED is deposited. Using electron beam lithography any kind of nanostructured pattern may be written into an electron beam resist. As depicted in Fig. 8.11 the nanostructure is transferred



8.11 (a–d) Fabrication procedure for a nanostructured OLED using electron beam (EB) lithography. Reprinted with permission from Fujita *et al.* (2005b). Copyright 2005, The Japan Society of Applied Physics.

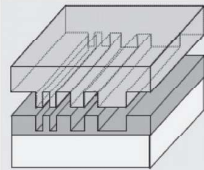
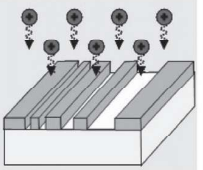
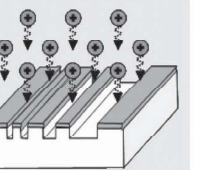
into the ITO layer. Then the OLED is fabricated using a standard procedure (Fujita *et al.*, 2005b). Even though this method is very versatile, it is only suitable for single proof-of-principle devices due to the serial fabrication procedure, which may take several hours of electron beam lithography for a single device. An alternative approach for generating periodic nanostructures is laser interference lithography (LIL). Here, two laser beams are brought to interference at the sample surface (Lupton *et al.*, 2000; Geyer *et al.*, 2008). A typical setup for LIL is depicted in Fig. 8.12. This method has been demonstrated to be suitable for rapid processing of large areas up to the square-meter range (Gombert *et al.*, 2004). A two-dimensional photonic crystal pattern may be achieved by multiple exposures and rotation of the sample.

Another cost-efficient and high-throughput method for obtaining nanostructured substrates is nanoimprint lithography (NIL). In NIL the nanopatterned surface profile of a stamp is transferred into a material by mechanical contact.

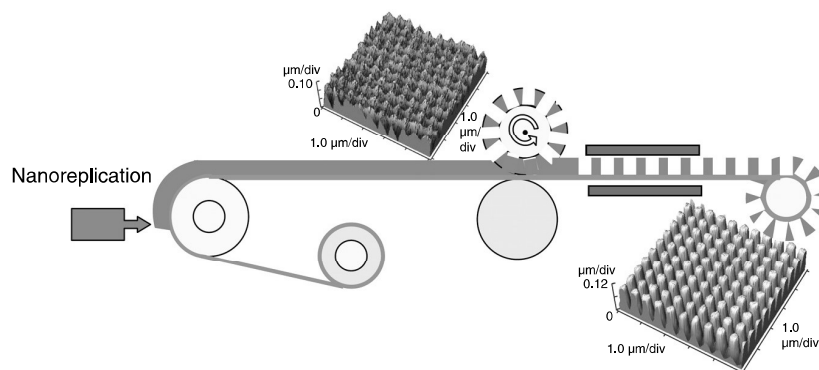


8.12 (a) Fabrication setup for laser interference lithography. (b) Two beams interfere at the sample surface causing a periodic pattern in the photoresist. Adapted from colour to grey-scale. Reprinted with permission from Hauss *et al.* (2011b). Copyright 2011, SPIE.

A comprehensive review of NIL is given by Schiff (2008). The stamp may be fabricated by electron beam lithography or LIL. In thermal NIL (T-NIL) a thin thermoplastic layer is moulded by a hard stamp using squeeze flow. This is also called hot embossing. In UV-NIL a liquid resin fills the stamp due to capillary forces and is subsequently hardened by UV exposure. Both methods allow for a parallel processing of a large surface area. As shown in Fig. 8.13 the pattern definition step is followed by a transfer of the pattern into the substrate by etching. The nanoimprint process may be integrated into a roll-to-roll fabrication method as demonstrated by Stegall *et al.* (2009) and depicted in Fig. 8.14.

Lithography	Pattern definition	Pattern transfer	
	Resist patterning	Residual layer etch	Substrate patterning
Nanoimprint lithography (NIL)			
Issues to be considered	3D rheology, inclusions, residual layer homogeneity, demolding, shrinkage, relaxation, distortion	Pattern fidelity and homogeneity, aspect ratio and contrast, surface contamination	Pattern fidelity, etch ration, topological and chemical contrast (hard mask), resist removal

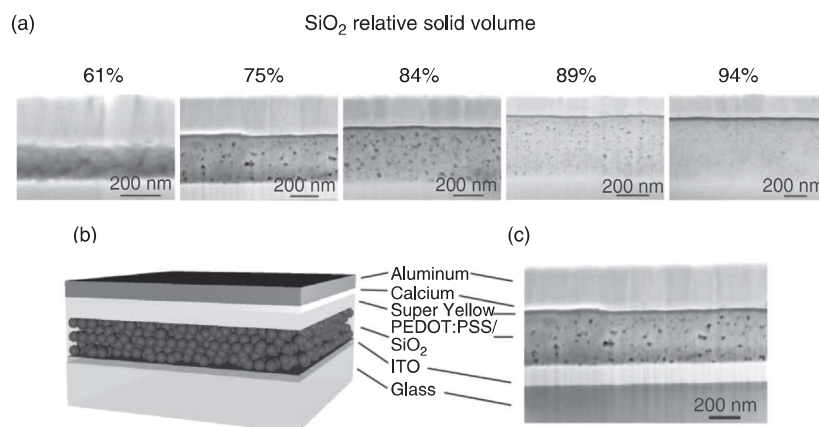
8.13 Fabrication procedure and issues to consider using nanoimprint lithography (NIL). Reprinted with permission from Schiff (2008). Copyright 2008, American Vacuum Society.



8.14 Schematic of fabrication procedures for roll-to-roll fabrication of nanostructured OLEDs. Reprinted with permission from Stegall *et al.* (2009). Copyright 2009, SPIE.

8.6.2 Fabrication of OLEDs with non-periodic nanostructures

In a top-down approach non-periodic nanostructures may be achieved similarly to periodic nanostructures by electron beam lithography and optional replication via nanoimprint lithography. Alternatively, bottom-up approaches may be applied. As shown by Riedel *et al.* (2011) and depicted in Fig. 8.15 nanoparticles may be blended into the organic layers. Inorganic nanoparticles in the PEDOT:PSS layer allow for a tailoring of the layer thickness, the layer refractive index and the scattering properties, while maintaining conductivity due to the organic matrix. Buckling patterns may be formed spontaneously on elastic material surfaces with thin metallic coatings resulting in quasi-periodic nanostructures (Koo *et al.*, 2010). Self-assembly for nanofabrication is, for example, reviewed by Gates *et al.* (2005). Alternatively, rough internal interfaces may be achieved by sandblasting, abrasion or etching (Riedel *et al.*, 2010c). Depending on the roughness of the interface, the deposition of a levelling layer may be necessary to prevent electrical shorts in the OLED.



8.15 (a) Series of scanning electron microscope (SEM) images of cross sections of OLEDs with composite organic/inorganic hole transport layers based on blends of PEDOT:PSS with different SiO₂ nanoparticle relative solid volumes. (b) Schematic and (c) SEM image of a cross section of an OLED containing a composite hole transport layer with SiO₂ nanoparticles. By blending inorganic nanoparticles into the PEDOT:PSS layer, much thicker layers are obtained. Depending on the nanoparticle material and size, the layer refractive index and the scattering properties can be adjusted. Reprinted with permission from Riedel *et al.* (2011). Copyright 2011, Wiley-VCH Verlag GmbH & Co. KGaA, Weinheim.

8.7 Conclusion

The external quantum efficiency for a standard OLED stack on a flat glass substrate is typically only about 20% due to radiative decay of excitons into guided modes in the substrate and guided modes in the OLED stack. In this chapter three different routes were investigated for improving the power efficiency by nanostructuring of the OLED. Firstly, the nanostructure may couple guided modes to leaky modes. For improved power efficiency, the nanostructure has to be designed such that the scattering coefficient of the nanostructure is higher than the absorption coefficient of the guided mode and the population of the guided mode with photons needs to be significantly higher than the population of the leaky mode. Secondly, the nanostructure may directly cause a redistribution of energy from guided modes to leaky modes and to non-radiative decay. The suppression of guided modes by the nanostructure is accompanied by an increase in the decay time of emitters. For highest efficiency improvements, a high refractive index contrast is needed, the emitters should be narrowband and specifically placed compared to the nanostructure, and a low non-radiative decay rate is needed compared to the radiative decay rate into leaky modes. Thirdly, nanostructuring the OLED at the electrode interfaces may cause local electric field enhancements, which may serve for control of carrier injection and turn-on voltage. This may be of particular interest as an alternative to additional polymer layers in solution processed devices, as the blending of nanoparticles into organic layers is simple and low cost.

In evaluating the efficiency enhancement after integration of a nanostructure into the OLED stack, care has to be taken in the design of experiments and the interpretation of effects. In order to judge if the 300% efficiency enhancement of the nanostructured OLED in Fig. 8.1 may be transferred from this proof-of-principle device to state-of-the-art OLEDs, it is necessary to understand the processes underlying the efficiency enhancement. For separating electrical and optical effects, it is helpful to characterise both the electroluminescence as well as photoluminescence. If an efficiency enhancement only is observed in the electroluminescence and not in the photoluminescence, the electrical properties of the OLED are changed without a successful coupling of guided modes to leaky modes. For the photoluminescence experiments it is important to ensure that the excitation efficiency of the emitter is not changed by the nanostructure. Also, in a photoluminescence experiment excitons are generated throughout the emission layer, while in the electrically excited OLED, carriers recombine at specific positions depending on carrier injection and carrier mobility. Both effects may cause an improved efficiency in the photoluminescence measurement, which is not observed in the electroluminescence. Furthermore, the excitation efficiency of some emitters may be directional and the emission polarization maintaining when excited with polarized light. This needs to be taken into account in particular for photoluminescence measurements on aligned polymer emitters. For distinguishing between the extraction of guided modes from the organic/ITO stack and the

extraction of modes from the glass substrate, the use of a macroextractor such as a large half-sphere is beneficial (Reineke *et al.*, 2009). The macroextractor extracts all modes guided in the substrate. Thus, if a nanostructured device with macroextractor shows a better efficiency than a non-structured reference device with macroextractor, this efficiency improvement may be attributed to the extraction of guided modes from the organic/ITO stack. Simulations of the extraction of substrate modes due to a grating in the OLED stack are given in Bienstman *et al.* (2007). In order to identify which guided modes are extracted from the organic/ITO stack, angle- and wavelength-resolved luminescence experiments are a valuable tool. In order to evaluate if the spontaneous emission properties of the emitter are changed, time-resolved photoluminescence measurements should be performed in order to determine the decay time. A change in the decay time is an indicator for changed spontaneous emission properties. On the other hand, this may also be caused by a change in the non-radiative decay time.

For the example in Fig. 8.1 further experimental results (Riedel *et al.*, 2010a) reveal that the electrical characteristics of the device remain unchanged for a flat Ta_2O_5 -layer and a nanostructured layer excluding local electric field effects. Angle- and wavelength-resolved electroluminescence experiments show peaks that can be attributed to the outcoupling of guided modes in the OLED stack. On the other hand, a broad efficiency improvement is observed for all angles and wavelengths. This can be explained when applying a large half-sphere as a macroextractor. With a macroextractor a similar broadband enhancement is observed leading to the conclusion that the grating structure causes a coupling of both guided modes in the substrate and guided modes in the OLED stack to leaky modes. Due to the high refractive index of the Ta_2O_5 intermediate layer, the nanostructure is particularly effective in outcoupling of substrate modes. Transferring this concept to state-of-the-art devices, it has to be taken into account that the Ta_2O_5 intermediate layer influences the optical modes in the cavity, which needs to be redesigned. Furthermore, as part of the efficiency enhancement is due to substrate mode extraction, this technology is competing with standard methods for structuring of the substrate-air interface. The intensity peaks in the emission spectrum attributed to the coupling of guided modes in the OLED stack are only obtained for a modification in the vicinity of the OLED stack. Different fabrication methods for integrating nanostructures into OLEDs were presented demonstrating that low cost and high throughput approaches are available.

8.8 Future trends

Today, research groups have demonstrated the successful integration of different types of periodic and non-period nanostructures into OLEDs. The reasons for efficiency enhancements have been investigated and are now understood. For commercialisation of nanostructured OLEDs, the major task is to optimize the

efficiency enhancement within the vast parameter set including the type of nanostructure, the position of the nanostructure in the OLED stack, the integration of additional layers, the design of the rest of the OLED, fabrication cost and time, etc. As this task is rather daunting, good design rules are needed to reduce the parameter space.

For an efficient nanostructuring that couples guided modes to leaky modes a good starting point is the question; What type of nanostructure can be integrated at acceptable cost in the 100-nm vicinity of the OLED stack that exhibits a period of the order of the wavelength of light and a high refractive index contrast? For evaporated devices the use of nanostructured ITO-substrates or of substrates with an underlying nanostructured high-index layer is most promising. For solution-processed devices the integration of low-index or high-index nanoparticles is an attractive alternative. Either way the scattering efficiency of the nanostructure should be maximised. Once the type of nanostructure has been chosen, the complete OLED stack needs to be redesigned such that a mode overlap of highly populated guided modes with the nanostructure is achieved and other desired OLED properties are maintained. In characterising the emission spectrum, distinct peaks of outcoupled guided modes should be visible for periodic nanostructures, while non-periodic nanostructures typically exhibit a broad emission spectrum.

Distinct peaks in the emission spectrum of periodic nanostructures cause unwanted direction-dependent colour and intensity impressions. Once an efficient nanostructure has been found, these effects may be eliminated using gratings with different periodicities at different positions or overlaid multiperiodic gratings. The design of the nanostructure will play a more important role in the future. In a top-down approach it is possible to design and fabricate nanostructures with more complex unit cells that allow for an improved engineering of the emission properties. This is already standard in the design of complex OLED stacks including microcavity effects, but has not yet been considered for the lateral nanostructuring of OLEDs.

In conclusion, the next step for the integration of nanostructures in OLEDs is the efficiency optimisation within the parameter space for achieving an efficient coupling of guided modes in the OLED stack to leaky modes. For the distant future it may be predicted that tailoring of the spontaneous emission properties using nanostructured environments will become standard, as this allows for a direct funnelling of the emitted photons into the desired modes.

8.9 Sources of further information and advice

In order to improve the extraction of light from OLEDs, it is essential to understand, in which modes the light is guided. *Optical Waves in Layered Media* (Yeh, 2005) gives a rigorous treatment of guided waves as well as surface plasmons in multilayer waveguides. Furthermore, it supplies calculation methods. Scattering of guided modes to leaky modes may be induced by periodic

or non-periodic nanostructuring. *Photonic Crystals: Molding the Flow of Light* (Joannopoulos *et al.*, 2008) gives a helpful introduction to the interaction of light with periodic nanostructures, while to study the scattering of light on non-periodic nanostructures I recommend *Wave Propagation and Scattering in Random Media* (Ishimaru, 1997). This book treats in detail the scattering of light on single particles and on differently concentrated distributions of particles.

Principles of Nano-Optics (Novotny and Hecht, 2006) is a good starting point to learn more about the spontaneous emission properties of emitters in nanoscale environments. In Chapter 8, the authors derive the spontaneous decay rate from quantum electrodynamics. Furthermore, they compare this result to classical theory and show that both are equivalent in the weak-coupling regime. Vahala (2003) presents a helpful review on the Purcell effect and different types of cavities realized to achieve strong coupling.

Enhancing the extraction efficiency of OLEDs using nanostructuring is a topic of fast-moving research. The newest results are presented in scientific publications and conferences and much progress is expected in the next few years.

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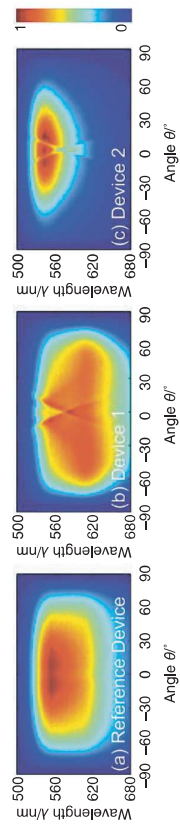


Plate 1 (Chapter 8) Wavelength- and angle-resolved electroluminescence measurements for the three devices shown in Fig. 8.6.

Modelling of light extraction from OLEDs

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Abstract: The novel concept of the light extraction modelling is proposed. It is based on the rigorous electromagnetic methods allowing for accurate modelling of complex organic light-emitting diode (OLED) structures including two-dimensional (2D) gratings, photonic crystals and scattering layers. This opens new possibilities for efficient design and optimization of a wide class of promising light sources.

Key words: OLED modeling, light extraction, scattering, diffraction.

9.1 Introduction

Design of light sources and displays based on organic light-emitting diodes (OLEDs) relies on analysis of complex structures aiming at optimizing the output parameters of the whole device. The main characteristics in such analysis are efficiency, brightness, angular uniformity, spectral (color) performance. All of them depend to a large extent on the optical properties of the structure, which contains light-emitting materials. A variety of nanostructured materials have been used recently to improve the OLED efficiency and to control light extraction. Photonic crystals are introduced in OLEDs to amplify light emission.¹⁻⁶ Periodic structures can also outcouple guiding modes.⁷⁻¹⁴ Scattering layers redirect light captured in the glass substrate and in the high-refractive OLED multilayer and homogenize the angular and spectral output diagrams.¹⁵⁻²⁰ Manufacturing of individual experimental samples becomes a complex, costly and time-consuming task. Therefore, the selection of the optimal device configuration needs numerical simulation.²¹⁻²⁵

Calculation of the optical characteristics of OLED structures refers to the theory of scattering and diffraction of electromagnetic radiation in the visible spectrum range in heterogeneous media with characteristic size of inhomogeneities from ten nanometers to several microns. This task is very complex and admits numerical solution only. Computational methods in the theory of light scattering and diffraction have been progressing for more than fifty years.^{26,27} There are established sufficiently powerful methods suitable for rigorously solving this problem. Radiation in active optical systems, light scattering in nano-structured optical media, and diffraction by one- and two-dimensional gratings are usually considered, however, as quite separate electromagnetic problems. Moreover, they are handled by different research groups. Therefore, an important issue is to choose a model interface giving the best access to the methods and techniques

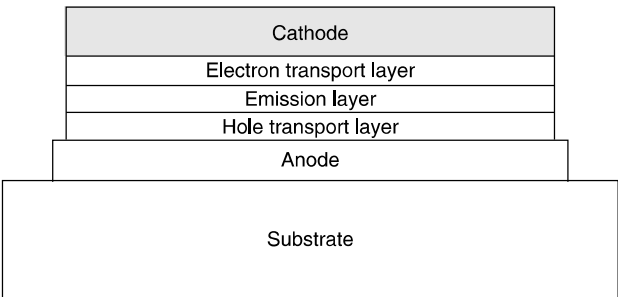
developed by different research communities to combine them in modelling OLEDs. The universal approach proposed here is based on the plane wave representation of the emitted field²⁸ together with the S matrix formalism²⁹ used to consider interplay between different parts of the OLED structure. The aim of this chapter is to present a computational model and numerical methods to simulate fast and accurately the optical properties of OLEDs aiming at their optimization for possible applications. Under the heading of optical properties we include the ability to calculate the following OLED characteristics:

- electromagnetic fields and intensity in near and far zones of the light-emitting structure;
- output spectral and angular intensity distribution;
- energy losses in each part (layer) of the multilayer structure;
- output electric and magnetic fields in non-radiating structure for a given incident wave.

9.2 Rationale of the approach in terms of the characteristics of the problem

An OLED is a light-emitting structure composed of plane layers with a thickness of up to hundreds of nanometers and lateral dimensions from a few millimeters to tens of centimeters (an example of a typical structure is shown in Fig. 9.1). From the optical point of view, such layers can be pure dielectrics, dielectrics with absorption, metals. Generally, each layer is characterized by complex permittivity. Some layers may be nanostructured, which significantly complicates the analysis of optical properties of the whole structure. Dielectric permittivity of such layers can be described by a spatially inhomogeneous function.

Study of optical properties of considered structures can be attributed to the theory of optical scattering and diffraction. In this case, the characteristic size of material inhomogeneities is comparable to the wavelength of the incident radiation (from 350 nm to 800 nm), which requires the smaller possible number of approximations and simplifying assumptions to the problem.



9.1 Schematic example of a plane-layered OLED-structure.

To date, quite a number of numerical methods have been developed in the theory of light scattering and diffraction. The methods analyze the problem of light scattering by individual particles and particle groups,³⁰ or consider a composite material as a kind of medium with modulated permittivity.³¹ Other methods focus on the problem of diffraction by periodic structures (diffraction gratings).³² We will see that these methods are also applicable to the scattering problem.

Light emission in OLEDs is due to singlet/triplet exciton radiative decay.³³ The size of the optical source is typically very small (of the order of or less than a few nanometers) compared with the radiated wavelength. This is why the classical vibrating dipole³⁴ is relevant as an electromagnetic source in the OLED modelling. The intensity in the emission line is usually far below the lasing threshold. This is why in OLEDs one deals with spontaneous emission.³⁵ All dipoles emit independently and linear Maxwell's equations describe entirely the optical system. The electromagnetic response at any frequency is considered as independent and the analysis is performed on the basis of monochromatic waves. Note that each source (dipole) radiates inside the multilayer. The reflected field interacts coherently with the dipole changing substantially the rate of its emission. Each dipole is linearly polarized. Its polarization is important in the multilayer context resulting in possibly different output efficiency.

9.3 Presentation of the emitting layers

9.3.1 Emitting dipole

The size of emitting sources not exceeding a few nanometers is very small with respect to the wavelength. Therefore, in optical analysis they are usually approximated by point dipoles. We consider radiation of a monochromatic Dirac point dipole with amplitude $\mathbf{p}_0$, located at point $\mathbf{r}_0 = (x_0, y_0, z_0)$ in a homogeneous medium with permittivity ϵ_p and permeability μ_0 :

$$\mathbf{p}(\mathbf{r}, t) = \mathbf{p}_0 \delta(x - x_0) \delta(y - y_0) \delta(z - z_0) \exp(-i\omega t) \quad [9.1]$$

The emitted electromagnetic field is given by its vector potential $\mathbf{A}$ ³⁶:

$$\mathbf{E} = i\omega \mathbf{A} - \frac{\nabla(\nabla \cdot \mathbf{A})}{i\omega \mu_0 \epsilon_p} \quad [9.2]$$

$$\mathbf{H} = \frac{\nabla \times \mathbf{A}}{\mu_0} \quad [9.3]$$

Potential $\mathbf{A}$ is found as a solution of the Helmholtz equation³⁷

$$\nabla^2 \mathbf{A} + k_p^2 \mathbf{A} = i\omega \mu_0 \mathbf{p}_0 \delta(x - x_0) \delta(y - y_0) \delta(z - z_0) \exp(-i\omega t) \quad [9.4]$$

where

$$k_p = \omega \sqrt{\mu_0 \epsilon_p} \quad [9.5]$$

The solution of [9.4] is a spherical wave

$$\mathbf{A}(\mathbf{r}, t) = -i\omega\mu_0\mathbf{p}_0 \frac{\exp\left(ik_p|\mathbf{r} - \mathbf{r}_0|\right)}{4\pi|\mathbf{r} - \mathbf{r}_0|} \exp(-i\omega t) \quad [9.6]$$

Emitted intensity is given by the Poynting vector

$$\mathbf{S} = \frac{1}{2} \operatorname{Re}(\mathbf{E} \times \mathbf{H}^*) \quad [9.7]$$

Integrating the radial component of $\mathbf{S}$ over 4π solid angle and applying Eqs. [9.2], [9.3], [9.6] and [9.7], yields the total intensity emitted by the dipole:

$$I = \lim_{r \rightarrow 0} \int_0^{2\pi} d\varphi \int_0^\pi S_r(\theta, \varphi) r^2 \sin\theta d\theta = \frac{\omega^2 \mu_0}{12\pi} \left| p_0 \right|^2 \operatorname{Re}(k_p) \quad [9.8]$$

Representing the fields via spherical waves is not useful for modeling emission in a multi-layer stack. In order to better fit the geometry of plane layers we represent Dirac dipole (1) in the reciprocal Fourier plane-wave basis (k_x, k_y) :

$$\mathbf{p}(\mathbf{r}, t) = \delta(z - z_0) \exp(-i\omega t) \frac{\mathbf{p}_0}{(2\pi)^2} \iint_{-\infty}^{\infty} \exp\left[ik_x(x - x_0) + ik_y(y - y_0)\right] dk_x dk_y \quad [9.9]$$

Solution [9.6] is then composed of plane waves [9.2] with corresponding Fourier amplitudes:

$$\begin{bmatrix} \mathbf{A}(\mathbf{r}) \\ \mathbf{E}(\mathbf{r}) \\ \mathbf{H}(\mathbf{r}) \end{bmatrix} = \frac{\exp(-i\omega t)}{(2\pi k_0)^2} \iint_{-\infty}^{\infty} \begin{bmatrix} \mathbf{A}(k_x, k_y) \\ \mathbf{E}(k_x, k_y) \\ \mathbf{H}(k_x, k_y) \end{bmatrix} dk_x dk_y \quad [9.10]$$

where

$$\mathbf{A}(k_x, k_y) = \frac{\omega\mu_0 k_0^2}{2k_{pz}} \mathbf{p}_0 \exp\left[i\mathbf{k}^\pm \cdot (\mathbf{r} - \mathbf{r}_0)\right] \quad [9.11]$$

$$\mathbf{E}(k_x, k_y) = \frac{k_0^2}{2i\varepsilon_p k_{pz}} \mathbf{k}^\pm \times (\mathbf{k}^\pm \times \mathbf{p}_0) \exp\left[i\mathbf{k}^\pm \cdot (\mathbf{r} - \mathbf{r}_0)\right] \quad [9.12]$$

$$\mathbf{H}(k_x, k_y) = \frac{i\omega k_0^2}{2k_{pz}} (\mathbf{k}^\pm \times \mathbf{p}_0) \exp\left[i\mathbf{k}^\pm \cdot (\mathbf{r} - \mathbf{r}_0)\right] \quad [9.13]$$

We denote by $\mathbf{k}^\pm$ the wavevectors of waves propagating in the positive and negative directions with respect to the z axis.

$$\mathbf{k}^\pm = (k_x, k_y, \pm k_{pz}) \quad [9.14]$$

$$k_{pz} = \sqrt{k_p^2 - k_x^2 - k_y^2}, 0 \leq \arg(k_{pz}) < \pi \quad [9.15]$$

Sign ‘plus’ is taken in [9.10] and [9.11] for $z > z_0$, sign ‘minus’ for $z < z_0$. Factors $k_0^2 = \omega^2 \mu_0 \epsilon_0$ are introduced in [9.10]–[9.13] to preserve field dimension in the reciprocal Fourier space.

Any plane wave is a superposition of TE and TM polarized waves. Considering the polarization of a plane wave is important since it is invariant in all reflections and transmissions. The amplitudes of the TE and TM components can be defined as follows:

$$\alpha_{TE} = \frac{k_y}{\gamma} E_x - \frac{k_x}{\gamma} E_y = -\frac{\omega \mu_0}{\gamma} H_z \quad [9.16]$$

$$\alpha_{TM} = \frac{k_y}{\gamma} H_x - \frac{k_x}{\gamma} H_y = \frac{\omega \epsilon}{\gamma} E_z \quad [9.17]$$

where $\gamma = \sqrt{k_x^2 + k_y^2}$ is the in-plane projection of the wavevector. Then, in a plane wave radiated by dipole [9.1], the amplitudes of such components $r_{TE, TM}^*$ are found from the relations [9.12]–[9.13], [9.16]–[9.17] (see, for example, refs 38 and 39):

$$r_{TE}^* = \frac{i\omega^2 \mu_0 k_0^2}{8\pi^2 \gamma k_{pz}} (k_y p_{0x} - k_x p_{0y}) \exp(-ik_x x_0 - ik_y y_0) \quad [9.18]$$

$$r_{TM}^* = \frac{i\omega k_0^2}{8\pi^2 \gamma k_{pz}} (\mp k_x k_{pz} p_{0x} \mp k_y k_{pz} p_{0y} + \gamma^2 p_{0z}) \exp(-ik_x x_0 - ik_y y_0) \quad [9.19]$$

The intensity radiated by the dipole, through any plane parallel to the plane XY, is defined by the z-projection of the Poynting vector [9.16]:

$$\begin{aligned} S_z(\mathbf{r}) &= \frac{1}{2} \operatorname{Re} \left(\int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathbf{E}(\mathbf{k}', \mathbf{r}) \frac{dk'_x dk'_y}{k_0^2} \times \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \mathbf{H}^*(\mathbf{k}^*, \mathbf{r}) \frac{dk_x dk_y}{k_0^2} \right) dx dy \\ &= \frac{(2\pi)^2}{k_0^4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S_z(k_x, k_y, z) dk_x dk_y \end{aligned} \quad [9.20]$$

Thus, the total intensity is found as the integral of plane wave intensities $S_z(k_x, k_y, z)$

$$S_z(k_x, k_y, z) = \begin{cases} \frac{1}{2} \left[|r_{TE}^+|^2 \frac{\operatorname{Re}(k_z)}{\omega \mu_0} + |r_{TM}^+|^2 \operatorname{Re}\left(\frac{k_z}{\omega \epsilon_m}\right) \right] \exp[-2 \operatorname{Im}(k_{pz})(z - z_0)], & z > z_0 \\ -\frac{1}{2} \left[|r_{TE}^-|^2 \frac{\operatorname{Re}(k_z)}{\omega \mu_0} + |r_{TM}^-|^2 \operatorname{Re}\left(\frac{k_z}{\omega \epsilon_m}\right) \right] \exp[2 \operatorname{Im}(k_{pz})(z - z_0)], & z < z_0 \end{cases} \quad [9.21]$$

Integrating S_z through planes $z = z_0 \pm 0$ over and below the dipole yields the total intensity emitted by the dipole:

$$\begin{aligned}
I &= \lim_{z \rightarrow z_0 + 0} \frac{(2\pi)^2}{k_0^4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S_z(k_x, k_y, z) dk_x dk_y - \lim_{z \rightarrow z_0 - 0} \frac{(2\pi)^2}{k_0^4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S_z(k_x, k_y, z) dk_x dk_y \\
&= \frac{\omega^2 \mu_0}{12\pi} \left| \mathbf{p}_0 \right|^2 \operatorname{Re}(k_p)
\end{aligned} \tag{9.22}$$

Obviously, this result coincides with [9.8].

9.3.2 Fields in a multilayer stack

We consider so far the radiation of a point source in a homogeneous dielectric medium. When dipole [9.1] is placed in a multilayer all the reflections should be taken into account. We suppose that all layers and interfaces are parallel to the OXY plane. Many efforts are usually made by authors to explain how to calculate amplitudes of plane harmonics in the multilayer. In fact, such analysis can be easily summarized using matrix techniques. An important comment is worth giving here. The transfer matrix technique, which is well explained in different textbooks, though it is easy in analytical implementation, leads to instabilities and loss of accuracy in numerical calculations while the S matrix technique²⁹ exhibits perfect stability and is much more preferable for numerical analysis of multilayer structures. This is why we introduce here the S matrix technique.

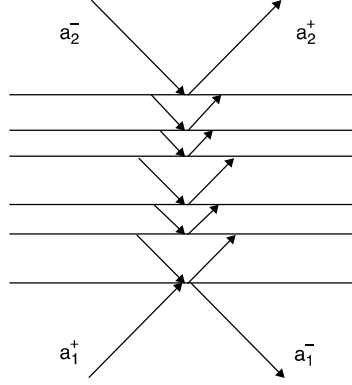
Reflection and transmission of a plane wave in a multilayer is described by S matrices which relate the plane wave amplitudes from both sides (side 1 and side 2 in Fig. 9.2) of a given structure:

$$\begin{pmatrix} a_1^- \\ a_2^+ \end{pmatrix} = S \begin{pmatrix} a_1^+ \\ a_2^- \end{pmatrix} = \begin{pmatrix} S_{11} & S_{12} \\ S_{21} & S_{22} \end{pmatrix} \begin{pmatrix} a_1^+ \\ a_2^- \end{pmatrix} \tag{9.23}$$

In fact, each S matrix contains two reflection and two transmission coefficients. Thus, the S matrix of an interface between two media with permittivities ϵ_1 and ϵ_2 consists of the Fresnel coefficients:

$$S_{TE} = \begin{pmatrix} \frac{k_{1z} - k_{2z}}{k_{1z} + k_{2z}} & \frac{2k_{2z}}{k_{1z} + k_{2z}} \\ \frac{2k_{1z}}{k_{1z} + k_{2z}} & \frac{k_{2z} - k_{1z}}{k_{1z} + k_{2z}} \end{pmatrix} \tag{9.24}$$

$$S_{TM} = \begin{pmatrix} \frac{\epsilon_2 k_{1z} - \epsilon_1 k_{2z}}{\epsilon_2 k_{1z} + \epsilon_1 k_{2z}} & \frac{2\epsilon_1 k_{2z}}{\epsilon_2 k_{1z} + \epsilon_1 k_{2z}} \\ \frac{2\epsilon_2 k_{1z}}{\epsilon_2 k_{1z} + \epsilon_1 k_{2z}} & \frac{\epsilon_1 k_{2z} - \epsilon_2 k_{1z}}{\epsilon_2 k_{1z} + \epsilon_1 k_{2z}} \end{pmatrix} \tag{9.25}$$



9.2 Plane wave reflections and transmissions in a multilayer.

The S matrix of a homogeneous layer with permittivity ϵ_l and thickness t_l is the same for both polarizations:

$$S = \begin{pmatrix} 0 & \exp(ik_{lz}t_l) \\ \exp(ik_{lz}t_l) & 0 \end{pmatrix} \quad [9.26]$$

To obtain an S matrix of a structure composed of two elements A and B one calculates first two S matrices S^A and S^B of the elements and then applies the following rule:

$$\begin{aligned} S_{11}^{AB} &= S_{11}^A + S_{12}^A S_{11}^B (I - S_{22}^A S_{11}^B)^{-1} S_{21}^A \\ S_{12}^{AB} &= S_{12}^A (I - S_{11}^B S_{22}^A)^{-1} S_{12}^B \\ S_{21}^{AB} &= S_{21}^B (I - S_{22}^A S_{11}^B)^{-1} S_{21}^A \\ S_{22}^{AB} &= S_{22}^B + S_{21}^B S_{22}^A (I - S_{11}^B S_{22}^A)^{-1} S_{12}^B \end{aligned} \quad [9.27]$$

The electric and magnetic field of a plane wave in terms of amplitudes of its TE and TM components are:

$$E_x^+ = \frac{k_y}{\gamma} a_{TE}^+ \mp \frac{k_x k_z}{\omega \epsilon_l \gamma} a_{TM}^+; E_y^+ = -\frac{k_x}{\gamma} a_{TE}^+ \mp \frac{k_y k_z}{\omega \epsilon_l \gamma} a_{TM}^+; E_z^+ = \frac{\gamma}{\omega \epsilon_l} a_{TM}^+ \quad [9.28]$$

$$H_x^+ = \pm \frac{k_x k_z}{\omega \mu_0 \gamma} a_{TE}^+ + \frac{k_y}{\gamma} a_{TM}^+; H_y^+ = \pm \frac{k_y k_z}{\omega \mu_0 \gamma} a_{TE}^+ - \frac{k_x}{\gamma} a_{TM}^+; H_z^+ = -\frac{\gamma}{\omega \mu_0} a_{TE}^+ \quad [9.29]$$

The intensity through any plane as follows from [9.20] equals⁴⁰:

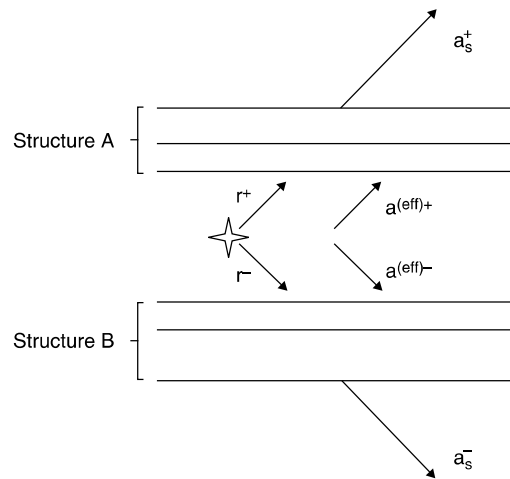
$$S_z = \frac{1}{2} \text{Re}(\mathbf{E} \times \mathbf{H}^*) = \frac{1}{2} \frac{\text{Re}(k_z)}{\omega \mu_0} \left(|a_{TE}^+|^2 - |a_{TE}^-|^2 \right) + \frac{\text{Im}(k_z)}{\omega \mu_0} \text{Im}(a_{TE}^+ a_{TE}^-) \\ + \frac{1}{2} \text{Re} \left(\frac{k_z}{\omega \epsilon_i} \right) \left(|a_{TM}^+|^2 - |a_{TM}^-|^2 \right) + \text{Im} \left(\frac{k_z}{\omega \epsilon_i} \right) \text{Im}(a_{TM}^+ a_{TM}^-) \quad [9.30]$$

Note that in the presence of reflected waves the energy transport can also be done by evanescent waves.

If the source is located inside a multi-layer structure, effective radiated power is changed because of interference with waves reflected at multiple interfaces between different media, composing the OLED structure. This strongly affects on the angular and spectrum characteristics of the source.

Formulae [9.24]–[9.27] are sufficient to calculate the S matrix of an arbitrary multilayer structure. To perform a rigorous electromagnetic analysis of the system we consider a source located at point $z=z_0$ (Fig. 9.3). Two structures (A) above and (B) below the dipole are characterized by their S matrices S^A and S^B .

The source emits plane waves of amplitudes r^+ and r^- , but the effective wave amplitudes differ from them because of multiple reflections and transmissions. The electromagnetic field emitted by the dipole is coherently added to the reflected and transmitted waves. This results in the corresponding amplitude change at the dipole location point. Effective wave amplitudes $a^{(eff)+}$ and



9.3 The source located between two structures.

$a^{(eff)-}$ between elements are found as a result of interference between all emitted and reflected waves:

$$\begin{aligned} a^{(eff)+} &= S_{22}^B a^{(eff)-} + r^+ \\ a^{(eff)-} &= S_{11}^A a^{(eff)+} + r^- \end{aligned} \quad [9.31]$$

These amplitudes are explicitly defined by matrix inversion:

$$\begin{aligned} a^{(eff)+} &= \left(I - S_{22}^B S_{11}^A \right)^{-1} \left(S_{22}^B r^- + r^+ \right) \\ a^{(eff)-} &= \left(I - S_{11}^A S_{22}^B \right)^{-1} \left(S_{11}^A r^+ + r^- \right) \end{aligned} \quad [9.32]$$

The effective intensity emitted by the dipole in this case is found as the difference between intensity above and below the source:

$$\begin{aligned} I_d &= \lim_{z \rightarrow z_0+0} S_z - \lim_{z \rightarrow z_0-0} S_z \\ &= \frac{1}{2} \left[\left(|r_{TE}^+|^2 + |r_{TE}^-|^2 \right) \frac{\text{Re}(k_{pz})}{\omega \mu_0} + \left(|r_{TM}^+|^2 + |r_{TM}^-|^2 \right) \text{Re} \left(\frac{k_{pz}}{\omega \epsilon_m} \right) \right] \\ &\quad + \text{Re} \left[r_{TE}^{+*} a_{TE}^{(eff)+} (z \rightarrow z_0 - 0) + r_{TE}^{-*} a_{TE}^{(eff)-} (z \rightarrow z_0 + 0) \right] \frac{\text{Re}(k_{pz})}{\omega \mu_0} \\ &\quad + \text{Re} \left[r_{TM}^{+*} a_{TM}^{(eff)+} (z \rightarrow z_0 - 0) + r_{TM}^{-*} a_{TM}^{(eff)-} (z \rightarrow z_0 + 0) \right] \text{Re} \left(\frac{k_{pz}}{\omega \epsilon_p} \right) \\ &\quad + \text{Im} \left[r_{TE}^{+*} a_{TE}^{(eff)-} (z \rightarrow z_0 + 0) + r_{TE}^{-*} a_{TE}^{(eff)+} (z \rightarrow z_0 - 0) \right] \frac{\text{Im}(k_{pz})}{\omega \mu_0} \\ &\quad + \text{Im} \left[r_{TM}^{+*} a_{TM}^{(eff)-} (z \rightarrow z_0 + 0) + r_{TM}^{-*} a_{TM}^{(eff)+} (z \rightarrow z_0 - 0) \right] \text{Im} \left(\frac{k_{pz}}{\omega \epsilon_p} \right) \end{aligned} \quad [9.33]$$

Note that the intensity is dependent on the amplitudes and phases of the reflected and transmitted waves. This indicates the fact that the multilayer changes the intensity emitted by a dipole with fixed amplitude.

9.3.3 Output intensity calculation

The part of intensity emitted by the dipole and not absorbed inside the structure goes in two adjacent semi-infinite media. If such a medium is a thick metal electrode the intensity is finally absorbed in it. If the medium is a transparent dielectric substrate the output intensity characterizes the efficiency of OLED emission. When the substrate is above the emitting dipole the output amplitudes are given by S matrix S^A :

$$a_s^+ = S_{21}^A a^{(eff)+} = S_{21}^A \left(I - S_{22}^B S_{11}^A \right)^{-1} \left(S_{22}^B r^- + r^+ \right) \quad [9.34]$$

The output intensity extracted to a semi-infinite medium of permittivity ϵ_s is found from [9.30]:

$$S_z = \frac{1}{2} \frac{\text{Re}(k_z)}{\omega \mu_0} \left| a_{sTE}^+ \right|^2 + \frac{1}{2} \text{Re} \left(\frac{k_{sz}}{\omega \epsilon_s} \right) \left| a_{sTM}^+ \right|^2 \quad [9.35]$$

Note that only waves with $k_x^2 + k_y^2 < k_s^2 = \omega^2 \mu_0 \epsilon_s$ contribute to the output intensity. In this case, the plane wave propagates in the substrate under angle $\theta = \arcsin(\gamma/k_s)$ with the z axis and azimuthal angle $\phi = \arccos(k_x/\gamma)$. The total intensity radiated into the substrate is found in accordance with [9.20] by integration:

$$\begin{aligned} I &= \frac{(2\pi)^2}{k_0^4} \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} S_z(k_x, k_y) dk_x dk_y = \frac{(2\pi)^2}{k_0^4} \int_0^{2\pi} \int_0^{\pi/2} S_z(\theta, \varphi) k_s^2 \sin \theta \cos \theta d\theta d\varphi \\ &= \oint_{2\pi} I_m(\theta, \varphi) d\Omega \end{aligned} \quad [9.36]$$

where $I_m(\theta, \varphi)$ is measured angular intensity which is inversely proportional to the output solid angle $d\Omega$:

$$I_m(\theta, \varphi) = (2\pi)^2 n_s^2 \cos \theta S_z(\theta, \varphi) \quad [9.37]$$

If the substrate is below the emitting dipole the output amplitudes are found by S matrix S^B :

$$a_s^- = S_{12}^B a^{(eff)-} = S_{12}^B \left(I - S_{11}^A S_{22}^B \right)^{-1} \left(S_{11}^A r^+ + r^- \right) \quad [9.38]$$

All the relations for the output intensity calculations rest quite similar to Eqs [9.36] and [9.37], the only change concerns the sign before terms k_{sz} , S_z , and $\cos \theta$. Note that calculation of integral [9.36] is simplified using rotational symmetry of the structure along the z axis.

9.3.4 External reflections and non-coherent return of the light

In many cases, the light is extracted from the structure to the air through a substrate. The substrate is too thick to preserve light coherence. This is why waves reflected back from the air–substrate interface do not interfere with emitted waves. Therefore, a correct analysis of such a situation includes calculation of light emission to the substrate by means of techniques developed in the previous sections (the air–substrate interface is disregarded at this stage); then, the air–substrate interface is introduced modifying the intensities. All formulae needed for the first stage of the analysis are given in the preceding section; in this section we present an algorithm providing intensity modification due to the air–substrate interface.⁴⁰

Presence of the air–substrate interface leads to two main consequences: first, all waves with in-plane wavevector projection $\gamma \geq k_{air}$ will be totally reflected back and guided in the substrate; secondly, in the case $\gamma \leq k_{air}$ emitted waves will be partially reflected at the interface resulting in decreasing output efficiency. Suppose the substrate is above the emitting structure. Let R_a and T_a be the reflection and transmission power coefficients at the interface

$$R_{aTE} = \left| \frac{k_{sz} - k_{az}}{k_{sz} + k_{az}} \right|^2, R_{aTM} = \left| \frac{\epsilon_a k_{sz} - \epsilon_s k_{az}}{\epsilon_a k_{sz} + \epsilon_s k_{az}} \right|^2, T_a = 1 - R_a \quad [9.39]$$

The reflection coefficient R_s from the structure is found as the square modulus of S_{22} element of the structure S matrix. Then, the total intensity I_a transmitted into the air after N reflections is

$$I_a = I \cdot T_a \frac{1 - (R_a R_s)^N}{1 - R_a R_s} = I \cdot (1 - R_a) \frac{1 - (R_a R_s)^N}{1 - R_a R_s} \quad [9.40]$$

where I is the intensity calculated in the absence of the air–substrate interface. The intensity lost due to re-absorption in the structure is

$$I_l = I \cdot R_a (1 - R_s) \frac{1 - (R_a R_s)^N}{1 - R_a R_s} \quad [9.41]$$

The rest of the intensity is ‘guided’ by the substrate:

$$I_s = I - I_a - I_l = I \cdot (R_a R_s)^N \quad [9.42]$$

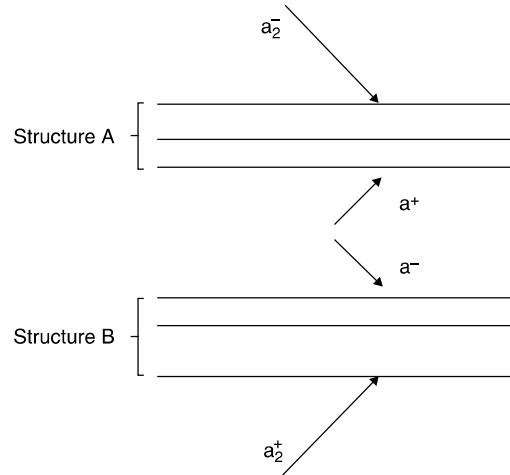
The effective number of reflections N depends on structure geometry and on wavevector projections k_x, k_y which determine the angles of light propagation in the substrate.

9.3.5 Energy dissipation

In order to trace fields in different layers we use the solution of the following problem. A structure is composed of two elements characterized by S matrices S^A and S^B , and two incident plane waves with amplitudes a_1^+ and a_2^- (Fig. 9.4). The incident waves have the same temporal and spatial frequencies, therefore, wave amplitudes a^+ and a^- between elements are found as a result of interference between all transmitted and reflected waves:

$$\begin{aligned} a^+ &= (I - S_{11}^B S_{22}^A)^{-1} (S_{21}^A a_1^+ + S_{22}^A S_{12}^B a_2^-) \\ a^- &= (I - S_{11}^B S_{22}^A)^{-1} (S_{11}^B S_{21}^A a_1^+ + S_{12}^B a_2^-) \end{aligned} \quad [9.43]$$

Thus, amplitudes $a^\pm(z)$ as well as corresponding intensity $S_i(z)$ can be rigorously determined at any point of the structure.



9.4 Two plane waves incident on a structure composed of two elements.

The intensity absorbed between planes $z = z_1$ and $z = z_2 > z_1$ in a layer of permittivity ϵ_l equals

$$I = \lim_{z \rightarrow z_2 - 0} (S_z) - \lim_{z \rightarrow z_1 + 0} (S_z) + I_d \quad [9.44]$$

where I_d is the intensity emitted by dipoles located in interval $z \in (z_1, z_2)$.

If there is a noncoherent return of the light (the case considered in the previous section) some part of the returned energy is re-absorbed in the structure. The proposed technique allows also for detailed analysis of such re-absorption. First, the returned intensity I_r is recalculated into the incident amplitude:

$$a_{TE}^- = \sqrt{\frac{2\omega\mu_0}{k_{sz}}} I_r, \quad a_{TM}^- = \sqrt{\frac{2\omega\epsilon_s}{k_{sz}}} I_r \quad [9.45]$$

Then formulae [9.43] and [9.44] are applied to calculate absorption in particular layers of the structure.

Thus, we have obtained all the necessary relations completely describing the propagation of waves in the plane-layered structures and directly applicable in numerical simulation.

9.3.6 Emission spectrum

So far all the characteristics have been calculated for a single dipole of given amplitude, polarization, frequency, and spatial position. To calculate the integral

optical characteristics of the structure one needs as pre-requisites the spectral, spatial and polarization distribution of emitting dipoles.

Contribution of the dipole radiation in different polarizations may be chosen with different weights. In most practical cases, however, a reasonable approximation is the assumption on uniform polarizations of the dipoles, and the average intensity can be expressed as the sum of the intensities emitted by the three mutually orthogonal dipoles $\mathbf{p}_1$, $\mathbf{p}_2$, $\mathbf{p}_3$:

$$|\mathbf{p}_1|^2 = |\mathbf{p}_2|^2 = |\mathbf{p}_3|^2 = \frac{1}{3}|\mathbf{p}_0|^2 \quad [9.46]$$

The first dipole is chosen to be orthogonal to wavevector $\mathbf{k}$, it emits TE-polarized waves with amplitudes

$$r_{1TE}^{\pm} = \frac{i\omega^2 \mu_0 k_0^2}{8\pi^2 k_{pz}} p_1 \quad [9.47]$$

The second dipole coincides with the projection of $\mathbf{k}$ into plane xy , the third one is parallel to the z axis. The last two dipoles emit TM-polarized waves with amplitudes

$$r_{2TM}^{\pm} = \mp \frac{i\omega k_0^2}{8\pi^2} p_2, \quad r_{3TM}^{\pm} = \frac{i\omega k_0^2 \gamma}{8\pi^2 k_{pz}} p_3 \quad [9.48]$$

An example of such spectral emission curves is taken from ref. 40. The power emitted to the substrate and to the air is also compared with calculated total effective emitted power and power losses in different layers. This is done via expressions [9.17] and [9.18] and the resulting spectral dependencies are shown in Plate II (see colour section between pages 414 and 415).

9.4 Theoretical methods in diffraction and scattering

9.4.1 Diffraction calculation

Among the methods for calculating the diffraction by one- and two-dimensional gratings, currently the most popular in practice are the Fourier Modal Method (FMM),⁴¹ also known as RCWA,⁴² the C method,⁴³ and different implementations of the FDTD method.⁴⁴ Certain progress is achieved in development of integral⁴⁵ and differential⁴⁶ methods, in the finite element method (FEM).⁴⁷ Obviously, each of these methods can find its own domain of expertise. Most efficient applications of gratings in OLEDs can be divided into two main groups.

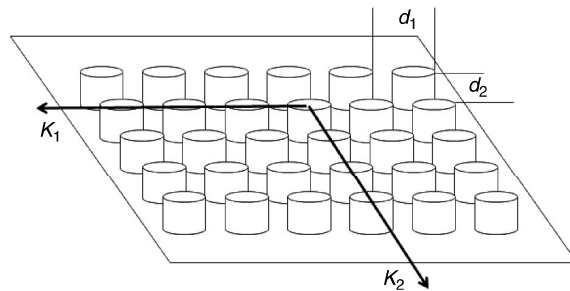
In the first group, the grating is initially made in the substrate and then reproduced throughout all layers including the metal electrode layer. This grating is usually not made very deep (several tens of nanometers) with a smooth profile (preferably, sinusoidal) so as not to perturb the electron/hole injection process. The best method for such multilayer smooth-profile grating modeling is the C

method. It is well developed for 2D gratings as well as for conical geometry of 1D gratings. The Rayleigh method which is now proved to be valid for such gratings⁴⁸ is very simple in implementation. It also gives analytical expressions for S matrix elements in the limit of small groove depth⁴⁹ which remarkably accelerates the grating calculation.

The second group combines OLEDs containing a special dielectric layer with strong periodical index (permittivity) modulation most often referred to in the literature as photonic crystals. The best accessible method for such gratings is the FMM. An important remark has to be made here. Many researchers extensively use this method though there is an immense difference between its variations in terms of accuracy and convergence. This difference concerns gratings with discontinuous permittivity and is mainly in how the normal and tangent electric field projections are developed in the Fourier basis. Without going into details, it is worth emphasizing for 2D grating the FMM implementation based on a paper by Schuster *et al.*⁵⁰ and for 1D grating the FMM modification by Lalanne *et al.*⁵¹ The FMM implemented with slicing⁵² exhibits very good accuracy and convergence for 1D gratings with arbitrary profile.

First, the following general notation is introduced relating to the diffraction grating and a two-dimensional (2D) grating of depth h periodical in the XY plane (Fig. 9.5) is considered. The grating vectors and the corresponding grating periods are $\mathbf{K}_{1,2}$ and $d_{1,2} = 2\pi/|\mathbf{K}_{1,2}|$, respectively. One-dimensional (1D) grating is periodical in one dimension and is characterized by single grating vector $\mathbf{K}$ and period $d = 2\pi/|\mathbf{K}|$. Evidently, 1D gratings are much easier to calculate and all the methods are better developed for this case. Note however that modeling 1D gratings in an OLED structure requires the general case of conical diffraction which is less considered in the literature.

In the Fourier modal method, the grating is supposed to be uniform in the vertical z direction. If this is not the case the grating layer is divided (sliced) into many sub-layers, which are then considered as uniform in the vertical direction gratings (so-called staircase approximation).



9.5 Schematic representation of a two-dimensional diffraction grating.

The diffraction solution in homogeneous layers under and above the grating can be represented by a Rayleigh-Fourier expansion. Any field component is either propagating or evanescent diffraction order. Its wavevector components in the XY plane are given by the grating equation:

$$k_{x,y}^{m_1 m_2} = k_{x,y}^{00} + m_1 K_{1x,y} + m_2 K_{2x,y}, \quad [9.49]$$

where m_1 and m_2 are diffraction orders and $k_{x,y}^{00}$ are wavevector components of the incident wave. The full wavevector projection in the XY plane is

$$\gamma^{m_1 m_2} = \sqrt{\left(k_x^{m_1 m_2}\right)^2 + \left(k_y^{m_1 m_2}\right)^2} \quad [9.50]$$

The z component of the wavevector is $k_{jz}^{m_1 m_2} = \sqrt{\omega^2 \mu_0 \epsilon_j - \left(\gamma^{m_1 m_2}\right)^2}$, $j=1,2$. Thus, the electric and magnetic field in the homogeneous medium are found by superposition of all diffraction waves:

$$\begin{bmatrix} \mathbf{E}_j \\ \mathbf{H}_j \end{bmatrix} = \sum_{m=-\infty}^{\infty} \left\{ \begin{bmatrix} \mathbf{E}_j^{m_1 m_2 +} \\ \mathbf{H}_j^{m_1 m_2 +} \end{bmatrix} \exp\left[ik_{jz}^{m_1 m_2} (z - z_j)\right] + \begin{bmatrix} \mathbf{E}_j^{m_1 m_2 -} \\ \mathbf{H}_j^{m_1 m_2 -} \end{bmatrix} \exp\left[-ik_{jz}^{m_1 m_2} (z - z_j)\right] \right\} \exp\left(ik_x^{m_1 m_2} x + ik_y^{m_1 m_2} y\right) \quad [9.51]$$

As in Section 9.3.1, the field of a plane wave is characterized by its tangent electric and magnetic field amplitudes [9.16] and [9.17]:

$$\begin{bmatrix} E_{jx}^{m_1 m_2 \pm} \\ H_{jx}^{m_1 m_2 \pm} \end{bmatrix} = \begin{bmatrix} \frac{k_y^{m_1 m_2}}{\gamma^{m_1 m_2}} & \pm \frac{k_x^{m_1 m_2} k_{jz}^{m_1 m_2}}{\omega \epsilon_j \gamma^{m_1 m_2}} \\ \pm \frac{k_x^{m_1 m_2} k_{jz}^{m_1 m_2}}{\omega \mu_0 \gamma^{m_1 m_2}} & \frac{k_y^{m_1 m_2}}{\gamma^{m_1 m_2}} \end{bmatrix} \begin{bmatrix} a_{jTE}^{m_1 m_2 \pm} \\ a_{jTM}^{m_1 m_2 \pm} \end{bmatrix}, \quad [9.52]$$

$$\begin{bmatrix} E_{jy}^{m_1 m_2 \pm} \\ H_{jy}^{m_1 m_2 \pm} \end{bmatrix} = \begin{bmatrix} -\frac{k_x^{m_1 m_2}}{\gamma^{m_1 m_2}} & \mp \frac{k_y^{m_1 m_2} k_{jz}^{m_1 m_2}}{\omega \epsilon_j \gamma^{m_1 m_2}} \\ \pm \frac{k_y^{m_1 m_2} k_{jz}^{m_1 m_2}}{\omega \mu_0 \gamma^{m_1 m_2}} & -\frac{k_x^{m_1 m_2}}{\gamma^{m_1 m_2}} \end{bmatrix} \begin{bmatrix} a_{jTE}^{m_1 m_2 \pm} \\ a_{jTM}^{m_1 m_2 \pm} \end{bmatrix}, \quad [9.53]$$

$$\begin{bmatrix} E_{jz}^{m_1 m_2 \pm} \\ H_{jz}^{m_1 m_2 \pm} \end{bmatrix} = \begin{bmatrix} 0 & \frac{\gamma^{m_1 m_2}}{\omega \epsilon_j} \\ -\frac{\gamma^{m_1 m_2}}{\omega \mu_0} & 0 \end{bmatrix} \begin{bmatrix} a_{jTE}^{m_1 m_2 \pm} \\ a_{jTM}^{m_1 m_2 \pm} \end{bmatrix}. \quad [9.54]$$

The solution of the diffraction problem is represented by the S matrix relating all the diffracted wave amplitudes to the incident wave amplitudes:

$$\begin{bmatrix} a_{1TE}^{m_1 m_2 -} \\ a_{1TM}^{m_1 m_2 -} \\ a_{2TE}^{m_1 m_2 +} \\ a_{2TM}^{m_1 m_2 +} \end{bmatrix} = S \begin{bmatrix} a_{1TE}^{m_1 m_2 +} \\ a_{1TM}^{m_1 m_2 +} \\ a_{2TE}^{m_1 m_2 -} \\ a_{2TM}^{m_1 m_2 -} \end{bmatrix} \quad [9.55]$$

The FMM and the C method are capable to deliver the S matrix of a given grating. The size of this S matrix depends on the number of diffraction orders taken into account. Calculating the dipole emission in an OLED structure containing a grating layer is done in the following way. Integration in the reciprocal k vector basis is made in coordinates $\gamma\varphi_{1,2}$ coinciding with grating vectors $\mathbf{K}_{1,2}$. Amplitudes of all waves which wavevector projections on the XY plane differ by some integer number of grating vectors $\mathbf{K}_1$ and $\mathbf{K}_2$ are coupled by the grating and can no longer be considered independently. This is why dipole [9.1] is represented in the following way:

$$\begin{aligned} \mathbf{p}(\mathbf{r}, t) &= \delta(z - z_0) \exp(-i\omega t) \frac{\mathbf{p}_0}{(2\pi)^2} J \int_{-\infty}^{\infty} \int_{-\infty}^{\infty} \exp[ik_x (x - x_0) + ik_y (y - y_0)] d\xi_1 d\xi_2 \\ &= \delta(z - z_0) \exp(-i\omega t) \frac{\mathbf{p}_0}{(2\pi)^2} J \int_{-1/2}^{1/2} \int_{-1/2}^{1/2} \sum_{m_1=-\infty}^{\infty} \sum_{m_2=-\infty}^{\infty} \exp[ik_x^{m_1 m_2} (x - x_0) \\ &\quad + ik_y^{m_1 m_2} (y - y_0)] d\xi_1 d\xi_2 \end{aligned} \quad [9.56]$$

where $k_{x,y}^{00}$ is defined as

$$k_{x,y}^{00} = \xi_1 K_{1x,y} + \xi_2 K_{2x,y} \quad [9.57]$$

and Jacobian J as

$$J = \frac{\partial(k_x, k_y)}{\partial(\xi_1, \xi_2)} = K_{1x} K_{2y} - K_{1y} K_{2x} \quad [9.58]$$

Thus, at any fixed pair of vector projections k_x^{00} and k_y^{00} under integral [9.56] the dipole radiates all diffraction orders with amplitudes:

$$r_{TE}^{m_1 m_2 \pm} = \frac{i\omega^2 \mu_0 k_0^2}{8\pi^2 \gamma^{m_1 m_2} k_{pz}^{m_1 m_2}} \left(k_y^{m_1 m_2} p_{0x} - k_x^{m_1 m_2} p_{0y} \right) \exp(-ik_x^{m_1 m_2} x_0 - ik_y^{m_1 m_2} y_0) \quad [9.59]$$

$$r_{TM}^{m_1 m_2 \pm} = \frac{i\omega k_0^2}{8\pi^2} \left(\mp \frac{k_x^{m_1 m_2}}{\gamma^{m_1 m_2}} p_{0x} \mp \frac{k_y^{m_1 m_2}}{\gamma^{m_1 m_2}} p_{0y} + \frac{\gamma^{m_1 m_2}}{k_{pz}^{m_1 m_2}} p_{0z} \right) \exp(-ik_x^{m_1 m_2} x_0 - ik_y^{m_1 m_2} y_0) \quad [9.60]$$

All needed S matrices are calculated in the next step. The S matrix of any part of the OLED which includes the grating layer has a dense structure because of non-zero coupling between all diffraction orders and polarizations. The S matrix of any multilayer free from gratings is a block-diagonal matrix where each small block is the S matrix of the multilayer calculated for the corresponding diffraction order and polarization. Evidently, the latter case can be calculated much faster. This is why the S matrices of multilayers without gratings are first calculated and then combined with the S matrices of grating layers. The rules of S matrix combinations [9.27] remain the same even for more complicated diffraction S matrices. Effective amplitudes $a_{TE,TM}^{(eff)m_1m_2\pm}$ in the layer containing the dipole are found by formulae similar to [9.32]:

$$\begin{pmatrix} a_{TE}^{(eff)m_1m_2+} \\ a_{TM}^{(eff)m_1m_2+} \end{pmatrix} = \left(I - S_{22}^B S_{11}^A \right)^{-1} \left[S_{22}^B \begin{pmatrix} r_{TE}^{m_1m_2-} \\ r_{TM}^{m_1m_2-} \end{pmatrix} + \begin{pmatrix} r_{TE}^{m_1m_2+} \\ r_{TM}^{m_1m_2+} \end{pmatrix} \right] \quad [9.61]$$

$$\begin{pmatrix} a_{TE}^{(eff)m_1m_2-} \\ a_{TM}^{(eff)m_1m_2-} \end{pmatrix} = \left(I - S_{11}^A S_{22}^B \right)^{-1} \left[S_{11}^A \begin{pmatrix} r_{TE}^{m_1m_2+} \\ r_{TM}^{m_1m_2+} \end{pmatrix} + \begin{pmatrix} r_{TE}^{m_1m_2-} \\ r_{TM}^{m_1m_2-} \end{pmatrix} \right]$$

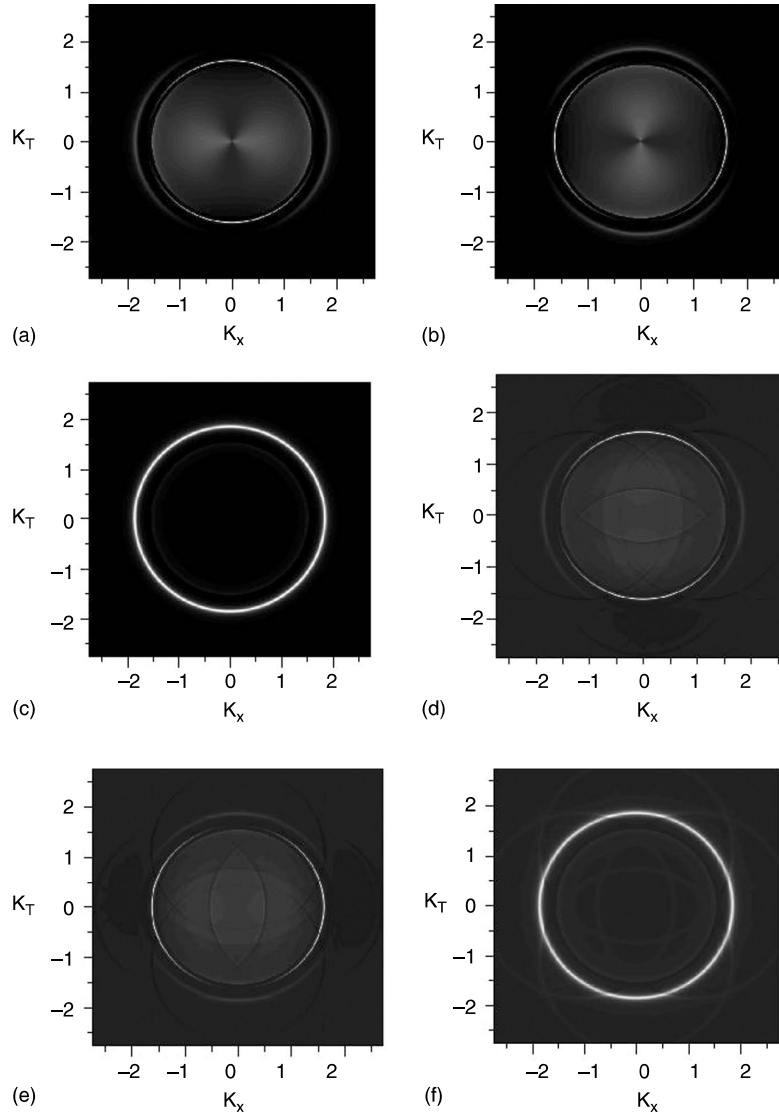
The output amplitudes are calculated by analogy to [9.34] and [9.38]:

$$\begin{pmatrix} a_{sTE}^{m_1m_2+} \\ a_{sTM}^{m_1m_2+} \end{pmatrix} = S_{21}^A \begin{pmatrix} a_{TE}^{(eff)m_1m_2+} \\ a_{TM}^{(eff)m_1m_2+} \end{pmatrix} \quad [9.62]$$

$$\begin{pmatrix} a_{sTE}^{m_1m_2-} \\ a_{sTM}^{m_1m_2-} \end{pmatrix} = S_{12}^B \begin{pmatrix} a_{TE}^{(eff)m_1m_2-} \\ a_{TM}^{(eff)m_1m_2-} \end{pmatrix} \quad [9.63]$$

The intensity in such a set of coupled diffracted waves propagates independently by each wave. This means that the total intensity is found as an arithmetic sum of intensities in all the diffracted waves using formula [9.35]. The same arguments are valid for intensity calculation in the interior of the multilayer (formula [9.30]), as well as for losses inside the layer and for energy emitted by the dipole (formula [9.33]). The important difference is at the integration stage. Now the integration is over intervals $\xi_1 \in (-1/2, 1/2)$, $\xi_2 \in (-1/2, 1/2)$, and all corresponding vector projections $k_{x,y}^{m_1m_2}$ as well as output angles $\theta = \arcsin(\gamma^{m_1m_2}/k_s)$ and $\varphi = \arccos(k_x^{m_1m_2}/\gamma^{m_1m_2})$ are found from [9.49], [9.50] and [9.57].

An example of angular intensity redistribution by grating is plotted in Fig. 9.6. The 2D sinusoidal grating with full groove depth 30 nm was reproduced through all multilayers. Figure 9.6 compares the intensity distribution in the k_x, k_y plane for a planar (Fig. 9.6a–c) and undulated structure (Fig. 9.6d–f) with three different dipole polarizations. Bright lines correspond to excitation of the non-radiative guiding modes. It is evident that the grating couples an important part of this energy into radiative modes lying in the center of the k_x, k_y diagram.



9.6 Intensity distribution in k plane for different dipole orientations. Planar structure: (a) p_x ; (b) p_y ; (c) p_z . Structure with sinusoidal interfaces: (d); p_x ; (e) p_y ; (f) p_z .

Calculation of the diffraction of the S matrix of a 2D grating is a time- and memory-consuming task. In almost all known rigorous methods the calculation time grows as the cube and the consumed memory as the square of the number of diffraction orders taken into account. This is why new implementation of the

Generalized Source Method (GSM)⁵³ is a very promising breakthrough of this limit. The GSM rigorously calculates 2D gratings with time and memory linearly proportional to the number of diffraction orders.

9.4.2 Light scattering modelling

Analysing numerical methods used in light scattering modelling first highlights the Mie theory,⁵⁴ which describes the scattering of light waves on a sphere and was developed in the early twentieth century. However, due to the fact that it is essentially the only exact analytical result on the scattering of electromagnetic waves, it is widely used nowadays in practice. In addition, the Mie theory is the basis of a number of numerical models describing the scattering of light by individual particles, whose shape is not very different from spherical.

In many experimental studies of light scattering in nanostructured systems where the authors have a reason to make the assumption that the material is a homogeneous matrix with spherical inclusions of another substance, the Mie solution is used as the first possible estimate for characterization of optical properties of the medium.^{55–57} The key parameters of the problem are the radius and material of the sphere and the environment material, and these parameters can be arbitrary without approximations. Detailed derivation can be found in the original work of Mie⁵⁴ and in a number of classical books.^{58–59} Here, only some formulae and ideas are given which are necessary for the survey.

The Mie solution is obtained by substituting solutions of the scalar Helmholtz equation in spherical coordinates, expressed in terms of spherical Bessel functions and associated Legendre functions $P_n^m(\cos \theta)$:

$$\psi_{nm}(r, \theta, \varphi) = z_n(kr)P_n^m(\cos \theta)\exp(im\varphi) \quad [9.64]$$

The vector field solution can be constructed by vector spherical harmonics defined as

$$\mathbf{M}_{nm}(r, \theta, \varphi) = \nabla \times (\psi_{nm} \mathbf{r}), \quad \mathbf{N}_{nm}(r, \theta, \varphi) = \frac{i}{k} \nabla \times \mathbf{M}_{nm} \quad [9.65]$$

A general solution for the fields $\mathbf{E}$ and $\mathbf{H}$ is found as a superposition of vector harmonics, with substitution of $z_n(kr)$ by spherical Bessel functions or spherical Hankel functions of first or second kind, respectively:

$$\mathbf{E}(\mathbf{r}) = \sum_{n=0}^{\infty} \sum_{m=-n}^n \left[a_{nm}^e \mathbf{M}_{nm}(\mathbf{r}) + a_{nm}^h \mathbf{N}_{nm}(\mathbf{r}) \right], \quad [9.66]$$

$$\mathbf{H}(\mathbf{r}) = \sqrt{\frac{\varepsilon}{\mu}} \sum_{n=0}^{\infty} \sum_{m=-n}^n \left[-a_{nm}^e \mathbf{N}_{nm}(\mathbf{r}) + a_{nm}^h \mathbf{M}_{nm}(\mathbf{r}) \right]. \quad [9.67]$$

Physically, functions $j_n(kr)$ describe the solution within the sphere, and the functions $z_n^{(1,2)}(kr)$ meet outgoing and incoming spherical waves outside the sphere.

Incident plane wave propagating in the direction defined by angles θ_{inc} and φ_{inc} is represented via spherical harmonics using the addition formula²⁷:

$$\exp\left[i\mathbf{k}\left(\theta_{inc}, \varphi_{inc}\right) \cdot \mathbf{r}\right] = \sum_{n=0}^{\infty} \sum_{m=-n}^n (2n+1) \frac{(n-m)!}{(n+m)!} i^n j_n(kr) P_n^m(\cos \theta_{inc}) P_n^m(\cos \theta) \exp\left[im(\varphi - \varphi_{inc})\right] \quad [9.68]$$

Finally, all the coefficients at incident spherical harmonics are found determining fields [9.66] and [9.67]:

$$a_{mn}^{(inc)e} = \left[-\sin \theta_{inc} P_n^{m'}(\cos \theta_{inc}) a_{TE} + \frac{im P_n^m(\cos \theta_{inc})}{\sin \theta_{inc}} \sqrt{\frac{\mu_0}{\varepsilon}} a_{TM} \right] \frac{(2n+1)(n-m)!}{n(n+1)(n+m)!} i^n \exp(-im\varphi_{inc})$$

$$a_{mn}^{(inc)h} = - \left[\frac{im P_n^m(\cos \theta_{inc})}{\sin \theta_{inc}} a_{TE} + \sin \theta_{inc} P_n^{m'}(\cos \theta_{inc}) \sqrt{\frac{\mu_0}{\varepsilon}} a_{TM} \right] \frac{(2n+1)(n-m)!}{n(n+1)(n+m)!} i^n \exp(-im\varphi_{inc}) \quad [9.69]$$

The advantage of such field representation in the Mie theory is that each harmonic is transmitted and reflected on the spherical interface of radius R in a single harmonic with the same indices m, n . Reflection coefficients determining scattered waves are

$$r_{mn}^e = \frac{a_{mn}^{(sc)e}}{a_{mn}^{(inc)e}} = \frac{j_n(k_1 R) \tilde{j}_n(k_2 R) - j_n(k_2 R) \tilde{j}_n(k_1 R)}{h_n^{(1)}(k_2 R) \tilde{j}_n(k_1 R) - j_n(k_1 R) \tilde{h}_n^{(1)}(k_2 R)} \quad [9.70]$$

$$r_{mn}^h = \frac{a_{mn}^{(sc)h}}{a_{mn}^{(inc)h}} = \frac{\varepsilon_1 j_n(k_1 R) \tilde{j}_n(k_2 R) - \varepsilon_2 j_n(k_2 R) \tilde{j}_n(k_1 R)}{\varepsilon_2 h_n^{(1)}(k_2 R) \tilde{j}_n(k_1 R) - \varepsilon_1 j_n(k_1 R) \tilde{h}_n^{(1)}(k_2 R)} \quad [9.71]$$

where

$$\tilde{z}_n(x) = z_n(x) + x z_n'(x) \quad [9.72]$$

Different authors modified the Mie solution for ellipsoidal particles⁶⁰ and particles with shells.^{61,62} From the standpoint of real system simulation, these solutions are interesting mainly as a reference for testing numerical methods.

To solve the problem of scattering of electromagnetic waves by objects whose shapes differ only a little from spherical, different efficient methods are developed such as the Separation Variable Method (SVM).⁶³ These methods are well suited for particles whose shape is not far from spherical, especially if they

have the axial symmetry. Similarly to the Mie theory they deal with fields represented by vector spherical harmonics and relate scattered amplitudes $a_{mn}^{(sc)e,h}$ with incident $a_{mn}^{(inc)e,h}$. Such a relation can be written in a matrix form

$$\begin{pmatrix} a_{mn}^{(sc)e} \\ a_{mn}^{(sc)h} \end{pmatrix} = T \begin{pmatrix} a_{mn}^{(inc)e} \\ a_{mn}^{(inc)h} \end{pmatrix} \quad [9.73]$$

Note that the so-called T matrix in scattering theory is quite different from the transfer matrix (T matrix) used in the multilayer analysis. It can be considered rather as an analogue to element S^{22} of the S matrix.

An important class of numerical methods, which are well suited for the study of individual particles with a smooth surface, are the methods of surface integrals. The most popular in this class is the null-field method (NFM).²⁷ The required surface integral equation for the NFM is obtained by integrating [9.65] with the help of tensor Green's function of the free space,⁶⁴ and then to use well-known Green's identities.⁶⁵ As a result, we obtain the equation relating the field throughout the space with a field on the surface of the scattering object. This equation is solved in two stages. First the null-field equation is solved and unknown tangential field components at the particle surface are expressed through the incident field. Then, the scattered field is determined outside the scattering particle. Note that the incident field and the scattered field are expressed in vector spherical harmonics, and therefore the problem reduces to solving the matrix equations for the coefficients of the T matrix [9.73]. This is why the NFM is also often called the T matrix method.⁶⁶

The above approaches were designed to study the scattering by a single particle. There is a way to extend them to calculate groups comprising many particles of different shape. The idea is to rigorously take into account the re-scattered field. Let T_i be the T matrix of the i -th particle centered at position, $\mathbf{r}_i$. It relates the coefficients at radiated spherical harmonics to those of incident ones. Evidently, all the harmonics are written in a spherical coordinate system originated at $\mathbf{r}_i$. Using the addition theorems (see for more details ref. 67), the radiated harmonics can be rewritten in another spherical coordinate system originated at a different point $\mathbf{r}_j$ related with the center of the j -th particle. When these two particles are separate the harmonics radiated by the i -th particle with coefficients $a_{imn}^{(sc)e,h}$ are transformed to the harmonics incident to the j -th particle with coefficients $a_{jmn}^{(inc)e,h}$. Such transformation is given by matrix relation:

$$\begin{pmatrix} a_{jmn}^{(inc)e} \\ a_{jmn}^{(inc)h} \end{pmatrix} = A_{ji} \begin{pmatrix} a_{imn}^{(sc)e} \\ a_{imn}^{(sc)h} \end{pmatrix} \quad [9.74]$$

Combining the inputs from all the particles with the incident field and applying [9.73] gives the following matrix equation on the scattered field:

$$\begin{pmatrix} a_{jmn}^{(sc)e} \\ a_{jmn}^{(sc)h} \end{pmatrix} = T_j \left[\begin{pmatrix} a_{jmn}^{(inc)e} \\ a_{jmn}^{(inc)h} \end{pmatrix} + \sum_{i \neq j} A_{ji} \begin{pmatrix} a_{imn}^{(sc)e} \\ a_{imn}^{(sc)h} \end{pmatrix} \right] \quad [9.75]$$

Finally, the T matrix of the group is found:

$$T = BM^{-1}C \quad [9.76]$$

relating the scattered and incident harmonics written in a system with some origin $\mathbf{r}_0$:

$$\begin{pmatrix} a_{mn}^{(sc)e} \\ a_{mn}^{(sc)h} \end{pmatrix} = T \begin{pmatrix} a_{mn}^{(inc)e} \\ a_{mn}^{(inc)h} \end{pmatrix} \quad [9.77]$$

where B is the line of matrices, B_i transforming scattered harmonics from the system related with $\mathbf{r}_i$ to that related with $\mathbf{r}_0$:

$$\begin{pmatrix} a_{mn}^{(sc)e} \\ a_{mn}^{(sc)h} \end{pmatrix} = B_i \begin{pmatrix} a_{mn}^{(sc)e} \\ a_{mn}^{(sc)h} \end{pmatrix} \quad [9.78]$$

Column C is composed of products $T_j C_j$, where matrix C_j transforms incident harmonics from the system related with $\mathbf{r}_0$ to that related with $\mathbf{r}_j$:

$$\begin{pmatrix} a_{jmn}^{(inc)e} \\ a_{jmn}^{(inc)h} \end{pmatrix} = C_j \begin{pmatrix} a_{mn}^{(inc)e} \\ a_{mn}^{(inc)h} \end{pmatrix} \quad [9.79]$$

Matrix M is defined as follows:

$$M_{ji} = \begin{cases} I, & i = j \\ -T_j A_{ji}, & i \neq j \end{cases} \quad [9.80]$$

The next important class of methods includes volume integral methods: the volume integral equation method (VIEM),⁶⁸ the discrete dipole approximation (DDA),^{69,70} and the general source method.⁷¹ As compared with surface methods, they are not limited to simple forms of scattering objects. However, these methods have less control over the accuracy of the obtained solution, especially in the case of metal inclusions.

In the method of VIE, the scattering particle is defined by the volume distribution of the permittivity, which is modified due to presence of the particle:

$$\varepsilon(\mathbf{r}) = \varepsilon_0 + \Delta\varepsilon(\mathbf{r}) \quad [9.81]$$

This makes it possible to rewrite the wave equation as

$$\nabla \times \nabla \times \mathbf{E} + \varepsilon_0 \omega^2 \mu_0 \mathbf{E} = -\Delta\varepsilon \omega^2 \mu_0 \mathbf{E} \quad [9.82]$$

and look for a solution in the form of volume integral

$$\mathbf{E} = \mathbf{E}^{inc} + \int_V k_0^2 \Delta\varepsilon \mathbf{G}_0(\mathbf{r}, \mathbf{r}') \mathbf{E}(\mathbf{r}') dV' \quad [9.83]$$

where the integration is over the volume of the scattering particle. In numerical treatment of the implicit equation [9.83], the problem is reduced to resolving a

linear algebraic system. It should be noted that the integration of [9.83] is complicated by the presence of singularity in the Green function.⁷²

Very similar to the method of volume integral equations are the DDA and its various modifications, such as the method of moments (MOM),⁷³ and the coupled dipole approximation (CDA).⁷⁴ In the DDA the scattering particle is represented as a set of discrete dipoles interacting one with another and with the incident field. This relationship can be written in the form of field equations at the points where the dipoles are located and is similar to the system obtained in the VIEM:

$$\left(\alpha_i\right)^{-1} \mathbf{P}_i + \sum_{j \neq i} \mathbf{A}_{ij} \mathbf{P}_j = \mathbf{E}_i^{inc} \quad [9.84]$$

where $\mathbf{P}_i$ is the i -th dipole polarization, $\mathbf{E}_i^{inc}$ is the incident field at the position of the i -th dipole, α_i is the i -th dipole polarizability, $\mathbf{A}_{ij}$ is the matrix expressing the field emitted by the j -th dipole at the location of the i -th dipole. In comparison with the VIEM, the DDA has no problems with the integration of singularities, however, it requires a set of free coefficients to define polarizabilities α_i . The most commonly used coefficients are given by the Clausius-Mossotti formula.⁷⁵ The accuracy of the method depends on the choice of the coefficients,^{76,77} and usually is less than the accuracy given by the VIEM for relatively large (of the order of several hundred nanometers) scattering particles. Figure 9.7 shows scattering on a group of 25 spheres calculated by the GSM.⁷⁸

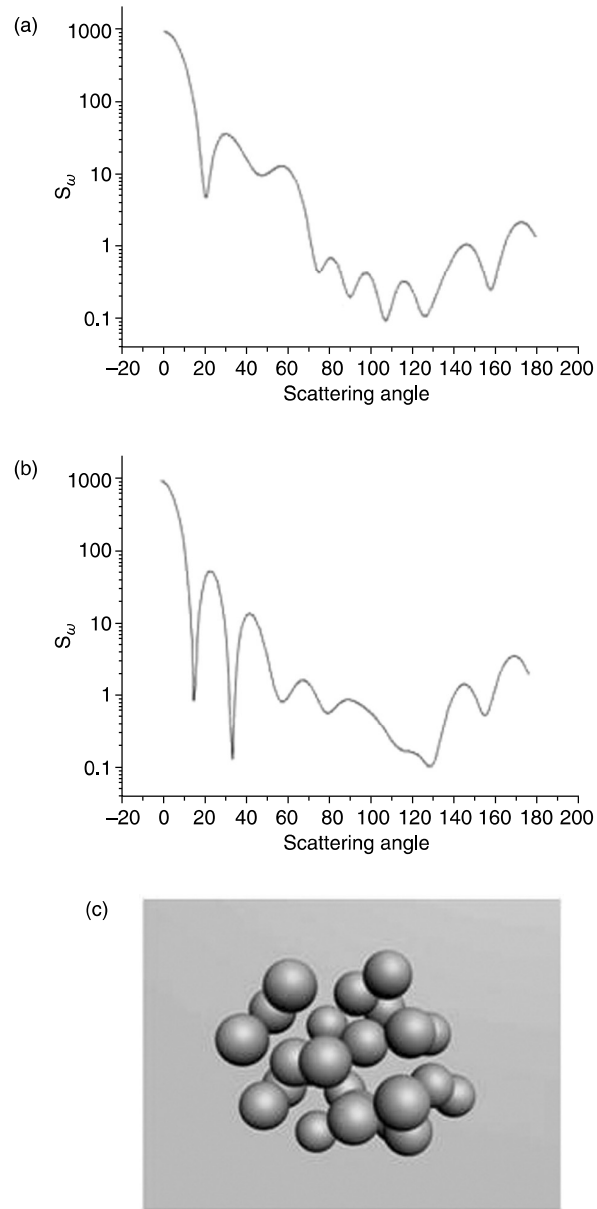
An important advantage of the methods of volume integral equation is the ability to analyze scattering from particles with very complicated form, but these methods are more suitable for the study of purely dielectric media. In the case of metal inclusions, fields are concentrated at the metal–dielectric interface, and this situation is better interpreted by the surface integral methods.

9.4.3 Scattering layer in a multilayer

The scattering layers in OLEDs are in an optical contact with the emitting multilayer structure. Therefore, a realistic model has to take into account all reflections of scattered light from the multilayer. The scattered field [9.24] and [9.28] is defined in the form of the vector spherical harmonics.^{18,19} It can also be transformed into a plane-wave basis. This operation is somewhat inverse to that given by Eq. [9.20]. First, the inverse formula is established:

$$j_n(kr)P_n^m(\cos\theta)\exp(im\varphi) = \frac{1}{4\pi i^n} \int_0^{2\pi} \int_0^\pi P_n^m(\cos\beta)\exp(im\alpha)\exp[i\mathbf{k}(\beta,\alpha) \cdot \mathbf{r}] \sin\beta d\beta d\alpha \quad [9.85]$$

Each spherical harmonic related with function $j_n(kr)$ is represented as an integral superposition of plane propagated waves. This is not valid anymore for scattered harmonics related with function $h_n^{(1)}(kr)$. Devaney⁷⁹ has proposed generalized plane waves



9.7 (a–c) Far field scattering diagram of a plane wave at $\lambda=550$ nm on an ensemble of 25 spheres of diameter 100 nm. Example is taken from ref. 78.

$$Q(\mathbf{k}, \beta, \alpha, \mathbf{r}) = \sum_{n=0}^{\infty} \sum_{m=-n}^n \frac{(2n+1)(n-m)!}{2(n+m)!} i^m h_n^{(1)}(kr) P_n^m(\cos \beta) P_n^m(\cos \theta) \exp[im(\varphi - \alpha)] \quad [9.86]$$

They are used to express scattered spherical harmonics in a way similar to integral [9.85]:

$$h_n^{(1)}(kr) P_n^m(\cos \theta) \exp(im\varphi) = \frac{1}{2\pi i^n} \int_0^{2\pi} \int_0^\pi P_n^m(\cos \beta) \exp(im\alpha) Q(\mathbf{k}, \beta, \alpha, \mathbf{r}) \sin \beta d\beta d\alpha \quad [9.87]$$

Such generalized plane waves represent both propagating ($\gamma < k$) and evanescent ($\gamma > k$) plane waves. Detailed description can be found in ref.79.

In fact, rigorous analysis of scattered field transformation to plane waves is not an easy issue. This is why the existing implementations use different strong approximations: not taking into account the back-scattering and reflection from the emitting structure, disregarding evanescent wave fields, etc. An alternative way of introducing the scattering layer which allows for avoiding such approximations is presented in the next section.

9.4.4 Scattering layer as a quasi-periodic structure

The problem is very complicated and, therefore, the method of its solution should be optimized as much as possible, even taking into account the capabilities of modern computers. This applies to both the calculation speed and the consumed computer memory. Most approaches that calculate the scattering on nanoparticles use the three-dimensional (3D) coordinate space. It turns out however that working in the reciprocal Fourier space one can consider orders of magnitude a few points lower to obtain the solution with the same accuracy. The second advantage is that in the reciprocal k -vector space the field is yet decomposed into plane waves. This signifies that such field solution is ready to be used in the frame of the S matrix technique and, hencefore, can be easily combined with that of a multilayer structure.

In numerical implementation, the k -vector space is discretized and truncated. The infinite continuum of k -vectors in the k_x, k_y plane is represented by some finite set. Moreover, these vectors form an equidistant mesh in the k_x, k_y plane in order to meet requirements of fast numerical techniques that implicitly use translation properties of the k -space. Such equidistant spectrum corresponds to a periodical function in the coordinate space. Thus, scattering on the real structure becomes diffraction on a virtual periodic structure. Such approximation is not very strong. Indeed, near the emitting source the scatterer remains nearly the same; all important changes concern those parts of the scattering layer that are far from the dipole and do not 'see' much its radiation. Some collective effects due to pseudo-periodicity can exist, however. Several authors propose to introduce perfectly matched layers (PML) between different grating periods to avoid such effects.⁸⁰

Starting from this point the scattering layer is considered as a 2D grating and the diffraction is calculated by one of the methods presented in Section 9.4.1. If the scattering layer is a pure mixture of dielectrics, the most common of the currently available methods is the FMM. However, the FMM is hardly applicable to the problem having very large computational complexity. The new implementation of the GSM⁵³ runs much faster, needs less memory and allows for calculating more complicated structures.

9.5 Analysis of OLED modes

OLED multilayers with permittivities different from that of their environment can be considered as planar cavities exhibiting spatial and spectral resonances. Such resonances are plasmons,⁸¹ guided,^{82,83} and leaky modes.⁸⁴ Detailed study of resonant solutions is necessary for two main reasons. First, because of their importance in connection with the output radiation efficiency of OLEDs. The modes store quite a lot of energy in comparison with the radiated energy. The second reason is rather technical and is related to all field and intensity responses exhibiting singularities near the resonances. This complicates numerical integration and leads to unpredictable errors. To avoid such pitfalls we propose a technique which carefully treats modal resonances.

Representation of solutions of Maxwell's equations as a superposition of modes in the waveguide structure is a standard electromagnetic approach. The principal issue in any modal method is the ability to calculate all eigenmodes of the structure. Such an algorithm should be fast, stable, precise, and capable of finding all the modes. All these requirements are satisfied in the method based on two different techniques. The first technique was originally designed for the analysis of propagating modes.⁸⁵ It also can be effectively applied to calculate plasmons and leaky modes in lossless structures. The algorithm is based on calculating the exact number of propagating modes in a given spatial interval of propagating constants. This ensures resolution of very close modes in structures that exhibit very weak coupling between the modes.

The second technique applies to structures with losses as well as to structures comprising gratings and scattering layers.⁸⁶ Leaky modes are characterized by complex propagation constants. They can be found as coordinates of poles in the field response to excitation by a periodic source located within or near the waveguide structure.⁸⁵ The approximate position of the pole is found by the first technique, and then refined using the method proposed in ref.⁸⁶. First, the structure is analyzed without loss, and then the exact coordinates of the poles corresponding to the real structure are found. At this stage, the propagation constants of degenerate modes and modes near the cutoff frequencies are very carefully calculated. The proposed algorithm also allows the precise modal field distribution needed to calculate the intensity integrals.

As from this point we suppose that all the OLED modes together with their modal fields are well defined. The complex (in general) modal propagation constant β_p gives the complex coordinates of the corresponding pole in the optical response. In an isotropic multilayer, value β_p is the same in all propagation directions. In structures with gratings and scattering layers it depends on propagation angle φ .

We fix some angle φ and get $k_x = \gamma \cos \varphi$, $k_y = \gamma \sin \varphi$. Consider an element of a resulting S matrix comprising singular parts that correspond to the modal poles. These parts can be extracted from the field amplitude response

$$a(\gamma, \varphi) = \sum_m \frac{k_0 a_m(\varphi)}{\gamma - \beta_{pm}(\varphi)} + a^{(reg)}(\gamma, \varphi) \quad [9.88]$$

where $a_m(\varphi)$ is the m -th mode amplitude and $a^{(reg)}(\gamma, \varphi)$ is a regular part of the response which is free from singularities. An elegant and fast numerical method of such extraction giving precise values of $\beta_{pm}(\varphi)$ and $a_m(\varphi)$ is developed in ref. 86. Note that all the poles $\beta_{pm}(\varphi)$ are reproduced with some amplitudes $a_m(\varphi)$ throughout all the resulting plane wave amplitudes. Numerical integration of regular parts of expressions containing amplitude [88] is made with a standard mesh. Near each modal resonance with center at $\gamma = \text{Re}[\beta_{pm}(\varphi)]$ and full width at half of maximum $\Delta\gamma = 2\text{Im}[\beta_{pm}(\varphi)]$ the mesh has to be adjusted to integrate the resonance peak with the needed accuracy.

When the OLED includes a grating layer, the modal resonances are reproduced in all the diffraction orders and each modal field is periodically modified. This is why all the modes will be represented through the corresponding diffraction orders in the integration interval.

9.6 References

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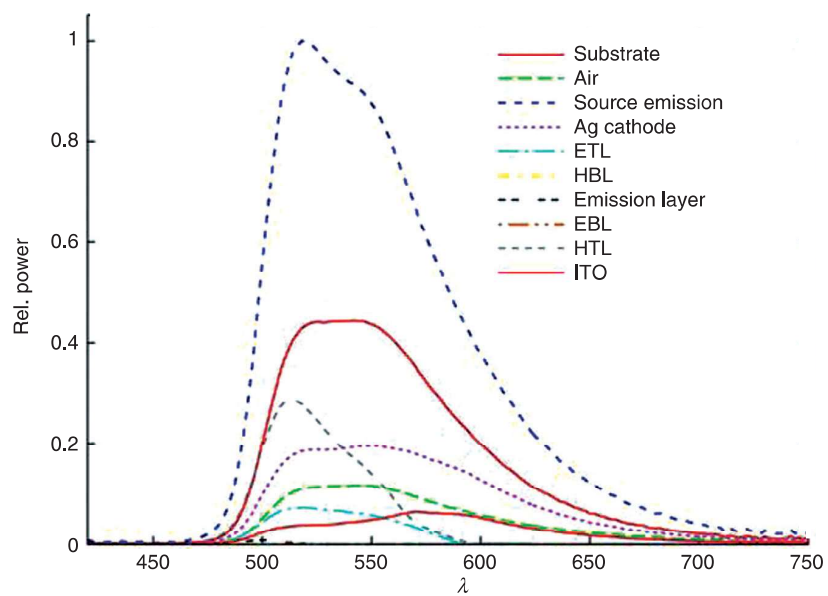


Plate II (Chapter 9) Effective emission, outgoing power and losses in each layer of the OLED structure. Example is taken from paper by Setz *et al.*[40].

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Abstract: This chapter provides an overview of the road map used to tune the colour and efficiency of organic light-emitting devices (OLEDs). A comprehensive introduction to the potential of OLED technology is first provided. Then attention is given to one way to obtain a multi-emission by a single phosphor, making use of platinum(II) complexes as phosphorescent emitters. OLEDs prepared using highly luminescent Pt(II) complexes containing cyclometallating bidentate and terdentate ligands are presented. These complexes with square planar configuration often lead to stacking and formation of luminescent aggregates. A brief description of the nature of these bimolecular excited states is reported. Taking advantage of this behaviour, many types of OLEDs, such as White OLED (WOLED), Near-InfraRed OLED (NIROLED) and Plant Growth OLED (PGOLED), are shown. Such devices fulfil the requirements to become an important part of 'green photonics'.

Key words: green photonics, OLED, electroluminescence, luminescence, phosphorescence, Pt complex, excimer, dimer, exciplex, WOLED, NIROLED, PGOLED.

10.1 Introduction

The world is coming to realise that solid-state lighting offers the promise of a green energy-saving technology. White organic LEDs (WOLEDs) are poised to fulfil that promise offering exciting new illumination forms and functionalities. Interest in the application of WOLEDs technology for general solid-state lighting applications and flat panel display backlights has been progressively increasing.¹⁻³ The power efficiency of WOLEDs, though still lower than that of inorganic LEDs, has steadily increased over the past ten years. OLED laboratory demonstrations have already achieved 30–60 lm/W, which is more than twice that of a typical incandescent light bulb (15 lm/W) and similar to the fluorescent bulbs (50 to 75 lm/W). In contrast to their inorganic semiconductor counterparts, OLEDs rely on electroluminescence (EL) from organic molecules to generate light. By tailoring the composition of the organic material, it is possible to create devices that emit red, green, blue or collectively white light when electrically driven. Today's state-of-the-art WOLEDs are able to offer 100 lm/W at 1000 cd/m² and high colour-rendering index (CRI)

* This chapter is dedicated to the memory of Professor Jan Kalinowski, who died on 18 December 2010.

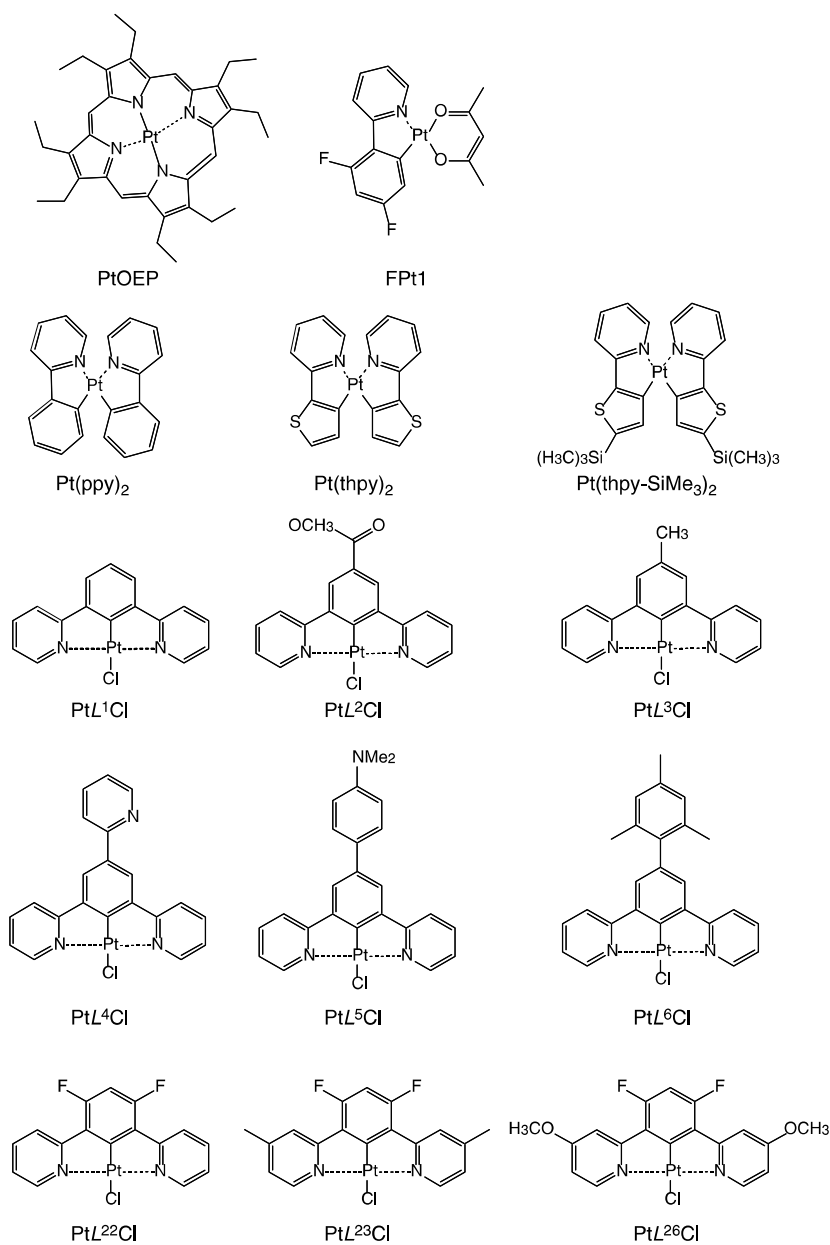
reaching 90 in a small device. It is anticipated that phosphorescent (PH) OLED technology will be able to break the 150 lm/W value by 2015. So far, PHOLEDs with active areas that are up to 25 cm² and 0.7 mm thick have been reported. Currently high-conductivity organic materials allow the operating voltage of PHOLEDs to be kept below 4 V. An LT50 index (the time taken for light output to decrease by 50% when the device is driven at a constant current) of 10 000 hours has been achieved on the laboratory scale (2 mm²) for warm-WOLED with an initial luminance of 1000 cd/m². This level of performance makes PHOLEDs very attractive for niche lighting applications such as night lights.

Meanwhile, recent improvements in PHOLED performance have inspired developers and designers to consider exploitation of the remarkable qualities of these unique diffuse light sources in other areas. They include low-to-medium brightness backlights for portable electronics (mobile phones, watches and personal digital assistants), automotive instrument panels, emergency-exit signs, novelty clothing, headwear and footwear lighting, decorations and safety and festive lighting.

Despite this recent progress there is still a significant amount of work to be done before high-efficacy white PHOLEDs will become a commercial reality. A variety of challenges to reach this goal can be identified. Many of them relate to synthesis and selecting organic materials and device architectures for low-cost manufacturing of larger-area lighting OLED panels. Given that organic materials have mainly very low conductivities, organic layer thicknesses in WOLED structures must be thin to ensure low voltage operation (<5 V). Alternatively, the layers can be doped to improve their conductivities. It appears, however, that dopants used to improve conductivities are generally also exciton quenching sites. Various strategies can be chosen in order to overcome these shortcomings such as the separation of emissive and conducting regions, insertion of electron- and hole-blocking layers, formation of very thin (<10 nm) emissive layers using several dopants that produce white light. There are several routes to cover the visible spectrum uniformly by WOLEDs emission. The most common approach is to use a stacked OLED structure with three separate emitters (blue, green and red)^{2,4,5} or through three emitters mixed together in a single emitting layer (EML) to achieve white emission.⁶ The most impressive characteristics of WOLEDs are those based on single emissive dopant, in particular square-planar Pt(II) complexes, where molecular excitons are harnessed to form triplet excimers or aggregates.⁷⁻¹⁰ They combine blue molecular phosphorescence with the red-shifted aggregate phosphorescence that yields white light.

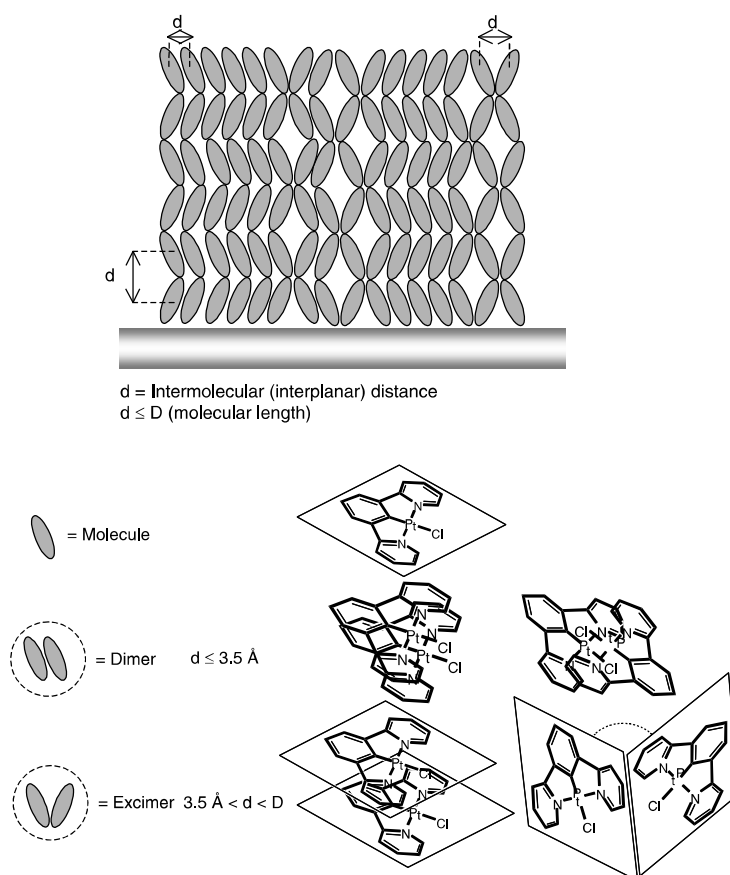
10.2 Multi-emission by a single phosphor

The efficient parallel phosphorescent emissions from mono-molecular (M-M) and bi-molecular (B-M) excited states¹¹ render the Pt complexes very attractive for organic optoelectronics. Figure 10.1 shows the molecular structure of more interesting Pt complexes as emitter in OLEDs. Among others, they allow the colour and efficiency of OLEDs to be effectively tuned.^{12,13} The square planar structures enable



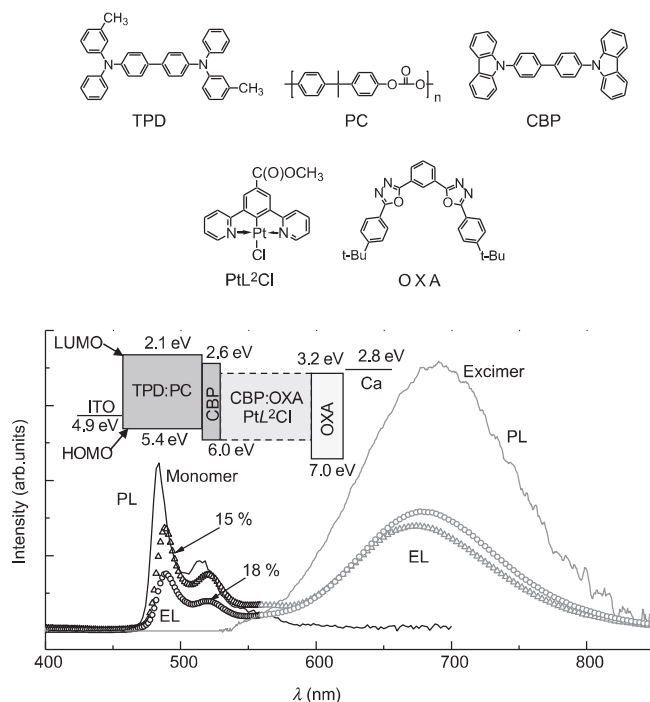
10.1 Molecular structures of some Pt complexes with porphirine, bidentate and terdentate ligands.

the Pt complex molecules to facially aggregate through attractive intermolecular interactions of Pt–Pt or ligand–ligand or a combination of these, thereby facilitating formation of B–M excited states, either in the ground state (dimers) or in excited states (excimers) (see Fig. 10.2) and will be discussed in section 10.3. Emission from B–M excited states is normally associated with a low quantum yield due to an increase in the rate of radiationless relaxation of the excited state, arising from increased intermolecular phonon interactions in extended molecular systems, and an overall reduction in the oscillator strength of the dimer due to the fact that only a fraction of the oscillator strength of the dimer transition is derived from the parent monomer transition.¹⁴ There have been, however, reports on molecules exhibiting



10.2 Bi-molecular aggregates in Pt complex neat film. The square planar structures enable the Pt complex molecules to facially aggregate through attractive intermolecular interactions of Pt–Pt or ligand–ligand or a combination of these, facilitating formation of bi-molecular states in the ground state (dimers) or in the excited state (excimers).

high singlet excimer efficiency ($\sim 75\%$),¹⁵ though triplet excimer efficiencies have long remained very low,^{16,17} until recent reports on the high efficiency PH and EPH from triplet excimers formed on heavy organometallic phosphor molecules. For example, red and near-infrared light-emitting devices (NIOLEDs) were demonstrated with external quantum efficiencies of up to $\varphi_{\text{EL}}^{\text{ext}} = 14.5\%$ ¹⁸ when based on a neat film of PtL^2Cl complex as triplet excimer emitter, showing photoluminescence (PL) efficiency of φ_{PL} (excimer) $\approx 35\%$.¹⁹ Moreover, φ_{PL} (excimer) = $74\% > \varphi_{\text{PL}}$ (monomer) = 49% has recently been reported for another Pt complex (PtL^{26}Cl).²⁰ Broad featureless emission from B-M excited states (excimers and dimers) becomes therefore even more attractive to the manufacturing of efficient red OLEDs and NIOLEDs^{18,19} as well as to the improvement of WOLEDs where a combination of molecular PH with the red-shifted excimer PH yields emission approaching white light based on single emissive dopant (see Fig. 10.3).^{7-10,21,22}



10.3 Normalized monomer (black figures) and excimer (grey figures) EL spectra at two different PtL^2Cl concentrations of the device shown in the inset. Indicated are the lowest unoccupied molecular orbital (LUMO) energies and the highest occupied molecular orbital (HOMO) energies of the materials used. Top: the molecular formulae of TPD, PC, CBP, PtL^2Cl and OXA. The photoluminescence (PL) spectra of low-doped (5%) samples (solid black line) and a 100% (solid grey line) evaporated PtL^2Cl film are shown for comparison. Reprinted with permission from Ref. 10. © (2007) American Institute of Physics.

10.3 The nature of emissive aggregates: excimer versus dimer

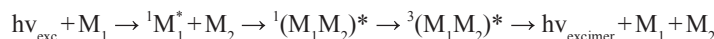
It is well known that the square planar configuration of Pt(II) complexes often leads to stacking and formation of aggregates and excimers^{23,24} which quenches the monomer luminescence. The resulting species may display their own, red-shifted photoluminescence and electroluminescence.^{2,25,26}

The broad band phosphorescence from Pt(II) organic complexes is often assigned to the radiative decay of the bimolecular excited triplet states constituting quantum mechanical entities, excimers, which are a result of excitonic (EX) and charge-transfer (CT) resonances optically or electrically imposed between two nearest-neighbour molecules (M_1 , M_2) and can be described by the function²⁷:

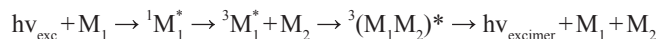
$$^3|M_1M_2\rangle^* = c_1|^3|M_1M_2\rangle_{EX}^* + c_2|^3|M_1M_2\rangle_{CT}^*$$

expressing the quantum mechanical mixing of the excimer formed by the EX resonance interaction and that resulting from the CT resonance interaction between two molecules (M_1 , M_2) of the emissive material. The coefficients c_1 and c_2 determine the contributions of the EX and CT interaction components to the excimer. The relation between amplitudes of the function and thus the excimer energy depend on the distance between the molecules M_1 and M_2 and their mutual orientation.

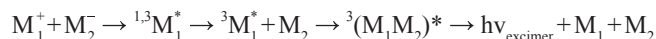
Excimer can be formed indirectly by optical excitation of the single molecule, M_1 or M_2 :



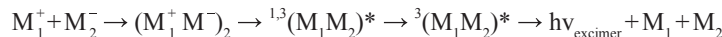
or



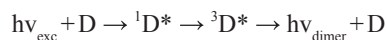
In electroluminescence (EL) by charge recombination:



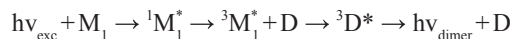
or directly from charge pair precursor



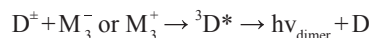
Alternatively, B-M excited states can be formed by the direct optical excitation of the ground-state, dimers, $D \equiv (M_1M_2)$:



and/or by their excitation as a result of the energy transfer from monomolecular triplet states:



In EL, the dimer-localized charge carriers can serve as recombination centres (charge traps), leading to the excited dimers as a result of direct recombination process on them



or through energy transfer with ${}^3M_1^*$ generated by the recombination $M_1^+ + M_2^-$ (M_3^-), where M_3 represents either the dopant or matrix molecule. The triplet dimer emission has been observed in neat films of Pt(II) porphyrin.²⁸

In addition and complementary to the excimer and dimer cases, when we have different molecules, one acceptor (A) and one donor (D), an exciplex (AD)* or CT complex (AD) can be formed in the excited or in the ground state respectively.^{29,30}

10.4 Mixing of molecular and bi-molecular emissive states to tune the colour and efficiency of phosphorescent OLEDs

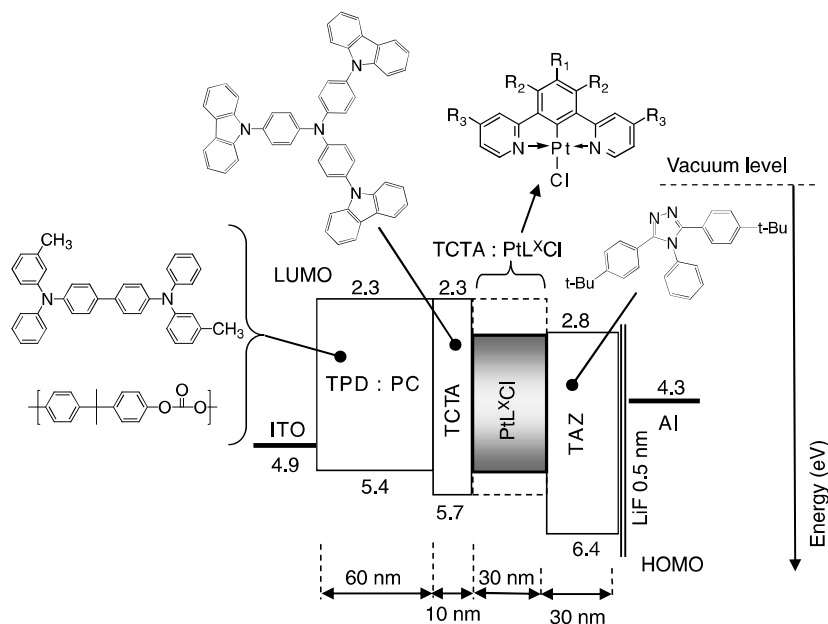
The emission spectrum and hence the colour of Pt(II) complex-based OLEDs depends on the strength of singlet–triplet mixing in emissive molecules, and on their propensity to form B-M excited states in the EMLs. In general, phosphorescence occurs from a mixture of ligand centred (LC) and metal to ligand charge transfer (MLCT) transitions.³¹ The relative importance of the MLCT and LC components depends on their energetic separation. For example, the MLCT component of PtOEP phosphorescence is very small because the porphyrin ligand has a significantly lower triplet energy (see Fig. 10.1 for chemical structure)³²: the emission is dominated by the LC transition giving relatively narrow PL and EL spectra centred at ≈ 650 nm.²⁸ Furthermore, the PtOEP triplet localized on the ligand experiences relatively inefficient spin-orbit mixing with the central Pt atom and consequently its lifetime may be as long as 100 μ s.²⁸ This long triplet lifetime increases the problem of triplet quenching in the triplet–triplet and triplet–charge carrier annihilation processes, which lead to a strong roll-off in the EL efficiency at high current densities.^{33,34} On the other hand, the emission from cyclometallated Pt complexes, such as those in Fig. 10.1, is typically attributed to a strongly mixed ${}^3\text{LC}$ –MLCT state.³⁵ Due to this behaviour, these Pt complexes present decay times of the excited state of about 10 μ s, one order of magnitude lower compared to that of PtOEP, reducing drastically the roll-off effect of their PHOLED.³⁶ At low complex concentration (≤ 5 wt%), in the so-called doped OLEDs, the formation of B-M excited states is inefficient and practically only the monomolecular (M-M) excited triplet states are generated in such EMLs. In doped OLEDs different molecules perform

distinctively the functions of electron-hole transport and of the emission. Such separation of functionality allows optimization of the device performance (see Fig. 10.4).

The doped PHOLEDs based on highly efficient N⁺C⁺N-coordinated complexes PtL^xCl (see Fig. 10.1), where L^x represents a cyclometallating terdentate ligand with various substituents on the central phenyl ring or on the pyridine rings, show monomolecular EL spectra with well-resolved structure and, due to optimized architecture, very high overall EL QE.^{37,22} Their EL spectra for 5 wt% PtL¹⁻⁶Cl-doped EML with their CIE colour coordinates are shown in Fig. 10.5, while Fig. 10.6 shows the EL spectra of 5 wt% and 100 wt% PtL²¹⁻²³Cl-doped EML and the PHOLEDs' colour quantified by CIE coordinates. The well-resolved EL spectra of the monomolecular excited state fall in the blue, green and yellow regions of the visible spectrum. The spectra of the F-substituted complexes are slightly blue-shifted, while the bi-molecular emissions fall in the orange, red and NIR regions. The EL relative to the PtL²⁶Cl-based EML gives the most blue-shifted spectrum with CIE coordinates (0.18, 0.27) and appears to be extremely sensitive to the concentration, the PHOLED colour shifting up to the red at high loadings (see Fig. 10.7). This is associated with a change in the EL spectrum caused by the formation and emission of excimers (see Section 10.3). At the same time, these PHOLEDs reveal good brightness and the highest EL QE (see Fig. 10.8), reaching ~20% ph/e at 30–35 wt% concentrations, partly due to the high phosphorescence efficiency of the complex in particular at high concentrations. For the photophysical parameters of the PtL^xCl complexes in question, see Table 10.1.

Judicious choice of PHOLED architecture contributes substantially to improvements in EL efficiency. As shown in Fig. 10.4, the devices consist of an ITO-coated glass anode transparent to the light generated in the EML. Holes are injected from the ITO anode and pass through TPD:PC and TCTA hole-transporting layers. They recombine in the EML with electrons that were injected from an Al/LiF cathode and transported through the electron-transporting layer of TAZ. The 10nm-thick TCTA layer, characterized by a triplet exciton energy E_T of 2.85 eV, has been used to block triplet exciton transfer from the Pt complexes (E_T < 2.6 eV) to the non-radiative triplet of TPD (E_T = 2.45 eV). The 30nm-thick layer of TAZ (E_T = 2.75 eV) plays a similar role of inhibiting quenching of the Pt complex triplet excitons at the cathode while at the same time blocking holes, both properties that enable the recombination process to be confined to a 30nm-thick EML layer. Such PHOLED architecture allowed maximizing of its performance parameters (for general mechanisms of PHOLED function see, e.g., Ref. 27).

The variation of the external EL QE vs current density changes with PtL²⁶Cl concentration (see Fig. 10.8b). The functional shape of the evolution can be explained on the basis of the unified approach that represents a quantitative description of EL QE versus j.³⁸ The external EL QE can be determined from

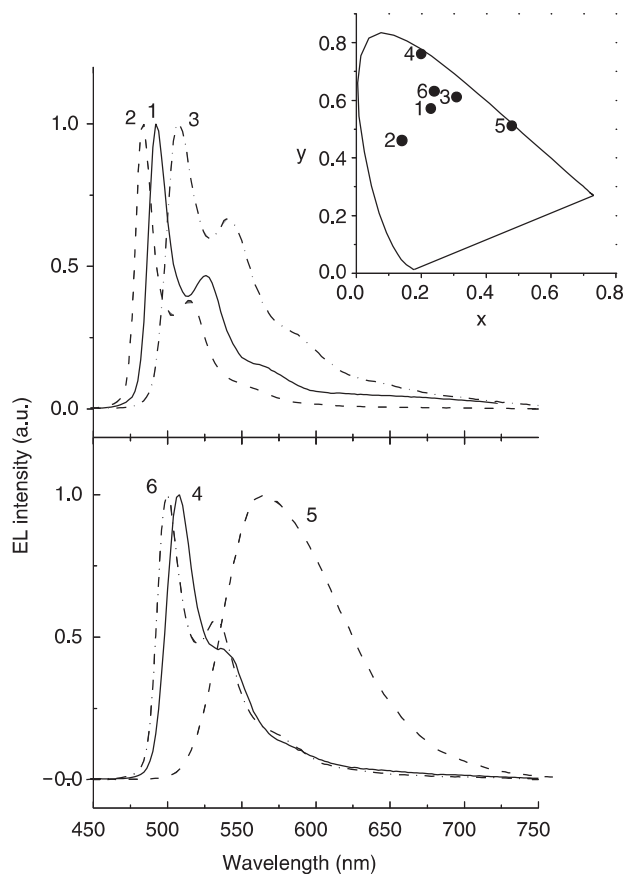


10.4 The architecture of the LEDs manufactured, and molecular structures of the materials used. These are completed with energy level diagram shown for understanding the exciton and electronic traffic within the devices. The highest occupied molecular orbital (HOMO) obtained for each material corresponds to its ionization potential. The lowest unoccupied orbital (LUMO) is equal to the molecular electronic affinity. The Fermi level positions for ITO and Al electrode contacts are added for completion. The positions of all the levels are indicated by the numbers in electronvolts relative to the vacuum level at energy zero. Reprinted with permission from Ref. 12. © (2010) Elsevier.

the general expression representing all electronic processes involved in creation and fate of n different excited states, modified by the phosphor concentration, c :

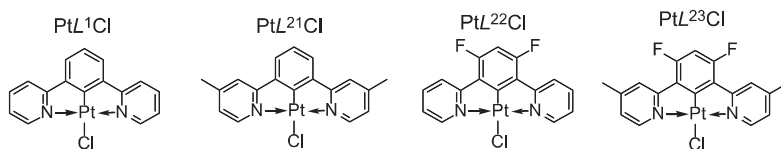
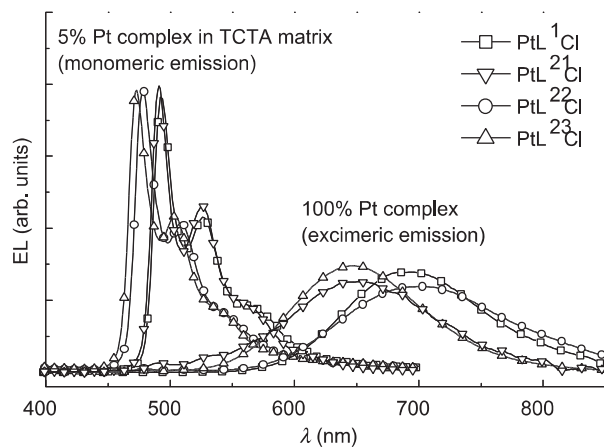
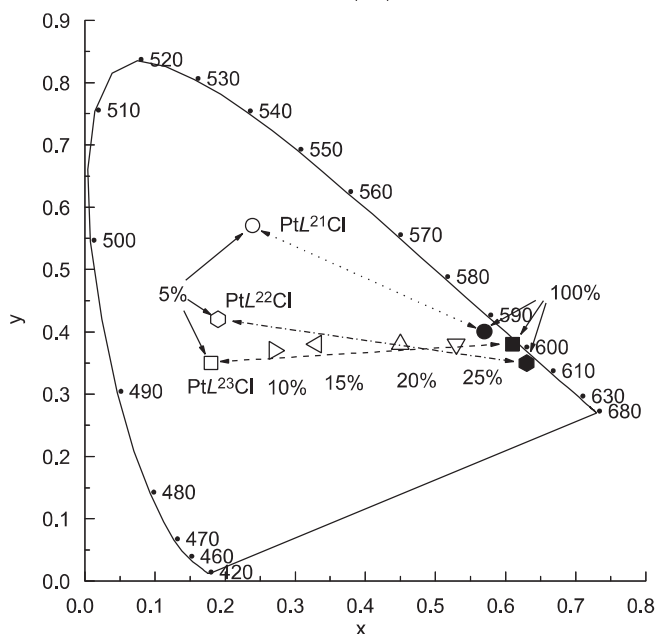
$$\varphi_{\text{EL}}^{(\text{ext})}(c) = P_{\text{R}}(c)P_{\text{d}} \sum_{i=1}^n P_{\text{si}} \xi_i(c) \varphi_i^{\text{PL}}(c) P_{\text{qi}}(c)$$

Here, $\xi_i(c)$ (< 1) is the light output coupling factor, accounting for OLED optical side modes escaping of usual front face detected EL light flux and dependent on the OLED's material composition, φ_i^{PL} is the quantum efficiency of the radiative decay of the excited state i created in the electron-hole recombination process, which is commonly identified with the photoluminescence quantum efficiency. The fundamental message of this equation is that the EL QE is a result of the

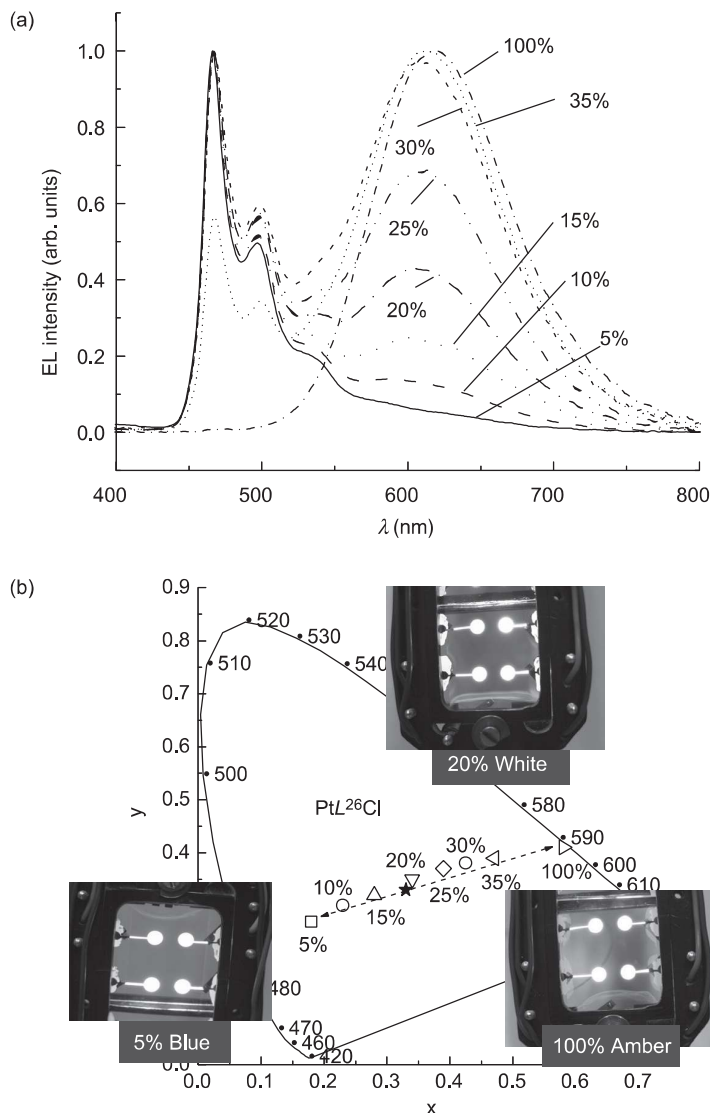


10.5 Electroluminescence spectra for devices having the structure as in Scheme 1 with different dopants: [PtL¹Cl] (1), [PtL²Cl] (2), [PtL³Cl] (3), [PtL⁴Cl] (4), [PtL⁵Cl] (5), [PtL⁶Cl] (6). The inset reports the corresponding CIE coordinates: (1)=[0.23; 0.57], (2)=[0.14; 0.46], (3)=[0.31; 0.61], (4)=[0.20; 0.76], (5)=[0.48; 0.51], (6)=[0.24; 0.63]. Reprinted with permission from Ref. 37. © (2007) Wiley.

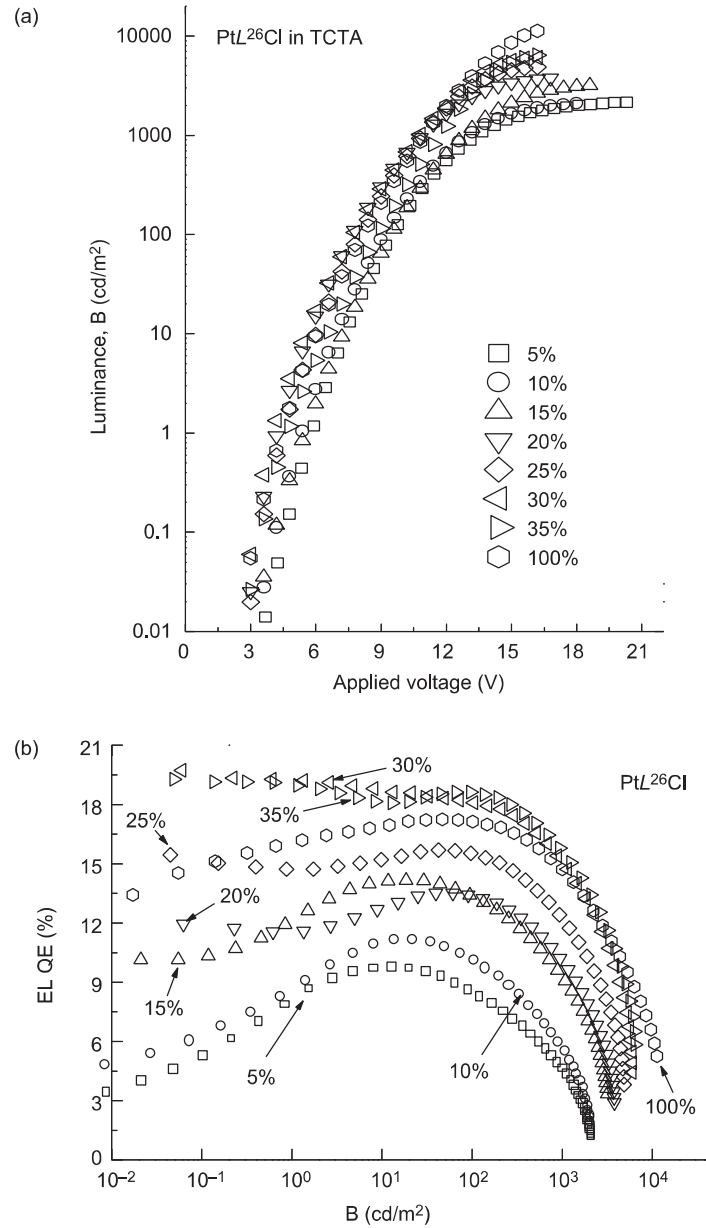
superposition of four independent processes operating in the OLED at the same time: P_R is the probability of the formation of a charge pair (CP) state, P_d is the probability of CP dissociation avoidance, P_{qi} is the escape probability of a quenching process by the final emissive i state, irrespective of the type of emissive material and OLED architecture, and P_{si} stands for the probability of creation of a singlet or triplet i th emitting state (for a detailed analysis see Refs 38 and 39).



10.6 Molecular structures of the Pt(N $\wedge$ C $\wedge$ N) complexes studied, along with their electroluminescence spectra from the 5wt% PtL_xCl complex-doped TCTA emitter layers of blend devices (left) and PtL_xCl neat film emitter devices (right). CIE coordinates of each of ten devices. Reprinted with permission from Ref. 22. © (2009) American Institute of Physics.



10.7 EL spectra (a), and CIE diagram (b) for LEDs with emitters of varying concentrations of PtL^{26}Cl . At low concentrations of the phosphor the LEDs are 'blue-based' (dominated by emission from the molecular triplet excitons), at high phosphor concentrations the LEDs become 'red-based' being dominated by the emission from phosphor excimers. The blue emission band practically disappears for 100% phosphor emitter (neat PtL^{26}Cl films). The LED with a 20 wt% content of the phosphor approaches closely a white light with CIE coordinates (0.33, 0.33). Examples of emission colours at various phosphor concentrations are given by photographs in the CIE diagram in part (b). Reprinted with permission from Ref. 12. © (2010) Elsevier.



10.8 Luminance (B) versus applied voltage (a) and EL QE vs B (b) at varying PtL²⁶Cl concentration in EML of devices from Fig. 10.3. Reprinted with permission from Ref. 12. © (2010) Elsevier.

Table 10.1 Photophysical and electrochemical parameters of the Pt(N⁺C⁻N) complexes in solution and neat solid films.

	Pt(N ⁺ C ⁻ N) complex	PL λ_{max} (nm)	ϕ_{PL} (%)	τ (μs)	E_{p}^{ox} (V) ^c HOMO (eV) ^d	$E_{\text{p}}^{\text{red}}$ (V) ^c LUMO (eV) ^d
PtL ¹ Cl	Solution ^a (monomer)	491	60	7.2	0.85	-1.61
	Film(excimer)	680	24 ^b	0.98	5.53	3.07
PtL ² Cl	Solution ^a (monomer)	481	58	8	0.89	-1.51
	Film(excimer)	684	35 ^b	1.07	5.57	3.17
PtL ³ Cl	Solution ^a (monomer)	505	58	7.8	0.79	-1.60
	Film(excimer)	675	31 ^b	1.1	5.47	3.08
PtL ⁴ Cl	Solution ^a (monomer)	506	57	9.2	0.95	-1.58
	Film(excimer)	680	22 ^b	–	5.63	3.10
PtL ⁵ Cl	Solution ^a (monomer)	588	46	12.4	0.61, 0.71	-1.64
	Film(excimer)	692	5 ^b	–	5.29, 5.39	3.04
PtL ⁶ Cl	Solution ^a (monomer)	501	62	7.9	1.00	-1.57
	Film(excimer)	682	20 ^b	–	5.68	3.11
PtL ²¹ Cl	Solution ^a (monomer)	487	73	6.8	0.62	-1.92
	Film(excimer)	652	5 ^b	0.2	5.30 ?	2.76?
PtL ²² Cl	Solution ^a (monomer)	472	85	13.6	0.73	-1.86
	Film(excimer)	700	35 ^b	1.0	5.41	2.82
PtL ²³ Cl	Solution ^a (monomer)	467	87	7.9	0.75	-1.80
	Film(excimer)	646	65 ^b	2.4	5.43	2.88
PtL ²⁶ Cl	Solution ^a (monomer)	461	71	7.8	0.75	<-2.20 (?)
	Film(excimer)	620	74 ^b	1.2	5.43	2.77 ^e (>2.5) (?)

Notes:^aPhotoluminescence data (ϕ_{PL} , τ) in DCM solution at 295K.^bCalculated using standard BASF LumogenF Red and integrating sphere.^cElectrochemical data in DCM or DMSO solution at room temperature. In some cases peak potentials of electrochemically irreversible processes are reported. The values are reported versus saturated calomel electrode (SCE).^dHighest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) levels (eV) as calculated from the redox potentials.^eCalculated employing the optical gap (E_{g}) as $E(\text{LUMO})=E(\text{HOMO})+E_{\text{g}}=5.43-2.66=2.77\text{ eV}$. It correctly falls above the value of 2.5 eV – a lower limit predicted from the reduction potential (row 1). Its exact value could not be determined because the reduction wave of the complex is obscured by the solvent.

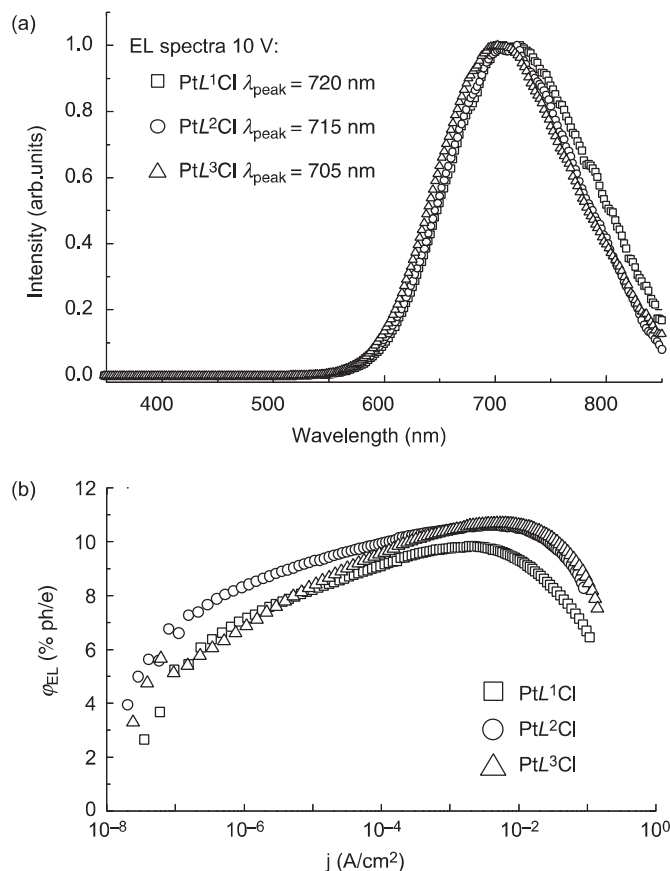
Source: Adapted from Refs. 12, 19, 22, 37.

10.4.1 Near-InfraRed OLEDs (NIROLEDs)

The extension of efficient OLEDs into the technologically important near-infrared (NIR) spectral range (NIROLEDs) is another challenge to scientists and engineers. Various approaches have been explored to obtain infrared emission from OLEDs. The use of rare earth complexes and small optical gap polymers has been attracting interest since lanthanide ions such as Er^{3+} or Nd^{3+} revealed NIR emission, and the polymer emission could be extended to a wavelength of 1000 nm. One of the most important shortcomings of the NIROLEDs is poor quantum efficiency and low power output. For example, forward light output of $100 \mu\text{W}/\text{cm}^2$ and only 0.1% of external quantum efficiency have recently been reported for NIR electrophosphorescence with a peak value at 720 nm from blends of polymeric host and an iridium(III) complex.⁴⁰ A dispersion of inorganic indium arsenide-based nanocrystals in conjugated polymers has been employed to improve the quantum efficiency but to no more than $\approx 0.5\%$ ph/e.⁴¹ Notable progress has been reported using Pt(II) tetraphenyl-tetrabenzoporphyrin [Pt(TPBP)] as dopant in Alq_3 EML, with narrow emission peaked at 772 nm having an EL QE of 8.5% at low power output.⁴² Only recently, the exploitation of excimer phosphorescence in neat films made of terdentate Pt(II) complexes has enabled the fabrication of highly efficient (up to 10% ph/e) NIROLEDs, as reported by my group¹⁹ (see Figs 10.9 and 10.10), opening up a new perspective for further improvements in this important branch of optoelectronics. Figure 10.10 shows very recently NIROLEDs based on neat films of $\text{PtL}^{27-29}\text{Cl}$ having very broad EL spectra with $\lambda_{\text{max}} \approx 775, 730, 730 \text{ nm}$ and EL QE_{max} $\sim 0.5\%, 1.0\%, 1.7\%$ respectively.⁴³

10.4.2 White OLEDs (WOLEDs)

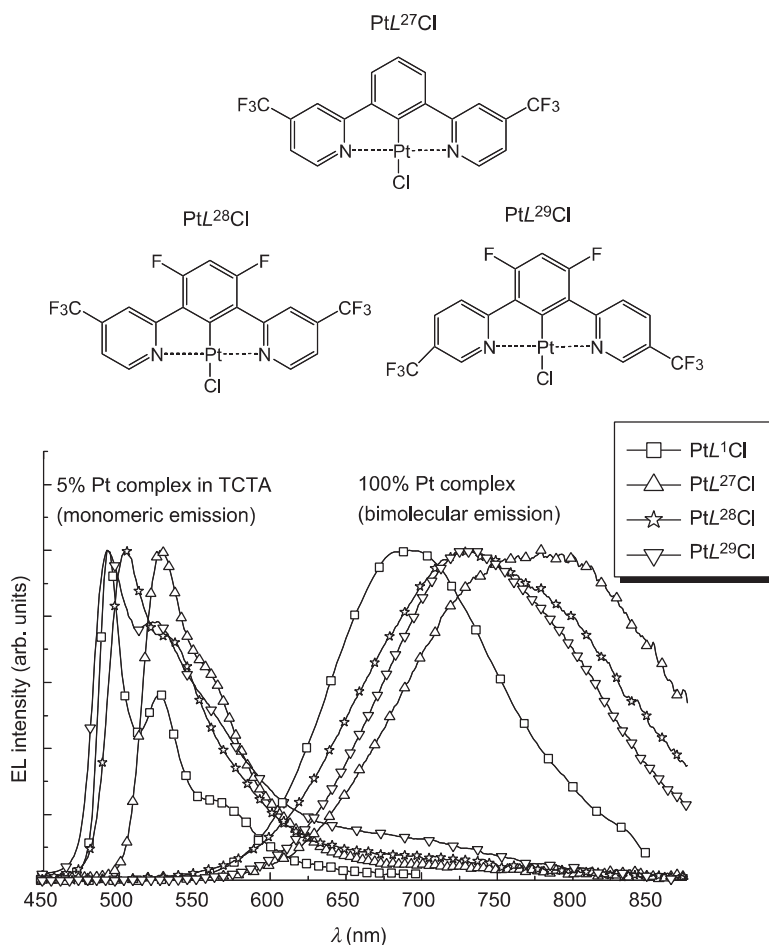
The high energy efficiency of a light source, measured by luminous efficacy (lm/W), is the primary motivation for development of WOLED for huge energy saving, but the colour quality is also a critical characteristic of light source for lighting. Colour quality is given from two different entities: chromaticity of light itself and colour rendition of the source, both of which are determined by its emission spectrum. The chromaticity of light is expressed in CIE (the Commission Internationale de L'Eclairage) 1931 coordinates (x, y) that are defined by calculating the tristimulus response of the colour.⁴⁴ The colour rendition of a light source is related to how natural the colours of objects look under a given illumination. This is described by the Colour Rendering Index (CRI), expressed as a value from 0 to 100. High CRI values indicate better colour rendition properties. This light quality parameter is better when the emission of the light source covers all the visible region like an ideal black-body radiator.⁴⁵ It is easy to understand that broadband emissions can fulfil this requirement while sources with narrowband spectra do not reach high CRI values. Also for these reasons OLEDs are better white light sources compared to inorganic LEDs.



10.9 EL spectra recorded at the applied voltage 10 V (a) and external EL quantum efficiency $\phi_{\text{EL}}^{\text{(ext)}}$ versus driving current density (j) (b) for NIOLEDs with PtLXCI ($X=1, 2, 3$) neat film as EML. Reprinted with permission from Ref. 19. © (2009) American Institute of Physics.

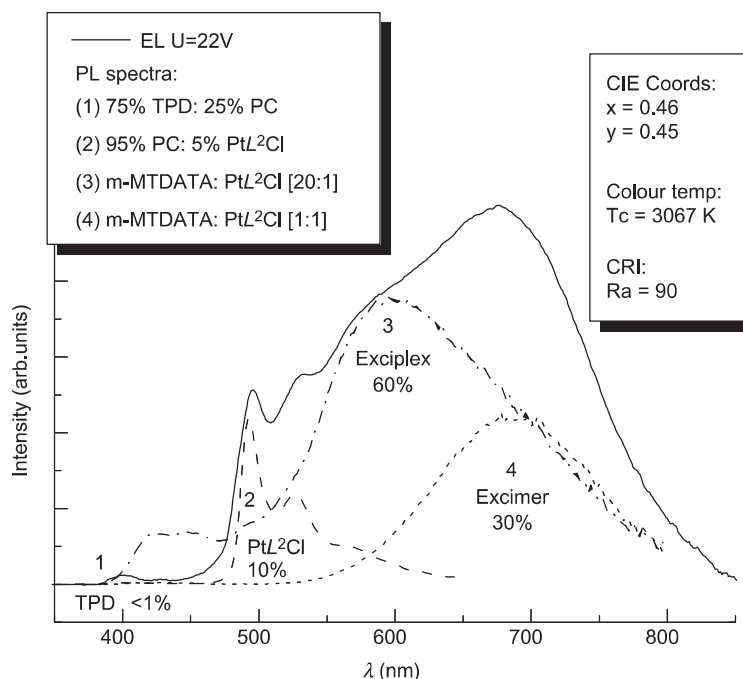
Several routes have been employed to realise WOLEDs. Typically, the fabrication of stacked² or multilayer⁴ OLED structures, with separated molecular emitters (blue, green and red) has been realised. Other approaches involve stacked RGB emitters,⁴⁶ fluorescent/phosphorescent emitters,⁵ multiple phosphor-doped emitters,⁷ phosphorescent triple-doped emitters⁹ or exciplex emission with mixed acceptors.⁴⁷ However, the OLEDs with the most impressive characteristics are those based on a single emissive dopant, in which molecular excitons are harnessed to form triplet excimers in addition to molecular excited states.^{7-10,21}

Electrophosphorescence from cyclometallated Pt(II) complexes with terdentate ligands has recently received wide attention due to their potential for tailoring the



10.10 Molecular structures of the Pt(N $\wedge$ C $\wedge$ N) complexes studied, along with their electroluminescence spectra from the 5wt% PtLXCl complex-doped TCTA emitter layers of blend devices (left) and PtLXCl neat film emitter devices (right) (X=27, 28, 29). Adapted from Ref. 43.

emission colour and efficiency of OLEDs.^{12,22,37,43,48–50} Many of the Pt(II) complex blend-based emitters show two phosphorescence bands located in the blue and red regions of the visible spectrum. Their contribution to the total emission output can be controlled by the concentration of the Pt(II) complex in a host matrix used for the preparation of the blended emissive layers. As shown in Figs 10.3, 10.6, 10.7 and 10.11, this feature has been employed for the fabrication of very high efficiency organic white OLEDs.



10.11 The electroluminescence spectrum (black lines) for WOLED reported in Ref. 21, recorded at a voltage of $U=22$ V. It is composed of three essential bands corresponding to the photoluminescence (PL) spectra of monomolecular triplet emission of PtL²Cl (dash line 2), triplet exciplex emission of m-MTDATA:PtL²Cl (dash-dot line 3) and excimer emission of PtL²Cl (dot line 4) with a small contribution from the molecular singlet emission of TPD, ¹D* (line 1). Reprinted with permission from Ref. 21. © (2007) Wiley.

Moreover, a new way to improve the white light quality has been reported by my group realising a WOLED based on monomer, excimer and exciplex emissions²¹ (see Fig. 10.11). Using electron donor-electron acceptor as EML, in which the broad emission band of an exciplex (see Section 10.2) and excimer emission are mixed, enabled us to form an efficient white device with particular high colour rendering index of CRI=90. In Table 10.2 the performance of the most advanced type of WOLEDs with highest CRI are reported.

10.4.3 Plant growth OLEDs (PGOLEDs)

High-brightness and low energy-consuming light sources look forward to optimize the photosynthesis process. Only a small amount of natural light (global radiation)

Table 10.2 Most advanced performance of selected WOLEDs.

WOLED structure	φ_{ext} [% ph/e]	η_p [lm/W] (B) [cd/m ²]	CIE ^a	CRI ^b	Comments and references
Fluorescent/ phosphorescent	34.0	81.0 (1000)	(0.43, 0.49)	72	Maximum values [51]
	11.0	22.1 (500)	(0.38, 0.41)	85	Values at 1 mA/cm ² [5]
	18.4	23.8	(0.38, 0.41)	85	Maximum values [5]
Multiple phosphor-doped emitters	5.2	6.4	(0.37, 0.40)	83	Maximum values [7] (B is not specified)
Phosphorescent triple-doped	12.0	26.0 (100)	(0.43, 0.45)	80	Values at 10 ⁻³ mA/cm ² (Ref.[2])
Phosphorescent triplet excimers	5.7	5.2 (500)	(0.40, 0.43)	81	Maximum values [9]
	15.5	9.5 (40)	(0.43, 0.43)	<60	Maximum values [10]
	18.1	11.8 (500)	(0.33, 0.38)	65	Values at $\approx$ 2 mA/cm ² [22]
	11.5	6.8 (500)	(0.34, 0.35)	74	Values at 2.5 mA/cm ² [12]
Phosphorescent triplet excimer/exciplex	6.5	9.0 (500)	(0.46, 0.45)	90	Maximum values [21]
Exciplex emission with mixed acceptors	–	– (425)	(0.32, 0.35)	90.4	No data for φ_{ext} and η_p are reported (Ref. [47])
Phosphorescent with no emitter specified	not reported	102 (1000)	not specified	70	Not specified [52]

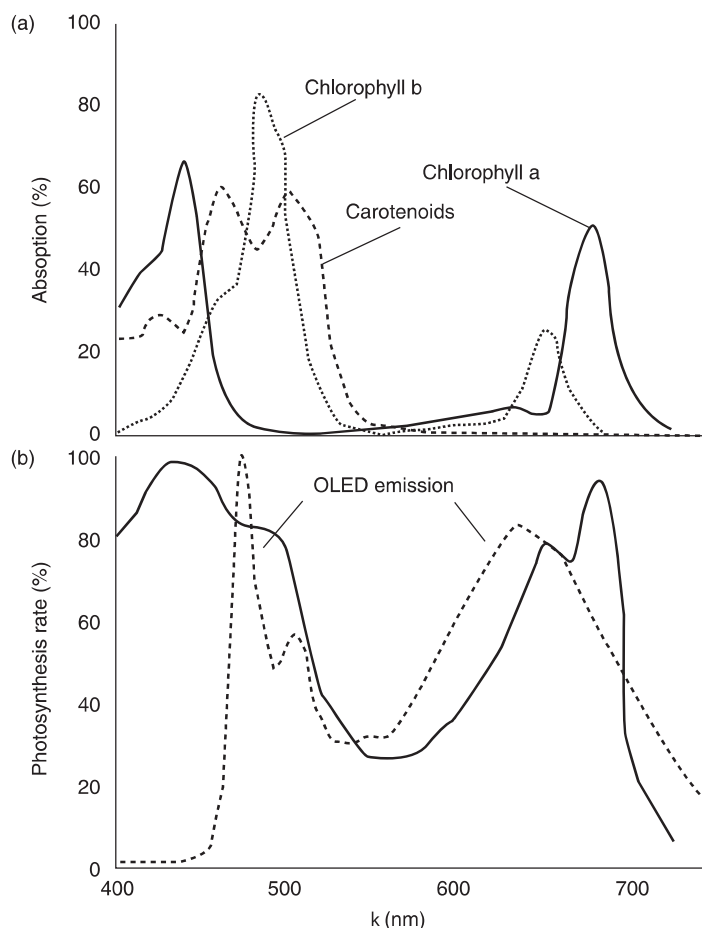
Notes:

^a CIE=Commission Internationale de l'Eclairage; ideal white light CIE coordinates are (x=0.33, y=0.33) and those for warm incandescent lamp light are (0.41, 0.41).

^b CRI=color rendering index; for ideal white light CRI=100.

Source: Adapted from Ref. 22.

is used by plants for growth, which is called 'growth light'. When a supplemental artificial light is used to enhance growth, its source is expected to produce growth light efficiently. With the development of ever-improving LEDs for lighting over the last decade, it is finally becoming more convenient to use LEDs as growth lights (cf. the NASA LED ultimate grow light). They can be used for several applications: hydroponics or soil, home or greenhouse. Researchers of NASA's

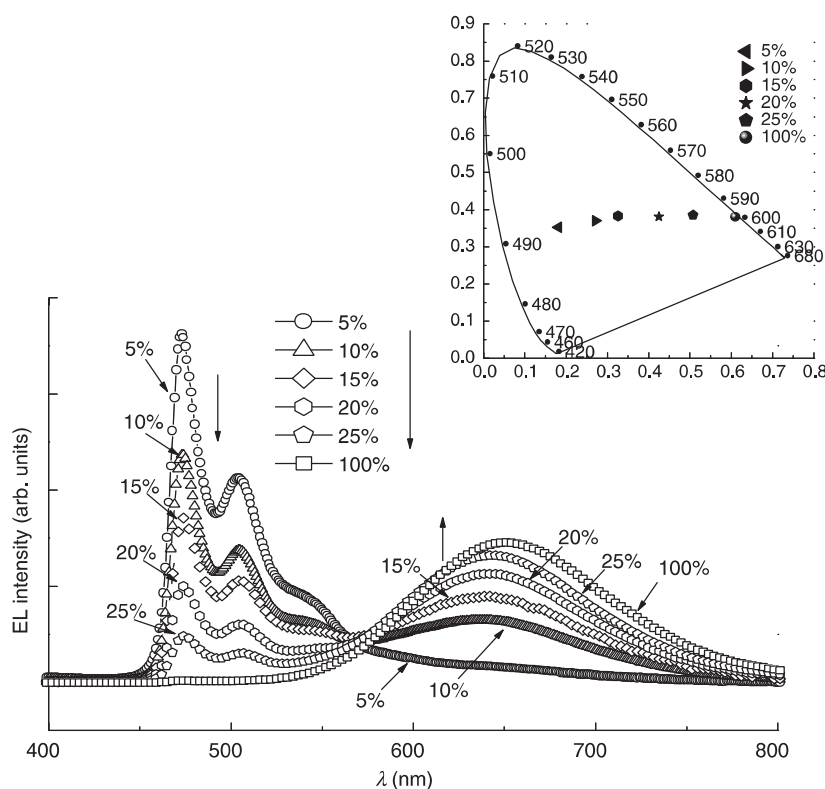


10.12 Absorption spectra of chloroplast chlorophyll-a and -b, and carotenoids (a), and action spectrum of photosynthesis compared with the emission spectrum of one of the present OLED (20wt% PtL²³Cl) (b). A remarkable correspondence between the OLED spectrum and the action spectrum (as taken from Ref. 53) can be observed. Reprinted with permission from Ref. 49. © (2008) Elsevier.

Kennedy Space Center are working on the application of LEDs in the fabrication of a salad machine that could enable space centre crews to grow and harvest their own greens within the next three years.

A typical inorganic LED is usually a small area source that emits an incoherent narrow-spectrum with the emission colour depending upon the composition and the condition of the semi-conducting material used. To convert such point light sources into solid-state lighting lamps, creating a uniform and homogeneous light

output, it is necessary to use optics which increase the weight and dimensions for the lighting systems. In contrast, organic LEDs for solid-state lighting represent a diffuse source of light and they are thus naturally suitable for large area general-lighting required for growing plants. The spectral distribution of light is one of the most important variables for optimizing plant growth. Researchers have found that blue and red light is essential for plant growth. Therefore, the most desired characteristic of OLED growth light is the combination of blue and red emission bands, following the action spectrum of the photosynthesis (see Fig. 10.12).



10.13 EL spectra, and CIE diagram (inset) for OLEDs with emitters of varying concentrations of PtL^{23}Cl . At low concentrations of the phosphor the LEDs are 'blue-biased' (dominating emission from the molecular triplet excitons), at high phosphor concentrations the OLEDs become 'red-biased' being dominated by the emission from phosphor excimers. The blue emission band practically disappears for 100% phosphor emitter (neat PtL^{23}Cl films). The OLED with a 15wt% content of the phosphor approaches closely a white light with CIE coordinates (0.33, 0.33) emitting device. Reprinted with permission from Ref. 49. © (2008) Elsevier.

The monomer and excimer emissions from single phosphor dopant emitters have been proven to be effective in the creation of such two-band emission spectra. Thus, manufacturing OLEDs that exploit the monomer and excimer emissions from single phosphor dopant emitters is potentially very promising for new plant growth light sources technology, since they create simultaneously the blue and red emission bands essential for plant growth. The first step on this way has already been taken as a series of plant growth OLEDs (PGOLEDs) has recently been reported by my group.⁴⁹ To achieve blue-to-red band proportions in the emission spectra of the PGOLEDs a proper composition of the LEDs' emitter is required (see Fig. 10.13), which corresponds to the action spectra of photosynthesis for different plants and their growth stage.

10.5 Conclusion and future trends

In this chapter I have sought to give a comprehensive and simply structured representation of the present state of the development of organic optoelectronic devices based on multi-emission by a single phosphor, in particular making use of square-planar, organometallic platinum(II) complexes as light emitters. The most important feature of such systems is the very high phosphorescence quantum yields of the monomer and the aggregates of these cyclometallated and rigid structures. Using Pt complexes with N $\wedge$ C $\wedge$ N terdentate ligands it is possible to easily tune their monomeric and excimeric emissions independently. This can be done by manipulating the substituents on the central phenyl ring (monomeric emission) and on the pyridyl rings (excimeric emission).

Certainly, another important feature is the propensity of these Pt(II) complexes to form bimolecular excited states such as excimers (or exciplexes when acting as electron acceptor species) and even more aggregated entities. The doping concentration of the phosphor complex material in the conductive molecular matrix of blend films determines the relative monomer-excimer-dimer EL emission and hence the colour of the emitted light can be tuned from blue to red with high efficiency. Tailoring the structure of the emitter, in turn, imposes intensive studies of a variety of organic molecules revealing the desired combination of short-wavelength molecular exciton and long-wavelength bimolecular (dimer, excimer and exciplex) emission spectra.

These features, combined with specially designed device architectures to optimise their performance, clearly allow the fabrication of highly-efficient OLEDs, NIROLEDs, WOLEDs or PGOLEDs, of which distinctive examples are described in the present overview. These findings have a direct impact on the design of new efficient organic optoelectronic devices based on multi-emission by a single phosphor.

This new class of organic emitters could be one of the best ways to fulfil the conditions, such as cost, lifetime, intensity, luminous efficacy and colour quality, for the commercialization of OLED products and it presents a great potential for further optoelectronic applications like organic light emitting transistors (OLET), luminescent solar concentrators, luminescent probes and sensors, etc.

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Optical characterisation of OLED emitters from radiation pattern analyses

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Abstract: Approaches enabling an accurate *in situ* determination of organic light-emitting diode (OLED) properties are discussed. Analysing the optical far field of electrically operating OLEDs with well adapted stack architectures reveals the profile of the emission zone, the internal dipole orientation, as well as the excited state's internal quantum efficiency. The methods are exemplarily applied to the well-known, triplet emitting guest host system of Ir (MDQ)₂(acac) blended in an α -NPD matrix.

Key words: optical analysis and simulation, dipole emitter orientation, profile of the emission zone, internal quantum efficiency.

11.1 Introduction

Since the first report of an organic light-emitting diode (OLED) by Tang and VanSlyke in 1987,¹ considerable progress has been achieved in improving the lifetime and efficiency of OLEDs as well as in studying the basic physics of such devices. The favourable prospects of these new organic semiconductor light sources rely amongst other features on their slimness, low weight and potentially very low fabrication costs. Moreover, the process of electroluminescence (EL) as the basic principle of light generation is extremely efficient and potentially yields one photon per injected charge. Most importantly, OLEDs are conceptually different from conventional, point-shaped light sources because the light is generated and emitted over a sizeable area of up to square metre dimensions.

Unfortunately, the overall performance of contemporary devices is limited by the rather low light extraction efficiency. This is due to the fact that the emission takes place in a high refractive index material and the energy of an excited emitter can be radiated into different optical channels of the OLED layered system. Hence, only a small fraction of the light energy is finally extracted from the device into the surrounding medium air. In order to perform comprehensive optical analysis and optimisation of the OLED layered system – which promise improved device efficiency – the optical features of the internal emissive process and the OLED layered stack need to be known. The availability of meaningful and reliable optical device properties is *the* fundamental

prerequisite for a quantitative optical simulation of OLEDs and sophisticated device engineering.

Frequently, photoluminescence (PL) experiments are performed to determine the spectrum of the emissive material as well as the molecular dipole orientation.²⁻⁴ However, PL experiments generally suffer from the fact that the initially photo-generated excited states are not necessarily identical to the excited states in EL operation.⁵ Furthermore, internal features such as the molecular orientation might depend on the exact deposition conditions and post-processing techniques.⁶ Consequently, *in situ* investigations of OLEDs are desirable and a promising approach is based on measurements of the optical far field of OLEDs in electrical operation combined with subsequent optical reverse simulations. A variety of more or less elaborate methods utilising the full angular, spectral, and polarisation resolved radiation pattern or some essential aspects of these have been proposed, allowing conclusions to be drawn to the profile of the emission zone⁷⁻¹⁴ and the transition dipole moment orientation.^{15,16} However, none of these studies provides information whether the investigated part of the radiation pattern holds sufficient information about the particular internal feature of interest, and none of these studies addresses the question of how the OLED's layered system could be tuned or adapted in order to increase the sensitivity of the internal feature of interest in the OLED far field.

In this chapter, approaches are discussed that enable an accurate *in situ* determination of the profile of the emission zone, the orientation of the transition dipole moments,¹⁷⁻¹⁹ and the (current dependent) internal luminescence quantum efficiency^{20,21} of OLED emitter materials. Initially introduced by Flämmich and co-workers, the outlined methods are based on measurements of the optical far field of electrically operating OLEDs and corresponding optical reverse simulation. A fundamental idea is to utilise devices with well adapted layered systems that optically enhance the visibility of the feature of interest.^{22,23} This allows for observing the internal properties of the dipole radiation in the OLED's far field with sufficient sensitivity. For experimental illustration, the methods are applied to a set of OLEDs containing the well-known small-molecular emissive material Ir(MDQ)₂(acac) blended in an α -NPD matrix.

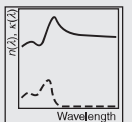
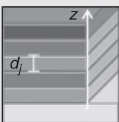
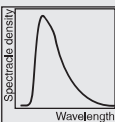
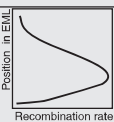
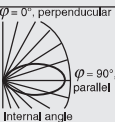
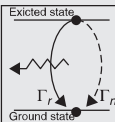
A general routine for a complete *in situ* characterisation of the *active* optical properties of OLED emissive materials²⁴ is demonstrated. Besides results that match the expectations and confirm common assumptions, the analysed phosphorescent emitter system exhibits the truly unforeseen feature of a mainly parallel dipole emitter orientation that opens up a novel and highly promising approach for OLED efficiency optimisation.

11.2 Optical modelling of OLEDs

For the purpose of optical modelling, the electroluminescent emissive process in OLEDs is considered as a dipole transition from an excited molecular state

into the ground state. It is important that the emissive event takes place in a microcavity and the interaction with the local environment plays a vital role. As a consequence, the radiation pattern of an OLED is generated by the interplay of the *active* optical properties of the emissive material and the *passive* optical properties of the layered system. With full details, the *active* optical properties of the emissive material are the internal EL spectrum, the profile of the emission zone, the orientation of the transition dipole moments, and the internal luminescence quantum efficiency; the *passive* optical properties of the layered system are the material refractive indices and the layer thicknesses. Whereas the *passive* optical properties (see Fig. 11.1) can be measured utilising standard spectroscopic methods such as, for example, ellipsometry²⁵ or reflection-transmission spectroscopy,²⁶ the *active* optical properties of the emissive system are more difficult to access.

In this section, the emission from an ensemble of emissive sites is briefly treated to model the radiation pattern and overall device efficiency of OLEDs. Then, the active optical properties of the emissive material (see Fig. 11.1) are discussed in detail one by one with special emphasis on available approaches towards their determination.

All materials in the stack		Emitter properties in electrical device operation			
Complex refractive index	Layer thickness	Internal spectrum	Profile of the emission zone	Dipole moment orientation	Luminescence quantum efficiency
					
$n(\lambda), \kappa(\lambda)$		$S(\lambda)$	$N(z)$	$g(\varphi)$	q
= <i>Passive</i> optical properties of the layered system		= <i>Active</i> optical properties of the emissive material			

11.1 *Passive* and *active* optical properties of OLEDs. Schematic illustration of the set of parameters that characterises an OLED for the purpose of optical simulation: the *passive* optical properties of the layered system (which are the material refractive indices and the layer thicknesses of all materials in the stack) and the *active* optical properties of the emissive material in electrical device operation (which are the internal EL spectrum, the profile of the emission zone, the orientation of the transition dipole moments, and the internal luminescence quantum efficiency).

11.2.1 Radiation pattern and device efficiency

The emissive dipole transition moment at vertical position z inside the emissive material has a defined orientation φ . The angular (θ , angle to the layered system normal) and spectral (λ , wavelength) radiant intensity $I^{dipole}(\theta, \lambda, z, \varphi)$ of a dipole emitter inside the OLED stack is simulated assuming a classical, continuously oscillating dipole source, yielding the emitted power $P^{dipole}(\theta, \lambda, z, \varphi)$ per solid angle $d\Omega$ and wavelength $d\lambda$ interval:

$$I^{dipole}(\theta, \lambda, z, \varphi) = \frac{d^2 P^{dipole}(\theta, \lambda, z, \varphi)}{d\Omega d\lambda} \quad [11.1]$$

In the following discussion, all power values of such classical dipoles are normalised with respect to the total irradiated power of a corresponding dipole in the homogeneous infinite emitter medium. The electromagnetic dipole fields in the system are evaluated using a transfer-matrix formulation of the well-known Green's function approach introduced by Chance, Prock, and Silbey.²⁷ For further details on the generation of the dipole fields see Danz *et al.*²⁸ and references therein. Consider a single, arbitrarily oriented dipole with respect to the surrounding layered system. Its classical emission pattern can be decomposed into contributions of three orthogonal dipoles ($\parallel$ TE, $\parallel$ TM, $\perp$ TM).^{29,30}

$$I^{dipole}(\theta, \lambda, z, \varphi) = \sin^2(\varphi) \cdot \left[I_{\parallel\text{TE}}^{dipole}(\theta, \lambda, z) + I_{\parallel\text{TM}}^{dipole}(\theta, \lambda, z) \right] + \cos^2(\varphi) \cdot \left[I_{\perp\text{TM}}^{dipole}(\theta, \lambda, z) \right]. \quad [11.2]$$

These orthogonal dipoles are illustrated in Fig. 11.2. They are specified according to their orientation with respect to the interfaces of the layered system (parallel ' $\parallel$ ', perpendicular ' $\perp$ ') and the corresponding polarisation of the emitted radiation (transverse electric 'TE', transverse magnetic 'TM'); the direction of measurement or observation is represented by the wave-vector k . Figure 11.2 indicates additionally the schematics of the internal radiation patterns of the dipoles in the homogeneous, infinite emissive material that are distorted in the presence of the interfaces of the layered system.

In order to ensure normalisation of power emitted from the dipole in the layered system, we utilise the equivalence between the probability for spontaneous emission of a photon via a dipole transition and the radiated power of a classical dipole source in the corresponding layered system.^{20,31}

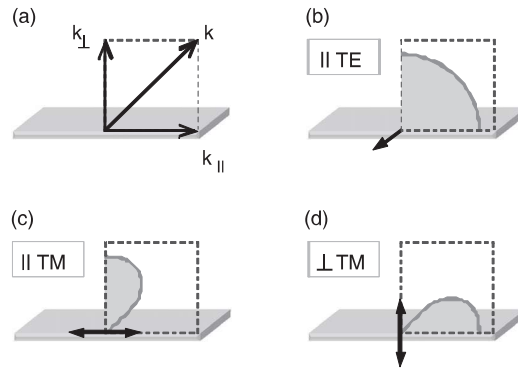
$$I(\theta, \lambda, z, \varphi) \propto \frac{1}{\Gamma_{rel}(q, z, \varphi)} I^{dipole}(\theta, \lambda, z, \varphi) \quad [11.3]$$

where $\Gamma_{rel}(q, z, \varphi)$ denotes the emission rate of the dipole at position z with orientation φ in the cavity normalised to the emission rate in the infinite emitter medium. Additionally, the relative transition rate depends on the internal luminescence quantum efficiency q of the emissive material. By means of Eq.

(11.3), the influence of the OLED stack on the rate of emission, often referred to as the ‘microcavity’- or ‘Purcell’-effect, is taken into account. A more detailed discussion of the relative transition rate and the q -value can be found in Section 11.5; moreover Refs.20,21,32, and 33 provide some further insight.

At this point it is worth noting that all calculations in this contribution are performed with a self-developed, in-house software tool,³⁴ although the applied optical model compares well to simulation tools established by other groups and discussed elsewhere.^{32,35,36} For simulation purposes, each layer within the OLED stack is assumed to have smooth, parallel interfaces and a certain thickness. The interaction between materials and radiation is considered by the wavelength dependent complex refractive index ($n+i\kappa$, with refractive index n and extinction coefficient κ). The emissive material is treated as loss-free ($\kappa=0$) when simulating the light generation process, whereas the complex-valued refractive index is used to describe light propagation through the emissive layer and all other layers of the multilayer system utilising a transfer-matrix method.³⁷

Emissive materials in real OLED devices can be treated as ensembles of incoherent radiators. Distributions in (i) emitter location z , (ii) dipole orientation φ and (iii) wavelength dependent spectral intensity account for (i) the profile of the emission zone, $N(z)$, (ii) the distribution of emitter orientation $g(\varphi)$, and



11.2 Three orthogonal dipoles. (a) The wavevector $\mathbf{k}$ (representing the direction of observation or measurement) and its two components oriented parallel ($k_{\parallel}$) and perpendicular ($k_{\perp}$) to the interfaces of the layered system (grey plane). The dipole transition moments (arrows) of the three orthogonal dipoles ||TE (b), ||TM (c), $\perp$ TM (d), with respect to the layered system are also illustrated. The indicated schematics of the internal radiation patterns of the dipoles correspond to those in the homogeneous, infinite emissive material and are distorted in the presence of the interfaces of the layered system.

(iii) the internal EL spectrum, $S(\lambda) = (hc/\lambda) \cdot \hat{s}(\lambda)$, respectively. The internal EL spectrum takes the photon energy hc/λ into account, where h denotes the Planck constant and c the speed of light in vacuum. The integrals of all distributions are normalised to one: $\int N(z) dz = 1$, $\int g(\varphi) \sin \varphi d\varphi = 1$, and $\int \hat{s}(\lambda) d\lambda = 1$. By this means, the integrated distribution yields a single emissive event in total while $\int S(\lambda) d\lambda$ corresponds to the mean photon energy with respect to the spectral distribution $\hat{s}(\lambda)$. The emission pattern of the OLED layered system or cavity $I^{cav}(\theta, \lambda)$ is obtained by an incoherent superposition of all contributions:

$$\begin{aligned} I^{cav}(\theta, \lambda) &= S(\lambda) \int_z \int_{\varphi} N(z) g(\varphi) \frac{I^{dipole}(\theta, \lambda, z, \varphi)}{\Gamma_{rel}(q, z, \varphi)} \sin \varphi d\varphi dz \\ &= S(\lambda) \left\langle \frac{I^{dipole}(\theta, \lambda, z, \varphi)}{\Gamma_{rel}(q, z, \varphi)} \right\rangle_{q, z} \end{aligned} \quad [11.4]$$

On purpose, $I^{cav}(\theta, \lambda)$ includes only optical effects due to the layered system. Electrical phenomena, like charge carrier injection and recombination, are excluded from the derivation so far. Consequently, it is this quantity which should be considered for optical analyses. It is related to the experimentally accessible spectral radiant intensity of a device $I(\theta, \lambda)$ by the formula:

$$I(\theta, \lambda) = (I_{inj}/e) \cdot \gamma \cdot \eta_{S/T} \cdot q \cdot I^{cav}(\theta, \lambda) \quad [11.5]$$

Equation 11.5 also includes (i) the number of injected charge carriers, I_{inj}/e , where I_{inj} denotes the current applied to the device and e denotes the elementary charge; the other terms in Eq. 11.5 express that the emission is proportional (ii) to the probability of charge carrier recombination and subsequent exciton formation γ , and (iii) to the generation of excited singlet as well as triplet states according to spin statistics, where allowed and forbidden transitions are regarded by the singlet/triplet-factor $\eta_{S/T}$. Additionally, (iv) the internal luminescence quantum efficiency q of the emissive system enters the radiant intensity.

The fraction of photons emitted from a device with respect to the infinite emissive material is given by an integration of the spectral and angular radiation pattern:

$$\eta_{out}^{cav} = 2\pi \cdot \int_{\lambda} \int_{\theta} I^{cav}(\theta, \lambda) / (hc/\lambda) d\theta d\lambda \quad [11.6]$$

It yields a measure of how the number of emitted photons is influenced by the presence of the layered system. It defines the overall device efficiency, represented by the well-known external quantum efficiency (EQE):

$$EQE = \gamma \cdot \eta_{S/T} \cdot \left\langle q_{eff} \cdot \eta_{out}^{class} \right\rangle_{q, z} = \gamma \cdot \eta_{S/T} \cdot q \cdot \eta_{out}^{cav} \quad [11.7]$$

giving the number of emitted photons per injected charge. The middle term of Eq. 11.7 is well established: in any microcavity the quantum efficiency of excited

state luminescence becomes system dependent due to near field effects, as regarded by the effective quantum efficiency q_{eff} . Furthermore, only a fraction of the internally generated light can leave the structure. This is taken into account by the classical outcoupling factor η_{out}^{class} , that gives the number of photons emitted from the layered system with respect to the number of photons generated inside the cavity. In this notation, however, q_{eff} accounts for the variation of the emissive rate due to the surrounding layered system, and the outcoupling-factor η_{out}^{class} is calculated by classical theory. Thus, both quantities, q_{eff} and η_{out}^{class} , depend on the emitter position z within the system as well as on the emitter orientation ϕ – a fact which is often disregarded. In order to transform q_{eff} to an emissive system specific constant, the internal luminescence quantum efficiency q is introduced into the right-hand side of Eq. 11.7. This gains the important advantage that the material-dependent quantities (γ , η_{ST} , q) are separated from the cavity specific effects (η_{out}^{cav}).

11.2.2 Internal electroluminescence spectrum

Typical emission spectra (indicated as in $S(\lambda)$ Fig. 11.1) of organic molecules are considerably broadened due to their complex morphology and disorder effects.³⁸ The resultant full width at half maximum of the emission spectrum is typically in the range of 0.3 eV and corresponds to 50–100 nm spectral width. By stacking several different emitter layers in an OLED, the cumulative emission can be tuned to virtually every colour, including white emission. Most white OLEDs contain blue, green and red emitter layers to create high quality white light, e.g. with a high colour rendering index or a desired colour temperature.

The internally emitted spectrum can be accessed easily from externally measured spectra by considering the spectral modification due to the cavity as discussed in detail by, for example Wasey *et al.*² or van Mensfoort and co-workers.¹¹ In order to minimise error propagation, the emissive sites should be placed in the system at positions where relatively weak changes of the interference conditions occur for differently located emitters.²²

11.2.3 Emission zone

Provided that the charge carriers are well distributed across the OLED area, the system is electrically homogeneous in the transverse direction and the active sites are homogeneously distributed in the plane of the layered system interfaces. The spatial distribution of the emissive sites simplifies to a one-dimensional function, the so-called profile of the emission zone (indicated as $N(z)$ in Fig. 11.1), that depends solely on the height z in the active layer. It is given by the charge-carrier recombination zone which is likely to be broadened by exciton diffusion.³⁵ The former mechanism of electron and hole recombination severely depends on the

particular properties of charge injection and charge transport in the whole OLED stack. It is primarily influenced by the properties of each single material but also by the constitution of all interfaces.³⁹ The latter attribute, the diffusion length of the excitons after their formation, is an emissive material specific parameter that can be measured indirectly only by experiments using sensing layers.⁴⁰ In multilayer small-molecular OLEDs the exciton formation zone is usually well localised in the thin emission layer, whereas polymeric OLEDs show typically a rather broad emission zone.⁴¹ The dominant type of charge carrier in the emissive layer and the balance point of the emission origin can be estimated by measuring the electronic properties of the involved materials and modelling the charge carrier dynamics in the device.⁴²

Approaches to measure the emission zone directly are based on measurements of the optical far field of OLEDs and subsequent optical simulations. A variety of corresponding methods have been proposed in recent years. Grüner *et al.* analysed the degree of polarisation in the emission from polymeric LEDs with the emission layer consisting of two regions of perpendicular macroscopic orientation prepared by the Langmuir-Blodgett technique.⁷ Scientists from the Cavendish Laboratory⁸ and, at a later date, Gather *et al.*¹⁰ investigated the forward emission from polymeric devices, while Granlund and co-workers compared calculated and experimental EL spectra from 5° to 60° emission angles.⁹ Members of the Philips Research Laboratories in Eindhoven suggested measuring the light emission profile in polymeric devices with nanometre spatial resolution from calculations based on up to 5 discrete dipole positions as sampling points in devices with up to 160 nm emissive layer thickness.¹¹ Perucco *et al.* investigated the impact of two fitting algorithms on the analysis of OLED-like numerical examples,¹² Kim and collaborators estimated the mean emission zone in phosphorescent OLEDs from current density dependent experimental luminous intensity data,¹³ Epstein and co-workers proposed a simplified method for the analytical extraction of the recombination zone location from emission pattern extrema,¹⁴ and Carvelli and co-workers estimated a spatial resolution for measuring the light-emission profile in OLEDs in the 10 nm range.⁴³ However, recently it has been demonstrated by Flämmich *et al.* that devices with adapted layered systems and resulting favourable interference conditions are essential to observe the origin of emission in the OLED far field accurately.²²

11.2.4 Dipole emitter orientation

The orientation of the transition dipole moments in spontaneously emitting materials utilised in OLEDs is determined by the molecular morphology of the particular material. Due to the OLED fabrication process, the dipoles are isotropically orientated in the plane of the layered system interfaces and only a non-isotropic distribution with respect to the layered system normal has to be considered (indicated as $g(\varphi)$ in Fig. 11.1). Thus, the fractions of all dipole

moments that are parallel $p_{\parallel}$ and perpendicular $p_{\perp}$ to the layered system interfaces are quantified by¹⁹

$$\begin{aligned} p_{\parallel} &= \int_0^{\pi/2} g(\varphi) \cdot \sin^2 \varphi \cdot \sin \varphi \, d\varphi \\ p_{\perp} &= \int_0^{\pi/2} g(\varphi) \cdot \cos^2 \varphi \cdot \sin \varphi \, d\varphi \end{aligned} \quad [11.8]$$

The normalisation $\int_0^{\pi/2} g(\varphi) \cdot \sin \varphi \, d\varphi = 1$ ensures that $p_{\parallel} + p_{\perp} = 1$.

As mentioned above, the emission from an arbitrarily oriented dipole can be decomposed into contributions of three orthogonal dipoles (ITE, ITM, $\perp$ TM) and, for the purpose of optical simulation, knowledge of the detailed orientation distribution $g(\varphi)$ is not necessary (see Eq. 11.2). The essential input parameter is the fraction of parallel and perpendicular dipole moments according to Eqs. 11.8 that contribute to the radiation pattern. Due to the isotropic in-plane distribution of the dipoles, a common reasoning is that the emission from OLEDs is generated by two parallel dipoles (ITE and ITM) and, depending on the emissive material, a fraction of ν perpendicular dipole contributions ($\perp$ TM), according to $p_{\parallel}:p_{\perp}=2:\nu$.

Considering polymeric materials deposited from solution by spin-coating, the polymer chains usually align in the plane of the film and the emissive sites tend to adopt this preferential orientation, as indicated by various photoluminescence and Raman studies.^{5,44} In the notation introduced here, materials with a purely parallel emitter orientation yield $p_{\parallel}:p_{\perp}=2:0$. However, it has been shown that some perpendicular dipole contributions have to be considered for polymeric devices as well.^{17,18} Moreover, the chromophore could be attached to a polymer side-chain rather than to the backbone, which would cancel any orientation-correlation suggested from the spin-coating process.

For a long time, vacuum deposited small molecule materials were believed to have no preferred emitter orientation due to their rather isotropic, small molecular structure.^{32,33,45} Such a complete random distribution corresponds $g(\varphi)=1$. A descriptive reasoning is that the radiation pattern is generated by one perpendicular dipole per two parallel dipoles: $p_{\parallel}=2/3$ and $p_{\perp}=1/3$, or $p_{\parallel}:p_{\perp}=2:1$. Just recently, strong birefringence accompanied by a preferred parallel orientation of the transition dipole moments in vacuum deposited, fluorescent small-molecular films was observed by Yokoyama and co-workers in PL investigations and attributed to the increased molecular length of the molecules.^{3,46} An expeditious approach to identify the orientation of the transition dipole moments in emissive materials under optical excitation of diode-like structures has been presented lately by Frischeisen and collaborators,⁴ and Flämmich et al. introduced a general method to measure the orientation of the emissive sites in electrically operating devices.¹⁷ By applying the latter two approaches, an unexpected, mainly parallel

orientation of the transition dipole moments was observed in phosphorescent materials very recently by Flämmich and collaborators,¹⁹ promising considerably enhanced optical outcoupling efficiencies for small molecule devices.

11.2.5 Internal luminescence quantum efficiency q

The internal luminescence quantum efficiency q is an intrinsic material property of spontaneously emitting materials and denotes the probability of the excited state to relax into the ground state radiatively, i.e., under emission of a photon:

$$q = \frac{\Gamma_r}{\Gamma_r + \Gamma_{nr}}, \quad 0 \leq q \leq 1 \quad [11.9]$$

It describes the ratio of radiative transitions (with the rate Γ_r) with respect to all transitions including competing non-radiative excited state depopulation (with the rate Γ_{nr}). In case of efficient emitters the radiative events dominate the non-radiative ones ($\Gamma_r \gg \Gamma_{nr}$; $q \rightarrow 1$), whereas inefficient materials provide many non-radiative decay channels and the emission of a photon is rather unlikely ($\Gamma_r \ll \Gamma_{nr}$; $q \rightarrow 0$).

It is well known that the spontaneous emission rate of a transition changes when the emissive system is placed in a microcavity or in a layered system^{31,47}: $\Gamma_r \rightarrow \Gamma_r^{cav} \equiv \Gamma_r^*$, whereas non-radiative transitions are assumed to be unaffected by the surrounding system: $\Gamma_{nr}^* \equiv \Gamma_{nr}$. Thus, the lifetime of an excited state and the total transition rate in a cavity become $1/\tau^* = \Gamma^* = \Gamma_r^* + \Gamma_{nr}$. The relative lifetime τ_{rel} and the relative transition rate Γ_{rel} (used in Eq. 11.3) become:

$$\frac{1}{\tau_{rel}} = \frac{\tau}{\tau^*} = \Gamma_{rel} = \frac{\Gamma^*}{\Gamma} = \frac{\Gamma_r^* + \Gamma_{nr}}{\Gamma_r + \Gamma_{nr}} \quad [11.10]$$

Similar to Eq. 11.9, the effective internal luminescence quantum efficiency q_{eff} can be defined

$$q_{eff} = \frac{\Gamma_r^*}{\Gamma_r^* + \Gamma_{nr}}, \quad 0 \leq q_{eff} \leq 1 \quad [11.11]$$

that is, the probability of the excited state in the cavity to relax in the ground state radiatively. This effective q -value is used in the typical formulation of the EQE equation (see middle term of Eq. 11.7).

In order to quantify the variation of the radiative rate due to the presence of the layered system, the equivalence between the probability for spontaneous emission of a photon via a dipole transition and the radiated power of a classical dipole source in the corresponding layered system is utilised (see Eq. 11.3 and for example, Lukos and Kunz).³¹ When the presence of a thin film cavity increases the total power radiated by the dipole, then the corresponding probability for the excited state to emit a photon will increase by the same factor⁴⁸.

$$\Gamma_r^* = F \cdot \Gamma_r = \frac{\rho_{tot}^{cav}}{\rho_{tot}^{hom}} \cdot \Gamma_r \quad [11.12]$$

By this means, the effect of the cavity on the radiative transition rate is expressed in terms of the total radiated power in the system ρ_{tot}^{cav} with respect to the one in the homogeneous medium ρ_{tot}^{hom} . The indices *hom* and *cav* refer to the dipole in the homogeneous medium and in a cavity, respectively. The relative transition rate according to Eq. 11.10 now becomes:

$$\Gamma_{rel} = 1 + q \left(\frac{\rho_{tot}^{cav}}{\rho_{tot}^{hom}} - 1 \right) = 1 + q(F - 1) \quad [11.13]$$

Thus, the variation of the emission rate can be evaluated when the internal luminescence quantum efficiency q of the emitter and the total emitted power in the cavity with respect to the homogeneous medium are known. This expression of the relative transition rate highlights: For the low q limiting case ($q \rightarrow 0$), where non-radiative transitions dominate the depopulation of the excited state, no influence of the cavity on the emission rate is present. By contrast, cavity effects have a pronounced influence and directly scale Γ_{rel} when employing high- q emitters. The latter case of $q \rightarrow 1$ is obviously the desired one for efficient OLED systems.

These considerations illustrate the outstanding impact of the q -value on the OLED performance: it is not only a multiplicative factor to the overall device efficiency (see Eq. 11.7) but is also related to the rate of radiative emission (see Eq. 11.13). Hence, the q -value significantly influences the optimal emitter position in planar devices and plays a crucial role for optical OLED optimisation strategies.^{20,32,33,49,50,51}

There are well known approaches to determine the q -value by means of photoluminescence experiments on single supported films using optical excitation as proposed by Greenham and co-workers.⁵² However, in addition to the two distinct excitation processes in optical and electrical operation, the local environment of an emissive site in an electrically excited device cannot be compared to its local environment under optical excitation: because the rate of phonon-mediated, non-radiative transitions, for example, severely depends on the local temperature, q usually changes with driving conditions and charge carrier densities.^{51,53} In order to consider these effects properly, an *in situ* measurement of q in electrical operation is desirable. The q -value is frequently estimated from the measured *EQE* of OLEDs.^{2,15,33,54} However, as follows from Eq. 11.7, this approach requires precise knowledge of the optical outcoupling efficiency and, more importantly, assumptions on the charge recombination probability γ and the singlet/triplet excitation ratio η_{ST} . The latter values are only rough estimates for small-molecular and polymeric material systems and thus a resultant q -value is debatable. Consequently, a relative measurement as introduced by Flämmich *et al.* would be preferable in order to reduce the number of assumptions involved in the analysis.²⁰

11.3 Experimental

Before proceeding to a detailed discussion of the experimental data and results in Section 11.4, the fabrication and stack architecture of the OLED systems under study is explained briefly. Furthermore, some issues of the inverse outcoupling problem are touched and the experimental methods are outlined.

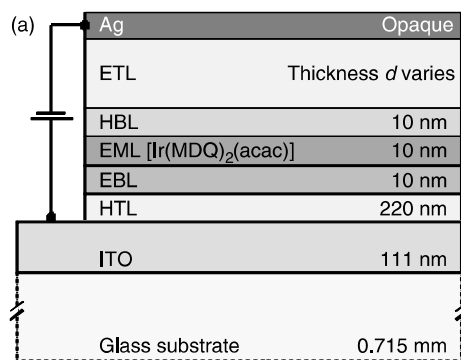
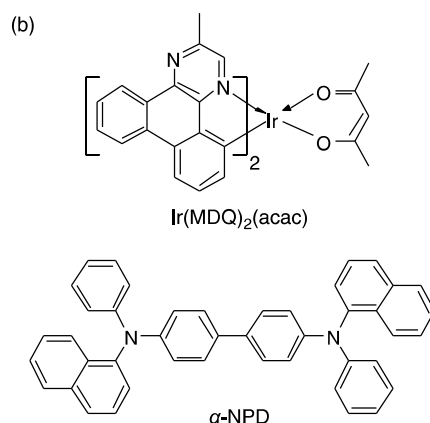
11.3.1 Layered system under investigation

The OLED samples, comprising several individually addressable circular pixels of 4 mm^2 area, were prepared at OSRAM Opto Semiconductors GmbH, Regensburg, by thermal evaporation of organic materials onto commercial ITO coated substrates. The layered structure was fabricated using standard evaporation techniques at a base pressure of 10^{-7} mbar and an evaporation rate of 0.05 nm/s . Doped electron-transport layer (ETL) and hole-transport layer (HTL) were used to improve the charge carrier transport, introducing the dopant by co-evaporation. This technique was also used for incorporating the emitter into the matrix material. Electron-blocking layers (EBL) and hole-blocking layers (HBL) were utilised to confine the charge carrier recombination zone within the emissive layer (EML). After cathode evaporation all devices were encapsulated with a glass lid containing a getter.

The stack architecture of the OLEDs is depicted in Fig. 11.3(a). The EML consists of the red triplet-emitting material iridium(III)bis(2-methylidibenzo-[f,h]quinoxaline)-(acetylacetonate) ($\text{Ir}(\text{MDQ})_2(\text{acac})$, 8 wt%) in a N,N' -bis(naphthalen-1-yl)- N,N' -bis(phenyl)-2,2'-dimethylbenzidine (α -NPD) matrix. $\text{Ir}(\text{MDQ})_2(\text{acac})$ is a typical emitter in today's high efficiency OLEDs and the mean wavelength of the emission spectrum is $\lambda = 630\text{ nm}$;⁵⁵ its chemical structure is shown in Fig. 11.3(b). A series of 9 devices with varying ETL thickness up to about 400 nm was fabricated.

11.3.2 The inverse outcoupling problem

The relations for the radiation pattern and EQE from an electrically operating OLED, as given by Eqs. 11.5 and 11.7, illustrate the fundamental reason why optical analyses from external device measures are not straightforward: externally measured device outputs are necessarily an average of all single emitter contributions. It is almost impossible to estimate features of the internal dipole radiation by starting from EQE measurements, because the EQE is an integral over all angular and spectral components. Furthermore, the other factors in Eq. 11.7 have to be known precisely in order to deduce meaningful results from the measured EQE . By contrast, angular, spectral, and polarisation resolved measurements of the radiation pattern are more likely to allow for conclusions about the emissive sites' properties.



11.3 Stack architecture, chemical structures of Ir(MDQ)₂(acac) and α -NPD. The layered system of the OLEDs is shown (a), alongside the chemical structures of iridium(III)bis(2-methyl-10-quinolinecarboxylate)-(acetylacetonate) (Ir(MDQ)₂(acac)) and N,N'-bis(naphthalen-1-yl)-N,N'-bis(phenyl)-2,2'-dimethylbenzidine (α -NPD) (b).

For optical analyses it is essential to separate the contributions from emitters with distinct locations or orientations in the optical far field. According to Eq. 11.2, parallel dipoles emit TE and TM polarised radiation, whereas perpendicular dipoles contribute to TM polarised radiation only. Hence, polarisation dependent measurements should allow for a separation of the contributions from parallel and perpendicular dipoles. By analysing the TE polarised radiation pattern, investigations of the internal EL spectrum $S(\lambda)$ and the emission zone $N(z)$ are performed independently of the dipole orientation. Keeping the internal spectrum and emission zone fixed while analysing the TM polarised radiation pattern, the

emitter orientation distribution $g(\varphi)$ remains the only unknown parameter that is adjusted to match TM experiment and simulation.

Solving the inverse outcoupling problem is based on performing a least-squares fit to the measured angle, wavelength, and polarisation dependent radiance of a device. In order to circumvent the complexity of absolute measurements and the consideration of absolute factors in Eq. 11.5, a non-absolute reverse simulation based on Eq. 11.4 is usually performed. A number of discrete emitter positions z within the emissive layer are assumed, each comprising an identical internal spectrum $S(\lambda)$ and orientation distribution $g(\varphi)$. Some investigations consider a single emitter position within the emissive layer.^{32,33} Other studies take an extended emission zone $N(z)$ into account, assuming a parametric distribution deduced from electrical considerations^{9–12} with numerically reasonable emitter position discretisations (e.g. $\Delta z \sim 10$ nm,¹⁰ or $\Delta z \sim 20$ nm).¹¹ Unfortunately, optical reverse simulations based on a large number of discrete emitter positions without assuming a distribution fail because the radiation patterns of emissive sites at different positions are not sufficiently distinct and not linearly independent. Regarding the orientation of the emissive sites, it is impossible to measure the detailed orientation distribution $g(\varphi)$, but rather the fraction of parallel and perpendicular dipole contributions ($p_{\parallel}; p_{\perp}$) that generate the radiation pattern (see Eq. 11.2).

11.3.3 Experimental methods

Prior to any analysis, the wavelength-dependent, complex dispersion data ($n+i\kappa$) of all materials involved have been measured by dispersion-model-free reflection-transmission-spectroscopy.²⁶ Subsequent spectral reflectivity analysis enables an exact determination of the deposited layer thicknesses.

In order to access the optical far field of the OLEDs, polarised angular radiation patterns have been recorded utilising a rotational stage where the OLEDs were mounted, and an optical detection system consisting of a wire grid linear polariser with attached achromatic waveplate, combined with a fibre coupled calibrated spectrometer. The resulting experimental intensity data $I(\theta, \lambda)$ possess a wavelength resolution of $\Delta\lambda < 5$ nm and an angular resolution of $\Delta\theta < 0.5^\circ$, as well as an intensity uncertainty below 2%. Unless stated differently, the OLEDs were driven at a current density of $j = 50$ mA/cm² using a constant current source.

The current-voltage characteristics of all OLEDs were also investigated to ensure similar electrical behaviour of the devices in spite of the different ETL thicknesses. Fortunately, the current-voltage curves revealed no significant difference between the devices with varying ETL thicknesses; a fact that is attributed to appropriate n-doping of the ETL.³³ As a favourable consequence, only optical effects need to be considered in forthcoming analyses, allowing a relative comparison of the performance of the devices from an optical point of view.

11.4 Routines for analysing the emitter properties

The characterisation of OLED emitter properties by optical analysis of radiation patterns of OLEDs in electrical operation has been established as an *in situ* investigation method in recent years. Most studies analyse the spectral emission of conventional devices and leave an important issue open to debate: does the investigated fraction of the OLED radiation pattern actually hold sufficient information about the internal feature of interest? In order to pursue this question systematically, the emission from a bottom emitting OLED stack (as depicted in Fig. 11.3, comprising Ir(MDQ)₂(acac) in α -NPD as emissive system as given in Section 11.3.1) is discussed in this chapter. Starting from very basic considerations of the internal dipole emission process it is exploited that the distance between the emissive sites and the metal cathode is most crucial to the overall optical device behaviour. Furthermore, the potential of polarisation resolved analyses to separate the contributions from differently oriented emitters is considered. A macroscopic glass-hemisphere is frequently attached to the OLED substrate in order to observe an extended fraction of the internal emission pattern. Since this increases the complexity of the experiments considerably, it is worth reviewing its advantages in comparison to conventional analyses of the far field pattern in air. By this means, a general routine is proposed that enables determining the internal features of particular interest with greatest accuracy and in a manner almost independent of the other *active* properties of the emissive material.

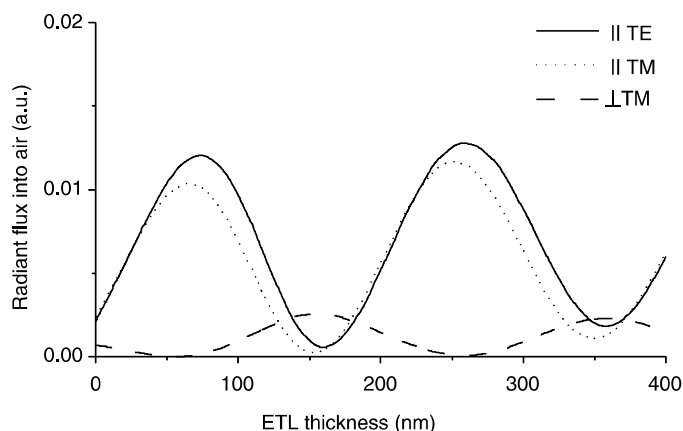
11.4.1 Dipole emission basics and emitter–cathode distance

It is well known that the emitter in a bottom-emitting OLED interacts with its reflected field from the mirror-like metal cathode. Consequently, the distance between the emissive sites and the metal cathode mainly determines the interference conditions at the position of the emissive sites. Varying the emitter–cathode distance, e.g. by varying the ETL thickness in the present OLED system, imposes the most pronounced effects onto the optical device properties. As a result, the ETL thickness is most crucial to enhance or suppress certain dipole contributions to the far field of the device.

To elaborate the different characteristics of the three orthogonal dipoles ($\parallel$ TE, $\parallel$ TM, and $\perp$ TM) in some more detail, their contributions to the OLED far field are discussed individually in the following. The radiant flux in air ($\Phi = 2\pi \int I^{dir}(\theta, 630\text{nm}) \cdot \sin\theta d\theta$) of the three orthogonal dipoles embedded in the OLED stack (shown in Fig. 11.3(a)) is calculated as a function of the ETL thickness and depicted in Fig. 11.4. Evidently, the emission from parallel and perpendicular emitters experiences opposite interference conditions. This is surprising at first because one expects a different interference behaviour for TE and TM polarised radiation due to a phase shift difference of approximately π (at moderate emission angles) upon reflection at the cathode. However, the typical character of dipole emission has to be taken into account as well: the interference behaviour

additionally depends on the initial phase relation of the relevant electromagnetic fields emitted by the dipoles in the backward direction towards the cathode and the forward direction towards the OLED substrate. The forward and backward emitted electric TE fields of a parallel oriented dipole (||TE) oscillate in phase initially. In the case of the magnetic TM fields, there is a π phase difference for a parallel emitter (||TM), but an in-phase-behaviour for perpendicularly oriented dipoles ($\perp$ TM).⁵⁶ Combining both effects, (i) the phase difference due to cathode reflection and (ii) the initial phase relation of the emitted fields, results in a similar interference behaviour for the TE and the TM waves of parallel dipoles (||TE, ||TM), but the interference effects of the radiation from perpendicularly oriented emitters ($\perp$ TM) are shifted by π , corresponding to a discrepancy in the emitter–cathode distance of a quarter wavelength. Thus, at emitter–cathode distances where parallel emitters experience constructive interference, destructive interference occurs for perpendicularly oriented emitters and vice versa.

Unfortunately, perpendicularly oriented dipoles emit most power in the direction parallel to the interfaces (see Fig. 11.2) and not in the desired perpendicular direction towards the outside medium air. As a consequence of this and the interference behaviour discussed above, the orientation of the emissive sites in the light-emitting material has a major impact on the device performance and overall efficiency – a fact which is well-known.^{15,17,18,32,49} Most common and optically optimised OLED stacks are designed to enhance the emission of parallel dipoles, as this allows extracting most power to the outside medium air (see Fig. 11.4 for ETL thicknesses $d=70$ nm and $d=260$ nm). Unfortunately, such



11.4 Opposite interference conditions for parallel and perpendicular dipoles. As a measure for the contribution to the OLED's far field radiation pattern, the calculated radiant flux in air at $\lambda=630$ nm is shown as a function of the ETL thickness for the three single dipoles embedded in the OLED stack depicted in Fig. 11.3(a).

optimised stack architectures trap almost all light generated by perpendicularly oriented dipoles inside the layered system or the substrate glass. As a result, the optical outcoupling efficiency for emitters with exclusively parallel orientation is about 50% larger than for isotropic oriented emitters.^{4,17–19} Within this context Fig. 11.4 illustrates the typical misery for light-emitting materials with isotropic emitter orientation: at the position for optimal outcoupling almost all light from perpendicular dipoles is lost inside the OLED stack.

11.4.2 TE polarisation: emission zone

As mentioned in Section 11.3.2, only TE polarised radiation should be considered if an investigation of the internal EL spectrum and/or emission zone is intended. Figure 11.5(a) depicts the calculated dependence of the radiant flux ($\Phi_{TE}^{air} = 2\pi \int I_{TE}^{air}(\theta, 630\text{ nm}) \cdot \sin \theta d\theta$) of TE polarised emission into air on the ETL thickness to illustrate the following arguments. The shape of the angular radiation pattern is related to the interference conditions at the position of the emissive site. Figure 11.5(b)–(k) shows the TE angular radiation pattern in air $I_{TE}^{air}(\theta, 630\text{ nm})$ according to Eq. 11.4 for some representative ETL thicknesses. For these calculations, the emissive sites were assumed to be located at three different positions in the EML: at the cathode sided interface of the EML ($z=10\text{ nm}$, upper plots), in the middle of the 10 nm thick EML ($z=5\text{ nm}$, middle plots), and at the anode sided interface of the EML ($z=0\text{ nm}$, lower plots).

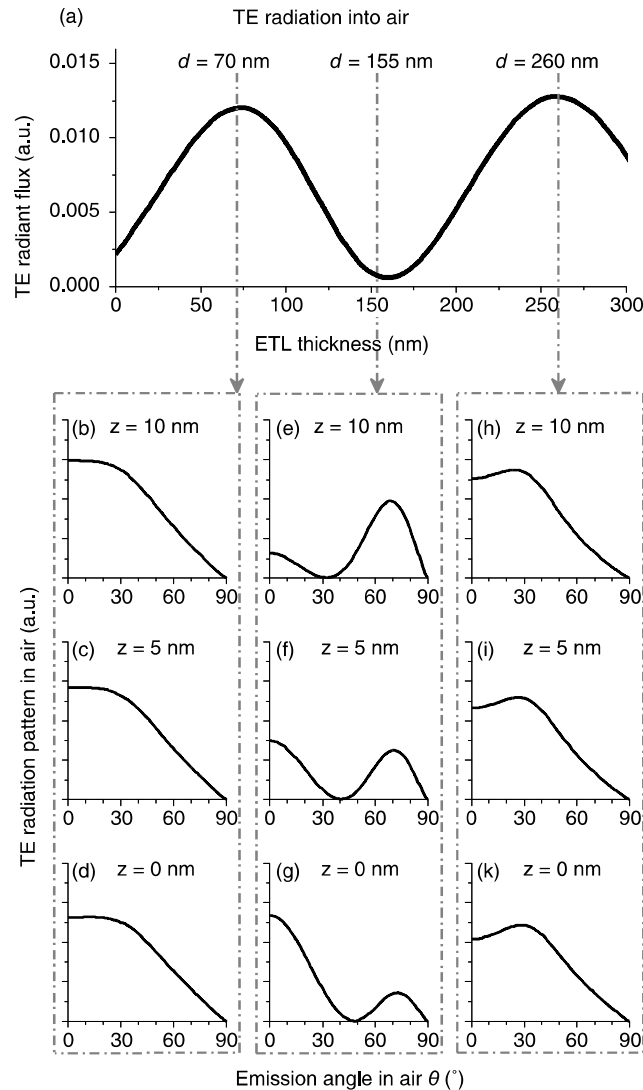
The characteristics shown in Fig. 11.5(b)–(d) and (h)–(k) correspond to emissive sites located around the first and second maximum of the TE polarised radiant flux into air, respectively. The angular patterns are nearly Lambertian like for these cases and all characteristics are very similar to each other due to the constructive interference conditions for moderate emission angles around these positions. By contrast, the angular characteristics of emissive sites around the minimum of the TE polarised radiant flux into air, as shown in Fig. 11.5(e)–(g), are significantly modulated and strongly deviate from a Lambertian emission pattern. Furthermore, the absolute emission intensity is considerably reduced due to destructive interference. Surprisingly, it can be seen that the angular characteristics vary considerably for the three emitter positions displaced by just a few nanometres in the 10 nm thin EML. For emissive sites in the middle of the EML (Fig. 11.5(f)), there is destructive interference for emission into oblique angles of $\theta=40^\circ$. This interference shifts significantly towards smaller or larger angles when considering emissive sites closer to or further from the cathode, respectively, causing a variation of the balance between radiation into normal or oblique angles. These considerations suggest that efficient OLEDs will not provide accurate information about the exact emission origin, whereas a detection of the emission zone in thin emission layers might be possible with adapted, inefficient stacks.

The right part of Fig. 11.5 illustrates similar characteristics to the left part, but for emission inside the OLED substrate that might be accessed experimentally by attaching a glass hemisphere to the substrate. The normalised TE polarised substrate radiant flux shown in Fig. 11.5(m) consists of an extended fraction of the internally generated angular radiation pattern. All angular patterns of emitters located around the maxima of the normalised TE polarised radiant flux into air (Fig. 11.5(n)–(p) and (t)–(v)) deviate significantly from a Lambertian emission due to the presence of leaky modes in the substrate. Again, angular spectra of different positions within the EML are rather similar to each other. The angular characteristics of emissive sites around the minimum of normalised TE polarised radiant flux into air (Fig. 11.5(q)–(s)) are again significantly modulated and the absolute emission intensity is considerably reduced. However, compared to the data from the minimum of the normalised TE polarised radiant flux into air in Fig. 11.5(e)–(g), there is much less effect of the exact emitter position in the EML on the radiation pattern shape. This is surprising at first because one expects the substrate radiation, containing an extended fraction of the OLED-internal radiation pattern, to yield more information than the emission into air. However, distinguishing between different emitter positions here is based on observing radiation pattern changes that are maximised at small emission angles. This sensitive interval is magnified in air because the transition from the substrate into air restricts the observed fraction of the OLED-internal radiation pattern.

This discussion holds two significant implications so far. First, adapted OLED stacks are essential for a sensitive detection of the emission zone. Second, the added value of complicated substrate pattern measurements is limited.

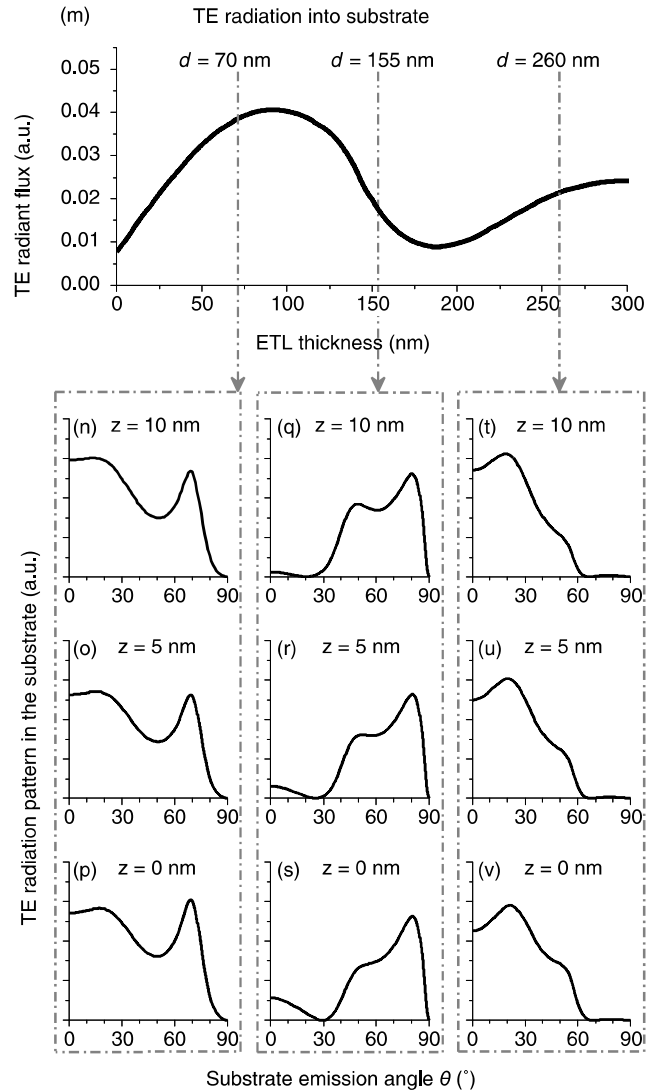
In order to verify the outlined necessity for an adapted stack architecture experimentally, two devices of the $\text{Ir}(\text{MDQ})_2(\text{acac})$ OLED series (see Fig. 11.3(a)) with two different emitter–cathode distances are analysed. Device [A] comprising an ETL thickness of $d=80\text{ nm}$ represents a conventional OLED structure that is optimised for maximum performance. Device [B] with $d=165\text{ nm}$ operates at a weak overall efficiency and is supposed to be well adapted to accurately measure emission zone in the $\text{Ir}(\text{MDQ})_2(\text{acac})\text{:}\alpha\text{-NPD}$ emitter.

Figure 11.6 shows the measured and calculated TE radiation patterns of the OLED [A]. As expected from a device in the first optical optimum in terms of emitter–cathode distance, the radiation pattern is rather Lambertian-like. Three different emission zones, sketched in Fig. 11.6(g), are assumed for simulating the experimental findings: a constant emission zone and two exponential emission zones with 2 nm $1/e$ width centred at the EML–EBL interface (anode side) and EML–HBL interface (cathode side), respectively. The corresponding formula are (i) constant: $N(z)=1/10\text{ nm}$; (ii) anode side: $N(z)=(1/2\text{ nm}) \exp(-z/2\text{ nm})$; (iii) cathode side: $N(z)=(1/2\text{ nm}) \exp(-(10\text{ nm}-z)/2\text{ nm})$. All three emission zones yield an excellent match between measured and simulated radiation pattern, as indicated by the low RMS deviation. In other words, this device structure generates a radiation pattern whose shape is completely insensitive to the exact emission origin and is, thus, unsuitable for measuring the emission zone.

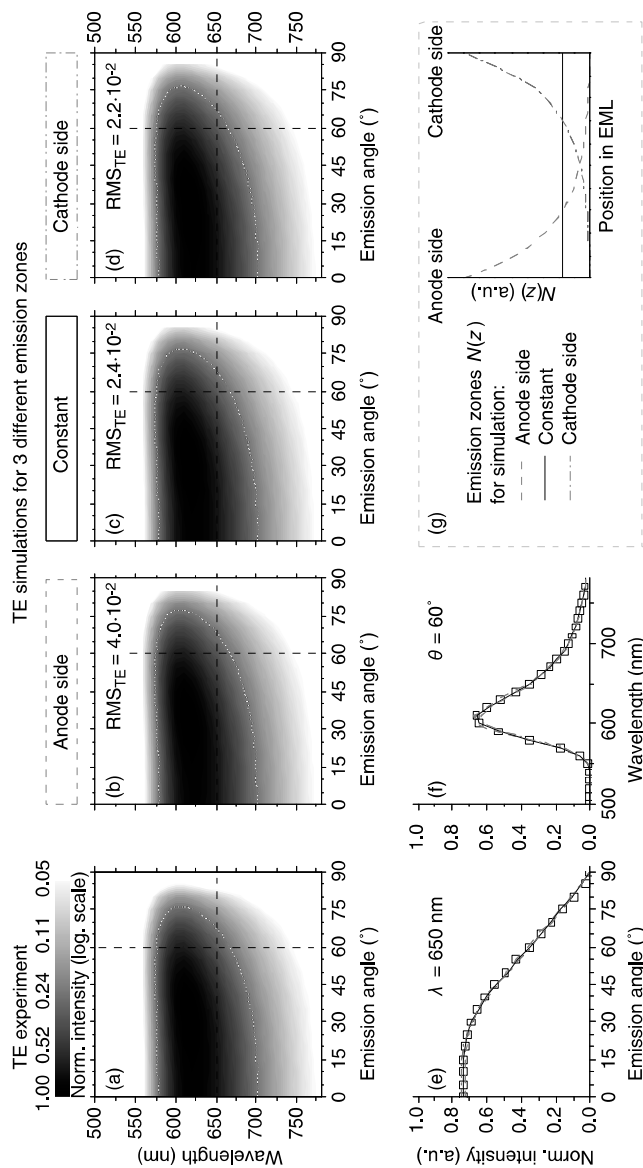


11.5 (a–v) TE radiant flux and single position radiation patterns. As a measure for the optical efficiency of the OLED stack, the calculated TE polarised radiant flux is shown versus the ETL thickness for radiation into air (a) and radiation into the substrate (m). The three outstanding ETL thicknesses correspond to two efficient devices ($d=70$ nm, $d=260$ nm) and one in the efficiency minimum ($d=155$ nm). For each of these three ETL thicknesses, TE polarised angular radiation patterns are shown for emission into air (left)

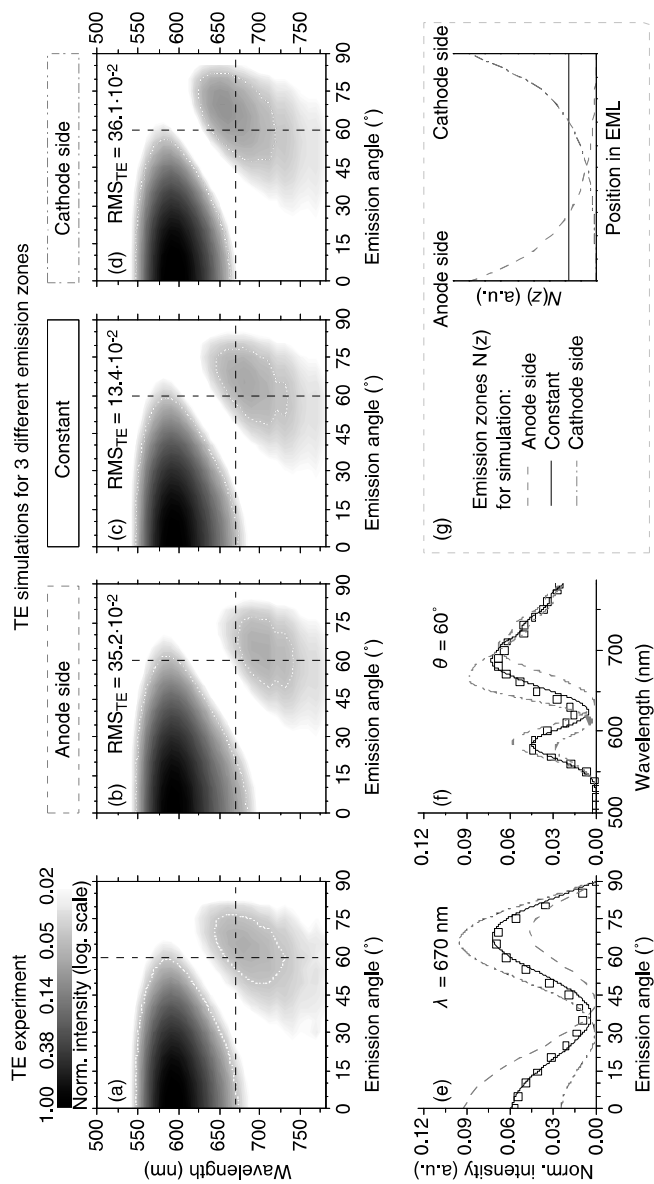
(Continued)



11.5 (Continued) and into the substrate (right), assuming light generation in infinitely thin sheets located at the anode side ($z=0 \text{ nm}$), in the middle ($z=5 \text{ nm}$), and at the cathode side ($z=10 \text{ nm}$) of the 10 nm thick EML, respectively.



11.6 Emission zone experiment using Ir(MDQ)₂(acac) OLED [A]. Experimental and theoretical TE polarised emission patterns of OLED [A] comprising 80 nm ETL thickness. Gray scale plots (a)–(d) exhibit a logarithmic intensity scale; the value 0.25 is accentuated by a white dotted line and cross-sections at $\theta=60^\circ$ and $\lambda=650 \text{ nm}$ are indicated by black dashed lines. Cross-section data plotted for $\lambda=650 \text{ nm}$ (e) and $\theta=60^\circ$ (f) contain experimental data (squares) and theoretical predictions (lines). Simulation results for three different emission zones (g) are shown: anode-sided [(b), dashed line in (e)–(f)], constant [(c), solid line in (e)–(f)], and cathode-sided [(d), dash-dotted line in (e)–(f)]. All assumptions yield a good match to the experimental data, indicated by the similar and low RMS_{TE} values.



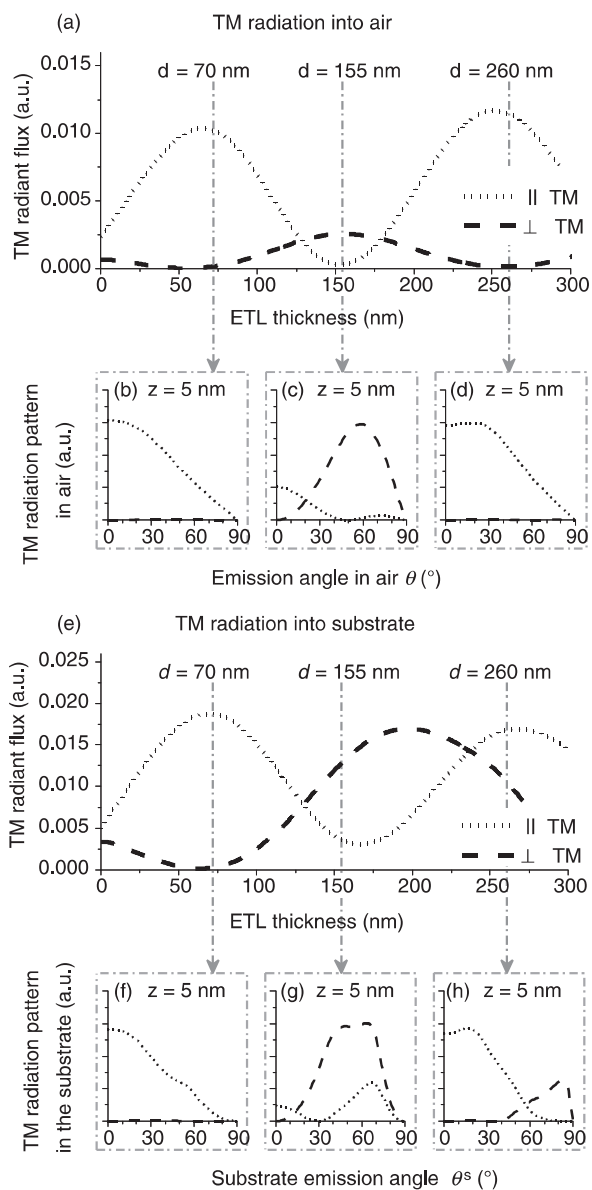
11.7 Emission zone experiment in Ir(MDQ)₂(acac) OLED [B]. Experimental and theoretical TE polarised emission patterns of OLED [B] comprising 165 nm ETL thickness. Grey scale plots (a)–(d) exhibit a logarithmic intensity scale; the value 0.05 is accentuated by a white dotted line and cross-sections at $\theta = 60^\circ$ and $\lambda = 670 \text{ nm}$ are indicated by black dashed lines. Cross-section data plotted for $\lambda = 670 \text{ nm}$ (e) and $\theta = 60^\circ$ (f) contain experimental data (squares) and theoretical predictions (lines). Simulation results for three different emission zones (g) are shown: anode-sided [(b), dashed line in (e)–(f)] and cathode-sided emission [(d), dash-dotted line in (e)–(f)] fail to yield a match to the experiment. A constant emission zone [(c), solid line in (e)–(f)] gives the lowest RMS_{TE} value and a perfect fit.

By contrast, the device structure of the OLED [B] is perfectly adapted for an emission zone measurement. According to Fig. 11.7, the angular and spectral location of the destructive interference condition significantly depends on the exact distance of the emissive sites to the cathode. In this context, Fig. 11.7(e) is most meaningful: the ratio of emission in forward direction and in oblique angles is significantly different for the three emission zones, and the angular position of destructive interference shifts considerably. Assuming a balanced, constant emission zone improves the overall agreement between experiment and simulation significantly compared to an exponential emission zone at either interface of the EML.

By this means, the emission zone in a 10 nm thin EML can be measured accurately utilising an adapted OLED stack architecture. Although α -NPD is known as a hole transporter, the result of a constant emission zone seems reasonable regarding the 10 nm EML thickness which is in the same order of magnitude as the exciton diffusion length in a comparable emissive system.⁵⁷

11.4.3 TM polarisation: dipole orientation

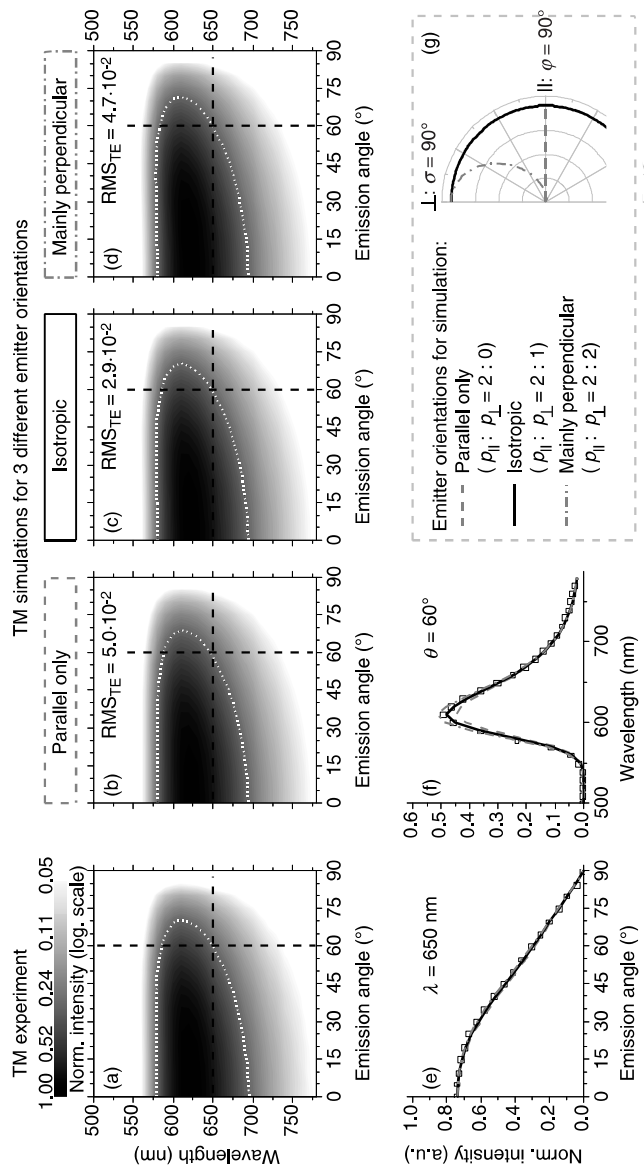
In order to sense perpendicular dipoles in the TM polarised optical far field of an OLED, their contributions to the radiation pattern must be sufficiently large compared to the TM polarised contributions arising from parallel dipoles. As a measure of the far field contribution, the radiant flux in air $\Phi_{TM}^{air} = 2\pi \int I_{TM}^{air}(\theta, 630nm) \sin\theta d\theta$ and in the substrate $\Phi_{TM}^{sub} = 2\pi \int I_{TM}^{sub}(\theta, 630nm) \sin\theta d\theta$ of the two TM dipoles embedded in the Ir(MDQ)₂(acac) OLED stack (Fig. 11.3(a)) is calculated as a function of the ETL thickness (see Fig. 11.8(a) and (e), respectively). The emission from parallel and perpendicular emissive sites is governed by opposite interference conditions as discussed in detail in Section 11.4.1. The interference conditions around the optical maximum enhance radiation from parallel dipoles and suppress light from perpendicular emitters (see Fig. 11.8(b) and (f)). Consequently, the distribution of the dipole moment orientation is almost impossible to obtain using standard, efficient OLED geometries which are optimised for maximum emission. Almost all light generated by perpendicularly oriented emitters is trapped inside such OLED stacks. This argument holds for both the air and substrate emission. By contrast, changing the emitter–cathode distance to the minimum of optical outcoupling yields a large far field contribution from perpendicular dipole moments accompanied by weaker outcoupling of the radiation from parallel dipoles (see Fig. 11.8(c) and (g)). This is the desired case for an emitter orientation analysis. Again, this rule is valid for both air and substrate emission. Measurements using a glass-hemisphere will yield a little more information for very large emitter–cathode distances only (see Fig. 11.8(d) and (h)), but offer no benefits compared to an emitter orientation investigation based on the radiation pattern in air utilising a well-adapted OLED layered system.



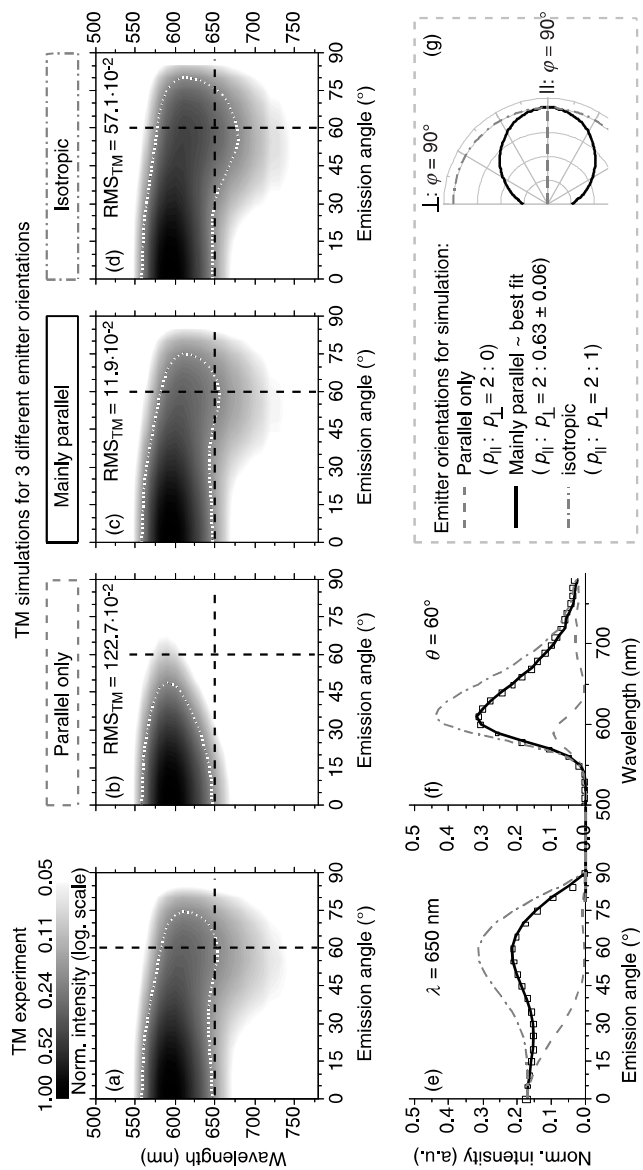
11.8 (a–h) TM radiant flux and radiation patterns. The TM polarised radiant flux of the two TM dipoles versus the ETL thickness is shown for radiation into air (a) and radiation into the substrate (e). For the three outstanding emitter positions, TM polarised angular radiation patterns are shown for emission into air (left) and into the substrate (right), split into the contributions from $\parallel$ TM (dotted) and $\perp$ TM (dashed) dipoles.

In order to verify these considerations from an experimental perspective, the two $\text{Ir}(\text{MDQ})_2(\text{acac})$ OLEDs [A] and [B] (ETL thickness $d=80\text{ nm}$ and $d=165\text{ nm}$, respectively, introduced in Section 11.4.2) are analysed. Figure 11.9 shows the TM polarised measured and simulated radiation patterns of the OLED [A] that is optimised for maximum optical performance. The simulations have been carried out for three different emitter orientations depicted schematically in Fig. 11.9(g): parallel, isotropic, and mainly perpendicular dipole orientation, with a ratio of 2 : 0, 2 : 1, and 2 : 2 contributions from parallel to perpendicular emitters, respectively. Notice that the distributions shown in Fig. 11.9(g) are normalised to the maximum value. The corresponding formulae are (i) parallel: $g(\phi)=\delta(\phi-\pi/2)$; (ii) isotropic: $g(\phi)=0.5$; (iii) mainly perpendicular: $g(\phi)=\exp(-(\phi^2/(0.32\pi^2)))$. Although these three emitter orientations differ significantly, all assumptions yield a perfect match between experiment and simulation. This is due to the fact that perpendicular dipole components are ‘invisible’ in the optical far field relative to the rather intense emission from parallel ones (compare Fig. 11.4 for $d=80\text{ nm}$). Although the assumption of an isotropic orientation delivers a slightly better fit, the difference for the other cases is minor. As a consequence, no information about the emitter orientation can be obtained from the radiation pattern of this conventional OLED stack that is optimised for maximum performance.

By contrast, the optical far field of an OLED is very sensitive to the contribution of perpendicular emitters if the layered system is designed to yield a weak outcoupling of radiation from parallel dipole moments. This is realised for the $\text{Ir}(\text{MDQ})_2(\text{acac})$ OLED [B], where the 165 nm thick ETL induces destructive interference for emitters aligned parallel to the layers, while it enhances the emission of perpendicularly oriented emitters into the air half space. As a result, this configuration is a particularly sensitive probe for studying the presence of perpendicular dipoles. Figure 11.10 shows the experimentally observed radiation pattern for TM polarised emission accompanied by representative simulation results. The destructive interference condition for radiation from parallel dipoles is perfectly illustrated in Fig. 11.10(b). The experimental TM emission obtained in oblique angles is significantly underestimated when assuming parallel dipoles only. This clearly indicates missing contributions from perpendicular dipole moments in the calculation. Including perpendicular dipole moments into the simulation enables accurate modelling of the measured TM polarised emission pattern across the whole spectral and angular range (see Fig. 11.10(c)). Interestingly, the expected isotropic emitter orientation clearly overestimates the measured radiation pattern (see Fig. 11.10(d)), indicating that less perpendicular dipoles contribute to the device emission. Surprisingly, a mainly parallel emitter orientation with $p_{\parallel}:p_{\perp}=2:(0.63\pm0.06)$ yields a perfect fit to the experimental data. The uncertainty of 0.06 is estimated from a doubling of the error function in the part of the radiation pattern that is highly sensitive to the exact emitter orientation.



11.9 Emitter orientation experiment using Ir(MDQ)₂(acac) OLED [A]. Experimental and theoretical TM polarised emission patterns of OLED [A] comprising 80 nm ETL thickness. Grey scale plots (a)–(d) exhibit a logarithmic intensity scale; the value 0.3 is accentuated by a white dotted line and cross-sections at $\theta = 60^\circ$ and $\lambda = 650 \text{ nm}$ are indicated by black dashed lines. Cross-section data plotted for $\lambda = 650 \text{ nm}$ (e) and $\theta = 60^\circ$ (f) contain experimental data (squares) and theoretical predictions (lines). Simulation results for three different emitter orientations [normalized polar-plots of $g(\varphi)$ are drawn in (g)] are shown: parallel [(b), dashed line in (e)–(f)], isotropic [(c), solid line in (e)–(f)], and mainly perpendicular [(d), dash-dotted line in (e)–(f)]. All assumptions yield a perfect match to the experiment, allowing no conclusion to the actual emitter orientation.



11.10 Emitter orientation experiment using Ir(MDQ)₂(acac) OLED [B]. Experimental and theoretical TM polarised emission patterns of OLED [B] comprising 165 nm ETL thickness. Grey scale plots (a)–(d) exhibit a logarithmic intensity scale; the value 0.2 is accentuated by a white dotted line and cross-sections at $\theta=60^\circ$ and $\lambda=650 \text{ nm}$ are indicated by black dashed lines. Cross-section data plotted for $\lambda=650 \text{ nm}$ (e) and $\theta=60^\circ$ (f) contain experimental data (squares) and theoretical predictions (lines). Simulation results for three different emitter orientations [normalized polar-plots of $g(\varphi)$ are drawn in (g)] are shown: parallel [(b), dashed line in (e)–(f)] and isotropic [(d), dash-dotted line in (e)–(f)] fail to yield a match to the experiment. A mainly parallel emitter orientation with $p:p=2:0.63$ [(c), solid line in (e)–(f)] gives a perfect fit to the experiment.

This truly surprising result is obtained in an operating OLED with the only difference to a conventional, optimised stack being a thicker ETL. It is the first notification of a phosphorescent emissive material with non-isotropic, mainly parallel aligned emissive dipole transition moments.¹⁹ This feature is probably related to the morphology of the α -NPD matrix blended with the Ir(MDQ)₂(acac) chromophore. However, the interaction of the asymmetric molecules during co-evaporation and the resultant predominantly parallel orientation of the dipole transition moments are not fully understood yet. Additional investigations potentially utilising more sophisticated spectroscopic techniques are needed in order to further exploit this effect.

As discussed above, the radiation pattern of OLEDs is generated by an ensemble of emissive sites. Assuming that the orientation of the emissive dipole moments $g(\varphi)$ follows, for example, a Gaussian distribution, the result $p_{\parallel};p_{\perp}=2:0.63$ means that the dipoles stagger around the preferred parallel direction with a 1/e-angle of about $\pm 67^{\circ}$. Notice that the mainly parallel emitter orientation of Ir(MDQ)₂(acac) has been confirmed independently using optically excited luminescence (see Flämmich *et al.*¹⁹ and references therein).

Both, the mainly parallel emitter orientation and constant emission zone have been confirmed by analysing the radiation pattern of another suitable Ir(MDQ)₂(acac) OLED of the fabricated series comprising 375 nm ETL thickness (data not shown), indicating that these *active* optical properties of Ir(MDQ)₂(acac) do not depend on the emitter–cathode distance. Furthermore, these *active* optical properties seem not to depend on the applied current density because radiation patterns recorded at $j=1\text{ mA/cm}^2$ and $j=100\text{ mA/cm}^2$ show identical relative characteristics.

11.4.4 Internal luminescence quantum efficiency q

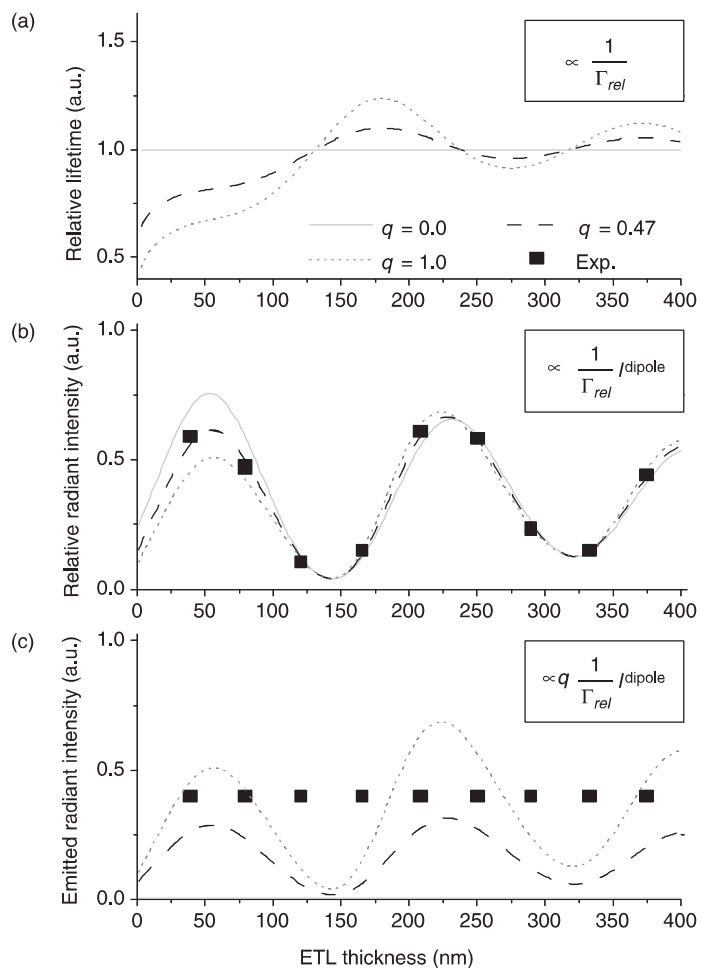
According to Eqs 11.4 and 11.5, the optically relevant factors to the experimentally accessible spectral radiance $I(\theta, \lambda)$ of a device are (i) the q -value, (ii) the relative lifetime of the excited states $\tau_{rel}=1/\Gamma_{rel}$ and (iii) the radiation pattern of a continuously oscillating dipole $I^{dipole}(\theta, \lambda)$:

$$I(\theta, \lambda) \propto q \cdot \frac{1}{\Gamma_{rel}} \cdot I^{dipole}(\theta, \lambda) \quad [11.14]$$

When placing an emitter at a certain distance to the cathode, the relative transition rate of the excited state (Γ_{rel}) depends on its interaction with all modes of the surrounding layered system. The q -value determines how much the relative transition rate is affected (see Eq. 11.13). This effect has a significant impact on the performance of the active layered system ($I^{cav} \propto I^{dipole}/\Gamma_{rel}$). Moreover, the q -value is a multiplier to the real emitted power ($I \propto q \cdot I^{cav}$) and the overall device efficiency.

In order to understand the role of the internal quantum efficiency in OLEDs and possibly derive a measurement concept for the q -value, the forward radiant intensity from the Ir(MDQ)₂(acac) layered system is discussed in detail in the following. For this reasoning it is useful to distinguish between (i) a measure that regards the optical effect of the cavity only ($I_e^{cav} = \int I^{cav}(0^\circ, \lambda) d\lambda$, yielding a relative or normalized radiant intensity using $I^{cav}(0^\circ, \lambda)$ according to Eq. 11.4) and (ii) a real radiant intensity that is absolutely scaled with q ($I_e = \int I(0^\circ, \lambda) d\lambda$ with $I(0^\circ, \lambda)$ according to Eq. 11.5). Figure 11.11 shows the relevant emission measures of the Ir(MDQ)₂(acac) layered system as a function of the ETL thickness for some representative q -values. The behaviour of the relative lifetime (τ_{rel}), i.e. the inverse transition rate ($1/\Gamma_{rel}$) of a representative emitter embedded in the middle of the EML, is depicted in the upper plot. The middle plot illustrates the effects due to the layered system ($I_e^{cav} = \int I^{cav}(0^\circ, \lambda) d\lambda$ using $I^{cav} \propto I^{dipole}/\Gamma_{rel}$ from Eq. 11.4), and the lower plot shows the corresponding real emitted radiance in forward direction. The case of low- q emitters ($q \rightarrow 0$) in Fig. 11.11(a) clearly exhibits no influence of the layered system on the relative transition rate ($q \rightarrow 0$ in Eq. 11.13, the transition rate is identical to the rate in the homogeneous emissive medium). In Fig. 11.11(b), the radiation pattern of low- q emitters is readily given by the classical radiation pattern and the modulation is again due to internal interference effects. Of course, the overall emission from a low- q emitter is fairly weak (see Fig. 11.11(c) for $q \rightarrow 0$). By contrast, the surrounding stack has a large influence on the relative rate for high- q emitters ($q \rightarrow 1$). The relative lifetime is very low close to the cathode and the relative rate is considerably enhanced. This is due to the fact that the emitter couples very efficiently to the surface plasmon propagating at the metal–ETL interface. As a result, the contribution to the far field radiation for high- q emitters is decreased in the first optical optimum (see Fig. 11.11(b)) because more energy is lost into the plasmon compared to the low- q limiting case. Of course, the overall emitted power in Fig. 11.11(c) is larger the larger the q -value is.

Based on the consideration of Fig. 11.11(a) and (b), an approach to measure the q -value is conceived²⁰: the emitter's q -value can be determined via the modified $\Gamma_{rel}(q)$ (see Eq. 11.13) by, for example, shifting the emissive sites through the device (e.g. via the ETL thickness). Based on a quantitative efficiency comparison of a series of OLEDs, each of which comprises a different emitter–cathode separation, the change in the radiative rate due to the modified surrounding layered system is scanned, enabling a determination of q by optical means.²⁰ For this purpose, Fig. 11.11(b) also shows the measured forward radiant intensity from all the devices of the Ir(MDQ)₂(acac) OLED series. The measured data is linearly scaled in order to match the theoretical prediction. An internal luminescence quantum efficiency of $q=0.47 \pm 0.1$ yields the best fit between experimental and simulated values. Because a relative comparison of experimental and simulated data is sufficient, two benefits arise: First, other factors that contribute to the absolute device emission (see Eq. 11.5) can be disregarded (as long as they are



11.11 The role of q in OLEDs and q of Ir(MDQ)₂(acac). The optically relevant emission measures of an emitter placed in the Ir(MDQ)₂(acac) layered system as a function of the ETL thickness are shown for some representative q -values: (a) the relative lifetime, (b) the effect due to the layered system ($I_{cav} = \int I_{cav}(0^\circ, \lambda) d\lambda$) and measured 0° -radiant intensity at $j = 50 \text{ mA/cm}^2$, and (c) the emitted radiant intensity ($I_e = \int I(0^\circ, \lambda) d\lambda$). The measured forward radiant intensity of all devices allows extraction of $q = 0.47$ as best fit between experiment and simulation.

constant). Second, the complexity of measuring absolute power values is omitted and an absolute calibration of the spectrometer is not needed.

It should be noted that the given reasoning to measure the q -value is not limited to the forward radiant intensity from OLEDs. In the same manner, for example the radiant flux, the EQE or the radiance into another emission angle (with or without a particular polarisation state) from several devices could be quantitatively compared. By this means, the proposed approach is similar to basic experiments on the fluorescence lifetime of molecular ensembles near interfaces.²⁹ Because the separation of the curves or rather the variation of the relative lifetime is largest at small ETL thicknesses (where the high- q emitters couple very efficiently to the surface plasmon), an increased number of devices in the first optical optimum would further enhance the accuracy of the measurement.

11.5 Further applications and optical analyses

The previous sections summarise how to analyse the OLED emitter *in situ*, i.e. within its charge carrier transporting environment. As the experimental examples illustrate, the proper knowledge of the system under consideration enables nearly perfect agreement of theoretical and experimental data. This is valuable not only for characterisation purposes but also for optical system engineering, for example the simulation-based optical design of complex stack architectures.

This section is intended to expand the scope of the introduced characterisation approaches. First, the method to measure the q -value by relative means will be applied to a further scenario of interest and the well-known current-dependent OLED efficiency roll-off will be investigated. Second, the unexpected mainly parallel emitter orientation of Ir(MDQ)₂(acac) in α -NPD will be discussed in some more detail in order to fully exploit the potential of oriented phosphorescent OLED emitters.

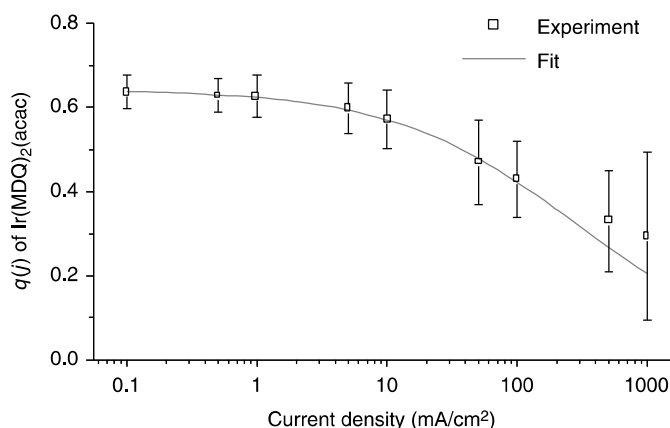
11.5.1 Current dependent device efficiency roll-off

The investigations of the q -value in the previous section are limited to a single current density ($j=50\text{ mA/cm}^2$). With increasing driving currents, however, the efficiency of OLEDs typically drops⁵⁸ which is disadvantageous for lighting applications at elevated brightness levels. This so-called efficiency roll-off is typically attributed to annihilation processes that are particularly important for the longliving triplet excited states in phosphorescent materials.⁵⁹ Since numerous interactions between the excited states and/or the charge carriers can lead to additional non-radiative excited state depopulation, a detailed discussion on the underlying mechanisms is beyond the scope of the present work. However, the method presented above provides a tool to measure the q -value in electrically operating devices by relative means and, thus, independent from other absolute

factors to the device efficiency such as, for example, the charge recombination factor γ that might depend on the current density as well.

The forward radiant intensity of the $\text{Ir}(\text{MDQ})_2(\text{acac})$ OLEDs was measured at different driving current densities ranging from 0.1 mA/cm^2 to 1000 mA/cm^2 . Extracting the q -value (as explained in detail in Section 11.4.4) yields the data shown in Fig. 11.12. The experimental q -values are almost constant at low driving currents $j < 10 \text{ mA/cm}^2$ and drop considerably for $j > 10 \text{ mA/cm}^2$. At current densities above 100 mA/cm^2 the resulting error bars increase considerably, indicating that the determined q -values are less reliable. This is possibly due to thermal effects or irreversible device modifications at these high driving currents. Thus, these values are excluded from further analysis.

A largely simplified function is fitted to describe the q -value roll-off versus current in a *qualitative* manner based on the following reasoning. The q -value is defined as the ratio of the radiative decay rate relative to the sum of all rates depopulating the excited state: $q(j) = \Gamma_r / (\Gamma_r + \Gamma_{nr} + \Gamma_{ad}(j))$. Here, $\Gamma_{ad}(j)$ accounts for additional non-radiative excited state decay that might be current induced (depending on the charge density $\rho(j)$ with the rate Γ_ρ): $\Gamma_{ad}(j) \equiv \Gamma_\rho \cdot \rho(j)$. For the sake of simplicity and to omit tedious manipulations, excited state density dependent depopulation processes are disregarded. It has been treated in detail elsewhere⁶⁰ and does not improve the description of the experimental data. Assuming a power law dependence of the current dependent charge carrier density

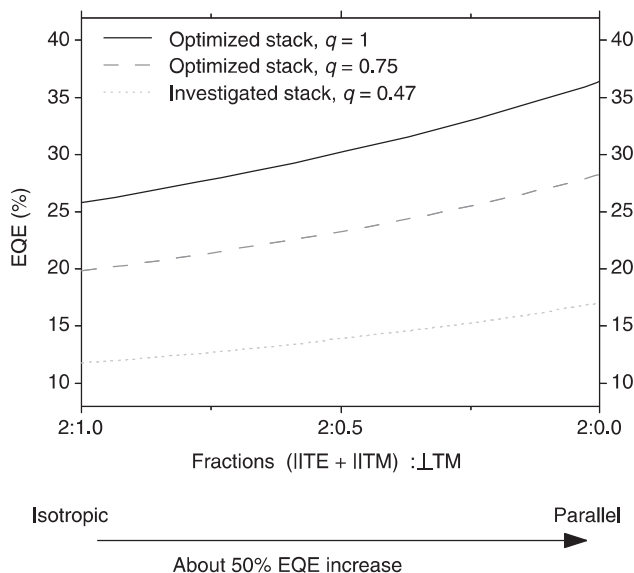


11.12 $q(j)$ of $\text{Ir}(\text{MDQ})_2(\text{acac})$. Determined q -values of $\text{Ir}(\text{MDQ})_2(\text{acac})$ plotted versus current density on a log scale. The value at 50 mA/cm^2 corresponds to the analysis depicted in Fig. 11.11. The line is a least square fit of the function $q(j) = q_0 / (1 + (a \cdot j)^m)$ to the data (allowing a *qualitative* description only; see text). One meaningful parameter is extracted: $q_0 = 0.64$.

yields $q(j) = q_0 / (1 + (a \cdot j)^m)$. Although this relation accounts for additional excited state depopulation due to current induced quenching and disregards annihilation due to an increased excited state density, one meaningful quantity is extracted from the fit: $q_0 = 0.64$, representing the low current limit ($j \rightarrow 0$) of q . It is the material parameter that would be measured in an infinite medium without interfaces and charge carriers present. Note that the fit-equation above is intended to illustrate the characteristic efficiency roll-off *qualitatively* only. It is not intended to derive quantities for any, current or excited state related, quenching effects. A purely excited state associated quenching model (results not shown) fits the data similarly well. Thus, a detailed determination of the corresponding molecular parameters and effects requires more extensive experimental investigations as, for example, presented in Ref. 60.

11.5.2 Oriented phosphorescent emitters boost OLED efficiency

The truly surprising result of a mainly parallel dipole emitter orientation in the phosphorescent small-molecular OLED emitter system of $\text{Ir}(\text{MDQ})_2(\text{acac})$ in α -NPD reveals the orientation distribution of active sites in phosphorescent small molecule guest-host systems is not necessarily isotropic. Although the common assumption of isotropy yields a fraction of $p_{\parallel} : p_{\perp} = 2:1$, a ratio of $p_{\parallel} : p_{\perp} = 2:0.63$ has been determined here, corresponding to a mainly parallel orientation. Consequently, one generally accepted argument applied to discussions of triplet emitting OLED devices must be revised. Beyond doubt, there are triplet emitters with isotropic orientation, but this attribute cannot be assumed generally. By contrast, emitter orientation based optimisation of OLED seems to be within reach, since in optically optimised devices parallel emitters preferably emit into air (see, e.g., Fig. 11.4) and reduce the effect of surface plasmon polariton excitation at the cathode as optical loss channel. This optimisation potential is illustrated in Fig. 11.13 which shows calculated *EQE*-values (according to Eq. 11.7) versus the emitter orientation. Considering the $\text{Ir}(\text{MDQ})_2(\text{acac})$ OLED stack depicted in Fig. 11.3(a) with an optimal ELT thickness of 250 nm, together with the $\text{Ir}(\text{MDQ})_2(\text{acac})$ emitter properties reported in this study, yields an *EQE* of about 13%. Assuming an optimised stack (HTL thickness of 65 nm) and a more efficient, still realistic emitter ($q = 0.75$) yields efficiencies of 20–30% (dashed curve in Fig. 11.13). A further emitter based optimisation toward an ideal quantum efficiency ($q = 1$) and an improved, predominantly parallel emitter orientation (with, e.g., a ratio of $p_{\parallel} : p_{\perp} = 2:0.14$ according to a realistic angular distribution with $\pm 22^\circ$ total width) could increase this efficiency to reach *EQE* values of about 35% (solid line in Fig. 11.13). Note that these efficiency values are given for the planar OLED system according to Fig. 11.3(a), avoiding more or less expensive internal or external outcoupling structures. A rough comparison of achievable *EQE* values according to Fig. 11.13 proves that a purely parallel orientation of the



11.13 Emitter orientation potential to EQE improvement. Calculated *EQE* (for $\text{Ir}(\text{MDQ})_2(\text{acac})$ stack shown in Fig. 11.3 (a) with ETL thickness of 250 nm vs. relative amount of perpendicular emitters ($p_{\parallel}:p_{\perp}=2:v$). Adjusting the HTL thickness to 65 nm and using $q=0.75$ emitters yields potential device efficiencies of 20–30% (dashed line). Extending the simulation towards ideal emitters ($q=1$, solid line) provides planar devices with efficiencies exceeding 35% *EQE*.

dipole transition moments boosts the efficiency of OLEDs by a factor of 1.5 compared to the commonly accepted belief of isotropic emitter orientation in phosphorescent materials.

Interestingly, *EQE*-values in excess of 30% – definitely not reachable with isotropic emitters (see Fig. 11.13) – have been reported recently for phosphorescent small-molecular emissive systems,⁶¹ but without giving a sound explanation for this unexpected high number. The results presented in this section clearly demonstrate that an *EQE*-value in this range is feasible – without any outcoupling enhancement structures – by using phosphorescent emitters with their transition dipole moments being mainly oriented in the substrate plane. This finding opens up unforeseen possibilities for OLED improvement by controlling the molecular orientation of the emissive material.

11.6 Conclusion and future trends

The *active* optical properties of the emitter materials are essential input parameters for quantitative optical analyses of OLEDs that already pave the way for optically

optimised stack architectures in highly efficient lighting prototypes and applications. Researches in both academia *and* industry are investigating optical loss channels in the OLED layered system by means of optical simulation tools in order to derive promising concepts for a further enhancement of the overall device performance. Besides other factors, the prospects of success of such optimisation strategies rely severely on the credibility of the optical input data.

An *in situ* characterisation of OLEDs by radiation pattern measurements and corresponding optical analyses is commonly performed by several research groups. Experiments under electrical excitation provide the inherent advantage over PL experiments that all possibly arising electrical side-effects are automatically included by the experiment. However, the strategic visualisation of the particular internal feature of interest is absolutely essential to such analyses in order to obtain meaningful, precise, and indisputable results. Based on this idea, the present work provides a guideline to measure the *active* optical properties of OLED emitter materials *in situ* by radiation pattern analyses. Reliable and widely applicable methods are introduced to determine the profile of the emission zone, the dipole emitter orientation, and the internal luminescence quantum efficiency of emissive materials from the optical far field emission of OLEDs in electrical operation. For this purpose the layered system has to be well adapted to optically enhance the sensitivity of the emitter features in the OLED far field. Due to basic characteristics of the internal dipole radiation, polarisation dependent measurements allow separation of the contributions from differently oriented dipoles during the analysis. Thus, the particular properties of the emissive material can be investigated almost independently from each other. Furthermore, it is reasoned that the common use of an index-matched glass-hemisphere in order to access the substrate emission is actually not advisable for OLED emitter characterisation by radiation pattern analyses.

The proposed characterisation procedures are applied to a set of OLEDs containing the well-known red phosphorescent small-molecular emitter Ir(MDQ)₂(acac). On the one hand, quite expected results are obtained, such as the constant emission zone in the 10 nm thin small-molecular emissive layer and the drop of the internal luminescence quantum efficiency with increasing current density. These commonly accepted findings confirm the introduced approaches in terms of their strategy as well as the way of performing the experiments and simulations. On the other hand, a novel and truly surprising result is found: a non-isotropic, mainly parallel emitter orientation in a phosphorescent small-molecular guest-host system.

Especially the latter result, that the well-known phosphorescent OLED emitter material Ir(MDQ)₂(acac) shows a mainly parallel emitter orientation in an α -NPD matrix, may have a tremendous impact on future OLED research activities. One generally accepted argument applied to discussions of triplet emitting devices must be revised and emitter orientation based optimisation of phosphorescent OLEDs seems to be within reach. Since parallel dipoles emit preferably into air,

the utilisation of smart emissive materials with advantageous molecular orientation is capable of boosting the efficiency of phosphorescent OLEDs by a factor of 1.5. Homogeneous systems without any presumably expensive internal or external outcoupling structure might deliver external quantum efficiencies in excess of 35%. Materials design, the influence of the matrix material and the substrate, as well as film deposition conditions are just a few parameters that need to be studied further in order to exploit the huge potential of the dipole emitter orientation in phosphorescent OLEDs.

The discovery of oriented phosphorescent emitters perfectly demonstrates how quantitative optical studies can provide an explanation of certain effects that were not understood before – such as an *EQE* in excess of 30% of planar systems. The novel optical *in situ* investigation tools presented in this contribution demand application on various scenarios of interest in future research and development activities. Analysis of white OLEDs (comprising blue, green and red emissive sites in one device) at various driving currents might provide interesting results concerning the interaction of the different chromophores (e.g. ‘triplet harvesting’) in electrical operation. *In situ* measurements of the emission zone in electrically driven devices can yield valuable information about charge carrier behaviour and injection phenomena when combined with sophisticated electrical modelling tools. Other mechanisms like electron- or hole-trapping, the influence of a varied n- or p-doping concentration and the exact required thickness of the electron- and hole-blocking layers might also be investigated by radiation pattern analyses of appropriate devices. Detailed studies on the internal luminescence quantum efficiency at different driving currents or device temperatures may provide valuable insight into the causes of the OLED efficiency drop at high current densities that is especially detrimental for high brightness applications. A combination with other established PL spectroscopic methods might be useful in some of these cases. For all mentioned studies, a feedback loop with material manufacturers is desirable in order to actually transfer the results and derived concepts into tomorrow’s applications.

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Printing techniques for the fabrication of OLEDs

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Abstract: Printed electronics offer a great opportunity for the development of large-area organic light-emitting diodes (OLEDs) with the potential for low-cost high-volume fabrication. This chapter provides a detailed overview of all the major printing and coating technologies. The capabilities and current limitations of each approach are discussed, underlining their current status of development for the manufacture of OLEDs. Discussed technologies include rotogravure, flexography, inkjet, screen, offset lithography printing as well as reverse gravure coating and slot-die coating methods.

Key words: roll-to-roll, printing technologies, organic and printed electronics, large-area OLEDs.

12.1 Introduction

In recent years there has been a growing interest in printing technologies for the fabrication of thin film large area electronic devices, such as organic light-emitting devices (OLEDs). This section will provide an overview of all the major printing technologies and print-related phenomena. Advantages and current limitations of each printing technology will be discussed, underlining their influence for the fabrication of OLEDs.

The purpose of printed electronics is the creation of electronic devices by printing means. During printing, inks are locally deposited over a substrate and then solidified creating a lasting pattern. In printed electronics, the inks are dispersions or solutions of functional materials with specific electrical or optoelectrical properties. By applying different layers of inks with different properties in combination, thin film electronic devices such as OLEDs are created.

In comparison to conventional silicon-based electronic manufacturing processes, printing offers the opportunity to manufacture devices in a continuous roll-to-roll fashion, at far higher manufacturing speeds, with minimum waste, lower cost, using a wide range of substrates (foils, rigid substrates or even papers) and operating at ambient temperature. Printing technologies are therefore indicated as crucial for the development of affordable mass produced large-area OLEDs. However, printing currently presents significant difficulties. Not all materials are printable; in order to be printable a functional material has to be

Table 12.1 Comparison of printed electronics vs. solid-state technology

	Printed electronics	Solid-state
Resolution	μm	nm
Deposit thickness	nm, μm	$\text{\AA}$, nm
Capital cost	Low-medium	High
Manufacturing speed	Fast	Slow
Economic run length	Small to large	Large
Materials	Under development	Developed
Substrate	Flexible, rigid	Rigid

dispersible or soluble, to be carried as ink. Secondly, printing as a rapid deposition process of particles or polymers does not achieve the level of molecular ordering and accuracy typical of processes such as vacuum deposition or photolithography (Gamota *et al.*, 2004). Printing processes are compared with traditional solid state technology in Table 12.1.

There is continuous research in ink development to overcome these constraints, and novel and better performing inks are continuously developed. An example is the current development of copper/silver inks for printing of conductive tracks. Historically, silver particle dispersions have been the main option as a low-temperature metallic printable conductor; copper particles could not be directly printed, due to their tendency towards oxidation (which renders copper non-conductive). With current research, novel conductive stabilised copper-based inks are being introduced to the market by several companies (e.g. Intrisiq Materials, Applied Nanotech, Novacentrix).

The following sections will introduce the basics of ink formulation and the range of printing technologies available, their applications, capabilities and constraints.

12.2 The inks for printing OLEDs

Ink formulation is a complex process that has to take into account the rheological requirements of the printing processes and the ultimate functional performance, which might be at odds with one another.

A conventional ink for graphic applications is constituted by four main components: colorant, solvent, binder and additives (Leach and Pierce, 1999; Gamota *et al.*, 2004). The colorant is either a pigment or a dye. Pigment is in the form of a dispersion of particles in the ink and dye as a solute. Pigment dispersions are typically preferred, being less expensive, more flexible and less susceptible to fading; a classic example of pigment is carbon black powder used in printing text. The selection of either pigments or dye will affect the rheology of the inks. Dyes, being in solution in the ink, will typically be associated with low viscosity inks (typically used for inkjet). Varying the concentration and size of pigments, instead,

will noticeably alter the viscosity of the ink, allowing a wide range of rheological properties. In functional inks, the colorant is substituted with the functional compounds of interest that are also present either as a dispersion of particles or (more rarely) as solute.

The second component is the solvent. This is the liquid medium; it is selected on the basis of its compatibility with the dispersed or solute phase, evaporation performance, wetting properties and viscosity.

Binders are typically a mixture of polymers, they facilitate the dispersion of the pigment in the ink and crucially they bind the particles together after the evaporation of the solvent creating the finished printed film. Finally, additives are compounds added in small amounts to improve performance of the inks. Examples are surfactants used to improve the wetting and dispersion of pigments, bactericides to avoid mould growth, optical brighteners, wax and silicone oils (to reduce friction). In the formulation of an ink these four components must be accurately selected and adjusted for the printing process.

Taking the example of a silver microparticle conductive ink, the silver acts as pigment being present as a micro-size particle dispersion. For this example ink, isopropyl alcohol can be selected as solvent, being a liquid compatible with the dispersed phase and easy to dry. Varying the size and concentration of the silver particles in the solvent will have a direct effect on viscosity of the ink. Increasing the concentration will result in increased viscosity with a higher risk of agglomeration of small particles, with risk of an uneven print. To avoid this issue, higher concentrations are typically associated with larger particles, which are easier to disperse. Printing processes (such as inkjet or gravure) that work with inks at low viscosity will therefore use smaller concentrations and smaller particles than ones with higher viscosity inks (such as screen printing). In recent years there has been a clear development in the formulation and commercialisation of silver nanoparticle inks. The stability of these dispersions is particularly difficult to maintain and specialised stabilisers are required.

The binder has to be added in measured amounts. Insufficient binder will generate weak printed structures, easy to scratch and damage; excessive quantities of binder will separate the silver particles rendering the structure non-conductive. As additive, a surfactant will be added to improve wetting performances and reduce agglomeration of the particles.

It is important to add that the solvent pigment dispersions, discussed in this chapter, are only a type of available inks. For graphic applications, ultraviolet curable polymer inks are also very common. In these inks, the colorants are dispersed in a liquid monomer blend that is cured under UV, without utilising any significant solvent. This polymeric blend acts as an insulator amid the dispersed phase and this limits the applicability of this kind of ink in functional printing. Ultraviolet curable inks are not currently significant for printed electronics and the manufacturing of printed OLEDs.

12.3 Printing technology classifications

Printing technologies are classified in two main categories (Kipphan, 2001; Gamota *et al.*, 2004):

- conventional printing processes (with a printing master);
- digital printing (without a printing master).

In conventional printing technologies, the image to be printed is predefined on a printing plate (the master). The printing plate is constituted by image areas and by non-image areas. When ink is provided to the plate, it transfers only onto the image areas and from there is deposited to the substrate (either directly or via an intermediate roller). These technologies are used for continuously reproducing the same predefined image; they typically offer high speed, high volume manufacturing capabilities with production runs varying from hundreds to millions of copies. Depending on the imaging technology and ink transfer mechanism there is a wide variety of master-based printing technologies. Each one crucially offers the ability to work with different kinds of ink rheology.

Conventional printing technologies particularly relevant for the current development of printed electronics and OLEDs include:

- Rotogravure
- Flexography
- Screen printing
- Lithography.

Digital printing technologies are identified as printing technologies without a print master. They offer the opportunity to deposit the ink where desired over the substrate without the constraint of a fixed image, allowing the creation, if required, of only a single copy of a desired image. Their development is historically associated with the diffusion of computers, which allow digital control of its components (e.g. ink ejection from nozzle in inkjet), hence the reference as digital printing technologies. In recent years several digital printing technologies have been developed. The two most widely available technologies are inkjet and electrophotography. For functional printing, inkjet is the most significant and widely applied masterless technology.

In the development of printed organic light emitting devices, these conventional and digital printing technologies cover different needs, complementing each other. Conventional printing technologies offer the speed and large-area processing capabilities required for mass-production, but require larger set-up cost. Inkjet, as masterless printing technology, covers instead the other end of the spectrum, being very useful for the development and functional study of technology demonstrators and for small and specialised production runs.

In the following sections, the presented printing technologies will be analysed one by one in detail, discussing their current use in the graphic industry, as the

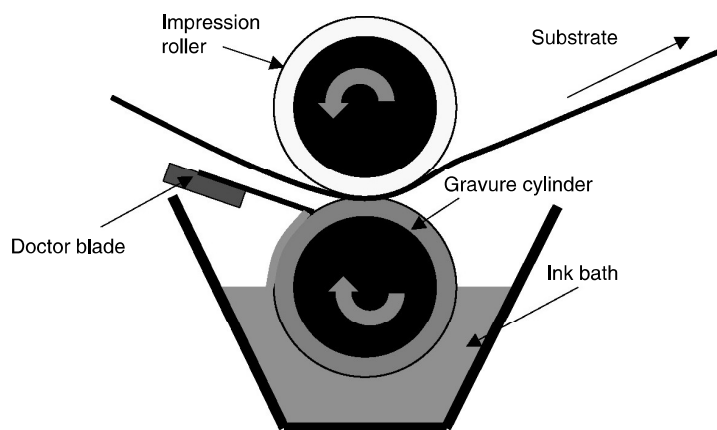
dominant and more mature printing market, and their capabilities for functional printing.

12.4 Rotogravure printing

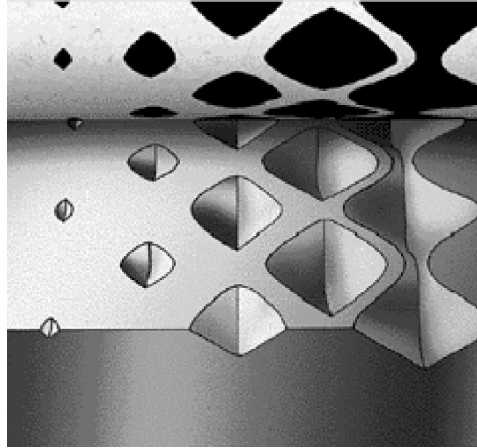
The rotogravure process is a high-volume high-resolution reel-to-reel printing process. Its basic working mechanism comprises an engraved cylinder, an ink bath, a blade referred to as the 'doctor blade' and a rubber covered impression roller (Fig. 12.1).

The image to be printed is engraved on a cylinder in the form of thousands/millions of microscopic recesses or cells. This engraved cylinder rotates in an ink bath where each cell is flooded with ink. The doctor blade is angled against the cylinder wiping away the excess of ink from the cylinder surface, leaving the ink only inside the cell cavities. Subsequently, the cylinder enters into contact with the printing substrate, while the impression roller presses the substrate against the cylinder. This area of contact is called the nip; here the ink is drawn out of the cell cavities and transferred to the substrate, forming printed dots. Larger cells, which will collect more ink, will release more ink onto the substrate, generating larger printed dots than smaller cells (Fig. 12.2). Finally the printed substrate passes through dryers that dry and fix the ink.

The use of finely engraved metal cylinders allows reproduction of high resolution images at very large volumes. The rotogravure process is typically used for roll-to-roll printing of flexible web substrates. Rotogravure presses are comprised of successions of printing units, one per each colour (or functional layer), and intermediate drying units. There is a wide range of gravure printing presses available, ranging from narrow web (50 cm) to very wide web (3–4 metres), reaching printing speeds of up to 1 km/min.



12.1 Schematic of the gravure process.



12.2 Different cells will print different dots (courtesy of European Rotogravure Association).

In the graphic industry, rotogravure is traditionally the printing method of choice where the quality of the print is paramount. Current large-volume markets for rotogravure include the production of high quality packaging and publication prints. Examples include flexible packaging for high-profit food (chocolate wrappers) or quality colour magazines (e.g. *National Geographic*) or catalogues (e.g. IKEA). Additional applications include large area coatings, wallpaper printing, wrapping paper and floor coverings.

12.4.1 The gravure cylinder

The gravure cylinder is at the heart of the rotogravure process. The gravure cylinder is engraved with the image to be printed and acts as the image and ink carrier in the process. Their size ranges from a width of around 50 cm up to 3–4 m and diameters from 10 cm up to 80 cm.

A gravure cylinder comprises a core cylinder that supports the engraved image-carrying layer. The core cylinder is usually made of steel, more recently, in the case of small size presses, of plastic. The engraved image-carrying layer is composed of an electroplated engravable soft material (copper). The image to be printed is engraved on this layer in the shape of small cavities. This soft layer is then protected by further electroplating a thin layer of a harder material (usually chrome). After polishing, the cylinder is then ready for printing.

Three engraving processes are available for the imaging of gravure cylinders on a production scale: electromechanical engraving, chemical etching and laser engraving. Electromechanical engraving is currently the dominant engraving process and is accomplished in lathe-style machines. While the cylinder rotates, a

diamond triangular faced tool, called a stylus, moves with a specific oscillation speed in and out of the cylinder copper surface, creating the cells. These cells have a characteristic pyramid shape. Depending on the shape of the stylus, the depth of the cut or contact length of the tool with the cylinder, cells of different size or aspect ratio can be created. Chemical etching and laser engraving allow much wider freedom in the imaging process, creating cells of different shape. In chemical etching, the copper cylinder is etched on the basis of a positive mask carrying the image. Chemical etching was the dominant process until the 1960s, using film masks. Recent advancements in imaging of chemically etched cylinder have been made using laser for a direct patterning of the mask. Laser engraving is a relatively recent process being introduced in the 1990s by Daetwyler Corporation. In this case the copper layer is replaced by zinc and a laser locally ablates it creating the cell patterns. On gravure cylinders, image areas can present engraved volumes of $<1\text{ ml/m}^2$ to typically 10 ml/m^2 leading to wet ink film deposit onto the substrate from $<0.5\text{ }\mu\text{m}$ to $>5\text{ }\mu\text{m}$ (before solvent evaporation). For special applications (such as coatings) much higher volumes can be engraved ($>100\text{ ml/m}^2$) creating very thick films.

12.4.2 Doctoring

The doctoring process is essential in metering the ink in to the cells. The doctor blade wipes off the excess of ink from the surface of the engraved cylinder, leaving the ink only inside the cell. The blades can be either steel or more rarely plastic. The requirements of the doctoring process limit the size and shape of the engraved cells. The gravure cylinder has to provide sufficient land (non-engraved) area support to the blade to allow a clean swipe process; excessive openings would cause risky deflections of the blade, damaging both blade and engraved features. To limit non-uniform wear of the blades in highly engraved areas, the doctor blade typically oscillates back and forth along the axis of the cylinder.

12.4.3 Impression roller

The impression roller is a rubber coated cylinder that compresses the substrate against the gravure cylinder ensuring a good contact and therefore a good transfer of ink. Impression rolls are smaller than the engraved cylinders (usual ratio 2:1) in order to achieve high contact pressures; these pressures tend to bend the impression roller in the middle, causing a non-uniform pressure distribution affecting the homogeneity of the transfer. Solutions to this problem include the use of back-up rollers to increase rigidity of the system or the use of deflection-compensated impression rollers, which adapt their shape to ensure a constant pressure.

Impression rollers can also improve ink release on the substrates (especially paper) through the use of so called 'electro-static assist'. An electrostatic charge

is applied on the impression roller generating an electromagnetic field between the impression roller and the gravure cylinder. This charge will attract the partially polarised ink, improving the ink transfer.

12.4.4 Rotogravure inks

Gravure inks need to be sufficiently fluidic to guarantee a good filling of the cells and doctoring action. They are therefore characterised by relatively low viscosity, typically within 50–500 mPa·s and low surface tensions; as such the percentage of solid content is typically limited to <30%. Higher viscosities are typically associated with lower print speeds. The inks are generally Newtonian (shear independent) in nature and can use either water as liquid medium or more commonly organic solvents. Highly volatile solvents are preferred for improved drying performances, due to the high speed of the process. An important consideration in the development of functional ink is the effect of the high shear forces at the doctoring. This could affect the functionality of the deposited functional compound.

12.4.5 Substrate

The main requirement for a substrate to be compatible with conventional gravure printing is that it is thin and flexible enough to pass between the gravure cylinder and the impression roller. Common substrates include paper and plastic films (PET, PEN, PP). Gravure is typically associated with roll-to-roll continuous printing, employing substrate reels several kilometres long. Sheet-fed printing by gravure over rigid substrates has been successfully tested on laboratory scale for functional printing (Bornemann *et al.*, 2011). Its large scale application is limited due to the high pressures at the nip and the hardness of the gravure cylinder. Printing over rigid substrates is typically achieved by offset gravure, where a rubber roll is used as an intermediate station to transfer the ink between the gravure cylinder and the substrate.

12.4.6 Rotogravure for functional printing

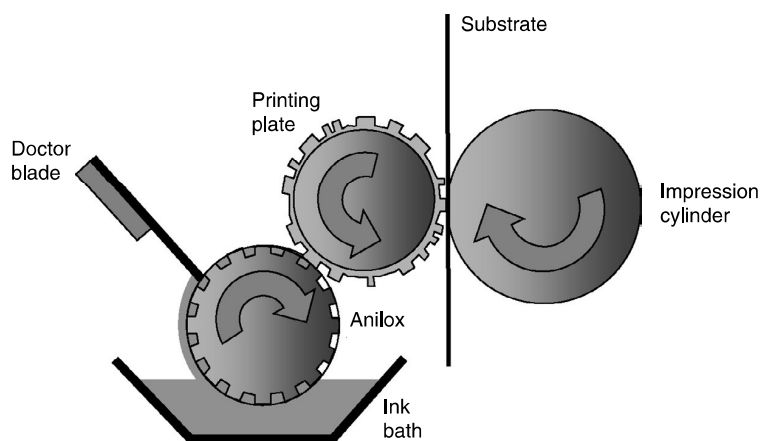
The high quality and long run printing capabilities of the rotogravure process make it one of the most interesting technologies for development of roll-to-roll mass produced thin film devices such as flexible printed OLEDs. Rotogravure operates with medium-low ink viscosities and a wide range of pigment sizes allowing working with a wide range of functional polymers and particles. Rotogravure printing allows an accurate patterned deposition of thin films of selected compounds. The traditional imaging technology limits the applicability of rotogravure in creating fine microstructures. As discussed, the images are created by engraving a succession of separated small cells rather than continuous

features. By depositing separated dots, the creation of continuous features is impossible without allowing the spreading of the ink, limiting the resolution and thickness for narrow elements, such as conductive tracks. In order to overcome this limitation, special engraving (e.g. continuous engraved channels instead of cells) has been successfully tested and conductive tracks down to 20 μm have been achieved (Clark, 2010). Due to the requirements of doctor blade support and ink flow the flexibility of this engraving type is limited.

12.5 Flexography

Flexography relies on a raised flexible plate to carry the image. Ink is transferred to the plate via an engraved cylinder known as an anilox roll. The surface of the anilox is covered with large numbers of uniform finely engraved cells, which are filled with ink from an enclosed chamber or ink bath. Sharp steel doctor blades remove the excess ink from the surface of the anilox ensuring only the cells contain ink (similarly to gravure). The anilox roll is brought into contact with the flexographic plate, thus only allowing transfer of the ink from the anilox roll to those areas where the relief image on the plate has made contact. The printing form is then brought into contact with the substrate to complete the printing process (Fig. 12.3).

Flexography has historically not been thought a high quality printing process, but through recent advances in plate technology and process control, the quality of printing has improved considerably, allowing flexography to compete in some markets with rotogravure and lithography. A great advantage of flexography is its ability to print over almost any substrate (cardboard, flexible plastic film, glass)



12.3 Schematic of flexographic printing process.

due to the flexibility of the image carrier and the low cost of the image carrier when compared with gravure for example. This makes the process particularly suitable for use in the packaging industry. Other markets for flexography include publications (some newspapers) and plastic bags. Flexographic printing presses can be either reel-to-reel or sheet-fed. The presses can reach up to 2 metres web width (e.g. 1.680m KBA Flexo-Courier presses used by the *Daily Mail*) with preference for narrower web presses in packaging. Print speeds can exceed 300 m/min.

12.5.1 Flexographic plate

The first flexographic plates were made from moulded or etched rubber. Currently, flexographic plates are commonly produced using photopolymers, which harden selectively when exposed to ultraviolet light. Different blends of photopolymer will produce plates of different hardness and resilience to chemical attack. For the manufacturing of an imaged plate, the starting point is an unexposed composite photopolymer sheet; this comes attached to a clear polyester backing film. The back of the sheet is exposed to UV for a predefined amount of time without any image creating the floor of the plate. A negative image of the artwork is placed on the top and exposed to UV, which cures and hardens the unprotected areas.

Flexographic plates are typically manufactured on a flat bed for ease of manufacture and to ensure an even controlled UV exposure. After being created the plates are mounted over the plate cylinder. The plates are typically attached through the use of a double-sided tape, called 'mounting tape'. These tapes come in various thickness and hardness, allowing various degrees of compressibility. When printing small features, soft tapes are usually preferred to prevent excessive compression and distortion of the photopolymer plate features. The plates are typically mounted on the cylinder manually with optical devices used to monitor their alignment. Mounting flat plates around a cylinder causes a distortion, a stretching of the outward-looking face of the plate; this is called the 'dispro' or 'distortion factor' and is usually compensated for at the design stage of the artwork. In order to avoid this distortion and improve alignment, recent work has been done in creating the plates directly over the plate cylinder, using alternative approaches such as direct laser ablation.

12.5.2 The anilox roller

The anilox roller is the primary ink metering system of the flexographic process. The surface of the anilox is uniformly covered with large numbers of finely engraved cells. Anilox rolls can be either ceramic with laser engraved cells or chromed with mechanically engraved cells (similar to gravure cylinders). The volume and shape of the engraved cells will determine the quantity of ink to be transferred. For fine printing, laser engraved ceramic aniloxes are preferred

allowing cells with deeper aspect ratio and higher volume capabilities. The total volume an anilox can hold is determined by the size and frequency of the engraved cells. The higher the frequency, i.e. the screen ruling, the lower the maximum achievable anilox volume will be. The choice of screen ruling also depends on the size of the features to be printed. Graphic art manuals recommend the use of anilox rolls with a screen ruling equivalent to $>5\times$ the image screen resolution (Kipphan, 2001). This is recommended to eliminate the 'dot dipping' phenomenon. This happens when the relief feature on the plate is too small compared to the anilox cell opening; the feature does not obtain enough support, dipping into the cells, leading to distorted printed patterns. The engraved volumes on an anilox can vary from $<1\text{ ml/m}^2$ to 40 ml/m^2 leading to wet ink film deposits on the substrate from $<0.5\text{ }\mu\text{m}$ to $20\text{ }\mu\text{m}$.

12.5.3 Flexographic inks

Flexographic inks need to be sufficiently fluidic to guarantee a good filling of the anilox cells but sufficiently viscous to guarantee feature consistency in the ink transfers between anilox/plate and plate/substrate. A wide range of viscosities are compatible with the flexographic printing process, typically ranging from 50–1500 mPa, with higher viscosities associated with lower print speeds. This permits the use of inks with a wide range of pigment concentrations. Concentrations of up to 40% or as low as $<1\%$ are acceptable. Flexographic inks can present Newtonian or shear thinning properties.

12.5.4 Substrates

A fundamental advantage of the flexographic process in comparison to rotogravure is its ability to work with a wide range of substrates both rigid and flexible. By controlling the pressure of engagement between plate and impression roller, very fragile materials such as thin glass sheets or corrugated cardboard can be printed. Common substrates includes paper and plastic films.

12.5.5 Flexography for printed electronics

Recent advancements in the flexographic process make it an interesting printing technology potentially competing with rotogravure for large scale manufacture of thin film printed devices. Flexography offers the advantage of a separate image carrier (that is also low cost and easy to handle) from the ink metering system (the anilox). This allows testing and provides variable film coating thicknesses without expensive re-imaging or re-engraving. This flexibility could offer flexography a competitive advantage over rotogravure in the development of novel devices.

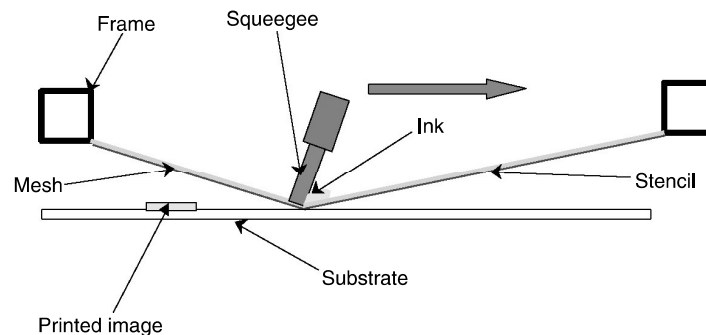
Furthermore, although traditionally associated with a lower image and line resolution than gravure, due to the squeezing of the ink between the plate and the

substrate, recent research (Deganello *et al.*, 2010, 2012a) demonstrated that flexography can mass-produce consistent fine features, such as conductive tracks. This is possible as the plate imaging process allows the definition of lines as continuous features and not as dots, combined with improved control in the pressure between plate and substrate. In these tests, flexography was used to produce a fine conductive grid aimed at reducing the resistance of the transparent anode layer for flexible OLEDs. In further tests, conductive track widths down to $50\text{ }\mu\text{m}$ have been achieved.

12.6 Screen printing

Screen printing relies on forcing the ink through a screen. The screen consists typically of a fabric mesh locally blocked by an imaged stencil. The screen is held over the substrate at a small distance, called the snap off gap. Ink is placed on the upper surface of the screen. A squeegee blade passes over the screen pushing the screen into contact with the substrate and forcing the ink through the mesh onto the substrate. The ink will pass only through the open areas of the mesh creating the desired image on the substrate (Fig. 12.4).

Screen printing has a unique place among conventional printing technologies: it covers a huge variety of markets. It can be used from an amateur level to large industrial scale operations in high-tech applications. Graphic applications cover the printing on fabrics and garments (e.g. t-shirts), the decoration of ceramics and plastic products. High-tech industrial applications include the printing of sensors, integrated circuits and solar cells. Among the various conventional printing technologies, screen printing is the most established in the printed electronic fields. Screen printing presses are usually sheet-fed, flat-bed systems, with production speeds up to 1000 copies/hour.



12.4 Flat-bed screen printing process.

12.6.1 The screen

The screen is the image carrier and ink metering system of the screen printing process. The screen consists of a stencilled fabric mesh. Historically the first meshes were made of silk, but currently meshes are primarily made by interwoven stainless steel or polyester threads. The frequency of the threads (number of threads per cm) will define the maximum possible image resolution, while the thickness of the threads will be the main factor in defining the thickness of the ink film deposit. A finer thread will lead to a thinner fabric and hence a lower ink deposit. Increasing the frequency of the threads will allow a higher resolution image; at the same time a higher frequency will require thinner threads to leave sufficient openings between the threads. Polyester meshes present mesh rulings in the range of 15–165 threads/cm with corresponding fabric thicknesses of 385 down to 43 μm , while stainless steel ones present mesh rulings of 31–154 threads/cm and fabric thicknesses of 215 down to 40 μm . Stainless steel meshes use typically thinner threads for the same resolution, allowing higher ink transfer, but are more delicate and fragile. On average, as a rule of thumb, the wet ink film thickness on the substrate will be just under half the thickness of the fabric. Screen printing is therefore associated with a relatively high wet film thickness deposit ($>10\mu\text{m}$).

In order to create the imaged screen, the mesh is tensioned and bonded to a frame. It is then coated with a photopolymer emulsion material. This is then cured by UV using a positive film of the image as a mask, creating the stencil. After washing, the screen is ready for print. During printing, the stencil (or emulsion layer) will act as the image carrier but it will also act as a seal ensuring a good edge definition of the image.

12.6.2 Screen inks

Screen printing is the printing process with the widest range of applications, hence with the widest variety of inks. The viscosity and composition of the ink must be matched to the fineness of mesh. Coarser meshes will require the use of higher viscosity inks (with higher solid content) to avoid dripping; the mesh opening will limit the maximum size of the pigments to avoid clogging (maximum ratio 1/10). Screen inks therefore present a wide range of viscosities (1 to 100 Pa·s) and solid content can be as high as 90%. The solvents used in screen printing usually have low evaporation rates to avoid drying in the mesh opening.

12.6.3 Substrates

Screen printing is used on almost any kind of substrate or surface, rigid or flexible. Screen presses are typically sheet-fed, printing one sample per time. By adapting the shape of the mesh and of the squeegee, screen printing can be used over complex shaped products such as ceramic surfaces.

For roll-to-roll web printing, a step-and-repeat approach on flat-bed screen presses can be used. Specialised rotary screen presses were developed in the 1980s allowing continuous roll-to-roll printing. In these rotary presses the screen is rolled in a cylindrical shape and consists typically of a rigid metal mesh. Ink is fed into the inside of the cylinder. While the cylinder rotates, the outside of the cylinder enters into contact with the substrate; the ink is squeezed by a squeegee (located inside the cylinder) out through the screen mesh on to the substrate.

12.6.4 Screen printing for printed electronics

Screen printing is the most mature printing technology for electronic and biomedical applications. It is extensively used in the manufacture of solar cells, integrated circuits and electroluminescent displays. It is used extensively in the fabrication of medical sensors.

Screen printing offers an incredible flexibility in terms of ink rheology and substrate. A screen press is much smaller than any flexo or gravure press allowing extensive laboratory research, albeit the process is primarily suited for small-medium print runs. In comparison to these other processes, it deposits a thick film. The print also tends to be less smooth, with the shape of the mesh sometimes retained in the print. The resolution of the printed features is limited by the mesh; conductive track widths of around 100 μm are typically produced. Through use of special meshes (such as by Asada mesh co.), narrower tracks (from 50 down to 30 μm) have been achieved.

12.7 Lithography

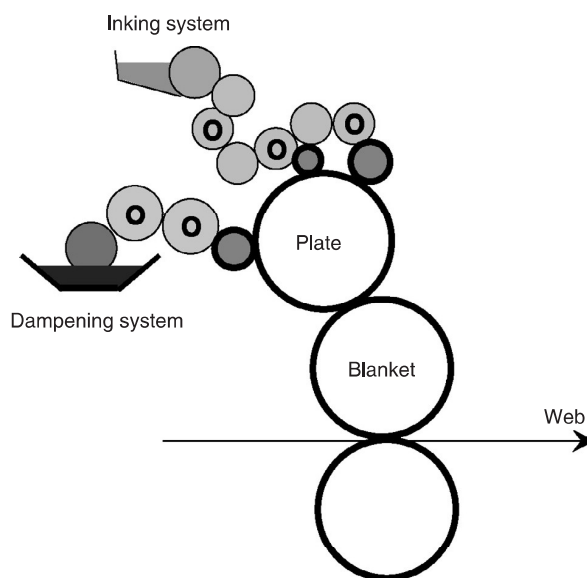
Lithography is the dominant conventional printing process in the graphics market. It is particularly used in the publication industry (magazines, newspapers, books); its application to printed electronics is currently limited.

In lithography the printing plate has the printing and non-printing areas on the same level. The difference is that while the printing areas are ink-receptive, the non-printing areas are ink-repellent. An inking system transfers the ink to the plate from an ink reservoir using a series of oscillating rollers, which ensure a uniform distribution and control of ink film thickness. The ink is typically transferred from the plate to the substrate through an intermediate carrier, a blanket; in this case the process is usually also called *offset printing*. Lithography is characterised by typically depositing a very thin wet ink film onto the substrate (1–2 μm thick).

Lithographic presses can vary from small-scale sheet-fed with print areas of A4 size to large-scale roll-to-roll web presses for magazine publications printing, reaching speeds of 600m/min. There are two main mechanisms for the determination of ink accepting/repellent areas on the plate; these are conventional offset printing and waterless offset printing.

12.7.1 Conventional offset printing

Conventional offset printing works on the principle that oil and water do not mix. The plate is commonly a thin aluminium sheet with the surface specially treated, making the non-image areas hydrophilic and the image area oleophobic. During the printing process, a dampening system transfers treated water from a reservoir through a series of rollers on to the plates, wetting only the non-image areas with a very thin film of water. The plates then enter into contact with the inking system, which provides an oily ink. The ink will wet only the image areas. Water and ink will be transferred to the blanket and then to the substrate (Fig. 12.5). This process is the current dominant offset printing technology, supported by the ease of manufacture and low cost of the plates and it is particularly suited for porous substrates such as paper.



12.5 Conventional offset printing.

12.7.2 Waterless offset printing

Waterless offset printing does not require a dampening system. In this system, the plate is coated with thin ink repellent coating, such as a thin silicon layer (indicatively $2\text{ }\mu\text{m}$ thick). The image areas are obtained by locally removing the repellent coating, creating ink-accepting recessed areas. The process requires specialised inks and specialised temperature control systems. By removing the

water from the process, there is a loss of its cooling effect on the plate. Any change in temperature would significantly affect the viscosity of the ink and hence its transfer; temperature control systems are therefore integrated in the presses, the most common of which is based on pumping coolant through hollow core rollers in the inking unit.

12.7.3 Offset lithographic inks

In the lithographic printing process only a limited range of ink viscosities, tack (e.g. stickiness) and chemical properties are used. Conventional offset tends to use oily paste inks with a high solid content. These inks are characterised by high viscosity (40–150 Pa·s), significant shear-thinning and elastic properties and large oil and binder content (30–50%). The shear thinning allows the ink to be uniformly distributed and to transfer thorough the inking system progressively, achieving thinner layers until the transfer to the plate. In waterless offset printing, the inks will tend to present a higher viscosity and tackiness than conventional offset ink, achieved through high-viscosity resins. This is required since it is essential that the ink presents a greater affinity for itself than it does for the silicon layer. In the case of multi-layering different colour inks, the inks must be graded by tack in order to avoid peeling: the first high, the second less so, the third lower and so on.

12.7.4 Lithography for printed electronics

The application of offset lithography to printed electronics is constrained by the complexity of ink properties required by the process. The process allows very high resolution (20–50 µm features) and it is widely utilised in graphics. Therefore there has been interest in the development of its functional applications. A range of conductive, dielectric inks have been produced albeit not reaching the same performances (to author's knowledge) as gravure or flexographic inks. A range of thin film devices have been produced: thermochromic displays, circuits and strain gauges (Southee *et al.*, 2008; Hay *et al.*, 2007). An interesting adaptation of the process to functional printing is the use of the dampening system as an image to transfer water-dispersed functional compounds. Offset printing has been employed for deposition of thin layers of PEDOT:PSS for the creation of organic field-effect transistors (Zielke *et al.*, 2005). However, the deposited layers presented a branched inhomogeneous morphology (Zielke *et al.*, 2005; Reuter *et al.*, 2007).

12.8 Inkjet printing

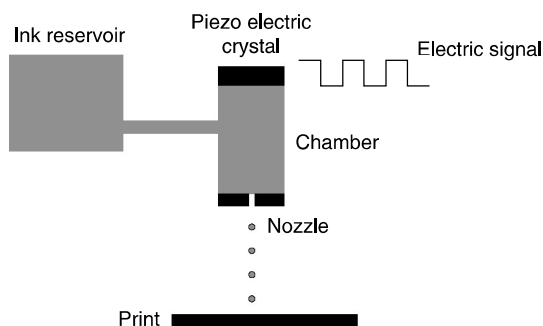
Inkjet printing operates by electronically controlling the production of microscopic droplets of ink that are then deposited on a substrate, hence producing the image.

There are three main methods available for the formation and deposition of droplets: drop-on-demand piezoelectric, bubble-jet, and continuous inkjet. Inkjet printers can vary from the common desktop size inkjet printers to large scale web operated presses.

12.8.1 Drop-on-demand piezoelectric inkjet

The ink is supplied to a chamber with a nozzle on one end and a piezoelectric crystal (PZT) on the other. Electric pulses control the expansion and contraction of the crystal, pushing the ink through the nozzle (orifice) and forming the droplets (Fig. 12.6). There are many variations in the piezoelectric inkjet architecture using different configurations of the piezo crystal, including tube, edge, face, moving wall and piston. Indicatively, droplets are formed with a frequency of 10–20 kHz.

The piezo-ink technology offers the capability to work with very small quantities of fluids at room temperature; it is therefore the most common technology for functional printing on a laboratory scale.



12.6 Drop-on-demand piezoelectric inkjet.

12.8.2 Drop-on-demand bubble jet

The ink droplet is formed by the ink being forced through the nozzle by the expansion of a gas bubble at the rear. This gas bubble is produced by locally boiling the ink through microheaters. The inks must therefore be compatible with the process, and contain a material that has to vaporise and tolerate high temperatures. This process is associated with frequency of 5–10 kHz.

12.8.3 Continuous inkjet printing

Continuous inkjet printing operates by selectively deflecting, through the use of electric charges, a droplet from a stream of droplets, which is produced by

the break-up of a continuous jet. This process allows an extremely high droplet generation frequency (1 MHz) and the creation of very small droplets. Difficulties in controlling the accuracy of the deflection mechanism means that continuous inkjet is typically used in fields where resolution is not essential (e.g. mailing).

12.8.4 Print quality and inkjet inks

The quality of the image will depend on the size of droplet and on its spreading over the substrate. The size of the droplet will be dependent on the rheology of the ink (surface tension and viscosity) and the nozzle diameter. Inkjet inks operate within a narrow range of low viscosities ($<10 \text{ mPa}\cdot\text{s}$) and surface tensions in order to be able to be ejected through the nozzle as droplets. In printing particle dispersion inks, the particle concentration has to be very low (indicatively $<5\%$) in order to maintain the low viscosity required. The particles also have to be very small in comparison to the nozzle diameter in order to avoid clogging (ratio 1/50, hence dye inks are favoured for graphic applications even if more expensive). The deposition rate of inkjet is therefore very low. Finer nozzles will deliver smaller droplets and hence higher possible resolution, at the cost of further reducing the particle size and the speed of manufacture. Typical droplet diameters are around $30\text{--}50 \mu\text{m}$. Printed features down to $20 \mu\text{m}$ (Hosokawa *et al.*, 2007) have been printed by specialised combinations of nozzles and ink, though features of $100 \mu\text{m}$ are more practicable. In order to increase the speed of printing, heads with multiple nozzles are the norm. In this case particular attention should be placed in recognising any clogging of a single nozzle.

12.8.5 Inkjet for printed electronics

Inkjet printing is the most studied and widely used printing process for the development of printed electronic demonstrators and the testing of novel functional compounds. A great advantage of inkjet is its ability to work with a very limited amount of ink, an important requirement in the early development stages of a material. Inkjet allows a great flexibility in imaging, without the need to produce a master. Its large scale applicability is limited by its low speed and solid content. For example, in order to produce conductive tracks the droplets must overlap and multi-layering is often required. This is different from graphic printing where the printed dots can be separated; hence manufacturing of functional devices by inkjet printing can be a particularly slow process. This is compensated on a laboratory scale by the large flexibility of the process. Another limit of the inkjet process is the limited size of printable compounds, which depend on the nozzle diameter. Inkjet printing technologies have been subject to continuous research and development in the last years, thus its large-scale applicability is expected to improve.

Table 12.2 Printing technologies comparison

	Rotogravure	Flexography	Screen printing	Offset lithography	Inkjet
Representative max resolution	Very high (<20 µm)	High (40–50 µm)	Medium (50–100 µm)	High (20–40 µm)	Variable (20–50 µm) droplet related
Deposit dry thickness	Variable (<0.1–5 µm)	Variable (<0.1–4 µm)	Thick (1–20 µm)	Thin (0.2–2 µm)	Very thin (< 0.5 µm)
Capital cost	High	Medium	Low	Low	Low
Manufacturing speed (for graphics)	Very high (1 km/min)	High (300 m/min)	Slow (<100 m/min) (20 sheets/min)	High (500 m/min)	Very slow (<10 m/min)
Economic run length	Large	Medium–large	Small–medium	Small–medium	Very small
Ink viscosity	Medium–low (0.05–0.5 Pa·s)	Medium–low (0.05–1.5 Pa·s)	High (1–100 Pa·s)	Very high (50–150 Pa·s)	Very low (<0.02 Pa·s)
Max % of solid content in ink	30%	40%	90%	90%	5%
Ink formulation	Flexible	Flexible	Flexible	Constraints	Constraints (particle size)
R2R/sheet-fed	R2R	R2R (sheet-fed)	Sheet-fed (R2R)	Sheet-fed/R2R	Sheet-fed (R2R)
Application	Large area/large volume production	Large area/large volume production	Large area/medium–small volume production	Large area/medium–small volume production	Small area/small volume production

12.8.6 Comparative table of printing processes

Table 12.2 compares the major printing processes discussed in this chapter. This provides an overview of the main characteristics of the processes. The values indicated in the table are only representative to help the reader in the selection of printing processes.

12.9 Coating processes

For covering entire surfaces rather than discrete patterning using printing technologies, coating processes can be used. These processes are typically not strictly classified as printing technologies, lacking the capability to create patterned structure on the substrate. Coating processes are anyway significant in the current development of printed electronics and can make use of similar formulations. Large-area thin film deposition of functional compounds is often achieved through coating processes, due to the perceived high level homogeneity of the obtained deposited layer. Patterning can then be obtained by subtractive means such as laser ablation or etching. The crucial limitation of this approach is the difficulty, time and cost in the accurate removal of single layers in multilayer devices without damage to the others. This approach is therefore useful for relatively unstructured large area devices, hence their interest for large-area OLEDs. On an industrial scale, two significant coating processes for thin substrates are reverse gravure and slot-die coating.

Reverse gravure is related to the previously discussed gravure printing process. This process makes use of an anilox but crucially the inked anilox does not rotate with the substrate web (as in gravure) but against it. The ink is drawn out of the cells by the shearing between the anilox and the substrate, depositing a thin film on the substrate. The thickness of the deposit will depend on the ink rheology and cell geometry.

In slot-die coating, the ink is forced out from a reservoir through a narrow slot by pressure and transferred onto a moving web. The slot is kept very close to the web, distanced by the cushion of liquid being coated. The thickness of the deposit will depend on the width of the slot, web speed, pressure, and ink rheology. Vacuum is often generated in front of the slot to avoid trapping of air in the ink cushion. By controlling the length of the slot it is possible to coat the entire surface of the moving web or to produce a striped coating. At its extreme, the process becomes nozzle printing, where the ink is extruded through a nozzle producing continuous narrow tracks in the direction of moving web. This striped coating presents several advantages in functional printing allowing a partial structuring. The process is recognised as being able to produce highly consistent, smooth layers.

12.10 Applications of printing technologies for OLEDs

Extensive literature has been published on the development and successful creation of OLEDs through a wide range of printing and coating technologies: inkjet, screen printing, gravure, flexography, slot-die coating.

The adaptability and selection of the most appropriate printing technology will depend on the OLED architecture, the desired volume production, and the substrate. The two main OLED architectures are small molecule organic light-emitting diodes (smOLEDs) and large molecule (polymer) light-emitting diodes (p-OLEDs). Printing research has so far been concentrated on p-OLEDs, due to the solution processability of the light-emitting polymer layer. Only limited research has been presented on the printing of smOLEDs. Flexography and gravure printing processes have been employed to deposit the small molecule layers as alternatives to vacuum deposition (Van den Hoonaard *et al.*, 2009; Bornemann *et al.*, 2011); this research showed small molecules could be processed by printing means, but that it is difficult to achieve the extremely thin and uniform layering required by the p-OLED architecture.

The structure of a basic p-OLED device can be extremely simple, consisting of a sandwich containing: a supporting transparent substrate, a transparent conductive anode, a hole transport layer (e.g. PEDOT:PSS), a thin light emitting polymer layer, and a metallic cathode (e.g. laminated aluminium layer). In this architecture, the main areas of research and application of printing technologies are in the deposition of thin films for the hole transport and light-emitting polymer layers, and the development of the transparent conductive anode. The suitability of the printing technologies will then also depend on the substrate and desired production volume.

12.10.1 Substrates for printed OLEDs

Glass is a common substrate for the manufacture of OLEDs; it is processed as individual sheets, whose planarity and rigidity facilitate a thin uniform deposition of the polymer layers. For small samples, it can be easily processed using laboratory deposition technique such as spin coating. Glass acts also as a vapour barrier, protecting the organic layers from water, allowing the production of OLEDs with long life spans. Screen printing and inkjet are printing technologies particularly suited for working with rigid substrates. Other printing methods, such as offset gravure, flexography and slot-die coating, can be adapted to the task, but tend to perform better with continuous substrates.

Commercially there is a major interest in substituting glass with plastic transparent films (PET, PEN), allowing flexible displays and large-volume, low-cost roll-to-roll processing. For this purpose, research and funding has been concentrated on the development of large-scale printing processes for OLEDs, such as direct gravure, flexography, and slot-die coating. However, a current

major obstacle to the wide adoption of plastic films is their high vapour permeability and the high cost and limits of current vapour barrier technologies for flexible substrates.

12.10.2 Deposition of thin films: hole transport and light-emitting polymer layers

For functionality purposes it is essential that the light-emitting polymer layer is thin (typically <100 nm), uniform and continuous. Any variation in its thickness would affect the uniformity of light output; any discontinuity would create highly detrimental shorts. Inconsistencies in the hole transport layer would cause similar issues.

In laboratory conditions, for very small scale samples, spin coating is the conventionally employed deposition method. Spin coating gives the desired film thicknesses and uniformities, but it is an unfeasible and wasteful method for coating over a large area and on any production scale.

For industrial large-area application, slot-die coating is recognised as being able to produce highly consistent, smooth layers (Kawaguchi *et al.*, 2009; Hetch *et al.*, 2011; Lee, 2012). To achieve highly consistent layers, slot-die coating needs to overcome flow instability issues at the beginning of the coating process, hence slot-die coating tends to perform best while working with large surfaces or as a roll-to-roll continuous process. The major limit of slot-die coating is its inability to pattern, which limits its application to small scale or integrated OLED devices in favour of large-area lighting applications.

Accurate patterning is necessary for the creation of more complex OLEDs and for the development of displays or matrix OLEDs, with different light-emitting polymer (hence different colours) areas next to each other. Through nozzle printing and selective slot-die coating, a partial structuring (in the direction of coating) is achievable allowing the manufacturing of displays (Chesterfield *et al.*, 2010) with the advantages in layer uniformity typical of traditional slot-die coating.

More complex patterning requires abandoning coating approaches for printing technologies. Inkjet printing has been extensively studied on the laboratory scale and has been crucial in the development and testing of printed OLEDs (Chang *et al.*, 1999; Shibusawa *et al.*, 2003; Villani *et al.*, 2009) but its slow speed limits its applicability to large volume productions.

Screen printing has also been successfully tested on a lab scale for the deposition of thin films and the creation of OLEDs (Lee *et al.*, 2009; Birnstock *et al.*, 2001; Todt *et al.*, 2011). However, large-scale manufacturing of thin films by screen printing is limited by layer dishomogeneity issues associated with the mesh topography and with the drying process.

Extensive research is invested in rotogravure for the construction of OLED devices. Its metering and imaging technology allows an accurate patterned

deposition of thin films, such as for the functional layers (20–100 nm) required by OLEDs. Examples of its application include the deposition of PEDOT:PSS as the hole transport layer or of various organic light-emitting layers (Kopola *et al.*, 2009; Hiroyoshi *et al.*, 2006; Lee *et al.*, 2010).

The homogeneity of the layers deposited by printing processes such as gravure, inkjet and screen printing tend to be constrained by the use of discrete dots (e.g. engraved cells for gravure, droplets in inkjet, mesh opening in screen) in the imaging. Research is ongoing into the minimisation of the roughness of the deposited layers. Rotogravure is an interesting process for this target thanks to its flexibility in ink rheology and controlled large volume deposition capacity (Kim *et al.*, 2010; Michels *et al.*, 2009). A possible alternative would be to employ printing processes that do not rely on dot patterning, such as flexography or offset. Research for these processes is still limited, but it has identified some limits in homogeneity possibly caused by instabilities at the ink/air interface during the splitting of the ink (Sauer *et al.*, 2011; Reuter *et al.*, 2007), an issue found also in gravure printing (Bornemann *et al.*, 2011).

In conclusion, the accurate and homogeneous deposition of thin films by printing still present some challenges, with a wide range of options depending on complexity of the pattern, area size and volume production.

12.10.3 Transparent conductive anode

The transparency and conductance of the anode is crucial for the performance of the OLED. The sheet resistance of the anode affects the uniformity of the light output, limiting the size of OLED displays. Indium tin oxide (ITO) coating is typically used, and is usually deposited by vacuum processing producing a thin transparent conductive layer. However, because of the limited conductivity and fragility of ITO layers, the high cost of indium and of vacuum deposition, alternatives are being sought.

Performance can be improved through the integration of a layer of ITO with a highly conductive metallic grid, improving the conductance and homogeneity of current distribution in the layer with minimal obscuration. The use of grids also allows the substitution of ITO with lower performing but solution processable (printable) transparent conductive coatings such as PEDOT:PSS or formulations based on silver nanowires or CNTs, for example.

Printing technologies can be employed for the manufacturing of the grids as a fast and affordable alternative to photolithography. In view of the sandwich structure of OLEDs, an important requirement for the grids is the smoothness of the conductive tracks to allow a uniform thin deposit of successive layers and large cross-sectional areas of the tracks to achieve the required conductance. Tests performed using screen printing with silver inks resulted in grids presenting excellent conductance (Galagan *et al.*, 2011; Todt *et al.*, 2011) but also difficulties in overcoating due to the high thickness of deposited tracks.

The flexographic printing process has been successfully tested over flexible substrate. High resolution conductive grids were printed over PEDOT:PSS coated film, obtaining tracks with low roughness, and sheet resistance of 3 Ohm/sq at 7% area coverage (Deganello *et al.*, 2012b). The smoothness achievable by the flexographic printing process is an important step forward and facilitates the over-coating of thin films. An interesting alternative solution to the issue of the line smoothness consists of embedding the printed tracks into the surface of the substrate, offering a planar smooth surface to be coated by a thin layer of conductive transparent coatings (Galagan *et al.*, 2011).

12.11 Conclusion

Printing processes are key technologies for the future development of OLEDs for large scale affordable production. This chapter provides the reader with an overview of the extensive range of printing technologies available for the development of OLEDs and other printed electronics products. While inkjet printing technologies are particularly suited for small scale and laboratory R&D, large area printing and coating processes such as screen printing, roll-to-roll rotogravure, flexographic printing and slot-die coating are of particular interest for large scale industrial production. Challenges have still to be overcome, such as reliable accurate and homogeneous deposition of thin films, depending on the complexity of the pattern to be printed, the area size and the volume production. Each printing and coating technology presents its own advantages and constraints in this respect. It can be expected that the first fully printed high volume OLEDs will be produced by integrating various printing and coating processes.

12.12 Acknowledgments

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Fluorenone defects in fluorene-based conjugated polymers

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Abstract: In this chapter the discovery, formation, effects and suppression of fluorenone defects in fluorene-based conjugated polymers are discussed. The discovery of how these defects are responsible for the formation of green emission from these polymers enabled methods, including improved synthesis methods and the design of new molecular and device structures, to be devised for its suppression. Comparisons are made to the behaviour of other bridged phenylene polymers which also illustrate the widespread applicability of the methods used for suppression of fluorenone defects to the optimisation of other classes of polymers.

Key words: polyfluorenes, luminescence, ketone defects, blue light-emitting diodes.

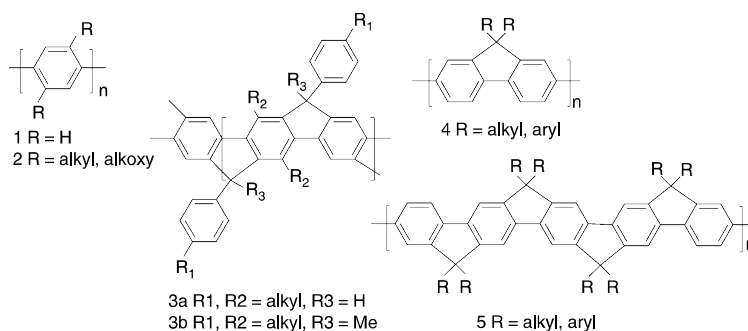
13.1 Introduction

Conjugated polymers have been intensively investigated as the active materials in organic electronics devices due to their intrinsic semi-conductivity. The first type of organic electronic device to have attained commercial viability is polymer light-emitting diodes (PLEDs) which utilise luminescent conjugated polymers as their active material (Grimsdale *et al.*, 2009). In order to attain the full advantages of this technology it is necessary to obtain efficient and stable emission in each of the three primary colours – red, green and blue. Of these, blue has proven the most difficult colour to obtain with acceptable colour purity, efficiency, and colour and device stability. The first of these problems arises because many blue-emitting materials show some emission in the green as well, to which the eye is much more sensitive than it is to blue light. This is soluble by appropriate design of material. The second arises because a blue-emitting material has an intrinsically large bandgap with a low lying highest occupied molecular orbital (HOMO) and a high energy lowest unoccupied molecular orbital (LUMO). This means that injection of holes into the HOMO at the anode and of electrons into the LUMO at the cathode may be inefficient as there are large energy differences between the emissive materials' frontier orbitals and the work functions of standard electrode materials. This problem is readily overcome by use of suitable charge injecting/transporting layers, and so is the simplest of the problems to deal with. The third problem forms the crux of this chapter. There are many examples in the literature

of PLEDs which show blue emission initially, but which produce other colours after the device has been operating for some time (not necessarily a long time) (Grimsdale *et al.*, 2009). This change in colour is often associated with a drop in device performance and may presage an imminent device breakdown. If one is going to overcome this problem it is vital to know what the underlying causes of it are. The investigation of the causes of colour instability in polyfluorene-based PLEDs represents one of the best and most instructive examples of how an understanding of how such a problem arises can lead to its solution. In this chapter I hope to show how the close collaboration between chemists and physicists has enabled significant advances to be made in understanding the fundamental processes that lead to unstable emission from conjugated polymers, and has led to the development of new methods for making conjugated polymers with greatly enhanced performance in PLEDs. While the details of the work are obviously unique to polyfluorenes, the sort of mutual interaction involved, especially the continuous mutual feedback between the synthetic chemists who understand the natures of impurities that can arise during chemical reactions or upon exposing a material to air or current, and the physicists who can detect the effects of chemical changes upon the properties. It is precisely by such interdisciplinary efforts that fundamental structure-property relationships are determined.

Of all types of blue-emitting materials, phenylene-based polymers have been the most widely studied as they have innately high bandgaps making them blue-emitters without the need for interrupted conjugation via incorporation of conjugation-breaking units or twisting of backbone by steric interactions between adjacent units (Grimsdale, 2010).

Phenylene-based polymers (Fig. 13.1) include single-stranded polyphenylenes such as poly(para-phenylene) (PPP, **1**) and soluble PPPs (**2**), in which there is only a single bond between each adjacent pair of phenylene units, ladder-type PPPs (LPPPs, **3**) in which all the phenylene units are tied together in a coplanar fashion by methine bridges, and so-called 'stepladder' polymers such as polyfluorenes



13.1 Typical polyphenylene-based conjugated polymers.

(PFs, **4**) and polyindenofluorenes (PIFs, **5**) in which only some of the phenylenes are linked by methine or other bridges.

Each of these classes of polymer has different optical properties with emission colours ranging from violet through to blue-green, so enabling the colour to be tuned by synthetic design – i.e. by controlling the number and nature of the bridges between the phenylenes and/or the side-chains on the polymer (Grimsdale and Müllen 2006, 2008).

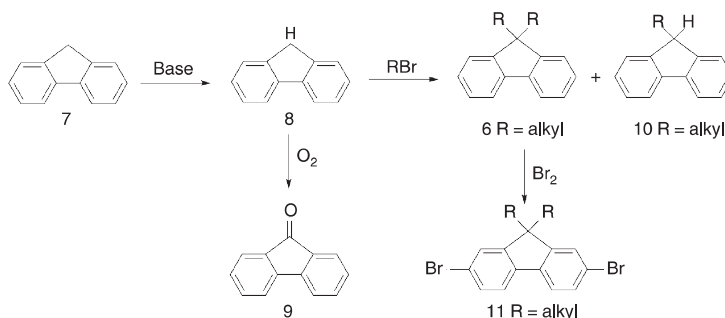
The parent poly(para-phenylene) (PPP, **1**) is a blue emitter but is insoluble, so films for PLEDs need to be prepared by precursor routes (Gin and Conticello, 1996). The problem associated with such routes is that the final conversion steps may leave the polymer films doped with acidic by-products which can corrode the electrodes, so soluble solution-processable polymers are preferable for PLEDs. Soluble PPPs **2** can be obtained by attaching suitably long alkyl or alkoxy side-groups onto the PPP backbone, but these produce emission which is significantly blue-shifted compared to PPP, as steric interactions between the side-chains induce marked twisting of the backbone reducing the effective conjugation (Grimsdale and Müllen, 2006). As a result their emission is mainly in the violet where the eye is relatively insensitive. To overcome the backbone torsion one can construct ladder-type polyphenylenes (LPPPs, **3**) in which all the rings are connected by methine bridges (Scherf, 1999). The flattening of the polymer backbone, which is apparent in the well-resolved vibronic structure and small Stokes shifts in LPPPs, also causes a red-shift in their emission compared to PPP. While blue emission has been observed for the parent LPPP **3a** bearing hydrogens at the bridgehead positions, as will be discussed later, this emission is unstable. The emission from other LPPPs such as Me-LPPP **3b**, which do not possess bridgehead hydrogens, is stable but is blue-green in colour. As a result the search for blue-emitting materials has concentrated on polymers with structures intermediate between the singly stranded PPPs **2** and the fully-ladderised LPPPs **3** – what are sometimes referred to as ‘step-ladder polyphenylenes’ in which some but not all of the phenylene units are linked by bridges (Grimsdale and Müllen, 2008). Random copolymers of **2** and **3** – the so-called ‘random step-ladder polyphenylenes’ have been investigated and it has been found that they produce emission which is less violet than for **2** and much more stable than for **3**, but the random nature of the structure of such polymers makes it essentially impossible to control their properties effectively. As a result, attention has focused on ‘regular step-ladder polymers’ with the breaks in the ladder structure occurring at strictly regular intervals. The simplest such polymers are polyfluorenes (PFs, **4**) in which every second phenylene has a bridge. As the amount of bridging increases, the emission becomes more red-shifted so that pure blue emission with the emission maximum around 440 nm is attainable from the polymers (**5**) containing ladder-type pentaphenylene units (Jacob *et al.*, 2004b), whereas PFs display violet-blue emission – otherwise known as a ‘deep blue’ – with emission maxima around 425 nm (Leclerc, 2001). Despite their not producing a really pure blue emission,

PFs with alkyl substituents on the bridgeheads – poly(dialkylfluorene)s or PDAFs – are the most widely studied class of blue-emitting polymers as their emission colour, while not a pure blue, is considered acceptable for device applications, and as we shall see in the next section, they are much more simple to prepare than polymers such as **5** with purer blue emission.

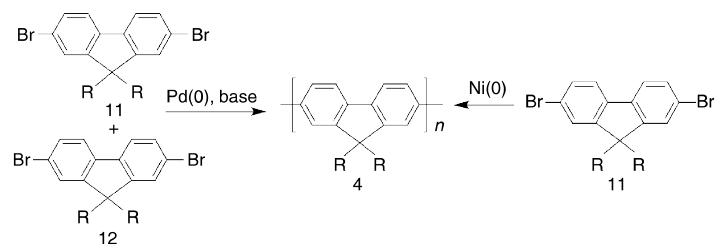
13.2 Synthesis of poly(dialkylfluorene)s

A particularly attractive feature of PDAFs is that the monomers are extremely cheap and easy to make. Alkylation at the C9 bridgehead position in fluorene (**7**) is extremely facile due to the acidity of the bridgehead protons, so that 9,9-dialkylfluorenes (**6**) are obtainable in high yield by treatment of **7** with an alkyl halide and base, usually under phase transfer catalysis conditions (Fig. 13.2). Some care is required to keep oxygen away as otherwise oxidation of the fluorenyl anion intermediate **8** will produce fluorenone (**9**) as a byproduct. Another potential problem with this reaction is that the product may contain traces of the monoalkylfluorene **10**, which are difficult to detect and remove. Bromination of **6** efficiently produces **11**, which can also be made in high yield by alkylation of commercially available 2,7-dibromofluorene. Both **6** and **11** can be used as monomers to make PDAFs.

PDAFs have been made by oxidative coupling of the monomer **6** with iron(III) chloride, but the products possess low molar masses and contain high levels of defects (Fukuda *et al.*, 1989, 1993). Most syntheses of PDAFs use Suzuki polycondensations of dibromomonomers **11** with the diboronates **12** (Schlüter, 2001; Sakamoto *et al.*, 2009), or Yamamoto couplings of dibromomonomers **11** (Yamamoto, 1992) as shown in Fig. 13.3. A group at Dow have developed an efficient Suzuki cross-coupling route leading to high molecular weight ($M_n > 100,000$ g/mol) PDAFs (Woo *et al.*, 1997; Inbasekaran *et al.*, 1998). Yamamoto-style polycondensations have also been used to prepare high molecular weight PDAFs by treating **11** with biscyclopentadienylnickel(0) and 2,2-bipyridyl



13.2 Alkylation of fluorene to produce monomers for PDAFs.



13.3 Suzuki (left) and Yamamoto (right) routes to PDAFs.

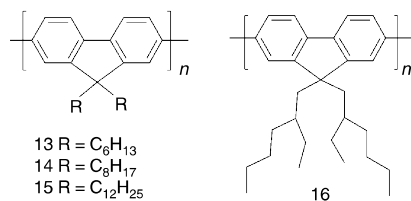
but the molecular weights cannot match those obtained from the most efficient Suzuki couplings. The Yamamoto method is experimentally simpler than the Suzuki method, making it an attractive method for obtaining samples of a new material in a research laboratory for evaluation, but the expensive nickel reagent must be used stoichiometrically, making it less attractive for industrial scale synthesis.

The development of efficient routes to the synthesis of PDAFs with high molar masses meets one of the requirements for using them as materials in PLEDs, but the main requirement for such devices is that they possess the right optical properties, and it is to their optical properties that we now turn.

13.3 Polyfluorenes as blue emitting materials

The emission from PDAFs is violet-blue (sometimes called 'deep blue') with a primary emission maximum at about 425 nm, and a secondary peak around 445 nm. The efficiencies for emission in the solid state for PDAFs are quite high (>50%), and their ready solubility in organic solvents plus high molar masses gives them good film forming properties (Neher, 2001). This combination makes them very attractive materials for making blue-emitting LEDs.

Some applications such as backlights for liquid crystal displays (LCDs) require polarised emission, which in turn requires aligned films. These can be produced from PDAFs with liquid crystalline properties. PDAFs with unbranched alkyl substituents, e.g. **13**, **14**, and **15** (Fig. 13.4), show two thermotropic nematic liquid crystalline phases whose phase transition temperatures decrease with increasing chain length (Teetsov and Fox, 1999). Annealing films of these polymers at a temperature just above the second liquid crystalline transition followed by rapid cooling enables the liquid crystalline order to be retained at room temperature (Grell *et al.*, 1997). Polarised PL and EL has been obtained from such a film of **14** deposited upon a rubbing aligned polyimide alignment layer (Grell and Bradley, 1999). Polarised EL has also been obtained from films of **14** deposited on a rubbing-aligned layer of poly(phenylene vinylene) (PPV) but the emission spectrum was slightly red-shifted due to some absorption by the PPV layer in the



13.4 Representative PDAFs with straight and branched chains.

region around 433 nm (Whitehead *et al.*, 2000a,b). By contrast, the polymer **16** with branched ethylhexyl chains displays only one nematic phase, while other polymers with branched alkyl chains are reported to show no thermotropic behaviour at all. Annealing of a film of **16** at 185 °C upon a rubbing-aligned polyimide layer followed by rapid cooling produced a film which emitted polarised EL with a high dichroic ratio (Grell *et al.*, 1999). Circularly polarised PL and EL emission has been obtained from polyfluorenes bearing chiral side-chains (Oda *et al.*, 2000a,b). Circularly polarised emission is also produced from a copolymer with a mixture of dioctylfluorene and chiral units, but with a much reduced degree of dissymmetry. This can be attributed to the achiral units preferring a planar conformation of the backbone, while the chiral-substituted units adopt a helical structure. A combination of a helical backbone conformation and liquid crystallinity thus appears to be essential for obtaining a high degree of circular polarisation.

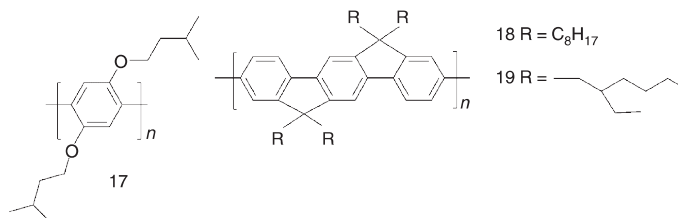
These optical and physical properties when combined with their ready synthetic availability made PDAFs appear to be very attractive candidates for blue-emitting PLEDs, but as we shall see in the next section a problem of colour stability became apparent when people started testing them in devices.

13.4 The green emission problem

The first reported blue-emitting PLEDs used poly(9,9-dihexyl-2,7-fluorene) (Fig. 13.4, **13**) made by oxidative polymerisation (Ohmori *et al.*, 1991, 1993, Uchida *et al.*, 1993). The emission efficiency was low, probably due in part to the poor quality of the polymers, and no further work was done on PF-based PLEDs until better quality materials became available. The first relatively efficient blue PF-based PLED used poly(dioctylfluorene) (**14**) prepared by Dow with the device efficiency improved by inserting a hole-transporting layer to improve hole injection and a low work function calcium cathode to enhance electron injection (Grice *et al.*, 1998). While device efficiencies high enough to be acceptable for potential commercial applications were obtainable by such methods it soon became apparent the blue emission from PDAFs was unstable, with a strong emission band around 530 nm appearing rapidly after annealing or upon running an EL device (Neher, 2001, Scherf and List, 2002).

As the other properties of PADFs made them extremely attractive candidates for commercial display applications, considerable effort has been made to develop stable blue emission from PDAFs.

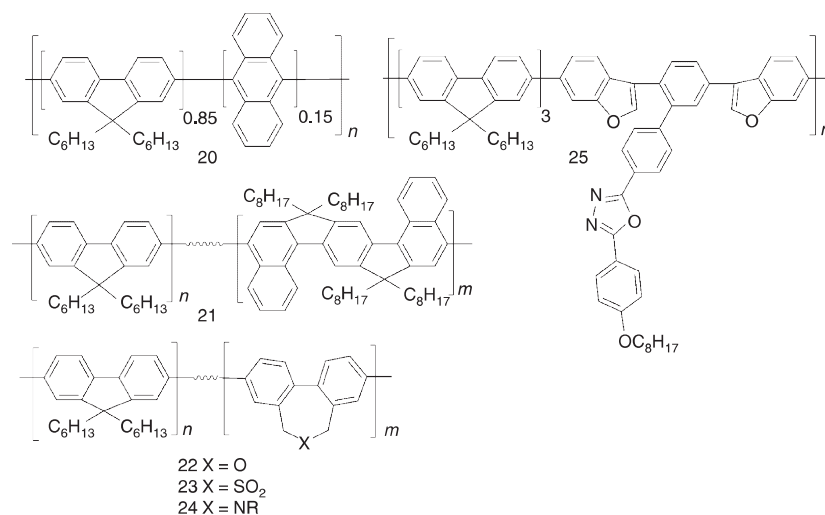
At first it was thought most probable that the source of the long emission was the formation of emissive aggregates – excimers. This was consistent with what was known about the behaviour of single- and double-stranded PPPs. It had been observed for soluble PPPs (**2**) that the electroluminescence (EL) emission was often red-shifted by the formation of aggregates which show longer wavelength, usually yellow, emission. For example, the EL emission from spin-cast films of a dialkoxy-PPP **17** (Fig. 13.5) contained the violet-blue band around 400 nm seen in the photoluminescence (PL) spectrum and a yellow-green emission band around 530 nm, whose intensity increased with time during device operation (Cimrová *et al.*, 1996). Films of **17** prepared by the Langmuir-Blodgett (LB) technique produced almost entirely yellow emission with the emission parallel to the dipping direction slightly red-shifted compared to the emission perpendicular to that direction ($\lambda_{\text{max}} = 536 \text{ nm}$ cf. 524 nm). That the yellow emission was due to aggregation was proved by blending **17** with a polysilane as the blend produced only blue emission around 400 nm (Cimrová *et al.*, 2000). As PADFs form aggregates as shown by the fibril-like morphologies in their films viewed by Atomic Force Microscopy (AFM), it seemed plausible that these aggregates could show similar emission behaviour to the aggregates of **17**. In the case of the LPPP **3a**, it had been observed that while solutions of LPPP **3a** displayed blue PL, in thin films the emission was dominated by a broad, featureless band in the yellow ($\lambda_{\text{max}} = 600 \text{ nm}$) (Hübert *et al.*, 1994), with the relative intensity of the blue and yellow bands being strongly dependent upon the method used to prepare the films, upon the solvent used, and upon the film thickness. The blue band disappeared completely upon annealing a film of **3a** at 150 °C. As a result, LEDs using **3a** have usually produced yellow EL (Grüner *et al.*, 1994), and when blue EL ($\lambda_{\text{max}} = 450 \text{ nm}$) has been observed from **3a** it was highly unstable, with the yellow band rapidly appearing (Hübert *et al.*, 1994). This yellow emission was attributed to excimers from the results of site-selective excitation experiments and time-resolved PL measurements (Mahrt *et al.*, 1995), and of photovoltaic



13.5 Polymers related to polyfluorenes which show similar long wavelength emission in LEDs.

experiments (Köhler *et al.*, 1995). Also consistent with this hypothesis was the obtaining of pure blue EL from blends of **3a** (1 wt%) in the wide bandgap polymer poly(N-vinylcarbazole) (PVK) (Grüner *et al.* 1994). The emission from such blends has also been shown to be unstable, turning white after less than an hour of device operation, which was attributed to formation of excimers due to the Joule heat produced by passage of electricity through the device (Yang *et al.*, 2000). Further supporting the excimer hypothesis was the observation that for the poly(tetraalkylindenofluorene)s (PIFs) **18–19** (Fig. 13.5) and their copolymers the degree of green emission seen in the solid-state PL and the EL spectra correlated with the degree of order, i.e. of chain aggregation, visible in their films by AFM (Grimsdale *et al.*, 2002). These polymers show similar optical and phase behaviour to the corresponding PDAFs **14** and **16**, but with slightly red-shifted emission (λ_{max} 430 nm) and higher phase transition temperatures (Setayesh *et al.*, 2000).

As a result, initial efforts to obtain stable emission from PDAFs concentrated on ways to suppress formation of excimers. One approach that has shown some success is to incorporate wide bandgap comonomers into the polymers. This was first observed in copolymers **20** made by the Yamamoto method (Fig. 13.6) containing dihexylfluorene and anthracene, which produced stable blue emission (λ_{max} = 455 nm) even after prolonged annealing (Klärner *et al.*, 1998, 1999a; Miller *et al.*, 1999). This was attributed to trapping of the exciton at the anthracene sites so that the emission came from them. A similar effect is seen in copolymers of anthracene with indenofluorenes (Marsitzky *et al.*, 2001a). Similar stability in emission colour has been observed for copolymers **21** containing 1–15 mol% of



13.6 Copolymers of fluorene with stable blue emission.

dinaphtho-s-indacene which display stable blue emission with emission maxima tunable between 448 nm ($m=1\%$) and 460 nm ($m=15\%$) (Guo *et al.*, 2009). Bridged biphenyls with long bridges are twisted which reduces their conjugation. Copolymers such as **22–24** containing 30–40 mol% of such units do not show the long wavelength emission seen for the fluorene homopolymers, though the EL efficiencies are lower which is attributable to poorer chain packing of the polymers which inhibits charge transport (Lim *et al.*, 2005). This shows an obvious problem with suppressing aggregation in conjugated polymers – the loss in efficiency due to reduced charge transport may outweigh any benefits in colour purity. To overcome this investigations have been made into using charge transporting comonomers to suppress aggregation without losing charge transport. For example, the copolymer **25** bearing electron-transporting oxadiazole side-chains is reported to show stable blue EL ($\lambda_{\text{max}}=434\text{ nm}$) with good efficiency (Zhang *et al.*, 2008). The stability of the emission from PDAFs has also been improved by incorporation into the main chain of hole-injecting 3,6-carbazole units (Xia and Advincula, 2001, Park *et al.*, 2009), or a combination of hole-transporting triphenylamine and electron-accepting diphenylsulfone units (Miller *et al.*, 1999), but the device results are not particularly good.

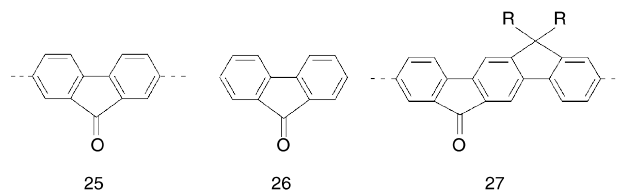
Other approaches towards obtaining stable blue emission from PDAFs through reduction of inter-chain interaction have included cross-linking the polymers using vinyl end-groups (Klärner *et al.*, 1999b), or attaching as end-groups or side-chains bulky groups, such as dendrimers (Setayesh *et al.*, 2001, Marsitzky *et al.*, 2001b) or silsesquioxanes (Lee *et al.*, 2004, Takagi *et al.*, 2005).

The methods described above to reduce aggregation or diminish its effects had some success in suppressing the unwanted long wavelength emission, but as we shall see in the next section, while they were being developed, evidence began to emerge that the cause of the green emission might actually lie in an emissive defect rather than an excimer, calling into question the whole basis of these research efforts.

13.5 Aggregate versus defect

While initially, as we have seen, the long wavelength emission band seen for PDAFs and for related polymers such as LPPP (**3a**) was believed to arise from excimers, evidence was found suggesting an alternative explanation for this emission, namely that it arose from defect sites – in the case of PDAFs fluorenone defects **25** (Fig. 13.7), presumably formed by oxidation of the fluorene units (Scherf and List 2002).

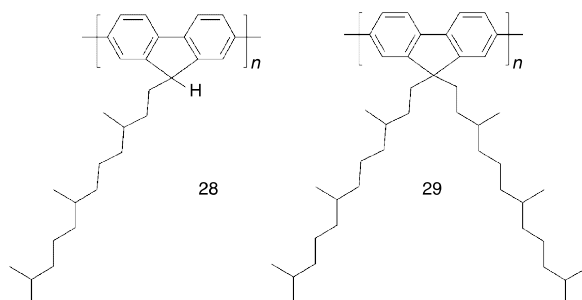
One example of such evidence for defect emission was seen in the substituted LPPP Me-LPPP (**3b**) (Scherf, 1999). The emission from **3b** is slightly red-shifted compared with LPPP **3a**, with an emission maximum at $\lambda_{\text{max}}=461\text{ nm}$ and a secondary peak at $\lambda_{\text{max}}=491\text{ nm}$, so that the emission colour is blue-green, but unlike **3a**, **3b** shows almost identical emission from films and solutions. There is



13.7 Proposed emissive defects in PDAFs and PIFs.

also a broad emission band from **3b** centred at 560 nm, which is much weaker than the corresponding yellow band from LPPP (**3a**), and the emission does not change upon annealing. This band was initially attributed to emission from aggregates (Haugeneder *et al.*, 2002), but it was later reported that it could be detected in the delayed fluorescence from both films and dilute solutions of Me-LPPP (Lupton, 2002). This is inconsistent with the emission coming from aggregates as dilute solutions should not contain any. It was therefore proposed that the long wavelength emission band originated from defects on the polymer chains. The defects would possess lower bandgaps than the rest of the polymer chain and so exciton migration should produce preferential emission from the defect sites which act as traps. The efficiency of such exciton trapping is illustrated by copolymers of fluorene containing emissive dyes as co-monomers. Such copolymers with only 1–2 mol% of emissive perylene dye co-monomers display emission exclusively from the dye units (Ego *et al.*, 2003). Even from copolymers containing only 0.005 mol% of orange-emitting co-monomers the orange emission is sufficiently strong to produce an overall white emission (Tu *et al.*, 2006). Since the green emission band from PDAFs closely resembles the solid state emission reported from fluorenone **26** (Ilharco *et al.*, 1997), it thus seemed quite plausible that it could arise from defects **25** and the slightly more red-shifted emission seen in related polymers could thus arise from similar defects, e.g. **27** for PIFs.

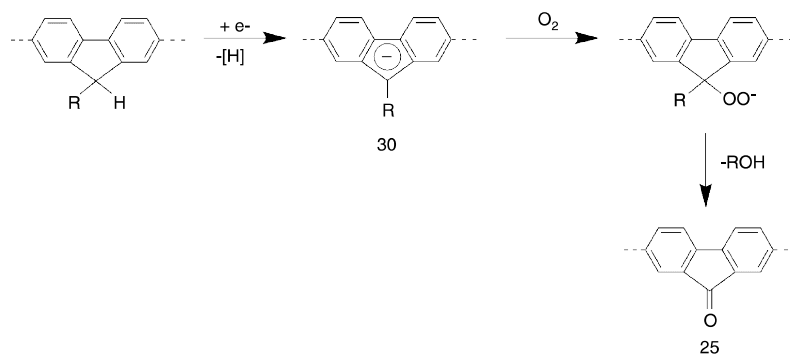
The crucial evidence for the presence of ketone defects came from studies on the monoalkyl and dialkylfluorene polymers **28** and **29** (Fig. 13.8), which were prepared by Yamamoto polycondensation. A strong carbonyl stretching band at 1721 cm^{-1} , which matches the ketone stretching band in fluorenone, was observed in the IR absorption spectrum of even pristine monoalkylfluorene polymer **28** (List *et al.*, 2002). The solid-state PL and EL spectra of **28** were dominated by a band at 533 nm which was also observed from the dialkylfluorene polymer **29** upon photooxidation or after running an LED for 30 minutes. This suggested the presence of ketone defect sites and that the long wavelength emission arose from energy transfer to them. The observed greater strength of this band in EL compared to PL spectra is explicable by the defects acting as charge trapping centres. The results of time-delayed PL experiments were also consistent with this hypothesis (Lupton *et al.*, 2002). This view was challenged by other researchers, who noted that the green emission appeared even when a film of a PADF was heated under a



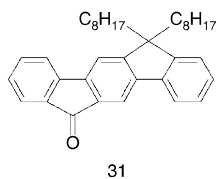
13.8 Mono- and dialkylated polyfluorenes used to prove ketone defect hypothesis.

nitrogen atmosphere, and who therefore suggested this ruled out oxidation (Zeng *et al.*, 2002). The crucial evidence was the fact that no long wavelength emission was observed when polymer **29** was heated at 200 °C under illumination in a dynamic vacuum ($<10^{-4}$ mbar) which rigorously excluded oxygen, but was observed upon heating in air (Gaal *et al.*, 2003). The appearance of the green emission even upon heating a film of a PADP under nitrogen was attributed to the presence of low levels of oxygen in the nitrogen, which suggests the extreme susceptibility of these polymers towards oxidation.

To account for the formation of the defect sites in pristine **28**, it was proposed that during the polymerisation, some of the alkylfluorene units were reduced by the nickel(0) to monoalkylfluorenyl anions **30**, which were then oxidised by atmospheric oxygen to the ketones **25** during the workup as shown in Fig. 13.9. The susceptibility of fluorenyl anions to attack by oxygen is well known and has been used as a means to prepare fluorenones in high yield by treating fluorenes with base in the presence of air (Pei *et al.*, 2002).



13.9 Proposed mechanism for formation of ketone defects **25**.



13.10 Model compound for defect in indenofluorenes.

Evidence for the presence of a similar defect **27** (Fig. 13.7) in the emission from PIFs has now also been found, backing up the idea of defects as a source of long wavelength emission in bridged phenylene polymers. A model compound **31** (Fig. 13.10) was made whose emission spectra closely matched the green emission band described above for the polymers **18** and **19** (Keivanidis *et al.*, 2005). Furthermore, when polymer **18** was made using a monomer in which strenuous efforts had been made to avoid underalkylation and thus a possible source of defects, the material was discovered to be a blue emitter in the solid state, though with slightly red-shifted emission compared to **19**; a difference which is plausibly attributable to aggregation of **18**.

13.6 Defect emission suppression

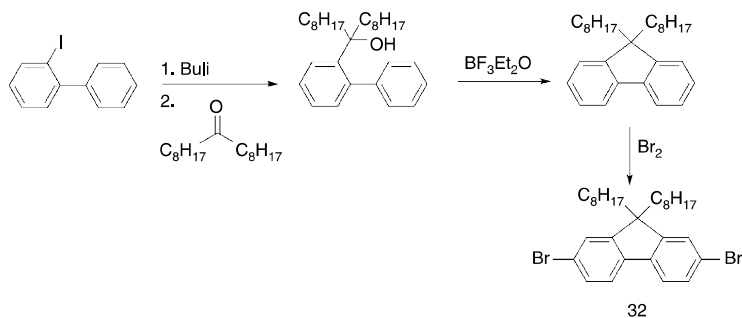
A number of approaches have been adopted to suppress the defect emission, either by removal or prevention of defects, or by reducing the effects of their presence. Some methods have been physical in nature, others chemical. As an early example of the first type, fractionation of **14** to remove low molecular mass material has been reported to reduce the long wavelength emission from it (Weinfurter *et al.*, 2000). This might seem a somewhat surprising result as one expects the probability of a polymer chain containing a defect to increase with increasing chain length. However, if the oligomers in the low molecular mass fraction assist in inter-chain charge and energy migration, removing them would reduce exciton migration to defect sites. Also fluorenone units on a polymer chain will reduce its solubility and so may hinder chain growth in solution; thus it is possible that a higher proportion of defects exist among low molar mass fractions.

Blending a PDAF with hole-transporting molecules has been reported to produce stable blue emission (Sainova *et al.*, 2000). This can be attributed to the dopants acting as hole traps, which reduces the amount of charge trapping at the defect sites and thus the emission from them. The fluorenone units are naturally electron accepting due to the oxygens in the ketone groups. More recently blends of **14** with low molar mass poly(phenyl ether) have been found to show more stable emission, which is attributed to the dopant hindering interactions between the polymer chains (Sirtonski *et al.*, 2010). However, the long-term stability of

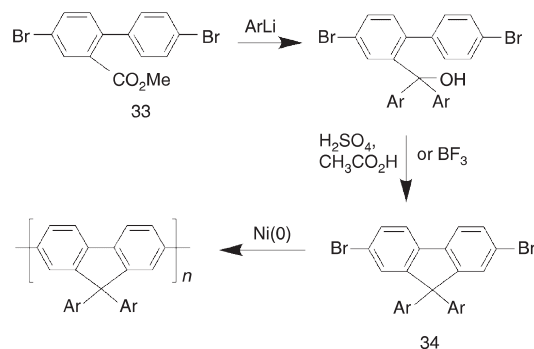
such blends with respect to phase separation is questionable, so the long term stability of emission from them is dubious. There is evidence that reduction of fluorene by calcium cathodes is implicated in the formation of ketone defects during LED operation, and this can be suppressed by introduction of a buffer layer between the polymer and the cathode (Gong *et al.*, 2003).

The surest approach to avoiding formation of ketone defects in PDAFs would be to ensure that the dialkylfluorene monomers contain no monoalkylfluorene impurities capable of being oxidised to the ketones. It has been reported that treating dialkylfluorene monomers with base to remove the monoalkyl impurities before polymerisation greatly enhanced the colour stability of the resulting polymers (Craig *et al.*, 2003), but as the impurities could not be detected either before or after this treatment, indicating they were present only in very low concentration, it was impossible to tell if they had been completely removed prior to polymerisation. This problem is surmountable by using a synthesis of 9,9-dialkylfluorenes (Fig. 13.11) which absolutely precludes the formation of monoalkylfluorenes (Cho *et al.*, 2007). Polymers made from the resulting 'defect-free' monomer **32** showed stable blue emission in initial tests, though lifetime tests to determine their absolute stability have yet to be reported. Incorporation of as little as 0.06 mol% of a monoalkylfluorene comonomer was found to lead to formation of a green emission band from the resulting polymers in an LED, thus further illustrating the sensitivity of the polymer emission properties to very low levels of defects—such levels of monoalkylfluorenes impurities in a dialkylfluorene cannot currently be reliably detected by NMR or other standard analytical techniques.

Unfortunately for the future prospects of PDAFs as blue emitters, a recent study has shown that ketone defects can be produced by degradation of their alkyl sidechains under aerial oxidation (Abbel *et al.*, 2009). This result implies that even defect-free polymers will not be indefinitely stable unless completely protected from oxidation sources, though acceptable lifetimes may well be possible for suitably encapsulated devices.



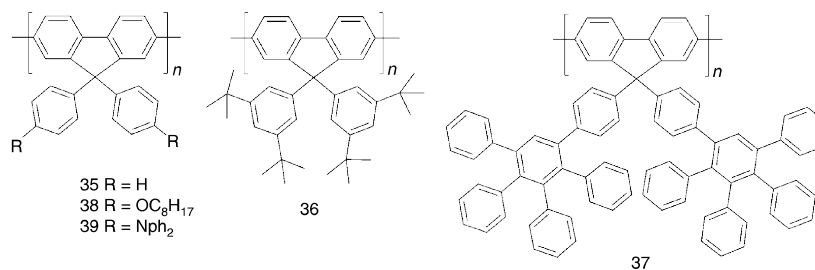
13.11 Route to dialkylfluorenes without monoalkylfluorene impurities.



13.12 Synthetic route to poly(9,9-diarylfuorene)s.

As aryl sidechains should be more stable towards oxidation than alkyl chains, polymers based on 9,9-diarylfuorenes are expected to display more stable blue emission than their dialkyl analogues. A general synthesis of polyfluorenes with aryl substituents at the 9-position has been developed (Fig. 13.12). This synthetic route precludes formation of the bridgehead hydrogens which are oxidised to ketones and the bulky aryl groups reduce inter-chain interactions, and hence exciton diffusion to any defect sites that might still be formed. As aryl groups, unlike alkyl groups, generally cannot be directly substituted onto the 9-position of fluorenes (for an exception see Fig. 13.15), the monomers **34** are prepared by addition of aryllithium reagents to the ester **33**, followed by ring closure using either sulphuric acid in acetic acid (Setayesh *et al.*, 2001), or Lewis acids such as BF_3 (Jacob *et al.*, 2004a). The polymers are then obtainable directly by Yamamoto polymerisation.

The diphenylfluorene polymer **35** (Fig. 13.13) is almost totally insoluble, but polymers such as **36** and **37** are processable from toluene (Setayesh *et al.*, 2001). The degrees of polymerisation for these polymers were rather low, with the dendronised polymer **37** having a M_n of only 10000 g/mol ($n=10$), probably due



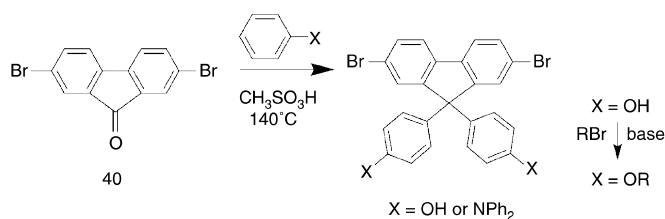
13.13 Poly(9,9-diarylfuorene)s.

to the bulkiness of the substituents. Polymer **37** is exceptionally thermally stable, with no significant mass loss being observed in Thermal Gravimetric Analysis (TGA) until 570 °C.

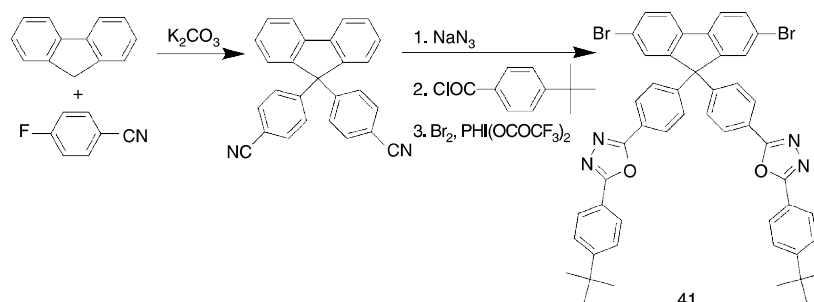
Stable blue PL emission has been obtained from films of both **36** and **37**, with no sign of an emission band at 530 nm even after annealing for 24 h in air at 100 °C, confirming that aryl substituents are less susceptible towards oxidation than alkyl groups. The dendronised polymer **37** shows blue EL with no defect emission observed even after several minutes' operation (Becker *et al.*, 2002; Pogantsch *et al.*, 2002). An obvious potential problem with the dendronised polymer **37** is that the bulky dendrimers might affect the photophysics of the polymer, and studies have confirmed that they do (List *et al.*, 2001; Lupton *et al.*, 2003; Pogantsch *et al.*, 2003a, 2003b). One particularly important effect is that the lifetime of triplet excited states is increased in **37** compared to PDAFs, which could reduce the efficiency of LEDs due to increasing singlet-triplet quenching (Pogantsch *et al.*, 2003b). The use of less bulky phenyl substituents to suppress the long wavelength emission thus appears to be advisable on physical grounds as well as those of synthetic simplicity.

A second way to attach aryl groups at C9, which has been used to make polymers **38** (Lee and Hwang, 2003) and **39** (Ego *et al.*, 2002), is by acid-catalysed condensation of activated aromatics such as phenol or triphenylamine with dibromofluorenone **40** (Fig. 13.14). Both these polymers show stable blue EL, and the hole accepting triphenylamine units in **39** improve hole injection into the polymer. The overall EL efficiency is no higher than for PDAFs however as the PL efficiency is lower – the use of copolymers containing triphenylamines on only some units is thus more promising as a method for increasing EL efficiency. This route is efficient and relatively simple but will only work with highly activated arenes.

Aryl substituents are considerably more bulky than alkyl sidechains (especially than *n*-alkyl ones) and so inhibit chain packing. This is demonstrated by the lack of liquid crystalline phases, and the absence of any signs of organization in the polymer films when studied by Atomic Force Microscopy (AFM) (Surin *et al.*, 2004). One consequence of this for device applications is that polarised emission is not obtainable from these materials by the methods used for PDAFs.



13.14 Addition of activated arenes to fluorenone.

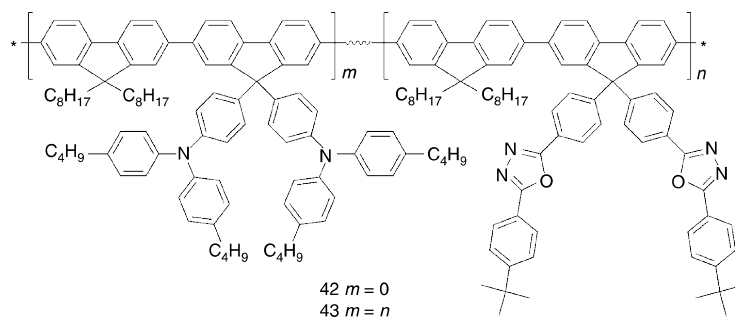


13.15 Synthesis of a fluorene with oxadiazole substituents.

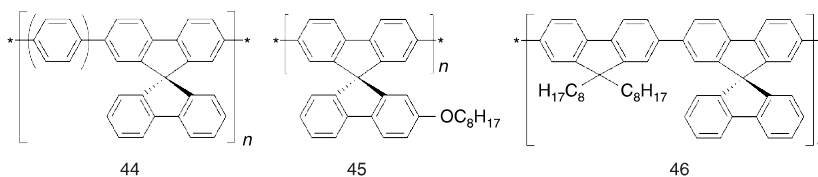
A third method for making diarylfluorenes involves nucleophilic substitution of 4-fluorobenzonitrile with the fluorenyl anion, followed by conversion of the nitriles to oxadiazoles via tetrazole intermediates (Fig. 13.15). This is the only example to date of the direct attachment of an aryl group at the fluorene C9 position, and was used to prepare a fluorene monomer **41** bearing two electron-accepting aryloxadiazole groups at the bridgehead (Wu *et al.*, 2003).

Due to the improved electron injection, the EL efficiency of the alternating copolymer **42** in a single-layer device is considerably higher than for the PDAF homopolymer **14** (0.52% vs 0.2%). The copolymer **43** (Fig. 13.16) bearing both hole- and electron-accepting groups has an even higher EL efficiency (1.21%) indicating the importance of balanced charge injection for obtaining high efficiencies in PLEDs (Shu *et al.*, 2003). The long-term colour stability of these materials has not been reported but they appear from the published data to be more stable than the PDAF homopolymers. Replacing the dialkylfluorene units with diarylfluorenes should further enhance the stability without losing efficiency.

Spirobifluorenes have an obvious structural affinity to diarylfluorenes and are prepared by methods analogous to the route to diarylfluorenes shown in Fig. 13.12.



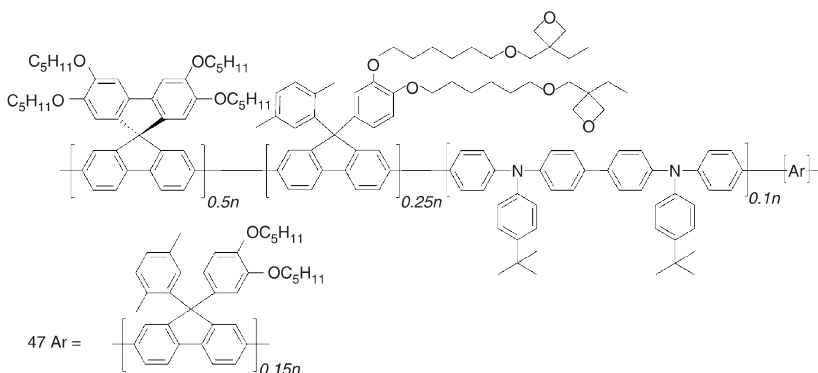
13.16 Fluorene copolymers with electron-accepting units at C9.



13.17 Polymers containing spirobifluorene units.

They have been found to be promising materials for use in blue OLEDs (Salbeck, 1996). As poly(diarylfuorene)s have proven to be stable blue emitters it comes as no surprise to find that similar stable blue emission has been reported from polymers containing spirobifluorenes (Fig. 13.17) such as **44** (Kreuder *et al.*, 1996) and **45** (Wu *et al.*, 2004). Due to their greater rigidity spirobifluorenes tend to be more crystalline and less soluble than diarylfuorenes, which affects the solubility of polymers containing them so the solubilising sidechains in **45** are necessary for ease of processing. The alternating copolymer **46** displays good solubility due to the dialkylfluorene units, and its emission is reported to be more stable than that from the fluorene homopolymer **14**, but green emission was still observed upon heating in air at 150 °C (Yu *et al.*, 2000). This presumably arises from oxidation of the dialkylfluorene units.

Crosslinkable copolymers with a variety of emission colours have been made by Suzuki cross-coupling of a spirobifluorene bisboronate with various dibromocomonomers (Müller *et al.*, 2003). Of these the diarylfuorene copolymer **47** (Fig. 13.18) produces stable blue ($\lambda_{\text{max}} = 457 \text{ nm}$) EL. The crosslinking is performed by illumination with ultraviolet light in the presence of a photoacid to induce cationic polymerisation of the oxetane rings. Comparison of the EL properties of

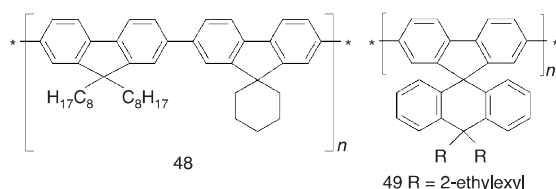


13.18 Cross-linkable blue-emitting copolymer containing spirobifluorenes.

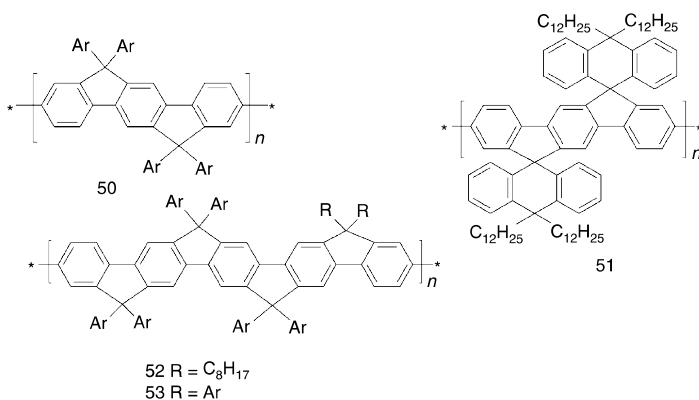
crosslinked **47** with a similar non-crosslinkable polymer showed that the crosslinking had no significant effect upon the luminescence of the materials, but by making the material insoluble assists in multilayer device fabrication as other layers can now be safely deposited upon the crosslinked material by solution processes such as spin coating without fear of dislodging it.

Other spiro-linkages have also been introduced at the C9-position of fluorenes in attempts to stabilize the emission (Fig. 13.19). Polymers with spirocycloalkyl groups such as **48** still produce green emission upon annealing (Grisorio *et al.*, 2005), whereas the polymer **49** with aryl groups at the bridgehead displays stable blue PL and EL (Vak *et al.*, 2004), which again demonstrates the greater stability of 9-aryl as compared to 9-alkyl fluorenes towards oxidation.

Similar stabilisation by using aryl substituents is seen in other bridged phenylene polymers. So for example poly(tetraaryllindenofluorene) **50** (Fig. 13.20) displays stable blue EL (Jacob *et al.*, 2003, 2004a), as does the polymer **51** with spiro linkages at both bridgeheads ($\lambda_{\text{max}}=445\text{ nm}$) (Vak *et al.*, 2005). For the pentaphenylene polymers **5**, while the blue EL emission from the partially arylated polymer **52** made using a dialkylfluorene (Jacob *et al.* 2004b) is more stable than that from PDAFs, a long wavelength emission band still appeared rapidly upon



13.19 Polymers containing other spiro-linked fluorenes.



13.20 Other aryl-substituted bridged phenylene polymers.

heating a film in air. By contrast the all-aryl polymer **53** was remarkably stable, with no sign of degradation being observed even after prolonged heating at 200 °C in air (Jacob *et al.*, 2005). This indicates the green emission band from **52** arises from oxidation of the alkylated bridgeheads, possibly indicating the presence of some bridgehead hydrogens, due to incomplete alkylation. Thus bridgehead arylation appears to be a general method for stabilising the emission from bridged phenylene-based polymers.

13.7 Conclusion and future trends

The fluorenone defect explanation for the green emission band in polyfluorenes (and of other ketone defects for the similar emission in other related polymers) now seems to be generally accepted, but inter-chain interactions play some part in the appearance of the long wavelength emission, as increased inter-chain interaction (aggregation) enhances exciton migration to the defect sites. Also there is evidence to suggest that ketone defects on different chains tend to aggregate due to dipole–dipole interactions and that the defect emission actually arises from excimers formed between two ketone defects (Chan *et al.* 2009). This has implications for designing methods to suppress the emission as it implies that the presence of defects can be tolerated as long as emissive dimers do not form. This would for example explain the increase in emission stability seen by blending PDAFs with other materials by Sirtonski *et al.* (2010). The details of the mechanism for the formation of the defects have also not yet been fully elucidated, which would affect the possibilities for minimising defect formation by structural design – e.g. if the abstraction of α -protons from the alkyl sidechains is a key step in the reaction (a plausible hypothesis) then substitution of those positions might hinder ketone formation. There thus remains considerable work to be done to fully understand the origins of the ketone defects and the green emission band associated with them, and to develop new and improved methods for their suppression.

The future commercial viability of fluorene-based polymers as the active materials in blue-emitting PLEDs is obscured by the commercial secrecy which shrouds the structures of the materials currently being used in prototype commercial devices, though it is widely believed that many of the existing blue-LEDs and full-colour LED-based displays do use them. At the moment it looks from a commercial perspective as if advances in device configuration and encapsulation are the simplest way to suppress the green emission for long enough to make dialkylfluorene-based polymers (which are the simplest and cheapest polyfluorenes to make) viable in commercial devices. But the more resistant polymers based on arylfluorenes or spirodifluorenes such as **47** look to be the best candidates for the long term. The story of how fluorenone defects were shown to be the source of the unwelcome green emission from fluorene-based polymers and how this knowledge could be used to develop effective methods to suppress it through improved molecular and device design and new synthetic procedures is

an excellent example of the sort of work needed to optimise emissive conjugated polymers for LEDs so as to enable them to meet the bright future so often predicted for them.

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Disruptive characteristics and lifetime issues of OLEDs

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Abstract: Nowadays, organic light-emitting diodes (OLEDs) have potential to disrupt the conventional and mainstream solid state lights (SSLs) and flat panel displays (FPDs) due to their numerous superlative characteristics like sunlight style color-temperature tunability, energy-saving, environmental-friendly, physiologically- and psychologically-friendly, and a very high color rendering index (CRI), etc. However, the commercial viability of OLEDs would strongly depend on their extrinsic and intrinsic lifetime because OLED efficacy and lifetime greatly suffer from exposure to atmospheric oxidants (moisture and oxygen). The effect of oxidants can be minimized by the use of abundant emerging encapsulation techniques while the intrinsic lifetime can be improved by a balanced device structure and high glass transition temperature based materials, etc.

Key words: OLED, disruptive characteristics, sunlight style, low color-temperature, very-high CRI, physiologically-friendly, psychologically-friendly, lifetime.

14.1 Introduction

Over twenty years have passed since the breakthrough discovery of organic electroluminescence by Tang and Van Slyke in 1987, when they reported the first small-molecule based organic light-emitting diodes (OLED) with multi-layer thin films.¹ Kido's group reported the first white OLED in 1993, having an efficiency less than 1 lm/W.² But it was an enormous breakthrough in the field of OLED devices because white OLEDs have been expected to open new designs for energy efficient solid state lighting (SSL) and flat panel display (FPD) technology. Since then there has been a continuous advancement in OLED research and development. Recently, Reineke and colleagues have reported a white OLED with p-i-n structure showing fluorescent tube efficacy of 90 lm/W at 1000 cd/m² by combining red-green-blue (RGB) phosphorescent materials and light-outcoupling enhancement techniques such as high refractive-index substrates and half-spheres.³ Particularly, this RGB white OLED showed a color rendering index (CRI) of 80, which is acceptable as an illumination source. Kido and his co-workers had developed an illumination acceptable CRI of 82 white OLED with an efficacy of 43.3 lm/W without any light-outcoupling

enhancement.⁴ Moreover, the efficacy of white OLEDs developed by Novaled and Dresden University has reached an 124lm/W at 1,000cd/m² with a three dimensional light extraction system.³

Due to some vital technical issues, i.e. low yield in OLED oriented thin film transistor (TFT) and insufficient lifetime at high luminance, OLED-based FPDs and SSLs industries have only lately risen markedly. In contrast, passive-matrix (PM)-based OLED technology has already been commercialized in portable display devices like mobile screens, camera screens, automobile audio systems, MP-3 players, etc. Sony has demonstrated the first 11 inches active-matrix (AM)-based OLED television (XEL-1) in 2007.⁵ At the present time, numerous major display market players (such as LG Display, Samsung, Mitsubishi, AUO, DuPont, Panasonic, GE, Toshiba, Cambridge Display Technology and Universal Display Corporation, etc.) have developed a long range of OLED display prototypes, and are still working on the advancement and most competitive display for commercialization.

OLEDs as innately surface-emitting light sources have a unique nature that allows great design freedom in producing a new concept of eco-friendly lighting. In early 2009, Osram introduced the first OLED-based functional table light,⁶ while in the same year Philips had started selling its OLED lighting panel, *Lumiblade*. Except for a few challenges such as increasing the lifespan, reducing manufacturing cost, and enlarging the area size, OLED devices have the potential to become the next generation lightings and displays because they have numerous superlative features over existing lighting sources and display technology.⁷ For example, energy-saving, plane-type emission, self-luminous, environmentally-friendly (less CO₂ emission and Hg free),⁸ physiologically-friendly, psychologically-friendly,⁹⁻¹⁶ sunlight-style color and color-temperature tuneable,^{17,18} a very high CRI,¹⁹ synthesized from sustainable materials, high freedom for design, broad color gamut, wide viewing angle (> 165°), higher contrast ratio, ultra-thin and light, flexible, stretchable, UV-free, IR-free, glare-free, flickering-free, transparent, dimmable and printable, etc.^{1,20-25} These disruptive characteristics would soon enable OLED as an ultimate technology for high quality display and lighting. The success of OLEDs would, however, also strongly depend on the device lifetime. Currently, large public funded projects run all over the world (e.g. United States, Japan, South Korea, Europe, and almost every major player in the lighting and display industries) have invested in research and development of white OLEDs. Hence, we will review in this chapter several disruptive characteristics and lifetime issues of OLED devices.

14.2 Disruptive OLED characteristics

Numerous disruptive characteristics of OLEDs will be revealed in this section. Some of the superior advantages explain why OLED technology will soon disrupt the mainstream FPD and SSL devices, while some would further enable the generation

of many innovative products only limited by our imagination. We are going to explain some noteworthy disruptive characteristics in the following sub-sections.

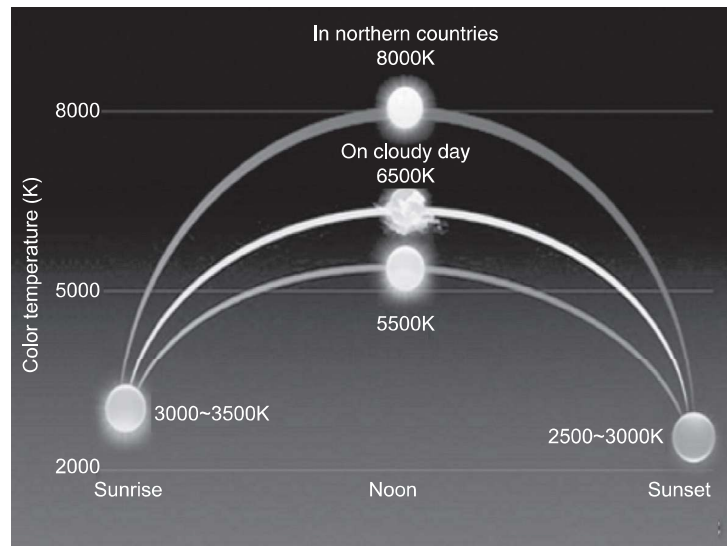
14.2.1 Sunlight-style characteristics

The nature of sunlight

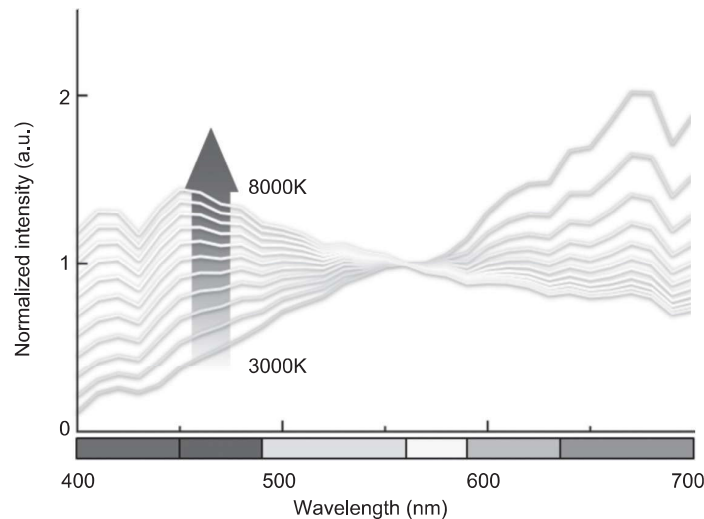
Figure 14.1 shows the color temperature of sunlight at different times, regions, and weather. The color temperature is 2500 K at dawn, 3250 K at dusk, 5500 K at noon (or 8000 K at noon in a high-latitude country), and 6500 K on a cloudy day. The spectra of sunlight with different color temperatures are shown in Fig. 14.2. They are continuous, and the intensity of blue-emission increases with the increase of color temperature.¹⁷

The importance of color temperature

Color temperature of light plays a crucial role in human physiology and psychology.⁹⁻¹⁶ High color temperature light stimulates the secretion of cortisol, a hormone that keeps people awake and active.^{9,11,15} High color temperature light also markedly suppresses the nocturnal secretion of oncostatic melatonin (MLT), increasing the risk of breast, colorectal, and prostate cancer. In contrast, low color



14.1 The color temperature of sunlight at different times, regions, and weathers.



14.2 The spectra of sunlight at color temperatures from 3000 to 8000 K.⁵²

temperature light has a lesser effect on MLT suppression, helps stabilize autonomic nerves, and provides a warm and comfortable sensation.^{13,14,16}

The benefits of using OLEDs

To get sunlight-style illumination, daylight color emission with a wide color temperature range is essential. However, current lighting devices give off only daylight color with a fixed color temperature. The latest white LEDs can be adjusted to a limited extent,^{26,27} but there still is an unpleasant glare and high-heat problems. Moreover, in order to obtain color temperature below 2500K, LED devices must decrease its blue emission, which in turn would greatly sacrifice efficacy.²⁸ Lately, the focus for OLEDs has been on developing devices with higher efficiency and a longer lifespan. While color-tunable OLEDs are common, monochromatic emission-dominant devices are not suitable for general lighting purposes. The challenge is to fabricate OLED devices capable of emitting light with a tunable color temperature that mimics sunlight.

Sunlight style OLEDs

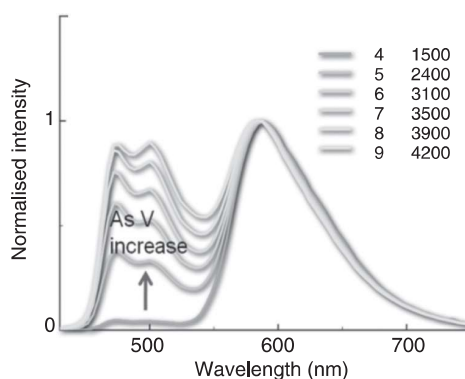
In 2009, Jou's group first demonstrated a single fluorescent OLED composed of daylight-complementary emissive constituents, that yield a sunlight-style emission with a color temperature ranging from 2300 to 7900 K (Plate III(a),

see color section between pages 414 and 415), with a power efficiency of 7.0 and 2.2 lm/W at brightness of 100 and 1000 cd m⁻², respectively.¹⁷ In Plate III(b), the resultant device shows significantly high luminescence at relatively low applied voltages, which increases from 20 to 5900 cd m⁻² for voltages increasing from 3 to 9 V. As shown in the electroluminescent spectra in Plate III(c), the device initially shows a predominantly red-emission spectrum at 3 V with CIE coordinates (0.48, 0.42), turns to pure white (0.33, 0.33) at 5.5 V, and becomes bluish white (0.28, 0.29) at 9 V.

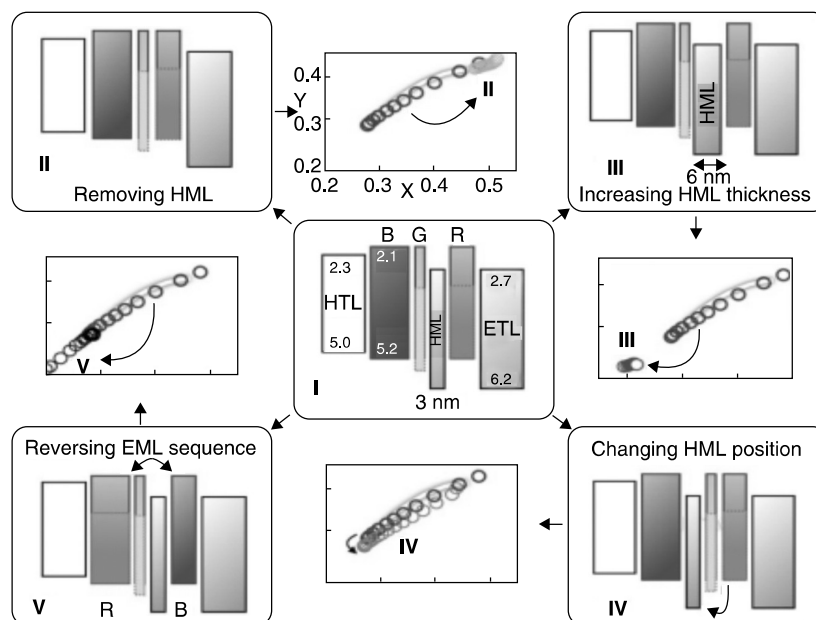
To enhance the device efficiency Jou's group in 2012 reported a sunlight-style device by replacing the fluorescent emitters with phosphorescent ones.¹⁸ The device power efficiency was improved from 7.0 to 25 lm/W at 100 cd m⁻² or from 2.2 to 17 lm/W at 1000 cd m⁻² with a resulting color temperature ranging from 1500 to 4200 K, as shown in Fig. 14.3.

Mechanism for color temperature tunability

It is noteworthy that the resulting emissive color and color temperature span of the OLEDs depended on factors such as emitter species efficiency and number, layer sequence and thickness, and doping concentration. Take the fluorescent sunlight-style OLED for example. To generate daylight colors better matching those of sunlight at all desired color temperatures, Jou's group switched from two daylight-color complementary constituents to three: the red, green, and blue light emitters. They deposited them onto transparent-electrode-coated glass with the blue light-emitting layer adjacent to the transparent cathode side and the red light-emitting layer adjacent to the aluminum anode side, coupling them with a hole-modulating layer (see Fig. 14.4). Figure 14.4 (I–V) shows the effects of the



14.3 In the phosphorescent sunlight-style OLED, the color temperature changes from 1500 to 4200 K as the voltage increases from 4 to 9 V.¹⁸



14.4 Effects of the hole-modulating layer (HML), the electron transport host material TPBi – 1,3,5-tris-(N-phenylbenzimidazole-2-yl)-benzene – and sequence of the multi-emitting layers (EML) on the color temperature and color temperature span of a sunlight-style, color temperature-tunable OLED. The effects are indicated by the emission track, against the daylight locus, on the CIE chromaticity space. Also shown are the energy-level diagrams of our device I and counterpart devices II–V for comparison. ETL is the electron-transport layer, and HTL is the hole-transport layer.¹⁷

layer sequence of blue and red emitters, the position and thickness of the hole-modulating-layer on the resultant color, and color temperature range of the OLED.¹⁷

Because the electron was a minor carrier in OLED devices, predominant holes were likely to move and accumulate near the aluminum anode, causing the recombination of the hole with the electron to occur mainly in the red emissive layer and to emit red light in the absence of the hole-modulating layer. On incorporating that layer, especially between the green and red light-emitting layers, a significant portion of holes would be retained in the blue and green layers. At low applied voltage, a small portion of electrons were injected into the blue and green emissive layers to recombine with the retained holes to emit blue and green light. They then mingled with the dominant red light to yield an orange-white light. As the voltage increased, increasing electrons injected into the blue

and green emissive layers formed a comparatively stronger blue and green light. That, consequently, shifted the emission from orange to pure-white and even blue-white.

OLEDs have a wider color temperature range due to their easy design of molecular emitters and their inherently diffused spectrum, enabling OLEDs to emit a wide variety of chromaticity and a continuous spectrum.²⁹ Plate IV shows a CIE 1931 chromaticity diagram. In 1931, based on the efforts of Wright (1928–29) and Guild (1931) on reconstructing relative color matching data, the CIE defined an original matching color function with a 2-degree field of view in the collection of the experimental data. Such a small view angle was chosen in order not to avoid stimulation of the rods outside the fovea centralis, which contains a dense concentration of cones. The cones are color receptors, therefore, subjects chosen by the CIE in 1931 were able to describe cone vision within the fovea. It should be noted that a 10-degree field of view was adopted in the CIE convention in 1964, since the 2-degree field was too small for many practical applications.^{30–32}

Plate IV shows the Planckian locus on the CIE 1931 chromaticity diagram. The curve traces all the chromaticity coordinates of blackbody radiators at different temperatures. By definition, if a light source has the same chromaticity coordinates exhibited by a blackbody at a specific temperature, at point B for example, the color temperature of the light source is 6000 K. Let us now consider two dashed segments, DE and FG. All the four points (D, E, F, and G) represent four colors on the spectrum locus. Due to the fact that all the chromaticities along the line joining any two points, such as D and E pairs or F and G pairs, on the spectrum locus can be achieved by mixing various combinations of these two pure colors, the chromaticities as well as color temperature at the intersection (point B) can be achieved either from mixing pure colors D and E pairs or from F and G pairs. The phenomenon is called metamerism and is the foundation of all color reproduction techniques.^{30–32}

14.2.2 Physiologically- and psychologically-friendly

Medical studies reveal intensive emission with high color temperature to impose drastic effects on suppressing melatonin (MLT) secretion. Frequent exposure to bright white light at night has been identified as one crucial carcinogen to several cancers.^{9–16} Physicians have long been calling for the development of MLT suppression-free illumination to safeguard human health.^{33–36}

The effects of color temperature on physiology and psychology

Light itself has been realized to have a dark side. Light sources used for work during the day should soon be banned for use at night, which was unveiled early by Stephen M. Pauley:

Since we are born into a world of artificial lighting, we do not give much thought to how light disrupts the normal 24 h circadian rhythms present in all organisms. Biological clock rhythms are found in all living things, even mice and algae. . . . 'the circadian clock depends on dark nights and bright daylight, where dark nights allow normal MLT production between 2 and 4 am and bright daylight entrains or re-sets the body clock. The system is triggered by photons of light reaching specialized cells in the retina of eyes.¹²

Therefore, a clear distinction between lighting purposes for use in daytime and at night must be clarified.

During the day or with intense light with high color temperature, the secretion of melatonin decreases and cortisol increases, helping people stay awake and improve work efficiency. At night or with low color temperature dim light, the melatonin level increases, helping people relax while preventing risk of cancers.

Figure 14.5 shows the color temperatures of various current light sources and their effect on MLT suppression at 100 lx. The respective color temperatures of the studied candle and incandescent bulb are 2000 K and 2500 K, with 5600 K for a cold-white fluorescent tube and 5700 K for a white LED. The time needed to suppress 50% of MLT secretion, for example, would be longer for a light source with a lower color temperature. According to the literature, it is 66 minutes for candle and 39 minutes for incandescent bulbs.¹¹ The secretion of MLT would also be less affected at a lower exposure dose according to the following formula³⁷:

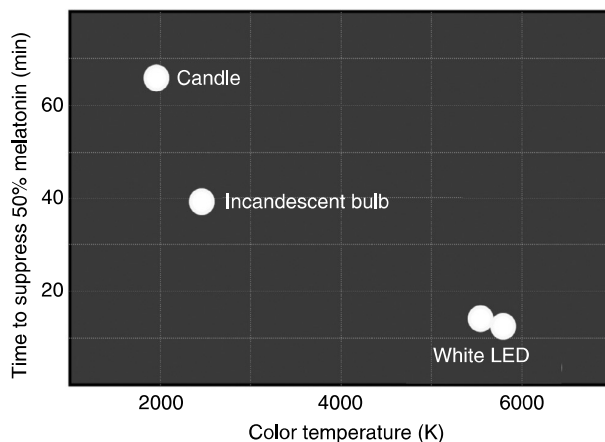
$$y = (y_0 - y_{\infty}) / [1 + ((x/x_{1/2})^s)] + y_{\infty} \quad (1)$$

where y is the extent of suppression with a total exposure dose of x , y_0 before exposure, and y_{∞} at saturation; $x_{1/2}$ is the dose required to reach half-saturation; $y_{\infty/2}$ is the slope of the curve between y_0 and y_{∞} .

In order not to disrupt human circadian rhythm, dim and low color temperature light sources are preferred for use at night. For visual effect, the ideal light source would be the one with a high color-rendering index and especially with a color temperature much lower than 2000 K.

A review of the color temperature of current lighting sources

Electrically driven lighting devices^{26,27,38–40} have gradually replaced most other traditional illumination measures from over a century ago. However, all current illumination devices, including modern electricity-driven lighting devices such as incandescent bulbs, fluorescent tubes, and the latest light emitting diodes, together with traditional hydrocarbon burning-based lighting tools, such as torches and candles, provide basic lighting needs but do not satisfy our desire for natural lighting, as from the sun, with a time-varying color temperature (Plate VI). For example, the color temperature is 2000 K for candles, 2700 K for incandescent bulbs, 2500–3000 K for warm-white fluorescent tubes, and 4000–5000 K for cool-white fluorescent tubes. The white light-emitting diodes use complicated



14.5 Effect of color temperature on the time required to suppress 50% of melatonin at 100 lux. The corresponding exposure times needed are adopted from the literature, and color temperatures are experimentally determined.

multichips, arrayed clusters or quantum-wells microstructure design to yield wide color temperature spans,^{41–43} but which are still insufficient to cover that of daylight, due to the lack of sufficient daylight-complementary constituents. To have high-quality lighting, emission with a daylight chromaticity and a color temperature span covering that of sunlight is essential, especially considering its strong effect on human psychology.^{44,45}

The fabrication of very low color temperature OLEDs

Jou's group demonstrated an approach to fabricate an OLED with low color temperature characteristics by using solution-process. The device exhibits a warm-white light emission with a color temperature of 2280 K, an external quantum efficiency (EQE) of 27.4%, and the efficacy of 38.8 lm/W at 100 cd m⁻² with a color temperature of 2320 K, 20.4% and 24.6 lm/W at 1,000 cd m⁻². The high efficiency may be attributed to the use of electroluminescence efficient materials and the ambipolar-transport host. Besides, the device architecture design enables excitons to form on the host and allows effective energy transfer from host to guest or from high triplet guest to low counterparts.⁴⁶ For light at night application, it is noteworthy to develop the high efficiency OLED with lower color temperature to be a physiologically-friendly light source. Therefore, a phosphorescent OLED with a color temperature ranging from 1880 K to 1940 K between 100 and 1000 cd m⁻² was proposed by Jou's group, which is lower than that of incandescent bulbs (2000~2500 K). The device still exhibits a high EQE

of 22.7% and high efficacy of 36 lm/W at 100 cd m⁻², or 20.8% and 29 lm/W at 1000 cd m⁻² by the incorporation of a blended interlayer to effectively distribute the entering carriers onto the available recombination zones.⁴⁷ For high-quality light for night, we further developed a high color-rendering index (CRI) device with lower color temperature by using fluorescent emitters. The device shows a color temperature ranging from 1773 K to 1830 K, which is much lower than that of candles (1800~2000 K), and a fairly high CRI of 87 between 100 and 1000 cd m⁻². The resultant efficiency is 6.4% and 11.9 lm/W at 100 cd m⁻², or 5.3% and 10.1 lm/W at 1000 cd m⁻². The reason for having the ultra-low color temperature and relative high CRI may be attributed to the significantly intensive deep red emission and five-band emitting from a single emissive layer. The high efficiency may be attributed to the employment of a smooth stepwise energy-level structure, enabling low injection barriers and balance carrier injection.⁴⁸

14.2.3 Very high color-rendering index (CRI) OLEDs

Defining CRI

Color-rendering index (CRI) is an important indicator of high-quality illumination, and four CRI bins represent different value ranges: very-high CRI (>90), high CRI (>75), medium CRI (>40), and low CRI (<40).⁴⁹

The importance of a very high CRI

Light sources with very high CRI have drawn much attention because objects can reflect under the very-high CRI illumination nearly the same color as that reflected under the sunlight with the same color temperature. Besides, no emission in the ultraviolet and infrared region was present, which made the very-high CRI device an ideal light source for application in museums, exhibitions, photography, and surgery, etc. Notably, very-high CRI light source has the highest market value of all, according to the DOE. It is estimated that the industry revenue of very high CRI devices will reach 400 million US dollars in 2015 and 750 million US dollars in 2020 (Plate V).

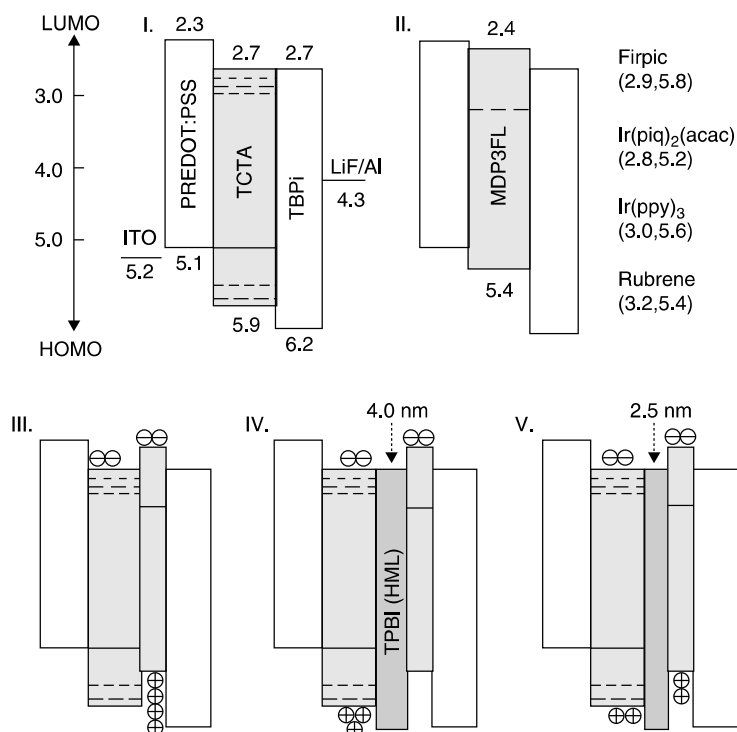
The benefits of using OLEDs

Although having 82 or greater CRI, current fluorescent lamps are not ideal light sources due to their intrinsically severe spiking, discontinuous emissive spectrum. Moreover, they show a relatively poor degree of resemblance with the emission of natural light from the sun. Typical incandescent bulbs exhibit 98 CRI, which would have been an ideal quality light source if not for its poor energy efficiency. As for the OLEDs, their inherently diffused emission is in favor of composing a light source with a continuous and smooth spectrum that prevents visual discomfort and yields a very high CRI. Therefore, OLED is a suitable candidate for obtaining

a very-high CRI. Numerous prior researches on OLED devices with high (>75) or very-high CRI (>90) demonstrate OLEDs to be capable of possessing a high CRI much greater than 90 as well as a high efficacy.²⁹

The fabrication of very high CRI-OLEDs

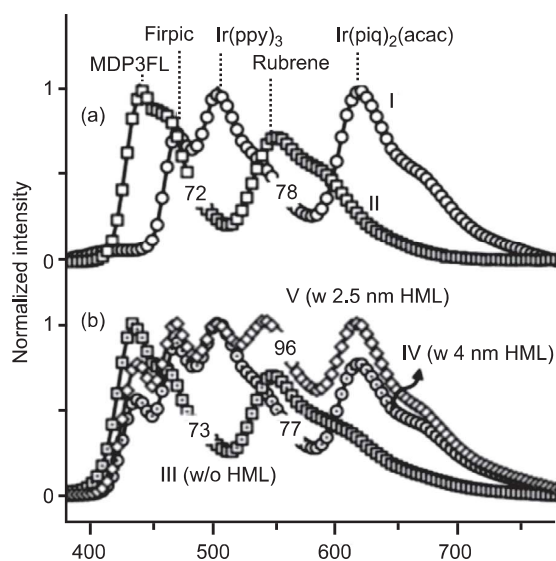
To achieve a CRI much greater than 90, OLED devices require multiple, usually more than three, complementary emitters with appropriate intensity. Jou's group fabricated a very-high CRI five-spectrum OLED with double white EMLs separated by a thin hole-modulation layer (HML) (Fig. 14.6), which enabled the



14.6 Schematic illustrations of the three-wavelength phosphorescent white OLED (Device I) and the two-wavelength fluorescent white OLED (Device II). Devices III–V are five-wavelength white OLEDs with the three-wavelength phosphorescent and two-wavelength fluorescent white emissive layers, where Device III contains no hole modulation layer (HML), Device IV 4 nm HML, and Device V 2.5 nm HML. With the use of an HML with a proper thickness (Device V), the entering holes and electrons can be well distributed into the two white emissive zones.¹⁹

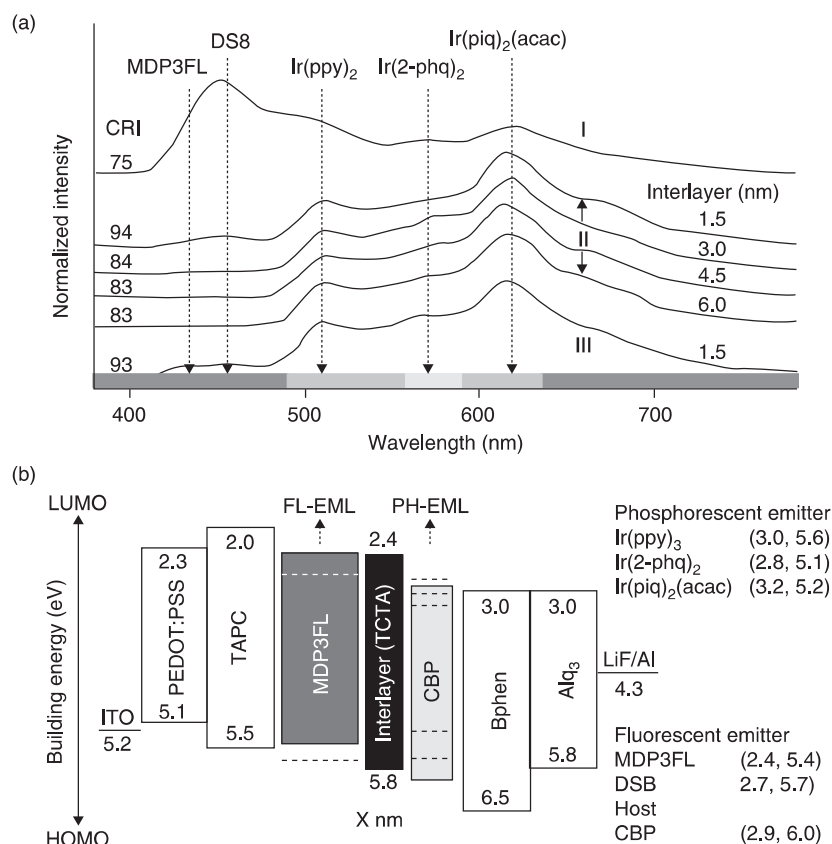
carriers to recombine in both emissive layers, hence achieving a maximum CRI of 98 with an efficiency of 8.3 lm/W at 100 cd m⁻².²⁹

Figure 14.7 shows the EL spectra and CRI values of the studied devices. Device I exhibited a three-wavelength white emission with a 78 CRI at 1000 cd m⁻². Device II exhibited an emission with two white light complementary colors with a 72 CRI. To obtain very high CRI, the two white EMLs were stacked to integrate their EL spectra. Without the HML, the resulting recombination occurred mainly in the second white EML, and showed correspondingly a CRI of 73. The major recombination would take place in the first white EML as the HML was 4 nm. The corresponding CRI was 77, similar to the 78 CRI exhibiting from Device I. Both devices (I and IV) showed nearly the same 3-band spectrum, clearly proving the employed HML was too thick, and hence most, if not all, entering holes were blocked by the HML having a 0.3 eV hole-injection barrier, and therefore retained in the first white EML. By reducing the hole modulation layer to 2.5 nm, the CRI was markedly improved to 96 (Device V), resulting from a balance emission of all five emitters, thereby producing a full wavelength spectrum with a very-high CRI.²⁹



14.7 The resultant EL-spectra of (a) the single white emissive layer containing OLEDs, Devices I and II, and (b) the double white emissive layers containing OLEDs, Devices III–V. A five-wavelength emission with 96 CRI at 1000 nits is observed as a 2.5 nm HML is employed, or 77 CRI if the HML is 4 nm. Only two-wavelength emission with 73 CRI is observed in the absence of the HML.¹⁹

Besides the above two white EMLs approach, very high CRI can also be obtained easily with the employment of five white light complementary emitters dispersed in two different EMLs. To develop this, Jou's group employed five emitters ranging from deep-red, orange, green, blue, to deep-blue to realize a wide and relatively continuous electroluminescent spectrum, as shown in Fig. 14.8(a). They developed a device architecture composed of fluorescent



14.8 (a) Electroluminescence (EL) spectral results of the studied white OLED devices with (Device II) and without (Device I) an interlayer. The highest CRI (94) appears in Device II with a 1.5 interlayer. Device III shows a much-improved power-efficiency while retaining a high CRI, 93, by using a different ETL (TPBi). (b) Energy diagram of the studied white OLED devices. Device I: without an interlayer, Device II: with an interlayer of 1.5/3.0/4.5/6.0 nm, and Device III: with the electron transporting layer of Alq_3 replaced by TPBi.⁵⁰

and phosphorescent emissive layers separated by a high triplet-energy interlayer as shown in Fig. 14.8(b). The design effectively balanced the distribution of excitons and modulated the recombination zone, improving the power efficiency and the CRI simultaneously. The resulting device achieved a high power efficiency of 23.3 lm/W at 100 cd m⁻², or 14.3 lm/W at 1000 cd m⁻² with a very-high CRI of 93.⁵⁰

14.2.4 High sunlight spectrum resemblance (SSR)

The benefits of using SSR

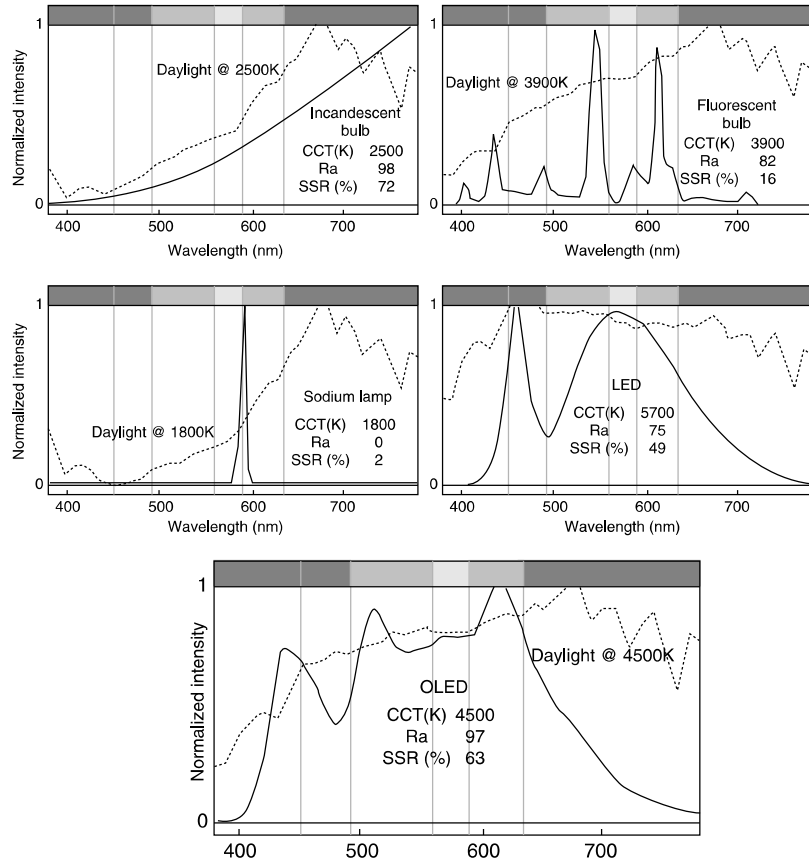
Sunlight spectrum resemblance (SSR) is a new indicator to characterize the extent of the emission spectrum of a given light source resembling that of sunlight, first proposed by Jou's group.⁵⁰ Since CRI alone cannot properly characterize a given light source,⁵¹ the proposed SSR, as well as color temperature, may together provide domain scientists and technological experts new aspects in research and/or development for improving or re-evaluating current light measures or devising new and better ones.⁵²

The SSR of current lighting sources

Lighting sources with a high color-rendering index (CRI) are desirable in color-critical applications such as photography and cinematography. Nevertheless, a high-quality lighting source should presumably have a high SSR. Figure 14.9 shows the CRI and SSR of an OLED compared with those of several conventional lighting sources. The studied incandescent bulb exhibits a 98 CRI and 72% SSR, while its power efficiency is only 15 lm/W. The studied fluorescent tube shows an 82 CRI with power efficiency of 90 lm/W, while its SSR is only 16%. The sodium lamp shows monochromatic light with a near 0 CRI and 2% SSR. The LED studied has a 75 CRI and 49% SSR. The four-wavelength OLED studied has a 97 CRI and 63% SSR, indicating that the desire for a sunlight-style high quality artificial lighting source can be realized by new OLED lighting technology.⁵²

14.2.5 Other outstanding characteristics

OLEDs also have many other merits that other lighting sources do not possess. These exclusive advantages are the basis of making OLED a killer technology. Coupled with the aforementioned superb disruptive characteristics, OLEDs have many other advantages for lighting applications, such as energy saving, mercury free, the ability to be built with sustainable raw materials, low driving voltage, plane-type (luminaire-ready), cold white emission with less high-heat production, thin, lightweight, flexible and rollable, etc.



14.9 Comparison of the CRI and SSR of an OLED with those of the studied incandescent bulb, fluorescent tube, sodium lamp, and LED.⁵²

Low driving voltage

OLED devices required a markedly low applied voltage. Even a couple of batteries are adequate to drive an OLED lighting panel. They can be driven even by several lemons or potatoes in series as shown in Fig. 14.10. The driving voltages are 3.7 V and 2.8 V for potatoes and lemons, respectively, which are low enough to mitigate safety concerns.

Thin and light

OLED panels are very thin, light, and easy to carry as they are only half of the thickness of traditional LCDs. The OLED TV developed by Sony, shown



14.10 Lemons and potatoes are able to drive OLEDs.

in Fig. 14.11, is only 3 millimetres thick from the side view. With the absence of the background light sources, they are capable of being made even lighter and slimmer.

Flexible OLEDs

Before OLED technology arrived, no lighting devices such as incandescent bulbs, fluorescent tubes, and LED light panels could be made flexible (Fig. 14.12). As an important product in new generation display and lighting, there are a lot of factors to be noticed when we are going to fabricate an OLED with impact-proof, shatterproof, thin and light, and easy-carrying characters. These factors are heat resistance of the substrate, resistance to moisture, the morphology and conductance of the anode on the substrate, encapsulation levels, bending abilities, etc.

Wide viewing angle

OLED displays have viewing angles greater than 165 degrees, therefore the side-view animation is as vivid and clear as that from the front view, which outperforms the traditional LCDs. Besides, no color aberration is observed from the side view. Hence, the OLED display technology can be adapted to TVs because the audience can view from different angles without aberration.

High contrast

OLEDs have surprisingly high contrast which LCDs cannot compete with. The Sony XEL-1 OLED TV shown in Fig. 14.11 has an ultra-high contrast of 1 000 000

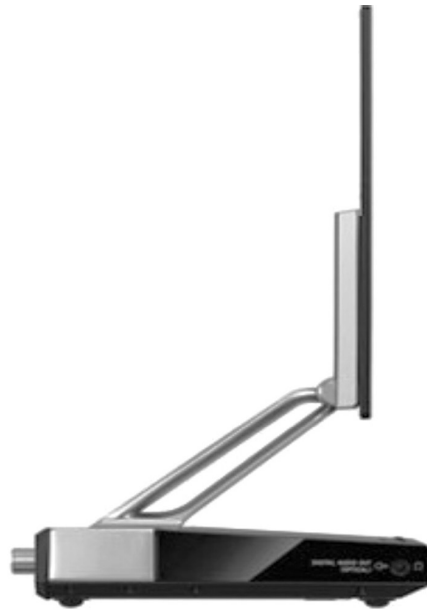
to 1. With higher contrast property, more minute details of dark region against light region can be resolved and even when the picture is displayed under the sun, the image is still very clear.

Fast response

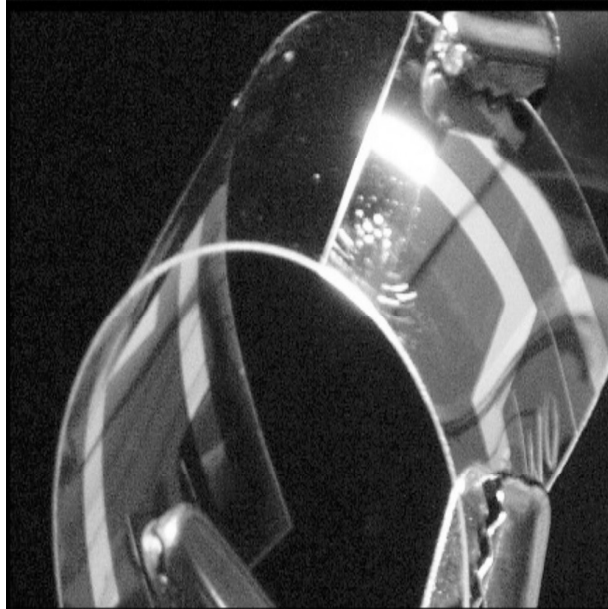
The response rate of OLEDs is about 100 times faster than that of LCDs (it is $50\mu\text{s}$ for OLEDs, and 5–25 ms for LCDs). Thanks to its high response rate, no evident motion blur will occur, which is one of the advantages of OLEDs for use in animations. On the contrary, LCDs have longer response time, resulting in retinal afterimages causing blurriness in human eyes when animation is displayed by LCDs.

Cold emission with less heat production

Incandescent bulbs have low efficacy, and are energy-consuming as well as producing wasted heat. For high efficacy LEDs, the biggest bottleneck to date is finding a way to improve the heat dissipation. It is, therefore, questionable that LEDs are highly efficient because at least 50% of energy was dissipated from the



14.11 Sony XEL-1 OLED TV.



14.12 Flexible OLED device.¹²⁴

chips to the package.^{28,53} OLEDs, on the contrary, belong to the cold emission type, which produce less heat and reduce the generation of waste heat.

Planar-type emission

Incandescent bulbs are point light sources. Fluorescent tubes are line sources and have a spiky emission which is far from that of natural sunlight. OLEDs, however, have diffusive light emitting characteristics (shown in Plate VII) that intrinsically dispel the problem of being stinging to human eyes due to concentrated beams. Therefore, OLEDs are suitable lighting sources for use indoors and in cars.

14.3 Lifetime issues

Although white OLEDs have almost reached the fluorescent tube efficacy,³ their operating lifetime remains a fundamental problem that limits their commercial applications.⁵⁴ Luminance degradation is one of the crucial problems for OLED device lifetime and consistency. OLED device lifetime is usually defined as the time that elapses as its brightness drops to half of its initial value under constant current operation.⁵⁵ A few mechanisms account for the decrease of

brightness with time. For example, the dark spot degradation is characterized by the increase of non-radiative area within the active area, and it depends on the stability of the electrodes.^{56–58} An unexpected drop to zero brightness is defined as entirety failure, which may arise from short-circuit between electrodes.⁵⁹ A nonstop long-term drop in device brightness is referred to as intrinsic degradation.

OLED lifetime can be measured as both operational lifetime and shelf life.⁵⁷ Operational lifetime is defined as the average number of hours of operation in which the initial brightness drops to 50% or 70% in more stringent application conditions,⁶⁰ whilst the shelf life is the length of time that an OLED device may be stored without affecting its performance for application. Under ambient conditions (room temperature, 50% relative humidity and without direct exposure to sunlight, etc.), shelf life is typically 10 years but elevated environmental temperature may reduce this. The lifetime and stability of OLEDs are affected by numerous factors. These factors can be divided into two groups: the intrinsic factors, such as low stability against heat, an unstable host, improper device architecture (e.g. high hole injection barrier), and electrode metals (In, Ca, Mg, etc.) out-diffusion; and the extrinsic or environmental factors such as atmospheric oxygen and moisture.⁶¹

14.3.1 Determining the lifetime of an OLED device

In the following sub-sections we will discuss in turn the techniques for OLED lifetime characterizations such as shelf life (sensitivity to relative humidity and oxygen) and operating lifetime (repeated oxidation, reduction and excitation cycles of a thin organic film).

As mentioned above, the OLED lifespan is typically characterized as the time it takes for the designated brightness to decrease to 50% or 70% of its initial value.^{62,63} This is a common metric in describing the life of lamps and other non-display light emitters, but which has little meaning for high information content displays because human eyes can easily recognize the minute non-uniformity in brightness on a display. Thus a 5–10% loss of luminous efficiency can result in a very visible burned-in image. A display with a claimed 20 000 hrs of life to 50% brightness, for example, might only have several hundred hours to 10% where burn-in would be a problem.^{60,61,63–65}

The OLED lifetime further depends on the specific applications. These specific applications are sensitive to the:

- loss of device functionality caused by dark spots formation;
- change in emission color;
- high heat generation at intensive brightness;
- loss in brightness with respect to operation time and driving voltage;
- device area size;

- environmental conditions; and
- pixel failure in displays etc.⁶³

Some companies, such as Vision Technology and Botest Systems GmbH, have developed lifetime measurement systems which can be used to monitor the lifetime of OLED devices accounting for the effects from the above factors.^{66,67}

14.3.2 Current lifetime records

Now we are going to discuss the latest lifetime records of both monochromatic and white OLEDs based on the reports from various academic and industrial research groups. For example, a high performance blue phosphorescent OLED developed by Konica Minolta had a lifetime of 16 000 hrs (at 1000 cd/m²) and CIE color coordinates of (0.16, 0.40), while the Universal Display Corporation (UDC) reported a lifetime of 9000 hrs (at 1000 cd/m²) for an OLED with CIE (0.18, 0.39). At CIE color coordinates (0.13, 0.22), a lifetime of 23 000 hrs (at 1000 cd/m²) for a fluorescent blue OLED had been reported by Idemitsu Kosan. UDC had also reported a 600 000 hrs lifetime for a phosphorescent green OLED with color coordinate of (0.33, 0.62) and a lifetime of 500 000 hrs for a red phosphorescent OLED with color coordinates (0.64, 0.36).

In 2010, numerous white OLEDs have been reported by major OLED lighting players. For example, Philips demonstrated an efficiency of 20~25 lm/W with a lifetime of 10 000 hrs, Osram 20~23 lm/W with 5000 hrs, Lumitech 11 lm/W with 30 000 hrs, Mitsubishi 28 lm/W with 8000 hrs, and New Energy and Industrial Technology Development Organisation (NEDO) program in Japan 37 lm/W with light out-coupling with 40 000 hrs. In early 2012 Mitsubishi Heavy Industries had reported a lifetime of 60 000 hrs for a 40 lm/W warm white OLED panel with color coordinates of (0.43, 0.42) and another efficient (25 lm/W at 3000 cd/m²) white OLED panel with a lifetime of 125 000 hrs with color coordinates of (0.38, 0.38) using materials from UDC.⁶⁶ Recently, UDC had reported the new lifetime data for both monochromatic (RGBY) and white OLEDs, as shown in Table 14.1 and Table 14.2.^{67,68}

Table 14.1 Performances of various RGBY PHOLED devices reported by UDC in SID 2011⁶⁷

UDC-PHOLED (at 1000 cd/m ²)	1931 CIE Color coordinates	Current efficiency (cd/A)	Operational lifetime (hrs) at LT 50%
Deep red	(0.69, 0.31)	17	250 000
Red	(0.66, 0.34)	24	600 000
Red	(0.64, 0.36)	30	900 000
Green	(0.34, 0.62)	78	400 000
Light blue	(0.18, 0.42)	47	20 000
Yellow	(0.46, 0.53)	72	1 400 000

Table 14.2 Recent advancement in various types of white OLEDs reported by UDC⁶⁸

UDC-PHOLED (at 1000cd/m ²)	Area (cm ²)	CRI	1931 CIE Color coordinates	Power efficiency (lm/W)	Operational lifetime (hrs) at LT 70%
Pixel	0.02	86	(0.475, 0.421)	72	55 000
Panel 1	15 × 15	83	(0.471, 0.413)	58	30 000
Panel 2	15 × 15	82	(0.446, 0.417)	62	18 000

14.3.3 Failure mechanisms

The failure mechanisms of OLED devices can be classified into two categories: intrinsic deterioration and extrinsic deterioration.⁶¹ Intrinsic deteriorations involve problems in the stability of organic thin film, interface between anode and organic layer, excited state stability, movement of ionic impurity, diffusion of transparent electrode metal into emission layer (indium migration mechanism), cation instability, large energy barrier for charge carriers, positive charges accumulation, and width of recombination zone.^{56,57,61,63,69,70,72–77}

Adachi's group has reported that a large energy barrier for hole injection at the interface of ITO/HTL (hole transporting layer) would lead to large joule heat generation. The produced heat would steadily cause local aggregation of organic molecules such as dimerization and crystallization of an amorphous HTL. These dimers and crystalline structures formed at the sites for hole trapping and a part of the injected hole build up a space charge. Simultaneously the large number of electrons accumulated in the emissive layer (EML) near the HTL/EML interface because HTL blocked the electrons within the EML. This directed the imbalance carrier injection in the EML. The excess electrons interacted with exciton at the HTL/EML interface and led to the non-radiative destruction of excitons with reduced luminance and lifetime.⁷³

Diffusion of electrode metal ions into the device's organic layers and its effect on device performance have been extensively studied in the last two decades.^{62,75–79} Electrode metal ions were moved due to an electric field constructed by direct current and reduced the device lifetime.⁷⁵ Haskal *et al.*⁷⁶ reported that the lithium (Li) diffused rapidly into organic materials from a Li/Al cathode, and thus shortened the device lifetime. Huang *et al.*⁷⁷ reported the strong correlation between the retardation of Al diffusion and the recovery of tris-(8-hydroxyquinoline) aluminum (Alq₃) and Photoluminescence intensity suggested that diffusion of Al into Alq₃ may be a major mechanism for Al-induced luminescence quenching in Alq₃ based devices. Lee *et al.*⁶² had investigated the metal diffusion from MgAg cathodes and ITO anodes. Diffusion of Mg from MgAg cathode into organic layer was limited to a depth of 2–3 nm and had not comprised a considerable effect on OLED device degradation, whilst the indium was substantially diffused into an

organic layer and increased the drive voltage. The device quantum and luminescence efficiency reduced since indium migrates from the ITO layer to the organic layer.^{62,77,78}

The lifetime of OLEDs driven by alternating current (AC) is longer than that driven by direct current (DC), which can be attributed to the AC field changing with time that prevents ions from diffusing into the organic layer. On the other hand, a DC field would cause ions to diffuse into the organic layer which will act as a quenching center that lowers the device lifetime and its efficiency.⁷²

Shen *et al.*⁷⁹ and Kondakov *et al.*⁸⁰ have reported the holes accumulation at the interface of organic layers formed a recombination center which could not emit light and reduced device luminance and lifetime. They have also proposed the operational degradation of an OLED device to be coupled with the accumulation of non-radiative recombination centers and luminescence quenchers in the emissive zone. It is an ordinary degradation mechanism affecting an extensive range of OLEDs with varying compositions and structures.

Due to poor thermal and excited state stability, an organic molecule may be distorted into intermediates or, worse, isomers. Kondakov *et al.*⁸¹ observed an 11% change in 4,4'-bis(N-carbazolyl)biphenyl (CBP)/(NPB) N,N'-diphenyl-N,N'-bis(1-naphthyl)-1,1'-biphenyl-4,4'-diamine ratio or 16% change in fac-tris(2-(2-pyridinyl)phenyl)iridium (Ir(ppy)₃)/NPB ratio for an OLED device subsequent to 2784 hrs use.

Generally, degradation that has not resulted from problems concerning materials and device structure is characterized as extrinsic (non-intrinsic) deterioration. Extrinsic issues effectively reduced the environmental stability of OLEDs because organic materials are highly sensitive to atmospheric moisture. Environmental exposure of organic materials leads to the formation of non-emissive spots within the device area.^{58,82} This non-emissive area is known as a dark spot, and it occurs if the device is not sufficiently protected from the atmospheric moisture and oxygen. Its growth would accelerate when the device is under electrical stress. The dark spot begins small but grows with time, thus reducing the emissive area and, subsequently, the total luminance.⁸³ Numerous researchers have extensively studied a large number of extrinsic factors and these are described as follows.

A heterogeneous thermal evaporation of organic materials causes a low adhesion between anode and organic layers. This leads to the permeation of relative humidity and oxygen in OLED devices and results in the dark spot's development. The final observation revealed the marked reduction in device lifetime.⁸⁴ Kim *et al.*⁸⁵ investigated the relationship between ITO surface roughness and current leakage in OLEDs. Surface roughness or spikes on the ITO surface resulted in corona discharge which induced the short circuit and current leakage problems. This resulted in the OLED device failure during operation.

An extensive amount of research has been carried out to understand the electrical and mechanical response of ITO thin film under stress because ITO is

one of the inorganic layers in an OLED device. The interfacial phenomena, between organic and inorganic layers, play a crucial role in device performance and stability. Poor interaction between organic and inorganic (e.g. ITO) layers caused the stratification that reduced the contact area and electron injection. Finally this poor interaction induced the dark spots and limited the device lifetime.⁸⁶⁻⁹¹

A bend test of a multilayer barrier that encapsulated a flexible OLED display has been carried out by Chwang *et al.*⁹² The display was bent under a tensile stress 1000 times around a cylinder of one inch diameter at a rate of approximately 12 bends/min. They reported that after 100 bends the display illustrated no damage. After 500 and 1000 bends they observed some mechanical cracks in the cathode that had not been observed before the experiment. Their group had not optimized the barrier layer properties and/or flexibility, however, the optimization of these characteristics should improve the display lifetime and flexibility.

Kim *et al.*⁹³ reported that successive deposition of cathode layers leads to pin hole formation and results in the penetration of moisture through the pin holes and leads to the formation of dark spots. Aziz *et al.*⁷⁰ attributed the development of dark spots to the growth of $\text{Mg}(\text{OH})_2$ at the $\text{Alq}_3/\text{Mg}:\text{Ag}$ interface coupled with local degradation of the Alq_3 layer. The growth of cathode bubbles (a domelike structure), which also leads to dark spot formation, is found to be caused by gas evolution from the galvanic corrosion of the cathode couple as well as from the electrolysis of penetrated moisture. They confirmed that the dark spot growth is principally associated with the degradation of the cathode layer.^{61,70,94}

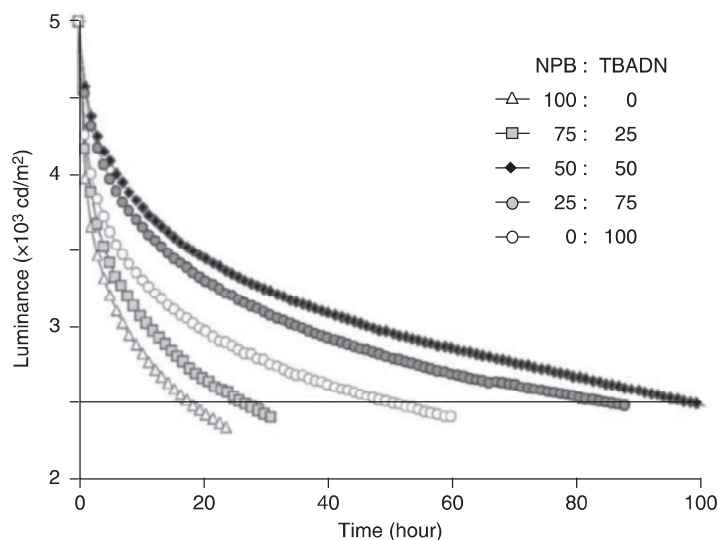
14.3.4 Improving the lifespan of OLED devices

Several research groups have extensively studied a large number of approaches to improve OLED device lifetime.^{75,95-97} Nowadays, it has already been proven that heat instability and the oxidation process of organic materials induce the sudden decrease or total loss of luminance due to the development of electrical shorts in the device. The development of shorts is attributed to catastrophic failure^{98,99} and extensively reduces the OLED device lifetime during operation.¹⁰⁰ Deepak *et al.*¹⁰¹ have reported the inefficient conversion of electrical power into light leads to increase in temperature of an OLED device. An increase of only a 10 K in an OLED device temperature during operation can lower its lifetime by more than 50%. Their group has performed a two-dimensional (2-D) heat transport analysis and reported that the device temperature can easily increase more than 10 K. To negate the heat effect throughout the operation, they proposed the both-side cooling technique for OLED-SSL panels and a thermal transport model for OLED-based FPDs. Researchers have developed numerous techniques to avoid the deterioration of OLED devices from operational heat. For example, Wu *et al.*¹⁰² synthesized a more thermally stable spirobifluorene-based 4,4'-bis(2,2-

diphenylvinyl)-1,1'-biphenyl (DPVBi) analogue, 2,7-bis(2,2-diphenylvinyl)-9,9'-spirobifluorene (DPVSBF). The presence of rigid spirofluorene linkage has effectively improved the material's glass transition temperature (T_g) and morphological stability, although it maintained most of the photophysical and electronic properties of DPVBi. The DPVSBF has shown a T_g of 115 °C which is approximately double from (64 °C) DPVBi. It was revealed that the DPVSBF-based OLED device has an operational lifetime 16 times longer than its DPVBi counterpart.

Jou *et al.*⁷⁴ have reported a long-lifetime, high efficiency white OLED with a mixed host in one of the double EMLs. These enhancements were attributed to a mixed-host structure, which effectively dispersed the carriers in a broad recombination zone and provided good thermal stability. Figure 14.13 shows the effect of a mixed-host ratio on the device lifetime. The lifetime was measured under constant current with an initial brightness of 5000 cd/m² at room temperature.

Recently, numerous researchers have paid more attention on the anode side to the modification of the ITO/HTL interface. Anode modification approaches involve various techniques, which can enhance the operational durability of OLED devices. For example, improvement of carrier injection may be achieved via self-assembled monolayers (SAMs) of dipolar phosphonic acids onto the surface of ITO glass. SAMs manipulated the Schottky energy barrier at the transparent conducting oxide anode layer (ITO)/organic layer interface,



14.13 Effect of a mixed-host ratio on the OLED device lifetime.⁷⁴

consequently the ITO work function increased.^{103–105} Numerous research groups have revealed an enormous enhancement of ITO anode work function and surface properties using oxygen plasma treatment.^{106–109} The OLED device lifetime is also enhanced by second order magnitude.¹⁰⁷ Choi *et al.*¹¹⁰ treated the ITO anode via SF₆ plasma and reported a significant improvement in power efficiency and stability of OLED devices based on poly[2-methoxy-5-(2-ethylhexyloxy)-1,4-phenylenevinylene]. SF₆ plasma treatment slightly reduced the ITO surface roughness. The surface content of fluorine has been found to be responsible for improvement.

Hashimoto *et al.*¹¹¹ deposited an iodogallium phthalocyanine (IGaPc) layer on ITO glass after various surface treatments (uv-ozone and oxygen plasma) and markedly improved the operational lifetime of an OLED device. Nüesch and his co-workers¹¹² have demonstrated huge shifts in the work function of ITO via acid and base treatment on the ITO surface. These huge shifts are caused by a double ionic surface layer. The opportunity to tailor the ITO work function by this method is of great interest in the fabrication of OLED devices where Ohmic charge injection is desired.

Mason and colleagues have presented the effect of oxidative and reductive treatments of ITO on the performance of EL devices. Oxygen glow discharge or uv-ozone treatments enhanced the surface oxygen concentration and greatly influenced the ITO work function.¹¹³ A low energy oxygen ion beam-treated ITO surface has depicted the lower operation voltage, very high brightness and significantly high operation half-lifetime, because ion beam treatment drastically reduced the ITO surface roughness.¹¹⁴

Besides ITO surface treatments, another method is the inclusion of a nanometer-thick organic interlayer with its HOMO between ITO and HTL layers to enhance hole injection. In 1996, Tang and his co-workers demonstrated an Alq₃ thin-film-based highly stable OLED device using a thin layer of copper phthalocyanine (CuPc) on the ITO surface. A noteworthy improvement in device stability is obtained because CuPc stabilized the hole-injection contact.¹¹⁵

An introduction of a thin magnesium (Mg) buffer layer (about 2.5 nm) between ITO and HTL drastically improved the operational stability in contrast to a device without a buffer layer. The Mg buffer layer had effectively blocked the indium ions diffusion into the organic layer and resulted in an extensive improvement in the device lifetime.¹¹⁶

Both efficiency and operational lifetime of a polymer LED can be markedly improved by inserting a thin insulating perylene layer between the ITO and HTL. The perylene thin layer provides a smooth morphology for HTL deposition, which retards metal migration, reduces local electrical field and prevents oxygen and moisture permeation. The device lifetime is improved and dark spot formation is overcome.¹¹⁷

McElvain *et al.*⁵⁷ had studied the dark spot formation and luminance diminution under constant voltage stress conditions. These dark spots have resulted from

delamination of metal at the Alq_3/Mg interface initiated by pinholes on the cathode surface. Baik's group investigated the ion-beam-assisted deposition of aluminum cathode on spin-coated poly-p-phenylene-vinylene (PPV). Their group has reported that the dense aluminum cathode inhibited the permeation of humidity and oxygen into the PPV thin film through pinhole defects and reduced the dark spot growth. An ion-beam-assisted aluminum layer deposition has extensively enhanced the lifetime of OLED devices.¹¹⁸

Due to the poor barrier performance of polymer substrates, a thin encapsulation technique is required on both sides of the device to prevent atmospheric moisture and oxygen penetration.¹¹⁹ Recently, a multilayer of atomic layer deposition (ALD)/molecular layer deposition (MLD) combination has been proposed by Dameron *et al.*¹²⁰ They reported that the effective water vapor transmission rates are also reduced for the $\text{Al}_2\text{O}_3/\text{SiO}_2$ ALD bilayer. It has been recommended that the rapid SiO_2 ALD layer successfully blocked pinholes in the Al_2O_3 ALD layer.^{119,120} Due to the excellent film integrity, the ALD barrier layer can easily prevent the diffusion of atmospheric moisture and oxygen.

The operational stability of OLEDs can be considerably improved by introducing a stable dopant such as rubrene, because the excited states of rubrene molecules are more stable than that of the hosts.¹²¹ Aziz and Popovic¹²² studied the stability of an OLED with a device structure of ITO/HTL/ $\text{Alq}_3/\text{Mg:Ag}$, in which different portions of HTL were doped with rubrene. Zhang *et al.*⁹⁶ reported the stability of a rubrene-doped HTL-based OLED is increased due to the specific energy levels of rubrene, which facilitate the carrier injection.⁹⁶ Rubrene acts as both a charge trap and a recombination center, proposed by Murata *et al.*⁹⁷ Enhancement in OLED operational stability is caused by rubrene molecules acting as hole traps in the HTL, thus reducing the formation of unstable Alq_3 cationic species.^{76,98,122}

Several researchers have proposed various types of encapsulation techniques. These hermetic seals are utilized to protect OLEDs from humidity and oxygen. Most common encapsulation techniques are made with inorganic materials, such as glass or metal lids. However, such materials are so large and heavy that they severely limit the application of OLEDs. Thin film encapsulation is the most promising technique for OLED device packaging. Nowadays, thin film encapsulation technology is one of the most challenging requirements to avoid the permeation of humidity and oxygen into flexible OLED devices. Kim *et al.*¹²³ have developed a new encapsulation technique using inert oils (e.g. silicone oil and mineral oil) as a liquid passivation layer. This liquid passivation layer strongly prevents the occurrence and growth of dark spots and significantly enhances the device lifetime in ambient conditions.

14.4 References

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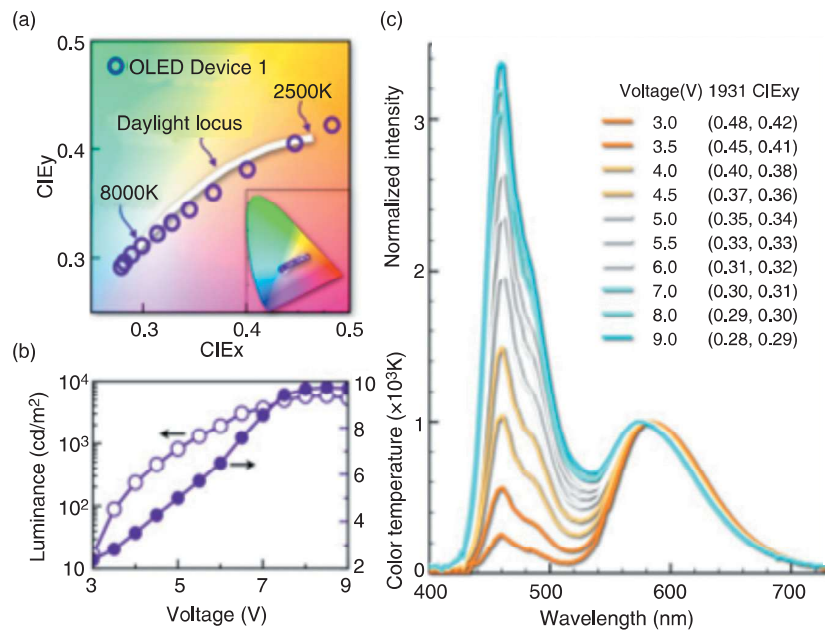


Plate III (Chapter 14) Emissive color and color-temperature characteristics of sunlight-style OLED device (a) The emission track on the International Commission on Illumination (CIE) 1931 chromaticity space, which characterizes color, matches closely to the daylight locus between 2500K sunset and 8000K sunlight in a northern country. (b) The color temperature changes from 2300 to 9700K and brightness from 20 to 5900 cd m⁻² as the voltage increases from 3 to 9V. (c) The electroluminescence spectra at various applied voltages. Three peaks, appearing at 460, 495, and 590 nm, correspond to the blue, green, and red emitters, respectively.

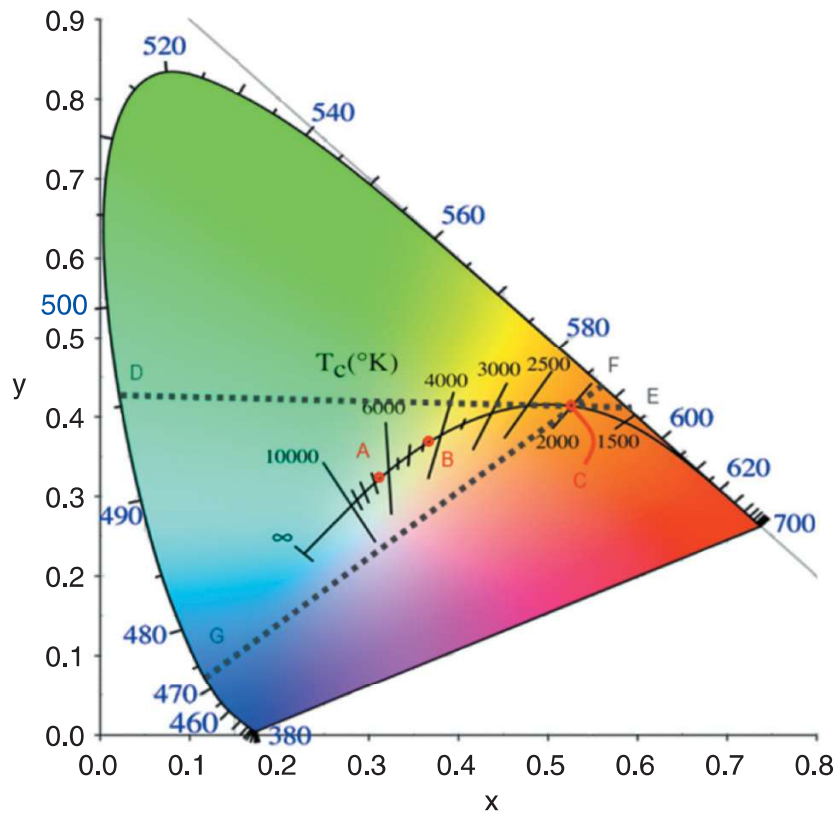


Plate IV (Chapter 14) Commission Internationale de l'Eclairage (CIE)
1931 chromaticity diagram with the locus of chromaticity coordinates
defined by blackbody radiators.

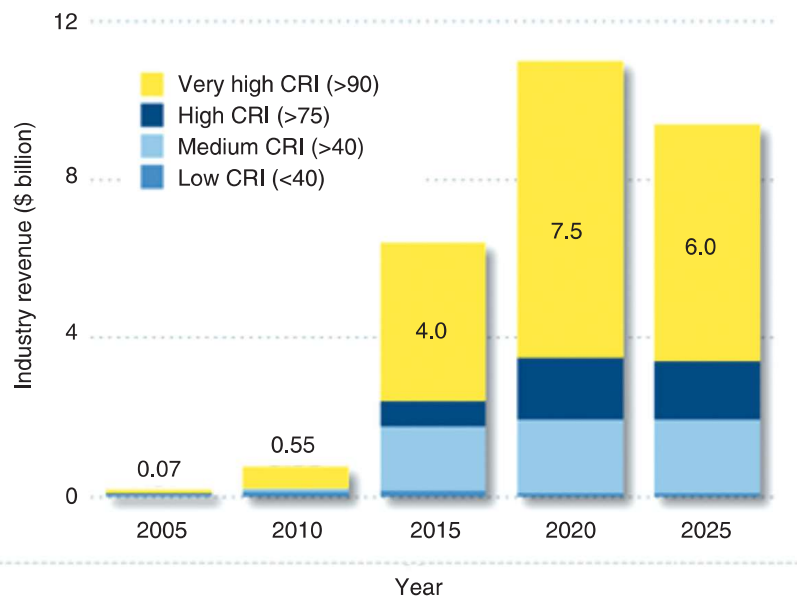


Plate V (Chapter 14) Industry revenue estimate from solid state lighting general illumination sale.

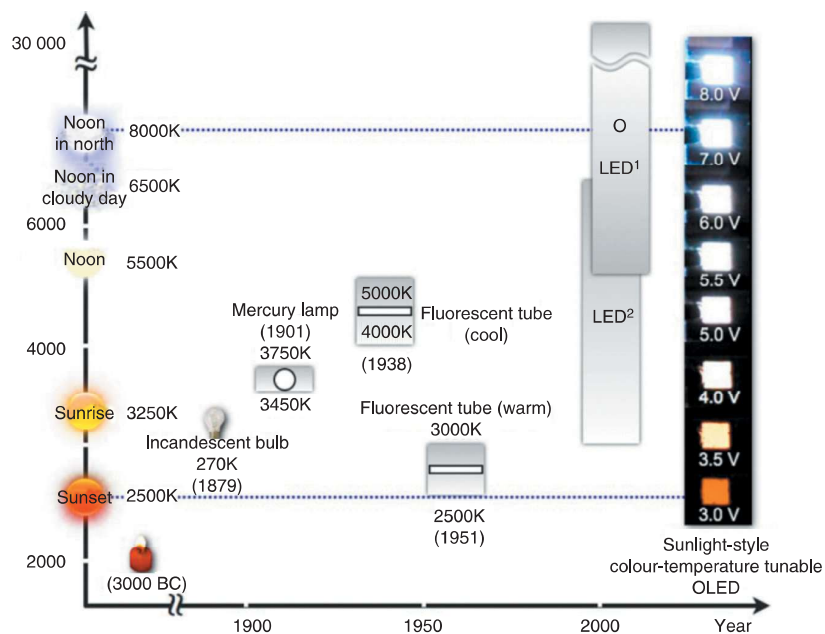


Plate VI (Chapter 14) Sunlight-style color-temperature tunable OLED with color-temperature span from 2300 to 9700K, compared against the color temperature and/or color-temperature span exhibited by candles, as well as typical electricity-driven lighting devices, including the point-type incandescent bulb, mercury lamp, and the latest LED, and line-type cool-white and warm-white fluorescent tubes. LED, using a multifaceted quantum wells microstructure design, shows a color-temperature ranging between 5000 and 20000K, and LED, using an arrayed LED clusters of multicolor combination, between 3000 and 6500 K.

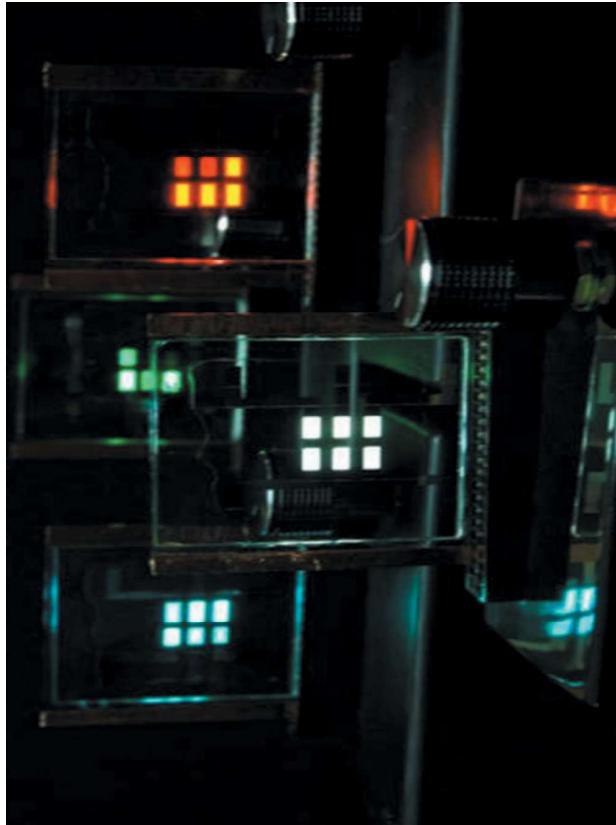


Plate VII (Chapter 14) RGB and white color emission of planar-type OLEDs.

Active matrix, organic light-emitting diodes (AMOLEDs) for displays

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Abstract: This chapter will focus on the creation of a business ecosystem around organic light-emitting diode (OLED) technology in displays. A history of flat panel ecosystem creation is also given in order to provide a proper framework for new emerging display technology and to enable the reader to see the challenges the new disruptive technology is facing in competition with mainstream technology. Lifetime issues have been a hot topic throughout the history of OLEDs. This parameter has been analysed in depth including the burn-in effect. The other main parameter is power consumption. OLED power consumption was at a disadvantage with LCD screens in the early days of development, but this is now turning to competitive advantage over LCDs. The potential for OLED TV is discussed as well as prospects for three-dimensional (3D) OLED TV.

Key words: disruptive innovations, business ecosystem, organic light-emitting device, lifetime, burn-in.

15.1 Introduction

The first organic light-emitting diode (OLED) devices were reported by Tang and co-workers from Kodak (Tang *et al.*, 1989) in the 1980s. Following this seminal work by the Kodak team, in 1990 light emission was also reported from large molecule polymer organic light emitting diode (PLED) devices (Burroughes *et al.*, 1990). Then in 1998 researchers at Princeton University and the University of Southern California were first to realize remarkably efficient OLEDs using a light-emission mechanism, today referred to as electrophosphorescence or phosphorescent OLEDs (PHOLEDs). The significance of this work was the first report of an OLED with 100% efficiency (Baldo *et al.*, 1998; O'Brien *et al.*, 1999). Building from the first report from the Kodak team to the high efficiency PHOLEDs from the Princeton/USC/UDC team, today OLED technology is challenging existing mainstream LCD technology in mobile phone displays and is poised to enter the TV market with excellent colours, thin structure and driving to lower and lower power consumption (Kim *et al.*, 2009). However, there have been challenges in scaling up the backplane technology and overall OLED display manufacturing processes, in addition to driving down cost for displays.

Clayton Christensen has defined a disruptive technology as one that either creates new markets or disrupts the existing markets with a lower cost solution.

OLED is in many ways fulfilling the definitions of a disruptive technology (Christensen, 1997, 2003), but not from a consumer's perspective. Existing mainstream LCD technology has improved image quality and response speed remarkably during the last 10 years and the difference in image quality between LCD and OLED has become rather small. However OLED has possibilities to simplify the production during the coming years and become a truly disruptive technology from a manufacturing perspective. Since the year 2000 the emerging OLED industry has focused on mobile display applications and there has been a lot of discussion about finding the so-called killer application for OLEDs, the application which is not possible with existing LCD technology. Today, the developing picture is one of approaching a new backplane technology for the thin-film-transistor (TFT) ecosystem, although one should not yet discount the killer application if OLEDs can realize some of the futuristic design concepts such as rollable or foldable or transparent display designs for these mainstream mobile products. Recently LGD demonstrated 55" OLED TV, which is able to show two different TV channels on the same screen. The viewers use special glasses to see their preferred content.

In 1970 Cathode Ray Tube (CRT)-based TVs and PC monitors were the mainstream technology. There had been LCD-based trials in the U.S. by RCA to develop LCD-based displays, but RCA had given up this development in 1974 and continued with its profitable CRT business. RCA sold the LCD license to the Japanese company, Sharp. In 1979 the disruptive innovations took place separately at Westinghouse in the U.S. and at Dundee University in Scotland. Researchers were able to demonstrate the light valve switching operation of liquid crystal cells by using a thin-film-transistor structure (TFT) on glass substrate to activate the switching phenomena. This combination enabled the flat screen development. Companies like Sharp, who had bought the LCD license from RCA to use the LCD technology in calculators and who did not need to protect their CRT business, saw the opportunity to move toward flat screen manufacturing. IBM needed displays for notebooks and PC monitors. Notebooks offered for this new TFT LCD technology a killer application, which could not be made with CRT. U.S.-based companies did not believe in LCDs, and without the TFT LCD innovation, passive matrix driven LCD alone was not useable for large screens. Here, robotics from the semiconductor industry concerning substrate handling was a key enabler. The companies in Japan had gained experience from passive matrix LCD small-scale manufacturing issues. The first TFT LCD flat panel line was opened in Japan in 1990 and that was the real kick-off for TFT LCD-based flat panel ecosystem creation. This ecosystem comprised companies working together for the same goal even though each company may have had its own different business. For example, robotics companies have semiconductor manufacturing companies and display companies, glass companies were needed to provide high quality glasses for TFT substrates, etc., so a strong systemic innovation process was adapted between Japanese companies (Maula *et al.*, 2006). All relevant documentation

was written in Japanese and translation into English took more than a year (Murtha *et al.*, 2001).

In the fourth quarter of 2007, TFT LCD televisions surpassed CRT-based TV units in worldwide sales (Gagnon, 2008). It had taken 28 years from the disruptive innovation of TFT LCD to an established mainstream position and 17 years since ramping up the first TFT LCD lines in Japan in 1990. Only a few CRT manufacturers were able to transfer their production to TFT LCD. All the U.S.-based companies such as RCA, Westinghouse and GE failed even though some of those companies had invested a lot of time and money into new display technology. Their shortcoming here was that they believed that LCD could never be suitable for TV, instead believing more in plasma technology. Europe totally missed the TFT LCD opportunity. Strong players like Thomson and Philips never invested in production lines of their own. Japanese and Korean companies survived better with the exception of Sony, who continued with their *Trinitron* production. Sony has been buying TFT LCD screens from different suppliers and has made numerous incremental innovations into driving mechanisms of TFT LCD screens, but Sony has not invested in their own TFT LCD lines.

All this has happened without any company or government orchestrating the systemic innovation process (Blomqvist and Armila, 2008). However, without the existence of an orchestrator, a healthy, well-functioning business LCD TFT ecosystem is in place, fulfilling consumers' needs. It seems to be that the common vision and foresight to one day have wall-hanging flat, lightweight TV screens has been enough to drive the systemic innovation actions needed to improve the overall performance of TFT-based LCD screens.

Around the year 2000 colour displays were introduced into mobile phones, first in Japan then followed by European and American markets. The technology was passive matrix LCD. The resolution of those displays was typically less than 130×130 . However the demand for higher resolutions started to grow due to more demanding applications in mobile phones and quarter VGA (240×320) resolution became the dominant design (Lääperi, 2003). This resolution was not achievable with passive matrix technology and therefore active matrix TFT LCD technology started to gain market share from passive matrix LCD displays. OLED displays were first introduced to markets in MP3 players and in car radios. When OLED displays were introduced to mobile phone markets those were used in front covers in fold concepts to indicate the incoming phone call or message. The technology was passive matrix driven, and resolutions were typically less than 100×100 , and those were monochromatic or area colour displays. OLED was competing with LCD with bright colours, wide viewing angle and without losing refresh speed in low temperatures. The prices of OLED-based displays were clearly higher than corresponding LCD prices, typically double. However, it was important for the emerging OLED industry to start the development of OLED manufacturing techniques by using passive matrix technology. The lifetime of passive matrix-driven OLED displays was too low to be used for the main display in mobile

phones and the use of passive matrix technology for full colour QVGA resolution displays was not feasible. Lifetime improvement and active matrix technology enabled OLED displays to emerge on mobile phones and smart phones in 2007. OLED has always been capable of providing bright colours and thin structure, but has suffered higher power consumption and much higher manufacturing costs even though there is great potential for getting manufacturing costs below corresponding active matrix LCD. Recent innovations in OLED emissive materials have reduced power consumption below backlight-driven LCD.

The killer application for active matrix TFT LCD displays was laptops. However, the killer application for OLED has not been found. That kind of killer application could be rollable or flexible displays for e-books or newspapers, but there are many technical challenges still on the road. OLED is therefore in competition with mainstream LCD technology (Moore, 2002).

15.2 OLED display business ecosystem creation

Taking a closer look at OLED related innovations, the basic innovations made by the Kodak team in the late 1980s were disruptive. However, the basic performance was very modest. The lifetime of these light-emitting devices was less than 100 hours and therefore no real applications could be identified. During the next 10 years the lifetime figures were improved, due to material development activities, to reach 5000 hours and the Japanese company Pioneer launched a car radio using a passive matrix-driven OLED display. OLED displays can be divided into two groups: Passive matrix OLED, which uses a simple matrix to operate pixel arrays; and Active matrix OLED (AMOLED), which requires TFTs to operate pixel arrays. Samsung SDI decided to start the PMOLED business first because it requires relatively small investment and the market entrance was less difficult. A partnership with NEC and creation of a joint venture called SNMD (Samsung NEC Mobile Display) for PMOLED manufacturing helped Samsung to enter the PMOLED market successfully. While expanding the PMOLED business, the AMOLED business team was spun off from the AMOLED R&D and began preparation of the AMOLED business in 2003. As far as IPR (Intellectual Property Rights) such as patents are concerned, the partnership with NEC in the PM business and generation of key IPR internally both in PMOLED and AMOLED made Samsung very competitive for establishing a business in OLED.

The steps taken in the OLED business ecosystem creation have some similarities with TFT LCD business ecosystem creation, but also show differences (Estrin, 2008; Iansiti and Levien, 2004). In both cases the mainstream ecosystem is felt to be gigantic compared to the emerging disruptive technology, and also in both cases the new disruptive technology is not coming from the low cost side of the application spectrum as defined by Christensen (Christensen, 1997, 2003). Both have been clearly more costly to produce (Lääperi and Torkkei, 2009a, b). TFT LCD TVs were clearly more expensive than CRT-based TVs, image quality was

lower, but the thinness and light weight was something consumers wanted. OLED technology will not have that kind of clear consumer benefit. Image quality is better than in LCD screens, thickness is reduced with no need for a backlight unit, the viewing angle is wide, dynamic range is wide and the response time far better than in TFT LCD screens. But these are, from a pure consumer's perspective, somewhat marginal features. However, all these features together may well become a good marketing tool. The new rising concern however, to reduce energy consumption as a result of worries over global warming, can be viewed as a critical competitive advantage for OLED TV during the coming years. Power consumption in small and medium displays may not have a direct impact on overall world energy efficiency, but energy efficiency is critical to these applications from the battery life perspective. Today's smart phones utilize active screens for hours per day. In pure mobile phone applications the display power consumption has only marginal effect. Typical use cases for smart phones are web browsing and even watching TV. At the same time consumers have wanted bigger screen sizes and more brightness from screens. All these have a tendency to increase power consumption. The difficult application for OLED screens has been web browsing, due to the large amounts of white background. Typical white ratios are between 70–80%. This was limiting the willingness of terminal makers to use OLED displays in smart phones, but recent improvements in power consumption have turned the situation upside down. Now AMOLED is more battery friendly than TFT LCD. On the other hand, TV and video application have been very favourable to OLED screens. The white ratio in TV and video applications is typically between 30% and 40%. In LCD screens the backlight is on all the time, and therefore the power consumption has been independent from content. It is clearly seen that improvement steps in OLED power consumption catalysed LCD panel makers to start to emulate OLED behaviour. The algorithms taking the content into account in LCD display drivers have been implemented. The idea is that with dark content the backlight can be reduced without reducing the image quality too much.

From one perspective, a difference OLED is facing compared to TFT LCD is the so-called killer product application. In the TFT LCD case it was laptops and notebooks, but CRT was not relevant for those applications. OLED can do everything TFT LCD achieves except to work in reflective, low power mode. In outdoor conditions OLED needs to use maximum brightness to compete with ambient light. But it has been difficult to find the application where LCD is not the relevant choice and OLEDs are. For this reason OLED is all the time in face-to-face competition with LCD in a 'parameter race'. The competitive positions have changed since the year 2000 when OLED was able to provide excellent image quality compared to the washed colours in LCD screens. But OLED was very power hungry and its lifetime was very limited as well. Today, LCD images are close to OLED image quality, but now OLED screens in many applications are consuming less power than LCD. Lifetime is no longer the limiting factor in small

and medium size OLED screens and their applications. Porter discusses this kind of competition among industry competitors in his book *Competitive Strategy* (Porter, 1980).

Samsung SDI, a panel maker and production line owner, has been in a key position in the OLED commercialization process. SDI had experience from the PMOLED manufacturing process and used the same evaporation process. The missing part was the backplane process. SDI had concentrated on providing passive matrix LCD displays, not TFT LCD panels. However, the TFT process suitable for LCD displays is not the same for OLED backplanes. OLED needs a more complex transistor structure for current drive instead of voltage drive as is used with LCD. Therefore SDI had to build a backplane line parallel to their OLED line and ramp up both. The discussions with Nokia and other potential customers set the required lifetime specifications and brightness requirements. SDI had several OLED material suppliers. Everyone had somewhat different material properties and lifetimes. SDI had to select a suitable material supplier for each colour and plan the size of an emissive area so that current densities were low enough to obtain the requested lifetime for the whole panel. It can be well stated that SDI was the orchestrator for the first commercial AMOLED panel development and manufacturing activities. The first generation model used fluorescent green and blue materials and UDC red phosphorescent materials to meet the lifetime requirements. UDC and Nokia met in conferences and exhibitions and noticed the great potential for power consumption reduction. Three party discussions between UDC, SDI and Nokia got a positive response from all members. The results from their discussions were the commonly understood drivers at the markets and a commonly agreed power consumption roadmap. Each company took that understanding into their organisations to better improve their contributions.

15.3 Lifetime and burn-in effect

The question concerning sufficient lifetime was asked frequently to all companies intending to use OLED displays. The lifetime is defined to be the time when the luminance has dropped to 50% of the initial luminance, $T(50)$. OLED material developers use acceleration methods in defining this lifetime. The acceleration will take place, when brightness of a pixel is increased. This means roughly that 50 000 hours lifetime ($T(50)$) will be obtained in 500 hours (21 days) by using ten times higher brightness than the planned maximum brightness.

Display makers had experience from LCD displays and the backlight units used behind the LCD panel. It has been the trend in Europe for mobile phone users to keep their mobile phone on all the time. As a result, the lifetime requirement of 30 000 hours was set by mobile phone terminal makers. This seemed an unobtainable figure among OLED developers in the early 2000s. It was realized by terminal makers that there were many ways to deal with lower lifetime figures,

but there was another difficult obstacle common to OLED and in general emissive displays, namely the so-called ‘image sticking’ or ‘burn-in’ effect. There was no data available to specify the requirements for OLED display from the terminal maker’s perspective. In order to find a reliable way to deal with this phenomenon, Nokia developed an excel based simulation program, which used different images to simulate typical daily usage. The daily usage pattern was then repeated to correspond to the desired number of years and the results were reviewed on suitable test images. The burn-in effect became visible sooner or later depending which were the lifetime figures of each colour, red, green and blue. This simulator was published in the SID conference 2007 (Lääperi *et al.*, 2007). The simulator gave at least one tangible way to define the sufficient lifetime. Nokia also conducted a user study in order to understand the consumer’s acceptance criteria concerning the burn-in effect. The results were published in the same SID conference and are shown in Table 15.1.

The simulator revealed that the lifetime itself was not the critical value. More critical was to deal with the burn-in sensitivity. Nokia increased the lifetime requirements from 30 000 hours to 50 000 hours based on the simulator results for mobile phone and smart phone applications and added dimming algorithms into the terminal software to handle the burn-in sensitivity. Dimming was used with LCD displays as well to decrease energy consumption. It should be noted that lifetime requirements and burn-in sensitivity are application specific. TV applications with sub-title texts and broadcasters’ logos may influence the necessary lifetime figures for OLED TV (Lääperi, 2009).

All emissive display technologies can suffer from image burn-in phenomenon. It was a hot topic during the early years of plasma displays and it was also an issue with LCD displays in the beginning. Stationary images or text with high contrast can cause the image to be slightly visible on the screen, even one image changing to another. Therefore it is also known as ‘image sticking’. The human eye is not very sensitive to absolute brightness changes, but is very sensitive to relative

Table 15.1 Results of the burn-in perception test

Luminance drop of worst pixels compared to best pixels	Description of burn-in effect
4%	Might be perceptible in some use cases, but not in general.
8%	Perceptible, but not annoying. Not likely to affect the perceived quality in typical use cases.
13%	Slightly annoying. Decreases the perceived display quality to some degree.
20%	Annoying. Easily seen in most use cases and likely to decrease the perceived display quality noticeably.

Source: Lääperi *et al.*, 2007.

differences between pixels. User tests have shown that test persons were able to detect a 4–5% relative brightness difference in burn-in effects (Lääperi *et al.*, 2007). This necessitated the introduction of T(95), the time elapsed when initial luminance has dropped by 5%. On the other hand absolute brightness can drop by 50% and it may be hard to detect without a reference display. This burn-in effect turned out to be an even more severe challenge for OLED display than lifetime itself. In mobile and smart phone applications OLED material developers have had to compromise to increase T(95) lifetime even though it would decrease T(50) lifetime. Terminal suppliers wanted to use OLED displays to utilise the bright colours and small thickness needed to study this burn-in effect in their own applications. Different applications are more or less sensitive to the burn-in effect. If the application is to show continuous live video on screen, burn-in effect will not occur. If the application is stationary menu items on screen for 24 hours per day, the menu items will burn into the screen within a matter of months. Therefore it is important to analyse each application. From burn-in perspective a black or white background did not influence burn-in sensitivity. What matters is the contrast between background and the object.

One effective way to avoid the burn-in effect in mobile applications is to reduce the brightness of the display after several minutes of non-user activity. By reducing the brightness by 50% the lifetime and T(95) both increase by 100%. By reducing the brightness to one tenth of maximum, the lifetime will increase by a factor of 100.

The lifetime history of OLED panels using different OLED materials is shown in Table 15.2. It can be seen that the required 50 000 hour lifetime figures in red and green were obtained in 2006. This table is an excellent example of the disruptive and systemic nature of OLED material development (Maula *et al.*, 2006). During the first half of the 2000s, the levels of lifetimes of OLED materials were below the useable level for mobile phone displays, and mainstream customers were not interested in OLED. As shown in Table 15.2, it was not until 2007 that when the blue lifetime exceeded the 30 000 hour level and approached the requested 50 000 hour level.

Table 15.2 Improvements of lifetimes (T(50) hours) of different colours in OLED panel

	2000	2001	2002	2003	2004	2005	2006	2007
FL Red	4000	6000	10 000	20 000	30 000	60 000	80 000	100 000
FL Green	3000	5000	7000	10 000	20 000	30 000	70 000	130 000
FL Blue	2000	5000	7000	10 000	20 000	22 000	25 000	40 000
PH Red		3000	8000	18 000	30 000	60 000	85 000	95 000
PH Green		3000	7000	11 000	22 000	25 000	40 000	60 000

Source: Samsung SMD.

Table 15.3 Improvements of lifetimes (T(50) hours) of phosphorescent OEL material (PHOLED)

	2005	2006	2007	2008	2009
PH Red	20 000	80 000	320 000	500 000	500 000
PH Green	40 000	100 000	250 000	250 000	500 000
PH Blue		3000	9000	13 000	15 000

Source: UDC.

When Samsung SDI launched their first AMOLED mobile display panels in 2006, the lifetime for red phosphorescent OLED (PHOLED) technology had reached commercial levels. Samsung SDI was therefore able to take advantage of the high efficiency of red PHOLED from the start to design and manufacture low power AMOLED panels. The next step has been to achieve commercial lifetime values for green PHOLED materials to further drive power down and development is ongoing to achieve blue PHOLED materials with long lifetime to complete the high energy efficiency materials set. A progression of the advancements in the lower power PHOLED technology is shown in Table 15.3.

Red PHOLED lifetime exceeded commercial requirements in 2008 so no additional increase was required for 2009. In the case of Green PHOLED lifetime a significant increase was obtained in 2009 to meet entry commercial requirements and continued research is being applied to blue to drive the lifetime to higher levels.

The lifetime figures for red and green phosphorescence in 2007 are displayed in Tables 15.2 and 15.3. Table 15.2 is for the whole OLED panel, while Table 15.3 is for the OLED pixel. There are several reasons for this difference, such as OLED stack design, process conditions and timing. It takes time to get new materials through the production process in the panel maker's production line. It is also crucial for terminal makers to understand the lifetime improvement steps and the power consumption reduction potential when developing new product concepts.

As mentioned earlier, OLED was invented by the Kodak team in the late 1980s. Since then Kodak has invested considerably into OLED materials and cell design. Kodak has the biggest number of OLED related patents. Kodak made a joint venture with Sanyo in the early 2000s, and they produced a digital still camera with the first commercial AMOLED display in 2003. The display got a relatively good reception from markets, but the yield problem in display production limited the volume rollout. Later Kodak and Sanyo dismantled the joint venture. Kodak was active in OLED material issues, and published conference papers. However, the business potential Kodak had been planning for was not realized in the timeframes Kodak had planned. Kodak made an exit from the OLED business in December 2009 after 20 years of investment. It is often expressed in the literature that the earliest pioneers are not the ones who become the leaders in mainstream markets.

Commercial OLED history started with passive matrix OLED displays. In 1997 Pioneer introduced a car radio/CD-player utilizing PMOLED display technology. Based on a DisplaySearch study (DisplaySearch, 2006), at the end of 2006 there were 29 OLED lines installed in 15 companies. A Low Temperature Poly Silicon (LTPS) process is needed in AMOLED displays to deal with an increased demand for electron mobility. The mother glass size in Samsung SDI was 730mm × 920mm, the largest among the reported lines. Motorola was the first company to use PMOLED displays in a mobile phone in 2000, but the phone was withdrawn from markets after a short time. The reasons for poor market withdrawal were: very bright, but power hungry, high contrast except in sunlight, thin package, but short lifetime, robust, but costly. AMOLED technology was not yet suitable for mobile phones. It took seven more years before Nokia, the market leader at that time, produced a mobile phone using AMOLED technology for the main display.

15.4 Power consumption

As mentioned, power consumption will be the key parameter in looking at the competitive advantages for OLED. Phosphorescent blue is still in the development process and is estimated to become available in a few years.

The basic difference in OLED compared to LCD is the way light is produced. OLED is an emissive device, and after activation it will radiate light. The colour of the light is dependent on the OLED material. LCD is a passive light valve. Light is generated in the backlight unit and is kept on as long as the user wants to look at the image. Light penetrates through the LCD stack through two polarizers and colour filters to the eyes of a user. More than 90% of light intensity is lost in an LCD stack and in colour filters. This fundamental difference gives OLED the opportunity to have a competitive advantage. Viewing web pages is the most demanding use from an OLED power consumption perspective due to a great amount of typically white background in images. TV and video application are much more OLED friendly, reducing power consumption to half or even less.

For mobile phones, power consumption of a screen does not have the same importance as in the smart phone category because the display will be dimmed during phone calls, and the display is active only during messaging or similar activities. The mobile phone category is also very price sensitive, and OLED penetration into that segment is dependent on OLED cost structure compared to LCD. This is a crucial point for OLED in the competition from mainstream technology. It may well happen that LCD will dominate mobile phone markets for a long time due to a well functioning, cost effective ecosystem. However, the OLED stack is clearly simpler, and may therefore around 2020 be able to become a more cost effective solution to produce low cost displays for small and medium display markets.

OLED development started with fluorescent materials. The lifetime figures improved rapidly during the 2000s, but the target for useful lifetime figures was high. We can clearly see that the OLED ecosystem had to first solve the lifetime challenge before the sales figures had any opportunity to grow. This was the 'basic requirement to compete' and this step was done mainly with fluorescent materials. The other key topic through the OLED history has been power consumption, and the next challenging target was to reduce the power consumption to the competitive level. However power consumption has not been so critical as lifetime. Lifetime has been a kind of showstopper, but due to the fact that in OLED displays power consumption is content dependent it has already been competitive in video application for years. Power consumption has moved during the OLED history from being disadvantaged to having competitive advantage compared to TFT LCDs.

15.5 OLED television

With OLED technology capable of producing displays with excellent colours, a wide viewing angle, fast response times and 'green' from an energy consumption perspective, it is more than obvious that the dream of every member of the OLED ecosystem is to enter into TV markets. The foresight is clear. However, there have been scaling challenges the ecosystem has had to solve. The challenge to realize large size TV such as 40" and above is to scale up the mother glass size similar to that used in TFT LCD production in order to reduce the manufacturing cost. The first AMOLED lines were using Generation 4 class (730mm × 920mm) and scaling up to Generation 8 (2200mm × 2500mm) required technological breakthroughs in both TFT backplane technology and OLED RGB colour patterning. These challenges are mainly solved, and LGD and Samsung are currently investing into Generation 8.5 lines. Typical mother glass generations are shown in Table 15.4.

OLED TV is undergoing intensive development and Samsung and LGD have been demonstrating 55" OLED TV in several exhibitions. LGD has announced

Table 15.4 Typical sizes of mother glasses of generations and the year when the corresponding TFT production line was first taken to production

	Gen 1	Gen 2	Gen 3	Gen 4	Gen 5	Gen 6	Gen 7	Gen 8	Gen 10
1st lines	1991	1994	1995	2000	2002	2003	2005	2006	2009
X (mm)	320	370	550	730	1100	1500	1870	2200	2880
Y (mm)	400	470	650	920	1300	1800	2200	2500	3130
Area (m ²)	0.13	0.17	0.36	0.67	1.43	2.7	4.11	5.5	9.0

Sources: DisplaySearch, Sharp, Corning, Samsung.

that it will start delivering 55" OLED TV during the first quarter of 2013. Scalability of backplane processes and improvements in OLED material utilization are the challenges which have been solved through systemic innovations. Today people are concerned about global warming, and households are looking more closely at how each of us could save energy. TV as such is a good object to focus attention on. PHOLED technology will be key here, as discussed above for mobile applications, to enable the most energy efficient OLED TV. The exhibited 40" OLED demo TV from Samsung, which was not optimized for low power, consumed around 40 W. OLED TV power consumption is expected to drop to half by the time those over 40" size OLED TV screens are commercially available. The estimated difference in power consumption figures between OLED and LCD is very wide. Estimations from Samsung SMD and UDC indicate power consumption of 20 W for a 40" FullHD OLED screen with typical TV content available in coming years, while at the same time TFT-LCD power consumption is estimated to be around 60 W with the same perceived brightness (OLED 400 nits, LCD 600 nits).

The way to apply OLED patterning on LTPS substrates has been to use evaporation techniques in a vacuum. This wastes a lot of expensive OLED material. A much more effective way is to print polymer type OLED materials onto the substrate. Companies like CDT have been working for a long time to make this happen (Patterson 2009). The challenges with polymer type OLED materials have been somewhat shorter lifetime figures compared to small molecule OLED material, which is used in evaporation chambers. The other challenge has been the uniformity of the printed OLED material. In big TV screens this is an important element. OLED material is today very expensive compared to liquid crystal material mainly due to the huge difference in the volumes produced. On the other hand, OLED displays will need only 1% emissive OLED material compared to the need of liquid crystal material in the same size LCD display. With the increased volumes the OLED material costs are coming down by orders of magnitudes.

The hot topic in the TV and entertainment industry is to move to three-dimensional (3D) TV. LCD panel makers have been improving the speed of LCD panels to enable the 3D experience. OLED TV does not have the same challenge, because OLED panel response time is some microseconds while LCD screen response is some milliseconds, three orders of magnitude difference. This short response time has been utilized by LGD by presenting two different TV channels on the same 55" OLED TV screen. The users are able to follow their favourite program by using glasses similar to 3D programs.

15.6 Conclusion and future trends

In the literature the business ecosystems have mainly been created under a strong orchestrating company like Microsoft, Cisco or Google. However, TFT LCD and OLED business ecosystem creation has happened without any company being

in such a position to orchestrate the ecosystem creation. As was mentioned earlier, in the mid 2000s there were 15 companies with established OLED lines, and in addition to that numerous companies developing OLED material, glass-based TFT substrates, evaporation equipment, etc. However, we have seen that Samsung SDI had the leading role in the OLED commercialization process, first PMOLED and then investing in AMOLED and LTPS lines. Nokia had a role in clarifying the lifetime requirements and power consumption targets and was willing to test OLED displays in mobile phone markets. UDC had a key role in power consumption reduction efforts during the second half of the 2000s. It should be noted that Samsung SDI was not the first company to make commercial panels. Pioneer was the first to introduce PMOLED-based products and Kodak and Sanyo were the first to have commercial products using AMOLED. It is pointed out by many articles and books that the first company to produce new disruptive technology is not necessarily the one who will be the winner in the mainstream phase. This also seems to be the case with OLED although we have not yet seen the mainstream phase in OLED business. The TFT LCD ecosystem is clearly the mainstream display technology, but was created without any orchestrator. In the TFT LCD case the common vision and foresight for lightweight, wall-hanging TV-seemed to be enough to drive companies to better and better systemic innovations. In the OLED business ecosystem, this foresight is not so strong. LCD TVs with LED backlight are thin and light enough to put on a wall. Now 'green' values are important to many consumers and efforts to save energy are regarded as important.

The competitive advantages and challenges of OLED technology have changed dramatically during the 2000s. The lifetime figures during the first half of the 2000s were a limiting factor for displays in mobile phones. As has been discussed, the lifetime figures improved significantly through systemic innovations and were at the usable level around 2006. The original competitive advantages concerning the image quality have not disappeared, but due to great improvements in TFT LCD displays the difference may be hard to notice. The discrepancy in panel thickness has similarly reduced. A new emerging competitive advantage is rising in the form of power consumption. Even though the so-called killer application has not been found for OLED technology, there are good candidates for that in the future. Flexible or even rollable OLED based displays have been demonstrated but there are still some years before the commercial phase for these is in place.

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15.8 References

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The technology and manufacturing of polymer OLED on complementary metal oxide semiconductor (CMOS) microdisplays

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Abstract: The integration of organic light-emitting diodes (OLED) with state-of-the-art complementary metal oxide semiconductor (CMOS) drive electronics can yield a high-resolution full colour information display technology with superior viewing performance. Its application in consumer electronics is limited only by the desire of technology users to view information ‘near-to-eye’ with a magnifying lens. Unfortunately such a limitation is significant and the future prospect of OLED microdisplays looks confined to specialist applications. In this article the technical constraints of integrating two very different technology platforms, OLED and CMOS, are discussed. The experience of an eight year technology development programme, from technology concept to high volume manufacturing, is explored with specific issues relating to technology integration and manufacturing being discussed.

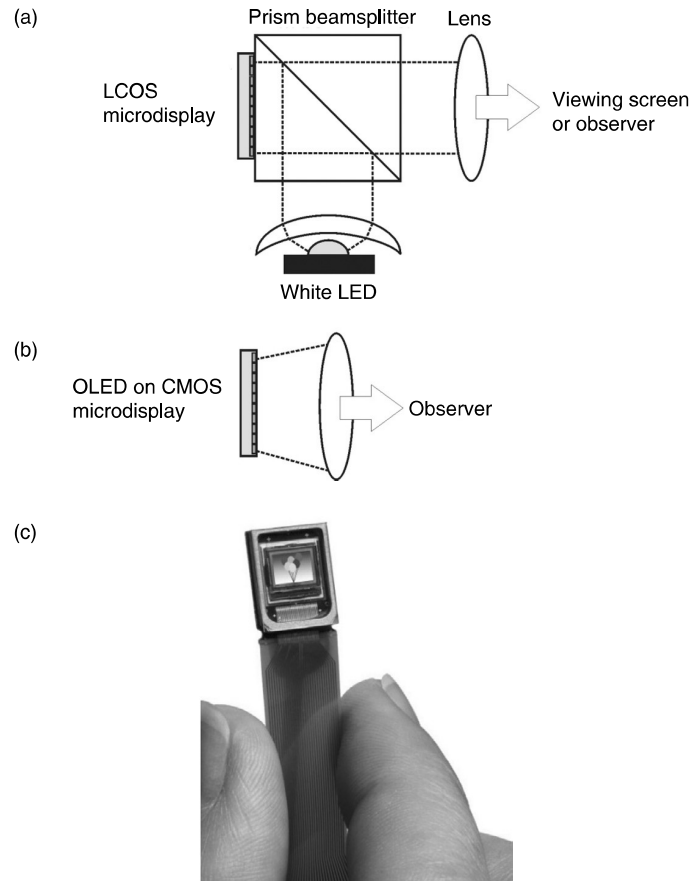
Key words: microdisplay, polymer organic light emitting diode, active matrix display, P-OLED, conjugated polymer.

16.1 Introduction

Microdisplays are a class of information display that are both physically small and of high image resolution. They typically require magnification to generate a useful image, in the far field in the case of projectors, or in a virtual field in the case of near-to-eye viewers. This chapter discusses the specific issues in developing and manufacturing a microdisplay product using polymer light-emitting materials and complementary metal oxide semiconductor microelectronics. Before embarking on a discussion on this technology and its manufacture a departure is made to summarize firstly the differences between the closest competing technology for organic light-emitting diode (OLED) microdisplays, LCOS, and secondly the history and status of OLED and specifically polymer OLED microdisplays. (see Fig. 16.1)

16.1.1 Liquid crystal on silicon microdisplays (LCOS) versus OLED on silicon microdisplays

The utilization of CMOS based very large scale integration (VLSI) electronics design and processing, for creating high resolution information displays, has its



16.1 (a) Typical LCOS display engine and (b) OLED on CMOS display engine illustrating the higher level of system complexity for the LCOS solution. (c) Photograph of Microemissive Displays ME3204 OLED on CMOS display viewed directly, without a magnifying lens.

origin with liquid crystal on silicon displays (LCOS) dating from the early 1990s. An excellent review of LCOS is given by Armitage, Underwood and Wu (2006). In LCOS an array of pixel electrodes control the molecular alignment of an overlaying liquid crystal layer via an applied bias voltage, such that the liquid crystal layer acts as an optical switch to polarized light. The top layer of the CMOS circuitry provides both a highly reflective layer from which incoming light to the display can be returned to the viewer, and an electrode whose voltage can be controlled. The liquid crystal is confined between the CMOS substrate and a transparent indium tin oxide counter electrode, pre-deposited on a glass substrate.

The post-processing of the CMOS with the liquid crystal layer and confining ITO electrode is done at wafer level before single display die are singulated and packaged along with a source of light and a viewing optic. Notably, to create a full colour display, red, green and blue images (with differently coloured and time-pulsed emissive light sources) are required to be time-integrated by the observer. The electronics required to control the timing of the light source and the display is typically provided by a second processor, adding complexity and cost to the display. LCOS microdisplays find application both in data projectors and in near-to-eye displays for digital cameras and personal viewers. It is in this second market that OLED on silicon can compete with LCOS for market share.

OLED based microdisplays offer some significant advantages over LCOS in terms of the near-to-eye market required for personal viewers and digital cameras. Since OLEDs are light-emissive there is no requirement for additional light sources or timing electronics. The simplicity of the OLED on CMOS solution when compared to LCOS leads in turn to a potentially lower power and lower cost solution. The viewing quality of OLED is excellent due to high contrast and high fill-factor of the emissive pixels. For personal viewers and electronic viewfinders where the display image is viewed using a magnifying lens it is important for the display pixels to appear continuous, without space between them, and it is also important to have high refresh rates.

16.1.2 History of the OLED on CMOS microdisplay

In the early 1990s AT&T Bell Labs made a series of reports describing the use of polymer OLEDs integrated on silicon substrates containing bipolar active circuits and photoreceivers. The application was photonic switching and optical interconnect rather than displays and is reviewed by Kim *et al.* (1994). In the late 1990s IBM developed a series of technology demonstrators including a fixed pattern monochrome green display of XGA resolution with 4 μm pixel pitch in 1998, a VGA (640 by 3 by 480) colour display with a 15 μm pixel pitch (3 stripes of 15 $\mu\text{m} \times 5 \mu\text{m}$) in 1999 and a VGA monochrome display (Levy *et al.*, 2002) with a 34.3 μm pixel pitch. Further integration of organic light-emitting diodes with CMOS electronic drivers, an 8 by 8 array of 90 μm organic light-emitting pixels, was demonstrated at the Optical Sciences Center at the University of Arizona as reported in 1999 (Mathine *et al.*, 1999). In recent years eMagin Corporation (formerly FEC Corporation) of Holmdel, New Jersey, has emerged as the primary commercial exploiter of molecular OLED on CMOS. The SVGA+ microdisplay by eMagin Corporation (see www.emagin.com) uses molecular OLED materials to produce a low-voltage, high-brightness, high-resolution solution for professional, military and other demanding applications. Lin *et al.*, (2002) briefly describe the CMOS backplane whilst Levy *et al.* (2002) describe some aspects of both the electronics and the optics of the device in more detail. More recently, in 2011, Sony released a molecular OLED microdisplay viewfinder for digital cameras.

16.1.3 Polymer OLED microdisplays

In contrast to the developments thus far described which have all utilized evaporated molecular materials as a basis for organic light emission, Heinrich *et al.* (1997) reported on the compatibility of solution-processed polymer OLED with CMOS. They used p-type Silicon as a hole-injecting lower-electrode and a very thin sputtered aluminium layer as the cathode. Light emission occurred upwards through the semi-transparent aluminium. The use of p-type silicon as the lower electrode is in contrast to the microdisplay described in this chapter which uses the top-level metal of the CMOS as the lower electrode. In a CMOS active matrix backplane, the Heinrich approach would require the OLED to sit side-by-side with the circuit and interconnect layers of the CMOS thus reducing the proportion of the pixel area available to emit light (rather like a conventional down-emitting active matrix OLED display) and would involve significant light leakage into the substrate with the accompanying circuit performance reduction and/or disruption (CMOS circuitry is extremely sensitive to light and great care is taken in optoelectronic CMOS devices like LCOS to eliminate any light leakage downward into the active circuitry through the incorporation of specially designed metallic light blocking layers). The OLED microdisplay devices in this chapter achieve emission from a very large proportion of the pixel area (between 70% and 80%) by placing the reflective electrode above the pixel circuit. In this case the lateral inter-electrode gap is minimal and determined by the critical metal-to-metal spacing as defined by the VLSI CMOS design rules.

The most prominent player in polymer OLED microdisplays over the last 10 years has been MicroEmissive Displays Ltd (referred to throughout the text as 'MED'). MED was a licensee of Cambridge Display Technology (CDT), an arrangement that allowed MED to make use of CDT's intellectual property in polymer-based light-emitting diodes in the microdisplay market. Having ceased to trade in 2008, it is MED's experiences of developing and producing polymer OLED microdisplays at high volume that this chapter focuses on. Overall we seek to emphasize, from the OLED point of view, the challenges of integrating polymer-OLED and CMOS technologies, providing normally unreported insights into the design and manufacturing of this novel technology.

16.1.4 The requirements of an OLED microdisplay

Before embarking on a description of the specific display technology developed by MicroEmissive Displays it is informative to provide a brief explanation of the most important factors that comprise the specification of a microdisplay, since it is these specifications against which the success of the technology is measured.

Resolution defines the total pixel count of a display and progress in information displays has been characterized by a drive to higher and higher resolutions. By definition such progress leads to more complicated design, since greater and

greater numbers of pixels must be written to each frame, and lower manufacturing yield since there are more circuit components to fail. For the consumer near-to-eye viewer markets targeted by MED, a minimum requirement of QVGA resolution was required (QVGA having $320 \times 240 \times 3$ sub-pixels) and MED's ME3204 product was designed and manufactured at this resolution, with a low target selling price of around \$10 (in 2007). VGA ($640 \times 480 \times 3$) is a more common resolution for personal viewers and no doubt future technology will be required to operate at SVGA ($800 \times 600 \times 3$) resolution and above.

The power consumption of a display designed to be used in portable battery operated devices is critical. For example, using a microdisplay as an electronic viewfinder in a digital camera instead of the higher power back-panel LCD display offers one way to extend battery operating life. For reasons already introduced, OLED microdisplays offer some of the lowest power microdisplay products because of system simplicity. In turn only a small fraction of power consumption in such an OLED microdisplay originates in the OLED materials themselves. MED's product ME3204, under typical video operation consumed around 20 W, of which less than 10% was OLED power.

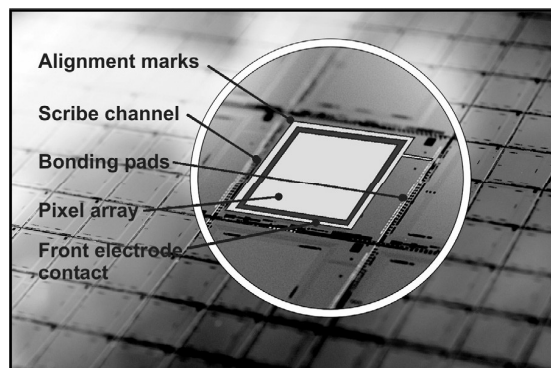
The colour tones and brightness of a display are two of the most important factors in assessing viewing quality. Both the white point, which defines skin tones and other colours that control the perception of 'lifelike' images, and colour saturation, that controls the vividness of images, are important to the viewer. Brightness is slightly less important for a microdisplay where the viewer is immersed in the viewfinder and external light sources are blocked. In this scenario luminance levels around 100 cd/m^2 are desired but levels as low as 30 cd/m^2 can be tolerated. Such a large range of tolerable luminance has significant impact on the degradation specifications of the OLED device. However, as we shall see, overall luminance degradation is far less important than both permanent and temporary differential ageing. For applications where the viewer is not enclosed and light penetrates from outside, luminance must be higher, and for see-through applications significantly higher at around 1000 cd/m^2 . Colour is specified and measured by the CIE 1931 standard. Luminance is an absolute measure of light energy leaving a surface, corrected by a function that describes the eye's natural spectral sensitivity to light.

Other factors that control viewing quality, and are especially important to OLED microdisplay technology, are the presence of defects. These typically manifest as non-emissive black spots (see Fig. 16.23) and other sources of non-uniformity that can either be smoothly varying across the display, have discrete boundaries in the display (see Fig. 16.5), or random luminance variation from pixel to pixel. For discrete zones in the image a threshold of between 2% and 5% uniformity is required. For local pixel to pixel variation a slightly higher threshold of 10% is acceptable. However, there can be no black spots or non-emissive zones in the display at all. Other artifacts that are characteristic of an OLED microdisplay are the presence of shadow images due to differential ageing of pixels that have

more overall usage. These ‘image retention’ artifacts can occur on a smoothly varying global level as in the typical presence of bright sky at the top of a digital camera image, or as discrete lines or blocks as in the presence of operating icons of the camera. The issue of image retention is discussed more fully in Section 16.3.1.

16.2 Device architecture for polymer OLED microdisplays

CMOS microelectronic devices are constructed using a series of layers of insulating or conducting material deposited sequentially on top of an n-type or p-type doped single crystal silicon substrate. Each layer (doped silicon, insulator and conductor) is patterned photo-lithographically such that its properties are modified laterally across the substrate. The combination of patterned doped silicon along with dielectric separation from conducting tracking can be used to form circuit components such as transistors and capacitors. Metal layers are used to connect the circuit components topologically such that complex electronic systems can be configured. It is the remarkable levels of integration of these circuit components that lead to the possibility of, among many other technologies, the high resolution microdisplay. In an OLED microdisplay each individual pixel may contain as many as 30 transistors to control the storage and release of charge to be converted to visible light by the OLED device layers. Different microelectronic component configurations, using different design rules, architectures and process nodes, can lead to different methods of driving the OLED device. It is outside the scope of this article to discuss these in detail. The book by Armitage *et al.* (2006) gives more detail on CMOS design for microdisplays and the article by Levy *et al.* (2002) illustrates one possible CMOS design. To summarise the options, the OLED is best driven by a certain current density in order to achieve a certain luminance. The current can either be supplied in a continuous analog form, or a more easily implemented pulse-coded digital form, where a particular time-integrated current for a particular luminance is constructed from a series of current pulses of different lengths; the pulse lengths being defined through combinations of digital bits of pulse. More advanced schemes contemplate the use of pixel-level control and feedback using integrated light-sensing elements in the CMOS circuitry. The drive current of each individual pixel could be adjusted to account for degradation of the OLED materials. While such schemes are relatively easily implemented on a global display level for global luminance degradation through extended usage by having a control OLED and control photodiode to the side of the main array, such a solution does not address the issues of short term differential degradation leading to image retention artifacts. To implement a pixel level feedback such that within each frame the luminance of each pixel is sampled and the drive current adjusted is a much more difficult proposition (Papadopoulos, 2009). However, the high levels of circuit integration possible with CMOS design and processing make this a possible avenue of future development.



16.2 An annotated photograph of the surface of a wafer of MicroEmissive ME3204 display die illustrating key components (from top to bottom of the list): the alignment marks in each die are used to align subsequent lithographic layers to each other and also used to align colour filters adhered in place over each pixel array; a scribe channel that isolates each display die and allows a space where the die can be sawn apart; bonding pads that allow connection of the display die to external circuitry; pixel array of Al metal electrodes; front electrode contact that provides an electrical connection from the top electrode of the OLED device to the display die backplane. Each 200 mm diameter wafer contains 667 display die.

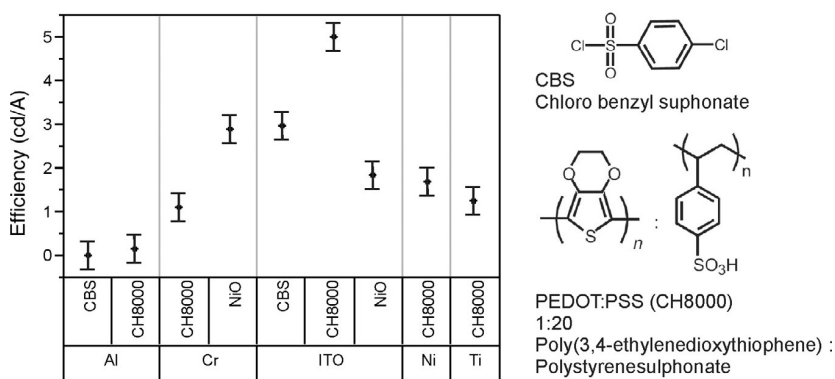
Historically, the layering of dielectric and conducting layers in CMOS led to a very bumpy top surface that would be of little use for integration with either LCOS or OLED device layers, since both technologies work with very thin uniform films of active organic material. It was the development of sophisticated planarisation techniques, described by Seunarine *et al.* (1999) amongst others, in response to the LCOS opportunity as developed in the 1990s, that resulted in the possibility of constructing a smooth planar electrode as a top layer of CMOS. For LCOS this top layer consisted of planar aluminium pixel electrodes between which sporadic micron high spacing pillars are fabricated. The pillars are used to maintain constant separation between the electrode surface and the ITO coated glass counter electrode such that the electric field required to control a certain degree of molecular switching of the liquid crystal molecule could be maintained.

For OLED device integration, on the other hand, the top layer is desired to be extremely flat both on a local length scale, but also across the whole semiconductor wafer. Surface topography introduced in regions between the pixel array and where large deep metal connection pads are present is particularly difficult to remove and if present can result in substantial local variation in the thickness of active organic layers deposited using spin coating. Particular care has to be taken in introducing metal 'pattern fill' to ensure local and global planarity. Once planarity has been achieved in this way attention can be turned to the electronic

function of the pixel electrode. In standard LCOS processing the metal used is high reflectivity, high purity Al and it is from this starting point that we embark on a discussion of the integration of CMOS and OLED (see Fig. 16.2 for an illustration of the physical layout of the top layer CMOS required for OLED integration).

16.2.1 PEDOT:PSS as a hole injection layer

Polyethylene di-oxythiophene doped polystyrene sulphonate (see Fig. 16.3 for structure) is a heavily doped conducting polymer that can be solution-processed from a waterbased suspension trading in various formulations under the Clevios™ brand (see <http://www.clevios.com> and Kirchmeyer and Reuter (2005) and references within). It has found widespread academic and commercial use in the fabrication of OLED devices due to good stability, ease of processing and a relatively large workfunction as required for low energy barrier hole injection into a variety of hole conducting organic semi-conducting materials. For a developer of polymer-based organic light-emitting diodes looking to integrate a hole injecting interface with a metal substrate, PEDOT:PSS is a sensible first choice for investigation. It is heavily doped and should form a barrier free electronic contact with the metal surface. In conjunction with certain metals PEDOT:PSS

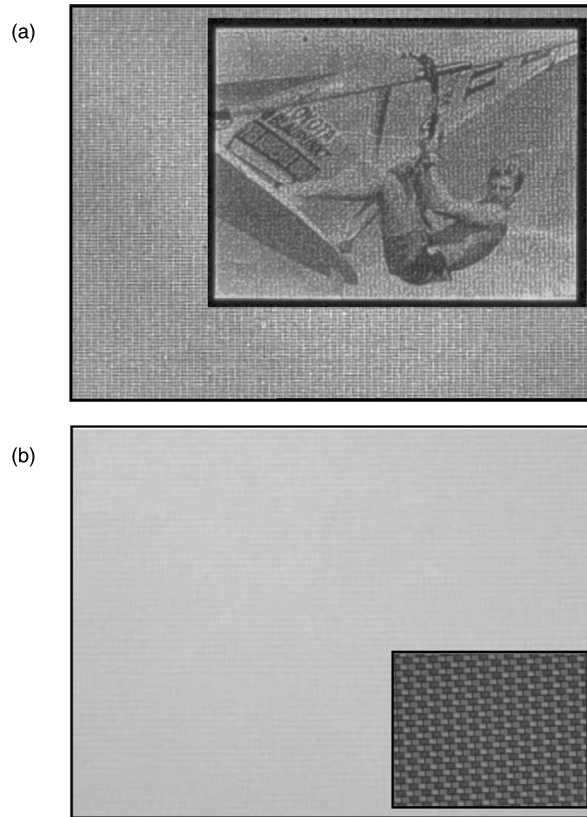


16.3 The results of experimentation into the compatibility of different metal electrodes with PEDOT:PSS hole conducting polymer. (Devices consist of electrode/hole transport layer/white light emitting polymer/ LiF (2 nm)/Ca (20 nm).) Electrode materials include Cr, Ti, Ni and ITO. Hole transporting materials include CH8000, CBS (structure of both shown in insert) and NiO. Cr, Ni and Ti electrodes provide device efficiency comparable in magnitude to that of benchmark ITO devices (differences can be accounted for by the optical properties of the metals in conjunction with microcavity effects). Al-based devices however are significantly poorer, using either CBS or CH8000, than the other metals, illustrating the difficulty in forming a good contact with Al metal.

does indeed form an effective hole injecting interface. In Fig. 16.3 results are shown from an experiment conducted by MED to identify the compatibility of different metal electrodes with PEDOT:PSS. Al, Ni, Ti and Cr were coated with either PEDOT:PSS (CH8000 grade), a monolayer of chloro benzyl sulphonate (as in the work by Khodabakhsh *et al.*, 2004) or NiO and the resulting anode then subsequently fabricated into an electroluminescent device with a white light-emitting polymer coated by spin coating from toluene solution followed by a thermally evaporated LiF/Ca cathode. The devices were encapsulated and tested. The result being that Ti, Ni and Cr (Fig. 16.3), metals showed acceptable (as a starting point for further investigations), $> 1 \text{ cd/A}$, luminance efficiency whereas Al, the key electrode metal in CMOS processing, showed very poor efficiency, $<< 1 \text{ cd/A}$, and unstable devices. The reactivity between acidic PEDOT:PSS and Al metal results in very low interfacial conductivity. A further negative of using Al in conjunction with PEDOT:PSS is the microcrystalline nature of the top layer Al found in CMOS processes. These crystals, which are typically around 2–3 microns in size, such that 5–10 fit within a single display pixel, result in very non-uniform luminance of neighbouring pixels. Figure 16.4 shows an electroluminescence micrograph of an early ME3201 QQVGA microdisplay that has Al pixel pads and a PEDOT:PSS hole injection layer. It is believed that the non-uniformity of light emission is a result of the reaction between Al microcrystals and the acidic PEDOT:PSS.

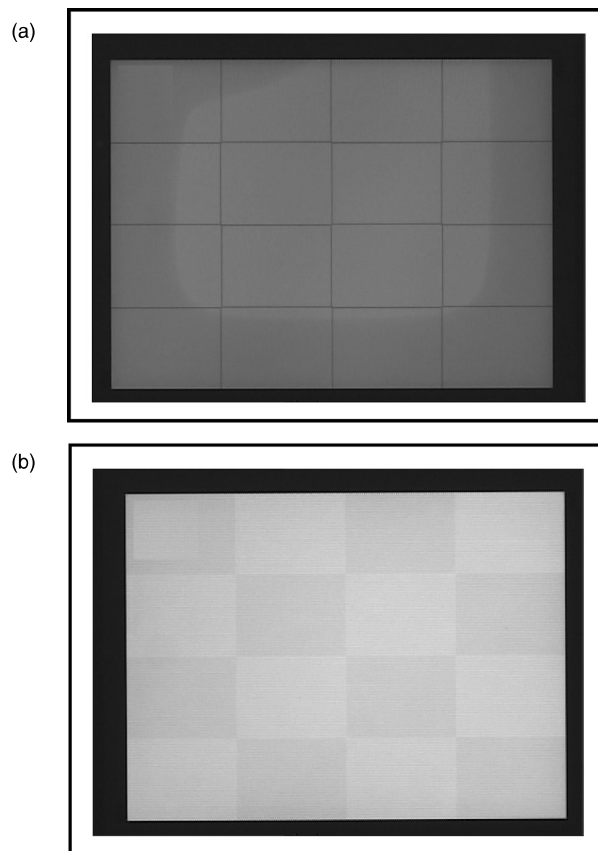
One possible solution to the incompatibility of Al and PEDOT:PSS is to eliminate Al from the top layer CMOS processes and replace it with a compatible metal such as Ti, Ni or Cr. However such ‘post processing’ of the top layers of the CMOS wafer is not particularly desirable since it not only introduces additional process steps that necessarily reduce the yield of the device, but such non-standard CMOS processing renders the process difficult to transfer from foundry to foundry. In particular, Ni and Cr metals are not found in CMOS processes and their introduction as sputtered layers is not easy to justify to the foundry. Ti is used in the passivation of vias and a process based on Ti pixel metal was negotiated by Microemissive for the production of its ME3202 product. However Ti itself is not particularly reflective and therefore has lower theoretical peak efficiency than comparative devices constructed using Al.

A second problem with the use of PEDOT:PSS as hole injection layers in microdisplay devices is its electrolytic behaviour due to the presence of ions of sodium. The nature of an information display is that there are not only electric fields in the transverse direction to the layers of thin films that make up the device, but electric fields in the orthogonal, lateral direction as neighbouring pixels are switched on and off. The migration of ions in these lateral electric fields can modify the transverse electronic properties of the layers into which, or from which, they drift. Microdisplays are particularly susceptible to these ion drift effects given the relatively close proximity and therefore high lateral fields compared to larger area displays. In the case of relatively large area OLED display



16.4 A photograph of two early MED prototypes displaying all white images (and in insert of (a) a surfer image, and in insert of (b) a magnified view of the individual RGB colour sub-pixels) The pixel uniformity of (a) is very poor and grainy whereas the uniformity of (b) is acceptable. Display (a) has Al/PEDOT hole injection interface and (b) has Ti/PEDOT interface.

devices such as that used in a mobile phone, the effect of ion drift is to reduce the effective emissive area of pixels (one solution to this 'pixel shrinkage' problem is described by Beuchel *et al.* (2003)) but the consequence in a microdisplay is more profound. Following a display condition that induces a high lateral field for a particular set of pixels, those pixels effectively switch off completely. Figure 16.5a illustrates the result of pixel shrinkage on a microdisplay comprising a PEDOT:PSS hole injection layer. A checkerboard image is displayed for a period of time, and immediately followed by a completely white image that should be uniform in appearance. It is clear from Fig. 16.5a that not only are the checks visible due to



16.5 Photographic results of an experiment carried out by MED to modify a PEDOT:PSS hole injection layer by incorporating Ca^+ ions in the deposited film. In (a) a test display with Ti pixel electrodes and a PEDOT:PSS layer followed by a white light-emitting polymer device. In (b) the PEDOT:PSS was modified by the incorporation of 300 ppm Ca. Following a checkerboard test (checkerboard image applied for 30s followed by all white test image) there are black stripes indicative of pixel shrinkage in the unmodified PEDOT device but no stripes in the modified device.

differential ageing of the driven and undriven pixels, but that at the interfaces of the checks the pixels are completely dark.

One solution to the pixel shrinkage problem is to actually increase the ionic content of the PEDOT:PSS film. Philips report the addition of CaOH (Beuchel, 2003; de Kok *et al.*, 2004) to significantly reduce the problem. An alternative, as implemented by MED, is to simply add Ca metal directly to the aqueous

PEDOT:PSS suspension. The result is an increase in pH of the formulation, but also a complete disappearance of the black stripes following the checkerboard test as shown in Fig.16.5b.

While such a solution resolves the pixel shrinkage issue, it creates additional problems. The conductivity of Ca doped (300 ppm in solution) PEDOT:PSS is about 10 times higher than undoped material, and the presence of high levels of Ca ions is a potential lifetime and reliability concern. When a constant current driven pixel architecture is used, a high lateral conductivity between pixels is highly undesirable since it results in current and therefore light being lost from the driven pixel. Such current loss can reduce both display efficiency and display contrast. A more satisfactory solution for hole injection is desired.

16.2.2 Metal oxide hole injection layers

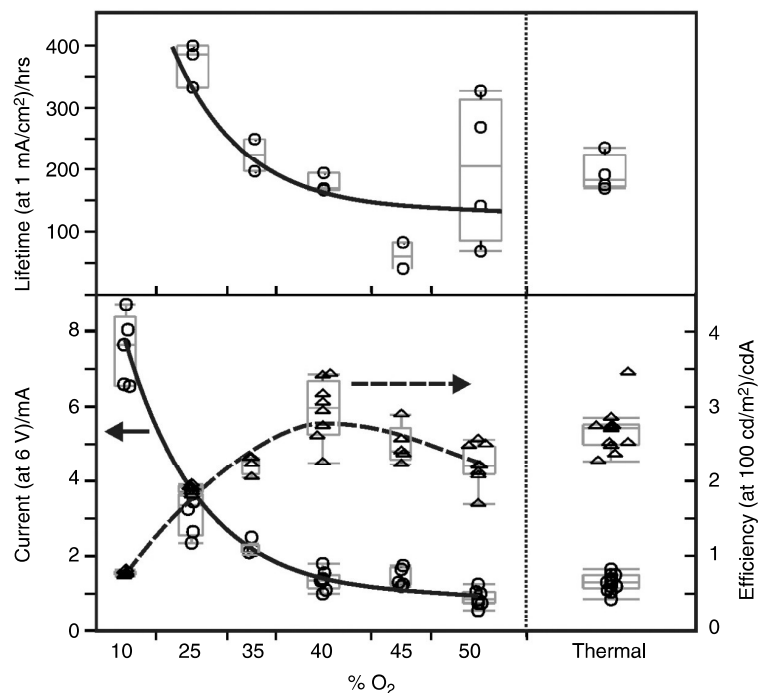
Transition metal oxides such as vanadium oxide or molybdenum oxide have been known to make excellent hole injection materials for OLED devices since first reported by Tokito *et al.* (1994). Recently there has been a significant volume of work showing excellent performance for particular test device architectures in both molecular OLED (Lee *et al.*, 2008; Xie *et al.*, 2008; Greiner *et al.*, 2010), polymer OLED (Buckley *et al.*, 2011), and even organic photovoltaic devices (Sun *et al.*, 2011 for example). One emerging explanation from all these reports, of the enhanced hole injection performance for Molybdenum oxide hole injection contacts with both molecular and polymeric tri-arylamine containing materials, is via charge transfer doping of the organic semiconductor at the MoOx interface. The use of either V_2O_5 , RuO_2 (Tokito *et al.*, 1994) or MoO_3 as a hole injection layer in conjunction with Al CMOS electrodes is a sensible alternative to the use of PEDOT:PSS. The specific choice of transition metal oxide and the determination of its processing conditions are driven by a number of competing factors. Firstly, for the injection of holes to blue or white organic light-emitting materials the metal oxide must have high workfunction (typically between 5.1 eV and 5.5 eV to match the frontier orbital energies of fluorene-based blue-emitting polymer semiconductors as used as base materials for white light generation by MED) to provide low barrier injection of holes in to the bulk of the active polymer layers. However the injection layer must also have low enough conductivity such that when a uniform layer of the oxide is coated continuously across a pixel array not too much (<5–10%) current is lost to neighbouring, grounded, display pixels. Finally it must be stable and provide good operating lifetime for the display. Lateral conduction between pixels can be tuned, not only through the conductivity of the material, but also through the thickness of the deposited layer, and to a certain extent the stoichiometry of the oxide.

While vanadium oxide has lower intrinsic conductivity (a 150 nm thick film was measured by Tokita *et al.* (1994) to have resistivity of 10^5 ohm cm) and is therefore well suited to the microdisplay device where low lateral conduction is

desired, the toxicity of V_2O_5 particles and requirement for manual interventions inside the deposition chamber of a production process meant that, for MED, a compromise choice of MoO_3 was preferred. MoO_3 has much higher conductivity (a 150 nm thick film was measured by Tokita *et al.* (1994) to have resistivity of 10^{-2} ohm cm) but is significantly less toxic than V_2O_5 . A reactive sputtering process was chosen to deposit the MoO_3 in production, it being the first layer deposited following receipt of wafers from the semiconductor foundry. However the natural state of the Al electrode surface is with a layer of native oxide around 2 nm thick. In addition to sputtering of a 3 nm layer of MoO_3 , an Ar sputter clean and then a 0.5 nm pure Mo passivation layer was deposited, to prevent, to a certain extent, the recurrent oxidation of the clean Al surface. This method was partly successful, but in reality loss in performance due to interfacial oxidation of Al metal and reduction of MoO_3 to MoOx was found to degrade device performance for MoO_3 layer thicknesses of less than 8 nm (Buckley *et al.*, 2011). A thicker MoO_3 layer would have resulted in better hole injection and consequent increase in lifetime through better charge balance, but such a film would have resulted in significant lateral current leakage, a consequent loss in display colour saturation and contrast, and an increase in overall power consumption. Figure 16.6 illustrates how the performance of white light-emitting diodes is dependent on the stoichiometry of MoOx as deposited by reactive sputtering. In this experiment conducted by MED a 5 nm MoOx layer was deposited on an Al electrode followed by a 40 nm layer of arylamine containing cross-linkable hole transporting material (patent of Inbasekaren and Yu, 2004) and a 67 nm film of white light-emitting polymer and a cathode bilayer of 2 nm LiF and 20 nm Ca. Lifetime testing was done from a constant current density and the increase in lifetime on reducing oxygen content of the MoOx film is largely due to increased hole current, which Fletcher *et al.* (2004) found to be stable in these devices. The efficiency of the devices peaks at around 3 cd/A at a sputter condition of 40% oxygen; this corresponds to a slightly reduced form of molybdenum oxide, and interestingly with similar performance to equivalent thermally evaporated MoOx injection layers.

16.2.3 White light generation in OLEDs

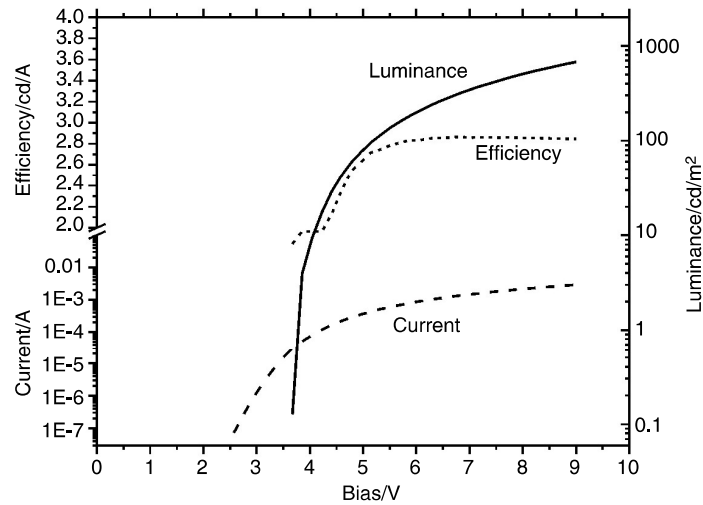
While the use of MoOx as a hole injection layer matches, more or less, the lateral conductivity and hole injection requirements of the OLED microdisplay device, so far there has been no discussion of light generation and optical outcoupling. Indeed, the very nature of using a metallic bottom electrode and opaque Si-CMOS substrate means that light must be emitted through an electron-injecting top electrode. The intrinsic requirements of such a cathode are, firstly a good degree of transparency, secondly a low energy barrier to electron injection, and thirdly high conductivity and good stability, or at least stable once hermetically encapsulated. The light-emitting material itself must provide transport to both



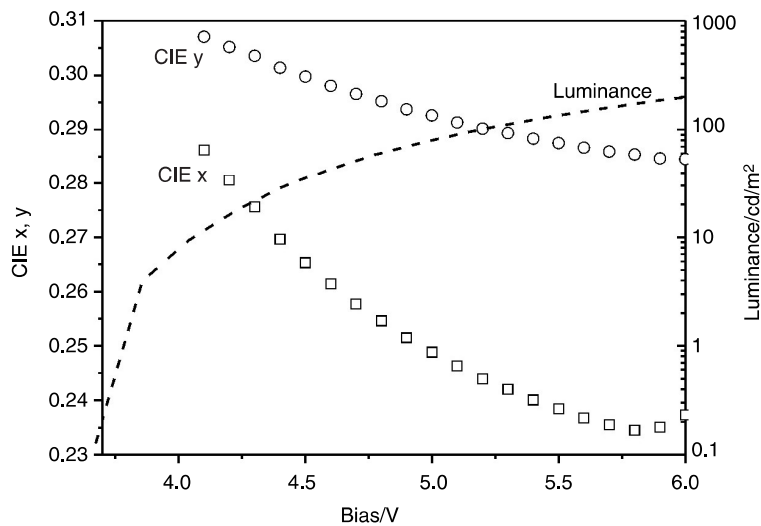
16.6 The results of an experiment undertaken by MED to investigate the effect of varying the oxygen content of the reactive sputter deposition of MoOx in white light-emitting Ti/MoOx/cross-linked arylamine hole transport layer/white light-emitting layer/LiF/Ca devices. Thermally evaporated MoOx of the same thickness (5 nm) used in the sputtered devices is shown on the right side of the figure.

electrons and holes, and in MED's display, the emission must be white such that red, green and blue sub-pixels can be formed by subsequent colour filtering by an array of lithographically patterned colour absorbing materials similar to those used in CMOS or CCD colour cameras. Details of colour generation for OLED microdisplays are discussed in Section 16.4. Figures 16.7 and 16.8 show typical voltage, current and luminance and voltage, luminance and CIE colour points for microdisplay product ME3204 respectively.

White emission is achieved by partial energy transfer from a high energy excited host component to a lower energy guest component (Buckley *et al.*, 2001). Light emission occurs from both the host and guest component and thus is comprised of multiple spectral contributions. The review by Farinola and Ragni (2011) describes guest–host systems that consist of co-evaporated molecular mixtures, partially phase-separated polymer blends and block co-polymer systems amongst others. Achieving stability in the colour both over extended operating lifetime and over a wide range of



16.7 Characteristic current-luminance-voltage curves for MED's ME3204 microdisplay product. To record these traces a test condition was implemented where the CMOS electronics is switched into an idle mode and only current flowing into the light-emitting polymer is recorded. The OLED power dissipation at 300 cd/m² (a typical operating condition) is around 6 mW.

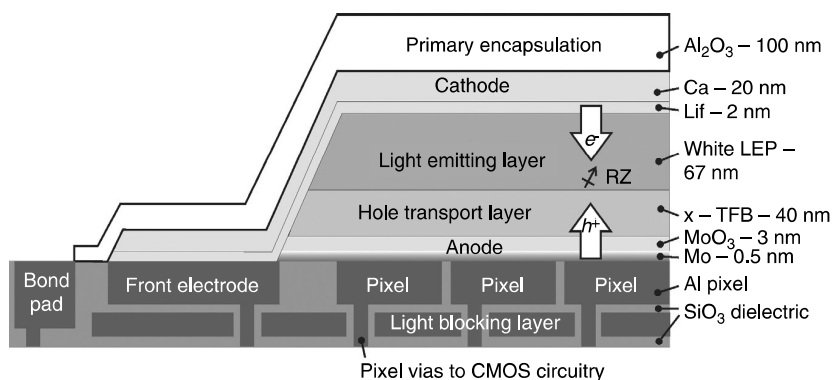


16.8 Characteristic luminance, CIE x, CIE y curves for ME3204 operated under test conditions. CIE x, y specifications exit at a window around 0.30, 0.31.

excitation densities (and therefore emission brightnesses) is not trivial. For fluorene-based polymeric systems developed by Wu *et al.* (2004) and further developed by Yamada *et al.* (2008) that were implemented in MED's display products, guest-host block co-polymers yielded the best colour stability. However even these systems, as demonstrated by Pounds *et al.* (2007), exhibit some shift in colour under increasing electrical stress, where at low electrical stress a redder emission is seen (at 50 cd/m^2 CIE x, y: 0.36, 0.34 for a typical three colour white described in Section 16.4) and at high electrical stress bluer emission is seen (at 500 cd/m^2 CIE x, y: 0.33, 0.33). The reason for such changes in the MED device architecture (see Fig. 16.9) is thought to occur from two sources. The first being a shift in the vertical location within the microcavity of the device where exciton formation occurs on increasing electrical stress, thus leading to a change in the relative outcoupling spectra of the device (see Section 16.4), the second being changes in the relative rates of direct and indirect electrical excitation of the guest chromophores. Greater direct excitation of the lower energy chromophore in a white emitting system leads to redder emission and greater direct excitation of the blue emitting host species leads to a bluer emission. It is likely that at low electrical stress direct excitation of the low energy red chromophore is relatively enhanced compared to the high electrical stress condition. Fortunately for pulse code modulation drive schemes, where a 256 level pixel grey scale is controlled by the switching of an 8 bit pulse scale, current stress levels in the materials remain constant, and colour artifacts are not noticeable.

16.2.4 Controlling charge balance

Long lived and efficient OLED devices are the result of a combination of stable efficient electroluminescent materials but also a result of a good balance between



16.9 Illustration of a cross-section through MED's ME3204 microdisplay device. RZ denotes the recombination zone, situated close to the interface between the hole transport layer and the light-emitting layer.

hole and electron densities in the light-emitting region. Since the hole injecting interface of MED's microdisplay device has been fixed due to consideration of lateral conduction of the MoOx film, good charge balance is achieved though a combination of an electron blocking layer and efficient electron injection.

Electron injection into blue fluorene based light-emitting polymers has been the focus of substantial research efforts in the early 2000s. Brown *et al.* (2001) reported device-based results and Greczynski *et al.* (2000) undertook a photoelectron spectroscopy investigation. In recent years, and in particular in commercial polymer OLED devices, Ba metal has been used preferentially as a cathode layer (illustrated in the online presentation material by Yamada *et al.*, 2008). The choice of Ba has been due to a combination of low workfunction and excellent electron injection into a range of light-emitting polymers, but also due to its ease of processing in electron beam evaporation. Disadvantages in the use of Ba include its extreme reactivity towards oxygen and water and, for MED's purposes, its relatively high optical density and low conductivity. Alternative cathode systems include combinations of low workfunction metals and alkaline and alkali metal salts such as LiF, BaF₂ and CsF. However all of these bilayer systems require, in the case of a microdisplay, a high conductivity, low optical density material that can act as a semitransparent conducting electrode layer. Sputtered conducting oxides such as indium tin oxide can be used as such layers, but typically the sputtering process results in damage to the underlying light-emitting polymers due to high energy bombardment by the sputtered particles. A low damage sputtering process is being developed (for a recent result in this field see Jeong *et al.*, 2010) but tends to have much lower deposition rates and was not seen as a viable option for MED. A combination of LiF and Ca layers does provide, for fluorene polymers, an acceptable combination of conductivity, workfunction and optical transparency. Table 16.1 shows some possible conducting metals as

Table 16.1 Table of resistivity, density and workfunction of available metals for use in polymer OLED cathode systems

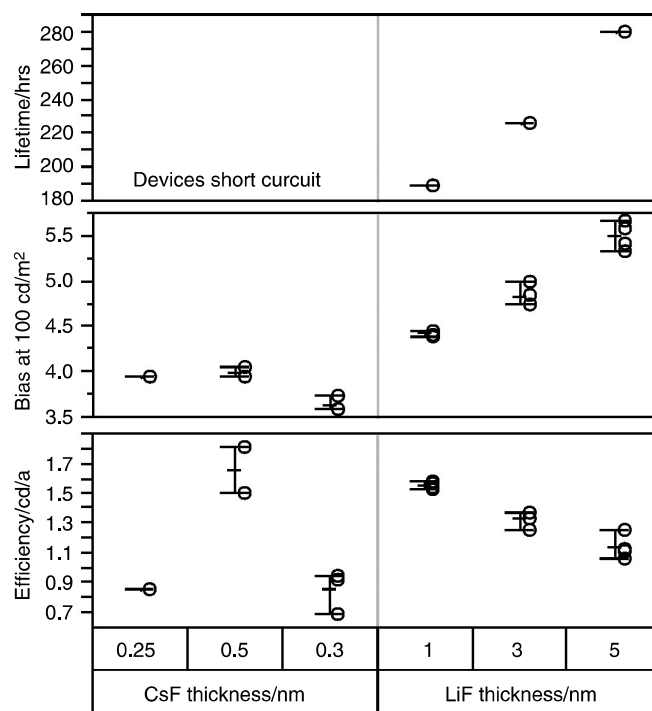
	Resistivity σ	Density ρ	Workfunction ϕ
	10^{-8} ohm m	g/cm ³	eV
Calcium	3.1	1.5	2.9
Barium	31	3.6	2.5
Aluminium	2.4	2.7	4.3
Chromium	13	7.2	4.4
Copper	1.5	8.9	4.6
Magnesium	4.0	1.7	3.6
Ytterbium	28	7.0	2.6

Source: Taken from Kaye and Laby online data www.kayelaby.npl.co.uk except workfunction of Yb taken from Nikolic, 1996.

parameterized by density, which is a strong indicator of optical density, resistivity, and workfunction. Ca metal provides an excellent compromise between all three equally important properties: low resistivity, low density and low workfunction. Brown (2001) and Greczynski (2000) report the relatively high stability of LiF/Ca interfaces with fluorene containing polymers such as 9,9'-dioctylfluorene-co-N-4-(butylphenyl)-diphenylamine (TFB) and poly(9,9'-dioctylfluorene) (F8). They show, using device results and photoelectron spectroscopy, that the LiF layer remains intact at the polymer/cathode interface. Such a result is an excellent indicator that the interface will remain stable during device operation and good lifetime performance is expected.

This is in contrast to the use of LiF/Al cathodes in molecular OLED devices where dissociation of LiF gives rise to a doping of Alq₃ with Li ions. In the case of Alq₃ the dissociated LiF is then stabilised by the doping reaction, however mobile Li ions are extremely undesirable in a device. Other alkali and alkaline earth metal salt such as CsF, CaF₂ or BaF₂ can result in similarly performing white emitting devices at first test when combined in a bilayer with Ca metal. However, in general, fluorides of Cs, for example, do not remain intact at the cathode interface and, as found with the use of Cs salts in the n-doping of molecular OLED device reviewed by Pfeiffer *et al.* (2003) relatively unstable devices result. On the other hand, fluorides of Ba and Ca, while stable, do not provide as effective electron injecting layers and efficiencies and lifetimes are somewhat reduced from those employing LiF/Ca interfaces. Figure 16.10 illustrates the compromise between lifetime, efficiency and operating voltage required to be negotiated when developing a display product using an alkali earth salt buffer layer as a cathode. Device results for different thicknesses of LiF and CsF cathode buffer layers are shown for a particular test device structure. While, in the case of LiF thickness, lifetime increases with LiF thickness, operating voltage and efficiency reduce. The stability of the buffer interface, which increases with thickness, is traded against reduction in efficiency and increase in operating voltage. CsF buffer layers, on the other hand, when implemented in very thin layers, produce very low operating voltage, indicating lower barrier to electron injection, but devices are liable to short circuit, indicating that the interface layer, while effective at time zero, is not stable. For MED's mass production process, a 2 nm LiF and 15 nm Ca bi-layer cathode was implemented.

Once electrons are successfully injected into the light-emitting layer, the remaining task of the device layers is to confine a high density of both electrons and holes in a particular region of the device. This is achieved successfully in polymer OLEDs by the use of an electron blocking layer. TFB has been reported by Kim *et al.* (2005) to be excellent in this role with a deep HOMO level (5.4 eV) and excellent hole mobility (recent measurements by Fong *et al.* (2009) gave a mobility of 0.01 cm²/Vs). However to achieve hole blocking function equidistant from cathode and anode, for optimum outcoupling, the TFB thickness is required to be between 40 and 50 nm. TFB is similarly soluble to white emissive polymers



16.10 Results of experimentation into different alkali earth metal salt materials as cathode buffer layers. The device structure was Ti/MoOx (5 nm)/TFB (40 nm)/White LEP (65 nm)/Buffer layer/Ca (20 nm). Lifetime is reported at a constant current stress of 1 mA and efficiency is reported at a luminance of 100 cd/m².

and a cross linking process is required to prevent washing part or all of a TFB layer when depositing the subsequent light-emitting layer. Such a material was developed by Dow Chemical (Inbasekaran and Yu, 2004) and an analogue of these reported materials was utilised in MED's device. In reality it was found that cross-linking led to a reduction in mobility of the material, and care was taken to ensure thermal curing did not over link the material. However, partial curing led to a partial washing during LEP coating and a reduction of the overall device thickness with corresponding changes in colour point, operating voltage and efficiency.

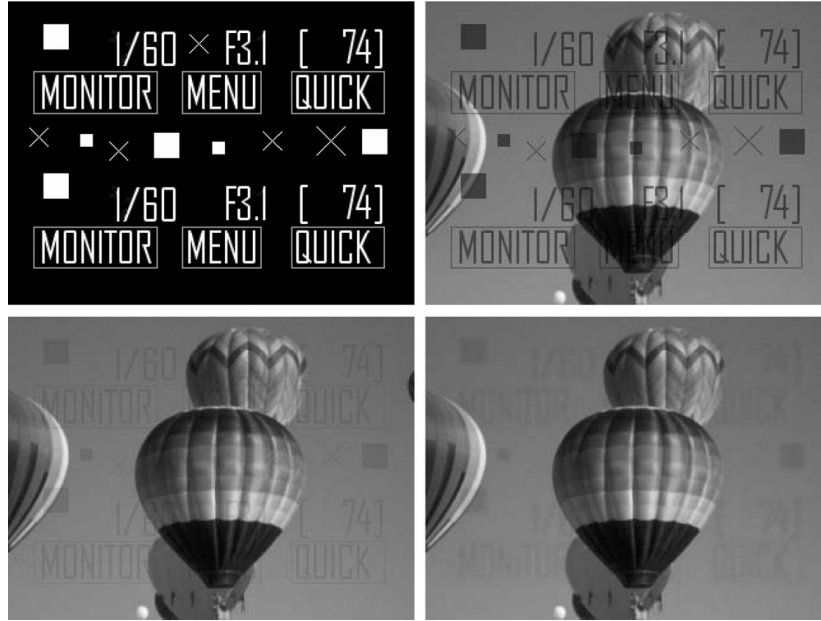
16.3 Artifact free images: the role of CMOS and OLED

All OLED devices suffer from loss of luminance during operation but the consequence of this degradation manifests in two independent ways. The first is

the threshold luminance below which the display product is no longer fit for purpose. Achieving acceptable product lifetimes in respect of this luminance threshold is relatively straightforward for mobile near-to-eye display applications where total operational time is limited by factors such as battery life, and product usage as reported by Lääperi *et al.* (2007), Buckley *et al.* (2009) and Cok *et al.* (2006). In the tests developed by Cok and co-workers for Kodak for OLED panel displays for digital cameras, a continuously looped still-image cycle test running non-stop for 10 days was estimated to be equivalent to 20 years operational use of the product. This corresponds to a usage duty cycle of only around 0.15%. However, the second manifestation of luminance degradation is in the appearance of image burn-in or image retention, where display icons, text or often used regions of the display such as bright sky at the top of the screen degrade faster than lesser used regions. The further important characteristic behaviour of many OLED device architectures is their ability to recover luminance efficiency somewhat following periods of stress as reported by Zou *et al.* (1998) and later and more importantly by van de Weijer *et al.* (2002) for Philips. Recovery in luminance efficiency is important in products where usage is sporadic, and most of the time the product is not being stressed. Recovery can add substantially to the functional lifetime of the display, as shown in the products developed by Kodak (Cok *et al.*, 2006). Figure 16.11 illustrates the effect of differential degradation following the application of an icon-based image on a picture image, typical of a digital still camera review mode. A 5% differential luminance reduction of the pixels stressed in the icon image clearly results in an unacceptable level of image retention. When the icon image is blurred by application over a range of pixels a 5% differential between the centre of the icon image blocks and the background image becomes acceptable.

16.3.1 Lifetime testing methodology

In developing a display technology based on OLED it is clearly important to test not only for long-term luminance degradation but also for short-term degradation that could give rise to image retention. Short-term and recoverable luminance degradation often occurs in OLED devices, where either ion drift modifies the charge injection and therefore charge balance of a device as hypothesized by Zou *et al.* (1998) or morphological effects in the polymer that give rise to slower recovery in efficiency concluded by van de Weijer *et al.* (2002). However, distinguishing between permanent and recoverable degradation is non-trivial since typically a number of parallel degradation mechanisms operate in a device with overlapping timescales, some of which are recoverable and some of which are permanent. A number of testing methodologies were implemented at MED in order to assess the stability of devices in this respect. Testing short-term (minutes) decay and recovery was implemented by testing the cyclic luminance loss of devices under an applied bias voltage. Typical data from an experiment to



16.11 Top left: image for camera menu screen. Top right: the effect of 50% reduction in luminance of pixels involved in the menu screen image overlayed on a typical camera image. Bottom left: the effect of 5% reduction in luminance for the menu screen pixels. Bottom right: the effect of moving the image origin within the display so that the menu screen image is blurred (5% luminance reduction).

investigate the compatibility of different cathode buffer layers with different white light-emitting polymers is presented in Fig. 16.12. White polymer 1 is more stable in a short-term cycle test when used in conjunction with a LiF buffer layer and white polymer 2 is more stable with a BaF₂ buffer layer.

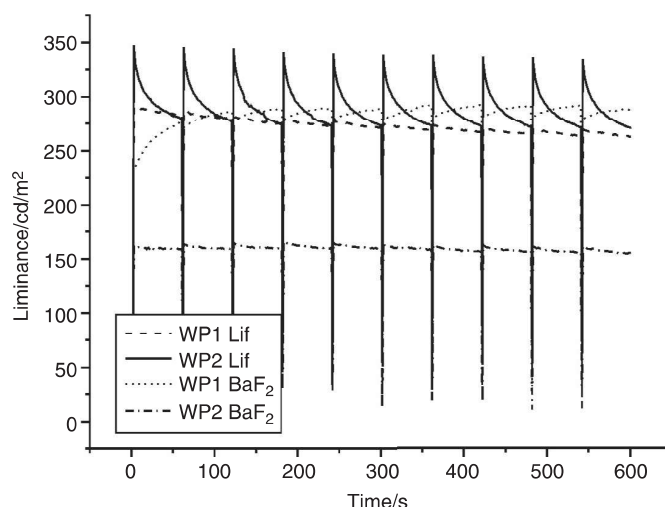
Long-term lifetime testing was also undertaken in order to measure the intrinsic operating stability of devices. In this case the steady state luminance decay was characterised by a stretched exponential function for luminance, L , as a function of time, t :

$$L = L_0 \exp(-(t/\tau)^\beta) \quad [16.1]$$

The initial luminance of the device is L_0 and the calculated time to half of L_0 , is $t_{1/2}$, and given by:

$$t_{1/2} = [0.693]^{1/\beta} \cdot \tau \quad [16.2]$$

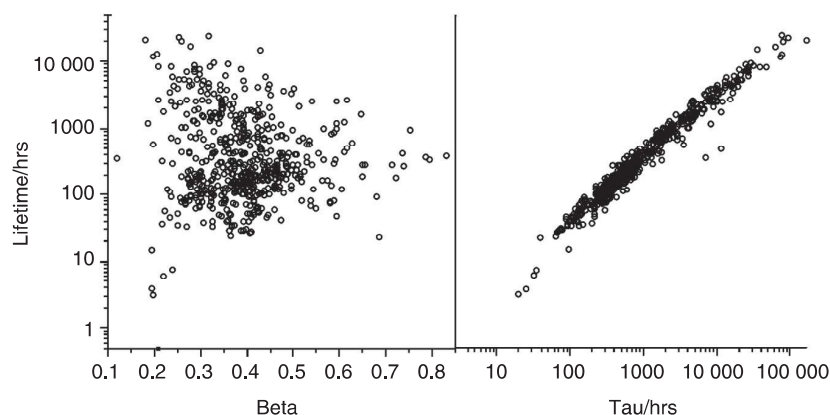
The stretch parameter β describes the steepness of the initial drop (explained well by Fery *et al.*, 2005), and the time constant τ describes the long-term luminance



16.12 Cycle test data for two different light emitting polymers in devices comprising two different cathode interface layers. The level of recoverable degradation depends on the compatibility of the polymer and cathode layer.

degradation. Figure 16.13 shows the correlation between the parameters τ and β and the time taken to half luminance, as measured in white OLED development devices fabricated by MED. Typically new white polymer materials, different anode materials (MoOx , V_2O_5 , PEDOT:PSS) and cathode materials (LiF, CsF, BaF_2 , NaF) and different combinations of layer thicknesses are included within the data. There is clearly strong correlation between the lifetime parameter τ and the time to half luminance, but surprisingly little correlation between β and time to half luminance. However β does significantly correlate to short time scale decay and the 5% threshold for differential ageing and observation of image retention. While there are phenomena observed that do not result in a stretched exponential decay, most OLED device degradation can be characterized by Equation 16.1. Brightwave, as illustrated by Parker (1999), where the luminance of a device initially increases for a short period of time, is one type of phenomena not able to be parameterized by the stretched exponential function. A second is the occurrence of catastrophic failure mechanisms whereby the degradation rate accelerates after a certain time, due to the presence of a feedback effect. However the long term degradation of luminance for a majority of OLED drive schemes and devices can be parameterized by the stretched exponential function.

One might also hypothesize that short-term degradation effects as seen in the cyclic testing shown in Fig. 16.12 would correlate with low values of β associated with steep initial drop in luminance in long-term testing. However, as seen in

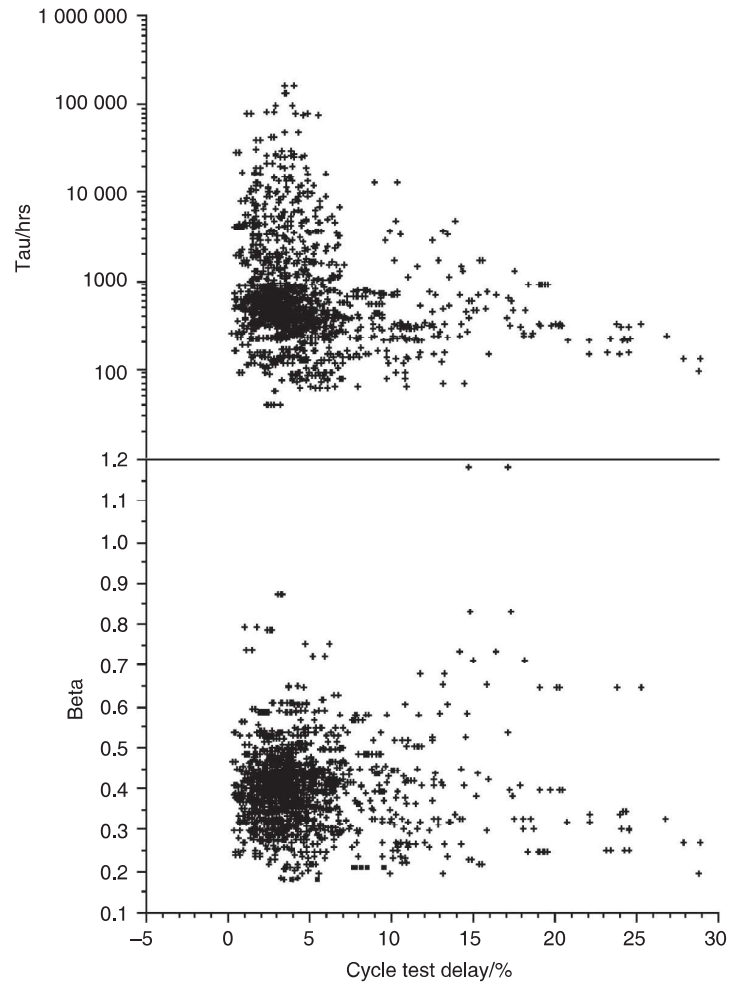


16.13 A scatter plot illustrating the correlation between lifetime (defined at time to half luminance) and fit parameters beta and tau. There are no long-lived devices with high beta but the overall correlation between beta and lifetime is poor, while clearly there is very strong correlation with the traditional time to half luminance measure of lifetime with tau.

Figs. 16.13 and 16.14, these effects in MED's developmental devices of polymer OLEDs seem uncorrelated. Even armed with information about short-term decay and recovery, and long-term degradation, it is difficult to assess the real operation lifetime of a display product since the time scales and duty cycles of the product will determine the actual, real time, degradation rate. Progress towards a real world product lifetime assessment was developed by measuring display luminance degradation over simulated operating cycles within a range of limits. The method of Buckley *et al.* (2009) allows extrapolation of a real operating lifetime for a typical product usage model. For example, for a mobile phone display with a 2% operational duty cycle (30 minutes display usage per day), the MED ME3204 product was calculated to have a 2.5 year operational lifetime when the 5% differential ageing criteria was applied. For higher usage applications, such as personal viewers linked to smart phones, the product lifetime would be proportionally less, and for digital still camera viewers with lower usage the lifetime would be higher.

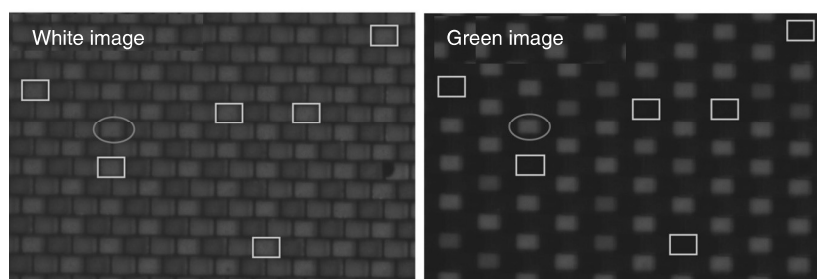
16.3.2 Delayed pixel switching

We shall briefly report one other display artifact, or failure mode, depending on your point of view, that in the ME3204 product gave rise to image imperfections. The problem was associated with the delayed switching of certain pixels under certain image conditions. It occurred primarily in images containing saturated

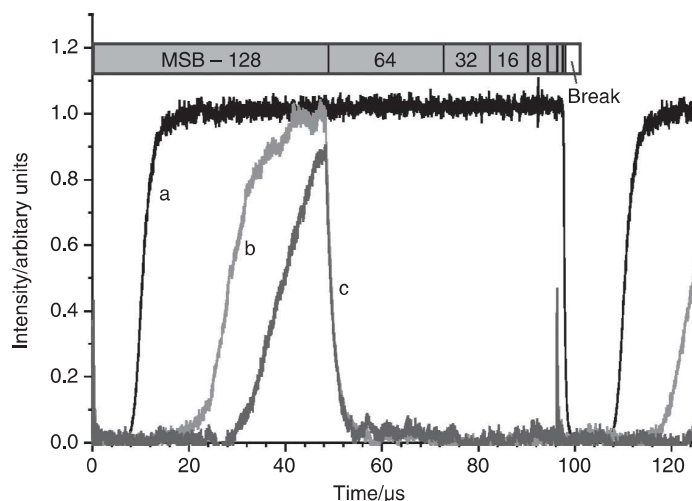


16.14 A scatter plot illustrating the correlation between beta and tau and the level of recoverable decay in the voltage-driven cycle test. Devices that are unstable in the cycle test clearly exhibit short tau and there are no long lived devices, with high tau, that have poor recovery and decay. Beta, however, is unexpectedly not correlated with the cycle test stability and illustrates that the time scales and therefore mechanism for initial drop as characterized by beta are not the same as the time scales for the decay and recovery in the cycle test.

colours, such that the pixels surrounding an affected pixel were switched off. The failure mode was termed 'lazy pixels' by those working on a solution. The problem seemed to arise from the presence of additional capacitance that needed to be charged before current could flow into the light-emitting layer of the OLED device. However, for many months it was not clear whether the parasitic capacitance was associated with the OLED device or the CMOS drive electronics. Figure 16.15 gives an illustration of the problem. Two different test images were written to an ME3204 microdisplay and the resulting electroluminescence image recorded using a high resolution microscope. The light emission of a particular portion of the pixel array was recorded under a full brightness all white image, and the same portion of pixels then recorded under a half brightness green image. Certain of the pixels in the green image show no emission, while they operate perfectly in the white image. The time resolved switching response of pixels affected by the problem and those that are not are compared in Fig. 16.16. In this test the pixel that exhibits delayed switching is shown to be delayed by around $20\text{ }\mu\text{s}$ under a particular test condition, while the promptly switching pixel exhibits a $<5\text{ }\mu\text{s}$ turn-on. One hypothesis that arose early on was that current leaking laterally from the driven pixel, to ground in the neighbouring un-driven pixels was preventing the OLED device of the driven pixel emit light. This hypothesis was quickly discounted since tests showed that the level of delay in the pixel switching was not correlated with the level of lateral conductivity of the anode interface layers. Further hypotheses relating to the discrete presence of cathode or anode defects that could influence the OLED capacitance also proved to be unfounded. Ultimately the problem was traced to the symmetry of the CMOS pixel transistor layout. A certain set of transistor gates exhibited mirror symmetry between neighbouring pixels. The switching response of these transistors was substantially affected by the state of the neighbouring pixel. The problem was



16.15 Electroluminescence test images from an ME3204 display illustrating the problem of 'lazy pixels'. The left micrograph is from an 'all white' image and the right from an 'all green' image. As described in the text the 'lazy pixels' take longer to switch on, resulting in no light emission at low grey levels.



16.16 A time-intensity trace of the luminance emission from three different individual pixels as captured by a photomultiplier tube and oscilloscope. The promptly switching pixel (a), a somewhat lazy pixel (b), and a very lazy pixel (c). The trace for (a) is for a full-on (255) grey level. The traces for (b) and (c) are for 50% grey level for just the most significant bit (MSB) of the pulse coded drive scheme.

identified through careful interrogation of test images where it was seen that the probability of a lazy pixel was higher in odd columns of the display.

16.4 The generation and control of colour

There are a number of different methods that could be used to achieve a full colour gamut for an OLED display. For example, firstly sub-pixelation by patterning separate areas of red (R), green (G) and blue (B) emitting materials; secondly, by the use of a white (W) emitter with patterned RGB colour filters (or indeed RGBW filter pattern); and finally by use of a blue emitter with B to G and B to R colour converters placed over two of the three sub-pixels. RGB emitters are usually the preferred method for OLED displays fabricated using shadow masked evaporated molecular materials or ink jet deposited polymer materials. However, the small pixel pitch in microdisplays (3 sub-pixels in a 10 μm to 20 μm pitch) presents serious technological challenges to these traditional patterning approaches.

The approach chosen by MED and currently in use by eMagin Corp (<http://www.emagin.com/>) is to use a white emitter with patterned RGB colour filters. This colour-by-white approach yields significant advantages for microdisplay

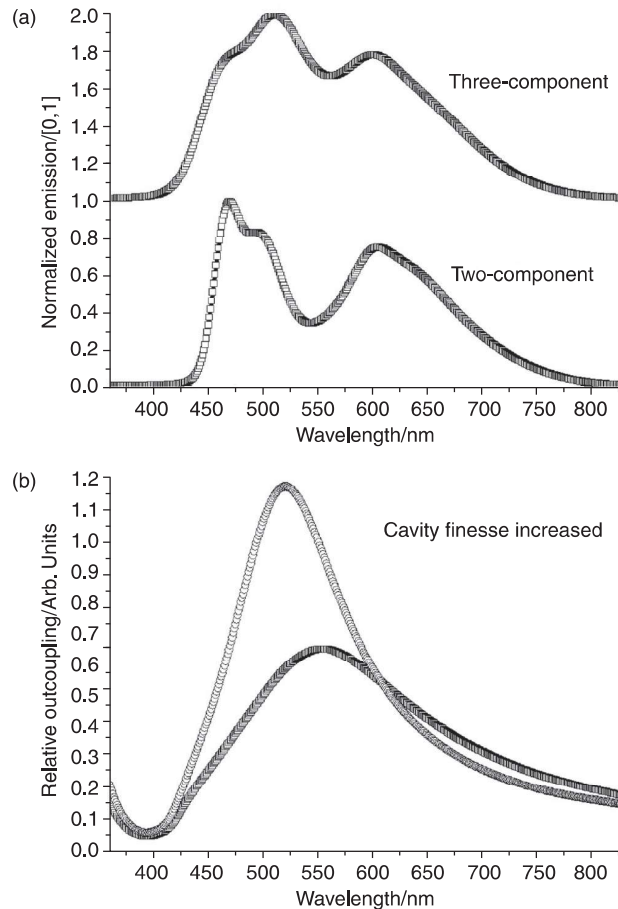
technology. It offers the simplest manufacturing process with no need for patterning of the active material, and also avoids differential ageing of the emitting polymer, as would be the case for patterned RGB emitters. The colour filters can be either deposited and patterned directly on top of the OLED layers as is implemented by eMagin, or through the simultaneous alignment, at wafer level, of a pre-fabricated wafer of colour filter arrays. Wafer level alignment was the process that MED opted for, mainly to reduce complex lithography processes in the manufacturing process, and partly to reduce the requirement of the OLED device to be compatible with the relatively high temperatures (at least 130°C) required for colour photo-resist processing.

The use of RGB sub-pixels on the microdisplay, as with most other large area display technology, relies on the observer integrating the emitted light spatially to produce the perceived image at the eye. In particular this means that the display can be well characterized by the RGB colour coordinates of the individual colour sub-pixels (in, for example, CIE 1931 XYZ colour space), together with the colour coordinates of the white point, produced when all sub-pixels are fully on. In MEDs technology, this colour gamut and white point are determined by the interaction of three specific spectral influences. Firstly the intrinsic electroluminescence spectrum of the light-emitting polymer, secondly, the spectral outcoupling profile due to microcavity interference from the partial reflectivity of the anode and cathode layers, and thirdly the relative absorption/transmission of the overlying colour filters.

16.4.1 The influence of the microcavity

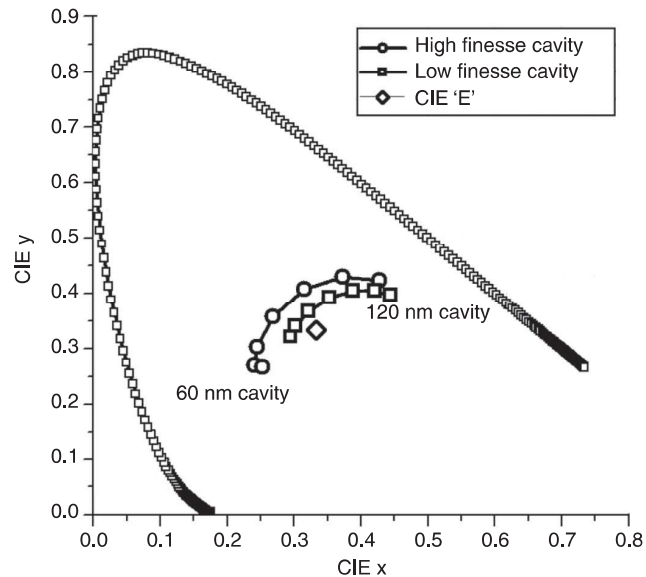
The generation of white light electroluminescence has already been commented on in this chapter (Section 16.2) and also covered in detail in Chapter 1. In this section we consider in detail two exemplar polymer emitters: a two-component emitter characterized by a significant separation between blue and red chromophores and secondly a three-component emitter where emission from the individual chromophores is less discrete and more uniform across the visible spectrum. Both give different flavours of white light emission as shown in Fig. 16.17a. It is believed that three-component systems should offer more flexibility in colour tuning than two-component systems. This may well be the case for bottom-emitting ITO polymer OLED displays, where cavity effects are less dominant. However, in top-emitting structures where microcavity effects are relatively strong, a full and balanced CIE gamut can often be better achieved through a two-component system.

The relative spectral outcoupling, from an emitter placed within a microcavity, will in general contain a peak at some wavelength. The spectral position of this peak is a strong function of the thickness of the cavity, and the width of the peak is a function of the finesse, or reflectivity of the cavity. This is illustrated in Fig. 16.17b where the relative spectral outcoupling is plotted for the same device



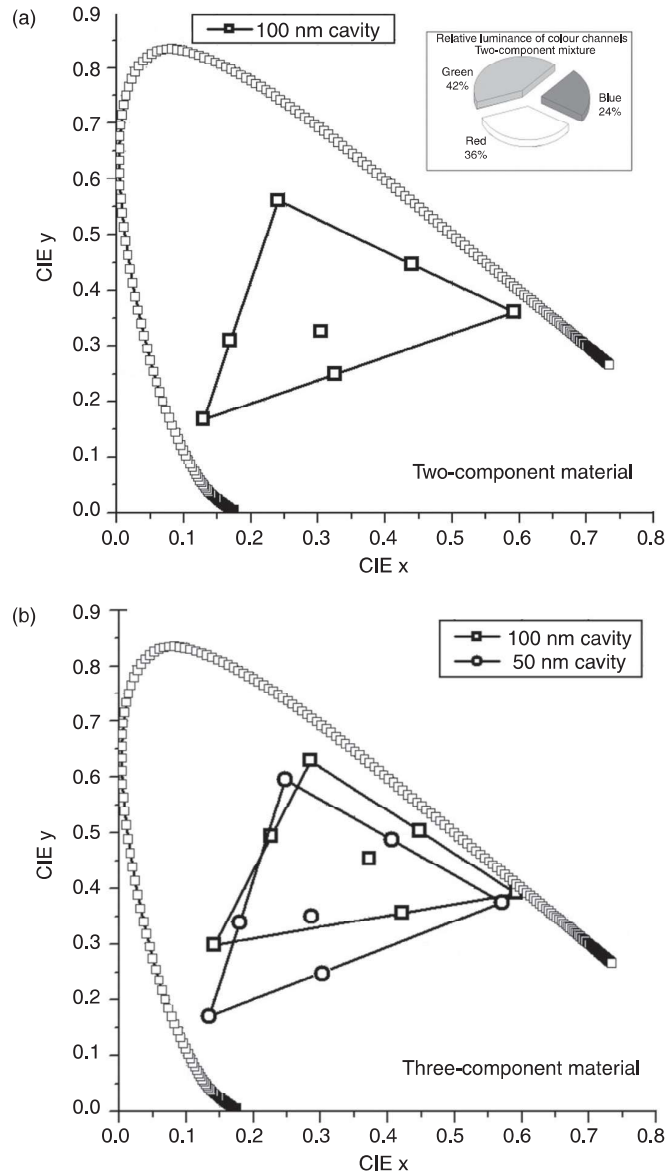
16.17 (a) Intrinsic emission spectra from two exemplar light emitting polymers: a two-chromophore co-polymer and a three-chromophore polymer. The emission from the three-chromophore polymer is broader with less drop in intensity in the green part of the spectrum. (b) The outcoupling spectra from high and low finesse cavities showing how increasing cavity finesse will increase the coupling of green light, and hence a reduction in the intrinsic emission spectrum in the green part of the spectrum is desired in order to generate even photopic output across the full visible spectrum.

but with a change in the metal anode to one that is more reflective, producing a cavity with greater finesse. Figure 16.18 illustrates the point that a change in the cavity properties can allow greater outcoupling, and thus a more efficient device, but at the cost of more strongly modulating the basic emission spectrum. The



16.18 The effect of microcavity thickness on the white point of a two-component polymer OLED device comprising an Al anode and semitransparent Ca cathode. The target CIE 'E' colour point is shown as a diamond for reference. Note that increasing the cavity finesse, by increasing the Ca thickness, has the effect of making the white point more green as the outcoupling spectra is narrowed.

product of the intrinsic emission spectrum and the outcoupling from the cavity determines the light reaching the colour filters. Thus an emission spectrum that has high intensity where the cavity coupling is weak and low intensity where the cavity coupling is stronger will lead to a greater uniformity in emission across the resulting output spectrum. Using a two-component polymer achieves this target more effectively than a three-component system, even though the three-component system has better intrinsic spectral coverage. Figure 16.18 demonstrates the effect that the cavity thickness has on the white point for displays with high and low finesse cavities and Fig. 16.19 shows the complete colour gamut for the two- and three-component systems under cavity architectures that result in a white point closest to the desired optimum for an information display of CIE 'E' at coordinates (0.33, 0.33). Varying the cavity thickness (by altering the polymer layer thicknesses) from 120 nm to 60 nm moves the white point from a red to blue colour via white. As would be expected, the effect is greater for the cavity with greater finesse. These considerations indicate that the combination of polymer and cavity requires careful engineering in order to produce a device that has a sufficient colour gamut whilst operating at a feasible voltage.



16.19 (a, b) The simulated colour gamuts of displays with two and three component emissive polymer materials. At a 'sensible' cavity thickness of 100 nm the three-component device in (b) exhibits a white point far from acceptable, with a yellow colour.

16.4.2 Colour filters and colour space

At the simplest level the colour filters modulate the emission spectrum from the cavity by transmitting or absorbing the particular wavelengths. The bandwidth of transmittance of the filter determines the saturation of the particular colour. Reducing the bandwidth has the effect of increasing the saturation of the colour and hence increases the possible colour gamut of the display. In general this can be achieved by increasing the thickness of the absorbing layer within the filter. However, this has the effect of reducing the luminance of the sub-pixel and hence altering the colour balance and white point of the display.

Since the microdisplay relies on spatial integration by an observer, the relative luminance values of the individual sub-pixels will determine the white point of the display. The white emission spectrum is simply the sum of the emission spectra from the three sub-pixels. In an ideal case the luminance emitted from each sub-pixel would be identical, and whilst this is very difficult to achieve, an acceptable gamut and white point can be achieved with a two-component polymer system. Figure 16.19a shows the colour gamut and white point, together with the conjugate colours (cyan, magenta, yellow), for a typical microdisplay based on a two-component polymer system, at a reasonable cavity thickness of 100 nm. The colour gamut is sufficiently large for most near-to-eye applications and the white point is very close to CIE 'E'. In contrast, Fig. 16.19b shows the equivalent data for a device with the same structure but based on a three-component polymer system. At the same cavity thickness the gamut is severely shifted towards the yellow region of the colour space. Reducing the cavity thickness of this device to 50 nm produces an acceptable gamut, but such a device would be unstable and highly liable to shunt failure.

16.5 Manufacturing issues

In this section a description of the MED manufacturing process is given. The experiences and challenges of integrating mature semiconductor processes with immature, poorly characterized or yet to be developed polymer OLED device processes are described. In Section 16.5.1 each process step is considered in turn. The equipment and metrology required to control the process are discussed alongside potential improvements. In Section 16.5.2 the yield of MED's process and product is discussed. Two example defect classes arising in the process are investigated. Finally some general issues about test and quality for the MED product are considered.

16.5.1 Process integration

The successful manufacture of OLED microdisplays is achieved by the integration of traditional and novel processes. All MED's process steps are based on

semiconductor tools and 200mm wafer handling. Figure 16.21 illustrates the full process, from receiving bare wafers with exposed Al pixel pads, front electrode connection and bonding pads, through wafer level processing, to final assembly into a display package. Each of the steps detailed in Fig. 16.21 is explained in the following sections.

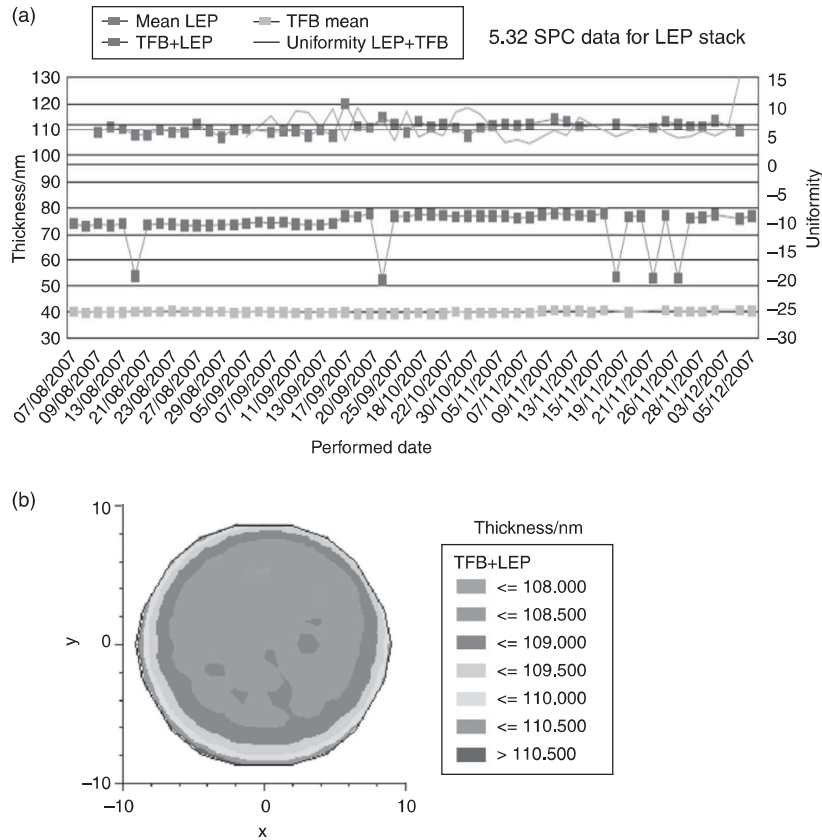
Anode deposition

A dual chamber sputter tool was used to surface condition and subsequently deposit the Mo/MoOx bilayer anode. The time for the process was less than 10 minutes. The resulting structure was found to be slightly hygroscopic and delay between exiting the loadlock of the sputter tool and progressing a wafer to polymer coating was minimized to less than one hour. Wafers that were delayed in processing following Mo/MoOx deposition were found to exhibit reduced efficiency and increased operating voltage. A mechanism for the dependence of the electronic structure on the uptake of water of MoOx anode interfaces for fluorene-arylamine hole transport polymers has recently been reported by Gwinner *et al.* (2011). The conclusion is that the LUMO energy of MoOx, to which electrons are transferred in the hole injection process, reduces from 5.4 eV for a pristine surface to less than 5 eV for a water contaminated surface, as such transitioning from a barrier-free interface with TFB to an interface with a 0.3 eV energy barrier. While such degradation is undoubtedly present, MED found that prompt processing from anode deposition to polymer coating resulted in a stable process with respect to hole injection.

Polymer deposition

Hole transporting and light-emitting polymer layers were coated using standard semiconductor spin coating equipment. Wafer to wafer, day to day, global and local intra-wafer uniformity of layer thicknesses are equally important to ensure repeatable OLED operating characteristics. Polymer layer thickness has the most significant impact on the white point of the displays (Fig. 16.20) where very small changes can result in non-conforming product. Individual layer uniformity of better than 1 nm (2% for the full 100nm stack) is required and can be achieved by careful control of the spin coating process. The generic coating process used by MED included, firstly, the dispense and uniform spreading of solution across the 200mm diameter wafer, secondly the closure of a lid on the spin bowl to ensure slow evaporation of solvent, and thirdly a very slow (<1000rpm) spin to remove excess formulation from the edge of the wafer during a controlled evaporation of the remaining solvent in the film. The surface wetting by the aromatic (m-xylene) solvent used in the formulation was excellent and spin comets or non-uniformities were rare.

The formulation concentration of polymer in m-xylene determines the viscosity and therefore the range of thicknesses that can be coated uniformly by modification



16.20 (a) A control chart of the mean thickness of test wafers constructed with hole transport layer and white light-emitting layer. Polymer thickness was measured after each deposition and the wafer to wafer uniformity is seen to be less than three nanometers. On 17 September the hole transport layer thickness was deliberately increased to 78 nm from 74 nm and this step change is clearly visible on the control chart. Note that missing data for the white emitter layer results in a spike point at 50 nm total thickness. (b) The intra-wafer uniformity of a particular test wafer is shown to be less than 5 nm. However, the majority of the wafer falls within the same 1 nm range at 108.5 nm. All measurements in this figure were made using spectroscopic ellipsometry, with sub nanometer precision.

of coating speed. Day to day variation in humidity and temperature (even in a controlled clean room) and batch to batch variation in the formulation due to subtle changes in molecular weight, storage conditions and age can lead to slight shifts in processing conditions in order to achieve specified thicknesses. Film

thickness was measured and controlled by the use of spectroscopic ellipsometry of individual layers coated on Al test wafers. Daily checks were performed on the process tool. Defects relating to dried polymer material in and around the spin bowl were measured by a light scattering particle counter and particles were minimized to less than 10 per test wafer by daily cleaning routines.

Polymer etching

Following the uniform deposition of a polymer bilayer across the whole wafer, those parts of the polymer film coating the bonding pads, cathode electrode contact and other inter-array regions are required to be removed such that reliable electrical connections and hermetic thin film encapsulation can be achieved. For reliable wire bonding complete removal of residual polymer is necessary from the bonding pads. For long-term reliable electrical connection between the 15 nm Ca cathode film and front electrode pad surrounding the pixel array it is also imperative that total removal of all residual polymer is achieved. For reliable encapsulation by subsequent multilayer deposition process it is further imperative that all polymer is removed from the regions onto which the encapsulation layers will be deposited. Any remaining polymer contamination will result in a pathway to the environmentally sensitive device layers such as the cathode, polymer and anode.

There exist a number of options in order to achieve patterning of the polymer layers such that they are present only on the pixel array. The first option (rather than spin coat the polymer layers) is to inkjet print blocks of polymer ink on the pixel arrays. However this method replaces the high yield, high throughput and easily controlled spin coating process with a substantially lower yield, slower and harder to control process. Following some initial trials it was concluded by MED that the process window for the use of inkjet printing to produce uniform displays was too small to be a competitive alternative to spin coating. A second option is to use laser ablation to remove the inter-array polymer. However such a process, while effective at removing polymer, requires very costly and relatively low throughput equipment and even with the implementation of suction in the ablation zone, results in broad (100s of μm) regions of debris next to the fully removed regions. Debris is not only a defect risk for the pixel array but it is harder to encapsulate using thin films due to a bumpy stochastic nature.

The method adopted by MED was the use of directional ion beam etching, with patterning of the etch being achieved by a proximity shadow mask. The process was implemented in the same vacuum cluster tool as the cathode and encapsulation deposition. It required two sequential etching steps using two different shadow mask sets to completely remove polymer from around the array. The first etch removed rectangular bars from the north and south sides of the pixel array, thus clearing bond pads and front electrode, but leaving polymer *in situ* on the east and west sides of the array such that a second etching step was required for total

removal. The ion beam generates a significant amount of heat, but this issue can be managed via three separate controls. The first is the backside cooling of the wafer by intimate contact to a cooled wafer holder. The second is by recessing the shadow mask over the pixel array such that the mask does not contact and conduct heat to the most sensitive part of the OLED materials. Finally a heat sink shadow mask that is deliberately not in contact with the wafer is held a short distance in front of the patterning shadow mask. This second mask conducts a significant amount of heat away from the sensitive regions. The combination of these three control measures resulted in an etching process that achieved a process time for complete removal of 20 minutes (using two etch chambers) while keeping the polymer layers on the array at less than 80 °C. It should be noted that precise manufacturing specification and control of the shadow masks was also required. The masks need to be made out of invar metal, one of the lowest expansion coefficient metals available, and the manufacturing process of these masks needs controlling to ensure that no sharp edges are present in the mask. Sharp edges scratch the metal layers of the wafer and lead to defect sites and a pathway for extrinsic degradation. The masks in all process chambers align to less than 50 µm across the wafer and are held in place by the use of a magnetic plate at the rear side of the wafer that is brought into contact once the wafer and mask are aligned. Thermal stability of the permanent magnets was achieved through a combination of form factor and materials choice.

Cathode deposition

LiF and Ca cathode layers were deposited by thermal evaporation using resistively heated baffled molybdenum boats taking 5 g material charges. The sources were kept at standby temperature between depositions with a resulting processing time of less than 10 minute per wafer. Careful degassing of Ca material is required when loading new material to the boats to ensure stable deposition rates. Both LiF and Ca materials were purchased from Testbourne Ltd and specific attention was paid to ensuring controlled particle size of 3–5 mm diameter pellets.

Once deposited, the cathode was immediately transferred to a second deposition chamber in order that a protecting layer of 50 nm thick electron-beam-evaporated Al_2O_3 be deposited. The Al_2O_3 prevented the thin 15 nm Ca layer from degradation in the vacuum chamber, and by degradation from the subsequent processing of the multilayer encapsulation. While electron beam evaporation has the risk of damaging sensitive organic layers by ionization by secondary electrons escaping from the deposition gun, by ensuring good grounding and magnetic confinement of the secondary electron flux, and a large source to substrate distance of around 40 cm, no secondary electron damage was observed.

A further advantage of the Al_2O_3 oxide layer, deposited through the same shadow mask as the cathode layers, was the possibility of using such oxide layer as an *in situ* hardmask to pattern the etching process. In this proposed process

improvement, rather than etching the polymer layers prior to cathode deposition (as is instinctively required to ensure electrical connection from the cathode to the front electrode pad), the first process is the deposition of LiF/Ca/Al₂O₃ through a shadow mask that partly covers the front electrode pad. The next, counter intuitive step is to etch in a single step the remaining polymer from the wafer using the ion beam. Thermal control by back-side wafer cooling is now vital to prevent damage to the polymer layers. Once the polymer is removed, the wafer is subjected to a final deposition of metal, either Ca or Al that covers the overlap between the Al₂O₃ layer and the front electrode. The etching process leaves just enough Ca exposed at the base of the Al₂O₃ layer that an effective and long-term reliable electrical contact can be fabricated from the nano-scale lateral overlap between the subsequent metal deposition and the underlying, pre-encapsulated Ca. Such a process was under development at MED as a way to reduce process time of the etch process, reduce the masking requirement of the etch, reduce the number of process steps, and provide a more reliable encapsulation in terms of lateral pathways for degradation.

Multilayer thin film encapsulation

MED used five bilayers of 500 nm thick planarizing acrylic polymer and 20 nm sputtered Al₂O₃ as an encapsulation. The process was licensed from Vitex Systems Ltd. The acrylic layer was deposited as a monomer liquid by vacuum spray deposition and cured using UV irradiation. The final Al₂O₃ layer was required to fully overlap the acrylic planarization layers in order to form a seal to the underlying wafer.

The multilayer process was effective in its protection from water and oxygen transmission vertically through the device. Details of the effectiveness of such multilayer encapsulation for OLED are given by Moro *et al.* (2004). Failure however is possible laterally if defects by mask scratching or other particles occur at the critical overlap between the multilayers and the oxide and metal surfaces of the display die.

Once encapsulated with the multilayers the wafer exits the cluster tool and can be tested using a standard semiconductor wafer probe tool, modified with the incorporation of a camera and spectrometer to record the light emitted from each display die. At this stage defective die can be identified and communicated to the subcontractor carrying out packaging processes such that defective displays are not assembled.

Colour filter lamination

Following test of the display wafer, a colour filter wafer is aligned and adhered in place to create colour display from the white light OLED arrays. The process is carried out in a cluster tool arrangement. The colour filter wafer is sprayed with a

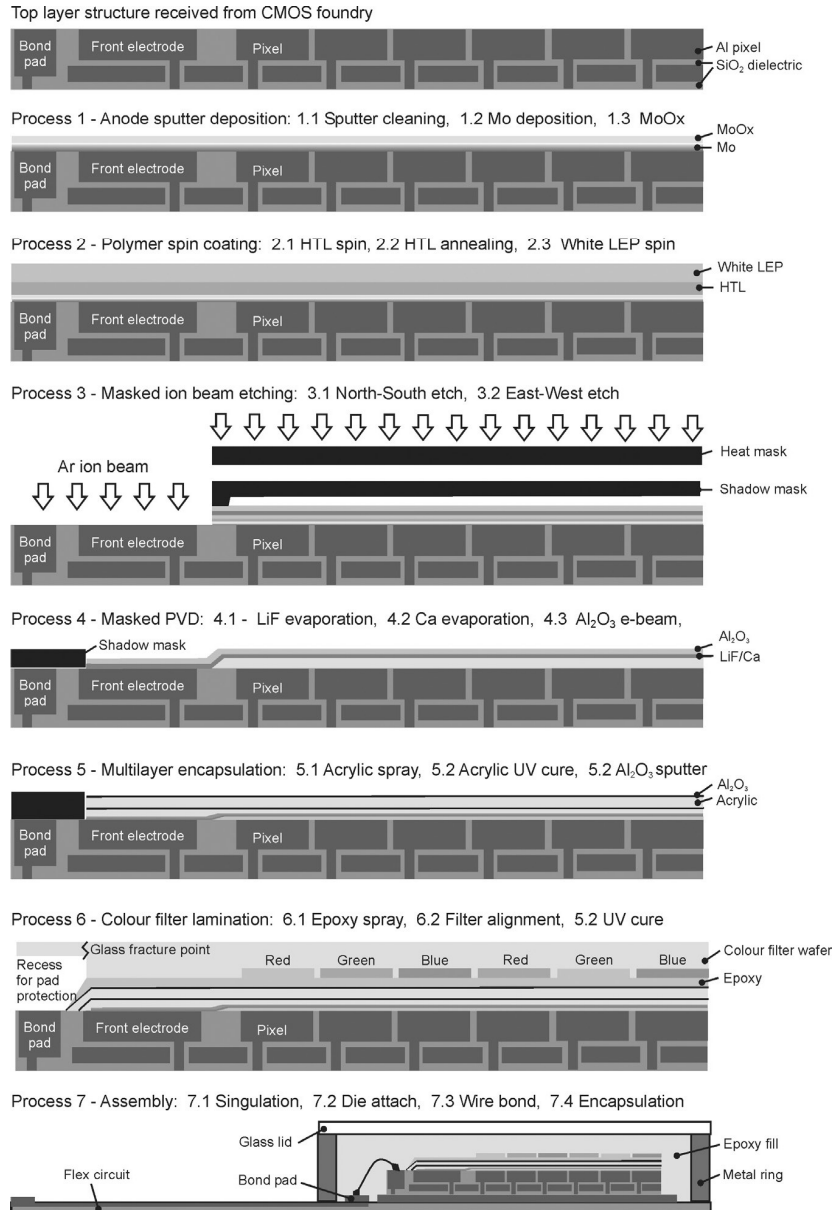
uniform coating of a formulation of visible light curing epoxy resin using methylethylketone as a solvent. A layer of several microns thickness is required such that when the colour filter wafer and display wafer are brought into contact the two wafers can slide across each other to enable precise alignment. A pre-alignment process is carried out under vacuum so that there is no bubble or void formation within the epoxy layer. The fine alignment process is then carried out by a modified anodic bonding tool (manufactured by EV Group) where x, y, z and θ control to less than 500 nm is possible. Finally, once aligned in all dimensions, the wafers are held in place and cured by UV and visible light exposure. The total process is around 15 minutes including 5 minutes UV curing. Visible light curing by the epoxy is important since much of the adhesive lies behind colour filters that strongly absorb UV light. It is also critical that the thermal expansion coefficient of the glass substrate containing the colour filter layers matches the expansion coefficient of the silicon wafer. The use of BK7 glass achieves this requirement.

There are several subtleties in the lamination process that are required. Firstly the bonding pads at the edge of the display die must be accessible following singulation of the wafer into individual display die, and secondly it is desirable to prevent epoxy contamination of the bond pads. While epoxy contamination can be removed by an O_2 plasma process at die level, such an intervention is certainly not desired. The solution to these problems is borrowed from LCD microdisplay production, and is to firstly incorporate relatively wide (100s of microns) recesses in the glass colour filter wafer by partly sawing into the glass above the region where the bonding pads will ultimately sit. The second stage, once the epoxy is sprayed onto the colour filter and after the display wafer and colour filter wafers have been brought together and adhered in place, is during the sawing process that allows the die to be singulated. Rather than sawing colour filter and display wafer in the same lateral location, a partial and offset saw cut is made to both sides of the laminate such that the laminate breaks either side of the recess where the bond pads lie, and the bond pads are opened up for access by the wire bonding tool. Partial sawing of the display wafer and colour filter wafer means that water, required to cool the sawing process, does not enter the recesses of the laminate and is not absorbed by the epoxy. However, the partially sawn laminate requires manual handling in order to break apart the individual display die. It was found that using a soft compliant surface underneath the wafer, and a certain, controlled amount of pressure on the laminate, the die automatically fall apart leaving the bond pads open on the north side of the die, and a lip of glass incorporating the machined recess on the south side.

Subcontract assembly

Once assembled into a laminate of colour filters and display wafer, the product is dispatched to a subcontract partner for singulation into individual display die, and subsequent mounting, bonding and encapsulating on a flexible circuit board that can be incorporated in the mechanical design of a final product.

496 Organic light-emitting diodes (OLEDs)



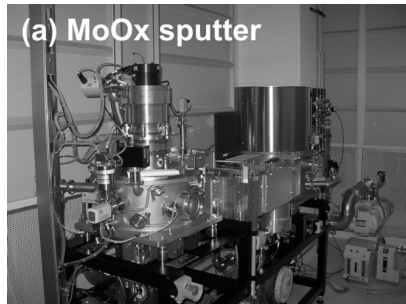
16.21 The MED process flow. Illustrating steps involved in the manufacture of polymer OLED microdisplays from receipt of wafers to packaging of individual display die.

16.5.2 Defects and yield

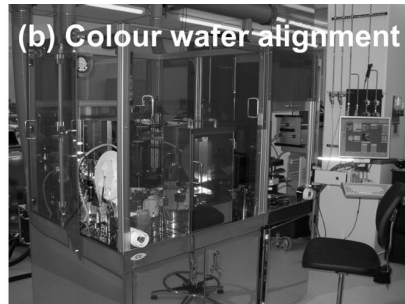
The overall yield of any display manufacturing process is a combination of electronic yield of the display backplane and the yield induced by visible defects once the display is viewed. Furthermore, and of critical importance for an OLED microdisplay, is that a clean defect-free image must be viewed not just at the beginning of a product's operational life but at the end as well. Failure modes for OLED displays are characterized by the growth of blackspots, where oxygen and moisture degrade electrode materials and active organic materials over time. The prevention of visible defects for an OLED display requires a combination of hermetic encapsulation of the device and the exclusion of water and oxygen from within the device. It is the presence of particles that reduces the effectiveness of encapsulation processes and also introduces reactive contamination to the active layers. Eliminating defects is the key to high yielding manufacturing of OLED displays and in this section two case studies of defects encountered by MicroEmissive Displays are presented. The scientific literature is relatively sparse in its reporting of an understanding of the mechanisms and methods for the prevention of defect-related blackspots. In the study by Kim *et al.* (2000) the growth rate of blackspots due to pinhole defects in an Al encapsulation layer used in their devices was measured. The blackspots observed were circular, and growth rate was controlled by the relative area of pristine and degraded regions of the device. The likely degradation mechanism to give rise to these blackspot defects is the oxidation and hydroxylation of low workfunction cathode materials such as Ba, Ca and Li. However, degradation of these materials is not the only mechanism that leads to blackspot formation. In work by Ji-Seon Kim *et al.* (2000) reports of a detailed Raman spectroscopic study of blackspot defects in polymer-based OLEDs is given and a conclusion is made that degradation was due to the de-doping of PEDOT:PSS hole transport material to a resistive rather than conducting layer by electrochemistry occurring between the light-emitting polymer, PEDOT:PSS, cathode materials. Reactive H^+ and OH^- species were associated with water penetration through pinholes in encapsulation layers. While this particular degradation route is specific to the polymer and cathode system of the devices under study it gives an example of the complex chemical processes that can be involved in blackspot formation. More recently, Bulle-Lieuwma and van de Weijer (2006) examined a polymer OLED device following stress applied for 500 hrs using surface science techniques that could measure the elemental composition of defect with vertical spatial resolution.

They concluded that the formation of Al_2O_3 clusters at the polymer/Ba/Al interface rendered the cathode interface insulating. While the solution to all three of these mechanisms is the improvement of encapsulation to prevent oxygen and water ingress to the active layers, the different conclusions illustrate that precise nature of the degradation chemistry is not simple.

MED observed many different characteristic blackspot defects during its device and process development and manufacturing. Typically, but not always, blackspots



(a) MoOx sputter



(b) Colour wafer alignment



(c) Looking down the cleanroom



(d) PVD cluster tool I



(e) PVD cluster tool II

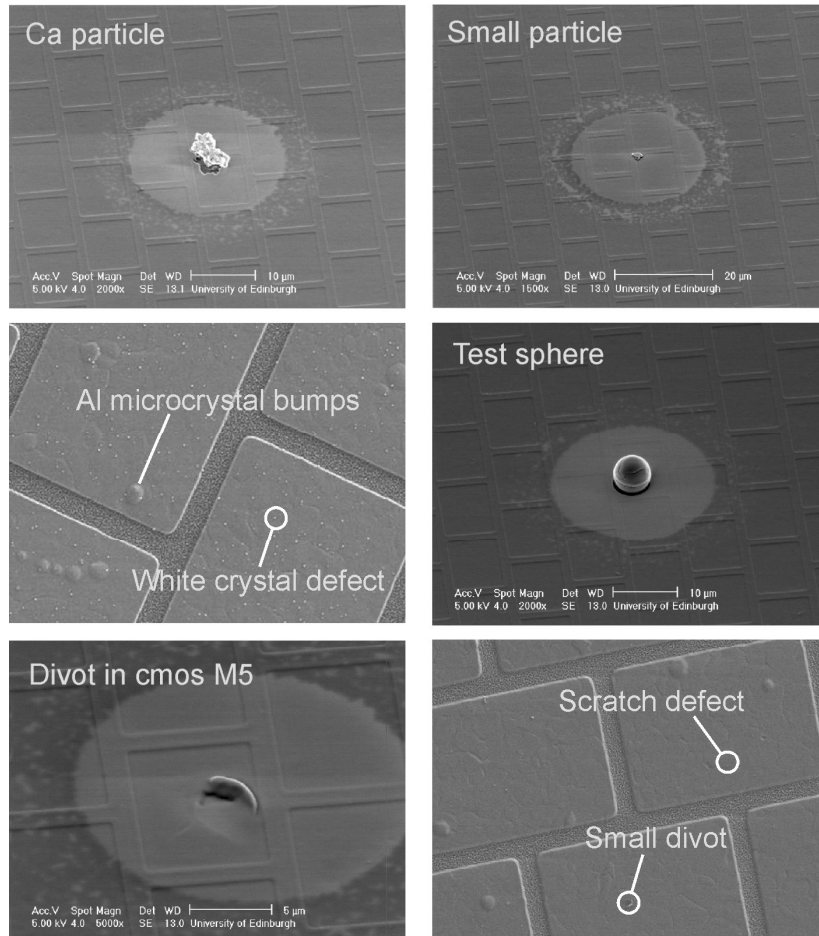
were associated with a visible defect on the wafer surface or deposited at a subsequent point in the process. Figure 16.23 illustrates some of the different defects that were discovered. The images are taken by SEM and the non-emissive region relating to the hydroxylation of the Ca cathode is visible by a contrast in image. All these particle defects give rise to a circular non-emissive blackspot, sometimes with a small halo surrounding it. The halo does emit light and its origin is not understood. The pixels in these images are 8 microns wide and 10 microns long.

Ca crystal defects

The first defect to be discussed in detail is one arising during the deposition of Ca metal in the cathode process. It was found that large and crystalline defects (shown in Fig. 16.23 and in Fig. 16.24) resulted from spitting during the thermal evaporation of Ca from open crucible sources. To achieve deposition rates required for OLED device fabrication of <1 nm/s, Ca must be sublimed. The lack of a molten surface gives rise to gas pressure pockets in the particles of Ca and the release of the pressure results in sparse but relatively large particles of Ca. The presence of a significant number of similar crystal-like particles (Fig. 16.23) was identified using a combination of particle identification using laser scattering and SEM-EDX. While expensive, this method of correlated one-by-one particle identification and inspection is the only way that large areas of substrate with very few defects can be investigated. A TEM section of one such particle is shown in Fig. 16.24. The EDX profile images show that the particle is Ca. The other layer structures: dielectric SiO_2 , Al metal electrodes, Al filled via, and C containing polymers are also highlighted by the EDX. The Pt capping layer is required for the sectioning process.



16.22 A photograph of the MED manufacturing line. (a) A two-chamber PVD tool is shown. In the far chamber Ar sputter cleaning removes native oxide from the Al pixels and in the near chamber Mo and then MoOx are sputtered with a pulsed DC power source. (b) CMOS and colour filter wafers are laminated together with sub-micron precision across the 200 mm wafer diameters. The process tool includes an epoxy spray station, a vacuum chamber for mechanical pre-alignment, a precision alignment station and a UV cure station. (c) A view along the cleanroom, notably during tool installation and qualification. Metrology equipment is seen on the right side of the cleanroom: back right, wafer probers for wafer level test; middle right, spectroscopic ellipsometer for film thickness measurement; and front right, particle counting equipment. At the back left is the colour filter lamination tool and at the front left is the loadlock to the MoOx sputter tools. (d) and (e) show PVD equipment for etching, cathode and encapsulation deposition. (d) shows the aluminium oxide sputter chamber for the multilayer encapsulation process; (e) shows two ion etch chambers, a thermal evaporation chamber and an electron beam evaporation chamber.

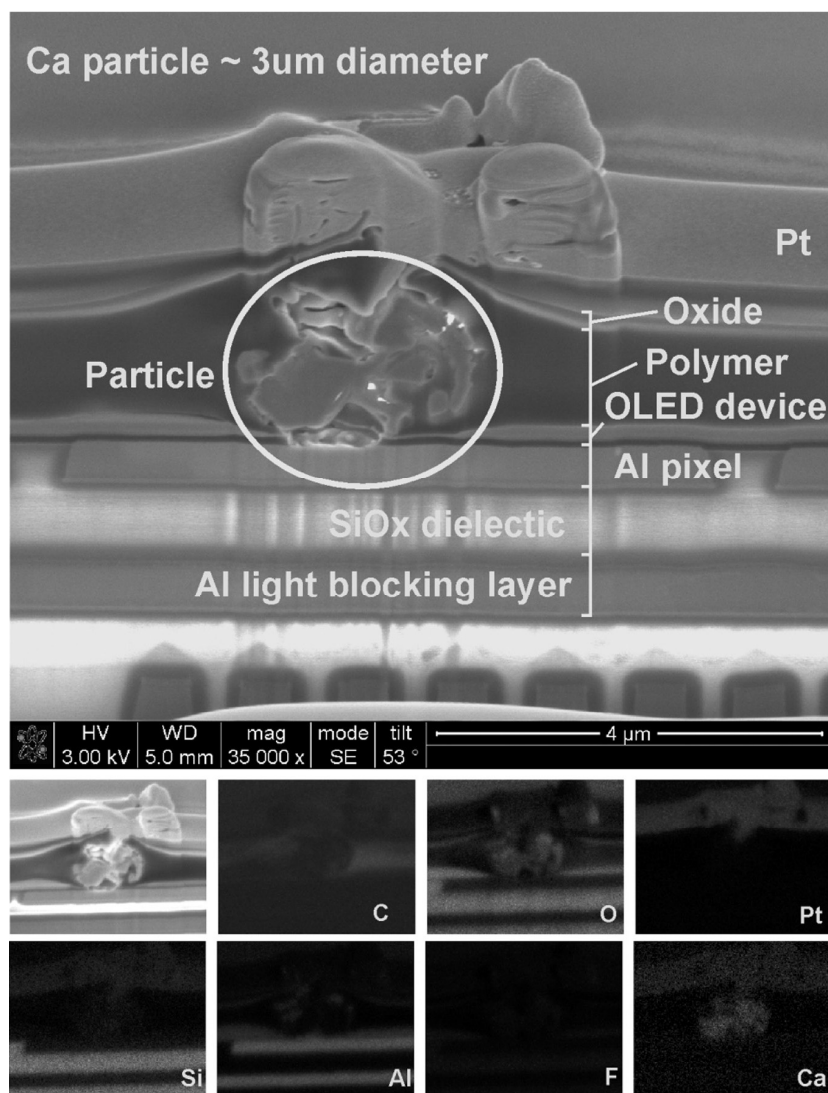


16.23 Different defect types present in the MED manufacturing process. Defects can be added to the wafer surface or present within the wafer surface. Both types are a risk for blackspot formation.

A solution to the Ca particle problem was found by preventing direct line of sight from the material and the wafer. A baffled Mo boat (see Fig. 16.26) was used and the Ca defect problem was eliminated.

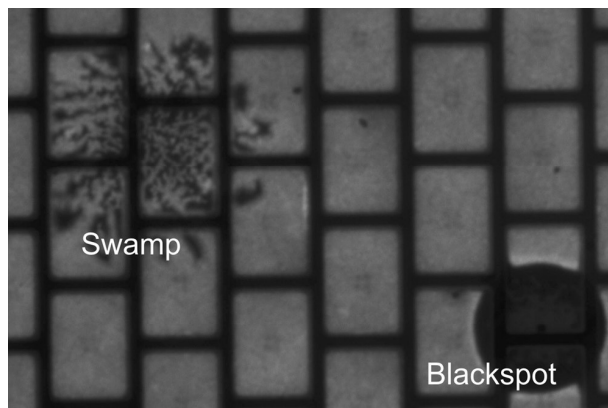
Swamp defect

The second type of defect that is described in detail is one that ultimately was not understood or completely controlled in MEDs manufacturing process. It was not



16.24 TEM section image through a Ca particle defect with EDX elemental analysis below.

associated with a particle but did result in blackspot formation following accelerated environmental ageing. The defect was therefore latent and placed at risk the long-term stability of MED's product. The defect was termed 'swamp defect' by those working on it and this is the term we shall use to refer to it in this section.



16.25 Electroluminescence image of swamp defect and a particle blackspot defect. The luminance uniformity within each pixel can be seen. A slight reduction of luminance is observed due to the thickening of the polymer films over the slight dimples caused by the via filling between metal 4 and metal 5 layers; non-emissive microspots are also seen within some pixels corresponding to micro-defects in the Al layer, either as insulating surface defects such as the white crystals seen in Fig. 16.23 or an other non-conducting surface contamination. The swamp defect is seen to be crystalline and not completely non-emissive.

Swamp defect was characterized by a non-circular, crystalline appearance and its presence was strongly related to the LiF layer in the device see Fig. 16.25 for a comparison between the electroluminescent appearance of blackspot and swamp defect. Removing the LiF layer eliminated swamp but made the device far more sensitive to other defect types. LiF, as explained in sections 16.2.3 and 16.2.4, is also required to achieve operating voltage, efficiency and lifetime performance. Swamp defect was also modulated by a number of other factors in the process, the most significant being the intimacy of the wafer with surfaces in the cluster tool vacuum system for etch of polymer and deposition of cathode layers. Many observations of the distribution of the defect density showed modulation with the proximity to chamber components including shadow masks, wafers handler and even chamber shield components.

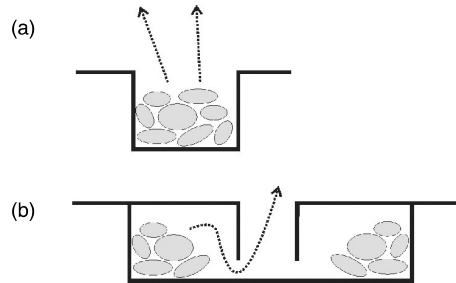
Only once was a manufacturing strategy introduced to control the defect. The LiF thickness was increased from 2nm to 4nm. This increase resulted in a catastrophic decrease of the luminance stability on accelerated environmental stress and LiF thickness quickly reverted to 2nm. Other methods that were developed to partially control swamp were: changing the LiF deposition source and material once the defect was observed; changing the LEP solution batch; changing Ca material and source; and reducing the etch temperature. None of

these solutions were guaranteed to work but all showed step changes in the presence of swamp at one time or another. Fortunately swamp defect was a rare occurrence for product produced on the MED production line, and was only once observed at all: an alteration in the frequency and method of mask cleaning introduced the defect on certain wafers.

One engineering solution to eliminate the defect was known to work. The implementation of an oxygen plasma process following the deposition of the polymer layers, to etch several nanometers from the LEP before processing in the cathode in the vacuum cluster tool. This method was shown to be successful in several repeat trials. The oxygen plasma modifies (through oxidation) the surface of the polymer in order to promote better adhesion between the thin LiF film and the LEP. The plasma is also likely to remove physically and chemically adsorbed species from the polymer surface, and also result in chemical defect sites (fluorenone sites for example) on the polymer surface. These different possible chemical modifications make the exact reason for the elimination of swamp defect difficult to deduce. The change in the interface chemistry due to oxidation does not appear to damage the bulk of the LEP, as device colour and performance are similar with and without plasma exposure. However, some loss of device performance is experienced, and along with the cost and timescale involved, this solution was not implemented.

The most likely strategic solution would have been to replace LiF from the device. A significant amount of work was carried out to look at alternative alkali metal salts as a direct replacement to LiF. The conclusion of this work, of which some of the results are explained in sections 16.2.3 and 16.2.4, is that no replacement was available with better or similar device performance to LiF.

One particularly interesting investigation of swamp defect utilized Raman microscopy is to map the difference in vibrational spectra of the underlying light-emitting polymer material. In Fig. 16.27 swamp defects, a particle induced blackspot defect and an un-degraded cathode region are compared. The vibration signature at around 1600cm^{-1} associated with in-plane backbone stretching of fluorene polymers (Ariu *et al.*, 2001) is seen to be an overlap of two peaks in all of the spectra. In the particle induced blackspot, where we suspect degradation is due to hydroxylation of the Ca cathode, the polymer under the degraded region exhibits equal strength from the two component peaks, whereas the polymer under the undegraded cathode shows a smaller contribution from the high energy peak. In the case of the swamp defect there is no difference in the characteristics of the 1600cm^{-1} peaks between the defect region and the undegraded background. The background intensity of the Raman spectrum is higher, and the microscopy image shows greater intensity, for both types of defect, in the defect regions due to higher reflectivity of the sample from the Al electrode. This adds weight to the hypothesis that the Ca in these regions has been oxidized or hydrolized becoming transparent. However the difference in the 1600cm^{-1} peak structure between swamp defect and blackspot defect shows that



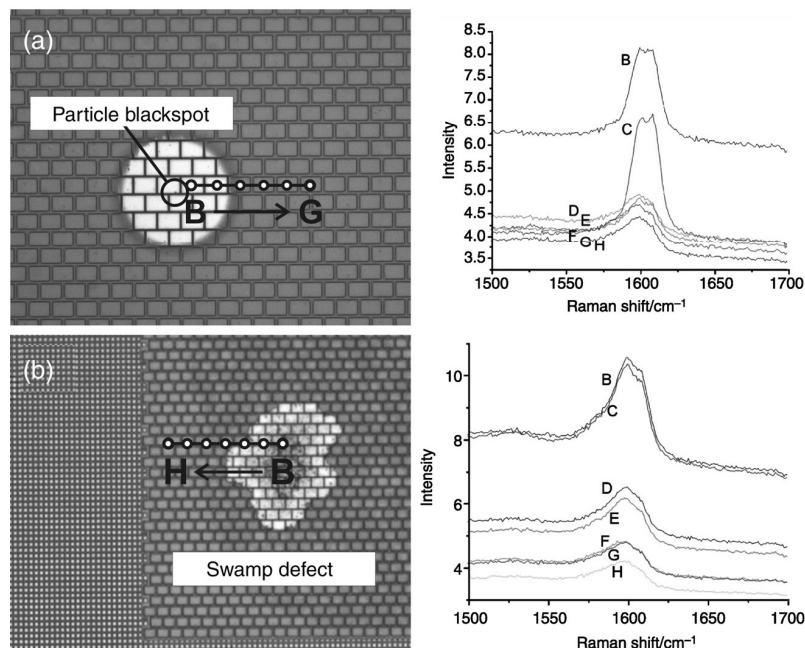
16.26 Alternative designs of Ca evaporation source. (a) Results in high density of particulates (b) controls particulates to a minimum by confining deposition vapour to that having diffused out of the baffle structure.

there is a chemical difference, possibly induced by differences in the LiF layer that explains the origin of the swamp problem.

16.5.3 Quality and testing

Our discussion of microdisplay manufacturing will be concluded with a short explanation of test and quality issues. As highlighted many times by those working in the development and implementation of testing methods at MED, the objective of any test department is to not have to test anything! The point being that once a manufacturing process is completely stable, all product will achieve specification and there is no need to test. The reality of developing a new technology and product is far from the zero test ideal. Test data not only allows non-conforming product, of which there is plenty, to be scrapped, it also gives important information regarding the performance of the manufacturing line, and indications of failure and instability. Financial forecasts rely on overall yield predictions and on return rate of parts failing in the field. The management of test methods and the analysis of test data is an important and complex task, especially for a product and process that are new and still under development.

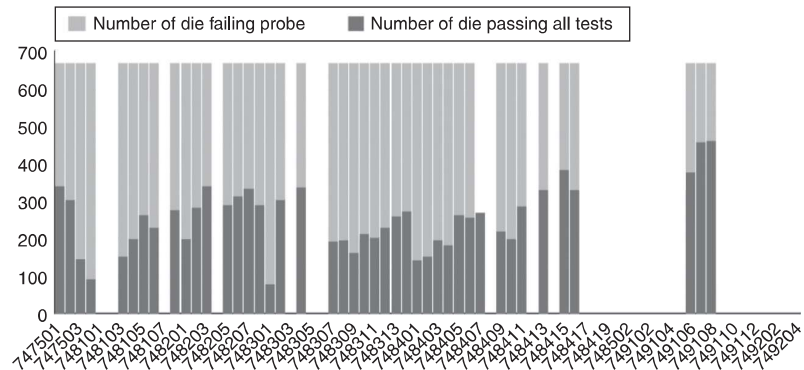
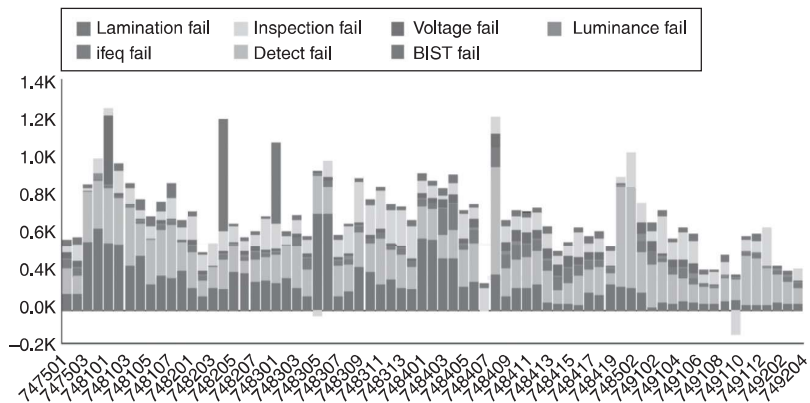
MED implemented three types of testing. Firstly each display die was tested at wafer scale to firstly give prompt feedback regarding the electronic yield status of incoming wafers, secondly to give prompt feedback regarding the production line and finally to identify non-conforming displays that could be discarded prior to assembly. There is a large cost associated with assembling and packaging large quantities of non-conforming displays and this was saved by individually marking non-conforming die at wafer scale for discard later. At the wafer test point electronic functionality (BIST in Fig. 16.28), luminance, operating voltage, leakage current (ifeq in Fig. 16.28) and defect density were measured. Two



16.27 Raman microscopy of defects. (a) The Raman spectroscopic profile of the 1600 cm^{-1} transitions for a blackspot defect due to a particle and subsequent cathode degradation from moisture ingress. (b) A similar profile for a swamp defect.

manual inspections were also incorporated in the overall test. One prior to lamination to identify poor etching and one post lamination to identify voids in the lamination epoxy, bond pad coverage or poor colour filter alignment. (These two inspections are identified as 'inspection fail' and 'lamination fail' in Fig. 16.28.)

The second product test point was following assembly and packaging and included a similar set of tests to those implemented at the wafer test point, but also colour points for red, green and blue test images were used. This final test determined conforming product that was shipped to customers. A summary of the specifications, yield at wafer test and final test process capability for MED production in 2007 is given in the table in Fig. 16.28. (Unfortunately a more comprehensive set of data showing yield progression to a maximum wafer yield of 70% and a typical monthly average yield of between 40% and 50% could not be retrieved for this chapter.)



	Mean	1 sigma	LSL	USL	Cp	Cpk lower	Cpk upper
Luminance	117.82	21.33	90.00	165.00	0.59	0.43	0.74
W CIE_x	0.2797	0.0140	0.25	0.34	1.07	0.71	1.43
W CIE_y	0.3054	0.0134	0.26	0.34	0.99	1.13	0.86
R CIE_x	0.5777	0.0233	0.50			1.11	
G CIE_y	0.4975	0.0195	0.46			0.64	
B CIE_{x+y}	0.2931	0.0245		0.36			0.91

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16.28 An extract from the monthly MED manufacturing report for December 2007. The display yield and failure pareto for each wafer is shown in the top two charts. The lower table charts the conformance of product based on final test data. The product specification, for optical characteristics, are shown as lower, LSL and upper, USL, specification limits and process capabilities, C_p and C_{pk} values are calculated based on a 6σ tolerance. Note that red, green and blue colour points in CIE 1931 space are single-sided specifications since a display cannot be too saturated in any of these colours.

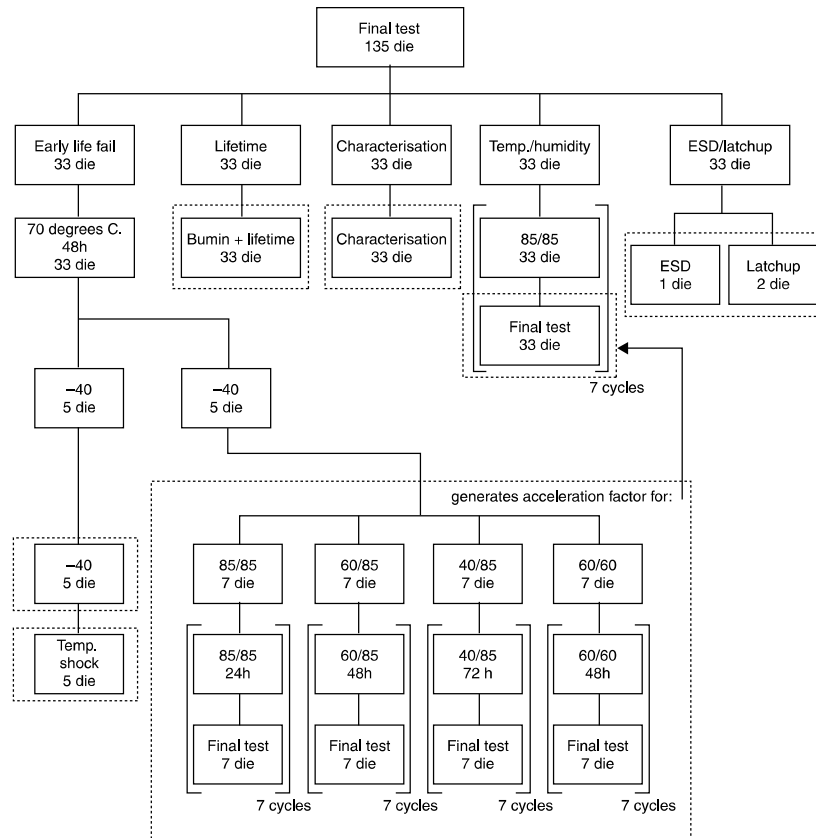
The third type of testing implemented was an accelerated ageing of a sample of displays from each wafer. Accelerated ageing was able to uncover encapsulation issues that would result in product failure in the field. Two displays from each wafer were tested at 85°C and 85% relative humidity for seven days. Each day a final test protocol was run on the displays and failures tracked. An expanded set of environmental and lifetime testing was also implemented to qualify a particular CMOS electronics revision or manufacturing process change. This qualification process is outlined in Fig. 16.29. The use of several different accelerated environmental conditions was able to determine an acceleration factor for degradation for the 85/85 sample test condition. Extended operational lifetime testing was included in the qualification protocol, however as noted in Section 16.3, the interpretation of steady state lifetime testing to measure actual product lifetime was more or less impossible and additional qualification using the custom-developed stochastic cycle test was eventually implemented. The qualification protocol also included standard qualification microelectronics tests such as electrostatic testing (ESD) and thermal shock testing.

Mechanical failure of the packaged displays typically resulted from delamination of adhesive bonded surfaces in the device. Limitations to the temperature that could be used to process die attach and other adhesives meant special materials needed to be used that were less reliable in bonding than more standard thermally cured microelectronics adhesives. While these delaminations did not necessarily result in failure of the OLED in the device, they did represent a package level failure that could not be tolerated in a product.

16.6 Conclusion and future trends

OLED on CMOS microdisplays provide an ideal match with a range of consumer markets such as personal viewers for watching film and TV, digital viewfinders for cameras and camcorders, accessories to mobile phones, and ultimately displays for viewing high information content from PCs. OLED microdisplay technology offers high levels of electronic and optical integration, very low power consumption and impressive image quality. In particular the image quality is perceived as higher than other NTE microdisplays due to high pixel fill factor ($>70\%$), fast switching speed ($\sim 5\ \mu\text{s}$) allowing for high refresh rates (up to 120 Hz in ME3204), extremely high intrinsic contrast ratio due to the emissive nature of display, and an unsurpassed clarity of image due to the simple and direct nature of the optical viewing system. An extremely small form factor can be achieved as the need for an external light source is removed, resulting in a single, simple package that can be integrated into many consumer products with ease.

It has been shown how MicroEmissive displays developed a device architecture and manufacturing process by negotiating a range of often conflicting issues relating to the integration of polymer OLED device, CMOS microelectronics and information display requirements. This account details processes and decisions



16.29 A chart illustrating the MED qualification protocol for display product. The range of environmental testing is required to calibrate an acceleration factor for the standard 85/85 testing used as a production sample.

that are not often documented and it is hoped that the learning from MEDs experience can be recorded such that, if at some point in the future there is an overwhelming demand for a high volume of low cost near-to-eye information displays, this record could help to implement a manufacturing process to produce them. In the meantime it is hoped that the examples given can provide a useful and interesting reference for other organic electronics manufacturing development.

16.7 Acknowledgements

Thanks are due to all those who worked for MED over the period 2000 to 2008. The enthusiasm, camaraderie and conflict of a start-up company with ambitions

for a worldwide, high volume consumer product are something quite amazing. The hard work and commitment from the supply chain is also acknowledged: Cambridge Display Technology, Sumitomo Chemical, Dow Chemical, Varitronix, Toppan, Dai Nippon, Advanced Neotech Systems, Vitex Systems, Scottech, Star Technology and many more.

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Abstract: Displays based on organic light-emitting diodes (OLEDs) are currently entering the market predominantly in mobile applications. In the future, OLED displays could even be transparent, which will enable a large number of applications that are beyond the reach of current display technologies. In this chapter we will have a closer look at AMOLED concepts and will address the technology behind transparent OLEDs. Approaches to achieve a transparent encapsulation for transparent OLEDs will be discussed. Finally, the recent progress in transparent driver electronics required for transparent AMOLED displays will be discussed.

Key words: transparent OLEDs, transparent thin film encapsulation, metal-oxide thin film transistors, see-through displays, active matrix backplane.

17.1 Introduction

In recent years, display technology has entered almost every part of our lives. As a human-machine interface, displays have become the central component of cellular phones, portable navigation systems and large area flat screen TVs, just to mention a few examples. The vast majority of these displays rely on liquid crystal technology and a steady improvement has led to higher resolutions, more brilliant images and lower energy consumption. Nevertheless, displays based on organic light-emitting diodes (OLEDs)¹ are expected to offer substantial advantages. As they do not require any backlighting at all, OLED displays offer outstanding levels of contrast, and can be viewed from every angle. They can be as thin as the substrate used, and even bendable devices have been introduced. Compared to established technologies, a further reduction in both energy consumption and also production cost can be expected. There are an increasing number of products where the display today is already based on OLED technology (e.g. cellular phones, digital cameras, etc.). In the future, three-dimensional (3-D) displays are expected to benefit from the high switching speed of OLEDs.

Transparent displays have received considerable public attention at recent showcases. There are applications where transparent displays or signage are very attractive and bring about additional benefits. In the off-state, a transparent display may appear as an ordinary window being just see-through. If activated this transparent device may be used to directly display information without the need

for bulky projection technology. Transparent displays could be integrated in the windows of vehicles in public transport (buses, trains, etc.) to provide information for an augmented reality of the outside world. There are countless design elements (e.g. in the automotive industry, hotels, public space, stores, etc.) which only become possible by using a see-through display.

When integrated in goggles, helmets or windshields they could be used to display essential information or warning messages that might help to save lives in road traffic or assist professionals in their job (e.g. surgeons, police or firefighters, etc.).

LCD technology is of limited use for the realization of transparent displays. As it requires an external light source and additional optical elements like polarizers and color filters, the overall maximum transmissivity is severely compromised. Other techniques, such as semi-transparent inorganic electroluminescent (EL) displays were proposed several years ago.² However, they have fundamental shortcomings such as high operating voltages ($\sim 200\text{ V}$) and low levels of achievable brightness ($\sim 100\text{ cd/m}^2$), limiting their day-time visibility. According to a standard released by the US Department of Defense, a transparent display would be required to provide at least a brightness of 5000 cd/m^2 for proper perception at daylight.³

Notably, OLEDs require only low operation voltages ($\sim 2\text{--}4\text{ V}$) and are readily capable of high brightness levels of 10000 cd/m^2 and higher. At the same time efficiencies in the order of 110 lm/W have been reported.⁴ Therefore, they appear the perfect building blocks of bright transparent displays. Owing to the large achievable Stokes shifts between absorption and emission in organic light emitting materials, OLEDs can be designed to transmit more than 80% of visible light.^{5,6}

The first transparent OLEDs were reported in 1996.^{7,8} Soon after that, an entirely transparent passive matrix OLED (PMOLED) display was demonstrated.⁹ For larger area high-resolution displays the active matrix (AM) driving scheme is mandatory. State of the art AM backplane electronics for LCD displays is based on amorphous silicon (a-Si).¹⁰ Since OLEDs are current driven devices the driving circuit will occupy a considerable amount of the pixel area. If the opaque silicon-based driver electronics occupies a substantial part of the active pixel area the overall transmittance is severely limited. Early reports using $\alpha\text{-Si}$ TFTs and transparent OLEDs led to 'transparent' displays with a transmissivity of only 20%.¹¹ Very recently, a transparent 14-inch AMOLED display has been shown using a backplane based on low-temperature polycrystalline silicon (LTPS).¹² The transmissivity in this case was somewhat higher but still only 38%. These figures are not sufficient for several applications (e.g. automotive windshields).

Recently, pixel driver electronics based on transparent TFTs has been envisaged.^{13,14} This novel branch of electronic thin film devices relies on metal oxide semiconductors which allow for TFTs with a transmissivity of more than 80% throughout the visible part of the spectrum. The first transparent AMOLED

displays using Indium Gallium Zinc Oxide (IGZO) TFTs as pixel drivers have been demonstrated^{15,16} and several prototypes of transparent AMOLED displays have already been shown by the industry at various consumer electronics tradeshows. Therefore one can be optimistic to see this exciting technology in real products in the near future.

In this chapter we will have a closer look at AMOLED concepts and the underlying device physics. In Section 17.2 we will address the technology behind transparent OLEDs; approaches to achieve a transparent encapsulation for transparent OLEDs will be discussed in Section 17.3; and finally, in Section 17.4 we will give an overview of the recent progress in transparent driver electronics required for transparent AMOLED displays.

17.2 Transparent OLEDs

Since most OLED-relevant semiconductors provide a large Stokes shift along with low intrinsic absorption losses, highly transparent OLEDs across the visible spectrum can be realized by employing transparent bottom and top electrodes. It turns out that the main technological challenge is the deposition of a transparent top electrode. In the following we introduce and discuss various concepts to realize transparent OLEDs.

17.2.1 Indium tin oxide

Today, indium tin oxide (ITO) is the most commonly used transparent electrode material. A 100 nm thick ITO layer shows a transparency above 80% in the visible part of the spectrum and concomitantly provides a low sheet resistivity of 20 Ω/sq . Those high quality ITO films are only obtainable through plasma-assisted deposition techniques such as sputtering, which is the established high-throughput process for uniform large area coating. However, the sputtering process can damage the OLED.^{8,17} One of the main impacts are sputtered In, Sn and O particles with a high kinetic energy. Another severe damage can occur from O^- ions which are accelerated towards the sample by the negative bias potential of the ITO target.¹⁸ Moreover, UV radiation and elevated temperatures during the sputtering process can deteriorate the OLED.¹⁹ Thus, buffer layers are necessary to protect the organic layers of an OLED against the particle bombardment during the sputter deposition of the top electrode. There are several requirements for such a buffer layer. Besides an effective protection, high transparency in the visible region and sufficient electrical conductivity are mandatory. In addition, the buffer layer should facilitate efficient charge injection from the ITO electrode into the organic transport layer. And finally, the buffer layer should form pin-hole free, homogenous thin films accomplishable with established and gentle large-area coating techniques. Several buffer layer concepts have been introduced which are discussed in the following.

Semitransparent metals

In 1996 Gu and co-workers reported the first transparent OLED using a semitransparent metal as ITO sputtering buffer.⁸ This report shows clearly the trade-off between transparency and protective properties. It was demonstrated that a semitransparent Mg-Ag alloy buffer layer can protect an Alq₃-based conventional OLED against a very gentle RF sputtering process (5 W, deposition rate 0.05 Å/sec). Still, devices with a Mg-Ag thickness of less than 75 Å were mostly shorted. For device with Mg-Ag thickness of 100 Å and more, working transparent OLEDs could be realized. However, the transparency dropped exponentially with increasing thickness of the Mg-Ag layer. Practically, the overall device transparency was only 40%. Note, several transparent displays, e.g. for automobile windshields, require a minimum total transmittance of 70% for safety reasons. Thus, to realize fully transparent OLEDs the thickness of the metal buffer layers is restricted to a very thin layer which can lead to insufficient protection against the ITO sputtering process.

Organic materials

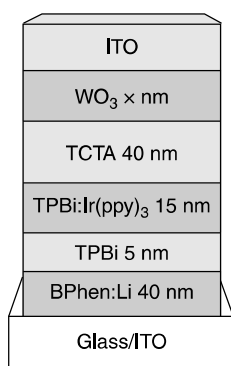
The use of an organic buffer layer, e.g. copper-phthalocyanine (CuPc), was first reported by Parthasarathy in 1998.²⁰ The conventional OLED showed a high overall transparency of 85% where the primary source of absorption is due to the 30–60 Å thick CuPc buffer. The effective sputtering protection was attributed to the extended π -system of CuPc molecules, which distribute the energy of impinging particles over several bonds. Yamamori and colleagues identified metal acetylacetonate complexes such as Mg(acac)₂, Ca(acac)₂, and Ni(acac)₂ as effective sputtering buffer layers.²¹ The best results were obtained with Ni(acac)₂ which was attributed to a dense and robust stacking structure, due to Ni-Ni bonds and an improved electron injection because of the formation of mid-gap states, analogous to CuPc buffer layers. Since those metal acetylacetonate complexes show almost no absorption in the visible region, devices with a very high transmittance of around 90% have been achieved. An inverted structure with pentacene buffer layer was demonstrated by Dobberty *et al.*²² In this study it was evidenced that the device performance is strongly coupled to the thickness of the pentacene buffer. An optimum was found at around 40 nm of pentacene. For thinner layers the protection was insufficient whereas for thicker layers optical absorption in pentacene limited the overall device performance. The best organic buffers are planar molecules with high packing density forming a polycrystalline structure. However, the surface morphology deteriorates the ITO film growth on top of these layers and consequently limits the transparency and conductivity of the TCO.²³ Dobberty and colleagues demonstrated that a spin-coated PEDOT:PSS layer on top of pentacene can lower the roughness and forms an effective hybrid buffer layer with ohmic hole-injection properties.²⁴ Here, the hydrophobic nature of pentacene prevents water penetration from the aqueous PEDOT:PSS dispersion

into the underlying organic layer. Transparent phosphorescent OLEDs with a hybrid pentacene/PEDOT:PSS buffer layer reached decent efficiencies of 32.5 cd/A and 12.2 lm/W at 100 cd/m² at an overall transmittance of around 75%. Although the hybrid buffer layer shows reasonable results, the vacuum break and the water introduced by the PEDOT:PSS wet process cause severe limitations as far as manufacturing is concerned.

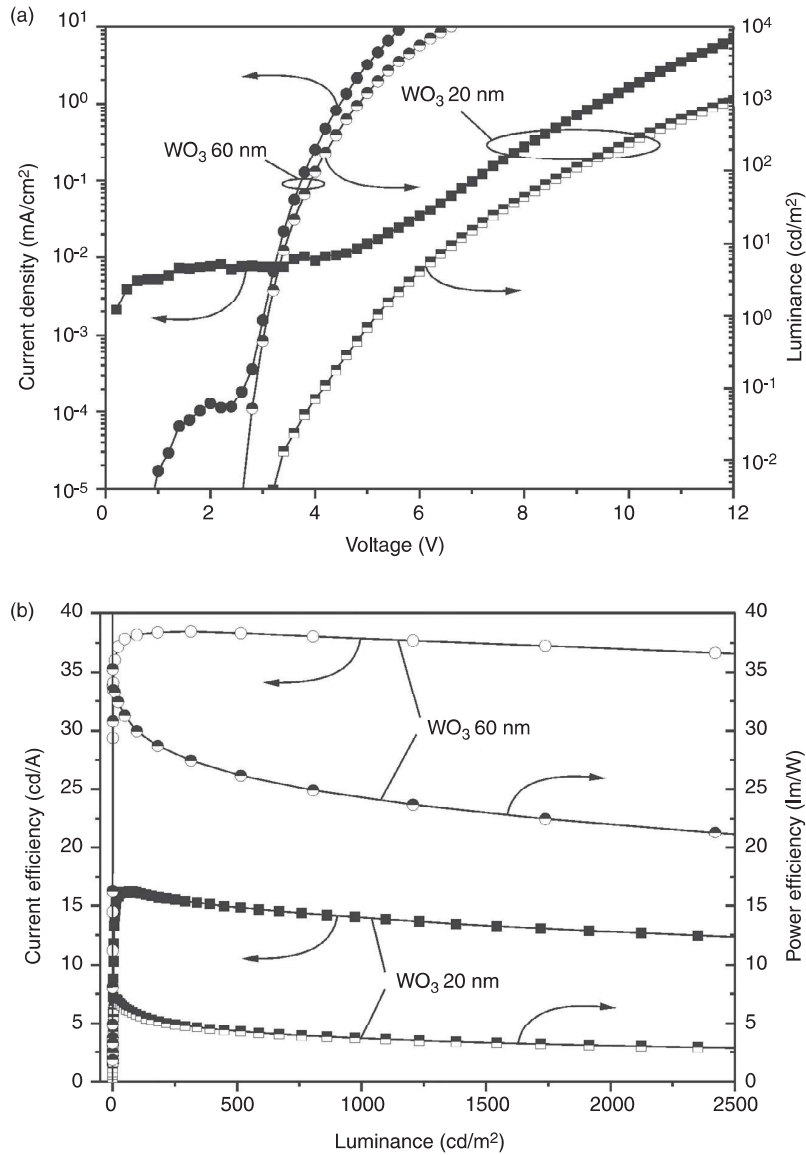
Transition metal oxides

More recently, transition metal oxides (TMOs) such as MoO₃, V₂O₅ and WO₃ have been introduced as sputtering buffer layer.⁶ In the following the properties of an inverted OLED with WO₃ buffer layer, as illustrated in Fig. 17.1, are discussed. The corresponding *L-I-V* characteristics are shown in Fig. 17.2.

WO₃ films with a varied thickness were thermally evaporated from a Knudsen cell. A 60 nm ITO thick electrode was sputtered on top using an optimized RF magnetron process at very low power levels of 0.16 W/cm² for the first 5 nm followed by a higher power level of 0.56 W/cm², yielding deposition rates of 6 nm/min. Figure 17.2 shows that a thin WO₃ layer (20 nm) is not sufficient to protect the underlying OLED against the particle bombardment from the sputtering process. A high leakage current and a rather low current and power efficiency were observed. Devices without WO₃ layer were mostly electrically shorted. In contrast, transparent OLEDs with 60 nm thick WO₃ layer showed a very low leakage current, and high efficiencies of 38 cd/A and 30 lm/W at 100 cd/m². The overall transmittance of those devices was higher than 78% in the visible region, even without the use of anti-reflecting coatings. Note, the low leakage current is comparable to that of conventional OLEDs with metal top contact.²⁵



17.1 Device structure of a transparent OLED with ITO bottom and top electrode. The thickness of the WO₃ buffer layer has been varied.



17.2 (a) Current density–voltage and (b) current efficiency–luminance characteristics of transparent OLEDs with 20 nm and 60 nm WO_3 buffer layer thickness.

To understand in more detail the role of the WO_3 buffer layer the ITO penetration depth was analyzed via secondary mass spectrometry (SIMS) measurements. To avoid In migration driven by the SIMS process the measurements were taken from the backside of a SiN membrane substrate. From the In concentration profile the ITO penetration depth was estimated to around 40 nm (Plate IX, see colour section between pages 414 and 415). The high leakage current observed for OLEDs with 20 nm WO_3 buffer layer can therefore be attributed to ITO particle penetrations deep into the transparent OLEDs. By increasing the WO_3 layer thickness to 60 nm, ITO particles are blocked by the WO_3 layer and an effective protection is provided. A structure analysis revealed that the WO_3 layer is composed of a nano-crystalline structure with grain sizes of 3–5 nm. It was therefore proposed that a WO_3 layer protects the OLED against the high kinetic particles due to a high cross-section and high collision-stopping power.

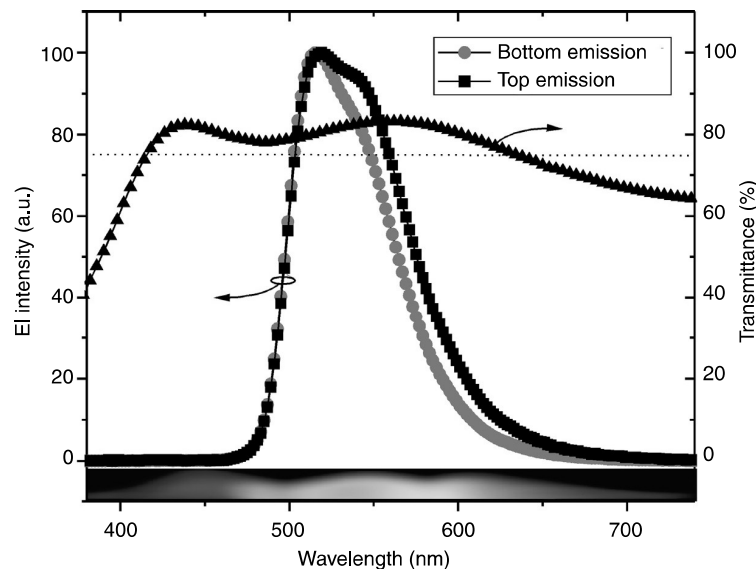
Similar results have been observed for MoO_3 as a sputtering buffer layer in organic solar cells by Schmidt *et al.*²⁶ Besides the effective sputtering protection, TMOs such as MoO_3 , V_2O_5 and WO_3 are also very efficient hole-injection materials. They exhibit very deep lying electronic states and are highly n-type doped due to oxygen vacancies.²⁷ The electron affinity, work function and ionization energy of WO_3 was measured via photoemission spectroscopy to values of 6.5 eV, 6.7 eV and 9.7 eV, respectively. In addition, energy level alignment studies of WO_3 /TCTA have revealed a large interface dipole which leads to a downwards shift of the vacuum level from WO_3 to the organic film, and the Fermi level is pinned close to the TCTA highest occupied molecular orbital (HOMO) level.²⁸ Electrons can easily overcome this energy barrier from the TCTA HOMO to the WO_3 conduction band (CB). Consequently, it has been proposed that the mechanism of the efficient charge injection via WO_3 occurs via an electron transfer for the HOMO of TCTA to the CB of WO_3 , a process which is also known as ‘charge generation’ in tandem OLEDs. The very large WF of TMOs such as MoO_3 , V_2O_5 and WO_3 allows for a direct hole-injection into organic hole-transport materials with large ionization energy such as TCTA.²⁹ This has led to a simplification of the OLED stack which is highly desirable in terms of processability and fail-safe manufacturing. Very recently, liquid processing of TMO has been demonstrated, which is another milestone for large-scale and high-throughput production of organic electronic devices.³⁰

17.2.2 Alternative TCOs

In view of the limited Indium resources worldwide the search for TCOs to replace ITO is of particular importance today. A very promising alternative is Al doped ZnO (AZO), because it is an inexpensive, non-toxic and abundant material with electrical and optical properties comparable to those of ITO. AZO films have been prepared by various deposition techniques such as sputtering and atomic layer deposition as bottom electrode. With pulsed laser deposition (PLD), high quality

AZO films with conductivities in the range of 2800 S/cm (sheet resistance 27 Ω /sq for a 130 nm thick film) can also be grown at room temperature which is important especially for the deposition of AZO electrodes on top of organic layers.⁵ Analogous to the sputtering process high kinetic energy particles emerging in the PLD process can damage the underlying OLED. As before, a TMO-based buffer layer has been identified as effective protection against the particle impact.⁵

The corresponding transparent OLED exhibits efficiencies of 27 lm/W and 44 cd/A at 100 cd/m². Figure 17.3 shows that the average transmittance in the visible region is around 73% whereas most losses are due to reflection at the multilayer OLED structure. The electroluminescence spectra, also given in Fig. 17.3, indicate that micro-cavity effects affect the out-coupling through the bottom and top contact. Without an additional capping layer nearly 70% of the emitted light is extracted through the bottom AZO electrode.



17.3 EL intensity and transmittance characteristics of an OLED with AZO bottom and top electrode.

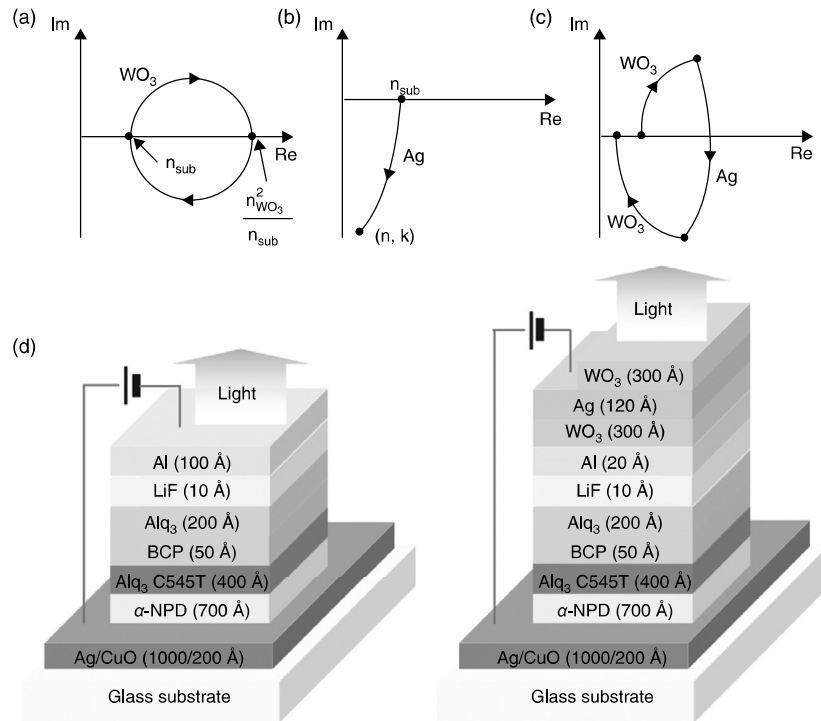
17.2.3 Multilayer – dielectric/metal/dielectric

As discussed above, a thin metal layer as the top electrode shows a trade-off between transparency and resistivity. A 10 nm thin film of Ag has an optical transmittance of only around 40%. In addition, semitransparent top electrodes induce micro-cavity effects resulting in a narrow electroluminescence spectrum. The main contribution of optical losses in metal thin films occurs at the metal/

dielectric interface, e.g. metal/air, due to surface plasmons, coherent electron oscillations induced by excitation, which leads to absorptions in the metal or reflections of the incident light. Materials with a large dielectric constant can suppress those surface plasmons coupling and therefore the dielectric/metal/dielectric multilayer structures can improve the optical transmittance. Several multilayer structures have been identified as transparent bottom electrodes for OLEDs such as ITO/Ag/ITO,³¹ ITO/Ag/WO₃,³² ZnS/Ag/WO₃³³ and ZTO/Ag/ZTO³⁴ allowing for high optical transmittance of over 80% and an improved sheet resistance smaller than 10–20 Ω /sq. Ag is the preferred interlayer because it has the highest conductivity of all metals and exhibits only low absorption in the visible region. As discussed above, the WO₃ layer in those OLED structures enhances not only the transmittance but also the hole-injection into the organic transport layer. Cho and co-workers demonstrated that ZnS/Ag/WO₃ multilayer transparent electrodes deposited on plastic substrates exhibit a superior mechanical flexibility compared to ITO electrodes.³⁵

Moreover, multilayer electrodes deposited by thermal evaporation such as WO₃/Ag/WO₃,^{32,36} MoO₃/Ag/MoO₃³⁷ and MoO₃/Ag/WO₃³⁸ have been used as transparent top electrodes with favorable optical and electrical properties in organic devices. Very recently, Hong and colleagues demonstrated that a WO₃ layer can fulfill the optimum zero-reflection condition with an Ag layer.³⁹ The optical matching via a WO₃/Ag/WO₃ multilayer is schematically shown in the admittance diagram (Fig. 17.4). Recall, zero reflection is given when the multilayer matches the refractive index of air (1,0). An increasing film thickness results in a clockwise rotation in the admittance diagram. A quarter and a half wavelengths are represented in a half and full circle, respectively. Ag is a material with an imaginary part of the refractive index. Because WO₃ is a high refractive index ($n > 2$) material, it is possible with a WO₃/Ag/WO₃ multilayer to return in the admittance diagram to the refractive index of air. With high index materials a relatively thick Ag layer can be used while maintaining the zero-reflection conditions. Such multilayer electrodes are comprised of 30 nm WO₃/12 nm Ag/30 nm WO₃ and show a high transmittance of around 93% and low sheet resistance of 7.2 Ω /sq. The electron injection was further improved by an additional thin LiF/2 nm Al interlayer, as shown in Fig. 17.4d.

In another report a multilayer electrode was proposed, in which a thin thermally evaporated Ag layer is sandwiched by layers of zinc tin oxide (ZTO), prepared by RF sputtering.³⁴ The favorable interface energy of ZTO and Ag allows for closed Ag layers at an Ag thickness as low as 6 nm. By comparing sputtered ZTO and evaporated MoO₃, it was found that closed Ag films and therefore higher conductivity are achieved at lower Ag thickness when deposited on ZTO as on MoO₃. Thereby, conductivities in optimized ZAZ multilayers are an order of magnitude higher than that of ITO and a concomitantly high transmissivity was achieved. Furthermore, the ZTO cap on top of ultrathin Ag not only improves the overall transmissivity of the electrode but, even more importantly, enables the



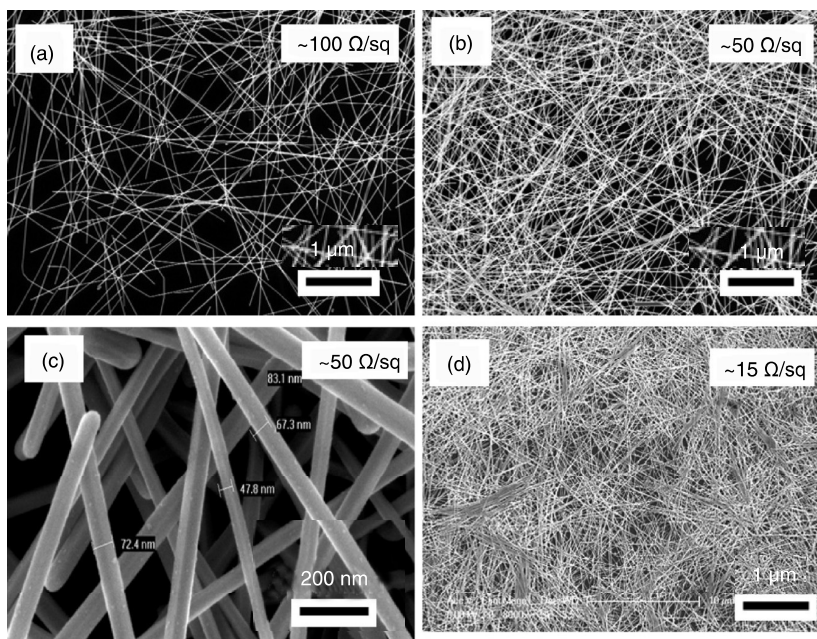
17.4 (a)–(c) Admittance diagram of WO₃/Ag/WO₃ multilayer.
(d) Schematic diagram of transparent OLEDs with different cathode structures.³⁹

stabilization of electrical characteristics of the electrode by suppressing Ag diffusion. It is well known that a severe issue of many TCO/Ag/TCO electrodes is their long term stability as thin Ag layers have the tendency to form agglomerates and discontinuous layers over time. Owing to the stabilizing effect of the sputtered ZTO cap, ZAZ is substantially more robust than other TCO/Ag/TCO multilayers.³⁴

17.2.4 Metal gratings and meshes

Highly transparent electrodes can also be realized with metal gratings or meshes in the nanometer scale. The conductivity and transparency depends on the dimensions of the metal lines and the distance between each line.⁴⁰ Kang and Gua demonstrated that OLEDs with transparent electrodes comprised of a Cu grating exhibit similar performance compared to a control device with ITO electrode.⁴¹ Periodic nanostructures, however, require cost-effective photolithography processing which is not applicable on top of an OLED. In addition, periodic nanostructures can cause parasitic optical interference effects.

Recently, Lee and colleagues reported on solution-based Ag nanowire meshes which are a promising alternative to metal gratings, because of the low processing and material cost, and high flexibility.⁴² Those meshes show electro-optical properties comparable to sputter deposited ITO electrodes. The Ag nanowires are synthesized by the reduction of Ag nitrate in the presence of poly(vinyl pyrrolidone) in ethylene glycol.⁴³ Figure 17.5 shows SEM images of Ag nanowires with different densities on PET substrates. With increasing film density fewer holes can be observed, which is important especially for a uniform electric field distribution across the film surface. The Ag nanowires diameter is in the range of 40–100 nm. An optimal sheet resistance of around 10 Ω/sq with an 80% transmittance was achieved.⁴⁴ To reduce the surface roughness, the Ag nanowire meshes were pressed between two steel plates by a mechanical manual presser of up to 81 GPa. Thereby, the surface roughness was lowered from 100 nm to 47 nm. Nevertheless, an additional planarization coating of a conducting polymer such as PEDOT:PSS was needed for a sufficient surface smoothness. It has also been observed that a large portion of light (up to 20%) is scattered in Ag nanowires, which is much larger than in ITO films. Lee and co-workers demonstrated that



17.5 SEM images of Ag nanowire films with different densities. The different densities of Ag NW films lead to different sheet resistances: (a) 100, (b and c) 50, and (d) 15 Ω/sq . The diameters of the Ag NWs are in the range of 40–100 nm.⁴⁴

solution-processed Ag nanowires meshes can also be used as a transparent top electrode without damaging the underlying organic layers by a simple lamination process.⁴⁵

17.2.5 Carbon nanotubes and graphene

The unique electronic properties of carbon nanotubes and graphene have led to an increasing research interest as electrode materials for OLEDs. So far only a few reports exist for bottom electrodes. The first OLED with multi-walled nanotubes electrode has been reported by Zhang *et al.*⁴⁶ With optimized single-wall nanotubes a sheet resistance of 160 Ω/sq at a transmittance of 87% has been demonstrated.⁴⁷ The surface roughness was reduced by using a PEDOT:PSS planarization layer. Up to now the performance of carbon nanotubes in OLEDs is still not superior to ITO electrodes. In addition, a severe drawback of carbon nanotubes are the high fabrication costs for large-area transparent conductive electrodes.

It is expected that the synthesis of graphene can be achieved at an industrial scale.⁴⁸ Since graphene is a zero-gap semiconductor with a very high Fermi velocity, individual planes have very high in-plane conductivity. In principle, charge carriers in an individual graphene sheet are delocalized over the entire two-dimensional sheet and can travel long distances without scattering. Very recently, Wu and colleagues demonstrated OLEDs on graphene thin films with electrical and optical performance almost comparable to that of a control device on ITO.⁴⁸ The graphene was 7 nm thick and exhibits a very low film roughness of <3 nm. However, the measured sheet resistance was still very high (800 Ω/sq). The first reports already showed the potential of graphene as an alternative electrode for OLED, however, further optimization in terms of film quality and thickness are needed to compete with ITO electrodes.

17.3 Thin-film-encapsulation of transparent OLEDs

17.3.1 Concepts and requirements

Gas diffusion barriers are important for various applications ranging from food-packing to flat panel displays or solar cells grown on plastic substrates. Owing to the sensitivity of many organic semiconductors to oxygen and moisture, OLEDs are a particularly demanding case.⁴⁹ Moreover, low work function cathode materials or electron injection layers based on chemically doped organic materials which are often used in OLED structures add to the sensitivity of the devices against ambient gases.⁵⁰ Without encapsulation a rapid degradation and a severely limited lifetime of the devices has been reported.⁵¹ A very commonly quoted figure for upper limits of the water vapor transmission rate (WVTR) of a particular barrier layer required to reach a minimum OLED lifetime of 10 000 h is $10^{-6} \text{ g}/(\text{m}^2 \text{ day})$.⁵² This value is based on an estimate of the amount of water required to corrode the reactive cathode material in a typical OLED. Aside from water

transmission, for the oxygen transmission rate (OTR) typical values to reach similar OLED lifetimes have been reported in the region of $10^{-5} \text{ cm}^3/(\text{m}^2 \text{ day})$ to $10^{-3} \text{ cm}^3/(\text{m}^2 \text{ day})$.⁵³ It is known that single polymeric materials like uncoated plastic foils cannot be simply laminated on top of an AMOLED, as a WVTR in the order of $1\text{--}10 \text{ g}/(\text{m}^2 \text{ day})$ does not fulfill the requirements of OLED encapsulation.⁵⁴ Organic devices are often encapsulated with a glass lid which is applied under inert atmosphere. Additionally some getter material is included to minimize the residual moisture in the cavity between the organic device. This approach not only suffers from substantial costs but it is not favorable for flexible and transparent OLED devices. Therefore, thin-film encapsulation strategies using metal oxide or nitride layers such as Al_2O_3 , SiO_2 , TiO_2 , or SiN_x are vigorously pursued. Transparent AMOLED displays are particularly demanding in this sense. In conventional OLEDs, where the light is emitted via the transparent glass substrate, the barrier functionality of the encapsulation layer is less relevant. In transparent OLEDs, the optical properties of the thin-film encapsulation are also of paramount importance. Ideally, the dielectric properties of the barrier layer can be used to tune the relation of light extraction from the top and bottom side of the display.

In this section, we will not be able to cover all aspects of barrier coatings in general. For additional reading on early work on diffusion barriers we refer to a review article of Chatham.⁵⁵ For recent results on barriers for AMOLED, the paper of Park *et al.*⁵⁶ provides an overview.

17.3.2 Techniques

Early work on thin-film permeation barriers was based on single layer systems prepared by plasma-enhanced chemical vapor deposition (PECVD) or sputtering. Poor barrier properties with a WVTR in the range of $0.1\text{--}0.3 \text{ g}/(\text{m}^2 \text{ day})$ have to be attributed to structural imperfections in the films or limited chemical stability.⁵⁷ Specifically, single layers of SiO_x ,^{58,59} SiN_x ,^{60,61} and SiO_xN_y ⁶² have been frequently studied as gas diffusion barriers. As a typical example, the WVTR of a polyethersulfone (PES) foil can be reduced from $50 \text{ g}/(\text{m}^2 \text{ day})$ to $0.3 \text{ g}/(\text{m}^2 \text{ day})$ by coating with a 100 nm thick SiO_2 layer using PECVD at 150°C .⁵⁸ A substantially lower WVTR of $0.01 \text{ g}/(\text{m}^2 \text{ day})$ has been obtained by using 100 nm of SiN_x instead of SiO_2 at the same deposition temperature.⁶⁰

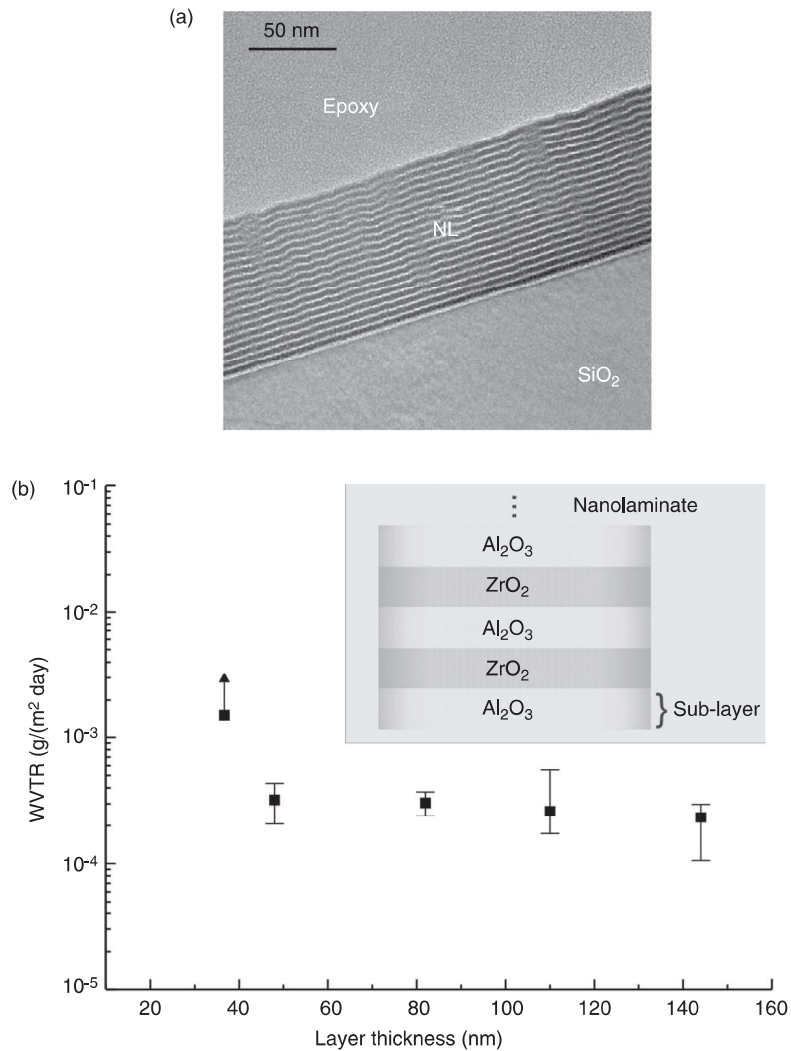
As a substantial improvement, multilayer barriers have been proposed by various groups.^{63–65} Specifically, General Electric Inc. have reported on graded multi-layers consisting of SiO_xC_y and SiO_xN_y , prepared by PECVD.⁶⁴ Thereby, substantially lowered WVTR values in the order of $10^{-5} \text{ g}/(\text{m}^2 \text{ day})$ have been achieved which are close to meeting the demands of OLEDs discussed above. At the same time, these barriers with a thickness in the order of several hundreds of nanometers show an average transmittance in the visible spectral region of 90%. Multilayers of SiO_x and SiN_x have been shown to yield a WVTR as low as

$3 \times 10^{-6} \text{ g}/(\text{m}^2 \text{ day})$.⁶⁵ As an alternative to all inorganic barriers a hybrid approach of inorganic/organic multilayers has been pursued and a WVTR of $2 \times 10^{-6} \text{ g}/(\text{m}^2 \text{ day})$ has been reported for Al_2O_3 /polyacrylate films.⁶⁶ From a production point of view, the alternating deposition of Al_2O_3 by a vacuum process and the polymer by a solution process may be problematic in terms of elevated production costs. Inorganic/organic hybrid barriers based on SiN_x /polyarylene multilayers may be prepared under similar vacuum processing conditions. A low WVTR of $7.4 \times 10^{-6} \text{ g}/(\text{m}^2 \text{ day})$ and a transparency of 88.4% has been achieved at a deposition temperature of 200°C .⁶⁷

A severe drawback of all discussed approaches is the use of plasma-based deposition techniques for the inorganic layers. Consequently, the application of these barriers on top of organic devices may be problematic due to potential plasma damage to the brittle organics or the electrode materials during the deposition process.^{54,68,69} A first report on the use of SiO_xC_y prepared by PECVD as encapsulation directly on top of a transparent OLED has shown the damage to the device inflicted by the plasma particles.⁶⁹ As a result, plasma-based approaches have thus far predominantly been used to form barrier layers on sufficiently stable polymer substrates without further (opto-)electronic functionality.

An alternative technique for the preparation of high quality barriers without the principal need for plasma activation is atomic layer deposition (ALD). In an ALD process the surface to be coated is sequentially exposed to a metal-organic precursor and a reactant (H_2O , O_3 , NH_3 , etc.).⁷⁰ The technique is known for excellent homogeneity of the resulting layers and an outstanding step coverage that is especially desirable for the preparation of dense and leak-tight barriers. Owing to the high reactivity of the precursors, ALD allows for the deposition of very dense films even at low temperatures ($< 100^\circ\text{C}$). The preparation of Al_2O_3 layers at room temperature states one example.⁷¹ Consequently, ALD is a promising technique to prepare encapsulation layers even directly on top of organic electronic devices. Early reports on ALD barriers based on single Al_2O_3 layers have evidenced low permeation rates.^{72,73} Very low WVTR in the order of $10^{-5} \text{ g}/(\text{m}^2 \text{ day})$ have been reported for Al_2O_3 films as thin as 10 nm which were grown at 120°C .^{73,74} However, deposition temperatures beyond 100°C might be critical because glass transitions temperatures for many functional OLED materials.

In spite of these outstanding barrier properties of a single Al_2O_3 layer, it has to be noted that Al_2O_3 is not stable and the WVTR itself has been shown to deteriorate substantially over time. It has been evidenced that Al_2O_3 films are easily corroded by exposure to H_2O vapors.⁷⁵ As a workaround, a bi-layer structure of $\text{Al}_2\text{O}_3/\text{SiO}_2$ or $\text{Al}_2\text{O}_3/\text{ZrO}_2$ has been proposed.^{75,76} Consequently, for increased reliability, multilayer ALD barriers are mandatory in which efficient sealing properties are accompanied by elevated chemical robustness.^{75,77} For $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminates grown at 80°C , see the transmission electron microscope (TEM) image in Fig. 17.6(a) and the inset to Fig. 17.6(b), a very low WVTR of $4.7 \times 10^{-5} \text{ g}/(\text{m}^2 \text{ day})$ has been measured in a climate cabinet at 70°C and 70% relative humidity.⁷⁷



17.6 (a) Transmission electron microscopy (TEM) image of an $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate prepared by ALD at 80°C . (b) Water vapor transmission rate (WVTR) vs. $\text{Al}_2\text{O}_3/\text{ZrO}_2$ nanolaminate thickness. WVTR measured at 80°C and 80% relative humidity. For thicknesses less than 37 nm a significant higher failure rate was observed. Inset: Scheme of nanolaminate structure.⁷⁶

The activation energy E_A of the WVTR through the nanolaminate was found to be 92 kJ/mol. Thus, the WVTR for the nanolaminate barrier at room temperature was estimated to be in the order of 5×10^{-7} g/(m² day). In a further study it was investigated how the variation of the nanolaminate thickness affects the WVTR. As depicted in Fig. 17.6(b), the WVTR does not substantially depend on the layer thickness as long as the thickness does not fall below a critical value of about 40 nm. Below 40 nm an abrupt increase of the WVTR was observed under environmental conditions of 80°C and 80% relative humidity. This can be attributed to a defect-dominated gas-diffusion, caused by pin-holes and/or micro-cracks, with decreasing layer thickness of the barrier.⁷⁸

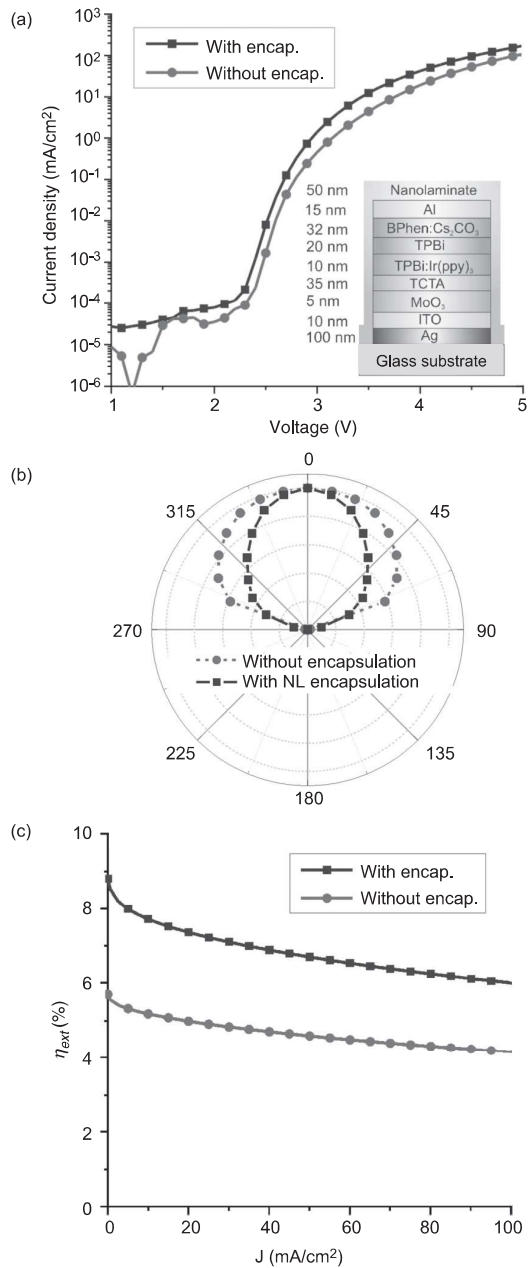
Aside from these obvious advantages of ALD processed barrier layers there are several challenges that need to be tackled in order to render ALD a serious production tool for organic electronic applications. There is the common belief that ALD is a substantially slower coating technique compared to sputtering and PECVD. On the other hand, ALD is inherently able to coat large areas and multiple substrates in a batch process – approximately 10 m² in one run. Therefore, a throughput as large as 0.6 m²/min for a 40 nm thick ALD layer has been claimed.⁷⁹

Typically, ALD is known as a batch processing technique at a reactor pressure of about 1 mbar. In an approach presented by Kodak, the concept of ALD has been extended to atmospheric pressure without the need for a reaction chamber.⁸⁰ In Kodak's process, a specially designed deposition head is used in which each reactant is confined to controlled regions along the substrate surface. Thereby, ALD is on the verge of becoming a module in a roll-to-roll production environment. Substantial recent work is now aimed at atmospheric pressure ALD with a coating speed of 1 nm/s.⁸¹ Even atmospheric pressure plasma assisted ALD has been introduced.⁸² As a result, the outstanding properties of ALD-deposited layers for applications such as thin film barriers will be available for continuous high-throughput manufacturing in the near future.

17.3.3 Atomic layer deposition (ALD) encapsulation of OLEDs

Effective OLED encapsulation has been reported for Al₂O₃ layers prepared by ALD.⁸³ The use of Al₂O₃/ZrO₂ nanolaminate structures as discussed above led to a further improvement of the encapsulation. State of the art pin OLEDs sealed by ALD have been shown to reach a lifetime of 8700 h and 22 000 h for Al₂O₃ and ZrO₂/Al₂O₃ encapsulating layers, respectively.⁸⁴ The lifetime of a reference OLED sealed with a glass lid and a getter was found to be in the same range.

As opposed to the previous discussion, where only the barrier functionality of the encapsulation layer is required, in the case of top-emitting or entirely transparent OLEDs, the optical properties of the thin-film encapsulation are also of paramount importance. Ideally, the dielectric properties of the barrier layer can be tuned to improve the light extraction from the top-emitting OLED. Figure 17.7 shows the study of a top-emitting OLED with an ALD encapsulation layer on top.



17.7 (a) I-V characteristics of the encapsulated OLED vs. neat devices directly after preparation. Inset: layer sequence of a top-emitting OLED structure with a 50 nm thick nanolaminate barrier layer on top. (b) Angular resolved light emission from the OLEDs. (c) External quantum efficiency η_{ext} vs. current density for the neat and encapsulated top-emitter.

The layer sequence of the OLED is based on a state of the art device with the peculiarity of a 15 nm thin aluminum top cathode that allows for some out-coupling of light. A maximum current efficiency of 27.5 cd/A (at 100 cd/m²) has been determined. Upon careful design of the optical properties of the encapsulation layer (thickness and composition) the amount of light extraction can be further increased. Specifically, in the present case a ZrO₂/Al₂O₃ nanolaminate (20/20 sub-cycles) structure with a thickness of 50 nm has been used. Under 0° observation angle the current efficiency almost doubles and reaches a value of 45 cd/A. It is well known that the capping layer may substantially alter the angular dependence of the top-emitter. This is also observed in an angle resolved light emission study as shown in Fig. 17.7(b). The radiation pattern narrows towards the forward (0°) direction. Substantially increased external efficiencies can be obtained by using metal-oxide-based top electrodes (e.g. ITO or Al:ZnO, see Section 17.2).

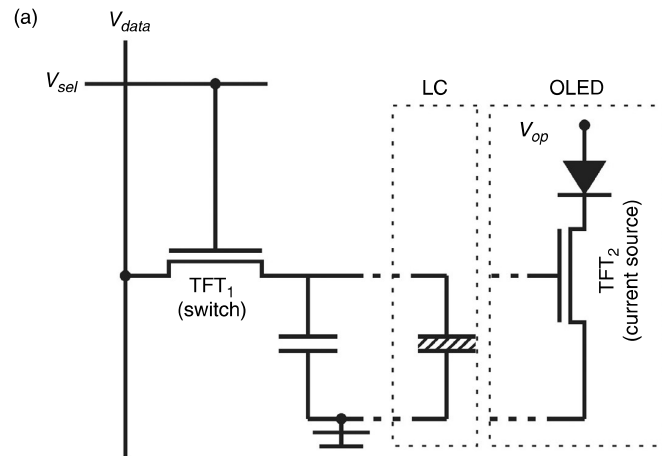
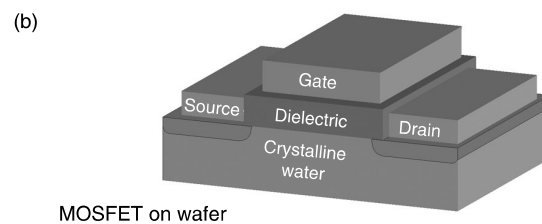
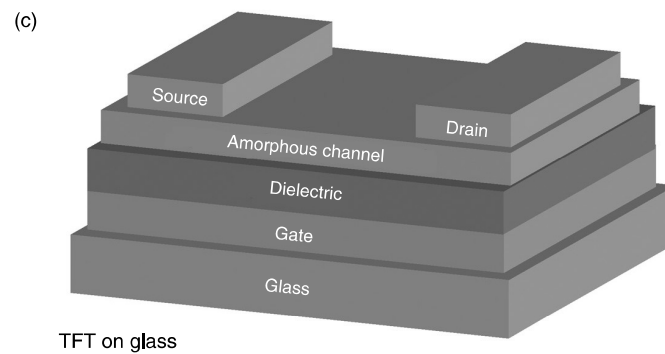
17.4 Transparent display driver electronics

17.4.1 Requirements

In the following section we will focus on the requirements of transparent display driver electronics. First it is explained why high resolution displays need electronic drivers and why OLED displays demand higher mobility and stability of the transistors compared to liquid crystal (LC) displays. Transparent amorphous oxide semiconductors (TAOS) are described as a promising alternative to state-of-the-art amorphous or polycrystalline silicon not only for transparent displays but also in general for active matrix OLED displays.

Addressing a high resolution matrix of OLED pixels requires a driving backplane. The matrix consists of m lines and n rows, accordingly $m \times n$ OLED-pixels – typically in the range of several millions. Two driving schemes have been developed. A passive matrix (PM) provides one contact line for each row and column, respectively. A pixel can be controlled by applying a voltage between the corresponding row and column. To address the entire matrix the rows are switched on sequentially. In PMOLED displays, at a certain time only one line is switched on. This means that the pixels need to be m times brighter than the display. Such large peak brightness reduces the lifetime and efficiency of OLEDs. Other issues of passive matrix driving are a limited contrast due to cross talk of neighboring lines and rows and limited brightness homogeneity due to ohmic losses in the transparent contacts. The active matrix (AM) driving scheme as shown in Fig. 17.8 can overcome these issues and provides a way to address large area high resolution displays.

To realize AM displays, an electronic circuitry underneath each pixel is needed. State of the art displays reach dimensions above 80 inches while the largest wafer is about 12 inches in diameter. It is obvious that display drivers cannot rely on standard silicon MOSFETs as schematically shown in Fig. 17.8(b). Instead the



17.8 (a) Simplest active matrix driving scheme for liquid crystal (LC) and OLED displays; (b) classical wafer based transistor; (c) thin film transistor (TFT) deposited on a glass substrate.

functional layers have to be deposited on a non-crystalline substrate like glass. Such transistors are called thin film transistors (TFTs) (Fig. 17.8(c)). The addressing is realized by the switching TFT₁. To define a line's brightness information the corresponding select contact (V_{sel}) is switched to high which makes all switching TFTs of that line conductive, so each capacitance is charged to data level (V_{data}). The charged capacitance stores the brightness information for each (sub)pixel in order to define the brightness. Each pixel now retains the brightness information until next addressing. Therefore each pixel in the matrix is always controlled by the voltage of the corresponding capacitance. In the case of LC displays the simplest pixel consists only of the LC cell itself. The LC cell is a passive device that modulates the display backlight. Once switched, LCs do not consume a significant current. Contrary to LCs, OLEDs are current-driven devices. The voltage-controlled OLED pixel consists of an OLED and a TFT₂ that serves as a current source (see right dashed rectangle in Fig. 17.8(a)). This way the OLED can be controlled by the capacitance voltage. As long as TFT₂ is used in the saturation regime the pixel brightness is not influenced by V_{op} . Consequently, the limited conductivity of transparent electrodes does not influence the homogeneity of the brightness of AMOLED displays.

While the current of TFT₁ determines only the switching speed of a pixel and therefore the resolution and refresh rate of a display, the current of TFT₂ directly determines the brightness of an AMOLED display. Assuming an OLED efficiency of 20 cd/A, for a brightness of 400 cd/m² a current density of 20 A/m² is needed. For a typical pixel size that means TFT₂ currents in the order of microamperes which lie significantly above the currents controlled by the switching TFT₁.

The current that can be driven by a transistor of a given size is determined by its field effect mobility. The larger the mobility the larger is the transistor current under equal conditions.

Figure 17.8(b) and (c) emphasize the difference between crystalline MOSFETs as they are used in microelectronics and TFTs that are used on large areas, e.g. in displays. Basically the field effect mobility of the devices depends on the charge carrier mobility of the channel material. In the case of silicon MOSFETs the crystalline silicon channel shows an electron mobility of 1.450 cm²/Vs.⁸⁵ In silicon this value critically depends on the crystalline order. On an amorphous substrate like glass it is not possible to epitaxially grow single-crystalline films. Instead, only amorphous or polycrystalline thin films can be deposited. The carrier mobility in amorphous silicon (a-Si) is around 1 cm²/Vs,⁸⁶ which is generally believed to be too small for driving the next generation of large and high resolution AMOLED displays. Nevertheless a-Si-TFTs have been very successful in driving LC displays. As long as the TFT remains largely conductive at select=high and non-conductive at select=low, small shifts of its transfer characteristics do not influence the brightness of the (sub)-pixel. In Section 17.3 we will explain how external stresses, such as gate bias stress, illumination, temperature or a change in

the ambient conditions, can indeed shift the transfer characteristics of TFTs which is critical for the OLED-driving TFT₂.

In order to prepare silicon-based TFTs that are more suitable for OLED driving with respect to their field effect mobility and stability, a technology for the crystallization of a-Si has been developed. However, one drawback of polycrystalline channels is a reduced homogeneity of the TFT parameters. Within the crystalline grains the mobility can be large, while the grain boundary builds a barrier for charge carriers.⁸⁷ Thus, statistical parameters like the number and orientation of grain boundaries will determine various TFT parameters.⁸⁸ In fact many efforts have been made to improve or compensate the uniformity of polycrystalline silicon (poly-Si) backplanes in order to successfully drive AMOLED displays.⁸⁹ However, especially for high performance large area displays, the homogeneity of amorphous channels remains highly desirable.

Transparent amorphous oxide semiconductors (TAOS) are promising candidates to fulfill the requirements for OLED driving by combining the great homogeneity of amorphous channels with an improved mobility compared to a-Si TFTs.⁹⁰

17.4.2 Transistors based on metal-oxides

In the absence of its crystalline nature the electron mobility of silicon is reduced by three orders of magnitude. Surprisingly, in other materials, such as ITO, the electrical performance depends much less on the crystallinity. The electron mobility of amorphous ITO ($33 \text{ cm}^2/\text{Vs}$)⁹¹ is less than 30% below that of single crystalline ITO ($42 \text{ cm}^2/\text{V}$).⁹² In 2004, Nomura *et al.*⁹³ explained this phenomenon with electron transport over large spherically shaped s-orbitals of heavy metal ions.

This phenomenon is fortunately not only found in highly doped TCOs like ITO. Rather, the ideal TFT channel consists of an intrinsic semiconductor, whose conductivity can be switched by small gate voltages. Various transparent amorphous oxide semiconductors, materials have been discovered that show a small density of free carriers and therefore qualify as channel materials in TFTs. Typical TAOS contain the heavy metal ions indium or tin with large s-orbitals to allow for high carrier mobility in the amorphous phase. To prevent crystallization, a mixture of at least two conductive oxides can be used.

In addition to the classical conductive oxides of zinc, tin and indium, TAOS can also include oxides that show only small conductivity in the pure form, like gallium, zirconium or hafnium oxide which leads to a large variety of channel materials. Especially, indium gallium zinc oxide (IGZO) and indium hafnium zinc oxide (IHZO) have evolved as promising TFT channel materials for display applications.^{93,94}

A systematic comparison of different TAOS materials has not yet been published. Here, as an example, we focus on the indium-free TAOS zinc tin oxide

(ZTO).^{14,95} The material shows a remarkable stability against bias stress and illumination which is necessary for an application in transparent displays. Fig. 17.9 shows a staggered bottom gate ZTO TFT.

All layers of a transparent TFT consist of transparent oxides. Typically Al_2O_3 or TiO_2 are used as dielectrics and TCOs like ITO or doped ZnO are used for the contacts. The TAOS channel is typically deposited by sputtering or PLD. Figure 17.9(b) shows the field effect mobility of ZTO channels of various compositions deposited by oxygen plasma-assisted PLD. For polycrystalline, pure SnO_2 (Zn content 0%) or pure ZnO (Zn content 100%) smaller mobilities are found than for the amorphous ZTO that contains at least 20% of each oxide. The amorphous nature of ZTO is verified by transmission electron microscopy (as shown in Fig. 17.9(c) and (d)).

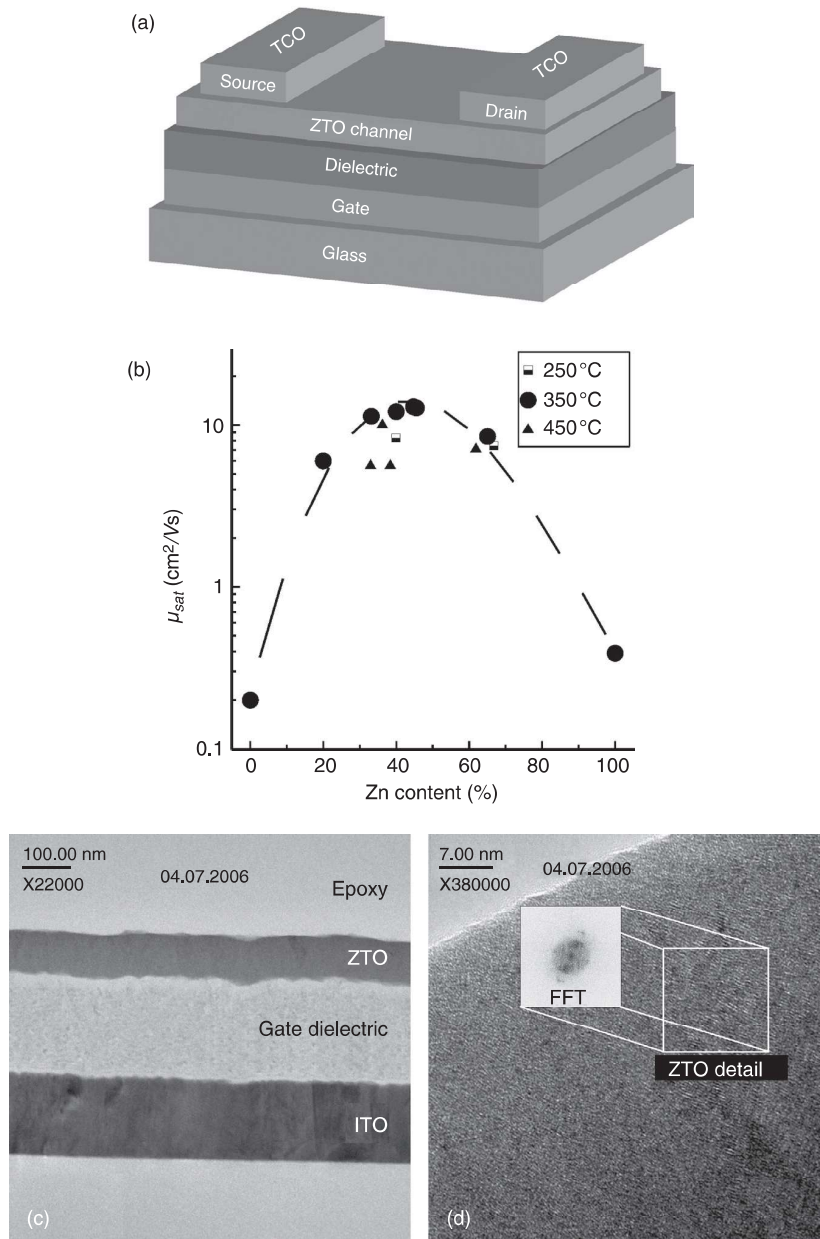
17.4.3 Stability/reliability

Amorphous layers always contain defect states that may reduce the device stability. In silicon it is well known that a gate bias stress causes shifts in the TFT device characteristics. While this may be acceptable in LC displays, it is a killer in AMOLED displays, as discussed above. Figure 17.10 shows the transfer characteristics of ZTO TFTs of different compositions before and after stressing with $V_g = 10\text{ V}$ for 1000 minutes.

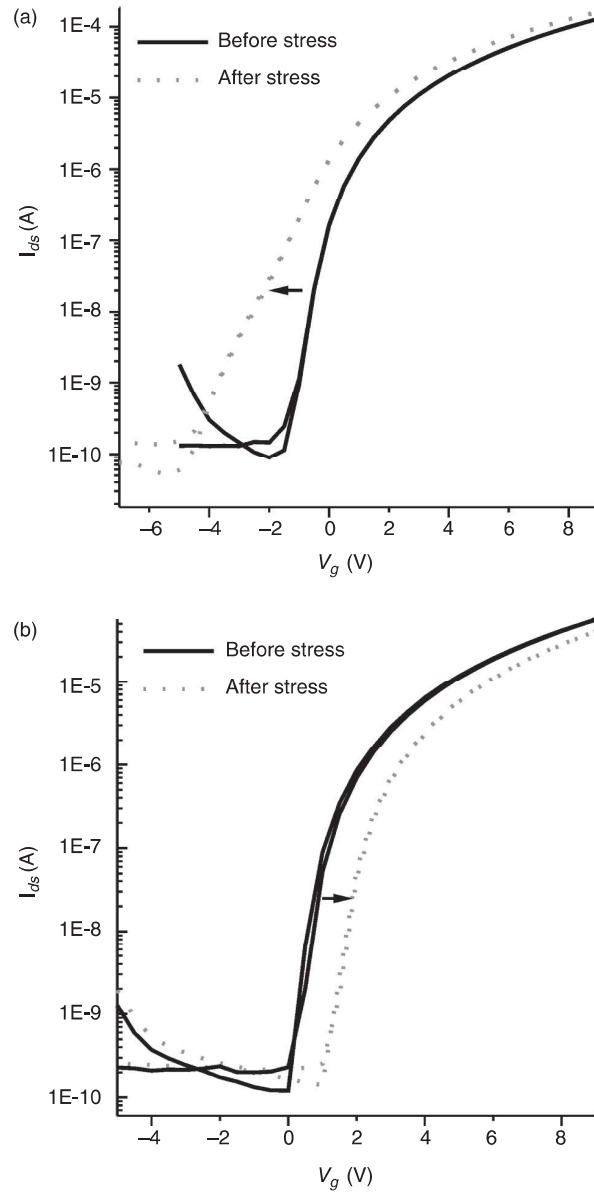
It turns out, that the composition of ZTO provides a parameter to ‘tune’ the stability of the TFTs against bias stress, as shown in Fig. 17.11(a). At a zinc content of around 50 percent a shift of the threshold voltage to smaller values is observed, while towards higher *and* lower zinc content an increase of the threshold voltage is found. From the different time dependence of the transfer characteristics shift and the different impact on its sub-threshold regime it can be concluded that negative shifts are dominated by defect state creation while positive shifts are caused by electron trapping into the dielectric, a phenomenon well known from amorphous silicon. For the application of ZTO-TFTs in AMOLED displays the dependency of ΔV_{th} on the composition is good news. It means that there may be ideal compositions where basically no shift of the TFT characteristics under stress is expected (large circles in Fig. 17.11). In fact, TFTs with a zinc content close to 36% (left circle in Fig. 17.11(a) show a very high stability against stress (Fig. 17.11(b)).

Strikingly, after a permanent stress for 1000 hours at a current of $I_{ds} = 188\text{ }\mu\text{A}$ (two orders of magnitude higher than that required for an OLED pixel in a display) the threshold voltage shifts by only 320 mV and the mobility changes by less than 1%. Such an outstanding stability against bias stress is unsurpassed by a-Si and appears very promising for the application of oxide TFTs in AMOLED displays.

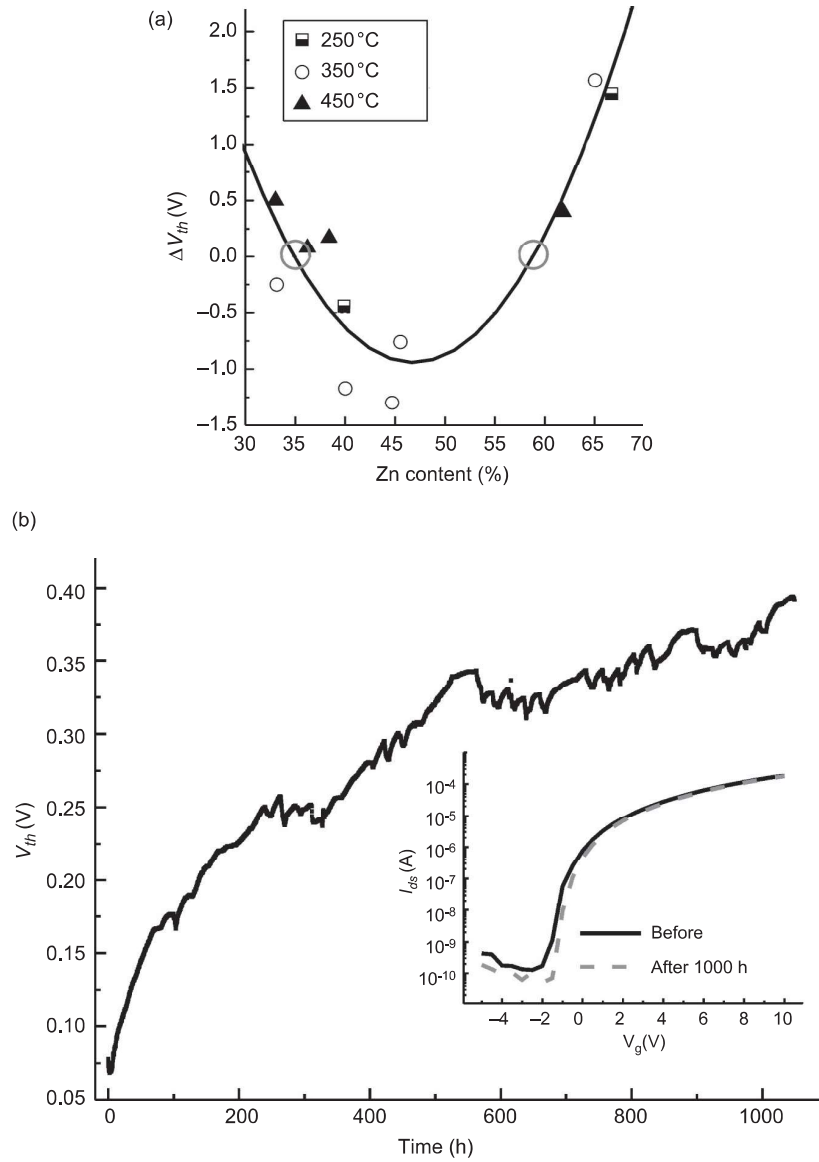
Transparent displays can in principle be realized using light shielded transparent or even opaque transistors as long as parts of the area remain



17.9 (a) Transparent ZTO TFT; (b) saturation field effect mobility of the device depending on the composition; (c) transmission electron micrograph (TEM) showing amorphous nature emphasized by Fourier transformed picture (d).



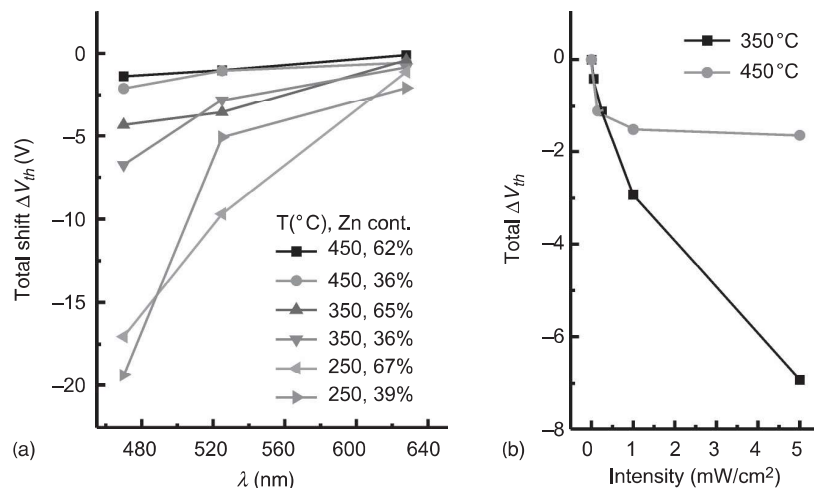
17.10 Shift of the transfer characteristic after 1000 minutes of stressing with $V_g = 10$ V for Zn content of (a) 45.5% (negative shift) and (b) 62% (positive shift).⁹⁶



17.11 (a) Threshold shift as a function of the channel composition⁹⁶ and (b) threshold of a TFT of 36% zinc content during 1000 h of stressing with $V_g = V_{ds} = 10$ V and $I_{ds} = 188$ μ A.⁹⁷

transparent. This way, a small AMOLED display of a transmission around 20% could be realized with an opaque amorphous silicon backplane.⁹⁸ Larger transmissivity values, however, can be realized with entirely transparent TFT backplanes. For such applications the channels are directly illuminated not only by the OLED light, typically in the range of 500–5000 cd/m², but also by external light. The question of how the TFTs react to illumination is therefore very important for transparent displays. Figure 17.12 shows the threshold shift upon illumination. As a light source, LEDs with spectra peaks at 628 nm, 525 nm, and 470 nm at an intensity of 1 mW/cm² were used. This is equivalent to a brightness of approximately 23 000, 50 000, and 6000 cd/m², respectively. The LED spectra represent the red, green, and blue color coordinates according to the National Television Systems Committee standard. As shown in Fig. 17.12(a), blue light has the strongest impact on the TFT characteristics as the photon energy is closest to the band gap of the ZTO channel. The processing temperature can be identified as the dominating parameter for the light sensitivity of the resulting device.

TFTs with channels deposited at 450 °C show a clear saturation of the threshold shift with increasing intensity of blue light. It has to be noticed that shorter wavelength, violet and ultraviolet light, can be blocked by transparent coatings. As blue illumination is most critical it can be concluded from Fig. 17.12(b) that the maximum threshold shift expected for these devices in a transparent display due to illumination is as small as 1.7 V.⁹⁹



17.12 (a) Total threshold shift of ZTO TFTs of different deposition temperature and composition after long-term illumination with blue (470 nm), green (525 nm) and red light (628 nm) (intensity 1 mW/cm²); (b) saturation of the total shift with increasing intensity for blue illumination (470 nm).⁹⁹

Gaining a better understanding of defects in TAOS materials and therefore stability issues of TAOS-based TFTs is an ongoing process.¹⁰⁰ It turns out that in addition to bias stressing or illumination, e.g. adsorption of species like oxygen or water on the channel surface, significantly influences the TFT.¹⁰¹ Therefore, the preparation of a dense ALD encapsulation that was described in Section 17.3 to successfully enhance OLED lifetime can in fact also affect the properties of the TAOS display backplane.¹⁰²

17.4.4 Transparent active matrix organic light-emitting diode (AMOLED) displays

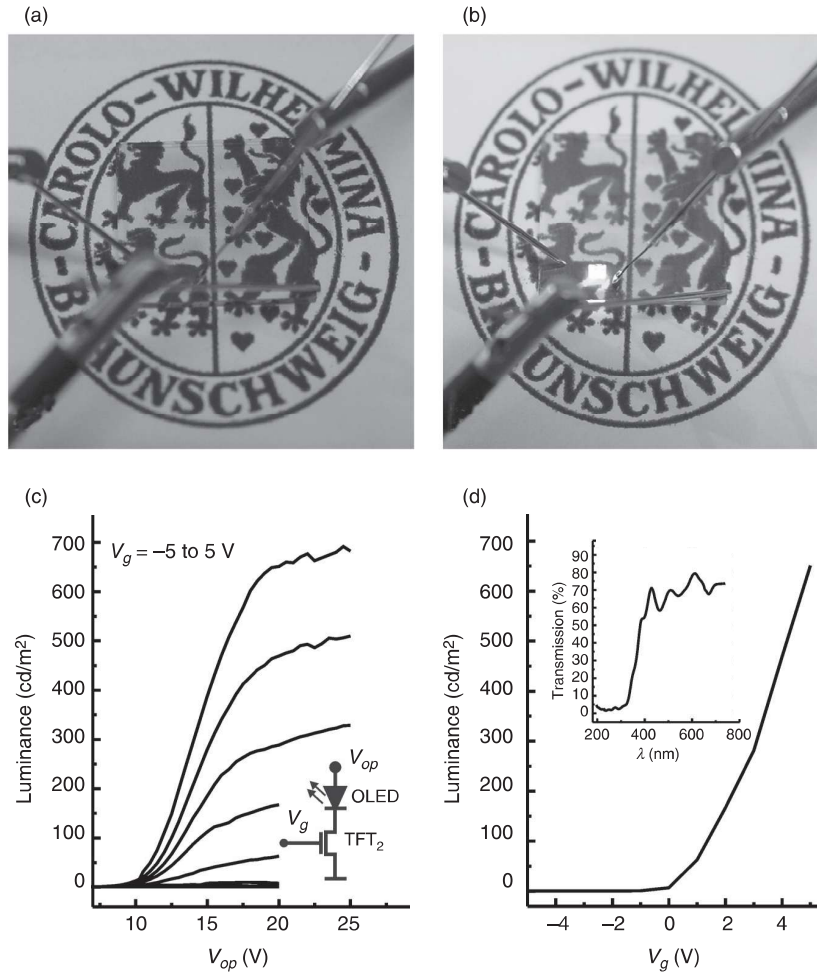
For the fabrication of transparent AMOLED displays transparent OLEDs need to be deposited on top of the transparent TFTs. In order to prove the technological compatibility transparent ‘smart pixels’ (Fig. 17.13(a,b)) have been prepared that consist only of the current source TFT₂ and the OLED, as shown in the right dashed frame in Fig. 17.8(a).¹⁴

A minimum transmission of 70% is found at positions where the light transmits the entire OLED and TFT stacks. A transparent display based on this technology will reach even higher values, especially with suitable antireflective coatings. It should be kept in mind that state of the art automotive windshields show a typical transmission of about 70% as well. With $1.5 \times 1.5 \text{ mm}^2$ the OLED is much larger than typical display pixels. Nevertheless the ZTO TFT of a channel width to length ratio of 10 is able to switch the pixel luminance between 0 and $>500 \text{ cd/m}^2$ with small gate voltages between -1 and 4 V (Fig. 17.13(c)). The results show that transparent OLEDs and TFTs can be monolithically integrated into highly transparent displays. To estimate the properties of such displays in terms of resolution and refresh rate, the switching speed of the active driver consisting of TFT₁, TFT₂ and the capacitor (see Fig. 17.8) has been investigated. First ZTO-based pixels of a size of $180 \times 240 \mu\text{m}^2$ could be addressed in less than 10 microseconds, providing HD resolution at refresh rates of about 100 Hz.¹⁰³ Very recently, the first entirely transparent displays based on TAOS backplanes have been demonstrated.¹⁵ Figure 17.14 shows such a display with a transmissivity of 45%.

The large mobility and stability of TAOS based transistors as well as their transparent nature make them attractive for the use as AMOLED drivers, especially in transparent displays.

17.5 Acknowledgements

The dedicated work of our collaborators and colleagues at the Institute of High Frequency Technology (TU Braunschweig) and the Physikalisch Technische Bundesanstalt (PTB) deserves particular acknowledgement. Moreover, the fruitful cooperation with our partners from academia and industry is highly appreciated.



17.13 (a) Transparent smart pixels consisting of a transparent TFT and transparent OLED in the off-state and (b) in the on-state, (c) luminescence in as a function of V_{op} and (d) as function of V_g including transmission spectrum.

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17.14 Transparent 2.4 inch QVGA display from AU Optronics Corporation using an IGZO backplane. The transmissivity is 45%.¹⁵

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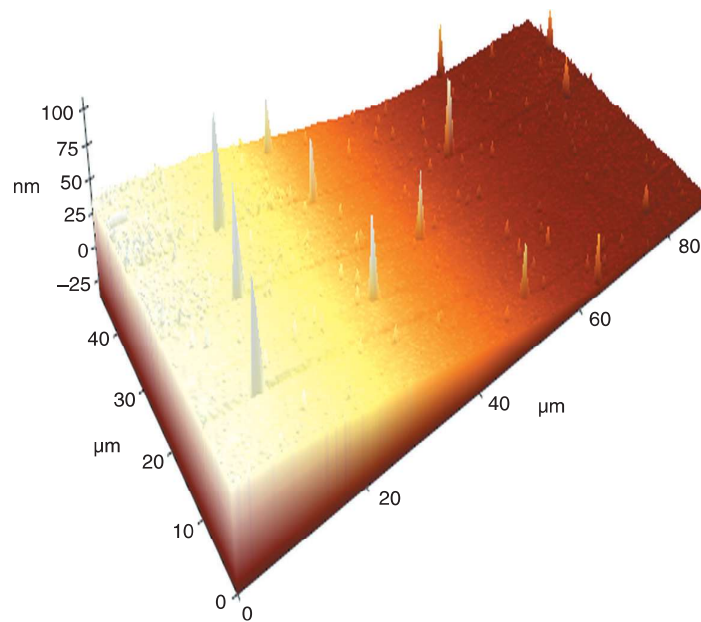


Plate VIII (Chapter 19) AFM image of sputter-patterned ITO measured on the slope of the patterned edge.

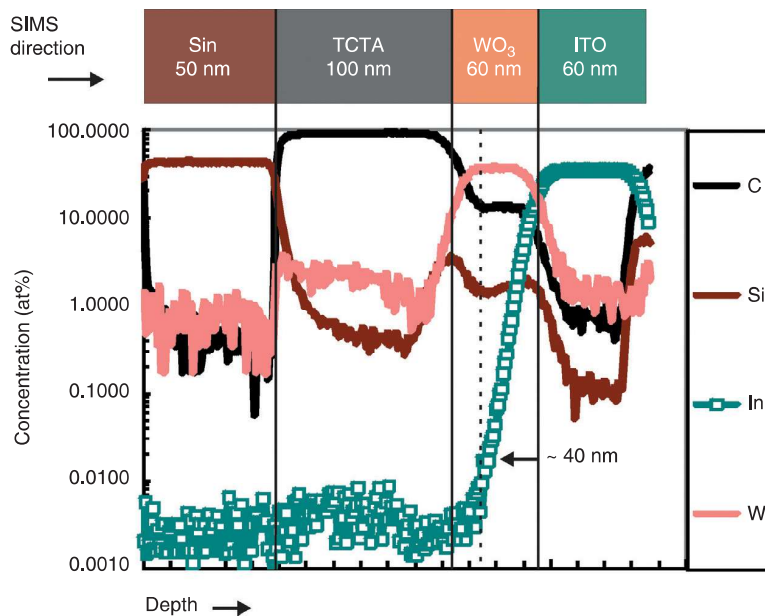


Plate IX (Chapter 17) Secondary ion mass spectrometry profile of the layer sequence: SiN/TCTA/WO₃/ITO measured beginning from the SiN substrate.⁶

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Abstract: In this chapter a brief overview of the evolution of organic light-emitting diode (OLED) technology has been presented and the key advantages and limitations of the OLED technology have been evaluated. The role of OLEDs in sensor technologies has been discussed. These include: (a) OLED based oxygen sensors, (b) OLED-based immunoassays, (c) OLED-based glucose sensors, and (d) OLED based hydrocarbon sensors. The rules that govern the design, fabrication and development of an optical, label-free bio/chemical sensor technology geared towards portable 'lab-on-a-chip' format applications have been discussed. The OLED sensor technology employs the use of nanotextured thin film surfaces packaged in a stacked vertical array format (Sun *et al.*, 2005). The intensity of emitted light from OLEDs is modulated as a function of the analyte concentration. The OLEDs are fabricated in a layer-by-layer configuration. The prototype sensor performance has been discussed for each of the four cases.

Key words: optoelectronic bio/chemical sensor, molecular detection, organic LED.

18.1 Introduction to sensors and sensor technology

The term sensor was originated from the Latin word 'sentire', meaning to perceive. Sensors were invented to measure a physical quantity and then process the data to generate an output stimulus which can be identified with an instrument or by an observer. As divergent from detectors, the sensors are employed to assess and quantify the variations of a measurand whereas the detector's function is simply to indicate the presence of the measurand. When the measurand is exposed to certain background changes or the parameter variations it alters one or more properties: mass, electrical conductivity, capacitance, etc. These variations can affect either directly or indirectly the output stimulus in a significant manner.

The primary purpose of the sensor invention has been to improve the life-style by monitoring the surroundings and by relaying the acquired data accordingly. Therefore, it is true that the sensors play a vital role in the current world.

Generally, sensors are made to be inexpensive yet reliable and consistent. They should provide accurate, stable, high resolution outputs; but most of all the sensors must be sensitive to the measurand and insensitive to the other measurable conditions. Each application of the sensor places diverse obligations

on the sensor platform, hence all the environmental effects such as temperature, humidity, shock and vibration, must be considered while building the device.

Nowadays, sensor technology has become an increasingly important area of study due to the need for physical, chemical and biological recognition systems. Embedded sensors of industrial process controllers play a prominent role in this development. There the sensors continually monitor to ensure the maximized efficiency while minimizing the production cost. Moreover, the automotive sensors help control the parameters to function properly. For example, an aircraft's control is dominated by the variety of sensors as they monitor position, wind speed, air pressure, altitude, life support, etc.

Parallel to these developments the sensors are now integrated for environmental applications to improve the quality of the lives of the people. Water quality monitoring and food quality monitoring are prominent applications of the sensors.

In the past few decades, the sensor technology was broadly spread through the field of health care and diagnosis to determine the function of biological systems. Recent research indicates the development of the sensors for a wide range of biochemical phenomena.

18.1.1 Biochemical sensors

Biochemical sensors are 'point-of-care' devices integrated to perform selective analysis through biochemical molecular recognition properties. Once the biochemical sensors are applied to a molecular recognition element, the transducer converts the response into an external measurable quantity which can be attained through the readout. Furthermore, biochemical sensors can be utilized to detect and diagnose not only a disease but also the presence of trace elements in the environment. Innovative bio-affinity sensors can employ proteins, DNAs, small molecules, aptamers or enzymes in performing the molecular recognition assays, which may lead to early diagnosis.

18.1.2 Transduction techniques

Sensor transduction techniques coupled with the various bio-receptors are presented in this section. The major transduction platforms include optical transduction, electrochemical transduction and mechanical transduction. As the focus of this chapter is on the use of organic light-emitting diodes as sensors, its primary detection modality is optical transduction. This section reviews the various optical transduction mechanisms that are currently in use in biochemical sensors.

Optical transduction is one of the most prominent transduction techniques. Optical sensors utilize the interaction of the optical waves. Wavelength-specific interactions with the sensor surface modulate the properties of the incident light such as its intensity and resonance and Q factor. These changes can be used to quantify the amount of the measureand. Mostly the intensity, frequency and the

polarization of the output stimulus get affected to indicate the presence of the measurand. The methods of the optical transduction are bioluminescence, photo- and electroluminescence, and Surface Plasmon Resonance (SPR). The focus of this chapter is to review biochemical sensors working and the optical transduction mechanisms of electro- or photoluminescence in the OLED format.

18.2 Introduction to organic light-emitting diodes

Electroluminescent devices using organic materials have been developed since the 1950s. Over the last half century organic thin films have been packaged in varying configurations in the sandwich format to develop light-emitting devices. Bernanose was the first to demonstrate light generation by applying high alternating current voltages to thin organic crystalline films of acridine orange and quinacrine (Bernanose *et al.*, 1953). The development of these organic luminescent devices was not suitable for practical device applications because of the high voltages required to drive the charge carriers into the organic crystal. In order to obtain significant light, voltages in the range of 30 V to 100 V were required to drive the device (Tang and Vanslyke, 1987). The structure of these organic luminescent LEDs comprised thin films of organic material such as anthracene (Gurnee and Fernandez, 1965). The power output efficiency of these devices was quite low, in the range of 0.1% to 0.05%. In addition, due to lack of long-term stability of these devices, they were not appropriate for commercial applications.

In general, the basic OLED structure consists of a stack of fluorescent organic layers sandwiched between a transparent conducting anode and metallic cathode. When an appropriate bias is applied to the device, holes are injected from the anode and electrons from the cathode; some of the recombination events between the holes and electrons result in electroluminescence (EL).

The first EL from an organic molecule, anthracene, was reported by Pope and coworkers in 1963 (Gustaffson *et al.*, 1992). They reported EL from a thick anthracene crystal (10 μm –5 mm), when a bias of several hundred volts was applied across it. Tang and VanSlyke (1987) reported a multi layered organic light-emitting diode (OLED), which worked on low operating voltages with improved performance parameters. These devices consisted of an organic layer, which was a sandwich of two organic films. These organic materials were mono-transport layers, i.e. they transported either the negative charges (electrons) or the positive charges (holes) and their morphological, recombination and luminescent properties were chosen such that they were compatible for the device construction and operation. In addition, low work function alloys comprised of materials such as magnesium and silver were used to inject electrons and improve the device efficiency. Since then, OLEDs have been of great interest because most of the organic materials that have been used as layers of thin films stacked on to each other have demonstrated extremely high fluorescent efficiency in the whole visible spectrum, color versatility, high brightness, wide angular emission profile and are

of light weight. This has made them extremely suitable for application in portable multi-color flat panel displays (Jung *et al.*, 2001).

Recently, there have been different types of organic luminescent devices using polymers that are known as polymer light-emitting diodes (PLED) (Gustafsson *et al.*, 1992), which have been fabricated using a thin film of conductive polymers that emit light when the device is biased. The device active area, i.e. the regions from which light emission occurs, has been micro structured through micro contact printing or ink jet printing techniques in order to improve the emission efficiency (Koide *et al.*, 2003). Polymers with derivatives of poly(p-phenylene vinylene) and poly(fluorene) have been used as conductive polymers that emit and absorb electrons respectively, forming the n-type and p-type layers of the device (Heeger *et al.*, 1993). These devices utilize the improved surface area to volume offered by surface texturing to improve the device performance metrics through controlled layer-by-layer deposition. These devices can be fabricated on rigid as well as flexible substrates, making them robust (Bharatan and Yang, 1998).

Other types of OLEDs that have been recently developed such as the transparent organic light-emitting device (TOLED) and stacked OLED (SOLED) (Gu *et al.*, 1996, 1999) have incorporated the advances in nanomaterial technology towards improving the device performance metrics. These include the incorporation of nanomaterial composites as well the use of hybrid organic and inorganic material. The inorganic materials include homogeneous as well as heterogeneous conducting as well as semiconducting material with varying geometries such as nanowires, nanotubes, nanospheres and other morphologies (Klauk, 2008; Zhou *et al.*, 2006; Piok *et al.*, 2003). These hybrids contribute to the generation of nanostructured surfaces which in turn improve the device performance metrics by multiple factors as compared to the micro structured OLED devices.

TOLEDs consist of transparent electrodes which can be used for anode or cathode or even both the electrodes. TOLEDs have been used in order to improve contrast and viewing angles of the display systems. SOLEDs consist of vertically stacked transparent OLEDs. These have been typically used for improved color characteristics and also for improved resolution (Hung *et al.*, 2001; Wu *et al.*, 2004; Li *et al.*, 2008)

18.3 Advantages and limitations of OLEDs

OLEDs have already achieved commercial success in display markets. Currently OLEDs are used in low information displays with limited size such as mobile phones, PDAs, MP3 players, digital cameras and some laptop cameras. The driving force behind this success is some advantages that the OLEDs enjoy. They are self-luminous, i.e. the efficiency of OLEDs is better than that of other display technologies without the use of backlight, diffusers, and polarizers. They are relatively low cost and are easy to fabricate. The roll-to-roll manufacturing process, such as inkjet printing and screen printing, is possible for polymer

OLEDs. They enable color selectivity as there are abundant organic materials to produce blue to red light. Lightweight, compact and thin devices can be designed using OLEDs with thickness as low as ~ 100 nm. They are extremely flexible; OLEDs can be easily fabricated on plastic substrates paving the way for flexible electronics.

One limitation of OLEDs is that they are highly susceptible to degradation by oxygen and water molecules. Organic materials are very sensitive to oxygen and water molecules which can degrade the device very fast (Sugiyama *et al.*, 2000). The biggest limitation of OLED is the lifetime of the device. With proper encapsulation, lifetimes exceeding 60 000 hours have been demonstrated. OLEDs have low glass transition temperature, T_g , for small molecular devices ($>70^\circ\text{C}$). So the operating temperature cannot exceed the glass transition temperature. The low mobility of OLEDs is due to the amorphous nature of the organic molecules.

18.4 Introduction to OLED biosensors

OLED biosensors are defined as analytical devices incorporating a biological sensing element which translates the chemical parameters of a system into an optical or electrical signal. OLED biosensors offer small, selective, and portable diagnostics for key biological substances. Such diagnostics could improve management of patients and allow testing in non-traditional settings. While most OLED biosensors are in the development stage, current research promises to meet several of the important measurement goals for selected metabolites, drugs and other important clinical molecules.

Enzyme technology was exploited as early as the 1950s with the development of an enzyme test strip (Baldo *et al.*, 1999) for the simple analysis of solutions, and the enzyme electrode is still the most commercially marketed biosensor for glucose monitoring.

18.4.1 Fluorescence biosensors

During the past decade there has been a remarkable growth in the use of fluorescence in the biological sciences, especially in development of biological and chemical sensors. Fluorescence is widely used for a range of biological and environmental applications ranging from environmental monitoring and clinical chemistry to DNA sequencing and proteomic analysis.

Due to the sensitivity of OLED fluorescence detection, it has become the single largest technique for analyzing biochemical analytes. Most recently there have been investigations in employing OLEDs that have been typically used for light-emitting displays towards developing optical biosensors. Kopelman and co-workers have demonstrated the development of bio-chemical sensors using OLED technology, and glucose as well as oxygen has been detected at parts-per-million concentrations using this technique (Savvate'ev *et al.*, 2002).

18.5 Types of OLED-based bio/chemical sensor technologies

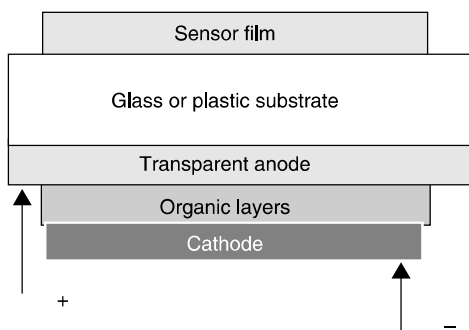
In this chapter four types of OLED-based bio/chemical sensor technologies will be reviewed. The first is the oxygen-based sensors and the second is the immunoassay-based sensors, the third is the glucose-based sensors and the fourth is the aliphatic hydrocarbon-based sensors. The structural configuration and the general principle of operation of these four sensor types are discussed.

18.5.1 OLED-based oxygen sensors

The field of photoluminescence (PL) and electroluminescence (EL) based chemical or biological sensors is growing rapidly (Aylott *et al.*, 2001; Savvate'ev *et al.*, 2002). Such sensors are typically composed of a sensing element, whose electro/photoluminescence (EL/PL) is monitored before and during exposure to an analyte, a light source which excites the EL/PL, and a photodetector (PD). Current light sources such as lasers and inorganic LEDs are bulky or require intricate integration procedures (Choudhury *et al.*, 2004a). In contrast, the structural integration of an OLED with a sensing element is simple, resulting in small-size devices (Choudhury *et al.*, 2004b; Shinar *et al.*, 2004) which are attractive for developing miniaturized sensor arrays for sensing applications (Choudhury *et al.*, 2004b; Shinar *et al.*, 2004). Solid state LEDs have been marginally used for gas sensing applications. The key issues in designing gas sensors have been the artifacts in the modulation of the refractive index due to the presence of the gas component. This has resulted in false positives in detection and has considerably reduced the sensitivity of the device. The second major limitation has been the inability to efficiently couple the optical light to and from the LED device. Lack of seamless integration of the heterogeneous components of the sensor system has resulted in a decrease in the dynamic range of detection as well as sensor performance metrics (O'Toole and Diamond, 2008).

The viability of structurally integrated OLED/luminescent sensors results from the intrinsic advantages of OLEDs as low-voltage, miniaturizable (Burke *et al.*, 2005), flexible (Trettnak *et al.*, 1995; Papkovsky *et al.*, 1995) and efficient light sources, and the dramatic improvements in OLEDs achieved over the past decade, which has led to their emergence in commercial products (Rosenzweig and Kopelman, 1996). These improvements include external quantum efficiencies and lifetimes which exceed 18% and 20000 hours, respectively, for green emitters (Lee and Okura, 1997; McDonagh *et al.*, 1998; Garcia-Fresnadillo, *et al.*, 1999) and 6% and 1000 hours, respectively, for blue emitters (Amao *et al.*, 2000). This section highlights the efforts of the Dallal and Shiner groups at Iowa State University towards the realization of OLED oxygen sensor platform.

The basic structure of the platform is shown in Fig. 18.1, where the OLED excitation source is deposited on one side of a glass substrate, while the



18.1 Basic structure of an integrated OLED/ fluorescence-based chemical and biological sensor.

sensing component is deposited on the other side of the substrate. Figure 18.1 shows a single pixel sensor format. In this configuration, applying the DC potential between the anode and the cathode excites the charge transfer within the organic sub-layers resulting in electroluminescence. Based on the selection of the organic dye components the emission wavelength is identified. The emitted light traverses through the transparent substrate to interact with the sensor surface onto which the analyte is immobilized. Interaction of the PL light with the analyte molecules modulates the light properties, mainly its intensity. Hence the intensity of light measured from the PD can be correlated to the dose of the analyte on the sensor surface. Equivalently, the OLED and sensing components can be fabricated on separate substrates and attached back-to-back. For complete integration of a compact sensor device, the position of the PD is of importance.

If the OLED is transparent, or consists of an array of pixels, the PD can monitor the PL that passes through the transparent OLED or between the gaps of the OLED array. For the oxygen sensor demonstrated in this work, the sensing element was a film consisting of ruthenium tris(4,7-diphenyl-1,10-phenanthroline) chloride (Ru(dpp)3) dye (Gillanders, 2004; Jorge *et al.*, 2004) embedded in a sol-gel matrix; the strong red PL of Ru(dpp)3 is quenched by collisions with O₂. The dependence of the PL intensity (*I*), as well as its lifetime (τ), on the oxygen partial pressure (O₂), is described by the Stern-Volmer equation

$$I_0/I = \tau_0/\tau = 1 + k\tau_0(O_2) \quad [18.1]$$

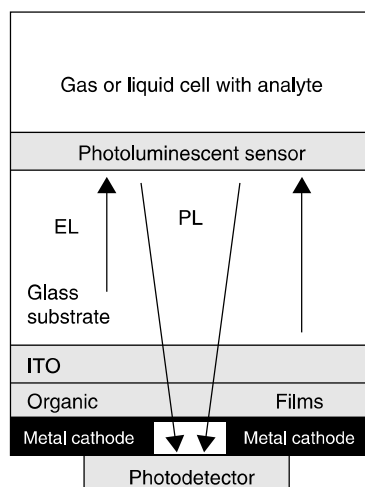
where the subscripts 0 denote values in the absence of a quencher and $k\tau_0$ is known as the Stern-Volmer constant. Experimental Stern-Volmer plots of $1/I$ or $1/\tau$ vs (O₂) should therefore be linear with identical slopes for a single type of luminophores in a given host, equally accessible to the quencher. Indeed, in solution, this predicted linear dependence was confirmed (Jorge *et al.*, 2004).

Methodology of oxygen sensing

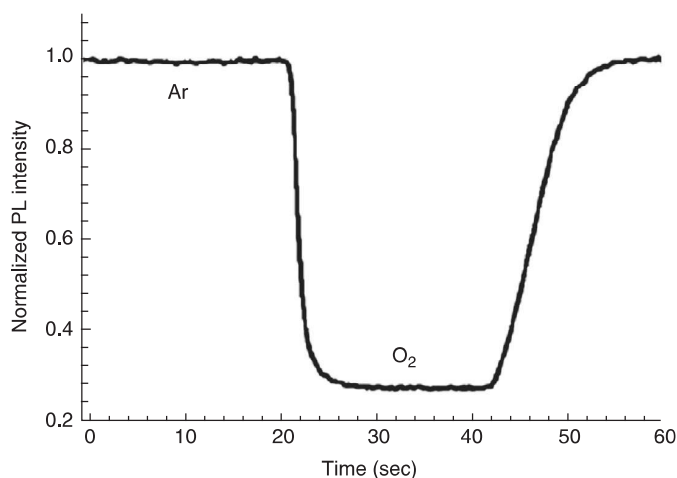
The oxygen sensing films were prepared by immobilizing Ru(dpp)3 in a sol-gel matrix. First, Ru(dpp)3 was blended with a sol, prepared from a methyltriethoxysilane precursor mixed with water and ethanol. The Ru(dpp)3-doped sol was spin coated on to cleaned, silanized glass slides and then aged at 70 °C. The resulting sensor films were optically transparent and crack free (Choudhury *et al.*, 2004a).

The EL of the OLEDs used in this study, which peaks at ~470 nm, strongly overlaps the broad PL excitation and absorption bands of Ru(dpp)3. However, there is minimal overlap between the EL and the PL of the Ru(dpp) dye, which peaks at ~600 nm. This situation is ideal for the OLEDs/sensing film combination of this study. The measurements on the Ru(dpp) sensor films excited by integrated DPVBi- or Pe:CBP-based OLEDs were performed in a flow cell with flowing oxygen/argon mixtures. Mixing was achieved by means of mass flow controllers, where the flow rates of the oxygen and argon varied, while maintaining a constant total flow rate of 500 sccm, thus generating varying oxygen partial pressures. For intensity measurements the OLEDs were operated in a dc mode with a forward bias of 9–20 V, or in a pulsed mode; for lifetime measurements, they were operated in a pulsed mode. The PD was a photomultiplier tube (PMT).

Figure 18.2 shows the configuration of the oxygen sensor and Fig. 18.3 shows the response of a typical oxygen sensor device, fabricated in a front detection geometry, to alternating flow of 7 psi Ar and O₂. As clearly seen, the PL intensity



18.2 OLED sensor in the front detection geometry for detecting oxygen species (redrawn from Choudhury, 2004a).



18.3 Response time of the OLED-based oxygen sensor (adapted from Choudury, 2004a).

in pure O₂ was only 27% of that in pure Ar (equivalently, the PL increased by a factor of 3.7 when the O₂ was replaced by Ar). The response time is 1–4 sec for a change in the PL intensity by a factor of 2.5–4.

18.5.2 OLED-based immunosensors

Immunosensors involve antibodies or antibody fragments as capture elements, often immobilized on a solid support, which bind specifically to antigens. In the ‘sandwich’ format, a primary antibody, which is attached to a surface, interacts with an antigen. The bound antigen is then allowed to interact with a secondary antibody, labeled with a fluorophore. This interaction results in a surface immobilized structure in which the antigen is ‘sandwiched’ between the primary and secondary antibodies. The labeled secondary antibody enables monitoring of the bound fluorophore PL that depends on the antigen concentration.

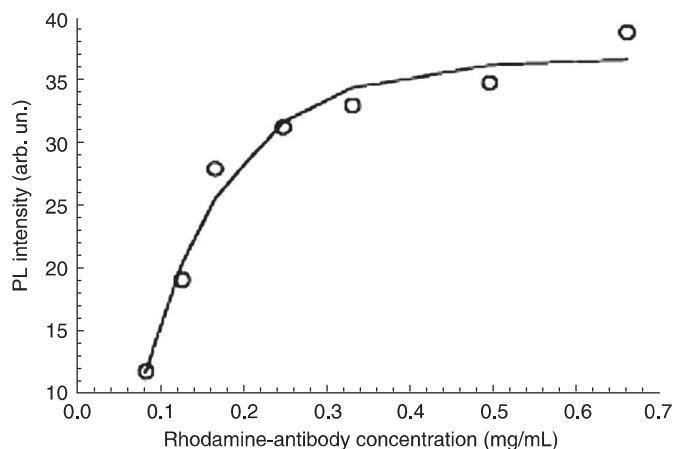
Immunosensor test methodology

To test the potential utility of OLEDs as excitation sources in structurally integrated immunosensors, the PL of the OLED was monitored with a Pierce rhodamine tagged rat IgG (host: goat) antibody to evaluate the detectable concentration range. An aqueous solution of the labeled antibody (3 µL) was placed in wells produced in a thin transparent poly(dimethylsiloxane) (PDMS) slab. The PDMS slab was attached to the opposite side of the OLED glass substrate, i.e. it replaced the sensor film shown in Fig. 18.1.

Figure 18.4 shows the results, which indicate that the current antibody level that can be detected is $\sim 0.3\text{--}0.4\text{ }\mu\text{g}$, which, for an antibody with a molecular weight of $\sim 150\,000$, corresponds to an antibody/antigen level of $\sim 2\text{ pmol}$, although the dynamic range is limited. Studies are under way to improve the dynamic range and to evaluate structurally integrated OLED/immunosensors on solid supports.

18.5.3 OLED-based glucose sensors

Recent commercial developments monitor subcutaneous glucose levels by impedance spectroscopy. However, these devices are largely limited to monitoring patterns and trends in blood sugar, and it requires daily calibration by a standard glucose meter. Its response is also affected significantly by motion, perspiration, and temperature. Glucose-sensing methods often rely on the enzymatic oxidation of glucose in the presence of glucose oxidase (GOx). The glucose concentration c_{Gl} can be determined by analyzing the reaction products (Li and Walt, 1995), or by measuring the photoluminescence (PL) intensity I or PL lifetime τ of an oxygen-sensitive dye, co-embedded from the films. Several approaches have been used to address these issues. For example, to address problems due to changes in the excitation source intensity, two fluorescent dyes, an indicator oxygen-sensitive dye and a reference oxygen-insensitive dye, have been incorporated together with GOx in a ratiometric nanosensor (Xu *et al.*, 2002; Cheon and Shinar, 2002; Li and Shinar, 2003). To account for possible variations in the oxygen concentration, cO which can compromise accurate glucose monitoring, two sensors, i.e. an oxygen sensor and a glucose biosensor, were used simultaneously (Li and Walt, 1995; Rosenzweig and Kopelman, 1996). The excitation sources for investigating



18.4 The PL (in arbitrary units) of a rhodamine-labeled anti-rat antibody as a function of the labeled antibody concentration. The data has been adapted from Choudhury, 2004a.

PL-based glucose biosensors have included Ar⁺ lasers operated at 20–40 mW (Xu *et al.* 2002, Rosenzweig and Kopelman 1996), Hg lamps (Xu *et al.*, 2002), or a fluorometer equipped with a 150 W Xe lamp (Wolfbeis *et al.*, 2000), and *cGl* was usually monitored via changes in the PL intensity *I*.

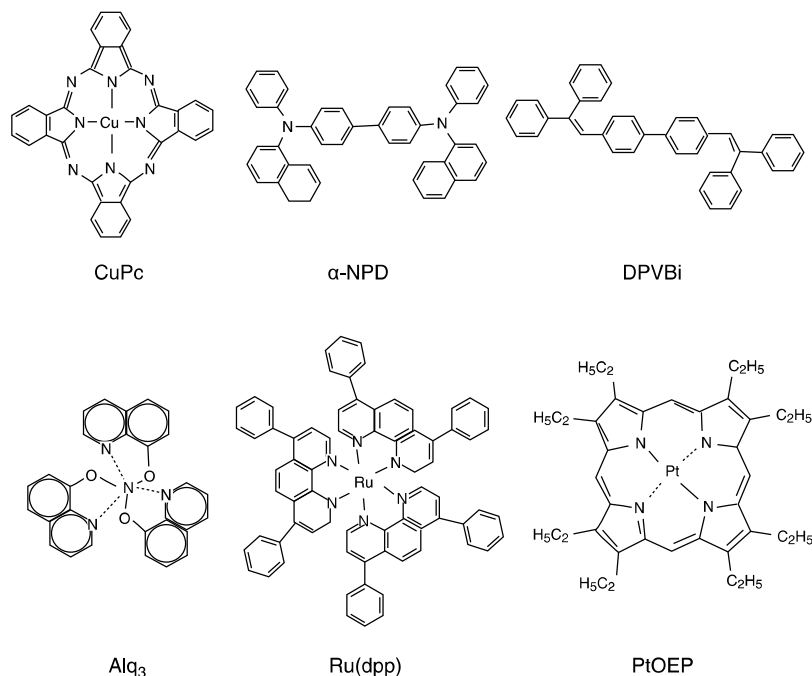
Choudhury *et al.* (2004a) have demonstrated a uniquely simple, structurally integrated platform for PL-based biosensing using a glucose biosensor as *cGl* is determined from either *I* or τ . Individually addressable OLED pixels, operable as the light source, are integrated with the sensing element. The OLEDs and the sensing element are fabricated on glass or plastic substrates, which are attached back-to-back, resulting in an extremely simple and compact device, which has the potential to advance the field of glucose sensing in various applications as well as PL-based biosensing technology for other analytes.

Blue OLED arrays were fabricated by vacuum evaporation of organic layers on 150–200 nm thick indium tin oxide (ITO) (the anode) coated glass (Li and Shinar, 2003). The organic layers consisted of a 3.5 nm thick copper phthalocyanine (CuPc) hole injecting layer, a 40 nm thick *N,N'*-diphenyl-*N,N'*-bis(1-naphthyl phenyl)-1,1'-biphenyl-4,4'-diamine (α -NPD) hole transport layer, a 40 nm blue-emitting 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl (DPVBi) layer (Li and Shinar, 2003), and a 4 nm thick tris (8-hydroxy quinoline) Al (Alq₃) electron transport layer (see Fig. 18.1 for the molecular structures). A 0.8 nm CsF buffer layer was deposited on the organic layers (Savvate'ev and Shinar, 2003; Li and Shinar, 2003), followed by the 150 nm Al cathode. The OLEDs were prepared as an encapsulated matrix array of $\sim 4 \text{ mm}^2$ pixels resulting from mutually perpendicular stripes of etched ITO and evaporated Al for 'back-detection'. Green Alq₃ OLEDs (Savvate'ev and Shinar, 2003; Friend *et al.*, 1999; Li and Shinar, 2003) were prepared by an identical procedure, in which the DPVBi was replaced by Alq₃. The total thickness of the OLED, excluding the glass or plastic substrate, was $\sim 0.5 \text{ mm}$. For *I* measurements, the OLEDs were operated in a pulsed mode with a forward bias of 8–15 V. For τ measurements, they were operated in a pulsed mode with a bias of 10–15 V, a pulse width of 1–100 μs , and a repetition rate of 20–25 Hz. It was determined that the pulse width, amplitude, or repetition rate had no effect on the measured τ .

Glucose-sensing methodology

Glucose sensing was achieved by:

- (i) Co-embedding GOx (EC 1.1.3.4, 162 units/mg type VII from *Aspergillus niger* (Sigma)) and the blue-absorbing-red-emitting dye tris(4,7-diphenyl-1,10-phenanthroline) Ru chloride (Ru(dpp)) in a sol-gel matrix (see Fig. 18.5).
- (ii) Depositing first a thin layer of the green-absorbing-red-emitting Pt octaethylporphyrin (PtOEP) as shown in Fig. 18.5 embedded in polystyrene, and then covering it with a thin layer of GOx in sol-gel. Ru(dpp) and GOx in aqueous solution also served as a sensing element.



18.5 The structures of copper phthalocyanine (CuPc), N,N'-diphenyl-N,N'-bis(1-naphthyl phenyl)-1,1'-biphenyl-4,4'-diamine (α -NPD), 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl (DPVBi), tris(8-hydroxyquinoline)Al (Alq3), tris(4,7-diphenyl-1,10-phenanthroline) Ru chloride (Ru(dpp)), and Pt octaethylporphyrin (PtOEP).

The sol-gel was prepared from 1 ml methyltriethoxysilane (MTEOS) precursor mixed with 0.18 ml water and 1 ml ethanol (Choudhury *et al.* 2004a). The mixture was sonicated for 1 h and then kept at 4 °C in the dark for 24 h. 10–30 mg Ru(dpp) was mixed with the sol-gel, while 5–50 mg GOx was dissolved in 1 ml water. A film was prepared by blending 0.5 ml of the Ru(dpp)-containing sol-gel with 0.5 ml of the GOx solution. The GOx and dye-doped sol-gel was either spin coated at 2000–4000 rpm or drop cast and spread evenly onto cleaned glass slides. The films were allowed to dry at 4 °C in the dark. The effect of the spin coating rate in this range was very small, resulting in slightly increased I for a given cGl with decreasing spin rate, probably due to an increased film thickness. The spin-coated films were visibly more homogeneous than the drop-cast films. Oxygen-sensing elements were prepared similarly but without the GOx. The resulting films were aged at 70 °C for 5–6 h or air dried for 2–3 days for Ru(dpp) or a few hours for PtOEP. PtOEP-based sensing elements were prepared by dissolving PtOEP in toluene (3.5 mg/ml) together with polystyrene (10 mg/ml). Thirty microliters of the mixture were evenly dropcast on a glass slide and allowed

to dry for 1 h. Next, 100 ml of a solution containing 7.5 mg/ml GOx were drop-cast on top of the PtOEP film and allowed to dry in the dark for three days. Solution-based sensing elements were contained in wells generated in poly (dimethyl siloxane) (PDMS) slabs. The solution contained 7.5 mg/ml each of the dye and GOx.

The sensor PL was monitored with a Hamamatsu 3456 photomultiplier (PMT) tube operated at 1000 V. The PL lifetimes were obtained by monitoring the sensor response following the application of the OLED pulse; the electroluminescence (EL) decay times for the DPVBi and Alq₃ OLEDs used in this study were dominated by the RC time constants of the OLED circuits, which were ~30 ns (Cheon and Shinar, 2004). The PL lifetimes of Ru(dpp) were calculated from the exponential decay from 0.5 to 13.2 ms. Similar values of the PL lifetimes were obtained when the lifetimes were calculated for other time ranges, starting at longer times. For the PL lifetimes of PtOEP, the range was 0.7–40 ms for 0 glucose to 0.7–150 ms for 5 mg/ml glucose. The experimental error in *I* and τ was $\pm 5\%$. The data has been adapted from Choudhury *et al.* (2004b).

18.5.4 OLED-based hydrocarbon sensors

A multi stacked organic light-emitting device has been designed by the Prasad group for detecting aliphatic hydrocarbons. This has been achieved by identifying the appropriate combination of organic polymers and anode and cathode material for achieving the most suitable device characteristics-reduced turn-on voltage for the purpose of chemical sensing. The device employs the nanotexturing in thin films to demonstrate measurable changes to the turn-on voltage and light intensity as a function of the chemical concentration. The organic light-emitting diode structure selected for this application consists of a stack of a metal oxide and metal sandwiching two electro active polymers that function as electron and hole transport layers respectively, with the following multi-stack configuration – ITO/TPD/AlQ₃/Al.

The device prototype demonstrates the detection of two specific simple aliphatic hydrocarbons in the liquid state – ethanol and methanol. We have demonstrated lower parts-per-million sensitivity, in detecting these two hydrocarbons. The key innovation associated with this chemical sensor technology is the fact that while the detection of the chemical agent is visual due to the change in the intensity of emitted light from the electroluminescent device, the sensor technology is label-free. This indicates that the chemical agents that have been detected (aliphatic hydrocarbons) have not been tagged with a fluorescent tag or an external chemical to make them luminescent. The chemical agents in their intrinsic form modulate the intensity of emitted light. The device prototype demonstrates potential towards developing a label-free, cost-effective, rapid, portable chemical sensor technology.

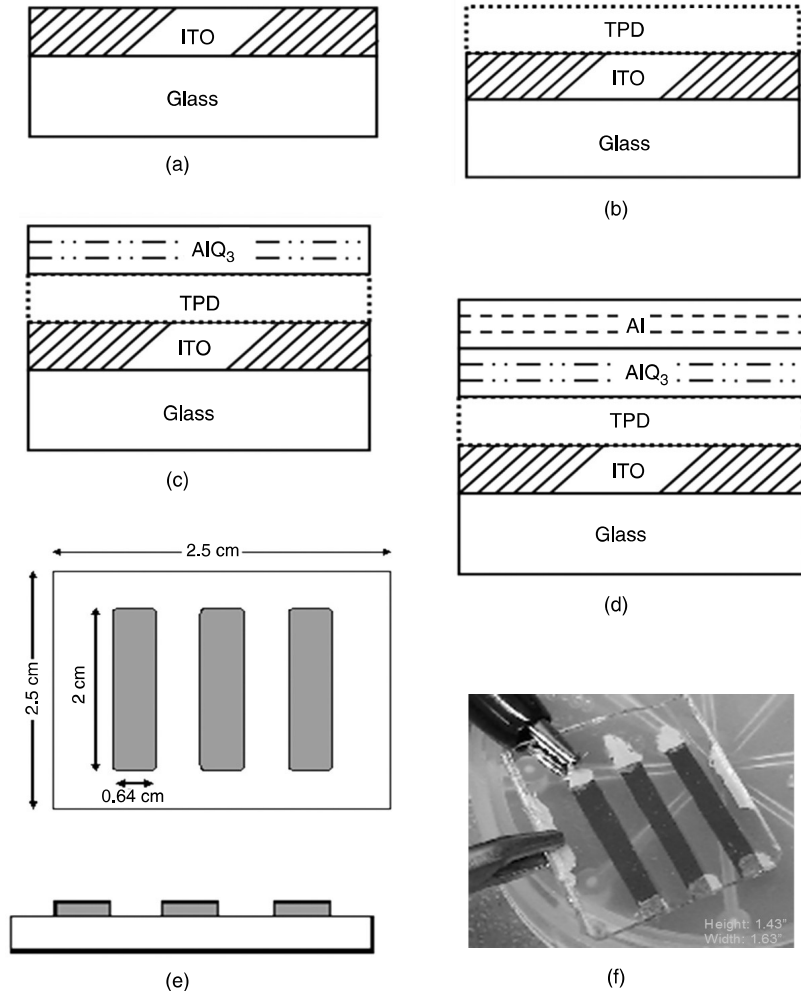
Design of the device

The device design has been adapted from Devabhaktuni (2009). The multi-stacked OLED was assembled on the anodic indium tin oxide (ITO) substrate. The OLEDs were fabricated on an ITO-coated glass substrate of size 2.5×2.5 cm. Each glass substrate had three OLEDs which were fabricated using a single mask. The process flow is shown in Fig. 18.6(a–d) and the mask schematic is shown in Fig. 18.6 (e). The mask is comprised of rectangular perforations on an optically transparent plastic. The dimension of each perforation was 2×0.64 cm. The mask was then fixed on to the ITO glass substrate for depositions of the various organic material layers for developing the multi-layer stack of the organic polymers. The mask was removed once the Al cathode was deposited.

The process flow for the fabrication of the OLED chemical sensor utilized the standard photolithography techniques. The substrate was glass coated with indium-tin-oxide (ITO) of thickness 100 nm with a sheet resistance of $20\text{--}30 \Omega/\text{m}^2$ (Sigma Aldrich Co, St Louis, MO.) The glass substrate was cleaned with isopropyl alcohol and DI water. TPD (*N,N*8-diphenyl-*N,N*8bis-3-methylphenyl-18-biphenyl-4-48-diamine) and AlQ_3 (tris-8-hydroxy quinoline aluminum) (Sigma Aldrich Co, St Louis, MO) of thickness about 300 nm were deposited over ITO to generate a nanotextured interface between the anode and cathode by the polymeric interface between TPD and AlQ_3 . The layers had a two step deposition process. First, TPD was deposited onto ITO by the two-step deposition process. The first step involved thermal vacuum deposition from tungsten boats at a pressure of about 10^{-5} Torr, with a deposition rate of about 0.2 nm/s and the formation of a 200 nm thick smooth layer of the polymer. The second step involved the drop coating of the polymer resulting in a roughened end surface of approximately 100 nm. The same process was repeated in reverse order for the second polymer AlQ_3 and resulted in a nanotextured polymer stack.

Aluminum was then deposited on top of AlQ_3 with a thickness 1000 nm using thermal vacuum deposition (Fig. 18.6(d)). These materials are selected since they can be deposited using the same thermal vacuum deposition without disturbing the structure of the diode. ITO functioned as the anode and Al functioned as the cathode, with organic polymer layers sandwiched in between them. These were the TPD/ AlQ_3 layers of polymer in the multi-stack. TPD was deposited on top of the ITO anode and AlQ_3 was deposited over the TPD layer. TPD functioned as the conductive polymer because the holes that were emitted from the anode got stacked in this layer. Also, in organic materials, holes are more mobile than electrons, so due to the electrostatic forces between the charge carriers holes moved from the TPD layer and are identified to be the conductive layer. AlQ_3 functioned as an emissive polymer that generated electrons, as the recombination took place in this region at the junction/interface of the AlQ_3 polymer.

Using silver epoxy the connections from the power supply were made to the OLED. The lead contacts were robust and adhered well on to the smooth surfaces



18.6 (a–d) Schematic representation of the various stages of the process flow of the layer by layer deposition of the various layers of the OLED device. (e) schematic representation of the mask used for device fabrication resulting in the formation of 3 OLED devices on a single substrate platform. (f) Optical micrograph demonstrating the OLED devices fabricated through the layer by layer process flow. (g) Scanning electron micrograph demonstrating the nanotexturing of the organic layer interface i.e. the interface between the P and N layer formed at the junction of TPD and AIQ₃. (Source: Devabhaktuni, 2009.)

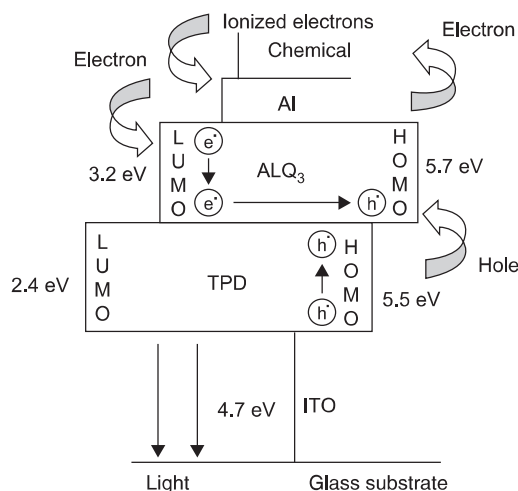
of the anode and cathode respectively. The epoxy was allowed to dry for a few hours and the contact leads were taken out from the epoxy and connected to the positive and negative terminals of a DC voltage connected to the supply. This resulted in the emission of light from the Al cathode as demonstrated in Plate X (a–c) (see colour section between pages 414 and 415).

Aliphatic hydrocarbon sensing

The sensing mechanism is based on the measurable variation to light intensity due to the effects of the specific chemicals on the cathode. The interaction of the ionized chemical species with a metallic cathode results in the modulation of the charge transfer characteristics within the vertical stack resulting in the modulation of the observable intensity of the emitted light. A specific change to the turn-on voltage and the intensity of emitted light was observed for the two chemicals. The integration of these two aspects results in the development of the ‘optical signature’ for the identification of individual chemicals.

The OLED functioned as a chemical sensor by forward biasing the device, with the anode being connected to the positive terminal of the power supply with respect to the cathode. This causes a stream of electrons to flow from the cathode towards the anode. So, the emissive layer is accumulated at the interface of the two organic polymer layers with electrons from the cathode. Simultaneously, due to the positive bias, the anode supplies holes to the conductive layer. As the voltage is increased the emissive and the conductive layers are accumulated with electrons and holes respectively. The electrostatic forces between the electrons and holes cause them to be attracted towards each other resulting in recombination, releasing energy in the form of visible light. Since the holes are more mobile in organic materials the recombination takes place in the emissive layer. This device cannot be operated in reverse bias because the layers only allow mono transport. Here TPD acts as the Hole Transport Layer (HTL), which means it allows the holes to pass through it, but will block the electrons. So, the electrons from the emissive layer are at the nanotextured interface of the two organic layers. It is thought that the nanotexturing may enhance the charge retention at the interface. This may be the reason for observing longer durations of recombinations occurring at the interface of conductive (P) and emissive (N) layers as compared to standard smooth thin film OLEDs.

When the chemical is added to the cathode of the OLED, the applied bias voltage ionizes the chemical-depending ionization potential of the chemical. Consequently, there are no electrons available in the emissive layer for the holes to recombine and release energy initially. As a result, when there is a change in the concentration of the specific chemical, there is a change in the electron concentration moving into the emissive layer. This produces a change in the observed intensity of emitted light. In addition, due to different ionization rates for the two hydrocarbons, the turn-on voltage changes accordingly. Figure 18.7 is



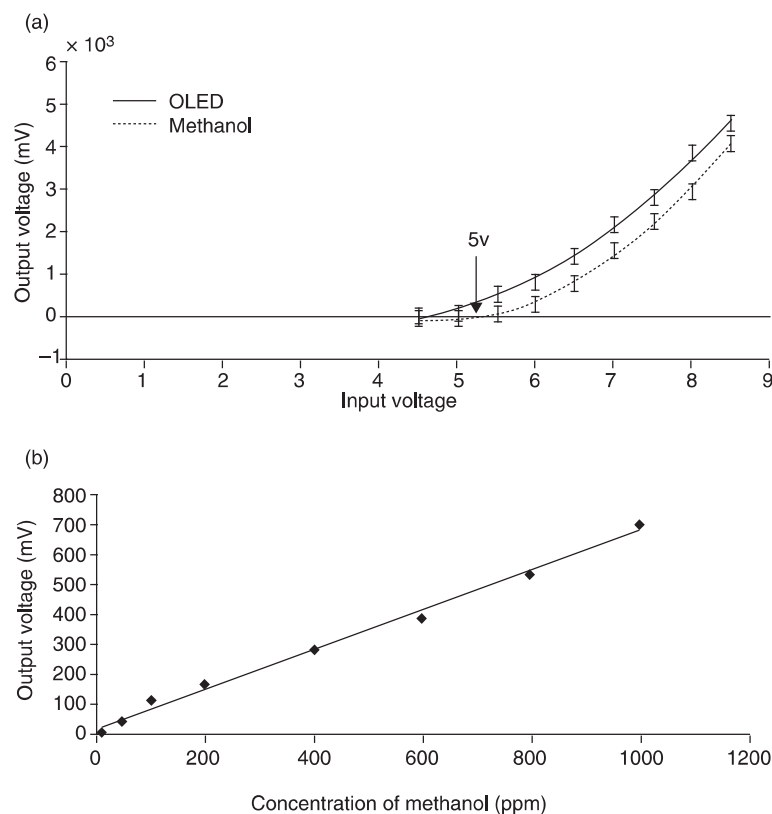
18.7 Energy band diagram of the nanotextured multi-stack demonstrating the HOMO and LUMO layers and the transport of the charge carriers through the nanotextured multi-stack.

the energy band diagram that shows the operation of the OLED in the normal light emission mode. The addition of the chemical perturbs the band height of the HOMO layer by pushing it down or pulling it up based on the ionization potentials of the chemicals that are tested, which in turn changes the threshold turn-on voltage for the device.

The characterization of the OLED chemical sensor was done by measuring the electroluminescent intensity of the device in the absence and in the presence of the hydrocarbons (ethanol and methanol). This was achieved by using a measurement set-up consisting of a photo diode and an oscilloscope as shown in color Plate X(d). Input voltage was applied to the device using a direct current supply source. Increasing the input voltage increased the intensity of the emitted light, which was measured using an oscilloscope and a photo diode. The photo diode converted the light energy into electrical energy that was in turn read by the oscilloscope. The change in the emitted light intensity was recorded for the two hydrocarbons over a range of concentrations: between 1000 ppm and 10 ppm for methanol and between 1000 ppm and 1 ppm for ethanol.

Methanol detection

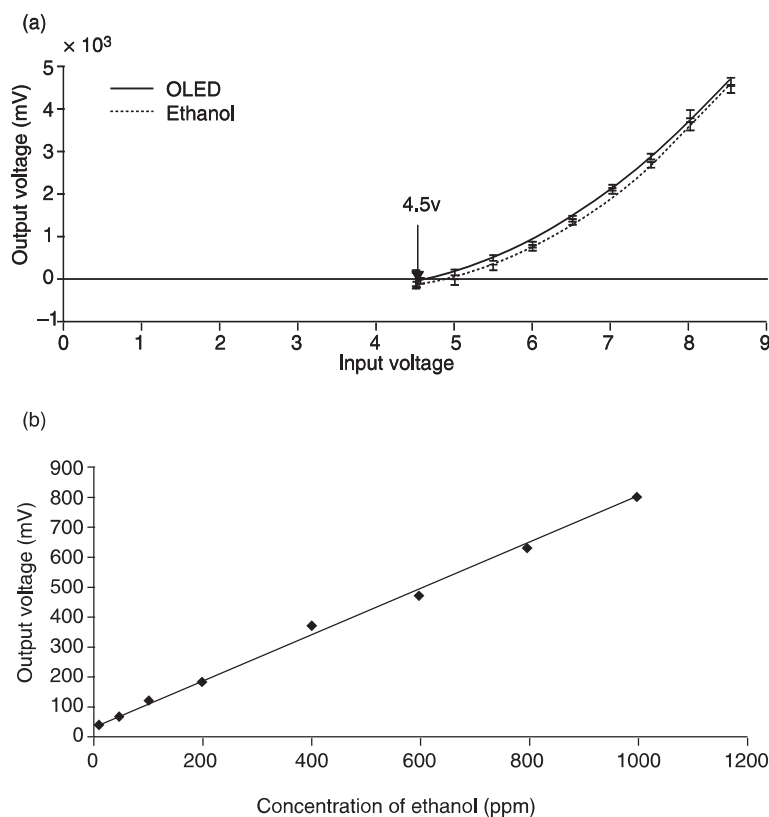
A specific concentration of methanol was injected onto the Al cathode surface and the volume of test sample dispersed onto the cathode surface was 10 μ l. After 5 minutes of incubation at room temperature, the turn-on intensity was determined. The intensity of the OLED with presence of the methanol is shown in Fig. 18.8(a).



18.8 (a) Graph showing the response of the OLED sensor to methanol. The representation is for concentration of 800 ppm of methanol. For the entire dynamic range the change in the output voltage follows a similar trend post turn-on voltage of 5V, but the absolute values of output voltages increased as the concentration of methanol increased. (b) Linear dynamic range of detection of methanol using the OLED chemical sensor. There was an increase in the output light intensity as the concentration of methanol increased and this translated to an increase in the output voltage from 30 mV to 700 mV. (Source: Devabhaktuni 2009.)

The presence of the hydrocarbon altered the intensity of the OLED from its normal emission intensity. The change in the turn-on voltage from baseline to methanol was identified to be 0.5 V from the control measurements of an OLED operating in the normal mode. The change in the bias voltage was attributed to the ionization potential of methanol, which is 10.85 eV (Novakovskaya, 2007). The ionization potential was smaller than that of DI water. As a result of this the

charge carriers in the conductive region changed, which in turn modulated the energy band diagram by pulling down the HOMO level which in turn would enable recombinations to occur at a lower threshold voltage. This event sequence resulted in two observations: first, the turn-on voltage was lower than that observed for DI water; and second, there was an observable change in the intensity of emitted light. The intensity variations were correlated to a voltage change from



18.9 (a) Graph showing the response of the OLED sensor to ethanol. The representation is for concentration of 800ppm of ethanol. For the entire dynamic range the change in the output voltage follows a similar trend post turn on voltage of 4.5V, but the absolute values of output voltages increased as the concentration of ethanol increased. (b) Linear dynamic range of detection of ethanol using the OLED chemical sensor. There was an increase in the output light intensity as the concentration of ethanol increased and this translated to an increase in the output voltage from 50mV to 800mV.

30 mV to 700 mV over the concentration range from 10 ppm to 1000 ppm as shown in Fig. 18.8(b). The increase in output voltage correlated to an increase in the output light intensity with an increasing concentration of the chemical. The linear dynamic range of detection for methanol was identified to be between 1000 ppm and 10 ppm. With a decrease in ionization potential there was a decrease in the threshold turn-on voltage, as observed from DI water to methanol (5.25 V for DI water and 5 V for methanol).

Ethanol detection

Similar to that of methanol, ethanol of 10 μ l volume was injected onto the cathode surface. Intensity of OLED with presence of the ethanol is shown in Fig. 18.9(a). The presence of the ethanol altered the intensity of the OLED from its standard intensity while operating under normal conditions. The intensity variations due to the effect of ethanol over the concentration range from 1 ppm to 1000 ppm, which was the linear dynamic range of detection, correlated to an output voltage change from 50 mV to 800 mV as shown in Fig. 18.9(b). The turn-on voltage in the case of ethanol was 4.5 V, which was lower than that of DI water and methanol and this was attributed to the ionization potential of ethanol which is 10.65 eV; that is lower as compared to the other two analytes. This measurement was in line with the trend of decreased turn-on voltage (5.25 V, 5 V and 4.5 V respectively) with a decrease in the ionization potential (12.58 eV, 10.85 eV and 10.65 eV respectively) as observed among DI water, methanol and ethanol (Devabhaktuni, 2009).

18.6 Conclusion

In this chapter research work has been summarized that demonstrated the potential of using an OLED for visual chemical detection of hydrocarbons from aqueous solutions. Detection of hydrocarbons, proteins, glucose and oxygen has been achieved by identifying the specific turn-on voltages and output intensities relevant to the bio/chemicals. The variation in the turn-on voltages and output intensities with each analyte is due to the difference in ionization potentials required by the chemicals to release the valence electrons. Nanotexturing of the emissive and conductive layer interface does contribute to the reduced turn-on voltages, which is important while designing low power sensors. Hence, by optimizing the nanotexturing it may be possible to more specifically control the OLED operating characteristics while functioning as a sensor.

Ionization potential for low ionic solutions is the highest; this suggests that it requires more energy for it to ionize and release the electrons, which may be the reason for the requirement of increased voltage to facilitate recombination between electrons and holes, thus increasing the turn-on voltage.

The OLED-based detection technique, despite being an optical detection technique, is still label-free. This has been achieved by exploiting the organic

nanotextured multi-stack OLED and perturbing the electron-hole recombination rate in the multi-stack organic layers. The advantage of using the nanotextured multi-stack OLED is that the bias voltage is reduced and this is due to the mono charge layers used for different charge carriers and the organic layers being mono-transport, i.e. they transport a single type of charge (either electrons or holes). The intensities of luminescence are in the range of the visible spectrum and the resulting color of the light is green. This spectrum depends upon the active layer, which in the current application is AlQ₃. Peak intensity occurs at 516 nm, which is green in the visible spectrum.

Despite the advantage of developing an optical label-free sensor there are multiple experimental process parameters that need to be optimized and controlled for proper functioning of these devices as sensors. In order for OLED to function properly the ITO layer (anode) thickness needs to be controlled before depositing organic layers. While depositing the organic layers when nanotexturing is needed, there should not be any pinholes. The gaps in the polymer layer during deposition are called pinholes due to their size and these pinholes affect the functionality of the OLED. The layers must be deposited keeping the stud (the mount to which the chip is attached) at a distance so that the other layers are not thermally perturbed, resulting in inactive layer depositions. By properly adjusting the thickness of the layers and optimizing the nanotexturing the OLED turn-on voltage can be reduced. The alignment of the photo diode impacts the maximization of the absorption of the emitted light.

The advantage with these OLEDs is that they operate both in pulsed mode and continuous mode power supply. However, for the sensing application these devices are operated in the continuous mode. In this mode, the energy bands of these organic semiconductors (emissive and conductive layers) are such that there is no temperature loss. OLED-based sensors are robust, portable, cost effective and fast. These types of sensors can find applicability in applications such as mining, and in chemical factories where there is a chemical spill for rapid, visual, label free indication of the trace presence of a toxic agent. This sensor is called label free because it does not use any external fluorescent tags or labels with the analyte that is tested but utilizes the modulation to the electroluminescent capability of the device as a function of the chemical analyte as a mechanism for chemical sensing. The disadvantages of the OLED sensor technology are their long term stability and re-use. With an increase in recombination the width of the junction barrier increases, therefore it becomes difficult for the charge carriers to break through the junction, thereby reducing the operating time. Using a multi-array cathode structure these OLED based chemical sensors can be used for multi-chemical sensing.

18.7 References

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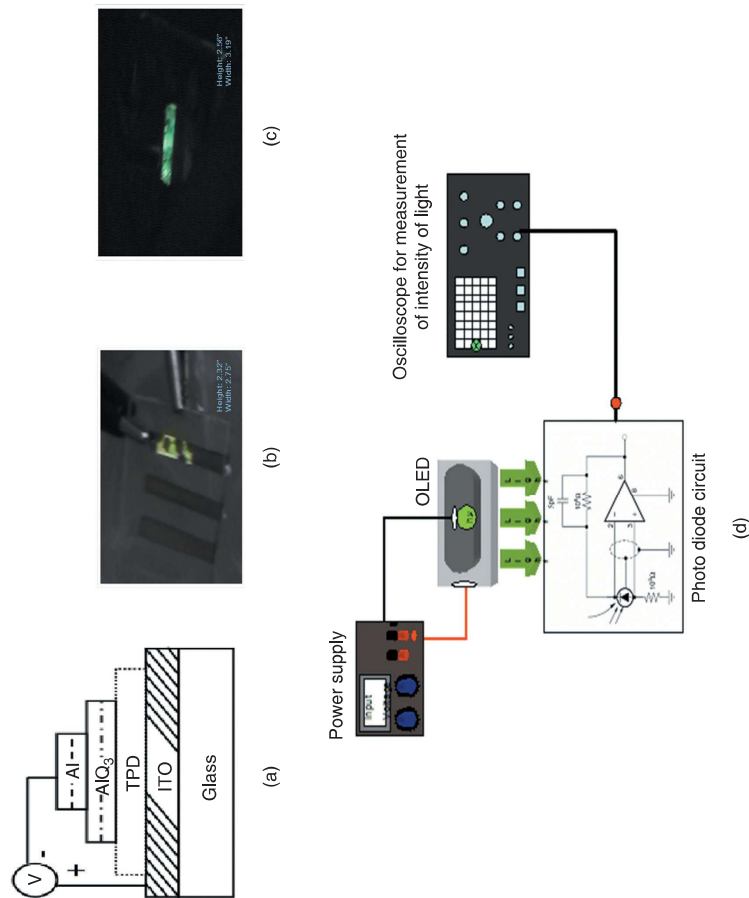


Plate X (Chapter 18) (a) Schematic representation of the multi-layer nano textured stack of the OLED device. (b–c) Optical micrograph demonstrating the functioning of the electroluminescent OLED device. (d) Schematic representation of the measurement circuit comprising an oscilloscope coupled to a photo diode circuit connected to the powered OLED that converts the output optical intensity from the OLED into a voltage signal. (Source: Devabhaktuni, 2009.)

Large-area OLED lighting panels and their applications

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Abstract: This chapter discusses the key issues related to the fabrication of large-area organic light-emitting devices (OLEDs) for lighting applications. It focuses on the origin of a short-circuit problem, luminance non-uniformity, hot spot, power loss, and heat generation and describes ways of suppressing them. The chapter then introduces three different application areas of large-area OLED lighting panels. They can be integrated with a solar cell for power recycling or inorganic LEDs for emotional lightings. The feasibility of using OLEDs for the application of visible-light communications (VLCs) is also reviewed.

Key words: organic light-emitting diodes (OLEDs), lighting, hybrid lighting system, self-powered OLED, visible-light communication.

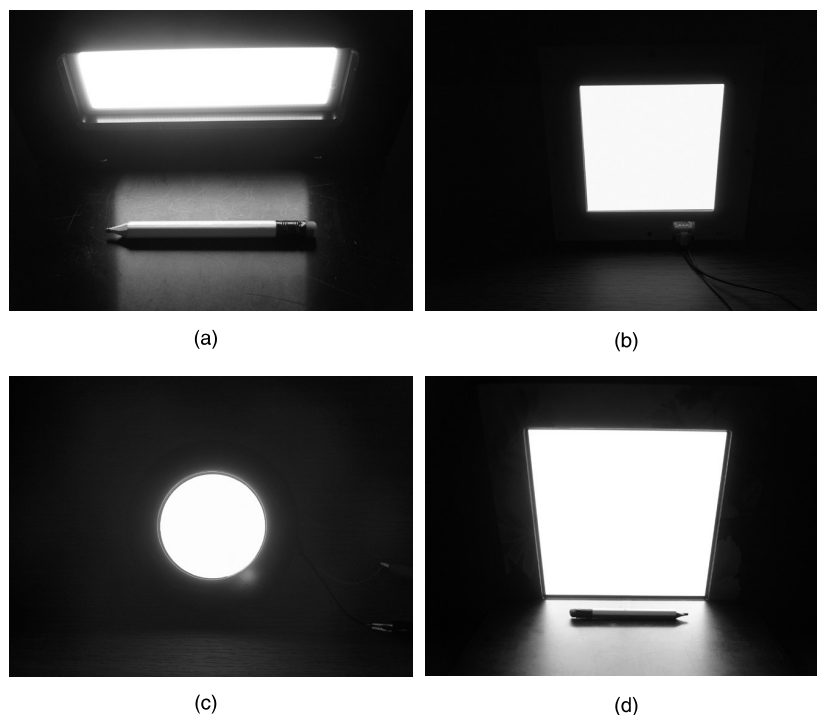
19.1 Introduction

Organic light-emitting diodes (OLEDs) are very attractive for display and lighting applications as they offer great potential for providing high power efficiency, low operational voltage, low operating temperature, and long lifetime (Tang and Vanslyke, 1987; Burroughes *et al.*, 1990; Reineke *et al.*, 2009; Sun *et al.*, 2006). As an innate surface-emitting light source for lighting applications, they can be operated at lower luminous intensity to get the same luminous flux simply by expanding the emission area. This feature is highly desired because it does not bring in much heat generation, thereby facilitating the implementation of large-area inflexible and flexible lighting systems (Kido, 2008). However, there still exist many technical issues in the development of large-area flat-panel OLED lightings. Fabricating large-sized panels entails several troublesome problems, for example a short circuit, non-uniform light emission, hot spot, power loss, and heat generation (Park *et al.*, 2009; Pohl *et al.*, 2008; Gärditz *et al.*, 2007; Kido, 2008). In this chapter we discuss the origin of those issues and provide the way of overcoming them. In addition to large-area surface emission and flexibility, another salient feature of OLEDs lies in their transparency (Ryu *et al.*, 2008; Yook *et al.*, 2008). This feature may create many application technologies in combination with other devices such as solar cells and inorganic LEDs (ILED). In parallel with the panel development, therefore, it is desirable to find their new application areas

in order to invigorate the OLED lighting industry further. In this chapter, we also introduce three different OLED application areas. One of them is to integrate a transparent solar cell with a transparent OLED lighting panel for the applications of self-powered light-emitting windows (Park *et al.*, 2010). Another one is to combine ILEDs with OLEDs for the applications of hybrid lightings (Park *et al.*, 2011). The other application area lies in a visible-light communication (VLC) (Park, 2010).

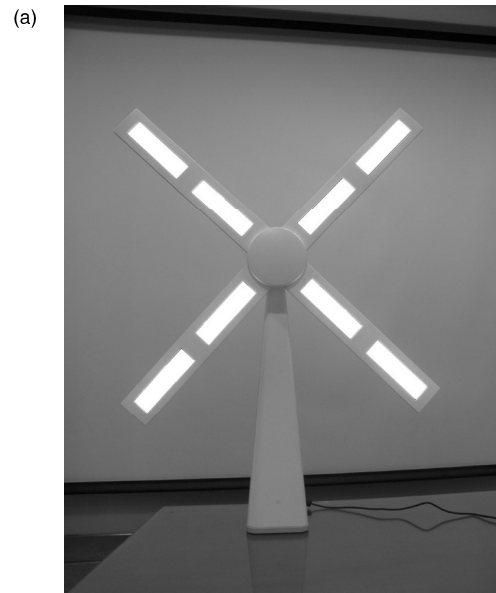
19.2 Fabrication of large-area OLED lighting panels

Shown in Fig. 19.1 are the images of light emission from various lighting sources; (a) rectangular ($30 \times 120 \text{ mm}^2$), (b) square ($70 \times 70 \text{ mm}^2$), (c) round (diameter=70 mm), and (d) square ($150 \times 150 \text{ mm}^2$) shaped panels. To meet some required luminous flux or develop new concept lighting systems, one may need to connect unit sources in series or parallel. Using such a tiling technology, we can fabricate various working mock-ups as presented in Fig. 19.2. The lighting



19.1 Images of light emission from (a) rectangular ($30 \times 120 \text{ mm}^2$), (b) square ($70 \times 70 \text{ mm}^2$), (c) round (diam=70 mm), and (d) square ($150 \times 150 \text{ mm}^2$) shaped large-area OLED lighting panels.

fixture of wings for a windmill in Fig. 19.2(a) is as thin as 4 mm. In Fig. 19.2(b), OLED lighting panels are used as indoor illuminations for cars, which could be feasible in real life in the near future. Like ILEDs, an OLED can be a point light source given that it is fabricated in a micro size. Though its

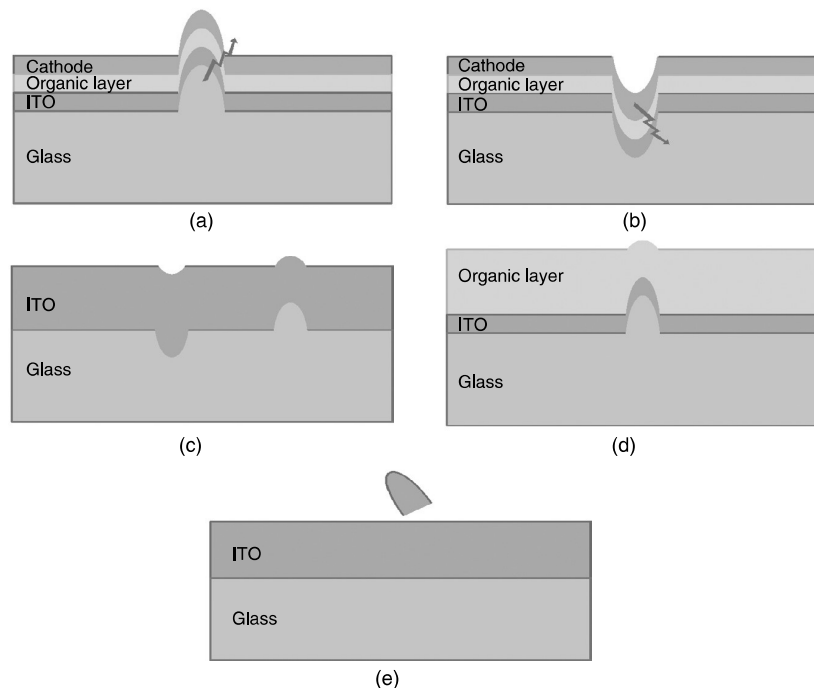


19.2 Working mock-ups using those lighting panels in Fig. 19.1 in the form of (a) windmill and (b) car.

luminous intensity can be comparable with that of ILEDs, yet its lifetime is much shortened at high luminance. To achieve the same luminous flux as ILEDs, therefore, it is desirable to utilize large-sized OLED panels. Although large-area surface emission is one of the advantages that OLEDs possess, there exists a limit in enlarging the emission area. As the panel size increases, the probability of the occurrence of a short circuit and hot spot is increased. Due to the limiting conductivity of transparent electrodes used in OLED devices, there also arise non-uniform light emission, power loss, and heat generation (Park *et al.*, 2009).

19.2.1 Short circuit

One of the tricky issues in the fabrication of large-area OLED lighting panels is a short circuit. It is induced dominantly by particles existing on a glass substrate and particles appearing during photolithography and evaporation processes (Park *et al.*, 2009). As seen in Fig. 19.3(a–b), they provide a short

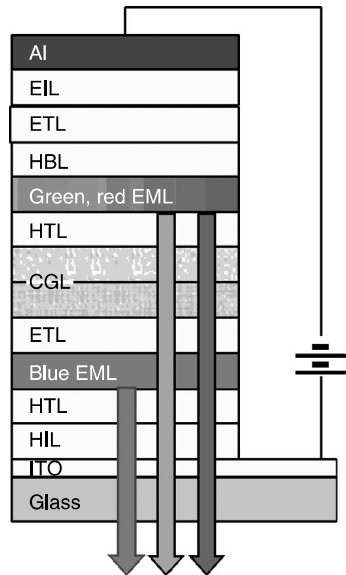


19.3 Schematic views of (a,b) the origins of a short circuit and (c)–(e) the ways to bypass it. (Source: Reprinted, with permission, from Park *et al.* (2009). Copyright © 2009 Institute of Electrical and Electronics Engineers.)

pathway for current flow, causing an instant current crowding. It also occurs when a photomask or metal mask is misaligned during the photolithography process or thermal evaporation. Upon emergence of a short circuit, the aluminum (Al) cathode melts. It also takes place as the bias voltage is varied, especially at low driving voltages. At high bias, current flowing through the device does not pass through the leakage channels due to high electric field intensity. At low bias, however, current is likely to find and pass through the leakage channels, thereby causing a short circuit. The chances of a short circuit occurring may increase with the size of the emitting area of OLEDs. As discussed below, large-area OLED panels require an auxiliary metal electrode on a transparent electrode (usually, indium-tin-oxide (ITO)). However, patterning the metallic grids inevitably may cause some damage to ITO (i.e., the surface roughness of ITO is degraded) and leave some debris (e.g., fine metal pieces) in the emission zone, which increases the probability of a short circuit. Namely, the short-circuit phenomenon is strongly related with the ITO surface condition. As such, a short circuit may show up more frequently in large-area flexible OLEDs than in inflexible OLEDs because more limitations exist in the fabrication of ITO films on flexible substrates. More seriously, it occurs even during a very stable operation, thereby bringing in a reliability issue. However, such a short circuit can be suppressed to a great extent (Park *et al.*, 2009):

1. by increasing the thickness of the transparent anode (ITO) as in Fig. 19.3(c), though the optical transmittance is sacrificed,
2. by coating a buffer layer on the transparent anode using a conductive polymer such as PEDOT:PSS (Na *et al.*, 2008),
3. by increasing the organic layer thickness in Fig. 19.3(d) (i.e., overall device thickness),
4. and/or by polishing the particles on the substrate or ITO film as in Fig. 19.3(e).

Of these, increasing the device thickness suppresses a short circuit with telling effect. The organic layer (device) thickness can readily be increased by adopting a tandem device structure without any compromise on the device performance (Liao *et al.*, 2004; Kanno *et al.*, 2006; Qi *et al.*, 2008). Shown in Fig. 19.4 is the device structure of a hybrid tandem white OLED. For white light emission, a fluorescent blue-emitting layer and a phosphorescent green- and red-emitting layer are connected in series by a charge generation layer (CGL). In this work, the CGL layer consists of Li-doped ETL (LG201) and HIL (LG101). Since many layers are stacked in this configuration, the overall thickness of a tandem white OLED device can be increased more than 200 nm. In fact, such a tandem device structure has been widely employed in fabricating large-area OLED lighting panels since it enhances the panel lifetime as well as the fabrication yield. One can also reduce the short-circuit phenomena through an aging (repair) process. Before sealing the OLED panels with a glass cover, we expose them to oxygen or moisture for dozens of seconds, and at the same time we apply the reverse bias to them at

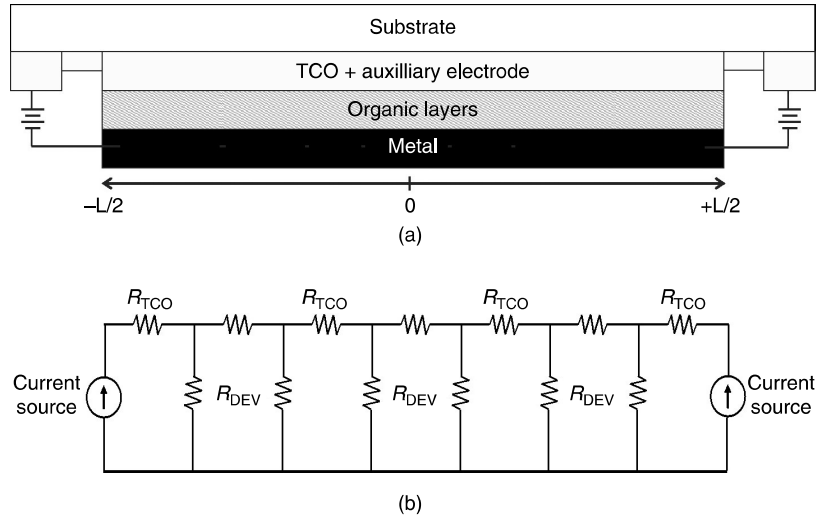


19.4 Schematic view of a hybrid tandem white OLED device structure. HIL stands for hole injection layer, HTL hole transporting layer, EML emitting layer, CGL charge generation layer, HBL hole blocking layer, ETL electron transporting layer and EIL electron injection layer.

about 10 V. By doing so, we can find that the overall device resistance increases up to $\sim 100 \text{ M}\Omega$ because the leakage channels are oxidized. It is known that exposing the OLED panels to moisture rather than oxygen is more effective against a short circuit. Although it is not the ultimate solution, it can suppress the initial short-circuit problem or enhance the lifetime a little more.

19.2.2 Non-uniform light emission

Due to the limiting conductivity of transparent electrodes, the injected current from the edges of the panel hardly reaches its central region, causing inhomogeneous light emission. As such, the light emission distribution must be taken into consideration from the beginning of the mask design for large-area OLED panels. It becomes serious at higher luminous intensity and for larger-sized OLED panels (Neyts *et al.*, 2006). Shown in Fig. 19.5 is the one-dimensional (1-D) equivalent circuit model of large-area OLED panels. If the effective horizontal resistance (R_{TCO}) of the anode is relatively higher than the vertical resistance (R_{DEV}) of the OLED device, most of current flows through the OLED device near the panel edges. In this case, one has to increase the vertical device resistance by increasing the device thickness with the aid of a tandem device structure. Namely, one has to



19.5 (a) Schematic cross-sectional view of the large-area OLED and (b) its 1-D equivalent circuit. (Source: Reprinted, with permission, from Park *et al.* (2009). Copyright © 2009 Institute of Electrical and Electronics Engineers.)

consider the ratio between R_{TCO} and R_{DEV} for enhancing the current uniformity over the panels. Another straightforward method for resolving this problem is to reduce the sheet resistance of transparent electrodes without decreasing of transparency. The commonly used transparent electrode (i.e., ITO) for anode shows the sheet resistance of $9 \sim 12 \Omega/\text{sq}$, which is still too high for large-area lighting panels. Another electrode structure employing a highly conductive metal (Ag) sandwiched between two conductive oxides has been introduced (Sahu *et al.*, 2008; Cattin *et al.*, 2010). Although it provides lower sheet resistance ($3 \sim 4 \Omega/\text{sq}$), the multi-stacking of different materials makes the patterning process difficult.

The other way is to utilize an auxiliary metal electrode that is deposited and grid patterned on ITO. As seen in Fig. 19.6, current flows through the low-resistance auxiliary metal lines to the central region, producing a highly homogeneous light distribution over a large area. The effective sheet resistance of such a structure can be expressed as (Neyts *et al.*, 2008):

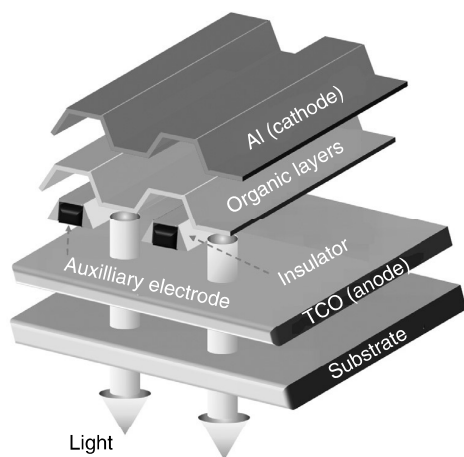
$$R_{eff} \approx \frac{2h}{\sigma wd} \quad [19.1]$$

where h is the apothem, w is the width, d is the thickness, and σ is the conductivity of metallic grids. In reality, there exists a tradeoff between the sheet resistance and the transmittivity of the grid on the selection of the ratio h/w since the transmittivity is determined by

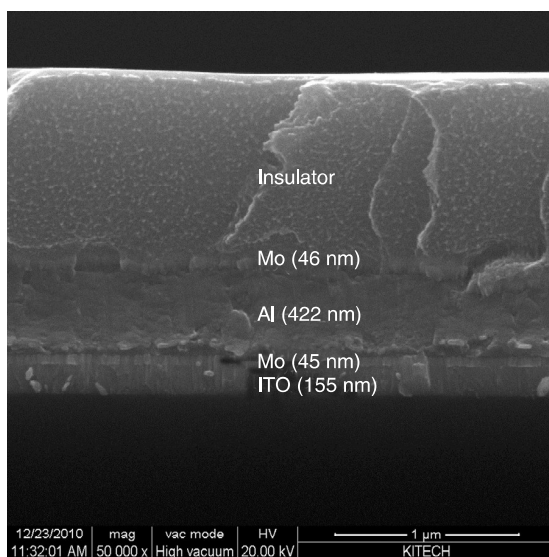
$$T = 1 - \frac{w}{h}. \quad [19.2]$$

Namely, increasing metal coverage (w/h) lowers the effective sheet resistance, but at the same time reduces the transmittivity, or rather the overall light-emitting area. Besides, the grid thickness (d) is also limited (typically 300~500 nm) because it should be covered with an insulating material on which very thin organic layers are then formed. Therefore, the conductivity (σ) of metallic grids is a key controllable parameter in reducing the effective sheet resistance and thus enhancing the device performance. Normally, Cr or MoNb/AlNb/MoNb is used as metallic grids.

Figure 19.7 shows the scanning electron microscope (SEM) image of a cross-section of the auxiliary metal electrode (Mo/Al/Mo) on ITO. The thickness of Mo and Al was measured to be 45 nm and 420 nm, respectively. The sheet resistance of 513-nm-thick Mo/Al/Mo is measured to be 0.09 Ω/sq . The width of the patterned metals and insulators is 150 μm and 190 μm , respectively. The distance between the patterned metal lines is ten times greater than the width of each metal line, namely, the ratio of the emitting area to the non-emitting area is 10:1. We have measured the luminance non-uniformity of large-area OLED panels using a two-dimensional (2D) color analyzer (CA-2000A, Konica Minolta) and presented the results in Fig. 19.8. As a reference device, we fabricated 30 $\times$ 120 mm² hybrid tandem white OLED panels without any metallic grids included. By the insertion of Mo/Al/Mo metal lines on ITO, the luminance non-uniformity is reduced from



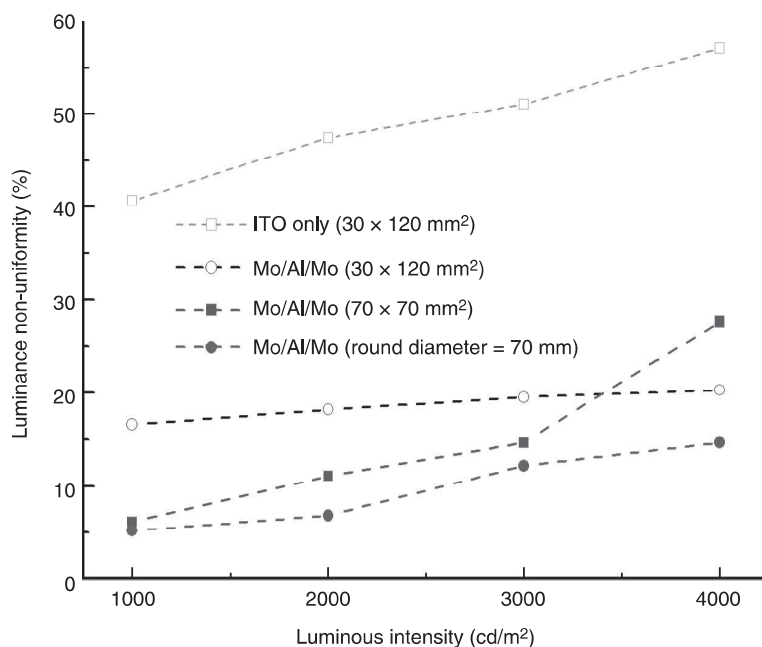
19.6 Layer structure of the large-area OLED with auxiliary metallic grids covered with an insulator. (Source: Reprinted, with permission, from Park *et al.* (2009). Copyright © 2009 Institute of Electrical and Electronics Engineers.)



19.7 Scanning electron microscope (SEM) image of a cross-section of Mo/Al/Mo metals on ITO.

57% to 20% at 4000 nit. One may place the metal lines either densely or sparsely with the aperture ratio unchanged. However, it is likely that deploying the metal grids densely is more desirable in that such a scheme is less vulnerable to the effect of particles. The shape of the metal grid also affects the luminance uniformity. It has been found that a hexagonal grid has lower voltage loss than a square grid with the same line width (Neyts *et al.*, 2008). For a square grid, inhomogeneity occurs at each corner. In this context, a round-shaped panel is expected to show more uniform luminance distribution. In Fig. 19.8, the square-shaped panels ($70 \times 70 \text{ mm}^2$) consist of the square-shaped Mo/Al/Mo grids ($150 \mu\text{m}$ in width), while the round-shaped one has the hexagonal grids ($h = 1 \text{ mm}$). It is observed that the round-shaped panel shows more uniform luminance distribution. As such, the metal grid pattern and light-emitting area are preferred to be in a round shape.

It is noteworthy that the uniformity of light emission can be enhanced further by a driving technique. One can divide the emission area into many sections, each of which is then controlled by an individual driving circuit. Namely, the luminance of each section is tuned and thus the luminance uniformity can be raised. However, it requires a very complex lighting system, causing a rise in price. The luminance uniformity can also be enhanced by reducing contact resistance between OLED electrodes and driving circuit boards. The contact area between them is preferred to be large so that current is injected into the panel from every direction. To this end, Ag pastes along with copper wires are commonly employed. Multi-pin



19.8 Measured luminance non-uniformity of various OLED panels as a function of luminous intensity.

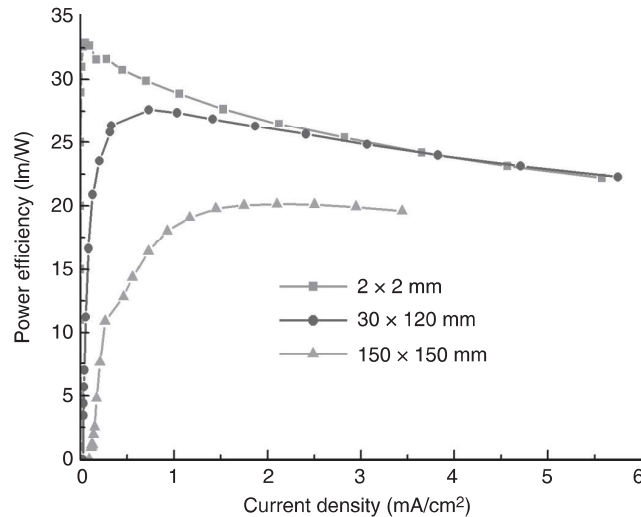
contacts are also used to suppress the contact resistance as well as the current non-uniformity (Park *et al.*, 2009).

19.2.3 Hot spots

Hot spots are normally induced by the spikes or rough surface of transparent electrodes along with particles. Though a hot spot occurs less frequently, it could be the main cause for shortening the device lifetime. Once spikes exist on transparent electrodes (Plate VIII, see colour section between pages 414 and 415), the current crowds at the spots and consequently local heat generation occurs (Plate XI) (Park *et al.*, 2011). Due to the hot spots, current flowing through the device gradually increases and eventually a short circuit-like phenomenon occurs. Upon emergence, with the aid of a heat sink, the local heat generated by the hot spots can be dissipated and thus its effect lessens to a great extent.

19.2.4 Power loss

As mentioned before, a large-area OLED panel suffers from a power loss due to the limiting conductivity of transparent electrodes. It causes a reduction of current



19.9 Comparison of power efficiency for different sized OLED panels (Cr metal line is used for 30×120mm and 150×150mm OLED panels). (Source: Reprinted, with permission, from Park *et al.* (2011). Copyright © 2011 Semiconductor Science and Technology.)

density and power efficacy. As evident in Fig. 19.9, about 20% reduction of the power efficacy on the 200×200mm OLED panel occurs, compared with the 2×2mm and 30×120mm OLED panels. Such a reduction in power efficacy could be recovered using more conductive auxiliary metal electrodes (MoNb/AlNb/MoNb, Cu, or Ag) on transparent electrodes. Furthermore, a decrease of current density results in a reduction of luminous intensity. To obtain the same luminous intensity, more current injection is demanded, inducing heat-related issues. To be released from this issue, we need to come up with a device configuration and material system showing high current efficiency at low current density. This entails various functional layers in the device configuration such as electron and hole blocking layers, interlayers for exciton blocking, etc.

19.2.5 Heat generation

Large-area flat-panel OLED lighting panels are not free from thermal-related issues. Like the conventional light sources such as bulbs, fluorescent lamps, and LEDs, the surface temperature of OLEDs is raised with increasing luminous intensity. Different from LEDs, however, OLEDs have a very short heat transfer pathway (i.e., 0.7-mm-thick glass substrate) between the internal heat source (i.e., light-emitting active area) and the outer device surface. In other words, the heat

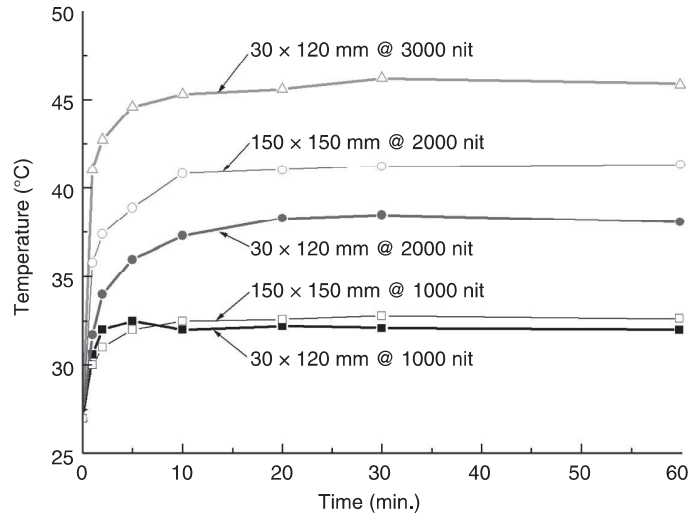
difference between them is very small, facilitating heat dissipation without using a bulk heat sink. Nevertheless, the Joule heating is also parasitic on the OLED devices. The heat flow in OLEDs is governed by the following equation expressed as

$$C \frac{\partial T(x,t)}{\partial t} = \frac{\partial}{\partial x} \left(k(x,t) \frac{\partial T(x,t)}{\partial x} \right) + \left[\frac{J_n(x,t)^2}{q\mu_n(x,t)n(x,t)} + \frac{J_p(x,t)^2}{q\mu_p(x,t)p(x,t)} \right] \quad [19.3]$$

where T indicates the temperature, k the thermal conductivity, C the volumetric heat capacitance, J the current density, μ the carrier mobility, n the electron density, and p the hole density. As expressed in Eq. 19.3, the Joule heating (the second term on the right-hand side) is induced by high current injection during operation. Due to Joule heating (Pohl *et al.*, 2008; Shin *et al.*, 2000), there occurs a reduction of luminance, short lifetime, and large spectral shift of OLEDs. To suppress the thermal degradation of organic molecules, the use of a heat sink is inevitable. This heat sink should be slim so as to show up the salient feature of ultra-thin OLEDs.

Shown in Plate XII is the heat distribution measured from 150×150 mm OLED panels with the Cr metal grids for different luminous intensity and in Fig. 19.10 the transient temperature variation for different panel size and luminance. One can see that as the luminance increases, the heat increases and at the same time heat distribution becomes non-uniform (Gärditz *et al.*, 2007). More seriously, heat is generated much more near the edges of the panel due most likely to the resistance of the anode. It means that more current flows through the device near the panel edges. From Fig. 19.10, it is observed that larger-sized OLED panels generate more heat to get the same luminous intensity. The smaller-sized (30×120 mm) OLED panel exhibits the maximum temperature of less than 50°C at the brightness of 3000 nit. As such, it is likely that small-sized OLED panels for auxiliary lighting applications requiring relatively low luminous intensity (or flux) may not need a heat sink. For general lighting applications requiring relatively high luminous intensity and flux, however, a heat sink is required for stable operation and long lifetime.

Considering the OLED device structure, heat dissipation is closely related to the encapsulation as heat transfers to a heat sink through encapsulation. Although the conventional glass encapsulation exhibits superior gas barrier properties, it shows poor thermal performance because nitrogen gas exists inside the device, which separates a heat sink from the OLED device without any contact involved between them. As evident in Plate XIII, the maximum surface temperature has been reduced only by 6°C (from 55.5°C to 49.6°C) with the aid of the heat sink. For experiments, we have employed a Polynetwork flexible heat sink (PN-FHB050N) in the form of bonding sheet. It consists of a $50\text{ }\mu\text{m}$ thick copper sheet and $35\text{ }\mu\text{m}$ thick thermal radiation layer. The bonding sheet has the thermal conductivity of $0.86\text{ W/m}\cdot\text{K}$. Recently, many researches have been conducted into



19.10 Transient temperature measured at various luminous intensities for different sized OLED panels. (Source: Reprinted, with permission, from Park *et al.* (2011). Copyright © 2011 Semiconductor Science and Technology.)

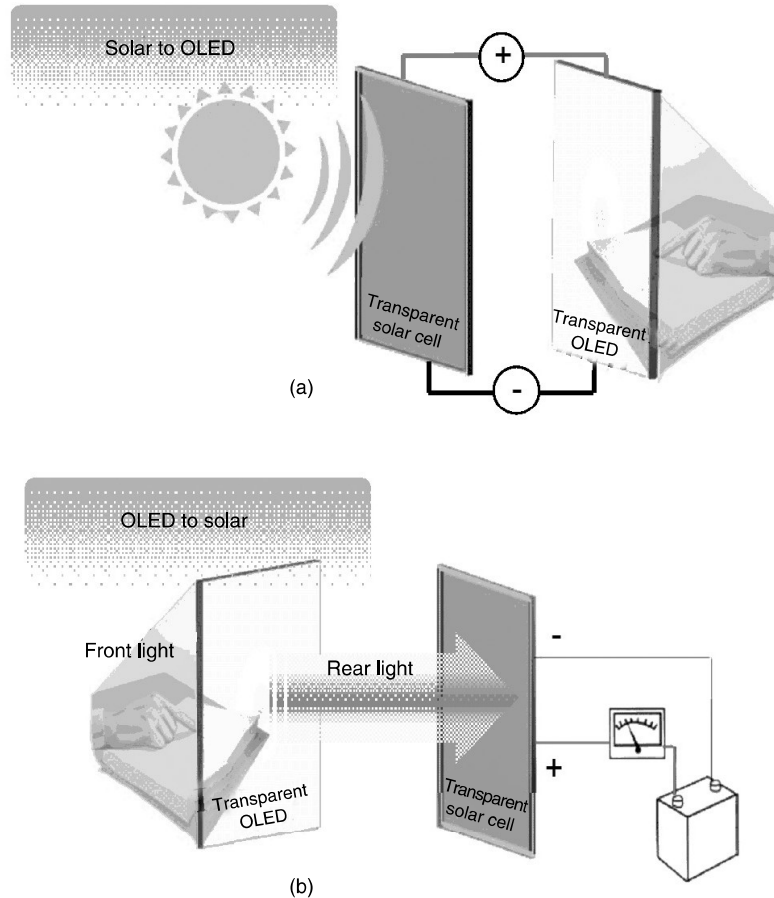
thin-film encapsulation (TFE) (Affinito *et al.*, 1996; Graff *et al.*, 2004; Charton *et al.*, 2006). Contrary to the glass encapsulation, the TFE method shows excellent heat transfer properties. It was demonstrated that the multi-heterojunction configuration and/or the low thermal conductivity of a polymer material in the TFE film have no impact on the thermal performance due to its extremely short heat transfer pathway (Park *et al.*, 2011).

The TFE layer is composed of alternating inorganic (50 nm thick Al_2O_3)/organic (500 nm thick polymer) multi-layers. As shown in Plate XIV, the maximum surface temperature is reduced from 58 °C to 33 °C. Such a large reduction in temperature (25 °C) results from a short heat transfer pathway of the TFE structure. The total thickness of the TFE layer (3.5 dyads) is only 3.2 μm . As such, heat generated in the emitting layer can be transferred to the heat sink and dissipated by it. However, its gas diffusion barrier property is not yet competent for industry applications. To dissipate heat effectively from the glass-encapsulation OLED structure, we have to eliminate nitrogen gas from the device. To this end we need an advanced glass encapsulation where the hollow glass cover is filled with a thermally conductive material through which a heat sink is in contact with the OLED device. Moreover, such a material should be capable of absorbing gas emitting from the OLED device or moisture diffusing into the device from the outside.

19.3 Integration of OLED lightings and solar cells

So far, we have focused on the fabrication of large-area OLED lighting panels. Now we introduce new application areas of those large-area OLED panels. One of the application areas would be a self-powered OLED lighting system that can be implemented by integrating OLEDs with solar cells. For a variety of applications with such a concept including light-emitting window glass for buildings and cars, a transparent OLED lighting panel is required together with a transparent organic solar cell (OSC). A transparent OLED and OSC can be fabricated simply by replacing an opaque thick aluminum cathode by transparent or semi-transparent cathodes such as Mg:Ag, Al/Ag, ITO/Ag/ITO, ITO/Ag/tungsten oxide (WO_3), $\text{WO}_3/\text{Ag}/\text{WO}_3$, etc. (Yook *et al.*, 2008; Sahu *et al.*, 2007). As shown in Fig. 19.11(a), the solar cell integrated with the OLED panel generates power by absorbing the sunlight in the daytime, which can be used for operating OLED lighting panels in the evening. The transparent OLED panel emits light on the front and rear sides. A light emitting from the front side would be used for illuminations, but a light from the rear surface may be wasted. As seen in Fig. 19.11(b), however, the wasted light can be recycled by the integrated solar cell for generating electrical power. In practice, OLED is readily integrated with OSC by depositing organic layers of OSC and OLED in series on a common glass substrate (Yang *et al.*, 2007). This approach was proposed to enhance the contrast ratio of OLED displays. The power recycling efficiency, defined as the ratio of the output power of a solar cell to the electrical input power of an OLED, has been achieved up to 0.26% on a pixel scale. Alternatively, the OLED can be integrated with OSC by depositing organic layers of OSC on one side of the common glass substrate and organic layers of the OLED on the other (opposite) side of the same (common) substrate.

To prove the feasibility of the power recycling using large-area ($30 \times 120 \text{ mm}^2$) white OLED panels, we have merged OSC and OLED into each other after they were fabricated separately (Fig. 19.12). The distance between OLED and OSC is set to be 1.5 mm and 9.5 mm. For experiments, we fabricated all-fluorescent non-tandem white OLED lighting panels that are composed of a 150 nm thick ITO pre-coated on a glass substrate, 35 nm thick 4,4'-bis[N-(1-naphyl)-N-phenylamino] biphenyl (NPB) for HTL, 30.5 nm thick AGH-001 (SFC) for EML, 30 nm thick ET-137 (SFC) for ETL, 1 nm thick lithium fluoride (LiF) for EIL, and 100 nm thick aluminum (Al) for cathode. In the EML, 2 wt% NRD-129 (SFC) is doped in the 0.5 nm thick EML layer (near the HTL/EML interface) for red emission and 3 wt% BD-02 (SFC) is doped in the 30 nm thick EML layer for blue emission. The luminance of the non-tandem white OLED is measured to be 2450 cd/m^2 at 5 V, 5042 cd/m^2 at 6 V, and 8953 cd/m^2 at 7 V. It exhibits the power efficiency of 10.7 lm/W at 4 V (at 1533 cd/m^2) and the maximum luminance of $83\,220 \text{ cd/m}^2$ at 10 V. We have employed the Oriel mono-Si reference solar cell with the National Renewable Energy Laboratory (NREL) KG5 filter. The active area of the reference

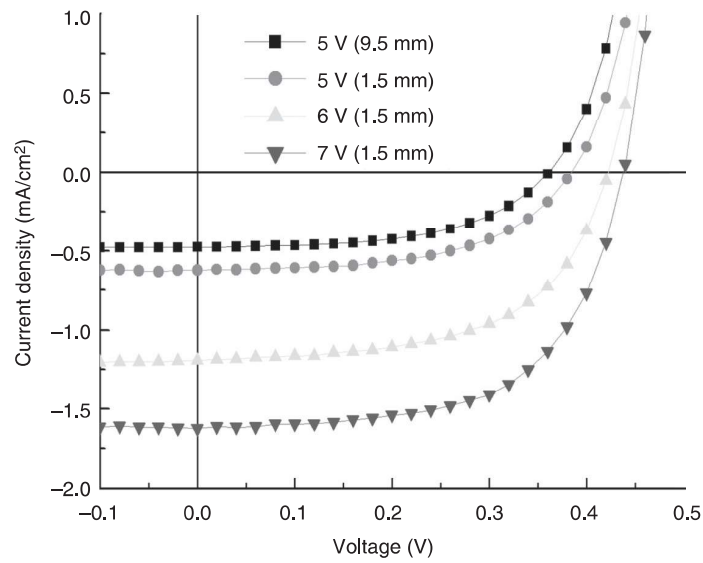


19.11 Schematic views of OLED-solar cell integration: (a) energy generation by solar cell from the sunlight and (b) energy generation by solar cell from the OLED light. (Source: Reprinted, with permission, from Park *et al.* (2011). Copyright © 2011 Semiconductor Science and Technology.)

cell is 3.991 cm^2 , a short-circuit current density (J_{sc}) is 11.34 mA/cm^2 , an open-circuit voltage (V_{oc}) is 0.502 V , a filling factor (FF) is 70.46% , and the conversion efficiency is 4.012% under AM1.5 with irradiation intensity of 100 mW/cm^2 . As demonstrated in Park *et al.*, (2010) and Fig. 19.13, J_{sc} is increased from 0.477 mA/cm^2 to 0.621 mA/cm^2 with decreasing distance, while a V_{oc} is increased from 0.36 V to 0.38 V and a FF from 54.52% to 55.59% . Therefore, it is obvious that

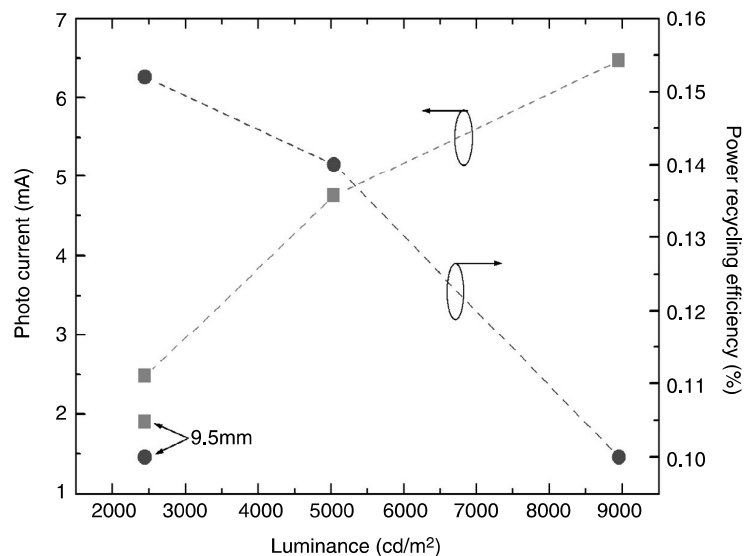


19.12 The test setup; the OLED panel sheds white light on the reference solar cell. (Source: Reprinted, with permission, from Park *et al.* (2010). Copyright © 2010 Institute of Electrical and Electronics Engineers.)



19.13 J - V characteristics of the reference solar cell under the illumination of the large-area ($30 \times 120 \text{ mm}^2$) OLED panel for different distances between solar cell and OLED and different bias voltages of OLED. (Source: Reprinted, with permission, from Park *et al.* (2010). Copyright © 2010 Institute of Electrical and Electronics Engineers.)

they should be merged into each other as closely as possible. Furthermore, J_{sc} , V_{oc} , and FF are shown to be raised to a great extent with increased luminous intensity of OLED. A J_{sc} is boosted up to 1.62 mA/cm^2 , a V_{oc} up to 0.42 V , and a FF up to 63.14% . Shown in Fig. 19.14 is the measured photo-current and power recycling efficiency with respect to the luminance of the white OLED. The photo-current is shown to increase, whereas the power recycling efficiency decreases with increasing luminance. The photo current is measured to be as high as 6.465 mA at 7 V and the maximum power recycling efficiency is 0.152% at 5 V . Although the output power of the solar cell is enhanced with increased input power of the white OLED, the power recycling efficiency is rather decreased. This is because the power efficiency of the white OLED is decreased as the current density (input power) is increased. Although the power recycling efficiency of 0.152% that we have achieved from the preliminary experiments seems a little low, it can be enhanced considerably by reducing the operating voltage of OLED, increasing its power, increasing the conversion efficiency of the solar cell, reducing the distance between solar cell and OLED, reducing the panel size, and matching the absorption spectrum of the solar cell with the emission one of the OLED (Park *et al.*, 2010).

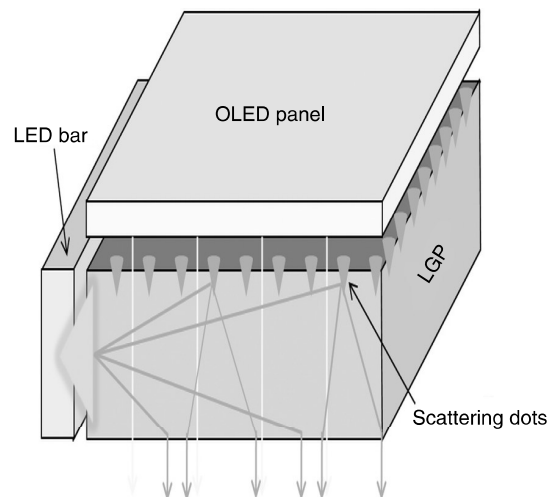


19.14 The measured photo-current and power recycling efficiency versus luminance. (Source: Reprinted, with permission, from Park *et al.* (2010). Copyright © 2010 Institute of Electrical and Electronics Engineers.)

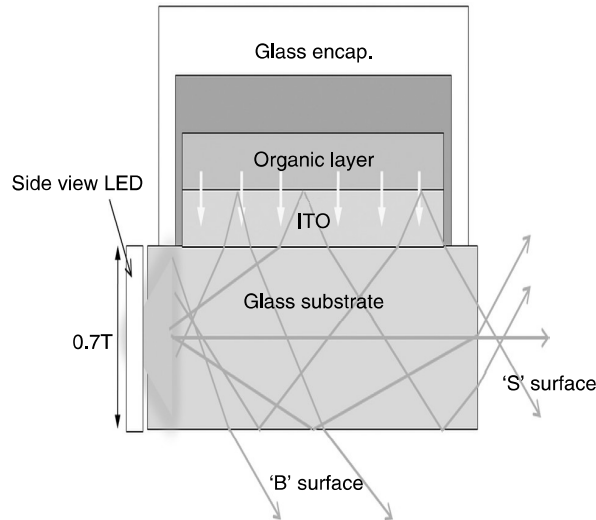
19.4 Integration of OLED and inorganic LED (ILED) lightings

Another application area of those large-area OLED lighting panels would be on a hybrid lighting system, which is based on a combination of ILEDs and OLEDs. They are so combined as to complement mutual weaknesses or rather to take advantage of mutual strengths (Park *et al.*, 2011). From an OLED perspective, the superior features of high brightness and long lifetime available from ILEDs are highly required. Meanwhile, large-area surface emission is attractive to ILEDs. Such a hybrid system is of great use in that OLEDs can be operated at low luminance by virtue of ILED light, enhancing the OLED lifetime, and furthermore the color temperature can readily be tuned by ILED light, enabling emotional lightings. The hybrid lighting system can be realized by deploying ILEDs on a side of a transparent light guide plate (LGP) with scattering dots (Fig. 19.15). With this configuration, uniform surface emission of ILED light is feasible. An OLED panel is placed at the bottom surface of the LGP. OLED light is emitted out from the transparent LGP and then mixed with ILED light. However, uniform surface emission of OLED light is hardly achieved with this scheme because the density of the scattering dots gets higher as the distance from the ILEDs increases. In this case, transparent scattering dots are preferred.

There exists a different way to combine them (Park *et al.*, 2011). In this configuration, side-view ILEDs are deployed at the edge of the OLED glass substrate as depicted in Fig. 19.16. The ILED light will pass through the

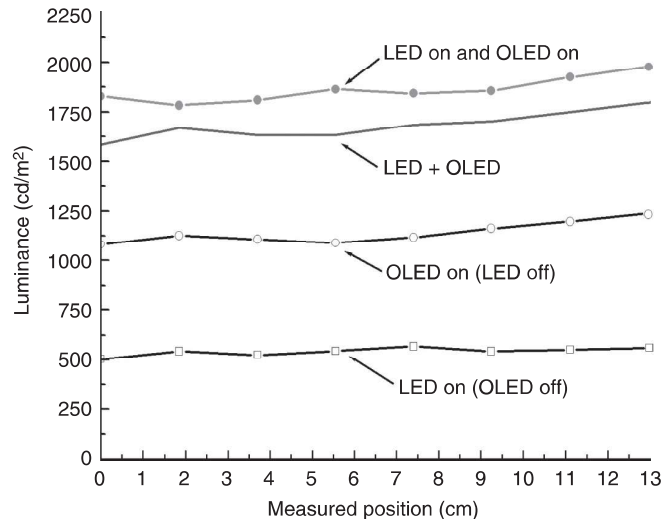


19.15 A hybrid lighting system using a transparent light guide plate (LGP) where light scattering dots are formed.



19.16 Schematic view of hybrid lighting system where an OLED is combined with an ILED. (Source: Reprinted, with permission, from Park *et al.* (2011). Copyright © 2011 Institute of Electrical and Electronics Engineers.)

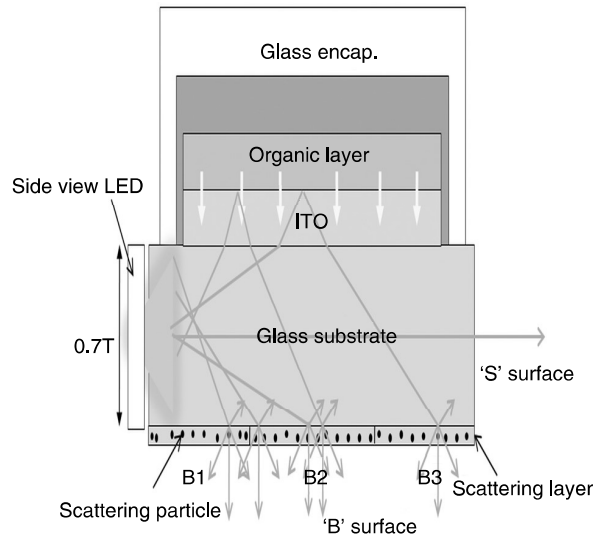
glass substrate of OLED. Some of the ILED light incident into the glass substrate will emit out of the light-emitting area of the OLED, which is then mixed with the OLED light, but most of the ILED light will propagate and emit out through the other sides of the glass substrate due to the direction of the ILED light rays and their total internal reflection (TIR). In reality, it was confirmed that almost half of the ILED light passes through the glass substrate and thus cannot be extracted in the perpendicular direction to the glass substrate. Plate XV shows the test setup where the green OLED panel ($30 \times 120 \text{ mm}^2$) is integrated with side-view green ILED bars. The green OLED device is composed of a 150 nm thick ITO pre-coated on a glass substrate, 10 nm thick LG-101 HIL, 25 nm thick 4,4'-bis[N-(1-naphyl)-N-phenylamino]biphenyl (NPB) for HTL, 25 nm thick 4,4'-N,N'-dicarbazolylbiphenyl (CBP) doped with tris(2-phenylpyridinate) iridium(III) (Ir(ppy)_3 , 8 wt%) for EML, 10 nm thick m-bis-(triphenylsilyl)benzene (UGH3) for HBL, 30 nm thick (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) (Bphen) for ETL, 1 nm thick lithium fluoride (LiF) for EIL, and 100 nm thick aluminum (Al). The side-view ILED bar shows the luminance of 2903 cd/m^2 at 7.5 V, 6554 cd/m^2 at 8 V, and 10908 cd/m^2 at 8.5 V. We have measured the luminance distribution along the horizontal line (120 mm) located at the center of the OLED emission area and present the results in Fig. 19.17. The



19.17 Measured luminance distribution from the test setup in Fig. 19.16. The solid line with no mark indicates the luminance obtained by adding the luminance of each lighting source. (Source: Reprinted, with permission, from Park *et al.* (2011). Copyright © 2011 Institute of Electrical and Electronics Engineers.)

measurement has been carried out when only the ILED bars are turned on, only the OLED panel is turned on, and both ILED bars and OLED panel are turned on. The luminous intensity obtained when both lighting sources are turned on is observed to be higher (about 10% increase) than that obtained after adding the luminous intensities measured from each lighting source (solid line without symbol in Fig. 19.17). It may arise from the interference between ILED light and OLED light. When they meet with different phases, the propagation direction of the light rays is changed. It is likely that such phenomena bring in the positive effect on the out-coupling efficiency. It may also result from a variation of some material parameters such as the refractive index of ITO under high current injection. The refractive index of ITO decreases as the temperature increases, which may release some ILED light from waveguided modes.

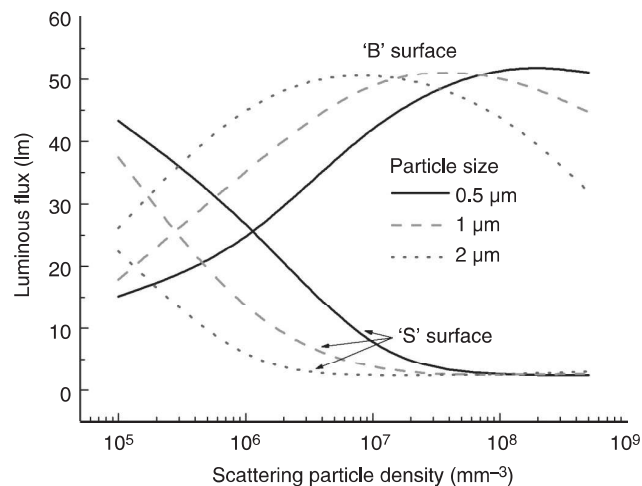
The key issue of this technique is to extract the ILED light without sacrificing the OLED light extraction because only about 15% of the ILED light is emitted from the 'B' surface. To this end, we introduce a scattering layer at the outer surface of the glass substrate (i.e., on the 'B' surface in Fig. 19.18). In reality, Asahi Glass Co., Ltd. formed such a scattering layer that is sandwiched between the glass substrate and ITO anode and showed experimentally that it indeed



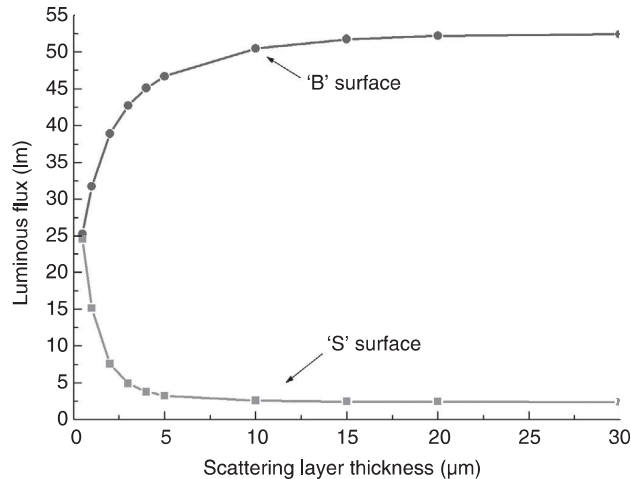
19.18 Schematic view of hybrid lighting system where an OLED is combined with an ILED with the scattering layer. (Source: Reprinted, with permission, from Park *et al.* (2011). Copyright © 2011 Institute of Electrical and Electronics Engineers.)

enhanced the out-coupling efficiency of OLEDs by suppressing the waveguided modes through light scattering. Therefore, the scattering layer can be placed either at the outer surface of the glass substrate or between the glass substrate and ITO anode. In the latter case, however, the surface morphology of ITO would be affected by the underlying scattering layer. Since we are more concerned with the light extraction of ILED, it would be better to place it at the outer surface of the glass substrate. In this work, the scattering layer is assumed to have the same refractive index ($=1.54$) as the glass substrate. In the scattering layer, scattering particles are formed and their size is of the order of $1\text{ }\mu\text{m}$. The scattering substance is pore, which has the refractive index of 1. In practice, pores can be introduced into glass materials by mixing of a glass powder with a foaming agent and subsequent heating (Beerkens, 1990). The density of the scattering particle should be high enough to scatter the ILED light effectively, though it depends on the particle size. In the absence of the scattering layer (Fig. 19.16), the ILED light incident onto the substrate/air interface cannot escape from the device given that a TIR condition is satisfied. In the presence of the scattering layer (Fig. 19.18), however, the ILED light will be scattered by the scattering particles, thereby enhancing the light extraction from ILEDs. We have investigated the effect of the scattering layer on the light extraction of ILEDs by way of

simulations using the ray-tracing tool (LightTool, Optical Research Associates). For simulations, the scattering layer thickness is set to be $15\text{ }\mu\text{m}$ and the luminous flux of the ILED is 100 lm . The ray-tracing simulation has been carried out by varying the scattering particle density and size. As shown in Fig. 19.19, the luminous flux from the 'B' surface is raised with increasing scattering particle density. At the same time, the luminous flux from the 'S' surface is reduced accordingly. It is noted that only about 15% of the ILED light is emitted from the 'B' surface without the scattering layer. However, the scattering layer enhances the light extraction of ILED from the 'B' surface by up to 50%. One can also find that the luminous flux varies depending on the particle size. Namely, for larger particle size, lower particle density is required to get the same luminous flux. But there exists an upper limit on the selection of the particle density above which the luminous flux is rather decreased. Shown in Fig. 19.20 is the calculated luminous flux as a function of the scattering layer thickness when the particle size and density are $1.0\text{ }\mu\text{m}$ and $1 \times 10^7\text{ mm}^{-3}$, respectively. It is demonstrated that more ILED light can be extracted with a thicker scattering layer. It appears that the scattering layer thickness should be at least $5\text{ }\mu\text{m}$ to effectively hinder a leak of ILED light through the 'S' surface.



19.19 Simulation results of luminous flux versus scattering particle density for different scattering particle sizes when the scattering layer thickness is $15\text{ }\mu\text{m}$. (Source: Reprinted, with permission, from Park *et al.* (2011). Copyright © 2011 Institute of Electrical and Electronics Engineers.)



19.20 Simulation results of luminous flux as a function of the scattering layer thickness when the particle size and density are $1.0\mu\text{m}$ and $1 \times 10^7\text{mm}^{-3}$, respectively. (Source: Reprinted, with permission, from Park *et al.* (2011). Copyright © 2011 Institute of Electrical and Electronics Engineers.)

19.5 OLED lightings for visible-light communication

The other new application area of large-area OLED lighting panels lies in visible-light communications. It would be feasible to use OLEDs not only as general illuminations but also as light sources for transmitting signals. Many groups have already researched ILEDs as a light source for VLC applications (Tanaka *et al.*, 2003; Komine and Nakagawa, 2003). Although there exist many key issues of OLEDs for VLC applications, one of the most significant is to increase the modulation speed of OLEDs. This is limited by the insulating behaviors of organic molecules or rather slow carrier dynamics. It also depends on the panel size since the device capacitance is increased in proportion to it (i.e., due to their capacitor-like behaviors). Furthermore, the response speed is affected by the space charges remaining inside the device (Park, 2010).

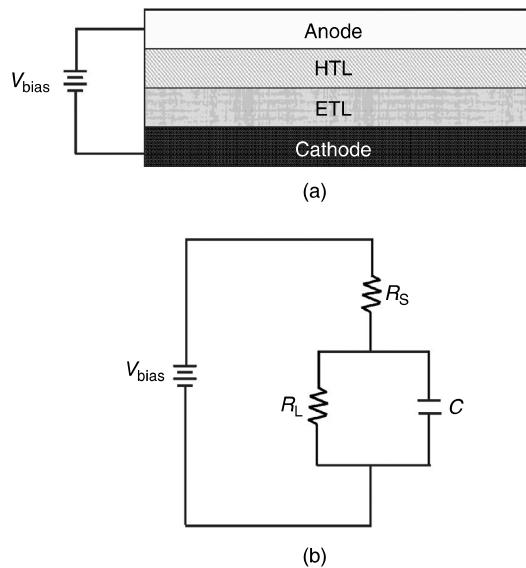
Shown in Fig. 19.21(a) is the device structure of a bilayer OLED and in Fig. 19.21(b) its equivalent circuit that consists of the device resistance (R_s) in series with the diode, the leak resistance (R_L), and the equivalent capacitance (C). The voltage across the capacitor is given as

$$V_C(t) = V_{\text{bias}} (1 - e^{-t/CR_s}) \quad [19.4]$$

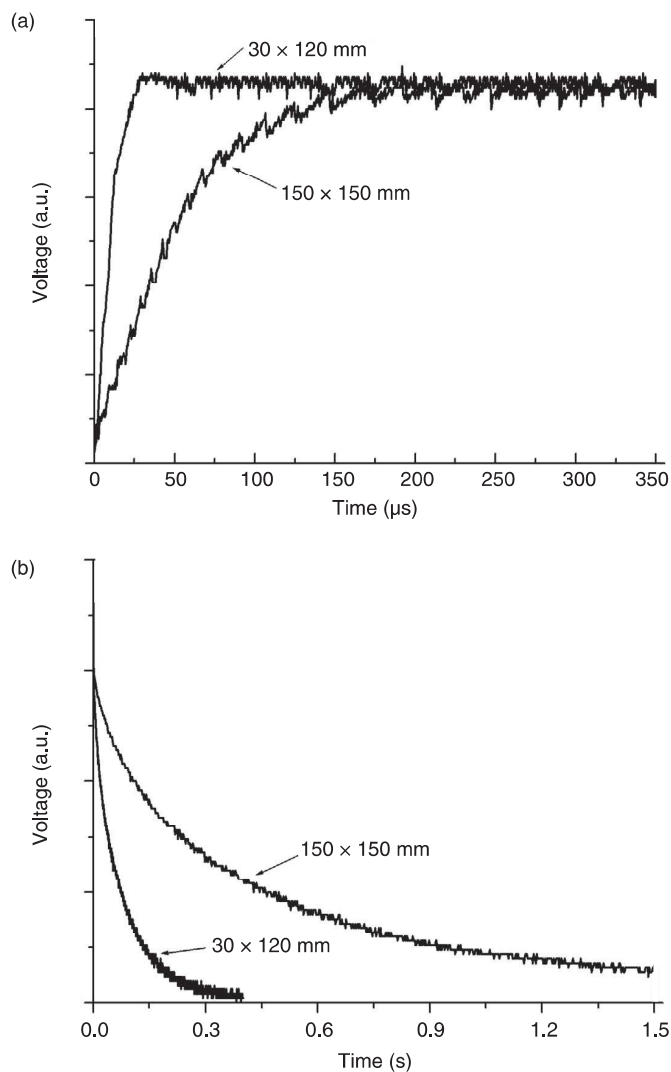
where CR_s is the time constant of OLED and C is expressed as

$$C = \epsilon_0 \epsilon_r \frac{S}{L} \quad [19.5]$$

with ϵ_0 (F/m) and ϵ_r defined as the permittivity of free-space and the dielectric constant of an organic molecule, respectively. L (cm) and S (cm²) indicate the device length (the distance between anode and cathode electrodes) and the surface-emitting area, respectively. The capacitance of the diode is increased in proportion to the dielectric constant and surface-emitting area (Eq. 19.5). Consequently, the EL response speed of large-area OLEDs would be reduced owing to an increase of the time constant (Eq. 19.4). To study exclusively the effects of the panel size on the response speed of OLEDs, we have observed the charge and discharge behaviors of 30×120 mm and 150×150 mm non-tandem white OLED lighting panels and presented the results in Fig. 19.22. The non-tandem white device is composed of a 150 nm thick ITO pre-coated on a glass substrate, 30 nm thick 4,4'-bis[N-(1-naphyl)-N-phenylamino]biphenyl (NPB) for HTL, 10 nm thick N,N'-dicarbazolyl-3,5-benzene (mCP) for an interlayer, 15 nm thick mCP for EML, 3 nm thick m-bis-(triphenylsilyl)benzene (UGH3) for HBL, 50 nm thick (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) (Bphen) for ETL, 1 nm thick lithium fluoride (LiF), and 100 nm thick



19.21 (a) Layer structure of a bilayer OLED and (b) the equivalent circuit of an OLED. (Source: Reprinted, with permission, from Park (2010). Copyright © 2010 Institute of Electrical and Electronics Engineers.)

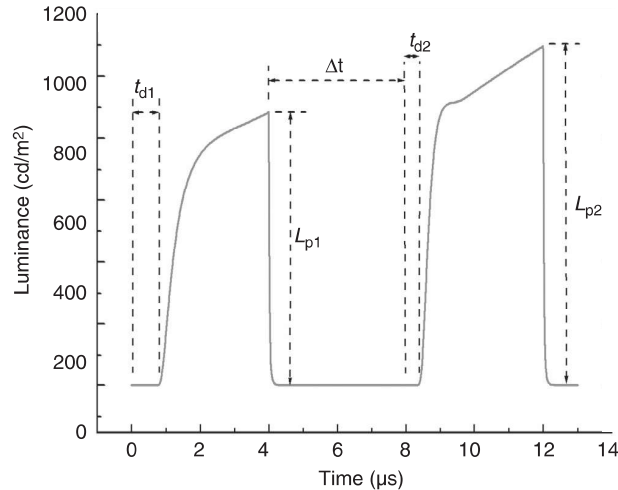


19.22 Measured voltages (a) upon turn-on and (b) upon turn-off for different sized large-area OLED lighting panels. (Source: Reprinted, with permission, from Park (2010). Copyright © 2010 Institute of Electrical and Electronics Engineers.)

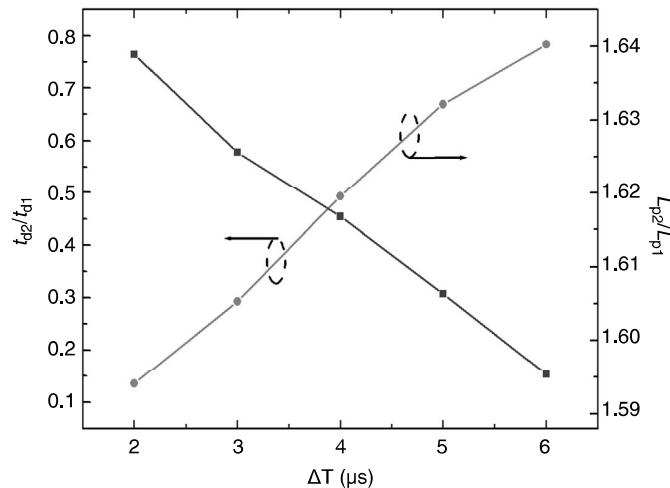
aluminum (Al). In the EML, 12 wt% bis[(4,6-difluorophenyl)-pyridinato-N,C²] (picolate) iridium(III) (FIrpic) and 0.4 wt% bis(2-phenylbenzothiazolato-N,C²) iridium(acetylacetonate) (bt₂Ir(acac)) are co-doped for white-light emission. As seen in Fig. 19.22, the larger-area OLED panel shows much slower charge and

discharge behaviors, originating most likely from an increase of the device capacitance. This result implies that the panel size should be reduced to get high modulation speed. Even so, large area OLED panels are preferred to obtain enough luminous flux for long-distance VLC applications. For this reason, there exists a trade-off between the response speed and luminous flux on the selection of the panel size. With attempts to find the way of increasing the modulation speed of OLEDs, we have carried out a numerical investigation of dynamic behaviors of OLEDs in response to single and double voltage pulses, device length, and various material parameters such as carrier mobility, exciton lifetime, and energy level offset in. For simulations, we have implemented a 1-D numerical model (Ruhstaller *et al.*, 2003; Park and Kawakami, 2006) that is composed of Poisson's equation, time-dependent drift-diffusion equations, and singlet exciton rate equation.

Due to the space charges remaining inside the device in the 'off-state', there exists a pulse-to-pulse interference that makes a significant impact on the dynamic response of OLEDs. Shown in Fig. 19.23 is the simulation result of transient luminance in response of the double voltage pulse. The pulse duration and separation (Δt) are chosen to be $4\ \mu\text{s}$. It is observed that the delay time (t_{d2}) of the second pulse is shorter than that of the first pulse (t_{d1}), while the peak luminance (L_{p2}) of the second pulse is higher than that (L_{p1}) of the first pulse. Upon turn-off,



19.23 Transient luminance in response to the double voltage pulses (pulse duration is $4\ \mu\text{s}$, pulse separation Δt is $4\ \mu\text{s}$, t_{d1} and t_{d2} are the delay time of the first and second pulses, respectively, and L_{p1} and L_{p2} are the peak luminance of the first and second pulses, respectively). Copyright © 2010 Institute of Electrical and Electronics Engineers. Reprinted, with permission, from (Park, 2010).



19.24 The ratio of the delay time (t_{d2}/t_{d1}) and peak luminance (L_{p2}/L_{p1}) as a function of the pulse separation (Δt). Copyright © 2010 Institute of Electrical and Electronics Engineers. Reprinted, with permission, from (Park, 2010).

the accumulated charges inside the device are discharged, yet it takes a long time to be fully discharged since holes penetrated into the ETL are discharged much more slowly due to very low hole mobility inside the ETL. Therefore, there always remain space charges inside the device if Δt is too short for charges to fully discharge. If this be the case, t_{d2} is always shorter than t_{d1} . Moreover, the peak luminance in response to the second pulse is amplified because carriers remaining inside the device upon turn-off (prior to the income of the second pulse) contribute to photon generation together with carriers injected by the second pulse. Shown in Fig. 19.24 are the ratios of the delay time (t_{d2}/t_{d1}) and peak luminance (L_{p2}/L_{p1}) as a function of the pulse separation (Δt). The ratio of the delay time is reduced by decreasing Δt , a direct result induced by a decrease in the number of discharged carriers, which also increases the ratio of the peak luminance. In this respect, the pulse separation is the critical factor determining the modulation speed of OLEDs for practical VLC applications. It was also demonstrated in Park 2010 that as far as the speedup of the device response is concerned, it appears to be desirable to apply higher bias voltage and reduce the device length. A reduction of the delay time induced by a variation of the carrier mobility, exciton lifetime, and energy level offset is less pronounced.

19.6 Conclusion

For large-area OLED lighting panels to be commercialized in the near future as a general lighting source, one has to first tackle those key issues such as a short

circuit, luminance non-uniformity, hot spot, power loss, and heat generation. With high-reliability large-area OLED panels, one can come up with several potential application areas including self-powered OLED lighting system, light-emitting windows, hybrid lighting systems, emotional lightings, and even application for sending information. Once those are feasible, the paradigm shift in the lighting industry will be indeed realized by surface-emitting OLED lighting panels.

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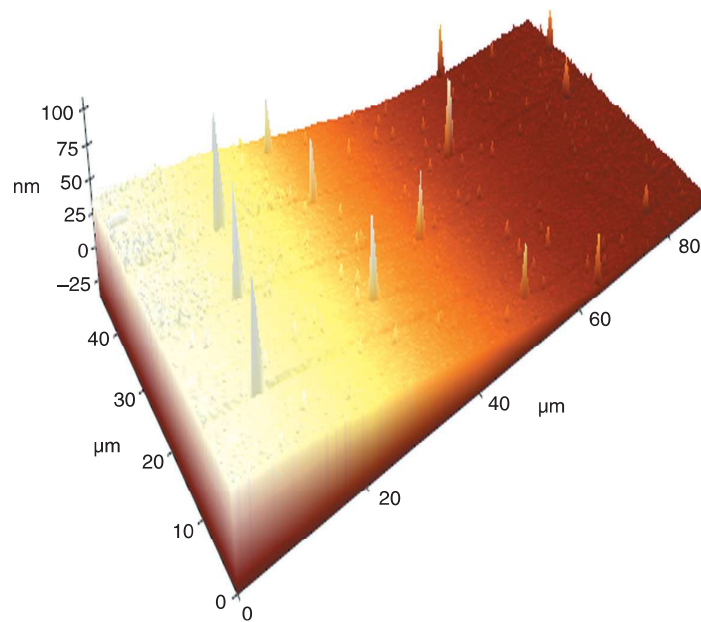


Plate VIII (Chapter 19) AFM image of sputter-patterned ITO measured on the slope of the patterned edge.

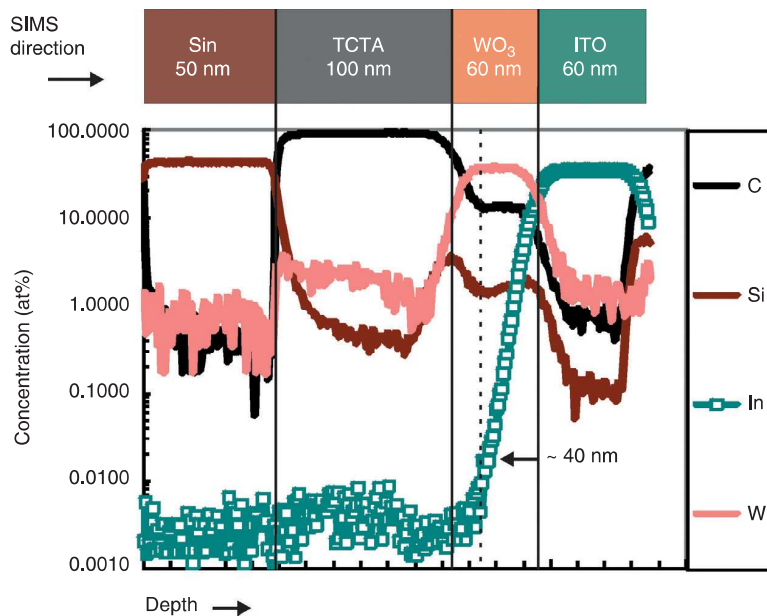


Plate IX (Chapter 17) Secondary ion mass spectrometry profile of the layer sequence: SiN/TCTA/WO₃/ITO measured beginning from the SiN substrate.⁶

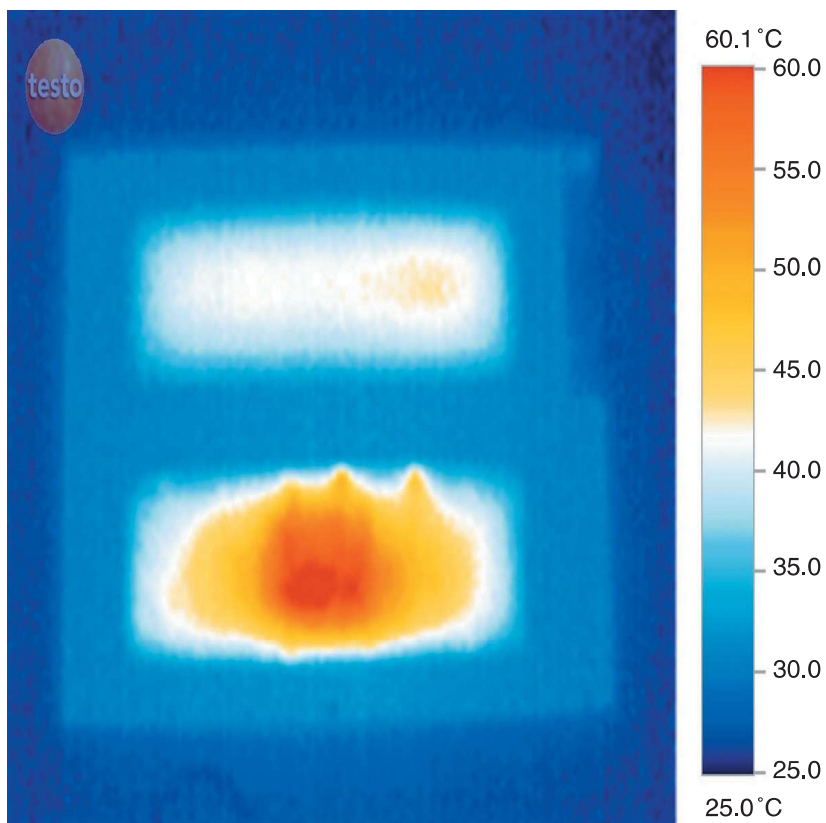


Plate XI (Chapter 19) The heat distribution over a large-area (30 mm x 120 mm) OLED panel measured at 2000 nit (Top: no spot appeared. Bottom: several spots appeared near the central region). Copyright © 2011 Semiconductor Science and Technology. Reprinted, with permission, from Park *et al.* (2011).

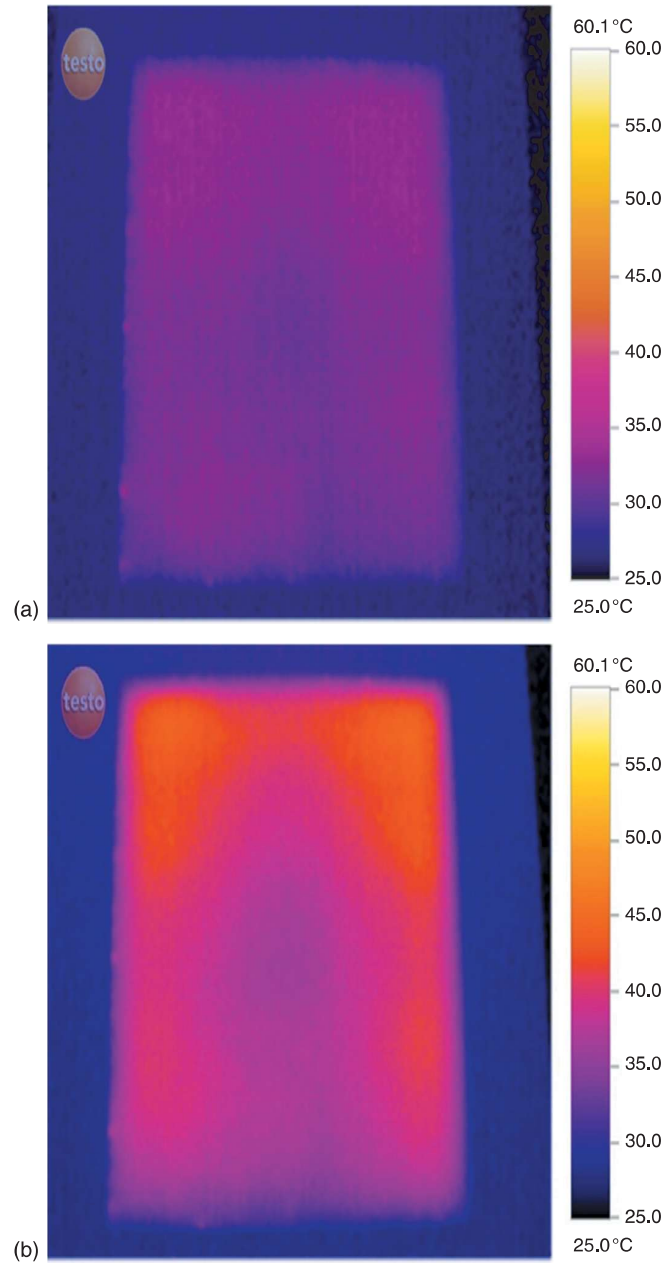
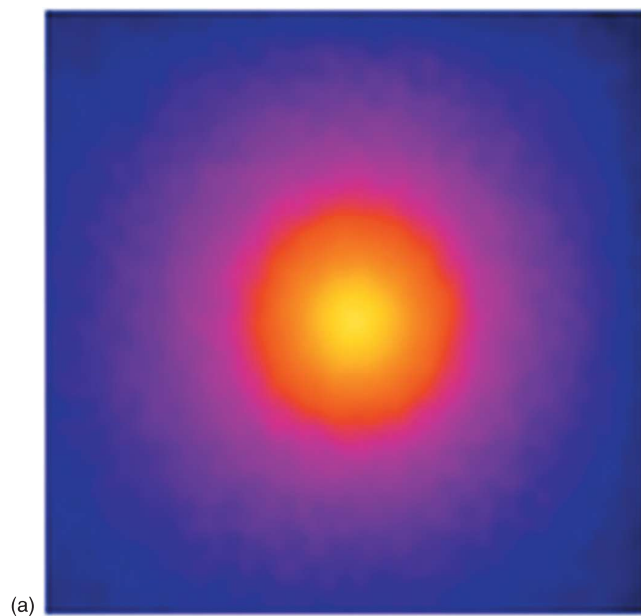
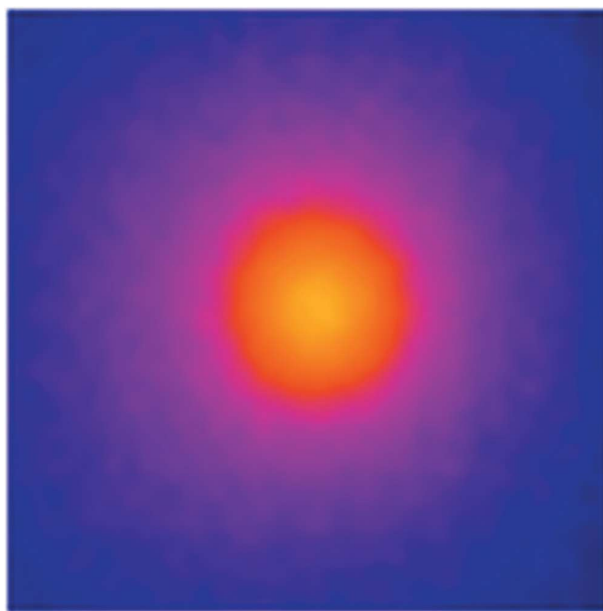


Plate XII (Chapter 19) The heat distribution over a 150 mm x 150 mm OLED panel measured (a) at 1000 nit and (b) at 2000 nit. Copyright © 2011 Semiconductor Science and Technology. Reprinted, with permission, from Park *et al.* (2011).



(a)



(b)

Plate XIII (Chapter 19) Surface temperature distribution over the glass encapsulated OLED (a) without and (b) with heat sink, and (c) transient variation of the maximum surface temperature measured at 7.5V. Copyright © 2011 Organic Electronics. Reprinted, with permission, from Park *et al.* (2011).

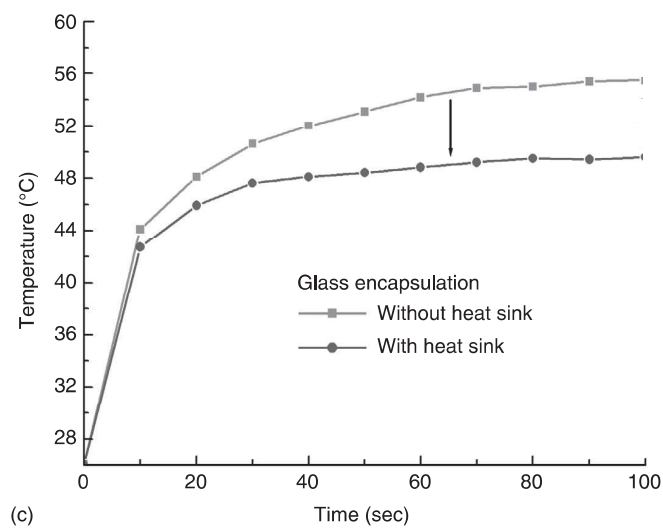


Plate XIII (Continued)

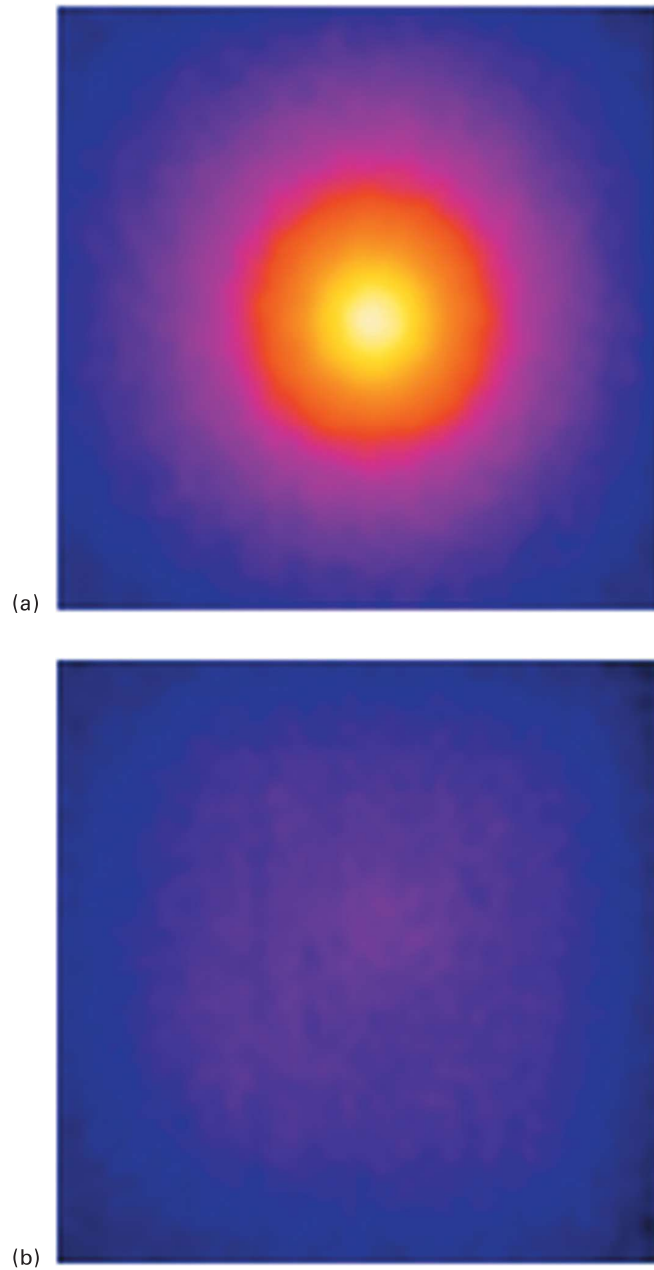
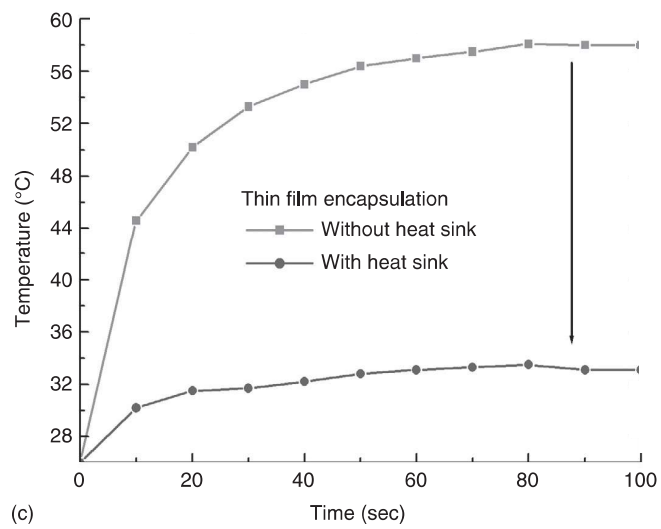


Plate XIV (Chapter 19) Surface temperature distribution over the thin-film encapsulated (3.5 dyads) OLED (a) without and (b) with heat sink, and (c) transient variation of the maximum surface temperature measured at 7.5V. Copyright © 2011 Organic Electronics. Reprinted, with permission, from Park *et al.* (2011).

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(c)

Plate XIV (Continued)

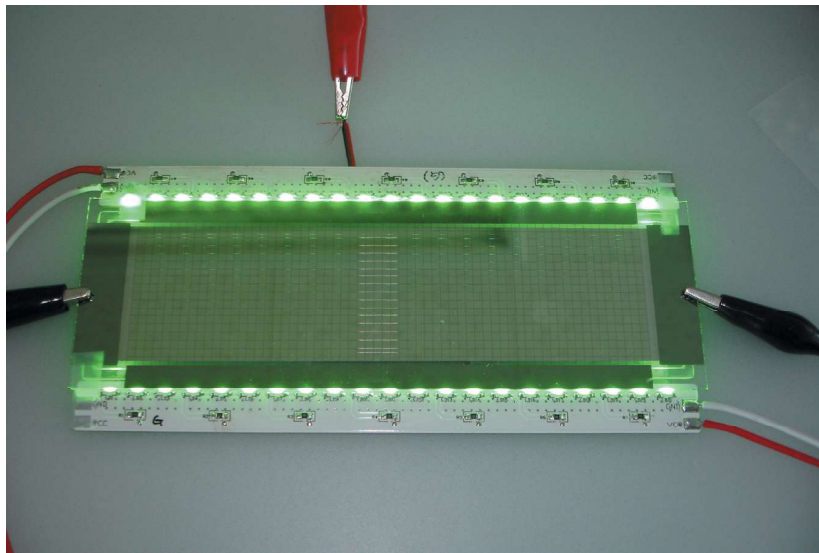


Plate XV (Chapter 19) The test setup; the green OLED panel ($30 \times 120 \text{ mm}^2$) is integrated with side-view green ILED bars. Copyright © 2011 Institute of Electrical and Electronics Engineers. Reprinted, with permission, from Park *et al.* (2011).

Lifetime determination procedure for OLED lighting panels and proposal for standardisation

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Abstract: A measurement setup and procedure for an accelerated testing of the luminance lifetime of large area organic light-emitting diodes (OLEDs) is presented. In a comprehensive study using more than 160 OLED panels of two manufacturers, a universal acceleration model has been developed which reveals excellent prediction capabilities. Based on these findings a recommendation for a generic lifetime measurement setup for large area OLED panels has been developed.

Key words: accelerated lifetime testing, acceleration model, lifetime extrapolation, standardisation.

20.1 Introduction

The lifetime of an organic light-emitting diode (OLED) can be defined as the period after which the OLED suddenly fails completely or when a soft failure occurs, i.e. when the value of one electro-optical parameter passes a certain threshold. The first case, of course, is highly undesirable and has to be ruled out by all measures applying suitable screening methods so that these devices can be identified before they reach the customer. The most obvious and therefore most severe soft failure is the degradation of the luminance below a fixed limit but there are other, secondary failure modes, too, like driving voltage rise, colour shift, loss of lateral luminance uniformity, etc. Since the requested lifetime of an OLED light source is several tens of thousands of hours, it is obvious that lifetime tests, on the one hand, have to be accelerated by applying non-standard operating currents or elevated temperatures and, on the other hand, degradation models have to be developed which allow for an accurate extrapolation of the actual product lifetime based on short-time measurements.

In this chapter, a lifetime testing setup and an acceleration and extrapolation model for the luminance lifetime will be presented which are meant to serve as a basis for a first proposal to lay out a standardised method for the lifetime

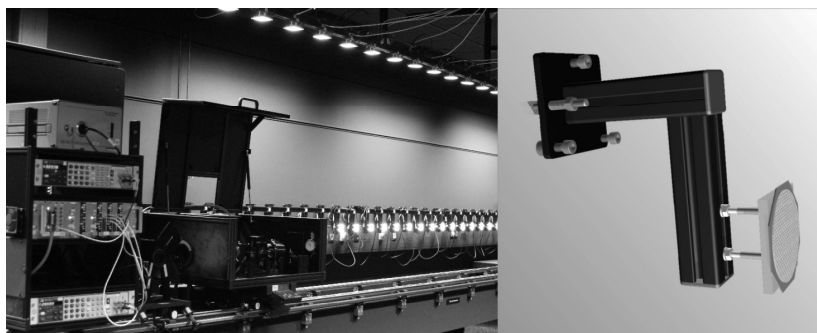
determination of large area OLED devices. It results from work done in the OLED100.eu European research project (09/2009–08/2011) with contributions from Osram, Physikalisch Technische Bundesanstalt¹ (PTB) and the Fraunhofer Institute for Photonic Microsystems (IPMS).

20.2 Lifetime measurement setup

The lifetime measurement setup, designed and built by PTB, allows for *in situ* measurement of electrical and optical parameters of the OLEDs, among them luminous intensity, spectral radiation, chromaticity coordinates, luminance and chromaticity distributions at various viewing angles.

20.2.1 Experimental setup

The basis of the investigations is a 17 m long photometer bench system to measure optical, thermal and electrical properties of up to 60 OLEDs. 30 OLEDs are mounted on the wall with horizontal light output direction and an additional 30 OLEDs are mounted at the ceiling facing downwards. One special characteristic of the setup is the possibility of *in situ* measurements: all OLEDs are operated continuously under stable thermal conditions. The measurement equipment is moving on a bench carriage system, detecting all relevant optical properties of each single OLED (see Fig. 20.1).



20.1 PTB's OLED lifetime measurement setup with several OLED types mounted on wall and ceiling. The image on the right-hand side shows an OLED mounted to the fixture. The fixture allows the alignment of all OLEDs with the optical axis of the detectors.

¹ The Physikalisch-Technische Bundesanstalt (PTB) is the national metrology institute of Germany providing scientific and technical services. PTB measures with the highest accuracy and reliability – metrology as the core competence.

OLED mount

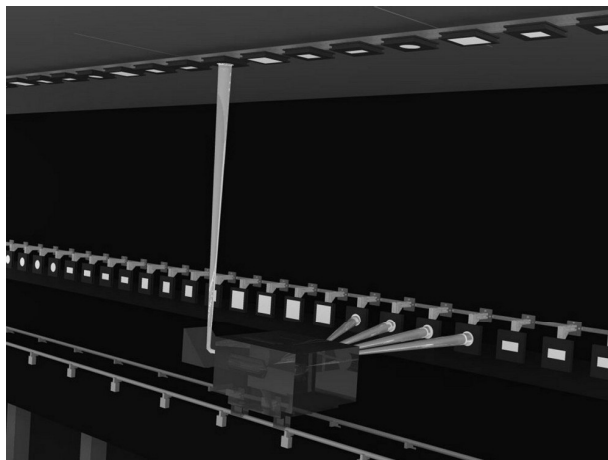
Each of the OLED panels is attached to a 10 mm thick aluminium plate with thermally conductive glue. The thermal conductivity of aluminium is more than two orders of magnitude higher than that of the OLED substrate and cap glass. This ensures a good lateral heat distribution across the active area of the device and stabilises the device temperature due to the large heat capacity of aluminium. The metal plate does not provide any remarkable cooling of the OLED since it does not add much to the superficial area. The plates are mounted to the fixture by means of thermally low conducting bolts with some clearance to the fixture, shown in Fig. 20.1 on the right, in order to assure that heat exchange with the environment occurs by convection and radiation only. A thermistor is attached to the backside of the aluminium plate and, in the following, when talking about the OLED temperature we are referring to the temperature measured by that sensor, knowing that it may differ from the actual OLED stack temperature.

Bench carriage system

A motor-driven bench carriage, equipped with several photometers, a spectroradiometer, and an imaging luminance measuring device (ILMD) are used for the optical measurements. The optical measuring devices are mounted on a rotating table in a light-tight cabinet with shutters. The possibility of moving and rotating the detectors freely along the 17 m long bench (parallel to the row of mounted OLEDs), combined with a limited field of view of the detectors allows for measuring not only under a perpendicular viewing angle but also under any viewing angle up to approximately 45°. For higher angles, crosstalk will occur, i.e. interference with adjacent OLEDs would disturb the measurement results.

Furthermore, a front surface mirror is installed beside the bench carriage to determine the photometric and radiometric properties of the OLEDs mounted below the ceiling. A sketch of the setup is shown in Fig. 20.2. Even though the measurement lab is a clean room, one has to consider that dust will deposit onto the mirror during the time the experiment is running. To correct the effect of dust, a monitor lamp is installed under the ceiling. This lamp is a scientific tungsten bulb with very stable light properties. The main advantage of this lamp type is that it does not show any ageing effects as long as it is not operated. The lamp is operated once a week to calculate a correction factor for the effect caused by dust on the mirror. In addition, PTB checked that the mirror does not cause significant changes to the reflected light due to polarisation effects for all tested OLED types.

The distance between the optical detectors and the front surface of the OLED for perpendicular viewing angles is approximately 1.65 m. Due to the Lambertian-like emission profile of the light emitted by the OLEDs and their maximum side length of less than 15 cm, it is assured that the measurement occurs under far field conditions. The correction for the extended OLED area is below 0.5% and is



20.2 PTB's OLED lifetime measurement setup. The cabinet on the bench carriage is shown in the front. The grey cones illustrate the field of view for different viewing angles. A front surface mirror beside the bench carriage reflects the emitted light of the OLEDs from the ceiling to the detectors inside the cabinet.

negligible for lifetime measurements. This enables the photometric inverse square law to be applied and the luminous intensity I of the OLED to be calculated from the illuminance E on the photometer and the distance d between photometer head and OLED:

$$I = E \cdot d^2. \quad [20.1]$$

Using the size of the active lighting area A_{act} of the OLED the luminance L is calculated as

$$L = \frac{I}{A_{act}}. \quad [20.2]$$

The definition of the active lighting area includes inner non-lighting areas due to defects but excludes non-lighting busbars and other mechanical structures.

The measurements are fully automated. This includes the movement of the bench carriage, changing the viewing angles of the detectors, the settings of photocurrent amplifiers as well as the data acquisition by digital voltmeters (DVM), the ILMD, the spectroradiometer, the temperatures of the devices and environmental quantities. The positioning uncertainty of the bench carriage system is in the range of a tenth of a millimetre. These minor deviations are negligible for measurement distances of about 1.65 m.

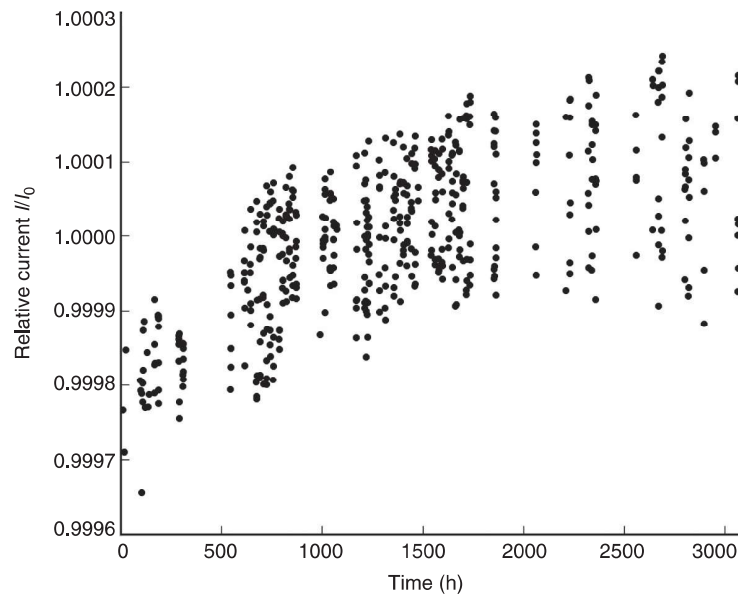
20.2.2 OLED operating conditions

Electrical conditions

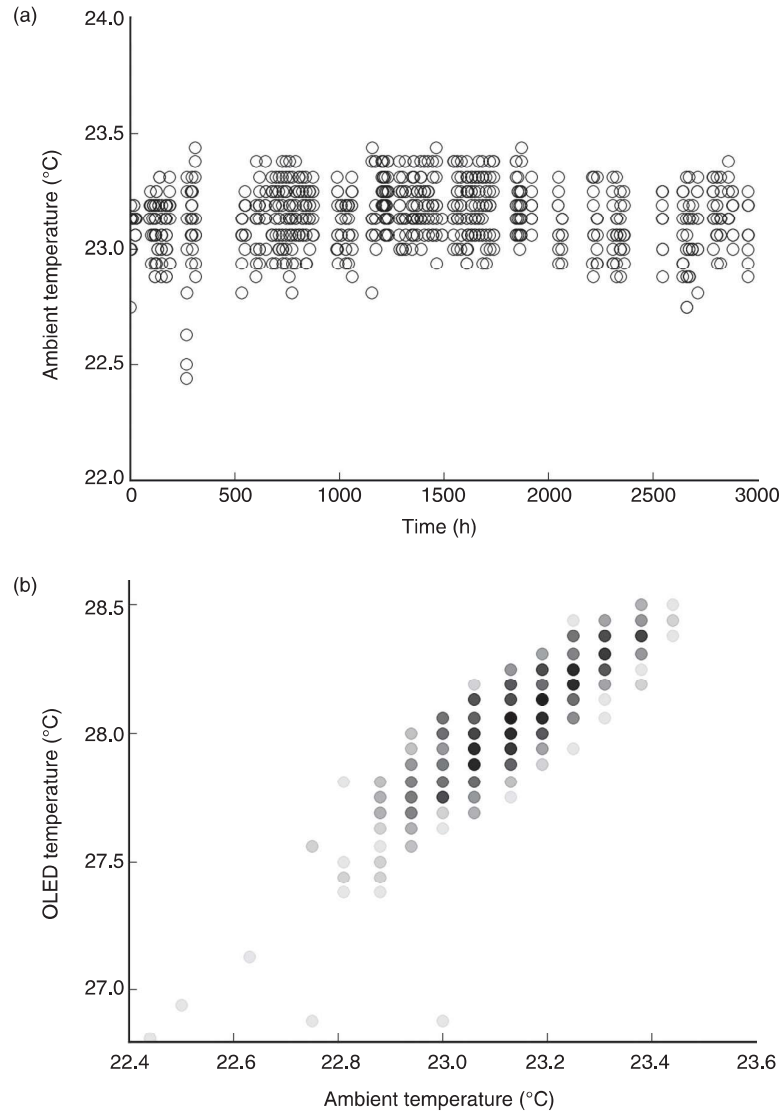
All OLEDs are operated under constant current conditions and the voltage is measured using the four-point probe method. A digital voltmeter (DVM) with a 60 channel multiplexer was used to measure each OLED voltage separately. Figure 20.3 shows the relative change of the OLED driving current during 3000 hours of operation. The variance is less than 0.1%. The voltage of the OLED device, though, depends on temperature and operating time due to device degradation.

Thermal conditions

The ambient temperature of the laboratory is controlled by air conditioning with a mean temperature of $23.0 \pm 0.5^\circ\text{C}$ as shown in Fig. 20.4(a). The OLED mounts, described before, are attached to the wall and the ceiling, respectively. Due to the insulating characteristics of the mount, the thermal equilibrium condition of the OLED mainly depends on the air temperature.



20.3 Relative change in the OLED driving current (I/I_0). The shown variation of the current in the range of $\pm 3 \cdot 10^{-4}$ is representative for all OLEDs and has a negligible effect on the optical properties as shown in the next section.

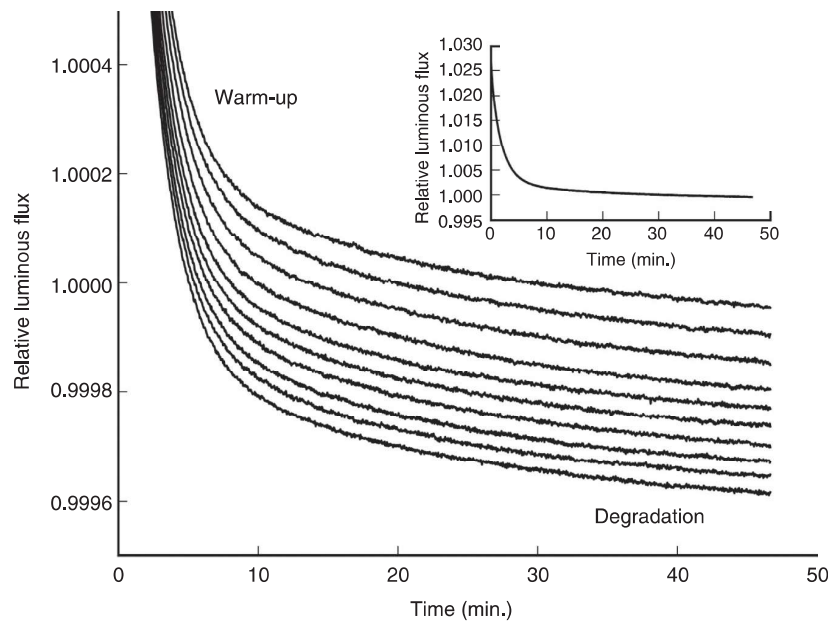


20.4 (a) Ambient temperature at the wall near the OLED fixtures over the course of 3000 hours of operation. (b) Correlation of OLED temperature and ambient temperature. The temperature difference between heatsink and ambient temperature for this specific OLED and operating condition is about 5.5°C.

OLED stack temperature

An essential requirement for OLED lifetime measurements is a good correlation between the ageing effects and the measured optical and electrical quantities. However, the optical properties are not only influenced by the OLED current I_{OLED} but also by the OLED stack temperature T_{Stack} . It has to be taken into consideration that the OLED stack temperature T_{Stack} strongly correlates with the OLED voltage U_{OLED} under constant current conditions. During the warming up phase, the luminance and the voltage of OLEDs usually show an exponential decrease until thermal equilibrium is reached. Afterwards the luminance decreases and the voltage increases due to ageing effects.

In Fig. 20.5, the decay of the total luminous flux of a burned-in OLED is shown. This OLED was driven for 47 minutes with a constant current and afterwards turned off for about 30 minutes. This procedure was repeated 10 times and the corresponding relative luminous flux is shown. As one can see, the warm-up time is in the range of 20 to 30 minutes and afterwards the OLED shows a more or less



20.5 Consecutive measurements of the luminous flux Φ_{OLED} emitted by an OLED during the warm-up phase measured in a temperature-stabilised integrating sphere with a diameter of 2.5 m. The plots are normalised to the flux value at around 30 minutes, at which thermal equilibrium has been reached and the decay thereafter is only due to degradation effects. The inset shows the relative flux during the first run in full scale.

linear decay of the luminous flux. The flux value emitted at thermal equilibrium is about 3% lower than that when the device is still at ambient temperature. After reaching equilibrium, the luminous flux value of each run is slightly lower than that of the preceding run.

Besides the total luminous flux Φ_{OLED} , the luminance L and colorimetric quantities (x,y) are important parameters of an OLED lighting panel. In preliminary tests we determined the dependence between these optical properties and small changes in the OLED voltage U_{OLED} and the OLED current I_{OLED} . A temperature-controlled heatsink with good thermal contact to the OLED stack was used for active control of the OLED voltage. Hence, we were able to measure luminance and chromaticity for different current/voltage combinations. The corresponding temperatures of the heatsink and luminance changes of the OLED are shown in Fig. 20.6. An increase of 1% in the applied OLED current results in a decrease in the luminous intensity of about 0.25% – as long as the OLED nominal voltage U_0 is kept constant. In contrast, an increase of about 1% in the OLED voltage for a constant current leads to a decrease in the luminous intensity of more than 2.5%!

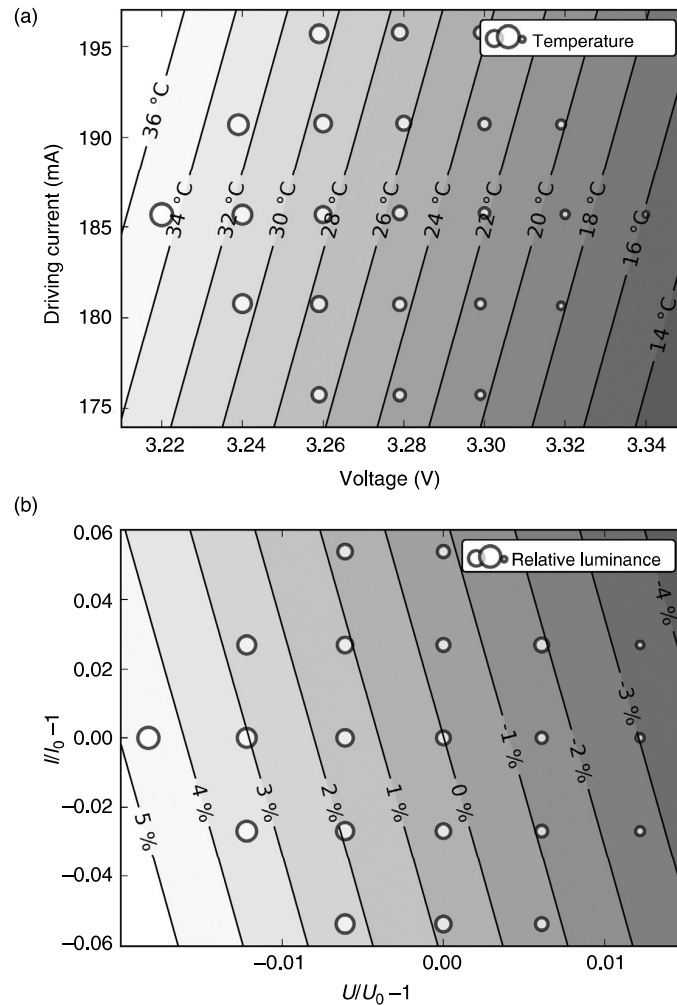
The good correlation between the stack temperature, the OLED voltage, and the luminance enables the correction of small changes in the voltage produced by variations in the heatsink temperature. Figure 20.7 shows the variation of the heat sink temperature and both the raw and corrected voltage of an OLED panel over the course of 3000 hours of operation. The effect of the temperature correction can best be seen in the inset plot of Fig. 20.7, which shows the residuals of the fit of a simple function to the raw and corrected voltage data. The temperature changes are below ± 0.7 K. The voltage increase during operation is about 5%.

20.3 Accelerated lifetime testing

It is highly desirable to get a good estimation of the product lifetime within a reasonable time and a limited number of measurements. The most obvious and thus primary parameter which defines lifetime is the light output of the OLED, measured as, e.g., luminous flux or luminance. Since nowadays the $L770$ – i.e. the operation time, after which the luminous flux drops to 70% of the initial one – amounts to several thousand hours and lifetime is expected to increase drastically due to a rapidly evolving technology, the need for time accelerated experiments or lifetime extrapolation methods is evident.

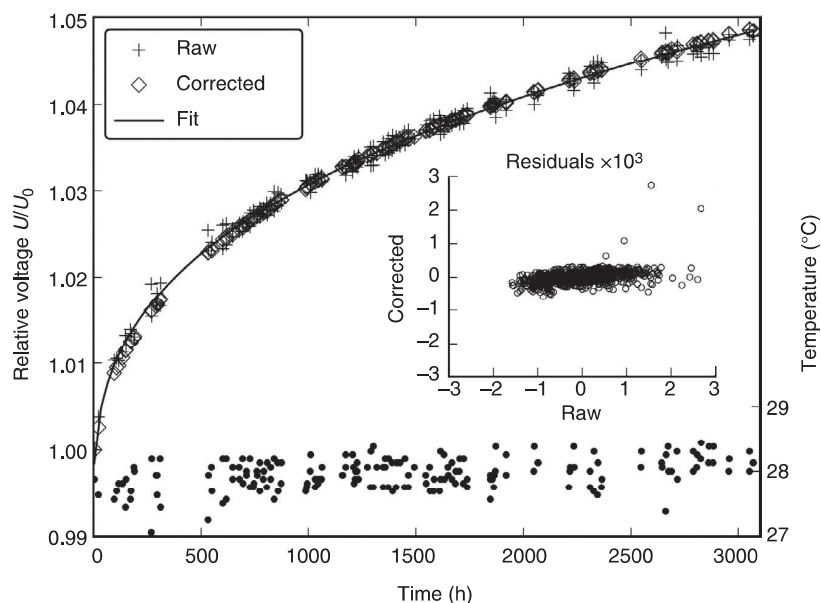
20.3.1 Lifetime stress relationship

In order to accelerate the occurrence of failures and obtain lifetime data, faster lifetime testing can be conducted under increased stress conditions. Common acceleration factors for OLED lifetime testing are elevated luminous flux or luminance output, which is proportional to the driving current in a good approximation for a broad range of current values, and the operating temperature. It has to be ensured that all other dependent optical and electrical parameters of



20.6 (a, b) Current-voltage diagram to visualise the correlation between current, voltage, and temperature. The OLED was operated under constant current conditions. The circles show the measured current/voltage combinations. Larger circles indicate higher temperature or luminance, respectively.

the OLED do not differ significantly from their values at normal operation. This holds especially for the uniformity of the luminance, since a very inhomogeneous luminance pattern will lead to locally distinct ageing conditions across the active area. In that situation it is questionable whether the degradation of the mean luminance is a good measure to conclude the luminance lifetime under normal



20.7 Voltage of an OLED and heat sink temperature over the course of 3000 hours of operation. The voltage has been corrected based on the measured temperature dependence of the voltage at constant current. The voltage rise during operation can be conveniently described by the simple function $U/U_0 = 1 + at^b$, with fit parameters a and b and time t . The inset shows the residuals of the fit to the raw and the corrected voltage.

conditions. Other parameters such as emission colour, angular emission characteristics, etc., are by design usually less dependent on driving current and temperature. In the following, the two most common acceleration conditions for OLED lifetime testing are discussed.

Arrhenius relationship

The Arrhenius relation is an empirical formula, relating the velocity of a chemical reaction to the absolute temperature. It is based on the idea that for a reaction to occur, the reactants have to acquire a minimum energy, called activation energy. The equation can be deduced from Boltzmann statistics and therefore has an exponential form:

$$R \propto e^{\frac{-E_A}{k_b T}} \quad [20.3]$$

where R is reaction rate, E_A is activation energy, k_b is Boltzmann constant $k_b = 8.617 \cdot 10^{-5}$ eV/K and T is absolute temperature.

Degradation mechanisms in OLEDs can indeed be related to irreversible microscopic chemical reactions (see e.g. Giebink *et al.*, 2008) and it is therefore not surprising that ageing follows the Arrhenius relation even though an exact understanding of the microscopic processes is still lacking. In the context of lifetime acceleration R is interpreted as the inverse of the failure time or lifetime LT .

$$LT(T) = Ce^{\frac{E_A}{k_b T}} \quad [20.4]$$

where C is the constant of proportionality.

In the following, the activation energy E_A will always be given in units of eV. The temperature-induced acceleration when increasing the temperature from T to T_{acc} is

$$AF(T_{acc}) = e^{\frac{E_A}{k_b} \left(\frac{1}{T} - \frac{1}{T_{acc}} \right)} \quad [20.5]$$

where T_{acc} is stress factor T (temperature) at accelerated condition and AF is acceleration factor with respect to standard condition.

Inverse power relationship

Another common observation in accelerated lifetime testing is that the system life is inversely proportional to the power of the applied stress (see any textbook on accelerated life testing), or more generally:

$$LT(X) = \frac{B}{X^n} \quad [20.6]$$

where X is stress factor related to either light output or driving current density, B is constant of proportionality and n is acceleration coefficient.

The acceleration for an experiment run at high luminance or driving current density is

$$AF(X_{acc}) = \left(\frac{X_{acc}}{X} \right)^n \quad [20.7]$$

where X_{acc} is stress factor X at accelerated condition.

The inverse power relationship in its simplest form with $n=1$ can be easily rationalised for OLED as a degradation process caused by the amount of charge flowing through the device (Popovic and Aziz *et al.*, 2002). Then, X corresponds to the current density. Since at moderate current densities the luminance L is proportional to the current density, in most publications on OLED lifetime testing L is used as stress factor (Popovic and Aziz, 2002). As L significantly depends on temperature when driven at constant current, we consider the current density as primary stress factor in our combined model.

It has to be noted that for convenient notation of the acceleration laws, the stress factor X is used as a dimensionless quantity equalling the value of the luminance or current density.

Complete acceleration model

We will use both stress factors discussed in the previous paragraph in order to accelerate the lifetime tests. Put together, one can expect the following lifetime for the accelerated experiment in dependence on temperature and driving current:

$$LT(T, X) = a \frac{e^{\frac{E_A}{k_b T}}}{X^n} \quad [20.8]$$

where a is the product of constants B and C . More conveniently, one can write the equation in so-called log-linear form. Each summation term therein corresponds to one stress type:

$$\ln(LT) = \ln a + \frac{E_A}{k_b T} - n \ln(X) \quad [20.9]$$

where X and T are stress factors related to luminance L or driving current density j and temperature T , respectively, with acceleration coefficients n and E_A . It will be shown that this stress–lifetime relation needs some extension in order to match the experimental findings. The agreement with the data could be increased significantly by introducing a temperature-dependent acceleration coefficient n as

$$n(T) = \frac{n'}{k_b T}. \quad [20.10]$$

This simple, hyperbolic dependence is especially convenient, as it does not need any additional fit parameter.

At high accelerating current densities it has to be considered that the device temperature may be increased with respect to its environment beyond measurement uncertainty. In case the temperature cannot be measured directly we can compensate for this heating effect in the model by making the device temperature T a function of driving current and ambient temperature T_{amb} such as

$$T(X) = T_{amb} + bX \quad [20.11]$$

where b is the fit parameter and T_{amb} is ambient temperature.

Here we assume that the heat generated by the OLED device is proportional to the driving current. Due to the typical exponential current-voltage characteristics of an OLED, the voltage changes only a little even if the current is increased to a multiple of its nominal value. Therefore the heating power mainly depends on the driving current.

In the following the lifetime–time stress relation and its extension, including the temperature dependence of n , will be referred to as models one and two.

20.3.2 Lifetime modelling

The availability of accurate models which describe the decay of the luminous flux over the lifetime is essential in order to extrapolate lifetime from short-time experiments. Lifetime information based on extrapolation from testing under normal operating conditions obviously has the advantage that the OLED is not operated beyond the specified limits and that hidden acceleration factors, like the influence of a strongly non-uniform luminance distribution on the lifetime, cannot affect the results. Since detailed knowledge about the microscopic processes which yield material degradation is not available, most models which describe the luminance decay of OLEDs are based on empirical observations. We will discuss three models and analyse their suitability for reliable extrapolation.

First, we discuss the well-known stretched exponential decay (SED) or Kohlrausch function (Kohlrausch 1854):

$$\frac{L(t)}{L_0} = e^{-\left(\frac{t}{\tau}\right)^\beta} \quad [20.12]$$

where t is time and, β , τ are fit parameters.

This Kohlrausch function is a widely successful empirical description of relaxation processes in disordered, amorphous or complex systems (Phillips 1996). It was considered for OLED degradation by Fery *et al.* (2005) as an approximate description of their specific model, which we discuss below as model three. Meerheim *et al.* (2006) discussed the use of the Kohlrausch function for extrapolating OLED degradation curves beyond the measured time range.

Secondly, we consider a model which is purely mathematical but which turned out to describe the luminance decay very well:

$$\frac{L(t)}{L_0} = 1 - bt^\gamma \quad [20.13]$$

where t is time and b , γ are fit parameters.

The fit parameter γ is in the range of 0 to 1 and the function's graph therefore has the shape of a negative non-integer root function. Therefore, we will call this the *generalised root* (GR) model in the following. Its obvious drawback is that it may yield negative values and thus has no physical meaning.

The third model was proposed by Féry *et al.* (2005). It results from an attempt to relate the luminance degradation to the quenching of microscopic emission centres. It is given as a differential equation in time and has to be solved and fit to the experimental data by means of numerical integration:

$$\frac{1}{\tau} \frac{d}{dt} \left(\frac{N}{N_s} \right) = e^{-A \frac{N}{N_s}} - \frac{N}{N_s} e^{-A} \quad [20.14]$$

where N_s and N are the total number and the number of quenched emission centres, respectively, and A and τ are fit parameters. Féry *et al.* (2005) comment that the solutions of their model can be approximately described by the stretched exponential decay function.

All models have in common that they need only two independent parameters to describe the luminance decay.

20.4 Data analysis and discussions

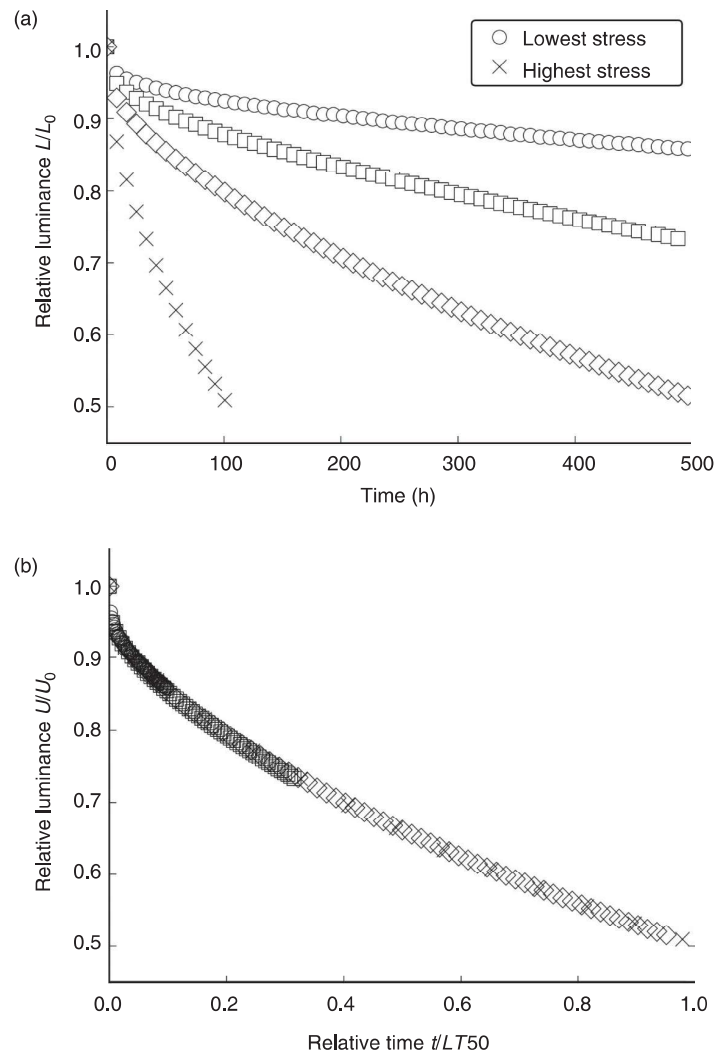
For this study, numerous lifetime tests have been taken out on OLED panels of various types. The panels differ in size, layout, assembly, and most importantly in the organic materials. Osram and IPMS apply different technologies for the composition of the OLED stack, both in terms of materials and layer sequence, resulting in significantly different operation conditions for current density and forward voltage. This means that lifetime and acceleration coefficients will also be different for those panels. The interesting task therefore is to find a model which can fit the lifetime of all panels, applying distinct sets of fit parameters.

Since the *in situ* lifetime tests at PTB are limited to a single temperature, additional lifetime tests on large area panels were taken out by the project partners. Only at PTB was it possible to perform all measurements without interrupting the OLED operation, i.e. all measurements were performed *in situ* in thermal equilibrium and the luminance was recorded by means of a luminance camera and a photometer. In contrast, at the other partner's laboratories, the large area OLEDs were measured initially, before the lifetime test began applying fast single-shot (OLED operating time smaller than 1 s) measurements of the forward luminance (Osram) and the luminous flux in an integrating sphere (IPMS). Then the OLEDs were operated under different stress conditions in a temperature-controlled environment and regularly measured in the same manner as the initial measurement.

In addition to data from large area panels, i.e. panels having an active area of $>30\text{ cm}^2$, data from small OLED pixels under various stress conditions has been provided by Osram and IPMS. The number and the range of distinct stress conditions that have been applied were much higher than what would have been possible using large area devices, thus the data base for the development of an acceleration model is much larger. The small size OLEDs made by Osram and IPMS have an active area of 4 mm^2 and 15 mm^2 respectively. The lifetime tests on those diodes have been taken out with *in situ* tracking of the emitted flux by a photometer placed in the near-field of the OLED pixel. The signal detected by the photometer is assumed to be proportional to the total luminous flux in good approximation. For the determination of the lifetime, this signal is normalised to its initial value and it is not necessary to know the absolute luminance value.

20.4.1 Analysis methods

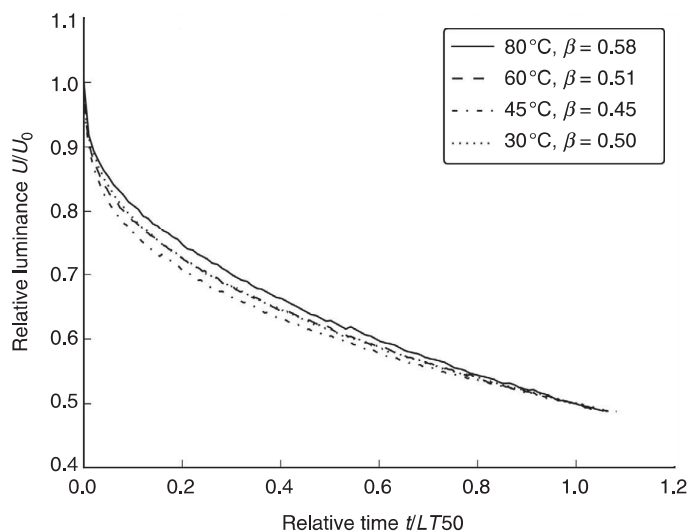
The small pixel data will be used to study the luminance degradation models and deduce an appropriate extrapolation method. Figure 20.8 shows the luminance decay of various devices operated at four distinct current density values from 5 up



20.8 (a) The luminance decay at various driving currents but constant temperature. (b) The time axis of each curve has been scaled so that the overall residual variance is minimised.

to 120 mA/cm^2 at a constant temperature of 25°C ; the curve with the steepest initial decay obviously corresponds to the highest driving current. Only two sets of devices have passed the 70% luminance level. For the other devices the lifetime will have to be extrapolated. By scaling the time axis, it is possible to map all curves onto a single one, shown in Fig. 20.8(b). This property holds for all pixel data of all partners and at all temperatures analysed in this study and proves that, using the current density as stress factor is a reasonable choice, the stress tests carried out at distinct stress levels differ only with regards to the time scale. Now, $LT50$ on the scaled time axis can be measured and by applying the inverse axis transformations on that value we obtain the extrapolated lifetime data of all devices. This scaling method allows lifetime extrapolation using luminance decay characteristics from accelerated testing without making any assumptions on the shape of the decay curve or applying a model. It has been applied wherever necessary throughout the whole analysis of the small pixel data to determine the lifetime.

As stated above, this method is only valid for luminance decay curves recorded at the same temperature. Figure 20.9 shows luminance degradation curves for the same device operated at constant current but at different temperatures. All curves are normalized to L_0 and $LT50$, respectively. The shapes of the curves differ considerably, which indicates that the acceleration mechanism induced by temperature might be more complicated than a simple Arrhenius type law with a



20.9 Luminance decay curves of IPMS OLED pixels at constant driving current but different temperatures as indicated in the legend. Also, the stretched exponent β of a stretched exponential decay (SED) fit is indicated.

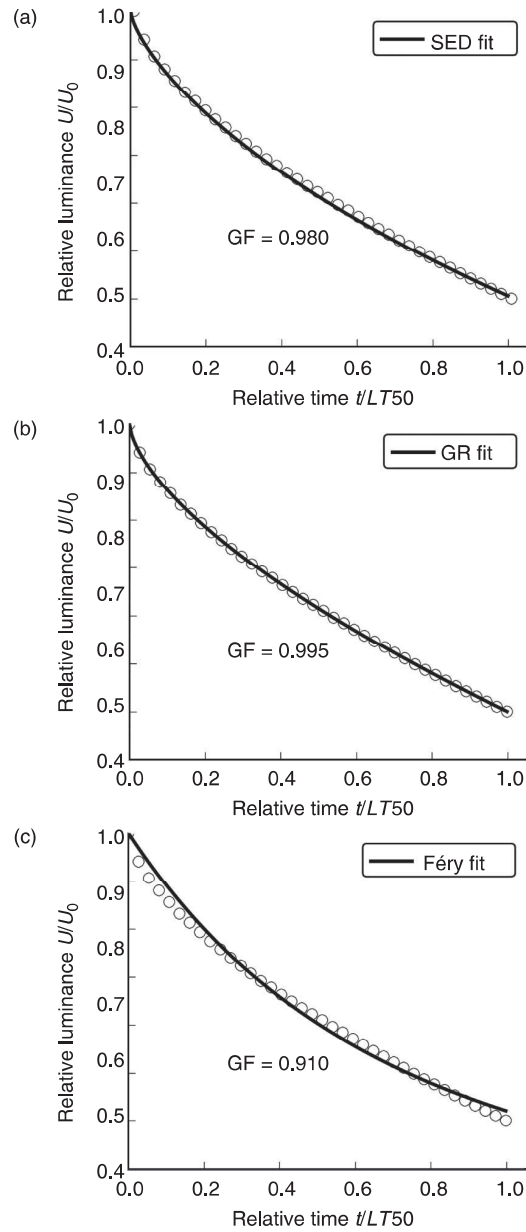
single activation energy. Again this seems to be a universal finding, since it holds not only for the curves shown here, measured on IPMS devices, but also for the data from Osram devices. Nevertheless, in the following we will still assume that temperature is a good stress factor and that the acceleration follows an Arrhenius relation, knowing that the determined activation energies will depend on whether the acceleration model is fitted to the $LT70$, $LT50$ data or any other degradation level.

If data from accelerated measurements is not available, extrapolation could still be carried out if an accurate model was available. Figure 20.10 shows fits of the three lifetime models presented before for the same data from an Osram device. The goodness of fit (GF), evaluated as

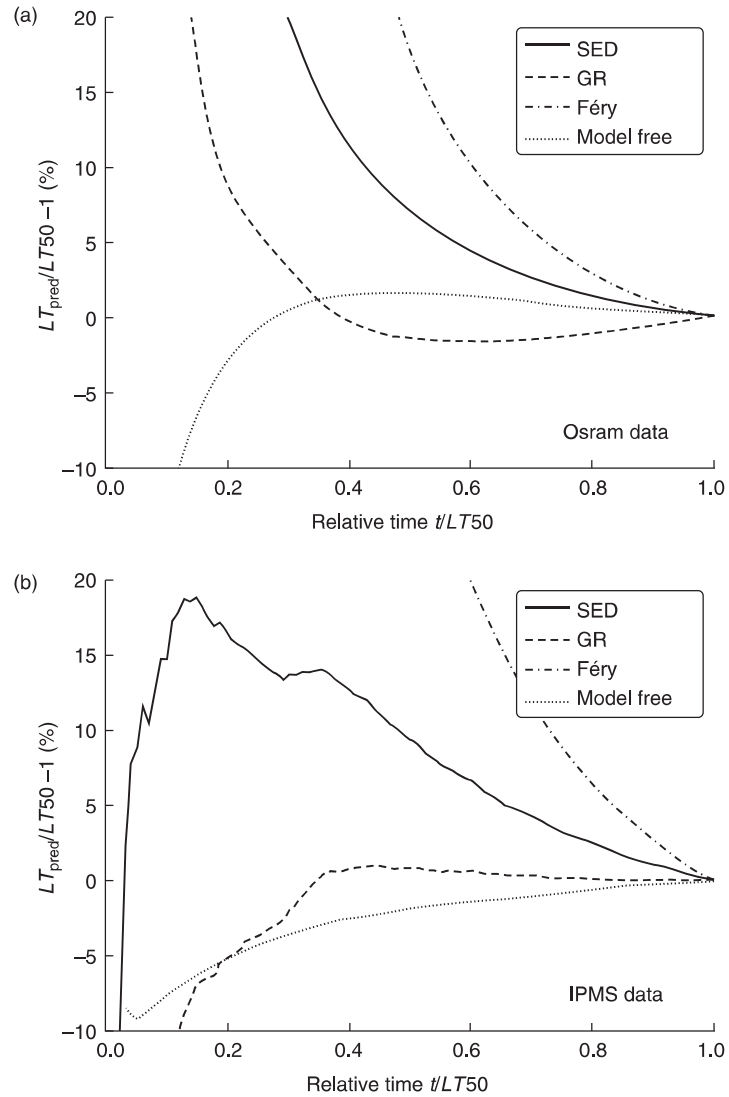
$$GF = 1 - \sqrt{\frac{\sigma_{res}^2}{\sigma_{tot}^2}} \quad [20.15]$$

where σ_{res}^2 and σ_{tot}^2 are the residual and the total variance of the data, is indicated in the graphs and is best for the generalised root model. The stretched exponential model performs well, too; only the Féry model shows significant deviation from the data. Note that even if the extrapolation of the generalised root model will eventually cross the abscissa at $L/L_0 = 0$, it provides the best fit for the data.

More important than showing good agreement with existing data is the ability of the model to extrapolate, i.e. to predict the characteristics of the decay curve in its future. Therefore we took the same data as in Fig. 20.10 and performed successive fits to an increasingly large subset of the available data and evaluated the $LT50$ value by extrapolation using all three models. If the model was a perfect description of the data and the noise of the data was small, we could expect that the extrapolated value would not change as a function of the number of data points used for the fit (provided that the number of data points is superior to the number of fit parameters). The results of this kind of analysis are shown in Fig. 20.11 for both IPMS and Osram small pixel data. The time axis is normalised to $LT50$; the data points represent the deviation from the predicted to the actual $LT50$. The Féry model turns out to give widely incorrect extrapolations for the $LT50$ of both types of OLEDs, even if data up to nearly $LT50$ is taken into account. The SED model performs considerably better, but only the GR model yields very good extrapolations already after about 30% of the expected lifetime for the data of both Osram and IPMS diodes. Even though the models are insufficient to describe the luminance decay exactly, it is possible to get accurate lifetime extrapolations by using the correction factors provided by this analysis from short-time measurements. The same procedure has been applied to the model-free extrapolation method presented previously. The results are shown together with the model-based extrapolations in Fig. 20.11. The prediction error is mostly below 10% even if the test has run for only about 10% of the expected lifetime.



20.10 Comparison of three lifetime models, fit to normalised luminance decay curves of an Osram device: (a) stretched exponential, (b) generalised root, (c) Féry model. The goodness of fit (GF) is indicated in each diagram.



20.11 Extrapolations based on successive fits to an increasingly large subset of the available data up to LT_{50} . (a) Shows Osram data; (b) shows IPMS data.

20.4.2 Acceleration model

As stated above, we will use the small pixel data provided by Osram and IPMS to develop an acceleration model. The stress factors are temperature, more precisely the temperature of the organic stack (in the following called device temperature), and either the initial luminance or the current density. Table 20.1 lists all stress conditions which have been tested. The highest and lowest applied driving current density correspond to a luminance of about 20 000 cd/m² and 1000 cd/m² for both Osram and IPMS devices respectively.

In order to provide a well defined temperature stress, the devices were operated in air convection ovens. Heat transfer from the devices to the surroundings occurs through convection and more importantly for small pixel devices by conductive heat transfer to the fixture of the device. For a broad range of driving current values, the temperature of the devices equals that of the oven within a range of ± 1 °C which is about the measurement uncertainty. For very high driving currents, it might happen that the cooling power is not sufficient and that the temperature of the devices is measurably increased due to significant self heating.

In general, the luminance is proportional to the current density in good approximation, becoming slightly sub-linear only at very high levels of luminance, but it also strongly depends on temperature. Considering that the electrical load defined by the number of injected carriers – if operated at constant current – should rather remain constant regardless of the operating temperature, it seems reasonable to assume that the acceleration law holds for the current density rather than the initial luminance. For better comparability between devices of different size but identical electro-optical performance, all lifetime data will be related to the current density rather than the current.

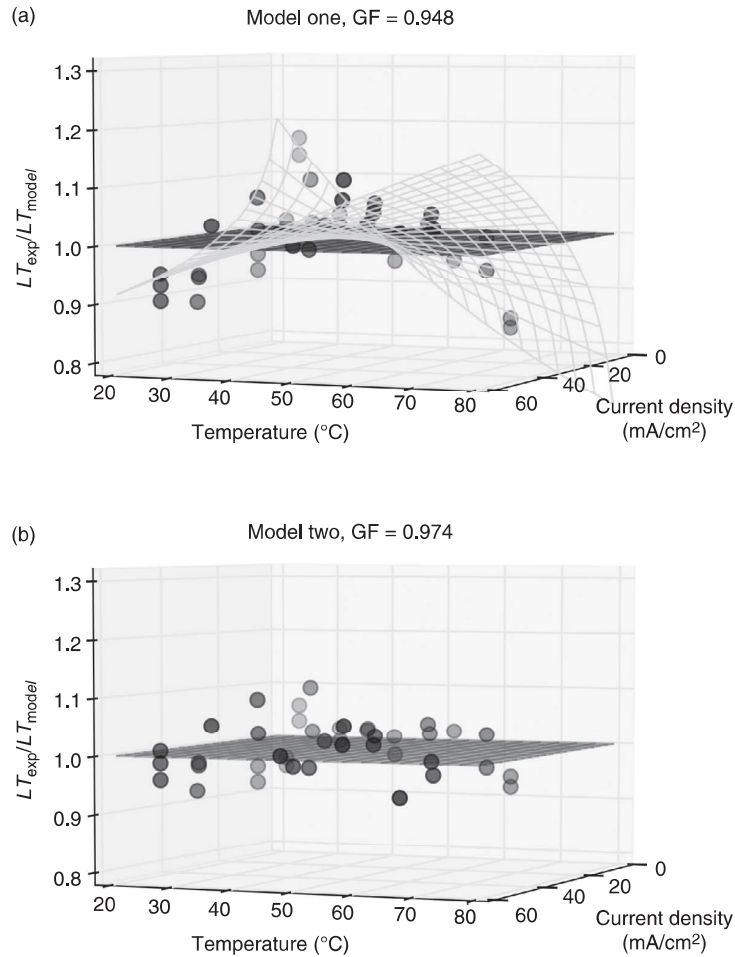
In the following, we will present the fits of the acceleration models proposed before to the collected *LT70* data as a function of temperature and current density. Mathematically speaking, this problem involves fitting a three-dimensional surface to a point cloud which we accomplished using least squares fitting. The fits were conducted on the logarithmic lifetime data. Assuming that the lifetime data is log-normally distributed, a fact which is confirmed by experimental findings, on a log-scale the data follows a normal distribution. A least squares fit on that data will thus be determined by the mean or *B50* value of the distribution,

Table 20.1 Stress conditions for all small pixel tests run by Osram and IPMS (at least two devices were tested at each condition)

Manufacturer	Current density (mA/cm ²)	T (°C)
Osram	5, 10, 20, 42, 55, 120	25, 35, 45, 55, 65
IPMS	1.65, 3.3, 10, 40	30, 45, 60, 80

i.e. that time after which the luminance of 50% of the devices passes the 70% threshold.

In a first step we used model one with constant acceleration coefficients (Eq. 20.9). In Fig. 20.12(a), the residual of the fit of model one to Osram data is shown. Apart from the scatter, a systematic deviation of the model from the data is visible. A closer look reveals that at high temperatures, lifetime is overestimated



20.12 (a) Residual plot of model one for the Osram lifetime data shown together with the difference between model two and model one as a warped grey surface. (b) Residual plot of model two for the Osram lifetime data. For clarity, the plots do not show the residual of the fit but $\left(e^{\ln(LT_{\text{exp}}) - \ln(LT_{\text{model}})} \right) = \frac{LT_{\text{exp}}}{LT_{\text{model}}}$.

at low current density and underestimated at high current density, while at lower temperatures the opposite is true. These characteristics can be very well accounted for by introducing the temperature-dependent acceleration coefficient n of model two (Eq. 20.10). This extension of the model can fit all data very accurately. For visualisation purposes, the difference between models two and one is shown in the residual plot of model one (Fig. 20.12(a)) as a warped grey surface which nicely follows the locations of the data points. Fig. 20.12(b) shows the residual plot of model two which no longer reveals any systematic deviation, and the goodness of the fit indicated in the plot is increased compared to model one.

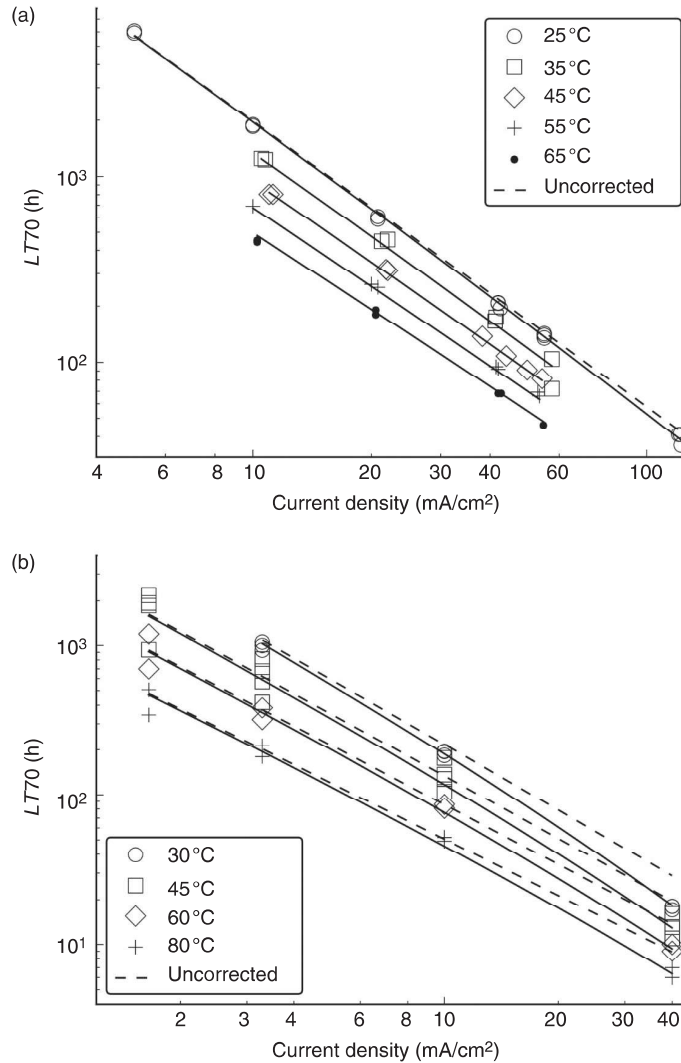
Looking at the IPMS data it turns out that at high current density the lifetime is generally overestimated. This might indicate that the device temperature at that current density is increased by self-heating effects. In fact it had been confirmed by measurements at Osram, that the temperature of their devices if operated at a current density of 120 mA/cm^2 is increased with respect to the surrounding by about $3 \pm 1^\circ\text{C}$. The effect is more pronounced in case of the IPMS devices, which is not surprising as their devices have an active area which is three times larger than that of the Osram diodes and the generated heat cannot be easily dissipated. Indeed, a fit of extended model two (denoted model two'), including the temperature correction as described before in Eq. 20.11, does increase the agreement with the experimental data further and yields a temperature correction at the highest driving condition, which amounts to about 3°C and 10°C for Osram and IPMS small pixel OLEDs respectively. The whole set of fitted parameters of the acceleration models for both types of OLEDs is shown in Table 20.2. The goodness of fit hardly increases when switching from model two to model two' in the case of the Osram data, indicating that the required temperature correction is small. In the case of the IPMS data, however, model two' does give a significantly better description of the data. Obviously the self heating of the devices is notable and cannot be disregarded.

For better visualisation, all Osram and IPMS lifetime data is shown in Fig. 20.13 grouped by temperature. The solid lines are fits of model two' to the experimental data using always the same set of fit parameters a , n , b and E_A for the whole set of data at all temperatures. The agreement with the data is excellent. The dashed lines are also evaluated using model two' but setting the fit parameter b , which reflects the temperature correction, equal zero. The further discussion of the data will be restricted to that subset of the Osram data which is not subject to notable self heating effects and for which no temperature correction is required, i.e. that fraction of the data up to current densities of 55 mA/cm^2 .

Again, as mentioned in the previous section, more interesting than the sole agreement with the data is the model's capability to predict the lifetime outside the tested parameter range. Therefore, we chose a subset of four conditions of the available Osram lifetime data representing rather high stress and repeated the fit,

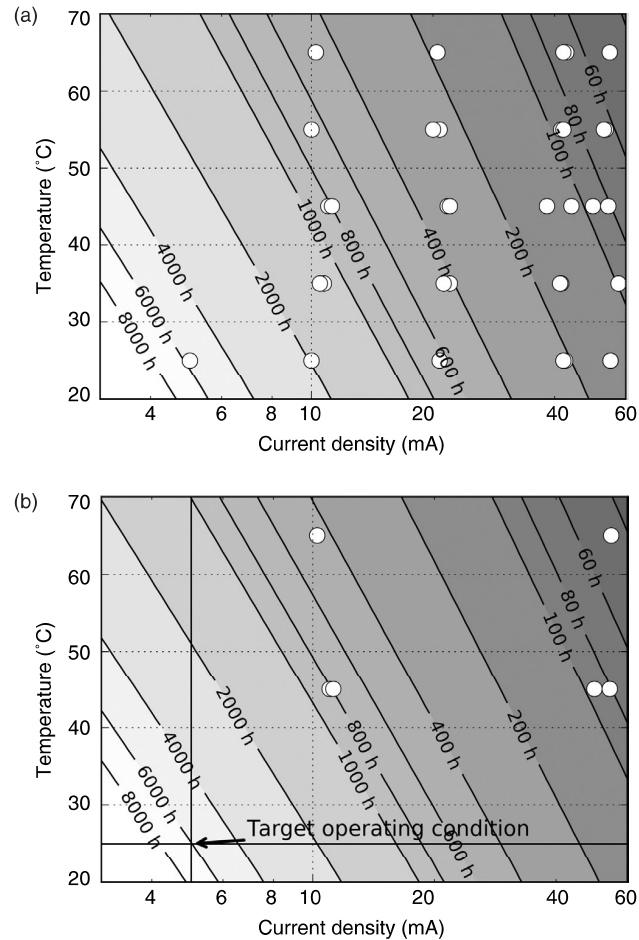
Table 20.2 Fit parameters and GF values of models one and two and model two with temperature correction, denoted two', for Osram and IPMS devices

Model	IPMS			
	One	Two	Two'	One
E_a (eV)	0.256 ± 0.008	0.388 ± 0.006	0.389 ± 0.006	0.268 ± 0.020
n or n' (eV)	1.510 ± 0.017	0.040 ± 0.000	0.039 ± 0.001	1.473 ± 0.031
b			0.033 ± 0.078	
$\ln a$	1.035 ± 0.299	-3.924 ± 0.212	-4.021 ± 0.243	-1.681 ± 0.707
GF	0.948	0.974	0.974	0.837
				0.882
				0.357 ± 0.016
				0.040 ± 0.000
				0.268 ± 0.103
				-4.891 ± 0.572
				0.894



20.13 Fit of model two to the Osram (a) and IPMS (b) small pixel LT70 data plotted in the common log-log plot of lifetime vs. stress. Data following the inverse power relationship appears linear in that plot. All parameters are fixed, only the temperature varies between the groups of data.

based on model two. The result is shown in Fig. 20.14: (a) the fit of model two to the Osram data is shown once more, this time as a greyscale plot of the fitted lifetime as a function of temperature and current density for the constricted data; (b) shows the results of the fit of model two to the subset of four conditions. The



20.14 (a, b) Pseudo colour plot of the fit of model two to the lifetime data of the Osram devices (white circles). The fit in (b) is based on only a subset of the available lifetime data as indicated by the white circles. Nevertheless the fits are almost equal.

fits are almost the same regardless of whether we use the full set of data or a small subset, proving the accuracy of the chosen model. Indeed, the prediction of the lifetime at the target operating condition of 5 mA/cm² and 25°C of 6060 hours, based on the model two fit to the subset of the data, nicely matches the actual mean lifetime measured under that condition, which is 5950 hours. Table 20.3 lists the lifetimes predicted by models one and two to the subset of the data. Model one generally underestimates the actual lifetime, also in the case of the IPMS data (not shown).

Table 20.3 Predicted lifetimes for the target operating condition of 5 mA/cm² and 25°C (the measured lifetime under that condition amounts to 5950 hours)

Model	One	Two
Pred. L_{T70} (h)	5030 ± 220	6060 ± 90

20.4.3 Large area devices

Those lifetime tests which are part of a product qualification process will have to be conducted on the actual product, i.e. a large area OLED panel. Most of the findings of the small pixel lifetime analysis, however, can be transferred and used for the analysis of the large panel tests. Nevertheless we expect an influence of the large area nature, e.g. the limited uniformity of the luminance, on the acceleration coefficients or even on the model. Lifetime testing on large area panels is considerably more costly compared to the small pixels, considering the required space in the testing equipment and the necessity of a powerful temperature control system, since the heat created by large area panels is notable, although rather small compared to inorganic LEDs. This part of the study on the large area devices was intentionally conducted using standard climate-controlled ovens which rely on convective heat transfer, without *in situ* tracking of the luminance. With that setup it was intended to evaluate whether the data collected by using this rather simple equipment is sufficient to conduct and run accelerated lifetime tests with good prediction capabilities. Also, since the OLED panels reveal a conventional cavity glass encapsulation, the OLED stack temperature is neither necessarily homogeneous across the active area nor easily accessible. Therefore we will relate the collected lifetime data to the oven temperature, knowing that this might introduce a systematic error.

The lifetime data presented in the following results from tests on circular OLED panels from Osram with an active area of 50 cm². The nominal driving current is 275 mA (5.5 mA/cm²); within the accelerated test the devices were operated with up to 400 mA at 60°C. Per stress level eight devices were tested. Table 20.4 lists the fit parameters of models one and two to the large area lifetime data and the prediction for the standard operating condition. The organic stack is similar to that of the small pixel OLEDs and except for process-related fluctuations the absolute lifetime and the acceleration coefficients, if determined using small pixel devices, should not differ much. However, the determined coefficients of the large area lifetime data differ significantly from those of the small pixel devices (Table 20.2). This is due to both testing and large area OLED-related effects which enter into the acceleration model. The convective cooling in the climate ovens cannot ensure that the temperature of the OLED devices exactly equals the control temperature; usually there is a constant offset between device and controlled ambient temperature. This offset is, in the first approximation, independent of the ambient

Table 20.4 Fit parameters of models one and two to the accelerated large panel lifetime data of the Osram devices and the corresponding predicted LT_{70} under normal operating conditions

Model	One	Two
Ea	0.317 ± 0.014	0.632 ± 0.015
n	1.942 ± 0.088	0.055 ± 0.003
$\ln a$	6.648 ± 0.863	-4.345 ± 0.510
GF	0.839	0.838
Pred. LT_{70} (h)	3285 ± 128	3318 ± 130

temperature, but it does depend on the OLED driving current. The higher the driving current, the larger will be the offset between oven and device temperature. This temperature-induced decreased lifetime will manifest itself in an increased acceleration coefficient n . The varying uniformity of a large area device at elevated driving currents or high temperature may also yield a differing set of acceleration coefficients compared to that of the small pixel devices.

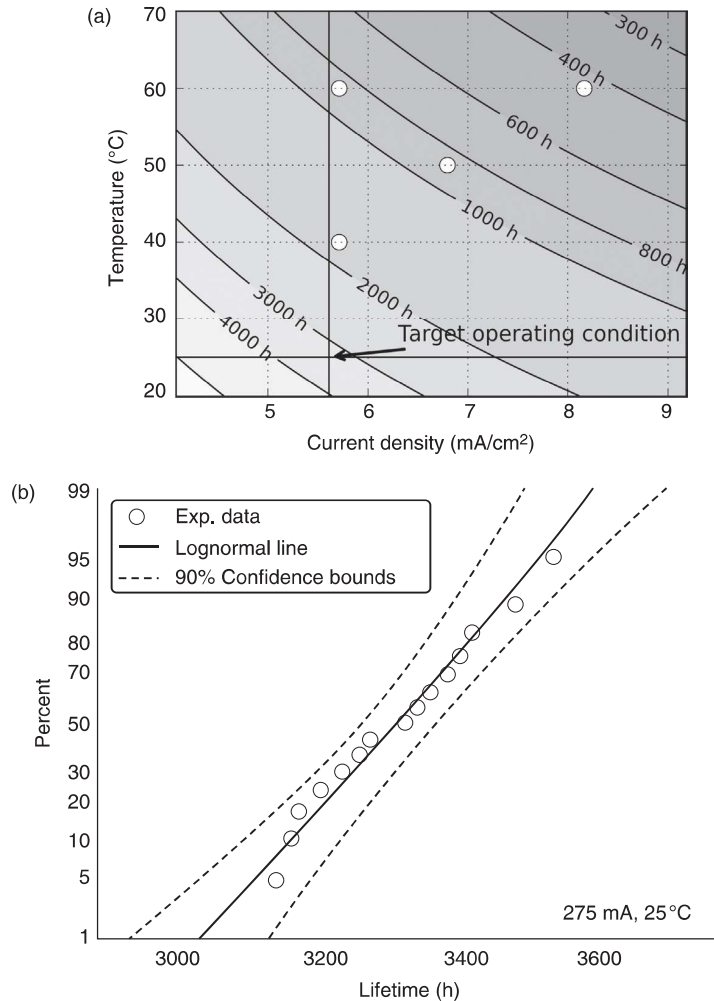
Both models one and two can be fitted to the data with low residual variance. The graph of Fig. 20.15(a) shows the evaluation of model two fitted to the lifetime data at the stress levels indicated by the white circles. The normal operating condition is indicated and the predicted lifetime amounts to approximately 3300 hours. The lifetime test under normal operating conditions has been conducted by PTB on an ensemble of 15 devices with a total duration of 1600 hours and the LT_{70} has been determined by extrapolation using the GR degradation model. The extrapolated LT_{70} is shown as a lognormal probability plot in the graph of Fig. 20.15(b). The B_{50} lifetime amounts to 3300 hours with a standard deviation of about 120 hours which very accurately matches the prediction made by the acceleration model even though the model includes contributions from several indirect acceleration factors as mentioned previously.

20.4.4 Secondary lifetime criteria

This study focuses on the development of a model for the acceleration of the luminance degradation. Nevertheless, secondary criteria, like voltage rise, loss of lateral uniformity and colour shift, which might also define an end-of-life incident, have been monitored too and will be discussed in this section. All data shown in the following results from the lifetime tests on the large area panels from the previous section.

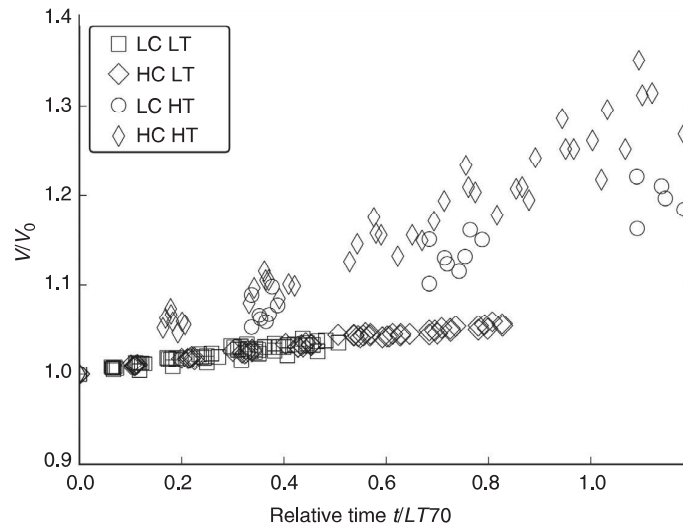
Voltage

The rise of the driving voltage during operation is at least from an application point of view a very important parameter. The voltage rise has to be considered



20.15 (a) Free fit of model two to Osram lifetime 70 data of large area OLEDs. (b) Lognormal probability plot of the extrapolated lifetime 70 data of the Osram devices run and measured at PTB under normal operating conditions. Fitted parameters: $B50 = 3297$ h, $\sigma = 120$.

when designing an electric driver. The system efficacy depends, among other things, on the voltage overhead which needs to be provided in order to make sure that the OLED may be operated during its whole lifespan without being affected by a voltage limit posed by the driver. When relying on accelerated lifetime tests it is therefore important to know whether the acceleration model for the luminance decay is able to predict the voltage rise during the lifetime. Figure 20.16 shows

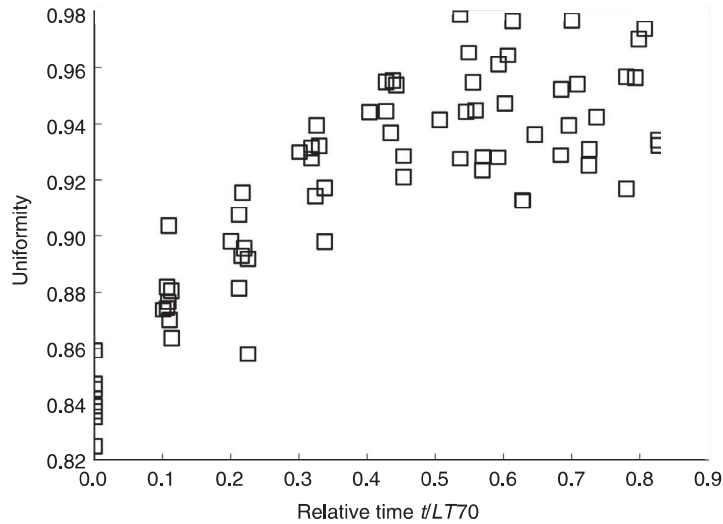


20.16 Relative voltage as a function of normalised time of large area devices, grouped by acceleration condition. LC and HC refer to low and high current, LT and HT indicate low and high temperature, respectively. The time axis is normalised to the luminance lifetime 70.

the voltage rise of the large area devices normalised to their corresponding luminance $LT70$. If the luminance degradation acceleration model held for the voltage as well, we would expect all data from all experiments to unite in a single (noisy) curve. Instead, we see that tests at equal temperature but distinct current do indeed reveal a comparable voltage rise; however, there is a clear dependence on temperature. Thus, the acceleration model holds very well with respect to current density but fails with respect to temperature.

Lateral uniformity

The lateral non-uniformity of both temperature and luminance caused by the finite conductivity of the electrodes is expected to change over the lifetime. The brighter and warmer areas of the device are subject to higher stress than the average, so that the degradation is faster there, reducing the local luminance at a higher rate than the mean luminance. Since luminance degradation is expected to be at least partly caused by a loss of conductivity of the organic layers, which manifests in the rising driving voltage during constant current operation, a laterally varying degradation rate will lead to a redistribution of the current profile through the device. This makes it difficult to predict the evolution of the uniformity over time. Fortunately, in most cases the initial non-uniformity decreases during the



20.17 Uniformity of the luminance of large area devices as a function of normalised time.

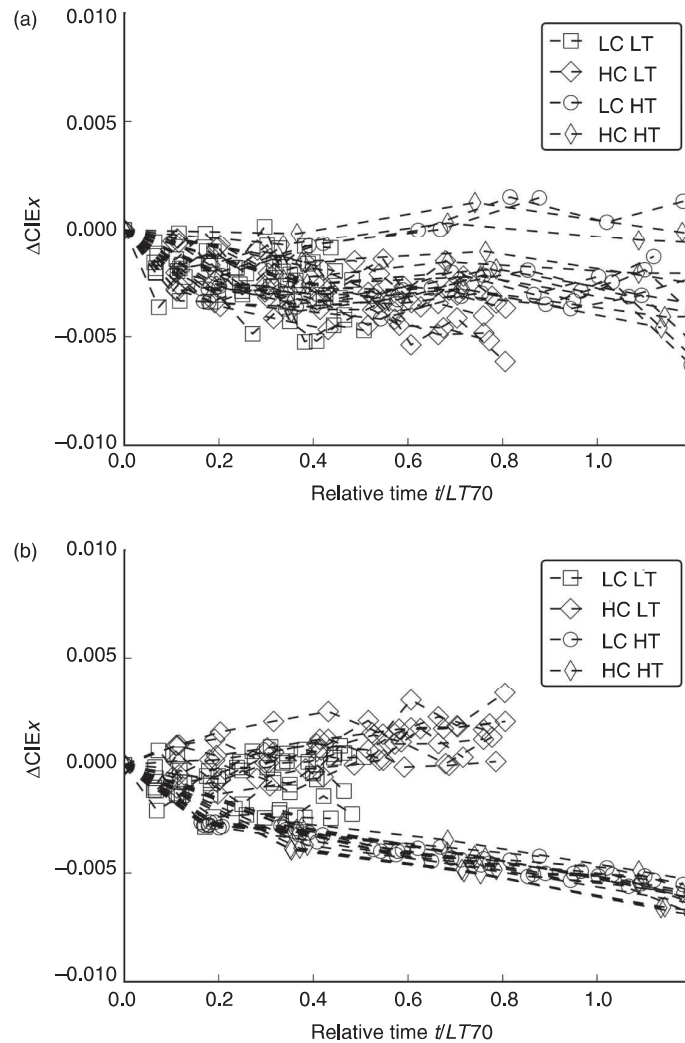
lifetime as shown in Fig. 20.17. The uniformity is calculated from the minimum and maximum luminance of the active area as

$$U = 1 - \frac{L_{\max} - L_{\min}}{L_{\max} + L_{\min}}. \quad [20.16]$$

The area of a measuring spot should be in the range of 1% of the OLED area.

Chromaticity

While the luminance degrades it would not surprise us if the emission colour changed too, even though a well-designed device will reveal only minimal changes. The chromaticity has been measured with a colour luminance camera in normal direction as we do not expect the angular characteristics to change significantly during the lifetime. The chromaticity coordinates as a function of lifetime, again normalised to the luminance lifetime 70, are shown in Fig. 20.18. The chromaticity changes only little during the lifetime. The CIEy coordinates corresponding to low and high current operation form a single group of time dependencies independent of temperature, confirming the validity of the luminance degradation acceleration model with respect to current density for the colour change vs. time. As previously, when analysing the voltage rise over the lifetime, this does not hold for operation at distinct temperatures. Interestingly, the CIEy coordinate tends to rise slightly if operated at low



20.18 (a, b) Relative colour coordinates as a function of normalised time of large area devices. LC and HC refer to low and high current, LT and HT indicate low and high temperature, respectively. The time axis is normalised to the luminance lifetime 70.

temperature and decreases at high temperature. This tendency is also present in the CIE_x data but less pronounced.

20.5 Conclusion

In this study, we have developed a three-parameter acceleration model for the luminance lifetime of OLEDs. Temperature and driving current – not the luminance as in many publications – were used as acceleration factors. The model includes an extension of a purely empirical nature to what was previously known in literature: a temperature-dependent acceleration coefficient for the current. With those enhancements we were able to fit both Osram and IPMS small pixel data with very good accuracy and give realistic predictions for the lifetime under normal operating conditions.

The testing setup for the accelerated lifetime tests of the large area panels used in this study did only match the minimum requirement: constant current operation in temperature controlled environments interrupted by regular measurements of the luminance. This has been done for two reasons: on the one hand, the present large area OLED devices do not allow the direct measurement and thus control of the OLED stack temperature due to the insulating properties of the glass cavity encapsulation. On the other hand, it could be verified that even with that setup, yielding acceleration coefficients which reflect a superposition of OLED intrinsic degradation properties with the systematic error of the test setup regarding the definition of the stress level, the models developed for the small pixel lifetime are still applicable and yield reasonable predictions. In that sense, the good agreement of the predicted and measured lifetime of the large area devices presented in the previous section is satisfactory but should not be overestimated.

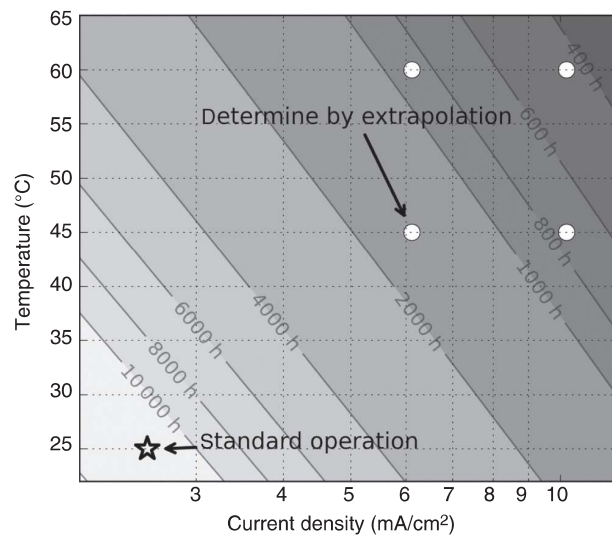
The emerging generation of OLED devices will be thin film encapsulated, eliminating the need for the gas-filled cavity between the back electrode and the cap glass. By applying a heat distributing material to the backside of the OLED, the temperature will be nearly constant throughout the whole active area. Controlling or measuring this well-defined temperature will result in similarly well-defined stress levels as in the tests of small-sized OLED devices. Eventually the differences in the acceleration coefficients between small and large area devices may be attributed solely to real OLED-related scaling effects, such as the varying luminance uniformity at distinct driving currents or temperatures.

Based on the findings, we make the following recommendations for conducting an accelerated lifetime testing procedure:

- Ensure a thermal environment which permits device temperature to be controlled or measured with an accuracy of 1 °C.
- Track the luminance decay *in situ* with a photometer. The initial flux will be determined at such time after which complete thermalisation is achieved, e.g. after one hour of operation.

- Test at least four distinct stress levels – one more than the number of parameters of the model – which span a rectangle as large as possible in the parameter space (refer to Fig. 20.19).
- Limit the current stress levels to an appropriate value in order to keep the uniformity of the luminance above a reasonable level.
- Choose an appropriate number of devices per stress level in order to keep the standard error of the prediction under standard operating conditions below 10%. This depends on the choice of the stress levels and the spread of the lifetime distribution.
- If feasible, determine the lifetime at the lowest stress level by a suitable extrapolation method in order to increase the total acceleration factor.

In order to establish a comprehensible lifetime determination procedure which can be understood and reproduced by any lamp, i.e. OLED, and luminaire manufacturer, the universality of the acceleration model has to be proven, i.e. whether any of the proposed models or any other model can fit the data of all manufacturers sufficiently well. This is a task which should be addressed in the international standardisation committee working groups on lifetime determination, e.g. TC2-68 of the *Commission Internationale d'Éclairage*, as soon as possible.



20.19 Exemplary lifetime map of an accelerated lifetime setup. The white circles mark the accelerated stress levels; the star indicates the standard operating condition.

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