

RESEARCH ARTICLE | OCTOBER 25 2004

High-efficiency and low-voltage *p-i-n* electrophosphorescent organic light-emitting diodes with double-emission layers

Gufeng He; Martin Pfeiffer; Karl Leo; Michael Hofmann; Jan Birnstock; Robert Pudzych; Josef Salbeck



Appl. Phys. Lett. 85, 3911–3913 (2004)

<https://doi.org/10.1063/1.1812378>



View
Online



Export
Citation



Cut Hall measurement time in *half*
using an M91 FastHall™ controller



Also available as part of a tabletop system and an option for your PPMS® system

High-efficiency and low-voltage *p-i-n* electrophosphorescent organic light-emitting diodes with double-emission layers

Gufeng He, Martin Pfeiffer, and Karl Leo^{a)}

Institut für Angewandte Photophysik, Technische Universität Dresden, D-01062 Dresden, Germany

Michael Hofmann and Jan Birnstock

NovaLED GmbH, Zellescher Weg 17, D-01069 Dresden, Germany

Robert Pudzich and Josef Salbeck

Universität Kassel, D-34109 Kassel, Germany

(Received 20 April 2004; accepted 13 September 2004)

We demonstrate high-efficiency organic light-emitting diodes by incorporating a double-emission layer (D-EML) into *p-i-n*-type cell architecture. The D-EML is comprised of two layers with ambipolar transport characteristics, both doped with the green phosphorescent dye tris(phenylpyridine)iridium. The D-EML system of two bipolar layers leads to an expansion of the exciton generation region. Due to its self-balancing character, accumulation of charge carriers at the outer interfaces is avoided. Thus, a power efficiency of approximately 77 lm/W and an external quantum efficiency of 19.3% are achieved at 100 cd/m² with an operating voltage of only 2.65 V. More importantly, the efficiency decays only weakly with increasing brightness, and a power efficiency of 50 lm/W is still obtained even at 4000 cd/m². © 2004 American Institute of Physics. [DOI: 10.1063/1.1812378]

Organic light-emitting devices (OLEDs) using phosphorescent dyes doped into charge-transporting hosts as emissive layers have attracted intensive attention¹⁻⁴ due to the highly efficient emission compared to conventional fluorescent OLEDs. Through radiative recombination of both singlet and triplet excitons, the internal quantum efficiency of the phosphorescent OLED can reach 100%,⁵⁻⁷ corresponding to an external quantum efficiency (EQE) of around 20% limited by the light outcoupling factor. Adachi *et al.*⁷ reported a maximum EQE of 15.4% by doping a green-emitting phosphorescent dye, tris(phenylpyridine)iridium [Ir(ppy)₃], into an electron-transporting host, 3-phenyl-4-(1'-naphthyl)-5-phenyl-1,2,4-triazole (TAZ). Ikai *et al.*⁶ employed a predominantly hole-transport (PHT) material 4,4',4''-tris(N-carbazolyl)-triphenylamine (TCTA) as a host for Ir(ppy)₃ and obtained an EQE of 19.2%. However, most of these high-efficiency phosphorescent OLEDs need high operating voltage, and the high efficiency is mostly obtained at very low current density and brightness, decreasing rapidly with increasing current. This is a challenge for applications such as high-brightness displays, passive matrix-driven displays, or OLEDs for lighting applications.

By introducing a *p-i-n* structure to an OLED, we have successively reduced the operating voltage for both fluorescent⁸ and phosphorescent devices^{9,10} in previous studies. The high conductive *p*- and *n*-doped layers enhance the charge injection from the contacts and reduce the ohmic losses in these layers.^{8,11-13}

The double-emission-layer (D-EML) concept for phosphorescent OLEDs was introduced by Zhou *et al.* in 2002.¹⁴ Here, we incorporate a D-EML structure into *p-i-n* phosphorescent OLEDs. The D-EML consists of two layers capable of ambipolar charge transport, one with a PHT character, one with a predominant electron transporting (PET) character;

both are doped with the phosphorescent dye. The D-EML OLEDs show significantly improved efficiency and much lower efficiency loss at high current density compared to conventional single-emission-layer (S-EML) OLEDs.

The OLEDs are prepared by thermal evaporation of different organic layers onto patterned, precleaned, and ultraviolet-ozone-treated indium tin oxide (ITO)-coated glass substrates in an ultrahigh-vacuum system without breaking the vacuum. The *p*- and *n*-doped transport layers, emission layers, and blocking layers are deposited in separate chambers, so the crosscontamination among the materials is avoided as much as possible. First, 100-nm-thick N,N,N',N'-tetrakis(4-methoxyphenyl)-benzidine (MeO-TPD)-doped with 2 mol. % of 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F₄-TCNQ) is deposited as hole injection and transport layer (HTL). This *p*-doped layer has conductivity approximately 10⁻⁵ S/cm and forms a quasi-ohmic contact with ITO that ensures easy hole injection via tunneling.¹⁵ Between the *p*-doped HTL and the emission layer (EML) system, an interlayer of 10 nm 2,2',7,7'-tetrakis-(N,N-diphenylamino)-9,9'-spirobifluoren (Spiro-TAD) is deposited. Next follows the D-EML system comprised of a layer of TCTA doped with 8 wt. % of Ir(ppy)₃ and a layer of an electron-transporting host like TAZ doped with the same concentration of Ir(ppy)₃. Then, another 10-nm-thick interlayer of a material with a high electron mobility and an appropriate lowest unoccupied molecular orbital (LUMO) level, e.g., 4,7-diphenyl-1,10-phenanthroline (BPhen) is deposited to prevent exciton quenching in the EML by the dopants in the electron transport layer (ETL). After that, a 50-nm-thick *n*-doped ETL is obtained by co-evaporation of BPhen with pure Cs from a dispenser source. Since the evaporation rate of Cs cannot be measured with a quartz thickness monitor, we prepared a series of doped BPhen layers with different Cs rate and calibrated by conductivity. For the OLED, we used a conductivity of

^{a)}Electronic mail: leo@iapp.de

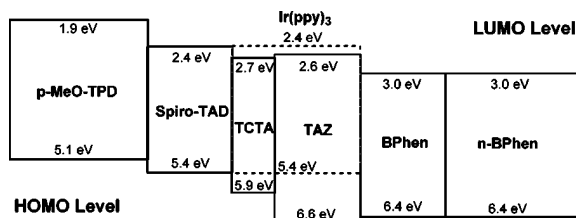


FIG. 1. Device structure of D-EML *p-i-n* OLED and the proposed energy level diagram.

10^{-5} S/cm. Finally, a 100-nm-thick cathode layer of aluminum was patterned using a shadow mask for a device active area of 3 mm². Except for the acceptor dopant F₄-TCNQ, all organic materials have been purified twice by vacuum gradient sublimation.

Current-voltage (*I-V*) characteristics of the OLED are measured in a vacuum with a Keithley SMU236, with the luminance obtained by mounting a silicon photodiode above the OLED to detect the light emitted in the forward direction through the transparent ITO substrate. The setup is calibrated by comparison with direct luminance measurements using a Minolta CS-100A luminance meter. The quantum efficiency is calculated under the assumptions that the emission pattern is Lambertian and electroluminescence (EL) spectra are angle independent.¹⁶ The EL spectra are recorded by a Sen-tronic PL-USB2000 spectrometer (spectrally corrected by comparison with a standard emitter) with an optical fiber attached above the OLEDs in the forward direction.

Figure 1 shows the structure of the *p-i-n* D-EML OLED discussed in the following and the energy level diagram of the device. The highest occupied molecular orbital (HOMO) and the LUMO values are extracted from literature.^{4,6,17}

The quantum efficiencies of D-EML OLEDs are much higher than that of the S-EML OLED we reported before,¹⁰ which has 20 nm Ir(ppy)₃-doped TCTA as an emission layer instead. A maximum EQE of 19.5% is obtained with a 5 nm PHT-EML with TCTA as a host, a 10 nm PET-EML with TAZ as a host and BPhen for the interlayer at the electron injection side. The *I-V* and luminescence-voltage (*L-V*) characteristics of this device are depicted in Fig. 2. Both *I-V* and *L-V* curves show a steep increase after the onset, which is one of the typical characteristics of *p-i-n* OLED. The operating voltage for a typical display application brightness of

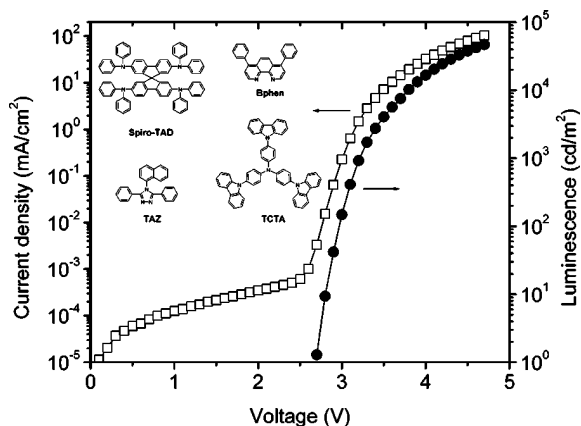


FIG. 2. Current density-voltage (open) and *L-V* (solid) characteristics of D-EML OLED with 5 nm PHT-EML and 10 nm PET-EML.

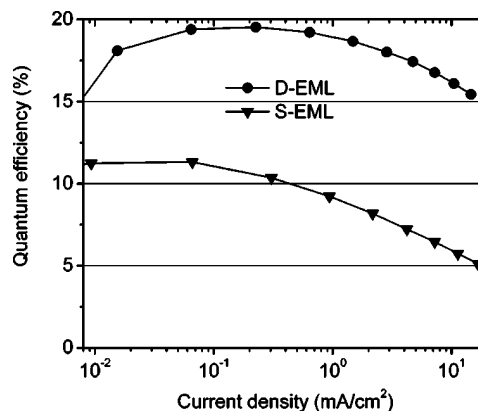


FIG. 3. EQE vs. current density for D-EML devices compared with the S-EML device.

100 cd/m² is 2.95 V, and 1000 cd/m² is obtained at only 3.21 V.

For *p-i-n* devices, both holes and electrons can be easily injected from anode and cathode to the organic layers so that the operating voltages are low for both S-EML and D-EML devices. Also, the S-EML structure using Spiro-TAD and Bphen for the blocking layers shows low operating voltage and very high efficiency. However, the plot of quantum efficiency versus current density shown in Fig. 3 reveals significant differences between S-EML and D-EML devices, which can be understood as follows: For the S-EML device, holes tend to accumulate at the interface of TCTA and Bphen due to the large energy barrier, and the recombination occurs in a shallow slab adjacent to this interface. The high density of triplet excitons may lead to enhanced triplet-triplet annihilation,¹⁸ while the high density of accumulated holes favors quenching of triplet excitons by charge carriers. Moreover, the occurrence of redshifted exciplex emission at around 460 nm in mixed layers of TCTA and BPhen proves that there is not only a large HOMO offset but also a significant LUMO offset between the two materials. Accordingly, we also expect some accumulation of electrons on the Bphen side of the interface and the formation of the TCTA-Bphen interface exciplexes that may lead to quenching of triplet excitons on Ir(ppy)₃ by Förster transfer to either Bphen-anions or exciplexes.

Some of these possible quenching mechanisms can be excluded when we replace the undoped Bphen layer by a layer of undoped TAZ of the same thickness. Having a higher LUMO energy than Bphen, electron accumulation at the interface is no longer expected and the photoluminescence of mixed layers of TCTA and TAZ shows only a superposition of TCTA and TAZ emission without any hints of exciplex formation. Such S-EML devices with TAZ as a hole blocking layer (HBL) show higher efficiency and higher operating voltage compared with the devices using undoped BPhen as HBL. The higher operating voltage can be attributed to the LUMO difference between BPhen and TAZ and lower electron mobility of TAZ. However, the efficiency also decreases substantially with increasing brightness due to either triplet-triplet annihilation or quenching of triplets by accumulated holes at the interface between TCTA and TAZ. In contrast, the D-EML structure can significantly reduce both possible quenching paths by widening the triplet generation zone and avoiding carrier accumulation at the interfaces of the EML and blocking layers.

There are two possible mechanism involved in exciton generation: Energy transfer from the host following carrier recombination on TCTA or direct charge trapping by Ir(ppy)₃. Since TCTA is predominantly a hole transporting material, while TAZ is a electron transporting material, excitons may form first on TCTA near the interface of TCTA and TAZ, and are then subsequently transferred to Ir(ppy)₃ in either PHT-EML or PET-EML. Alternatively, as the HOMO level of TCTA (5.9 eV) is much lower than that of Ir(ppy)₃ (5.2–5.6 eV), holes injected to the TCTA can easily be trapped by Ir(ppy)₃ due to the large energy difference, or the holes can be injected directly to the Ir(ppy)₃ sites and transported by hopping via Ir(ppy)₃ sites. Although the energy difference between the HOMO of TCTA and TAZ is as large as 0.7 eV, the holes can also be directly injected into the HOMO of Ir(ppy)₃ sites in the TAZ layer and perform hopping steps between the Ir(ppy)₃ sites. Then, the formed Ir(ppy)₃ cation can capture an electron from TCTA or TAZ to form an exciton, leading to efficient Ir(ppy)₃ emission. This process can even take place if the Ir(ppy)₃ LUMO is higher than the TCTA or TAZ LUMO, because the LUMO of Ir(ppy)₃ is shifted downward by reduced electron–electron repulsion when the molecule is positively charged.¹⁰ Both processes can spread the emission zone from PHT-EML to both layers although we are unable to determine which process is dominant. Thus, the recombination zone is not limited to the thin slab in the PHT part of the emission layer, but expanded to the Ir(ppy)₃-doped PET part of the emission layer. The reduced quantum efficiency roll off at large current density with D-EML structures shown in Fig. 3 is ascribed to a reduction of both triplet–triplet annihilation and triplet–hole quenching.

An important feature of the D-EML structure is its self-balancing character not being based on abrupt barriers, but rather on smooth transitions between regions with different mobility for the charge carriers: Electrons enter the EML system via an electron transporting host, are slowed down by an ambipolar host with lower electron mobility, and are likely to recombine before reaching the high barrier to Spiro-TAD. As to holes, we have already pointed out that hopping between dopant sites may be involved in both host materials. However, the effective hole mobility for this process may still be markedly different for the two matrices because the height of the tunneling barrier between two dopant sites depends on the HOMO level of the matrix. Therefore, also the holes are gradually slowed down and are likely to recombine before reaching the high barrier to the BPhen blocker.

The structures discussed above contain a number of materials with a low sublimation temperature or glass transition temperature, namely F₄-TCNQ, MeOTPD, TAZ, and undoped Bphen. To obtain robust devices, we replaced these materials with thermally more stable compounds with similar electrical properties and energy levels. The resulting green-emitting *p-i-n*-type phosphorescent D-EML devices have an even slightly better performance (Fig. 4): A power efficiency of 82 lm/W is obtained at 10 cd/m², falling to 77 lm/W at 100 cd/m², and 64 lm/W at 1000 cd/m². The improved power efficiency is partly due to an even lower operating voltage, 2.65 V for 100 cd/m², probably due to the use of a matrix material for the PET-EML with a higher electron mobility than TAZ.

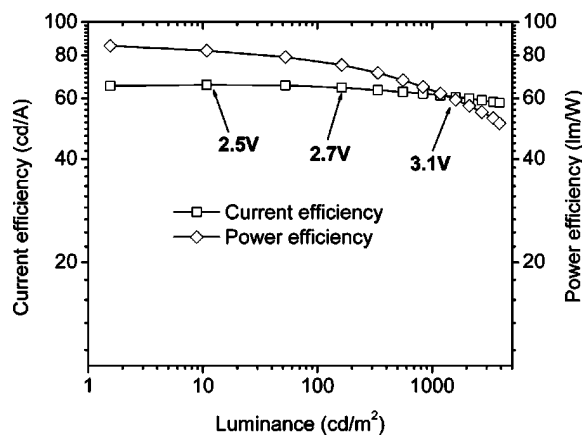


FIG. 4. The current efficiencies (square) and power efficiencies (diamond) of an optimized D-EML OLED.

As we will discuss in more detail in a subsequent paper, the improvement of device stability is another advantage of applying D-EML structure OLEDs: The interface between the EML and the HBL is typically a critical issue for long-term stability in S-EML OLEDs.¹⁹ This supports the interpretation that the improved stability for the D-EML avoids accumulation of charges at interfaces by its self-balancing character.

The authors thank the German Secretary for Education and Research (01BD151) and the Deutsche Forschungsgemeinschaft (Leibniz prize).

- ¹M. A. Baldo, D. F. O'Brien, Y. You, A. Shoustikov, S. Sibley, M. E. Thompson, and S. R. Forrest, *Nature (London)* **395**, 151 (1998).
- ²M. A. Baldo, S. Lamansky, P. E. Burrows, M. E. Thompson, and S. R. Forrest, *Appl. Phys. Lett.* **75**, 4 (1999).
- ³M. E. Thompson, P. E. Burrows, and S. R. Forrest, *Curr. Opin. Solid State Mater. Sci.* **4**, 369 (1999).
- ⁴C. Adachi, M. A. Baldo, S. R. Forrest, S. Lamansky, M. E. Thompson, and R. C. Kwong, *Appl. Phys. Lett.* **78**, 1622 (2001).
- ⁵C. Adachi, M. A. Baldo, M. E. Thompson, and S. R. Forrest, *J. Appl. Phys.* **90**, 5048 (2001).
- ⁶M. Ikai, S. Tokito, Y. Sakamoto, T. Suzuki, and Y. Taga, *Appl. Phys. Lett.* **79**, 156 (2001).
- ⁷C. Adachi, M. A. Baldo, S. R. Forrest, and M. E. Thompson, *Appl. Phys. Lett.* **77**, 904 (2000).
- ⁸J. Huang, M. Pfeiffer, A. Werner, J. Blochwitz, S. Liu, and K. Leo, *Appl. Phys. Lett.* **80**, 139 (2002).
- ⁹M. Pfeiffer, S. R. Forrest, K. Leo, and M. E. Thompson, *Adv. Mater. (Weinheim, Ger.)* **14**, 1633 (2002).
- ¹⁰G. F. He, O. Schneider, D. S. Qin, X. Zhou, M. Pfeiffer, and K. Leo, *J. Appl. Phys.* **95**, 5773 (2004).
- ¹¹B. Yamamori, C. Adachi, T. Koyama, and Y. Taniguchi, *Appl. Phys. Lett.* **72**, 2147 (1998).
- ¹²J. Blochwitz, M. Pfeiffer, T. Fritz, and K. Leo, *Appl. Phys. Lett.* **73**, 729 (1998).
- ¹³X. Zhou, M. Pfeiffer, J. Blochwitz, A. Werner, A. Nollau, T. Fritz, and K. Leo, *Appl. Phys. Lett.* **78**, 410 (2001).
- ¹⁴X. Zhou, D. S. Qin, M. Pfeiffer, J. Blochwitz-Nimoth, A. Werner, J. Drechsel, B. Maennig, K. Leo, M. Bold, P. Erk, and H. Hartmann, *Appl. Phys. Lett.* **81**, 4070 (2002).
- ¹⁵J. Blochwitz, T. Fritz, M. Pfeiffer, K. Leo, D. M. Alloway, P. A. Lee, and N. R. Armstrong, *Org. Electron.* **2**, 97 (2001).
- ¹⁶T. Watanabe, K. Nakamura, S. Kawami, Y. Fukuda, T. Tsuji, T. Wakimoto, S. Miyaguchi, M. Yahiro, M.-J. Yang, and T. Tsutsui, *Synth. Met.* **122**, 203 (2001).
- ¹⁷C. C. Wu, Y. T. Lin, K. T. Wong, R. T. Chen, and Y. Y. Chien, *Adv. Mater. (Weinheim, Ger.)* **16**, 61 (2004).
- ¹⁸M. A. Baldo and S. R. Forrest, *Phys. Rev. B* **62**, 10967 (2000).
- ¹⁹R. C. Kwong, M. R. Nugent, L. Michalski, T. Ngo, K. Rajan, Y.-J. Tung, M. S. Weaver, T. X. Zhou, M. Hack, M. E. Thompson, S. R. Forrest, and J. J. Brown, *Appl. Phys. Lett.* **81**, 162 (2002).