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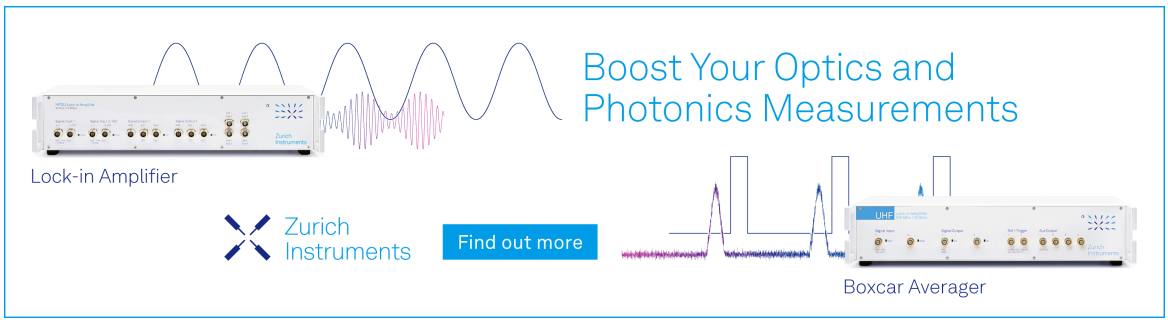

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Very high-efficiency and low voltage phosphorescent organic light-emitting diodes based on a *p-i-n* junction

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Green phosphorescent organic light-emitting devices (OLEDs) employing tris(2-phenylpyridine) iridium doped into a wide energy gap hole transport host have been studied. N,N,N′,N′-tetrakis(4-methoxyphenyl)-benzidine doped with 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane is used as a hole injection and transport layer, 4,7-diphenyl-1,10-phenanthroline and cesium are coevaporated as a *n*-doped electron transport layer, and an intrinsic emission layer is sandwiched between these two doped layer. Such a *p-i-n* device features efficient carrier injection from both contacts into the doped transport layers and low ohmic losses in these highly conductive layers. Thus, low operating voltages are obtained compared to conventional undoped OLEDs. By modifying the device structure, we optimized the carrier balance in the emission layer and at its interfaces. For the optimized device, the maximum power efficiency is 53 lm/W, and a luminance of 1000 cd/m^2 is reached at 3.1 V with a power efficiency of 45 lm/W. © *2004 American Institute of Physics.* [DOI: 10.1063/1.1702143]

I. INTRODUCTION

Since Tang's report[1] on the efficient organic light-emitting device (OLED), OLEDs based on either polymers or small molecules have attracted intensive research interest due to their promising applications in full-color flat panel displays. In conventional fluorescent OLEDs, only the generated singlet excitons contribute to the light emission under electrical excitation. However, the branching ratio for singlet-to-triplet generation of excitons is predicted to be 1:3 by spin statistics, a rule which is also confirmed by experiments for small molecules based OLEDs.[2] Accordingly, the maximum internal quantum efficiency is limited to 25%. Phosphorescence is a way to overcome this limit as phosphorescent materials can harvest both singlet and triplet excitons.[3–6] The recent demonstration of high efficiency electrophosphorescent OLEDs has shown the prospect of achieving 100% internal quantum efficiency.[7–9]

To obtain good charge balance and thus high efficiency, multilayer devices comprising electron/hole injection and transport layers are usually fabricated. The voltage drop across these layers requires more power to drive the devices, leading to lower power efficiency. Recently, however, a few reports[10–13] have shown that increasing the conductivity of organic semiconducting layers by doping with either electron donors (for electron transport materials) or electron acceptors (for hole transport materials) can significantly reduce the voltage drop across these films. By introducing this approach to OLEDs, we have successfully demonstrated a fluorescent *p-i-n* type OLED[13] with an operating voltage of 2.55 V for 100 cd/m^2. Pfeiffer *et al.*[14] extended this approach to small molecule electrophosphorescent OLEDs. By doping a green-emitting phosphorescent dye, tris(phenylpyridine)iridium [Ir(ppy)$_3$], into a thin N,N′-dicarbazolbiphenyl (CBP) host layer, they achieved 100 cd/m^2 at 2.65 V with a luminous power efficiency around 28 lm/W (8% external quantum efficiency). Since the theoretical limit for the internal quantum efficiency of phosphorescent OLEDs is 100%[3,5,7] and around 20% of the generated photons are actually coupled out of the device,[7] there is still some room to improve the efficiency of such *p-i-n* structures. In this work, we test a predominantly hole-transporting host material for Ir(ppy)$_3$ with different thicknesses of the emission layer to reach a much higher quantum efficiency with still low operating voltage.

II. EXPERIMENT

The OLEDs are prepared by thermal evaporation of different organic layers onto precleaned indium tin oxide (ITO) coated glass substrates in an ultrahigh vacuum system at a base pressure of 10^{-8} Torr without breaking the vacuum. First, a 100-nm-thick layer of N,N,N′,N′-tetrakis(4-methoxyphenyl)-benzidine (MeO–TPD) doped with 2 mol % 2,3,5,6-tetrafluoro-7,7,8,8-tetracyanoquinodimethane (F_4–TCNQ) is deposited as hole injection and transport layer (HTL). This *p*-doped layer has a conductivity of approximately 10^{-5} S/cm and forms a quasi-ohmic contact with ITO.[13–16] To prevent excitons generated in the emission layer from diffusing into the heavily doped and highly conductive HTL where nonradiative quenching might occur, an electron blocking layer of 10 nm 2,2′,7,7′-tetrakis-(N,N-diphenylamino)-9,9′-spirobifluoren (Spiro-TAD) is deposited, followed by an emission layer of 4,4′,4″-tris(N-carbazolyl)-triphenylamine (TCTA) doped with 8 wt. % of Ir(ppy)$_3$. Then, a hole and exciton blocking buffer layer of 10 nm 4,7-diphenyl-1,10-phenanthroline (Bphen) is deposited, which has a very high electron mobility.[17] After that, a 50-nm-thick *n*-doped electron transport layer (ETL) is obtained by coevaporation of Bphen with pure Cs from a

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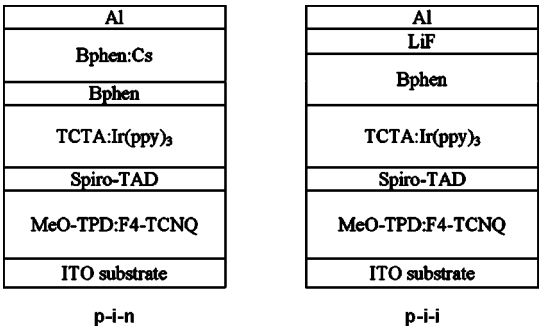

FIG. 1. Device structure of *p-i-n* and *p-i-i* OLEDs.

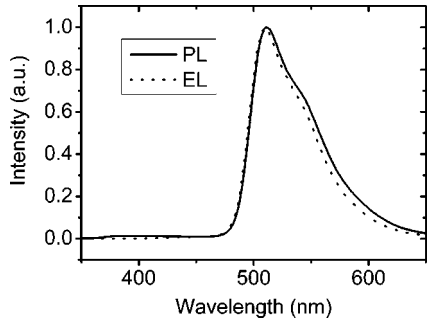

FIG. 2. PL of $Ir(ppy)_3$ (8% wt. %) doped TCTA excited at 330 nm (solid line) and EL of the *p-i-n* OLEDs (dotted line).

dispenser source. As the evaporation rate of Cs cannot be measured with a quartz thickness monitor, we prepare a series of doped Bphen layers with different heating power for the Cs dispenser and measure the conductivity in coplanar contact geometry. For the OLEDs, we use a source power where a conductivity of 10^{-5} S/cm is achieved. For comparison, devices without Cs doping are fabricated, which have an ETL of 50 nm undoped Bphen and then a 1-nm-thick layer of LiF to improve electron injection. Finally, a 100-nm-thick layer of aluminum is deposited as cathode for both kinds of devices (Fig. 1). Except of the acceptor dopant F_4–TCNQ, all organic materials have been purified twice by vacuum gradient sublimation. To avoid cross contamination, *p*-doped, *n*-doped, and undoped layers have been prepared in separate evaporation chambers of a cluster tool.

The current density–voltage ($J-V$) and luminance–voltage ($L-V$) characteristics of the OLEDs are simultaneously measured under vacuum conditions with a Keithley SMU236 and a calibrated silicon photodiode. The electroluminescence (EL) intensity was measured by mounting the calibrated silicon photodiode above the OLEDs to detect the light emitted in forward direction through the transparent ITO substrate. The quantum efficiency is calculated under the assumptions that the emission pattern is Lambertian and EL spectra are angle independent.

III. RESULTS AND DISCUSSION

A possible mechanism for electrophosphorescence is via energy transfer from host to guest. Here, a hole transport material, TCTA, is chosen as a host material for the phosphorescent dopant because of the good overlap between the photoluminescence (PL) spectrum of TCTA and the metal-to-ligand charge transfer absorption of $Ir(ppy)_3$.[8] This indicates the possibility of efficient singlet transfer from TCTA to $Ir(ppy)_3$. It is confirmed by the photoluminescence results. Figure 2 shows the photoluminescence of $Ir(ppy)_3$ (8 wt. %) doped TCTA film excited at 330 nm, which is around the maximum absorbance of TCTA while the absorption of $Ir(ppy)_3$ around 330 nm is low and features a low quantum yield of photoluminescence.[18] However, only $Ir(ppy)_3$ emission is observed during the excitation. The same is true for the electroluminance spectrum even driven at 40 mA/cm^2. No host emission indicates that efficient energy transfer occurs between the host and dopant.[4] As to triplet energy transfer, there is no direct indication from photoluminescence. However, the occurrence of efficient guest phosphorescence proofs that the host triplet level is above the respective guest level. An alternative mechanism for guest emission under electrical excitation is hole trapping on $Ir(ppy)_3$ sites and subsequent electron capturing. As the highest occupied molecular orbital (HOMO) level of TCTA (5.9 eV) is much lower than that of $Ir(ppy)_3$ (5.2–5.6 eV),[8,19] 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. Then, the formed $Ir(ppy)_3$ cation can capture an electron from TCTA to form an exciton. Note that this process can even take place if the lowest unoccupied molecular orbital (LUMO) of $Ir(ppy)_3$ is higher than the LUMO of TCTA because the LUMO of $Ir(ppy)_3$ is shifted downwards by reduced electron–electron repulsion when the molecule is positively charged.

The $L-V$ characteristics of the OLEDs are shown in Fig. 3. Here, the $L-V$ characteristics of a *p-i-n* OLED with Cs doped Bphen are compared with a *p-i-i* type OLED where, instead of the doped Bphen layer, undoped Bphen is used as an ETL and an interlayer of LiF is added below the Al contact. Although the evaporation of Al onto LiF liberates Li which moves into the Bphen thereby acting as dopant for the underlying organic layer to improve electron injection,[20] the

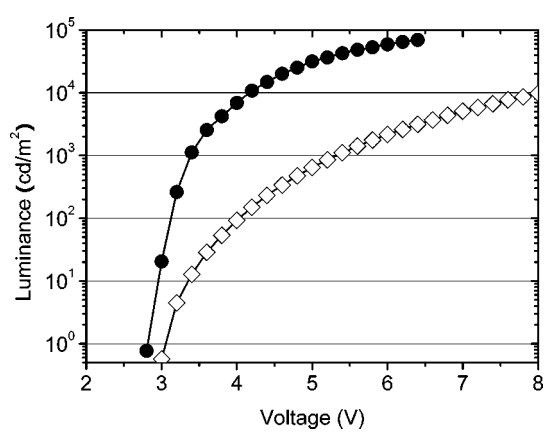

FIG. 3. EL intensity vs applied voltage for TCTA:$Ir(ppy)_3$ based phosphorescent OLEDs. Shown are data for a *p-i-n* sample (circle), compared with a *p-i-i* sample (diamond) with the layer sequence ITO/MeO–TPD:F_4–TCNQ (100 nm)/Spiro-TAD (10 nm)/TCTA:$Ir(ppy)_3$ (5 nm)/ETL-system/Al, where the ETL-system is Bphen (10 nm)/Cs-doped Bphen (50 nm) for the *p-i-n* sample and Bphen (50 nm)/LiF (1 nm) for the *p-i-i* sample.

bulk doping effect can be neglected with respect to the thick Bphen layer. To make it more comparable, we choose two devices with the same emission layer thickness of 10 nm. Each device has the maximum external quantum efficiency of around 13.5%. However, the *p-i-n* sample reaches 100 cd/m^2 at 3.1 V, with the luminance increasing dramatically at higher voltage and a luminance of 10 000 cd/m^2 is achieved at only 4.2 V. In comparison, the *p-i-i* OLED operates at much higher voltage with a flattening $L-V$ curve. It requires 4 V for 100 cd/m^2, and more than 8 V for 10 000 cd/m^2. If we reduce the thickness of the emission layer to 5 nm, the operating voltage can be even lower without efficiency loss as discussed later.

There are two possible reasons that could explain the low operating voltage in the *p-i-n* OLED. First, the *p-i-n* device can get easy carrier injection from both anode and cathode, while in the *p-i-i* device, there might still be an injection barrier for electrons at the Al/LiF cathode. Second, low ohmic losses occur in the doped Bphen layer with high conductivity compared to the undoped Bphen layer in the *p-i-i* device, thus most of the electric field is dropped over the intrinsic emission layer (EML), which enhances carrier injection and transport in the EML.

Besides operating voltage, another important parameter to characterize device performance is quantum efficiency. Although very high efficiency phosphorescent OLEDs based on green phosphor, $Ir(ppy)_3$ and $Ir(ppy)_2acac$, have been report previously, the high efficiency is mostly obtained at very low current density and brightness, and decreases rapidly with the increase of current.[4,7] For example, Adachi reported one of the best green phosphorescent OLEDs with undoped transport layers. It reaches almost 100% internal quantum efficiency, and the power efficiency at 100 cd/m^2 is 29 lm/W, dropping to 20 lm/W at 1000 cd/m^2 and 13 lm/W at 10 000 cd/m^2. For comparison, the performance of our *p-i-n* devices with 5 and 20 nm emission layer is shown in Fig. 4. The device with 5 nm emission layer reaches a power efficiency of 52 lm/W at 100 cd/m^2, falling to 45 lm/W at 1000 cd/m^2, and 24 lm/W at 10 000 cd/m^2.

Even as compared to Pfeiffer's previous study on phosphorescent *p-i-n* OLEDs, our latest results show further significant improvement in device performance. Apart from optimized preparation conditions and high material purity, another advantage of our *p-i-n* structure is that we use Cs instead of Li as the dopant for *n* doping. Compared to Li atoms, Cs atoms have larger size, which reduces the probability of Cs diffusing into the emission layer to quench the excitons. Using Li, undoped buffer layers have to be at least 25 nm thick to obtain the full efficiency. Using Cs, however, 10 nm of undoped Bphen between the emission layer and the doped transport layer are enough to avoid any quenching. On the other hand, we find that, if Cs is used, the driving voltage of the OLEDs rapidly increases with the thickness of the undoped buffer layer which is another hint that Cs hardly penetrates into the nominally undoped region.

As compared to Pfeiffer's previously reported device, the actual combination of materials used for the emission layer and the two adjacent undoped buffer layers is somewhat different even though the energetic arrangement and the basic function of the layers is very similar. If we compare the host material CBP used by Pfeiffer *et al.* and the TCTA used here to the analogous noncarbazole compounds N,N′-bis(3-methylphenyl)-N,N′-diphenylbenzidine (TPD) and 4,4′,4″-tris(N,N-diphenylamino)-triphenylamine (TDATA),[21] we conclude that TCTA should have a lower ionization energy than CBP just as TDATA has a lower ionization energy than TPD. The same is probably true for the electron affinities. Moreover, we find that mixed layers of TCTA and Bphen show a redshifted photoluminescence spectrum as compared to the individual components. This

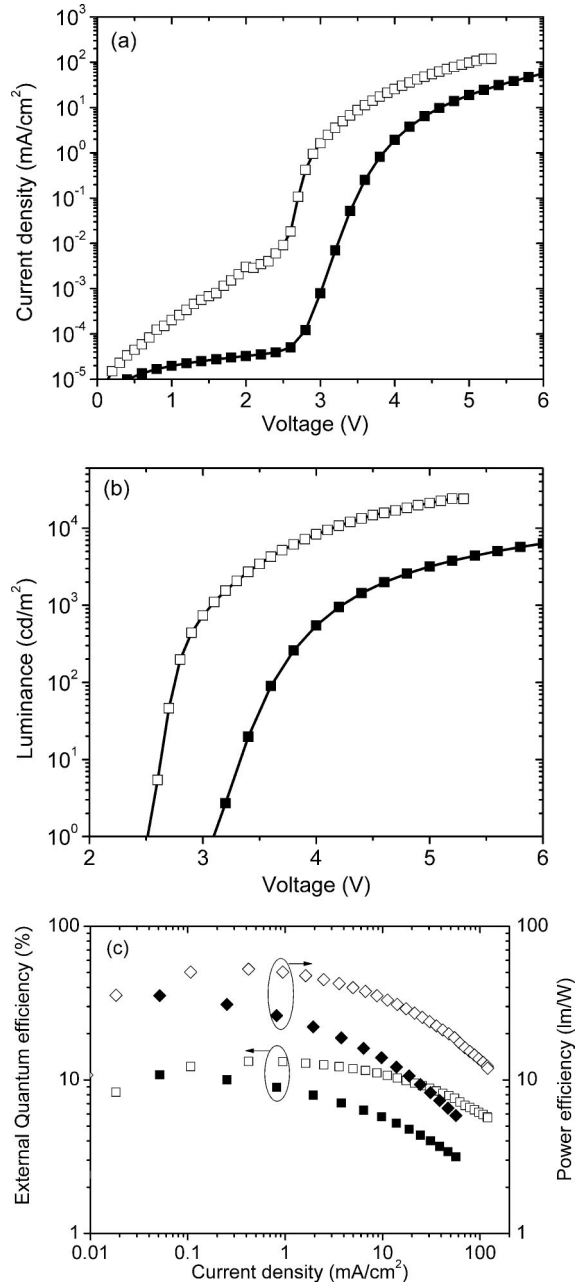

FIG. 4. (a) $J-V$ characteristics, (b) $L-V$ characteristics, (c) the external quantum (square) and power efficiencies (diamond) of the OLEDs with 5 nm (open) and 20 nm (closed) thickness of emission layer. The layer sequence of the devices is ITO/MeO–TPD:F_4-TCNQ (100 nm)/Spiro-TAD (10 nm)/TCTA:$Ir(ppy)_3$ (5 or 20 nm, respectively)/Bphen (10 nm)/Bphen:Cs (50 nm)/Al.

TABLE I. External quantum efficiency, power efficiency, and operating voltage of *p-i-n* OLEDs with 20, 10, and 5 nm thick of emission layer. Some efficiency values from literatures are listed as well.

		100 cd/m^2			1000 cd/m^2			10 000 cd/m^2		
	η_{ext} (%)	V (V)	η_p (lm/W)	η_{ext} (%)	V (V)	η_p (lm/W)	η_{ext} (%)	V (V)	η_p (lm/W)	η_{ext} (%)
Adachi	~20		29			20			13	
Pfeiffer	~10		28			27			16.5	
EML20 nm	11.3	3.5	32	10.5	4.2	19	7.2			
EML10 nm	13.2	3.1	44	12	3.4	33	10	4.2	19	7.1
EML 5 nm	13.7	2.75	52	13	3.1	45	12.6	4.1	24	8.8

exciplex-type emission is a hint that there is not only a large offset in the HOMO levels, but also a significant LUMO offset between the two materials so that an exciplex formed by a hole on TCTA and an electron on Bphen is the lowest excited state (more details about these spectroscopic studies will be presented elsewhere). Therefore, we believe that hole injection from Spiro-TAD into TCTA is easier than electron injection from Bphen into TCTA. Thus, holes are likely to accumulate at the interface of TCTA and Bphen after injection due to the large barrier between them. Referring to Ikai's paper,[8] the HOMO level of TCTA is 5.9 eV, while the HOMO level of Bphen is much lower, around 6.7 eV.[4] Such a big difference (0.8 eV) prevents holes from being injected into the Bphen layer. Furthermore, the accumulation of holes at the interface changes the internal electric field distribution, and facilitates electron injection and transport. When the electrons arrive at the interface, they will be injected into the emission layer and recombine with the holes gathered at the interface very fastly and efficiently, and form excited states (excitons). However, even if the excitons are generated efficiently, efficient light emission can only be obtained when the excitons are confined in the emission layer.[8,14,22] Hence, the buffer layers between emission layer and *p*-doped hole-transport layer or *n*-doped electron-transport layer are very important. Otherwise, the excitons will be easily quenched by F_4-TCNQ or Cs in the doped layers. Here, we successfully confine the excitons in the emission layer using Spiro-TAD and Bphen as buffer layers. No efficiency loss is observed even when the thickness of emission layer is as low as 5 nm. Both Spiro-TAD and Bphen provide nearly complete isolation of the emission layer from the conductive dopants, as well as good confinement of both carriers and excitons in this region.

From the earlier considerations, one should expect that, for an ideal choice of buffer layers, the quantum efficiency should be independent of the thickness of the emission layer as neither charge carriers nor excitons should be lost at one of the interfaces. However, the data summarized in Table I for a series of the *p-i-n* OLEDs with 20, 10, and 5 nm thickness of emission layer show that reducing the thickness of the emission layer not only lowers the operating voltage, but even increases the quantum efficiency. The reason for this surprising phenomenon is not finally understood, but a possible explanation is a follows: As mentioned earlier, an exciplex can be formed when a hole on TCTA meets an electron on Bphen at the interface, which should be avoided. In this respect, the close vicinity of the hole injecting layer in OLEDs with a very thin emission layer may be an advantage as it facilitates a process that does not involve holes on TCTA: Holes are injected from Spiro-TAD directly into $Ir(ppy)_3$ sites in the doped TCTA, perform a few hopping steps between the $Ir(ppy)_3$ sites, and subsequently capture an electron as described earlier. As the recombination zone is close to the interface of TCTA and Bphen for all emission layer thicknesses,[19] it is easier for holes to reach the recombination zone by hopping on $Ir(ppy)_3$ molecules for thinner emission layers. We speculate that this generation process, which does not involve excitons on the matrix as an intermediate step, is responsible for the remarkably high quantum yields observed here.

IV. CONCLUSIONS

In conclusion, we have demonstrated highly efficient green-emitting phosphorescent OLEDs using a hole-transport material TCTA as host with a *p-i-n* structure. The power efficiency using a 5-nm-thick emission layer is 52 lm/W with 100 cd/m^2 at 2.75 V and 45 lm/W with 1000 cd/m^2 at 3.1 V, which is much higher than the OLEDs reported to date at the same brightness. This is a promising approach for low-power display devices.

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