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Improved electrophosphorescence efficiency for organic light-emitting diodes using the cohost with stepwise blending profile

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ABSTRACT

A tris(2-phenylpyridine) iridium doped phosphorescent organic light-emitting diode using a mixed host with stepwise blending profile was demonstrated. We adopted the mixture of 4,4′,4″-tris(N-carbazolyl) triphenylamine and 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene as the host in the emitting layer. By using a stepwise blending ratio profile of the two host materials, a peak external quantum efficiency of 17.7% and a peak power efficiency of 45.7 lm/W were attained, which increased by 59.5% and 60.9% relative to the optimal uniform blending ratio profile based device, respectively. The efficiency improvement was attributed to the multiple exciton formation interfaces, which could expand the recombination regions.

1. Introduction

Phosphorescent organic light-emitting diodes (PhOLEDs) have attracted much attention in recent years because they can achieve a maximum internal efficiency of 100% in principle due to the use of both the singlet and triplet excitons by mixing between the singlet and triplet resulted from the heavy metal effect [1,3–7]. The enhancement of the electroluminescent (EL) efficiency of PhOLEDs, however, presents two obstacles, one of which occurs during the exciton formation process. There is hardly a host material which has a very good bipolar transporting character, since the bandgap of the phosphorescent hosts must be large enough for achieving efficient emission of dopants, so the exciton formation would be rather difficult and the efficiency would be low. The other obstacle occurs during the exciton diffusion process. Due to the long lifetime of the triplet excitons, triplet–triplet annihilation [2] and polaron–triplet annihilation [2,3] would largely depress the EL efficiency of the PhOLEDs. To conquer the first obstacle, mixed host, i.e., cohost structure has been adopted [4], as a result the performances of the PhOLEDs were improved by using the blend of two host materials which respectively has electron- and hole-transporting property. But facilitating the carriers transporting also leads to the accumulation of large numbers of excitons at HTL/EML and EML/ETL interfaces, here HTL, ETL and EML denote hole transporting layer, electron transporting layer and emitting layer, respectively. This would result in the triplet–triplet annihilation or polaron–triplet annihilation. To overcome the second obstacle, researchers managed to expand the recombination region or promote the exciton diffusion. Such as, Yang et al. enhanced the current efficiency by inserting a layer of 4,7-dipheny-1,10-phenanthroline (Bphen) into the EML [5]. However, due to the hole blocking character of Bphen, the bias voltage of the device must be increased, resulting in a low power efficiency which acts as a very important factor for actual applications. Quantum well structure was also used to extend the recombination region [6], but the bias voltage was largely enhanced too. Therefore, if we could expand the recombination region without enhancing the bias voltage, that is conquer the two obstacles synchronously, the efficiency of the PhOLEDs would be largely increased.

In this paper, we demonstrate a structure of PhOLEDs, which can not only facilitate the exciton formation but also broaden the exciton formation region. A stepwise blending of TCTA/TPBi was used as the cohost, and $Ir(ppy)_3$ was the dopant, here TCTA, TPBi, and $Ir(ppy)_3$ denote 4,4′,4″-tris(N-carbazolyl) triphenylamine, 1,3,5-tris(N-phenylbenzimidazole-2-yl)benzene, and tris(2-phenylpyridine) iridium, respectively. Since the TCTA is a hole transporting material and TPBi is an electron transporting material [4,7,8], the TCTA/TPBi stepwise blending cohost can facilitate the carrier injection and transporting in the EML. On the other hand,

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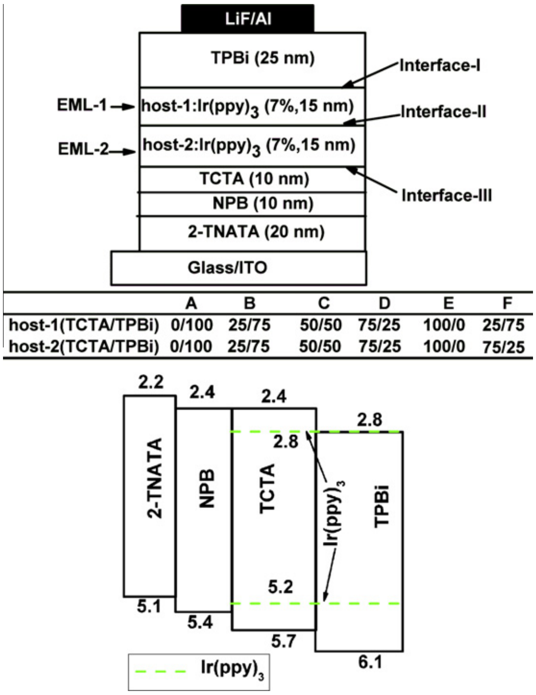
the stepwise blending of TCTA and TPBi means that the electron and hole mobility would be different at different position of the EML, so the carriers would pile up at these interfaces between the positions with different carrier mobility, i.e., the recombination region would be expanded because of the TCTA/TPBi stepwise blending cohost. Because of the two advantages, the efficiency of the PhOLED was largely enhanced.

2. Experimental

The PhOLEDs were prepared by thermal evaporation of organic layers onto precleaned indium tin oxide (ITO) coated glass substrates in a vacuum system at a base pressure of 3×10^{-4} Pa without breaking vacuum. Thermal deposition rates for organic materials, LiF, and Al were about 1, 1, and 10 Å/s, respectively. EL spectra were measured with an OPT-2000 spectrophotometer. The luminance–current–voltage characteristics were measured with a Keithley model 2400 power supply combined with a ST-900 M spot photometer and were recorded simultaneously with measurements. The OPT-2000 spectrophotometer and ST-900 M spot photometer are made by Beijing Normal University. Fig. 1 shows the architecture of the present PhOLEDs. Six PhOLEDs (devices A–F) with different EMLs were fabricated, ITO/2-TNATA (20 nm)/NPB (10 nm)/TCTA (10 nm)/EML-1 (15 nm)/EML-2 (15 nm)/TPBi (25 nm)/LiF (1 nm)/Al (200 nm), where 2-TNATA and NPB are 4,4′,4″- tris(2-naphthylphenylamino)triphenylamine and 4,4′-bis(N-phenyl-1-naphthylamino)biphenyl, respectively. In our PhOLEDs, 2-TNATA and NPB are used as hole injection layer and HTL; the 10-nm-thick TCTA acts as the electron blocking layer; the 25-nm-thick TPBi acts as the ETL and exciton blocking layer; LiF as an electron injecting layer, and Al as cathode electrode. The employed hosts for device A, B, C, D, E, and F are composed of the blends of TCTA and TPBi with different ratios, which are shown in Fig. 1. For device A, B, C, D and E, the TCTA contents in the EML are uniform, i.e., the EML-1 and EML-2 are the same in each PhOLED. While for device F the TCTA/TPBi is 25/75 in EML-1but in EML-2 the TCTA/TPBi is 75/25.



	A	B	C	D	E	F
host-1(TCTA/TPBi)	0/100	25/75	50/50	75/25	100/0	25/75
host-2(TCTA/TPBi)	0/100	25/75	50/50	75/25	100/0	75/25

Fig. 1. Schematic structure, the contents of the EMLs and the energy band diagram of the PhOLEDs.

3. Results and discussion

The forward current density–voltage (*J*–*V*) and external quantum efficiency (EQE)-J of the PhOLEDs are shown in Fig. 2a and Fig. 2b, respectively. The inset of Fig. 2a shows that all PhOLEDs emitted bright green light with a peak wavelength at around 510 nm originating from the Ir(ppy)$_3$ triplets. For devices A–E, with the uniform TCTA/TPBi blending ratio profile in EML-1 and EML-2, the maximum EQE was 11.1% (device B). This indicates that the electrons and holes are more balanced in the EML of device B than other devices among the devices A–E. While for device F, with the stepwise TCTA/TPBi blending ratio profile, a peak EQE of 14.7% was obtained. The highest current density was obtained in device B indicates that TCTA/TPBi = 25/75 is the best ratio for carriers injection in EMLs. We also note that the current density of device F followed device B and was almost the same with that of device B at bias voltages of below 8 V. This suggests that the stepwise blending structure would not increase the driving voltage of PhOLEDs. Therefore, as shown in Fig. 2c, a high power efficiency of the device F is also harvested.

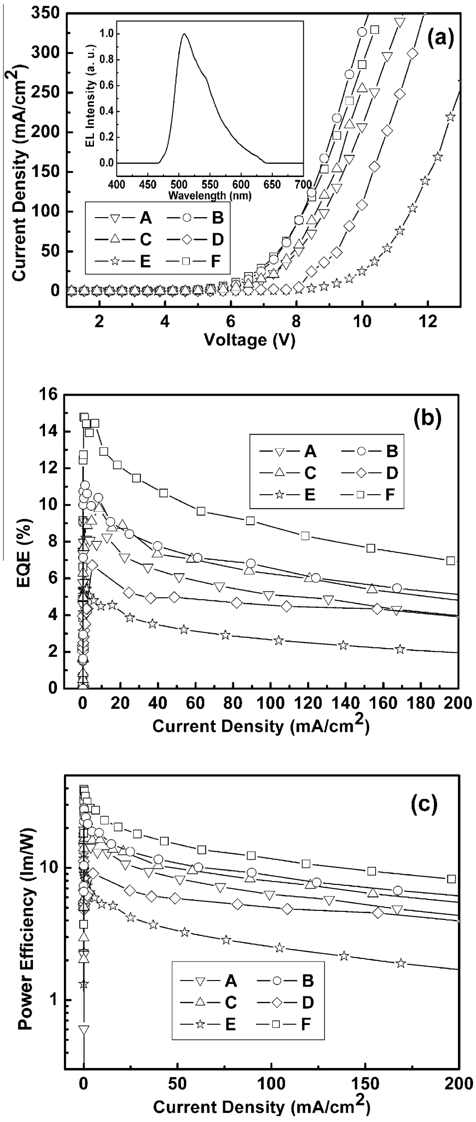


Fig. 2. (a) Current density–voltage characteristics for devices A–F. Inset: EL spectrum of PhOLEDs. (b) Current density dependencies of the external quantum efficiencies for devices A–F. (c) Current density dependencies of the power efficiencies for devices A–F.

The EL improvements of device F can be expressed as bellows. If the electrons (holes) flow from a layer with a high electron (hole) mobility, μ_n (μ_p), into a layer with a low electron (hole) mobility, the electrons (holes) would pile up at the interface between the two layers. The exciton formation probability, which is $\sim n \times p$, is thus significantly higher at the interface as compared with the EML bulk. In other words, excitons would mainly form at the interface where large densities of holes and electrons accumulate, with correspondingly low generation in the bulk of the EML [9]. It is well known that TCTA is a hole-transporting host and TPBi is an electron-transporting host. For devices A–E, the hosts in EML-1 and EML-2 are the same in each device. So $\mu_{n/p}$(EML-1) = $\mu_{n/p}$(EML-2), the carriers would only accumulate at interface-I and interface-III but not at interface-II. However, for device F, μ_n (EML-1) > μ_n(EML-2) and μ_p(EML-1) < μ_p(EML-2), so the electrons and holes would largely accumulate at interface-II. In other words, the recombination zone was expanded. As a result, the efficiency is observely increased. To find out whether the holes and electrons largely pile up at interface-II or not, we respectively fabricated the device G and device H:

Device G: ITO/2-TNATA (20 nm)/NPB (10 nm)/TCTA (10 nm)/DCJTB (0.1 nm)/TCTA:TPBi (50:50, 15 nm)/C-545T(0.1 nm)/TCTA:TPBi (50:50, 15 nm)/DCJTB (0.1 nm)/TPBi(25 nm)/LiF (1 nm)/Al (200 nm).

Device H: ITO/2-TNATA (20 nm)/NPB (10 nm)/TCTA(10 nm)/DCJTB (0.1 nm)/TCTA:TPBi (75:25, 15 nm)/ C-545T(0.1 nm)/TCTA:TPBi (25:75, 15 nm)/ DCJTB (0.1 nm)/TPBi(25 nm)/LiF (1 nm)/Al (200 nm).here DCJTB and C-545T denote 4-(dicyanomethylene)-2-(t-butyl)6-methyl-4Hpyran and 10-(2-benzothiazolyl)-1,1,7,7-tetranethyl-2,3,6,7-tetrahydro-1H,5H,11H[l]benzo-pyrano[6,7,8-ij]-qcinolizin-11-one, respectively. The spectra of the device G and device H at different current densities are shown in Fig. 3a and b, respectively. The red and green emission bands peaked at about 595 nm and 510 nm are originated from DCJTB and C-545T, respectively, as well the blue emission comes from NPB. Relative to the red emission intensity, the green emission intensity of device H is much higher than that of device G. Thereby, we can conclude that a large number of charge carriers pile up at interface-II in device F. Furthermore, the higher efficiency of device F should not be attributed to the change of emitting layer thickness relative to the devices A–E. When the PhOLEDs are working the excitons would form only on Ir(ppy)$_3$ molecules because the electron blocking characteristic of TCTA (the hole blocking characteristic of TPBi) prevent the electrons (holes) from transferring onto the TCTA (TPBi) molecules. As we known that the exciton formation zones are located within 5 nm of the EMLs adjacent to their boundaries [9,10] and the Ir(ppy)$_3$ excitons would not migrate out of these zones because the energy of the TCTA or TPBi triplet exciton is much higher than Ir(ppy)$_3$. In other words the excitons would be limited within their respective exciton formation zones. In an EML there at most are two exciton formation zones (10 nm altogether), the width of each EML in devices A–F (30 or 15 nm) are all larger than 10 nm. Therefore, the exciton formation zones in these PhOLEDs do not affect each other and the emitting layer thicknesses of these PhOLEDs do not affect the EL efficiency either.

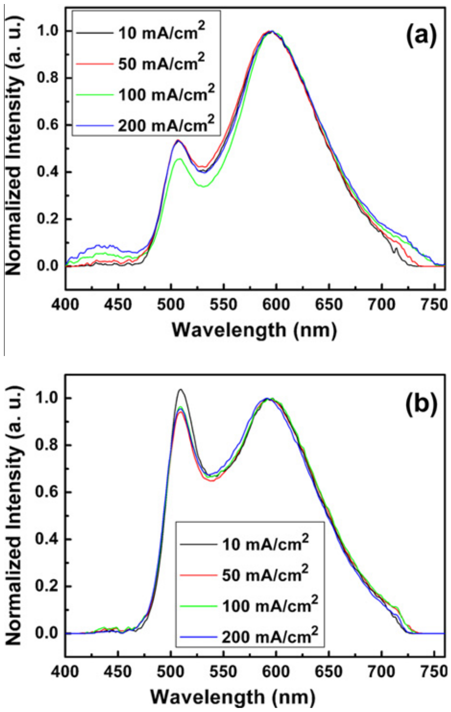


Fig. 3. The EL spectra of the device G and device H at different current densities.

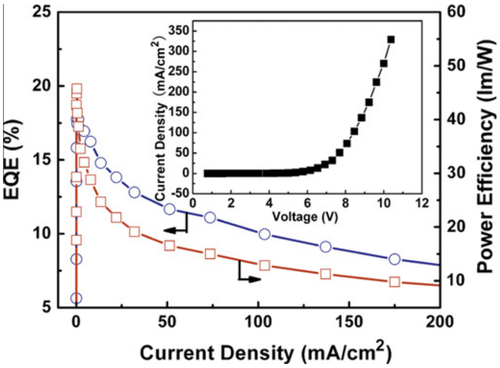


Fig. 4. Current density dependencies of the external quantum efficiencies and power efficiencies for the three EMLs based PhOLEDs. Inset: current density–voltage characteristics for the three EMLs based PhOLEDs.

To further improve the EL performances of the PhOLEDs, a three EMLs based device with the structure of ITO/2-TNATA (20 nm)/NPB (10 nm)/TCTA (10 nm)/TCTA:TPBi: 7 wt.%Ir(ppy)$_3$ (80:20, 10 nm)/TCTA:TPBi: 7 wt.%Ir(ppy)$_3$ (50:50, 10 nm)/TCTA:TPBi: 7 wt.%Ir(ppy)$_3$ (20:80, 10 nm)/TPBi (25 nm)/LiF (1 nm)/Al (200 nm) was fabricated. In the device, four carrier accumulation interfaces were formed. Fig. 4 shows the performances of the device. A peak EQE of 17.7% and a peak power efficiency of 45.7 lm/W were obtained.

4. Summary

In conclusion, we demonstrated high efficiency PhOLEDs by using stepwise blending ratio profile of TCTA/TPBi as the host. A peak EQE of 17.7% and a peak power efficiency of 45.7 lm/W were achieved, respectively. The stepwise blending profile can efficiently expand the recombination region and possibly minimizing the triplet–triplet exciton quenching, so that 59.5% increase in the external quantum efficiency and 60.9% increase in the power efficiency were obtained relative to the optimal uniform blending ratio profile based device, respectively. The concept of “stepwise blending” can be also extended to the “continuously graded” profile to further enhance the EL efficiency of the PhOLED devices.

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