Increased performance of an organic light-emitting diode by employing a zinc phthalocyanine based composite hole transport layer*

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We demonstrate that the electroluminescent performances of organic light-emitting diodes are significantly improved by employing a zinc phthalocyanine (ZnPc)-based composite hole transport layer (c-HTL). The optimum ris-(8-hydroxyquinoline)aluminum (Alq_3)-based organic light-emitting diode with a c-HTL exhibits a lower turn-on voltage of 2.8 V, a higher maximum current efficiency of 3.40 cd/A and a higher maximum power efficiency of 1.91 lm/W, which are superior to those of the conventional device (turn-on voltage of 3.8 V, maximum current efficiency of 2.60 cd/A, and maximum power efficiency of 1.21 lm/W). We systematically studied the effects of different kinds of N'-diphenyl-N,N'-bis(1-naphthyl)(1,1'-biphenyl)-4,4'diamine (NPB):ZnPc c-HTL. Meanwhile, we also investigate their mechanisms different from that in the case of using ZnPc as buffer layer. The specific analysis is based on the absorption spectra of the hole transporting material and current density–voltage characteristics of the corresponding hole-only devices.

Keywords: organic light emitting diodes, composite hole transport layer, zinc phthalocyanine

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1. Introduction

With potential application in the fields of flat-panel display and next generation solid-state lighting, organic light-emitting diodes (OLEDs) have attracted considerable attention.[1–4] It is extremely important to obtain low driving voltage and high efficiency for accomplishing the widespread applications of OLEDs.[5–8] The hole carriers are always the majority carriers which manage the turn-on voltage of the device as compared with the electron carrier in OLED.[9] But for the multi-layered device structure, the highest occupied molecular orbital (HOMO) of hole transport layer (HTL) is generally higher than the work function of indium tin oxide (ITO) anode, which results in the hole injection barrier that leads to the increasing of the turn-on voltage.[10] Many efforts have been to design the appropriate configuration for carrier injection and transportation. For example, inserting a buffer layer between ITO and hole transportation layer will reduce the energy barrier to enhance hole injection.[11,12] And chemical doping in organic semiconductors is another important technique to realize low driving voltage and high efficiency of OLEDs.[13–15]

Copper phthalocyanine (CuPc) is most commonly used as hole injection layer in OLED, and it is demonstrated that the utilization of CuPc can improve the device efficiency. However, the insertion of CuPc often leads to substantial increase in device turn-on voltage.[12] Recently, various metal oxides such as MoO_x,[13] WO_3,[14] and ReO_3[15] have been introduced as hole injection layer or dopant. Especially it has been reported that MoO_3 is used as an effective p-dopant in N'-diphenyl-N,N'-bis(1-naphthyl)(1,1'-biphenyl)-4,4'diamine (NPB) to improve the device efficiency and lower the turn-on voltage.[16] But MoO_3 is an inorganic substance which has relatively high growth temperature.[16] Zinc phthalocyanine (ZnPc) is a promising candidate for solar-cell applications because it is easily synthesized and non-toxic to the environment.[17–19] In this paper, we introduce ZnPc into Alq_3-based OLEDs, and we find that ZnPc-doped NPB used as c-HTL not only increases the current efficiency but also significantly reduces the operation voltage, so that the power efficiency increases automatically.

2. OLED with a ZnPc based c-HTL

2.1. Experiment

The patterned ITO-coated glass (with a sheet resistance of 20 Ω/square) substrates were scrubbed and sonicated consecutively with acetone, ethanol, and deionized water in sequence. All of the organic layers were thermally deposited in a vacuum at a rate of ∼ 0.1 nm/s monitored *in*

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situ with the quartz oscillator. The absorption spectra were measured by ultraviolet/visible spectrometer (UV2550, Shimadzu). The current–voltage–luminance characteristics were measured with a PR650 spectra-scan spectrometer and a Keithley 2400 programmable voltage–current source. All the samples were measured directly after fabrication without encapsulation in ambient atmosphere at room temperature.

2.2. Results and discussion

In this paper we investigate the EL performances of the devices with composite hole transport layers, and we choose NPB as hole transport material and ZnPc as dopant. Table 1 shows the lowest unoccupied molecular orbital (LUMO) and HOMO of three kinds of materials chosen in the experiment.

Table 1. The LUMO and HOMO of the materials.

	LUMO/eV	HOMO/eV
ZnPc	3.34	5.28
NPB	2.45	5.46
Alq_3	3.1	5.8

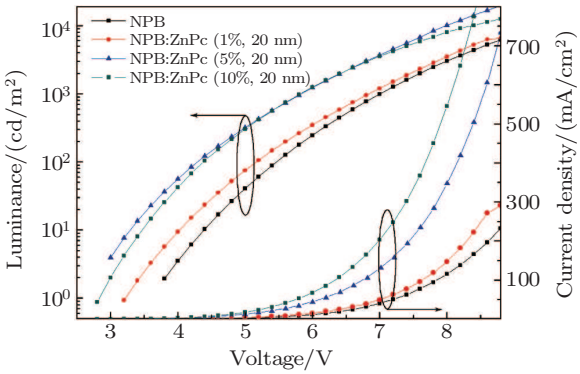


Fig. 1. (color online) Current density–voltage–luminance (J–V–L) characteristics.

For all the devices, 50-nm Alq_3 layer is used as the emitting layer and electron transport layer. The devices fabricated are as follows: ITO/NPB:ZnPc(0%, 1%, 5%, 10%; 20 nm)/NPB(30 nm)/Alq_3(50 nm)/LiF(1 nm)/Al(100 nm). Figure 1 shows the current density–voltage–luminance (J–V–L) characteristics. As can be seen in the figure, the device with 5% concentration exhibits better performance than the others, the turn-on voltage is lowered to 2.8 V compared with the value of 3.8 V of the device with neat NPB as hole transport layer. And the luminance at 3 V of the 5% doped device reaches 3.9 cd/m^2, at 9 V it reaches 19790 cd/m^2, which is much higher than those of conventional devices. Meanwhile the current efficiency and power efficiency both have some improvement shown in Figs. 2(a) and 2(b). These results indicate that the EL performances of OLEDs could be improved by introducing a composite hole transport layer (c-HTL) with NPB doped ZnPc.

In order to investigate the characteristics of the thickness dependence of the device and to further improve the EL performance of device, another series of OLEDs composed of ITO/NPB:ZnPc(5%, X = 10, 20, 30, 40 nm)/NPB(50-X nm)/Alq_3(50 nm)/LiF(1 nm)/Al(100 nm) structures are fabricated.

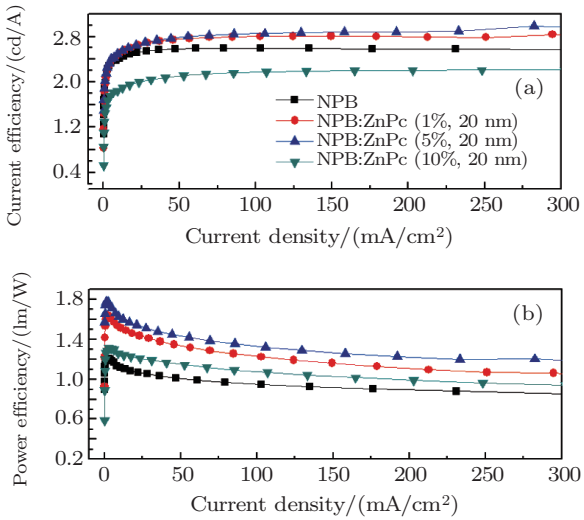


Fig. 2. (color online) (a) Characteristic curves of current efficiency versus current density and (b) power efficiency versus current density.

The J–V–L characteristics of these devices are shown in Fig. 3. And the device with 30-nm c-HTL exhibits the best efficiency in the devices with different thickness values of c-HTL shown in Figs. 4(a) and 4(b). The maximum current efficiency of 3.40 cd/A and power efficiency of 1.91 lm/W are obtained from the optimum device with 30-nm c-HTL, which are much higher than the values of 2.60 cd/A and 1.15 lm/W obtained from a conventional device. When the doped layer is over 30 nm in thickness, more excitons or electrons leak into the c-HTL, which may cause aggravated quenching so that the efficiency decreases obviously.

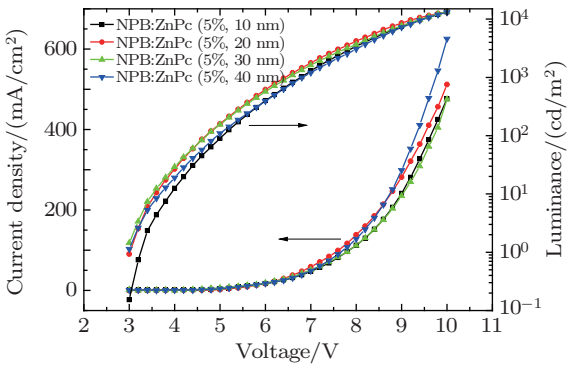


Fig. 3. (color online) Current density–voltage–luminance (J–V–L) characteristics.

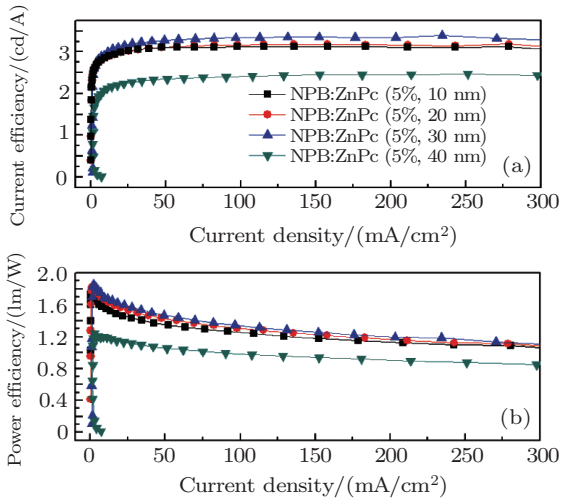


Fig. 4. (color online) (a) Characteristic curves of current efficiency versus current density and (b) power efficiency versus current density.

We also investigate the EL performances of the buffered devices with different thickness values of ZnPc as buffer layer evaporated on the ITO. The devices fabricated in this study are as follows: ITO/ZnPc(X nm, X = 2, 5, 10, 15)/NPB(50-X nm)/Alq3(50 nm)/LiF(1 nm)/Al(100 nm). Both the brightness and the current density are improved with the increase of thickness of ZnPc, and the optimum thickness of ZnPc is 10 nm. The buffer layer is useful for smoothening the surface of ITO and improving the injection of holes but its efficient is less than that in the case of the c-HTL, and the much thicker buffer layer leads to imbalance of carriers injected into emissive layers, which will reduce the efficiency. Table 2 gives the values of turn-on voltage, maximum current efficiency, and power efficiency of the above devices.

Table 2. Electroluminescent characteristics of the devices with different thickness values of the ZnPc buffer layer.

	Turn-on voltage/V	Max current efficiency/cd·A^{-1}	Max power efficiency/l mW^{-1}
ZnPc buffer layer 2 nm	3.8	2.63	1.15
ZnPc buffer layer 5 nm	3.6	2.64	1.21
ZnPc buffer layer 10 nm	3.5	2.73	1.35
ZnPc buffer layer 15 nm	3.5	2.15	1.13

Figure 5 shows the current density–voltage characteristics of nominal single-carrier devices and the fabricated configurations that are ITO/NPB(50 nm)/Al, ITO/ZnPc(50 nm)/Al, ITO/NPB:ZnPc(1%, 50 nm), ITO/NPB; ZnPc(5%, 50 nm)/Al. It reveals the abilities to inject and transport holes in both the single and composite HTL. It is shown that the hole-only device with ZnPc serving as c-HTL exhibits a higher current density than that with neat NPB serving as hole transport layer, which exhibits a similar trend of J–V characteristics for the corresponding complete devices because holes are the majority carriers in our fabricated devices. The energy of HOMO of the doped ZnPc is 5.0 eV,[20] which is smaller than that of NPB (5.5 eV). As the efficiency of the hole injection is controlled by the Schottky height at the anode/organic interface, the c-HTL leads to more efficient hole injection. In this case, the holes injected into the doped hole transport layer are first trapped by the ZnPc molecules and then transport along the ZnPc molecules by a hopping mode. From the experiment we can see that the 5% concentration is large enough to form carrier transport channel and the doped system could exhibit the better hole injection and transport capability, which results in a lower operation voltage. Because of a relatively similar hole mobility between ZnPc and NPB molecular,[18] the transport of holes in the c-HTL will not sharply aggravate the imbalance of the carriers injected into the Alq_3 emissive layer. And the increase of hole current is shown to enable the increase of electron current, thereby improving the hole–electron balance. We consider that the devices with better performance will be achieved by optimizing the doping concentration and the thickness of doped layer.

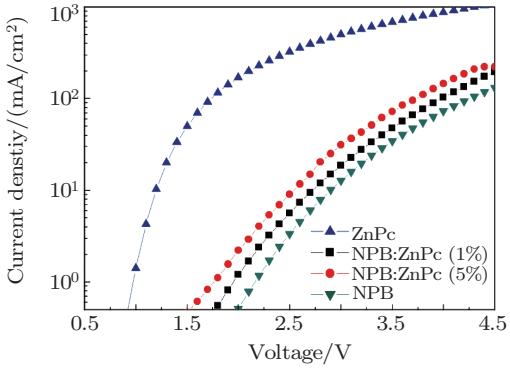


Fig. 5. (color online) Current density–voltage characteristics of nominal single-carrier devices.

The absorption spectra are measured by means of UV 2550 and Fig. 6 exhibits the absorption spectra of neat NPB (in the inset at the top right corner), and a series of ZnPc-doped NPB with different thickness values of the doped layers. The fabricated configurations have glass substrate/neat NPB or glass substrate/NPB:ZnPc(5%, X nm; X = 10, 20, 30, 40 nm)/NPB(50-X nm). We consider the absorption between 630 nm to 700 nm is intrinsic peaks of ZnPc.[20] With the increase of thickness of ZnPc, its intrinsic peaks grow and strengthen. The phenomenon is quite different from that in the case of MoO_3-doped NPB which has additional absorption peaks that come from charge transfer complex.[21] Since there appears no new substance, the mechanism of leading to the

lower turn-on voltage of the device with c-HTL should be further investigated. We speculate that this is due to the change in the HOMO level of the c-HTL which forms a gentle hole injecting channel.

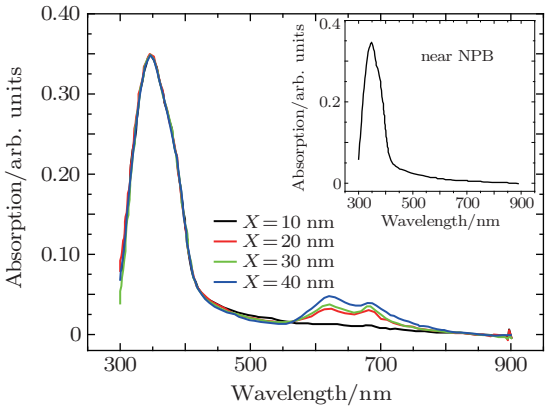


Fig. 6. (color online) Absorption spectra of neat NPB (in the inset at the top right corner) and a series of ZnPc-doped NPBs with different thickness values of the doped layers.

3. Conclusion

In this paper, we demonstrated that the EL performances of OLEDs could be improved by introducing the ZnPc-doped c-HTL. We also systematically investigated the role of doping ZnPc into NPB HTL. The results show that Alq_3-based OLEDs exhibit some better electroluminescent performances with lower turn-on voltage (2.8 V), higher current efficiency (3.40 cd/A), and power efficiency (1.91 lm/W) than conventional structures. The maximum current efficiency and luminous efficiency are enhanced by a factor of 1.3 and 1.6 respectively, and the turn-on voltage is reduced by 1.0 V. According to our assumption, the performance of the device can be further improved by introducing a more efficient electron transporting layer, balancing the charge injection, and optimizing the thickness of each layer.

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