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The performance enhancement in organic light-emitting diode using a semicrystalline composite for hole injection*

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A semicrystalline composite, 3, 4, 9, 10 perylenetetracarboxylic dianhydride (PTCDA) doped N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB), has been fabricated and characterized. An organic light-emitting diode using such a composite in hole injection exhibits the improved performance as compared with the reference device using neat NPB in hole injection. For example, at a luminance of 2000 cd/m^2, the former device gives a current efficiency of 2.0cd/A, higher than 1.6cd/A obtained from the latter device. Furthermore, the semicrystalline composite has been shown thermally to be more stable than the neat NPB thin film, which is useful for making organic light emitting diodes with a prolonged lifetime.

Keywords: semicrystalline composite, hole injection, organic light-emitting diode
PACC: 7860F, 7855K, 7380L

1. Introduction

Organic light-emitting diodes (OLEDs) are becoming more and more important for flat-panel displays and have tremendous potential applications in future lighting.[1,2] In OLEDs, the control of hole injection and transport is important for obtaining balanced electron and hole concentrations in the emission zone, thereby improving the device efficiency.[3−5] Moreover, the hole transport layer (HTL) tends to crystallize due to the Joule heating during device operation, which ultimately degrades the stability of the device. One of the most powerful solutions is to insert a hole injection layer (HIL) between indium-tin oxide (ITO) and the HTL.[6−8] Since copper phthalacyanine (CuPc) has merits, such as high thermal and chemical stabilities, the device stability can be significantly enhanced by inserting the CuPc between the ITO anode and the N,N'-di(1-naphthyl)-N,N'-diphenylbenzidine (NPB) layer.[9] However, CuPc is believed to decrease the hole injection into the HTL, thus leading to an undesirable increase in the device operating voltage.[10] Therefore, it is necessary to develop new HIL to enhance the hole injection and decrease the operating voltage. The organic semiconductor material 3, 4, 9, 10 perylenetetracarboxylic dianhydride (PTCDA) has unique characteristics of transporting holes in the direction perpendicular to the molecular plane, and it has been used as an HTL in OLEDs.[11,12] In this paper, we find that PTCDA-doped NPB as a hole injection layer not only reduces the operation voltage, but also enhances the device efficiency and the stability.

2. Experimental details

The OLED devices were fabricated in an organic molecular beam deposition system (OMBE) with a base pressure of about 2×10^{-5}Pa. The anode was of a commercial ITO-coated glass with a sheet resistance of 30Ω/□. The substrates were cleaned sequentially with de-ionized water, acetone, and ethanol, and finally treated in the UV-ozone for about 15min. The organic layers were deposited in sequence according to the device structures listed in Table 1 (see Section 3). NPB and Alq_3 were used as hole transport and emit-

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ting/electron transport layers, respectively. PTCDA was used as a dopant in NPB. All of organic materials were purified by a home-made sublimation system prior to the use. Finally, a LiF/Al cathode was deposited on the top.

The current–voltage–luminescence ($I-V-L$) characteristics of the devices were measured by an ST-86LA spot photometer and a computer controlled Keithley electrometer 617 under the ambient condition. The emission area of the devices was 0.01 cm^2 as determined by the overlap area of the anode and the cathode. The optical absorption spectra of organic thin films were obtained by using a UV–visible spectrometer (UV-3100). X-ray diffraction (XRD) measurements of organic thin films were obtained from an x-ray diffractometer (D/max-RB). Optical microscopy was performed with a Union SDZ2 optical microscope equipped with a Nikon DXM1200F digital camera before and after the thermal treatment.

3. Results and discussion

Figure 1 shows the UV–vis absorption spectra of undoped NPB, PTCDA and NPB: 10wt% PTCDA films (50nm thick) on quartz substrates. The absorption of NPB: 10wt% PTCDA film is attributed to the co-absorption of NPB and PTCDA, and no new absorption band is present, demonstrating that there is likely to be no chemical reaction between NPB and PTCDA.

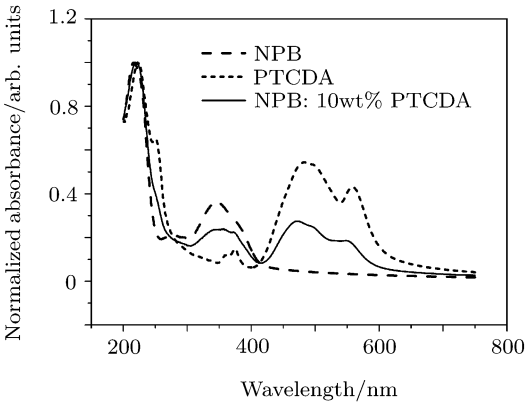


Fig.1. Normalized UV–vis absorption spectra of undoped NPB (dot line), PTCDA (dash dot line) and NPB: 10wt% PTCDA films (solid line) (about 50 nm) on quartz substrate.

The x-ray diffraction patterns of PTCDA and NPB: 10wt% PTCDA films (50 nm) on quartz substrates have been shown in Fig.2. For the PTCDA doped NPB film, there are a prominent peak present at 2θ=27.6°, corresponding to diffraction from the (102) plane of the PTCDA phase, and a broad peak present at 2θ =21.0°, assigned to the reflection from the quartz substrate. The diffraction peak does not disappear, and just the intensity decreases compared with that of the pure PTCDA film. This clearly demonstrates that the PTCDA doped NPB film is semicrystalline. The semicrystalline composite has been shown to be more thermally stable than the neat NPB thin film (see Fig.6), which is useful for making organic light emitting diodes with a prolonged lifetime.

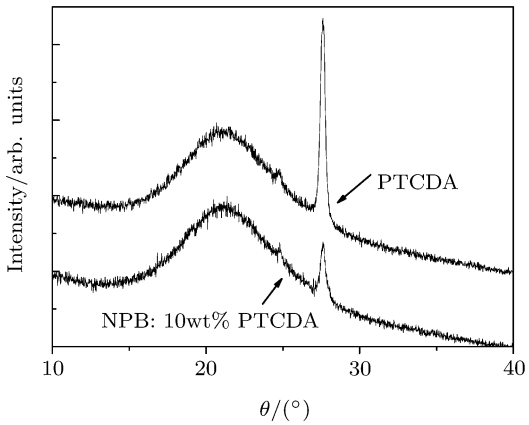


Fig.2. XRD measurements for 50 nm thick PTCDA (dash line) and 50 nm thick NPB: 10wt% PTCDA films (solid line) on quartz glasses.

Five types of devices were fabricated with hole injection layer (HIL)/ hole transport layer (HTL) structures, as shown in Table 1. The thickness of Alq_3 was 60 nm for each of these five devices. On the top of organic layers were LiF (1nm)/Al (120 nm) cathodes under identical conditions. The differences among them lie in the HIL and HTL. The basic devices were A and B, which had the undoped HILs. Device C, D and E each had a thin PTCDA-doped NPB layer that functioned as a hole injection layer. The total HIL and HTL thicknesses of all the devices each were kept constant to compare their relative influence on device performance.

Table 1. HIL and HTL structures for various OLEDs used in this work. For all devices, 60 nm Alq_3 was used as the bifunctional electron transport/emission layer, and LiF / Al bilayers were used as the cathode.

device	injection layer/nm		hole transport layer/nm	
A			NPB	80
B	PTCDA	5	NPB	75
C	NPB: 5 wt % PTCDA	10	NPB	70
D	NPB: 10 wt % PTCDA	10	NPB	70
E	NPB: 30 wt % PTCDA	10	NPB	70

Figure 3 shows the current density–voltage–luminance characteristics of various OLEDs listed in Table 1. The device B with a thin PTCDA layer as an HIL exhibits an operation voltage of 9.3 V at 20 mA/cm^2. In contrast, the devices with PTCDA-doped NPB layers show significantly reduced operation voltages. For example, the devices C, D, and E show the operation voltages of 5.8, 5.6, and 5.7 V at 20 mA/cm^2, respectively. It is well known that an energy offset, the difference in potential energy between transporting channels, exists at any heterojunction. In organic electronic materials, such energy offsets have been shown to be an important factor limiting the injection of current at the organic–organic interface.[13,14] Since the highest occupied molecular orbital (HOMO) level of PTCDA is 6.8 eV,[15] the bare ITO would produce a strong injection-limited hole current. However, the PTCDA-doped NPB film has been found to behave similarly to the NPB but for a slight difference, such a mixed layer may serve as an interlayer between ITO and NPB to help holes move from the ITO to the NPB. These results indicate that doping of PTCDA in the NPB layer effectively enhances the hole injection and transport compared with the pristine layer. The power efficiency–luminance–current efficiency characteristics of various OLEDs listed in Table 1 are also shown in Fig.4. Whole doped devices maintain high current efficiencies at a high luminance level. For example, the devices C, D, and E show improved current efficiencies of 2.0, 2.0, and 1.9cd/A at 2000cd/m^2, respectively, as compared with a current efficiency of 1.6cd/A for the device A with an undoped NPB layer. The increasing of PTCDA doping concentration has no effect on the performance of the doped devices. The improvement in current efficiency of the doped devices may be qualitatively explained by more balanced hole and electron injections.

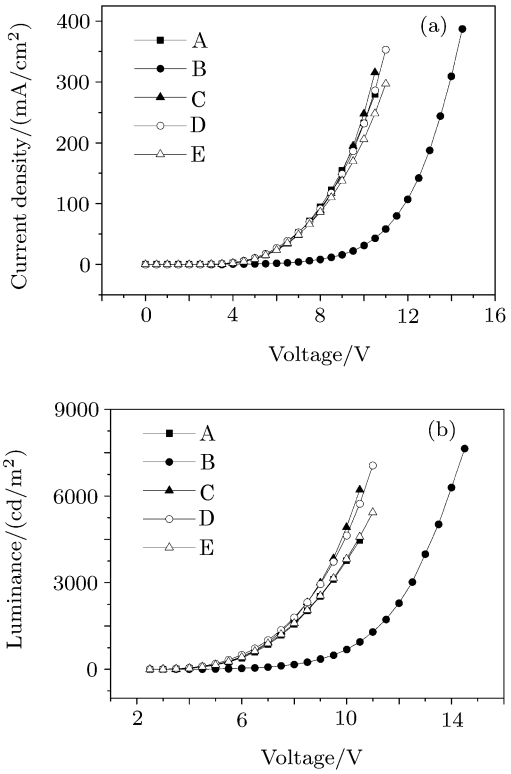


Fig.3. Plots of current density–voltage (a) and luminance–voltage (b) characteristics for various OLEDs listed in Table 1.

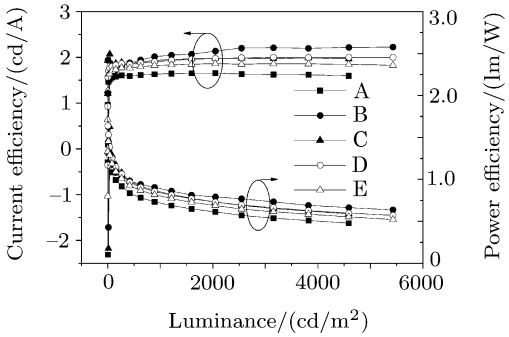


Fig.4. Plots of current efficiency and power efficiency versus luminance for various OLEDs listed in Table 1.

To investigate hole injection and transport characteristics of the PTCDA-doped NPB layer, the hole-only devices with the structures of ITO/ NPB: 10% PTCDA(10 nm)/ NPB(110 nm)/Al and ITO/NPB (120 nm)/Al were fabricated. As shown in Fig.5, the $J-V$ characteristic for the device with an undoped NPB layer follows general trapped-charge-limited current (below 1.5V) and space charge limited current (above 1.5V) models.[7,16] In contrast, it is clearly shown that the hole-only device with an NPB:10% PTCDA/NPB layer exhibits ohmic-like $J-V$ characteristic. The electrical conductivity was calculated to be 2.1×10^{-6}S/cm. Still, at a bias of 3V, a current density of 467mA/cm^2 is achieved higher than the 101 mA/cm^2 of the device with an undoped NPB layer. These results clearly indicate that PTCDA doping in NPB enhances the hole injection and transport at ITO /organic interface.

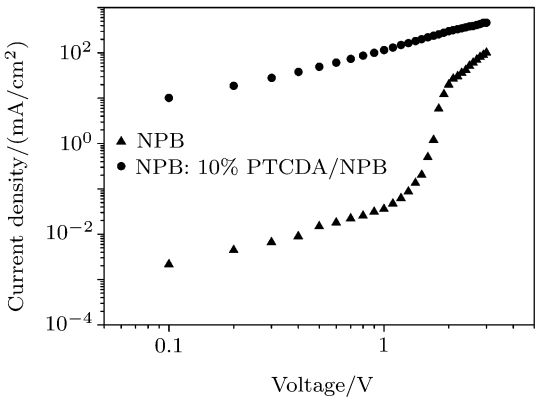


Fig.5. The current density–voltage characteristics of the hole-only devices with NPB: 10wt% PTCDA (10 nm thick) /NPB (110 nm thick), and undoped NPB (120 nm thick).

To study the influence of PTCDA doping on the thermal stability of the NPB film, pure NPB films (sample A), pure PTCDA films (sample B) and NPB: 10wt% PTCDA films (sample C), were deposited on the same ITO substrate. Both samples were 50 nm thick and annealed for 1h at 120°C in an oven. Figures 6(a) and 6(b) show the optical micrographs for the undoped NPB films after the annealing at room

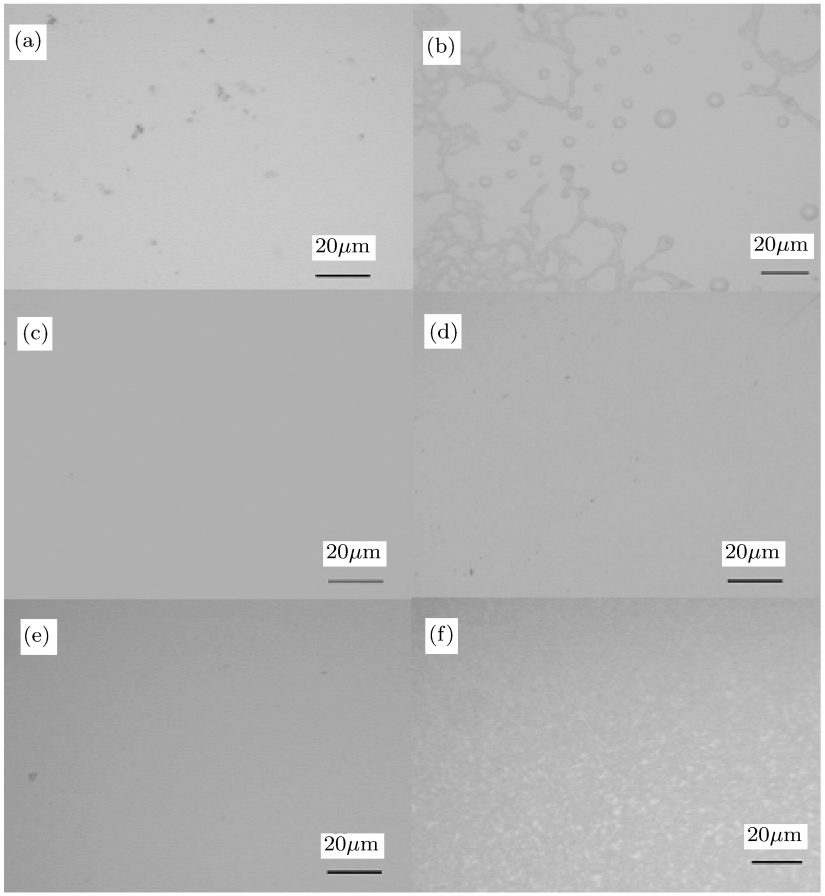


Fig.6. Optical micrographs of the undoped NPB (50 nm thick) sample A: (a) before and (b) after annealing at 120°C; the PTCDA (50 nm thick) sample B: (c) before and (d) after annealing at 120°C; and of 10wt% PTCDA-doped NPB (50 nm thick) sample C: (e) before and (f) after annealing at 120°C.

temperature. The morphology shows lots of dewetting spots even before the annealing. After annealing, delaminated spots grew larger in some areas and then spread to almost all regions of the sample as shown in Fig.6(b). This phenomenon indicates pure NPB films tend to crystallize at 120°C. In contrast, 10 wt % PTCDA-doped NPB films, as shown in Fig.6(e) display an almost featureless morphology before annealing, indicating the formation of smooth film. Remarkably, as shown in Fig.6(f), after being stressed at 120°C, the immense dewetting spots do not exist any more as compared with the undoped NPB films annealed. The data suggest that the doped layer prevents the HTL from dewetting from the substrate as well as precludes the HTL from crystallizing. The results clearly show that the PTCDA-doped NPB layer has the improved thermal stability. For the pure PTCDA films (Figs.6(c) and 6(d)), no features are observed before annealing, and the morphology is unchanged even after the annealing, indicating the stabilization of the PTCDA film. So doping PTCDA in NPB films prevents the NPB from crystallizing. Otherwise, the PTCDA is known to be an electron acceptor, whereas hole transport molecules are known to be strong electron donors. When NPB is mixed with PTCDA, the electron acceptor PTCDA gains charges from the hole-transporting molecules. Such a charge transfer provides a permanent dipole force cross-linking NPB molecules. This crosslinking will produce a thermoset molecular film and thereby enhance the long-term stability of the OLEDs. Although our previous optical absorption studies failed to find the clear evidence for a strong chemical bond formation, such an adhesion improvement has previously been observed in C60-doped NPB films.[17] Detailed mechanisms about doping-induced enhancement of device stability are under further investigation.

Owing to the restriction on the encapsulation condition in our laboratory, we measured the durability characteristics of two devices at an initial luminance of 2000cd/m^2 through an continuous dc operation under ambient condition. The device with an undoped NPB layer shows a half-lifetime of only 72h, whereas the device with a 10% PTCDA-doped NPB layer exhibits a half-lifetime of 94h. This suggests that the doping of PTCDA in the NPB layer can improve the long-term stability of OLEDs.

4. Conclusions

We have investigated the promising electron acceptor PTCDA-doped NPB as hole injection layer for OLEDs. Mechanically, the doped films have been shown to have very good thermal stability as compared with the NPB layer. The Alq_3-based OLEDs with PTCDA-doped NPB layers exhibit much reduced driving voltages of 5.6–5.8 V and current efficiencies of 1.9–2.0cd/A at 2000 cd/m^2 due to the enhancement of hole injection and transport. The OLEDs with PTCDA-doped NPB layers show improved device stability, which is mainly attributed to the stabilization of the NPB film morphology.

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