

White organic light-emitting devices fabricated by spin-coating molecular materials

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White organic light-emitting device (WOLEDs) employing molecular mixed host (MH) is demonstrated by spin-coating. The spin-coated film functions as light-emitting layer and hole transporting layer, with the former formed by spin-coating solution containing MH of NPB (N,N'-Bis(naphthalene-1-yl)-N,N'-bis(phenyl)-benzidine) and MADN (2-methyl-9,10-di(2-naphthyl)anthracene), blue dye (4,4'-bis[2-(4-(N,N-diphenylamino)phenyl)vinyl]biphenyl) and yellow dye (5,6,11,12-tetraphenylnaphcene). The performances of the devices made with different mixed ratio of MH are investigated. It is found that the device performances depends on the MH ratio, and under the optimal NPB:MADN ratio (60:40), the WOLEDs show a maximum luminance of 24 671 cd/m² and a current efficiency of 5.8 cd/A for the practical luminance of 1000 cd/m². The effect of MH ratio on device performances can be attributed to the difference of hole mobility between the NPB and MADN.

white organic light-emitting devices, small-molecular materials, mixed host, spin-coating

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White organic light-emitting diodes (WOLEDs) have very promising applications in areas such as full-color flat-panel displays, liquid-crystal-display backlighting and large area illumination. For these purposes, high-throughput, large-area manufacturing techniques with low-cost have to be established to drastically reduce production costs. Currently, the techniques for manufacturing WOLEDs can be classified into two categories, namely the vacuum deposition based on molecular materials and the solution processing mainly used for polymeric materials. It is well known that vacuum deposition allows us to realize complicated multi-layer structure and render excellent device performance such as high efficiency [1], but it is a relatively costly process. The alternative, the solution processing is suitable for low cost, large area manufacturing technology such as

screen-printing, inkjet printing [2] and so on, and hence is more desirable for large-scale manufacturing.

In the past few decades, the research on solution processed WOLEDs has predominantly focused on polymers as emitters or binders. These solution-processed WOLEDs, which were based on polymer blends [3–5] or dyes-doped conjugated [6] or non-conjugated [7–9] polymers, showed good efficiency and luminance. For instance, the best efficiency reported was 16 lm/W [5] and 7.6 cd/A [10] for WOLEDs based on polymer blends and 17.7 cd/A for WOLEDs based on dyes-doped polymer [6]. Yet, despite their high efficiency, most of WOLEDs based on polyfluorene-type polymers are prone to suffer from the photo- and/or electro-degradation processes during operation [11]. Furthermore, for some conjugated polymer, interactions between the molecules in the solid state can lead to dimer, excimer or aggregate formation [12], which can cause quenching of

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the luminescence. Besides, they usually have low triplet energies, which makes them unsuitable to serve as the host for blue/green phosphorescent emitters [13]. As for the non-conjugated polymer, such as poly-N-vinyl carbazole, it is a host material with suitable triplet level for phosphorescent emitters, but its use often leads to high operating voltages [14] and consequently low power efficiencies. In addition, the polymer purity is currently low due to the difficulty to purify and the presence of chain defects [15].

In contrast, the molecular materials used for WOLEDs seem to have more advantages in comparison with polymers. For instance, the variety of molecular materials that can be used for host of phosphorescent/fluorescent emitters are numerous, and they are easy to achieve high purity. Recently, some papers [16,17] have demonstrated OLEDs by spin-coating molecular materials. However, WOLEDs fabrication by spin-coating molecular materials have been rarely reported, yet its investigation is significant because this approach is expected to reduce manufacture cost and avoid the complexity of co-deposition process in thermal evaporation.

In this paper, WOLEDs employing molecular mixed host (MH) is demonstrated by spin-coating. The white light-emitting layer (EML) is formed by spin-coating solution that contains the molecular MH of MADN and NPB, with the former doped with the blue dopant 4,4'-bis[2-(4-(*N,N*-diphenylamino)phenyl)vinyl]biphenyl (DPA VBi) and the yellow dye 5,6,11,12-tetraphenylnaphacene (rubrene). The solution-processed WOLEDs show high luminance and stable white-emitting behavior under a driving voltage, and the complexity of co-evaporation in the vacuum deposition for WOLEDs is avoided.

The devices based on MH structure were fabricated on indium tin oxide (ITO)-coated glass with the structure, ITO/EML(50 nm)/BCP(10 nm)/Alq₃(30 nm)/LiF/Al. BCP (2,9-dimethyl-4,7-diaphenyl-1,10-phenanthroline) was used

as the hole blocking material and Alq₃ (tris(8-hydroxyquinoline)aluminum) as electron transporting material. The EML for all the devices was composed of molecular MH of MADN and NPB, which was doped with DPAVBi and rubrene. Six NPB:MADN blends (weight ratio), 100:0; 80:20; 60:40; 40:60; 20:80 and 0:100 were investigated. The doping concentration of dye DPAVBi and rubrene are summarized in Table 1.

The device fabrication is performed as follows. The chlorobenzene solution containing MH materials and blue and yellow dyes were spun over the patterned, precleaned ITO-coated glass substrate to serve as the EML (50 nm), and then it was baked at 80°C for 40 minutes. After the baking, the sample was loaded into the vacuum chamber to deposit the BCP (10 nm), Alq₃ (30 nm) and the cathode, LiF (0.6 nm)/Al (80 nm), by thermal evaporation.

The films used for the atomic force microscopy (AFM) investigation were built in the same way. The film thickness was measured by an ellipsometer and was about 50 nm. The electroluminescence (EL) spectra and CIE coordinates of the devices were measured by a spectrometer (PR650) and the current-voltage-luminescence characteristics were analyzed by a Keithley 2602 source meter.

Figures 1(a)–(f) show the AFM images of organic films spin-coated on top of ITO with NPB:MADN ratios of 0:100, 20:80, 40:60, 60:40, 80:20 and 100:0, respectively. From Figures 1(a)–(f), it can be seen that all the films show a pin-free and smooth surface morphology. The surface roughness of the film with NPB:MADN ratio of 0:100 and 100:0 in terms of root-mean-square (RMS) is 0.344 nm and 0.285 nm, respectively, as shown in Figures 1(a) and 1(f). From Figure 1, we can clearly see that introducing the NPB into MADN have a little effect on the surface roughness of the spin-coated film. For instance, when the NPB:MADN mixed ratio is varied from 20:80 to 80:20, the surface

Table 1 EL performances of devices with different NPB:DPVBi ratios

No.	Weight ratio				Performances		
	NPB	MADN	DPAVBi (x%)	rubrene (y%)	Maximum luminance (cd/m ²)	efficiency at 1000 cd/m ² (cd/A)	CIE(x,y) 4 V/9 V
A	80	20	4	0.7	20661	6.9	(0.447,0.459)/(0.435,0.459)
B	80	20	4	0.4	20542	5.6	(0.409,0.433)/(0.383,0.423)
C	80	20	4	0.3	20315	4.6	(0.337,0.388)/(0.314,0.380)
D	100	0	4	0.27	14114	3.9	(0.315,0.386)/(0.275,0.336)
E	80	20	4	0.27	21505	4.9	(0.315,0.387)/(0.292,0.385)
F	60	40	4	0.27	24671	5.8	(0.321,0.391)/(0.305,0.393)
G	40	60	4	0.27	23376	5.8	(0.313,0.388)/(0.306,0.394)
H	20	80	4	0.27	17153	5.3	(0.311,0.370)/(0.291,0.365)
I	0	100	4	0.27	7237	2.9	(0.341,0.412)/(0.329,0.408) ^{a)}

a) The CIE coordinates at 5V/μV, respectively.

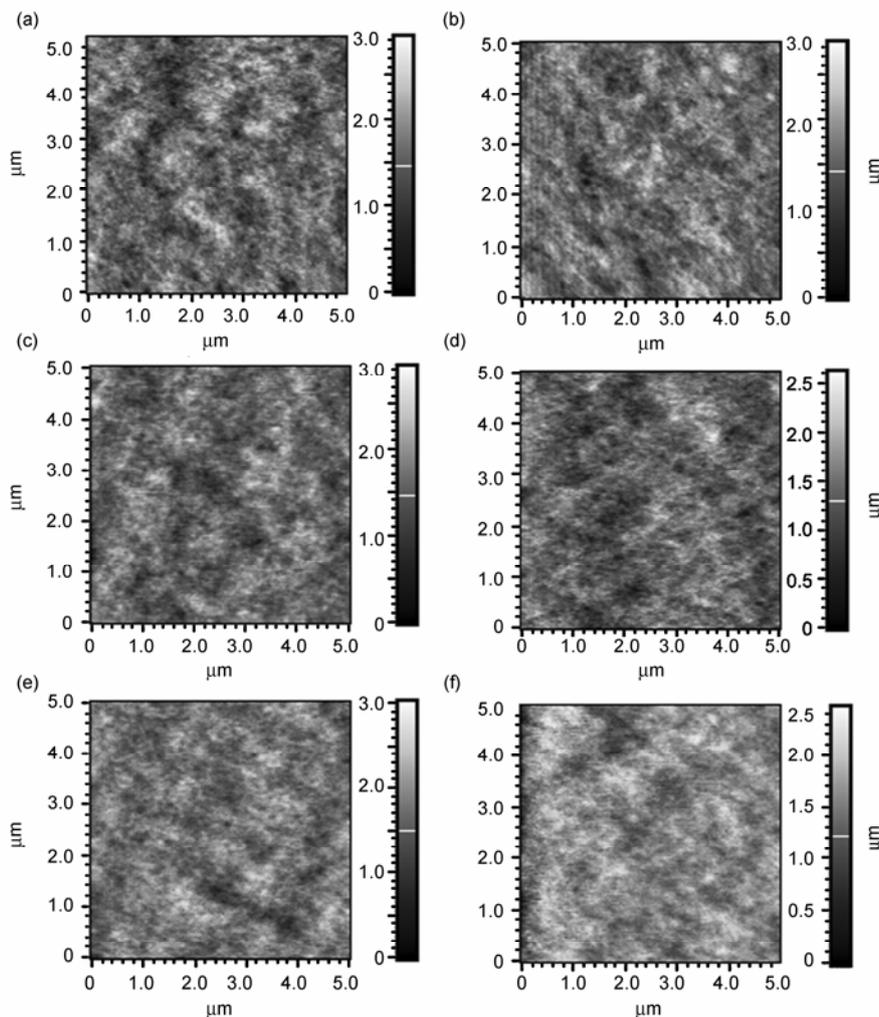


Figure 1 The AFM images of films with NPB:MADN ratios of (a) 0:100 (RMS=0.344 nm); (b) 20:80 (RMS=0.303 nm); (c) 40:60 (RMS=0.304 nm); (d) 60:40 (RMS=0.293 nm); (e) 80:20 (RMS=0.292 nm) and (f) 100:0 (RMS=0.285 nm). (scanning size: 5 μm \times 5 μm).

roughness of the spin-coating films in RMS only changes from 0.303 nm to 0.292 nm, as shown in Figures 1(b)–(e). This result of AFM investigation indicates that well-defined, uniform films made of NPB, MADN and their blends can be achieved by spin-coating chlorobenzene solution, and these spin-coated films can be used for EML of WOLEDs.

Figure 2 shows the normalized EL (a.u.) spectrum of devices A–C, and E, in which the doping concentration of rubrene varies from 0.27% to 0.7%. Here, the ratio of the molecular MH of NPB:MADN is selected to be 80:20 and the doping concentration of DPAVBi is fixed at 4%, which is an optimal value in the range of 2%–7%. As shown in Figure 2, when the doping concentration of rubrene is 0.27%, the intensities of the blue and yellow emissions are nearly equal and their CIE coordinates are (0.30, 0.38), indicating that white-emitting can be obtained under this doping concentration. As the doping concentration of rubrene is increased, the relative intensity of the yellow emission increases, indicating that more energy is transferred from MH

and DPAVBi to rubrene. When the concentration of rubrene is 0.7%, the intensity of yellow emission is significantly higher than that of the blue emission and the device shows yellow-emitting. Basing on the above results, the doping concentration of DPVABi and rubrene is fixed at 4% and 0.27% respectively in the following investigation for the effect of MH ratio on device performance.

Figure 3 shows the current density-voltage (J - V) characteristics of devices D–I with different MH ratio. At a given current density, the voltages of these devices decrease steadily with the increasing NPB concentration in MH and the MADN and NPB host device show the highest and lowest voltage, respectively, as shown in Figure 3. The dependence of J - V characteristics on MH ratio can be attributed to the effect of MH ratio on hole-transporting property. The reason is that the hole mobility of NPB ($10^{-4} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) is significantly higher than that of MADN ($\sim 10^{-6} \text{ cm}^2 \text{ V}^{-1} \text{ s}^{-1}$) [18]. Increasing the NPB concentration thus improves the hole transport, hence decreases the operation voltage. This

explanation is also supported by Tsai et al. [19] Their results show that the voltage of hole-only devices at a given current density decreases when the mixed NPB concentration in NPB:MADN is increased. In addition, the hole-injecting barrier of different materials also have an effect on the J - V characteristics of device, while the effect of MH ratio on hole-injection character here can be neglected because of the nearly equal HOMO (highest occupied molecular orbital) energy of MADN (5.5 eV) and NPB (5.4 eV) [19].

EL characteristics of all devices are summarized in Table 1. Figures 4(a) and 4(b) show the luminance-current density and current efficiency-luminance characteristics of the devices D-I. As shown in Figure 4, the maximum luminance and current efficiency of the devices (E-H) are higher than that of NPB (D) or MADN (I) host device, and the MADN host device shows the lowest luminance (7237 cd/m^2) and current efficiency (2.9 cd/A at 1000 cd/m^2), which can be attributed to low hole mobility of MADN. Among all the devices, the device with NPB:MADN ratio of 60:40 (F) shows the best performances, for instance, its maximum luminance reaches $24\,671 \text{ cd/m}^2$ at the current density of 1000 mA/cm^2 and current efficiency is up to 5.8 cd/A for an applicable luminance of 1000 cd/m^2 . This is because the optimal MH ratio can balance the holes and electrons in EML, hence improving the luminance of the device [20]. In addition, it was found that the device with NPB:MADN ratio

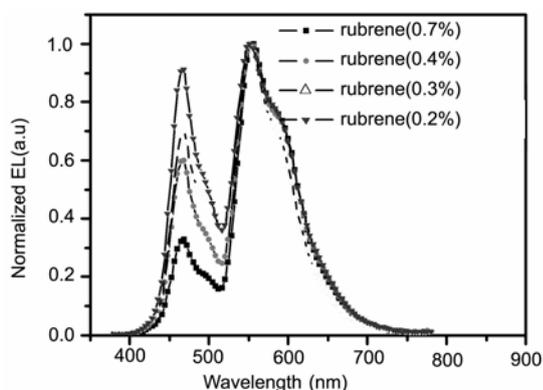


Figure 2 The normalized EL (a.u.) spectrum of devices A-C, and E with varying concentration of rubrene.

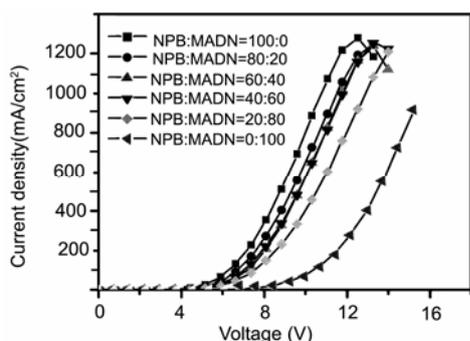


Figure 3 The current density-voltage (J - V) characteristics of devices D-I.

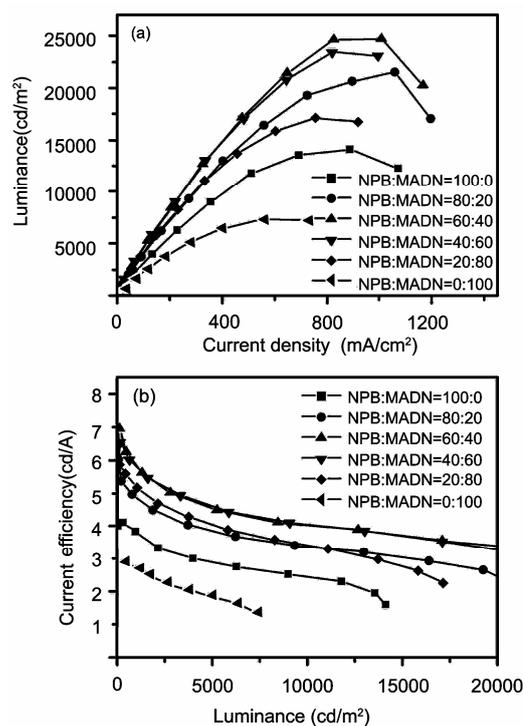


Figure 4 (a) The luminance-current density; (b) current efficiency-luminance characteristics of devices D-I.

of 40:60 (G) showed nearly equal luminance and current efficiency when the current density was below 500 mA/cm^2 . When it was above 500 mA/cm^2 the luminance and current efficiency of device G were slightly lower than that of device F.

Figures 5(a), (b) and (c) show the normalized EL (a.u.) spectra of devices I, F and D at various voltages, as well as CIE coordinates in the right. The EL spectra of the three devices show two main peaks at 468 nm and 552 nm originated from the emission of DPAVB i and rubrene, respectively. As shown in Figures 5(a) and (e), with the increasing driving voltage, the EL spectra of device I and F are almost the same. The CIE coordinates of device I change from (0.341, 0.412) at 5 V to (0.329, 0.408) at 11 V, which is only a change of $(-0.012, -0.004)$, and the CIE coordinates of device F change from (0.321, 0.391) at 4 V to (0.305, 0.393) at 9 V, the change of CIE coordinates are $(-0.016, 0.002)$. In the EL spectra of device D shown in Figure 5(c), when the driving voltage is increased from 4 V to 9 V, the intensity of blue emission increases more rapidly than that of yellow emission and its CIE coordinates shift from (0.315, 0.386) to (0.275, 0.336), the change of CIE coordinates are $(-0.040, -0.050)$. The blueshift effect of device D under the increasing applied voltage is attributed to the saturation of the rubrene molecules located at narrow recombination zone [21]. The stable color coordinates of devices F and I can be attributed to ambipolar carrier-transporting character of MADN, which shift the re-

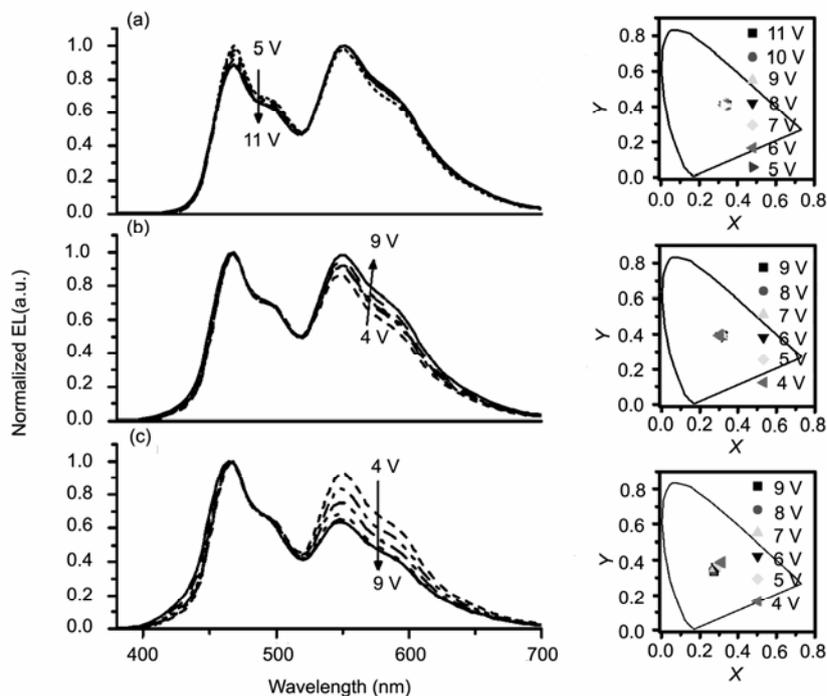


Figure 5 The normalized EL(a.u.) spectra of devices I, F and D at various voltages, as well as CIE coordinates. (a) device I, (b) device F, (c) device D.

combination zone into body of the EML and consequently avoid the saturation of rubrene molecules. In all the devices, the role of BCP is expected to prevent holes from entering electron-transporting layer and confine all the electron-hole pairs in the EML for efficient recombination.

In conclusion, we investigated solution-processed films of NPB, MADN and their blends, the AFM results show that well-defined, uniform films of NPB, MADN and their blends can be achieved by spin-coating. Using the spin-coated films of the blends of NPB and MADN doped with DPAVBi and rubrene, which serves as EML, a novel WOLEDs was demonstrated. The solution-processed WOLEDs show a maximum luminance of 24671 cd/m² and a current efficiency of 5.8 cd/A at a practical luminance of 1000 cd/m². This approach is expected to reduce manufacture cost and avoid the complexity of co-deposition process in thermal evaporation, and it is possible for this approach to be used for other molecular materials to achieve better performance.

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