Solution-processed organic films of multiple small-molecules and white light-emitting diodes

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A B S T R A C T
We investigated characteristics of solution-processed films of 4,4'-bis(2,2-diphenylvinyl)-1,1'-bibenyl (DPVBi), N,N'-bis(naphthalene-1-yl)-N,N'-bis(phenyl)-benzidine (NPB), and their blends, and it was found that the spin-coated films of NPB, and blends of NPB and DPVBi, though having lower densities, were more uniform than their vacuum-deposited counterparts. Using the spin-coated films of NPB:DPVBi as mixed host, doped with blue dye (4,4'-bis(2-(4-(N,N-diphenylamino)phenyl)vinyl)biphenyl) and yellow dye (5,6,11,12-tetraphenylnaphacene), new white organic light-emitting devices (WOLEDs) were demonstrated. The luminance (maximum luminance of 35822 cd/m²), efficiency (5.3 lm/W (100 cd/m²) and 8.3 cd/A (1000 cd/m²)) and stability of these solution-processed devices are better than or equivalent to the vacuum-deposited one, which was expected as an alternative route to the fabrication of small-molecular WOLEDs, reducing the cost of devices and avoiding the complexities of the co-evaporation of multiple dopants and host materials in the vacuum deposition.

1. Introduction

White organic light-emitting devices (WOLEDs) have highly promising applications in areas such as full-color flat-panel displays, liquid-crystal-display backlighting and large area illumination. The white emission from WOLEDs are generally obtained by mixing complementary (e.g., blue and yellow or orange) or primary colors (red, green, and blue). Many approaches have been proposed to achieve white light emission, such as doping several dyes into one [1–4] or more emissive layers (EMLs) [5–7]. In WOLEDs with multiple EML structures, two or more EMLs are physically separated from each other. Thus the location of exciton recombination and the doping concentra-

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ogy such as screen-printing, and inkjet printing [11]. In the past decades, organic materials in solution processing for fabricating devices are mainly polymers [12–15]. Alternatively, many solution-processible organic molecules were designed and synthesized to fabricate the light-emitting devices by spin-coating, such as dendritic molecules [16–18], oligomers [19], spiro-molecules [20,21], and binuclear metal chelates [22,23]. Recently, Lee et al. have also reported a spin-coated blue light-emitting devices based on 2-(t-butyl)-9,10-bis(2-naphthyl) anthracene [24], which combines the simple materials of OLED and low-cost process of solution processing. Thus, it is desirable to develop solution-processed devices based on high-efficient molecular materials which films were usually made by vacuum-deposition.

In this paper, we investigated the characteristics of spin-coated films of DPVBi (4,4'-bis(2,2-diphenylvinyl)-1,1'-bibenyl), NPB (N,N'-bis(naphthalene-1-yl)-N,N'-bis(phenyl)-benzidine) and their blends, which were widely used in fabrication of OLEDs by vacuum-deposition. It was found that the spin-coated small-molecular films of NPB, and blends of NPB and DPVBi, though having lower densities, were more uniform than their vacuum-deposited counterparts. We demonstrate WOLEDs based on solution-processed films of the blends of NPB and DPVBi. In these WOLEDs, the white EML was formed by spin-coating a solution containing mixed hosts (MH) of NPB and DPVBi, blue dopant 4,4'-bis[2-(4-(N,N-diphenylamino)phenyl)-vinyl]biphenyl (DPAVBi) and yellow dye 5,6,11,12-tetraphenylnaphacene (rubrene). Besides avoiding complexity of co-evaporated process in vacuum deposition, these devices show high luminance and stable white-emitting under different driving voltages.

2. Spin-coated molecular films

The chemical structures of DPVBi, NPB, blue dye DPAVBi and yellow dye rubrene are shown in Fig. 1(a). The chlorobenzene was used as a solvent for dissolving these molecular materials. The solution-processed films of blends of NPB:DPVBi were fabricated as follows. The blends with NPB:DPVBi weight ratio of 0:10, 1:9, 1:4, 3:7, 2:3, 3:2, 4:1, 10:0 were first dissolved in chlorobenzene (14 mg/ml), the solution was then spin-coated on indium tin oxide (ITO)-coated glass substrates to form a film with a thickness of 50 nm (1000 rpm). Finally, the spin-coated films were transformed to the oven for baking. Following previous reports [25], the spin-coated films were baked at 80 °C for 30 min in the oven to guarantee the removal of residual solvent of chlorobenzene. The surface morphology was investigated by AFM and 10× microscope objective with a numerical aperture of 0.3 (Nikon, Japan). The thickness and refractive indices of the films were measured by an ellipsometer.

Fig. 2 shows the microscope images of spin-coated films of NPB:DPVBi with different mixing ratios. Fig. 2(a)–(h) corresponds to NPB:DPVBi ratio of 0:10, 1:9, 1:4, 3:7, 2:3, 3:2, 4:1, and 10:0, respectively. Fig. 2(a) shows the spin-coated film of DPVBi, where significant crystallization and coagulation of DPVBi was observed. These effects are due to the low glass-transition temperature \( T_g \) of DPVBi (64 °C) during the annealing process [26]. If the NPB (10%) is blended with DPVBi (90%), however, crystallization of the spin-coating film of the blends was reduced as shown in Fig. 2(b). With the increasing NPB concentration in the blends, the crystallization of spin-coated film of the blends was further reduced as can be seen from Fig. 2(c) and (d). As the NPB concentration is increased to 40%, the crystallization and coagulation can no longer be observed (see Fig. 2(e)–(h)). The suppressing of the crystallization and coagulation of DPVBi can be attributed to two factors. One is that the NPB molecules in the blends function as defects and hence prevents the formation of an ordered crystal of DPVBi. This phenomenon is similar to a previous report [10], where the glass-transition temperature of NPD:rubrene was found to be higher than that of pure NPD(4,4'-bis[N-(1-naphthyl)-N-phenyl- amino]-biphenyl) because the doped rubrene serve as defects. The other is that a polymer with a high \( T_g \) was reported to effectively suppress the crystallization and coagulation of molecular material in molecularly doped polymers [27]. Since NPB has a \( T_g \) of about 95 °C, it is effective on preventing the crystallization and coagulation from happening in spin-
coated films and thus provides these films with better thermal stability.

Fig. 3 shows the surface morphology of spin-coated and vacuum-deposited films by atomic force microscopy (AFM). Fig. 3(a) is the surface of the ITO film, on which other organic materials were deposited or spin-coated. The root-mean-square of surface roughness ($R_{\text{RMS}}$) of ITO film is 1.51 nm. Fig. 3(b)–(f) is the surface morphology of spin-coated films of the blends with NPB:DPVBi ratios of 0:10, 1:9, 1:4, 3:7, 2:3, 3:2, 4:1, and 10:0, respectively. The AFM investigations indicate that...
The spin-coated films of NPB, and NPB:DPVBi blends are more uniform than the vacuum-deposited ones. The refractive indices of the spin-coated films can be obtained by spectroscopic ellipsometry, which can be used.

Fig. 3. The AFM images of ITO films (a) \(R_{\text{rms}} = 1.51\) nm and spin-coated films with NPB:DPVBi ratios of, (b) 10:0 \(R_{\text{rms}} = 0.319\) nm, (c) 3:7 \(R_{\text{rms}} = 0.247\) nm, (d) 2:3 \(R_{\text{rms}} = 0.254\) nm, (e) 3:2 \(R_{\text{rms}} = 0.277\) nm, (f) 4:1 \(R_{\text{rms}} = 0.312\) nm, and the vacuum-deposited films with NPB:DPVBi ratios, (g) 10:0 \(R_{\text{rms}} = 1.62\) nm and (h) 3:2 \(R_{\text{rms}} = 0.91\) nm (scan size: \(5 \times 5\) \(\mu\)m).
to evaluate the porosity of the films. The refractive index ($n_f$) of the film can be expressed as $n_f = n_s(1-q) + n_p q$, where $n_s$ and $n_p$ are the mean indices of skeleton of the film and the pore space, respectively, and $q$ is the porosity, or the fractional volume of the pores in the film [28]. So the refractive index, $n_f$, is inversely proportional to $q$, the porosity of films. Fig. 4 shows the refractive index of spin-coated films of NPB, the blends of NPB and DPVBi (3:2), and their vacuum-deposited counterparts. It was found that the refractive indices of spin-coated films of NPB and the blends of NPB and DPVBi (3:2) were smaller than those of vacuum-deposited counterparts. These showed that the spin-coated films were more porous and had lower density than the vacuum-deposited ones. How to deposit more dense molecular films by solution-processing will be a challenge in future research.

3. Fabrication and performances of WOLEDs

Based on spin-coated films of NPB:DPVBi, the device structure of WOLEDs in our experiments is ITO/EML (50 nm)/BCP (10 nm)/Alq3 (30 nm)/LiF/Al. BCP (2,9-dimethyl-4,7-diphenyl-1,10-phenanthroline) is used as hole-blocking material and Alq3 (tris(8-hydroxyquinoline)aluminum) as electron-transporting material. The spin-coated EML consist of MH doped with blue dye DPAVBi (4%) and yellow dye rubrene (0.27%) [29]. The composition of the EMLs used in six devices (labeled as A, B, C, D, E, and F) is summarized in Table 1. The six devices A, B, C, D, E, and F have different NPB:DPVBi weight ratios, which are 10:0, 4:1, 3:2, 2:3, 1:4, and 0:10, respectively. The details of device fabrication are as follows: (1) the chlorobenzene solution (~14 mg/ml) was spin-coated on clean patterned ITO-coated glass substrates to obtain a film of 50 nm thickness; (2) the spin-coated films of the devices A–D were annealed at 80 °C for 30 min and that of the devices E and F were annealed at 80 °C for 10 min to avoid the crystallization of spin-coated films; (3) the samples A–F were then loaded into a vacuum chamber to have the BCP hole-blocking layer (10 nm thickness), electron-transporting layer (30 nm thickness) and the cathode, LiF (0.6 nm)/Al (100 nm) deposited by thermal evaporation. The schematic energy-level diagram of the devices is shown in Fig. 1(b). The photoluminescence (PL) spectra of the films were measured with a fluorescence spectrophotometer (Fmax-4, JY Co.) and the absorption spectra were measured with U3010 (Hitachi Co.). 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 Keithley 2602 source meter and Luminance meter.

The EL characteristics of devices A–F were summarized in Table 1. Fig. 5(a) and (b) shows their luminance–current density and current efficiency–luminance characteristics. Among all the devices, device C shows the best performance, it presents a power efficiency of 5.3 lm/W (100 cd/m²) and current efficiency of 6.5 cd/A at a luminance of 1000 cd/m² and a maximum luminance of 35,822 cd/m² at 11.7 V. The luminance and current efficiency of the devices with MH (B–E) are higher than that with only NPB (device A) or DPVBi (device F). As we can see, device A shows a current efficiency of 3.83 cd/A (1000 cd/m²) and a maximum luminance of 14,113 cd/m², while device F shows a current efficiency of 0.65 cd/A (1000 cd/m²) and a luminance of 1476 cd/m².

The higher efficiency and luminance of devices B–E can be attributed to the blend of NPB and DPVBi used as MH, which effectively adjust the hole-injecting/transporting of devices by varying the ratio of the blend. DPVBi is a light-emitting material with intense fluorescence in the blue region [30], and NPB is widely used as a hole-transport material, whose hole mobility ($10^{-4}$ cm² V⁻¹ s⁻¹) is much higher than that of DPVBi and the hole-injecting-barrier

![Fig. 4. The refractive indices of the spin-coated and vacuum-deposited films of NPB and the blends of NPB:DPVBi (3:2).](image)

| Weight ratio | Performances | CIE (x, y) | 4 V/9 V
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<tr>
<td>NPB</td>
<td>DPVBi</td>
<td>DPAVBi (%x)</td>
<td>Rubrene (%y)</td>
</tr>
<tr>
<td>A</td>
<td>10</td>
<td>0</td>
<td>4</td>
</tr>
<tr>
<td>B</td>
<td>4</td>
<td>1</td>
<td>4</td>
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<td>C</td>
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*The CIE coordinates at 6 V/12 V, respectively.

**Devices G and H have the structure as ITO/PEDOT:PSS/EML/BCP/Alq3/LiF/Al.**
rier of NPB from ITO (0.3 eV) is lower comparing to DPVBi (0.8 eV) [30,31]. So the blend of NPB and DPVBi used as MH play the roles of both hole-transport layer (HTL) and EML in WOLEDs, and the hole injection and transport in WOLEDs can be adjusted by changing the ratio of NPB and DPVBi in EML, which could improve the balances of carriers (holes and electrons) in EML and achieve the high performance of devices.

In order to distinguish the energy-transfer processes in the EMLs of the WOLEDs, the absorption and PL spectra of the dyes, the MH and the dye-doped MH films are investigated. Fig. 6(a) shows the absorption spectra of DPAVBi and rubrene in chlorobenzene solution, and PL spectra of DPVBi, NPB and DPAVBi in films. In Fig. 6(a), there is a large spectral overlap between the fluorescent band of the MH (NPB:DPVBi) and the absorption bands of both DPAVBi and rubrene, which indicates that the lowest singlet-excited states in the MH can be energetically transferred to the dyes (DPAVBi or rubrene) via Förster energy transfer. In addition, the spectra overlap between the fluorescent band of DPAVBi and the absorption band of rubrene suggests that the energy-transfer process between them can happen. Fig. 6(b) shows the PL spectra of the mixed NPB:DPVBi film (3:2), the DPAVBi (4%), rubrene (0.27%) and both DPAVBi (4%) and rubrene (0.27%) doped films. The excitation peak wavelength was at 350 nm for all the PL measurement. The DPAVBi and rubrene show a peak at 468 and 550 nm, respectively. In Fig. 6(b), no emission from the MH is observed in PL spectra of MH doped by DPAVBi, indicating that the energy in the excited MH molecule is completely transferred to DPAVBi with a doping concentration of 4%. On the other hand, a strong emission from MH is observed when the MH is doped with rubrene, suggesting the energy transfer from the MH to rubrene is incomplete with the doping concentration of 0.27%. When we doped both DPAVBi (4%) and rubrene (0.27%) in the MH, nearly comparable intensity of blue and yellow-emitting band are observed, which implies that the energy in the MH is shared by both dyes.

Fig. 7(a)–(d) shows the EL spectra of devices A–D under different applied voltages, where the EL intensity is normalized to the blue wavelength peak, and the CIE coordinates are shown in insets. As can be seen, the devices B–D with MH show quite stable CIE coordinates with various applied voltages. The CIE coordinates of device C change from (0.305, 0.390) at 4 V to (0.320, 0.392) at 9 V, in which the change of CIE coordinates is only (0.015, 0.002), while the CIE coordinates of device A with NPB as host shift from...
(0.315, 0.386) to (0.275, 0.336), showing a change of
(−0.040, +0.050). According to previous reports [32,33],
the blueshift under increasing applied voltages in WOLEDs
with lightly doped rubrene is attributed to the saturation
effect of the rubrene molecules, which could account for
the spectral variation of device A with NPB host doped
with little amount of rubrene (only 0.27%). Therefore the
stable color coordinates of devices B–D with MH are due
to DPVBi in the blends that has an electron-transporting
character [30,34], which transports electrons to the bulk
of the EML effectively and consequently avoids the satu-
ration effect of rubrene molecules. In addition, the role of
BCP in WOLEDs is expected to prevent holes from entering
electron-transporting layer and confine all the electron-
hole pairs in the EML for efficient recombination, which
also helps stabilize the color coordinates of WOLEDs.

The device performance of above device C still has
room for improvement if we introduce a hole-injection
layer such as poly(3,4-ethylenedioxythiophene):poly(sty-
rene sulfonate) (PEDOT:PSS). Fig. 8(a) and (b) presented
the comparison of efficiency and stability of solution-pro-
cessed WOLEDs (device G) and the vacuum-deposited one
(device H). The devices G and H have the same struc-
ture as ITO/PEDOT:PSS (50 nm)/EML (50 nm)/BCP
(10 nm)/Alq₃ (30)/LiF (0.5)/Al(100 nm), in which the PED-
OT:PSS was introduced as hole-injection layer, and EML
consisted of the same ratio of NPB, DPVBi, DPAVBi, and
rubrene as device C in Table 1. The water-dispersed PED-
OT:PSS mixture was spin-coated on the top of ITO to form
a film with a thickness of 50 nm. As for the solution-pro-
cessed WOLEDs (device G), the fabrication of EML was
the same as device C except the annealing condition is
changed to be 130 °C for 15 min in the oven. As for the vac-
uum-deposited one (device H), the EML was formed by
vacuum deposition of a solution-promixed deposition tar-
got with mixed hosts DPVBi and NPB doped with DPAVBi
and rubrene [35]. In Fig. 8, device G shows a current effi-
ciency of 8.3 cd/A at the luminance of 1000 cd/m² and an

over 70 h lifetime with initial luminance of 690 cd/m²,
which were better than or equivalent to those of vac-
uum-deposited one, device H. In addition, the efficiency
of device G was comparable to that of the vacuum-depos-
ited multilayer WOLEDs based on the DPAVBi and rubrene
as dopants in previous reports, in which the reported best
efficiency is 7.7 cd/A (112 cd/m²) [33] and 10.9 cd/A
(10 mA/cm²) [36]. So, solution-processed molecular films
in our works provide a new route for the easy and simple
fabrication of WOLEDs without the sacrifice of device performance.

4. Conclusion

We have investigated solution-processed small-molecule films, such as DPVBi, NPB, and their blends. The more uniform films of NPB and the blends of DPVBi:NPB can be achieved by spin-coating, though having a lower density, in comparison with their vacuum-deposited counterparts. With the spin-coated films of DPVBi:NPB doped with DPAVBi and rubrene, which serves as the EML, a new WOLEDs were demonstrated. The solution-processed WOLEDs show the considerable efficiency and stability, which were prior or equivalent to the vacuum-deposited counterparts.

Solution-processed small molecular films are expected to be a new route to fabricate their WOLEDs to reduce manufacture cost and avoid the complexity of the vacuum co-deposition process.

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References

[29] The doping concentration of DPAVBi was optimized over the range of 2–7 wt% in NPB:DPVBi (80:20) structure for blue emission, and an optimal value is 4 wt%. For all of MH devices, the white emission can be obtained when the concentration of rubrene is 0.27 wt%.
[35] The solution-promixed deposition target was prepared as follow: the blends with NPB:DPVBi weight ratio of 3:2 doped with 4% DPAVBi and 0.4% rubrene were first dissolved in chloroform (C24 H10 mg/ml), then the solution was transformed to the oven and baked at 80 °C for 30 min to remove the solvent chloroform. The same process can be found in the report of Jwo–Huei, Jou et al. (SPIE, 6999 (2008) 69992S).