



White organic light-emitting devices with a solution-processed small molecular emission layer

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ARTICLE INFO

Article history:

Received 29 June 2011

Received in revised form 18 March 2012

Accepted 23 March 2012

Available online 30 March 2012

Keywords:

White organic light-emitting devices

Small molecule

Solution process

ABSTRACT

A white light-emitting device (WOLED) was fabricated with a solution-processed single emission layer composing a small molecular mixed-host (MH) of N,N'-bis(naphthalene-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) and 4,4'-bis(2,2-diphenylvinyl)-1,1'-bibenyl (DPVBi) by codoping blue dye of 4,4'-bis[2-(4-(N,N-diphenylamino)phenyl)vinyl]biphenyl (DPAVBi) and red dye of 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTb) into the MH. White light emission was realized in an OLED with 1.15 wt.% DCJTb and 4 wt.% DPAVBi doping concentrations. A maximum luminance of 13,638 cd/m² and a current efficiency of 5.7 cd/A were obtained in the device. These results demonstrate that WOLEDs can be realized through solution-processed small molecular emitting layer, which reduced the cost of devices and avoided the complicated co-evaporation of multiple dopants and host materials in the vacuum deposition.

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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 [1–3]. In order to obtain white emission from organic light-emitting devices, a general strategy is to use different organic materials, which emit at different primary colors to fully cover the whole visible spectrum range [4–9]. Currently, there are many approaches reported to realize WOLEDs, mainly by employing multiple emissive layers (EMLs) in which each layer emits a primary color [4–6], or a single EML doped simultaneously with different color light emitting materials [7–9]. Small molecular WOLEDs can be fabricated by the co-evaporation of different emitting dyes and host materials in a single or multilayer structure [6–9]. The doping concentration of dyes must be controlled carefully to obtain balanced white emission, which is a difficult task to achieve in the co-evaporation process and usually leads to a fabrication process of great complexity, poor reproducibility and high cost. Several methods have been reported to avoid the complexity of co-evaporation and reduce the manufacturing cost [7,10–16]. Solution-premixed deposition source is an effective method to avoid the complexity of co-evaporation process [7,13–16], where, the dopants and hosts are

mixed prior to the device fabrication process through solution mixing and drying. However, for this method to be possible, compatible material systems have to be found to match each other.

As an alternative approach, solution-processing is a more desirable technique for low-cost manufacture because it is easy to realize co-doping of several dopants and compatible with low-cost, large area manufacture technology such as spin-coating [17], ink-jet printing [18] and screen-printing [19]. In the past few decades, the research on solution-processed WOLEDs has predominantly focused on polymer blends or dye-doped polymers [20–22]. Although light-emitting polymers are considered to be suitable for solution process, the efficiency and lifetime of polymer-based devices are lower than that of vacuum deposited small molecular devices. Recently, solution processed small molecule thin films have drawn much attention because it was found that highly efficient small molecular materials, which were usually used in vacuum-deposition, can be utilized in this process, thus having the aforementioned advantages [17,23]. Solution-processed OLEDs employing small molecules as hosts show good performances that were comparable to the vacuum-deposited counterparts, with much improved process feasibility [24]. Thus, it is a good strategy to develop OLEDs based on solution processible small molecules, which would open up exciting possibilities for commercialization of OLEDs for displays and lighting.

On the other hand, to ensure high performance, it is important to balance the injection of holes and electrons in the emissive layer. This can be achieved in vacuum-deposited small molecular

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devices by stacking different functional layers. However, it is difficult to form multilayer structures by the solution process because of the dissolution of the former layer by the later solution. One effective method to obtain a lower driving voltage and higher efficiency in WOLEDs is to use a mixed-host (MH) structure instead of a single-host structure [7,17,25–27]. An appropriate combination of a hole-transport-type host and an electron-transport-type host was effective in reducing driving voltage and increasing device efficiency [25–27].

In this work, high efficiency WOLEDs employing dyes doped small molecular MH are demonstrated via solution-process, which avoids the complexities of the co-evaporation of multiple dopants and host materials in the vacuum deposition. A soluble small molecule MH system consisting of hole-transport-type material N,N'-Bis(naphthalene-1-yl)-N,N'-bis(phenyl)-benzidine (NPB) and electron-transport-type material 4,4'-bis(2,2'-diphenylvinyl)-1,1'-biphenyl (DPVBi), which possesses a good solubility and film forming properties without crystallization issues, has high carrier mobility characteristics for holes and electrons. Using this MH, we fabricated single emissive layer WOLEDs, which is doped with blue dye of 4,4'-bis[2-(4-(N,N-diphenylamino)phenyl)vinyl]biphenyl (DPAVBi) and red dye of 4-(dicyanomethylene)-2-t-butyl-6-(1,1,7,7-tetramethyljulolidyl-9-enyl)-4H-pyran (DCJTB). These WOLEDs show high luminance and efficiency, which are comparable to that of vacuum-deposited devices. The complexity of co-evaporation process and high costs are effectively avoided in our production process. As a consequence, solution-processing of small molecular OLEDs is expected to be a new and growing route for fabricating multi-components WOLEDs.

2. Experimental

The devices based on the MH structure were fabricated on indium tin oxide (ITO)-coated glass with the structure, ITO/PEDOT:PSS(30 nm)/EML(45 nm)/BALq(40 nm)/LiF(0.5 nm)/Al(100 nm). Poly(3,4-ethylenedioxythiophene):Poly(styrenesulfonate) (PEDOT:PSS) and bis(2-methyl-8-quinolinato)-4-phenylphenolate aluminum (BALq) were used as the hole-injection layer (HIL) and electron-transport layer (ETL), respectively. DPAVBi and DCJTB co-doped NPB:DPVBi MH was used as white EML.

For all of devices, the relative composition of two host materials and the doping concentration of DPAVBi in the EMLs were fixed at 6:4 and 4 wt.%, respectively, which were optimized in the blue devices. The devices A, B, and C have different DCJTB doping concentrations, which are 1.0 wt.%, 1.15 wt.%, and 1.3 wt.%, respectively. In the experiment, the EML materials were dissolved in chlorobenzene to prepare the solution with concentration of 14 mg/ml. The water-dispersed PEDOT:PSS mixture was spin-coated on the top of ITO substrate at a spin speed of 2000 rpm for 60 s. The PEDOT:PSS layer was baked at 120 °C for 30 min. It has a thickness of ~30 nm and acts as the HIL. The EML was then prepared on this HIL by spin coating, and then it was baked at 120 °C for 10 min. The thickness of the light emitting layer is found to be about 45 nm. After baking, the BALq layer (40 nm) and the cathode LiF (0.5 nm)/Al (100 nm) were deposited by thermal evaporation in a vacuum chamber at a pressure of 5×10^{-4} Pa, respectively. The schematic energy-level diagram of the devices is shown in Fig. 1.

Ultraviolet-visible (UV-Vis) absorption and photoluminescence (PL) spectra were measured with UV-Vis spectrophotometer (U-3010, Hitachi Inc) and fluorescence spectrophotometer (FluoroMax-4, HORIBA Jobin Yvon Inc). The film thickness was measured with an ellipsometer. The current-voltage-luminescence characteristics were measured with Keithley 2602 source meter and Luminance meter. Electroluminescence (EL) spectra and Internationale d'Eclairage (CIE) coordinates of the devices were analyzed

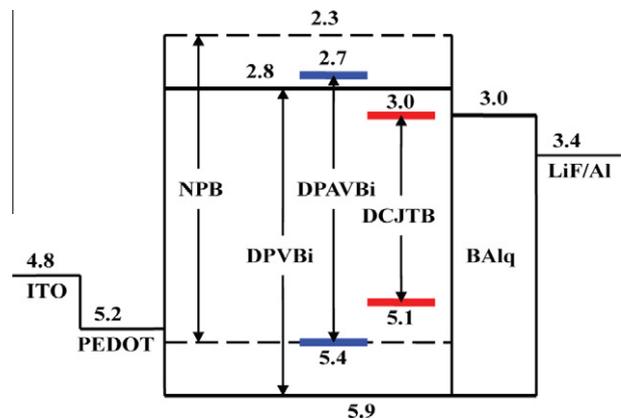


Fig. 1. Energy level diagram of the fabricated WOLED.

with a spectrometer (PR650). All measurements were carried out under ambient conditions at room temperature.

3. Results and discussion

The light emissions from the dopants in EML are known to be occurred by either energy transfer or carrier trapping [28]. In general, a significant spectral overlap of the host emission and the dopant absorption is a key requirement for the efficient energy transfer, whereas for the efficient hole or electron trapping, the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) energy levels of the dopant must fall within the energy gap of the host [29]. Fig. 2a shows the absorption spectra of DPAVBi and DCJTB in chlorobenzene solution, and PL spectra of DPVBi, NPB, and DPAVBi in films. In Fig. 2a, there is a partial spectral overlap between the fluorescent band of the MH (NPB:DPVBi) and the absorption bands of both DPAVBi and DCJTB, which indicates that the lowest singlet-excited states in the MH can be transferred to the dyes (DPAVBi or DCJTB) via Förster energy transfer. In addition, the spectra overlap between the PL of DPAVBi and the absorption of DCJTB suggests that the energy-transfer process between them can happen. Fig. 2b shows the PL spectra of the mixed NPB:DPVBi film (6:4), the DPAVBi (4 wt.%) and both DPAVBi (4 wt.%) and DCJTB (1.15 wt.%) doped films. The excitation peak wavelength was at 350 nm for all the PL measurement. In Fig. 2b, 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 wt.%. When we doped both DPAVBi (4 wt.%) and DCJTB (1.15 wt.%) in the MH, the blue and red-emitting bands are observed, which implies that the energy in the MH is shared by both dyes.

Fig. 3a shows the normalized EL spectra of devices A–C at 10 V. The EL spectra of the devices show two emission bands: a blue band from DPAVBi and a red band from DCJTB. The device with 1.0 wt.% doping concentration of DCJTB, device A, emitted bluish-white light with a strong intensity of the blue emission, while the device with 1.3 wt.% doping concentration of DCJTB, device C, yielded a yellowish-white EL spectrum. The intensity of the blue band gradually decreased with the increase of doping concentration of DCJTB. White emission was obtained in device B with 1.15 wt.% doping concentration of DCJTB. The CIE coordinates of device B biased at 10 V were (0.31, 0.39). The results demonstrate that a white emission can be realized through co-doping two fluorescent dyes into the MH in the same EML.

The normalized EL spectra of device B at different driving voltages are shown in Fig. 3b. With the increasing driving voltage, the

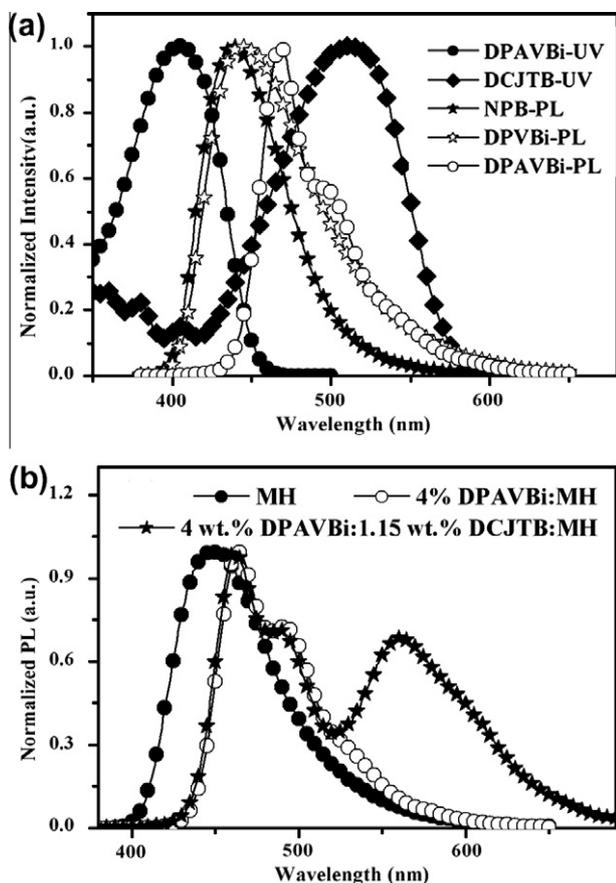


Fig. 2. (a) The absorption spectra of DPAVBi and DCJTBT in chlorobenzene solution and PL spectra of pure NPB, DPVBi and 4 wt.% DPAVBi doped into PMMA films, and (b) PL spectra of MH (NPB:DPVBi = 6:4) film, DPAVBi (4 wt.%) doped MH film, and both DPAVBi (4 wt.%) and DCJTBT (1.15 wt.%) doped MH film.

CIE coordinates shift from (0.36, 0.41) at 5 V to (0.29, 0.38) at 12 V, in which the variation of CIE coordinates is (−0.07, −0.03). Similar phenomena had been found by other authors [17,28]. For example, Hsiao et al. reported that the change of CIE coordinates in 5,6,11,12-tetraphenylnaphacene (Rubrene) doped WOLED was (−0.05, −0.05) as the luminance increased from 100 to 8000 cd/m² [28]. Wang et al. also found that the CIE coordinates of WOLED with Rubrene as dopant shifted from (0.32, 0.39) at 4 V to (0.28, 0.34) at 9 V, showing a change of (−0.04, −0.05) [17]. The blue-shift under increasing applied voltages in device B can be attributed to the carrier trapping by the DCJTBT molecules and the concentration quenching [30–32]. According to the energy level diagram of the fabricated white OLED in Fig. 1, the HOMO and the LUMO of DCJTBT are located within the energy gap of MH. Thus, the red emission has two possible excitation ways: not due to the energy transfer from MH, but from the direct recombination of injected carriers at the red dopant sites [30,33]. At low current injection, some excitons were directly formed and radiatively released on the DCJTBT through the carrier trapping mechanism, which can be confirmed through comparing the PL spectra of the EML (Fig. 2b) with the EL spectra of the device (Fig. 3b). At high current injection, in light of the fully charge-occupied DCJTBT molecules, additional excitons could be formed on the host molecules due to the saturation effect of the DCJTBT molecules [28,34]. Additionally, the concentration quenching may be another reason for the color shift due to the higher doping concentration of DCJTBT. Aggregate formation at high concentrations provides sites for non-radiative recombination, which reduce the possibility for radiative emission [32].

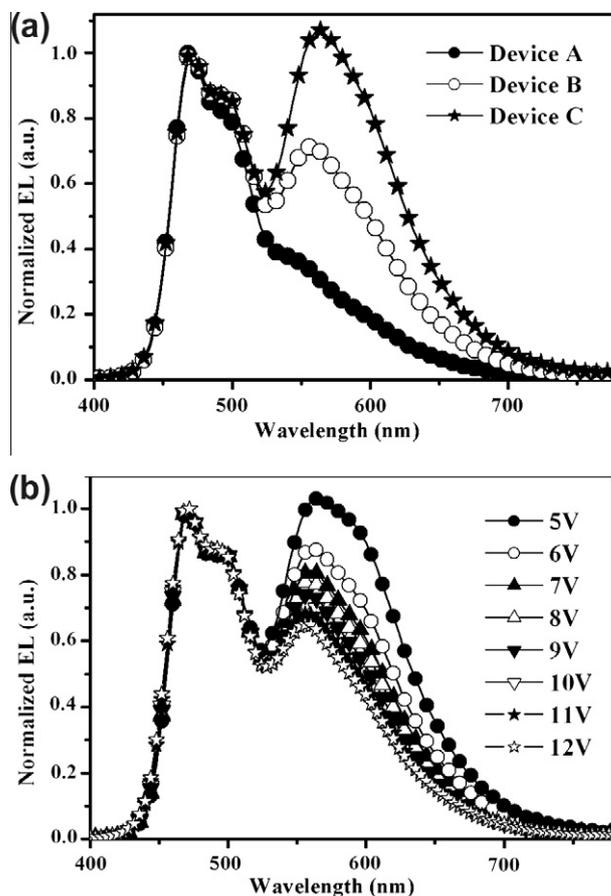


Fig. 3. (a) The normalized EL spectra of the devices A–C at 10 V and (b) normalized EL spectra of the device B at different driving voltages.

The injected charge carriers in the emission zone would be easily trapped by the dopant due to a higher concentration of DCJTBT (1.15 wt.%) throughout the EML. The recombination on the DCJTBT sites increases with increasing doping concentration. It follows that the spectra shift of WOLEDs is very sensitive to the doping concentration of DCJTBT [28,32,34]. The current-induced color shift can be improved by using a lightly doped EML [32]. Lin et al. reported color stable WOLEDs by utilizing double-EML structure with different doping concentration of DCJTBT [32], in which the concentrations of DCJTBT in EML1 and EML2 were 0.05 wt.% and 0.2 wt.%, respectively. This graded doping structure greatly confined the number of carriers trapping on DCJTBT molecules at the interface and controlled the current-induced fluorescence quenching.

Fig. 4 shows the current density-voltage, luminance-voltage and current efficiency-voltage characteristics of devices A–C. It can be seen from Fig. 4a that the operation voltage significantly increases with the concentration of DCJTBT doping. The strong DCJTBT concentration dependence of the current–voltage characteristics indicates that the DCJTBT molecules dispersed in the MH play the role of charge carrier trapping sites in the processes of EL [35]. It can be seen from Fig. 4b that the devices A–C had quite similar luminance–voltage characteristics. The maximum luminances of the devices A–C are 13,755 cd/m², 13,638 cd/m², and 14,838 cd/m², respectively. In Fig. 4c, the current efficiency increases with the concentration of DCJTBT doping. As we can see, the peak current efficiencies of devices A, B and C achieved are 5.6 cd/A, 5.7 cd/A, and 6.2 cd/A, respectively. In comparison with previously reported WOLEDs based on the fluorescent dyes as dopants, the efficiency of device B was comparable to that of the vacuum-deposited WOLEDs [16,36–37]. For example, Khan et al. reported p-bis(p,N,N-diphenyl-amino-styryl)benzene (DSA-Ph) and DCJTBT doped multilayer

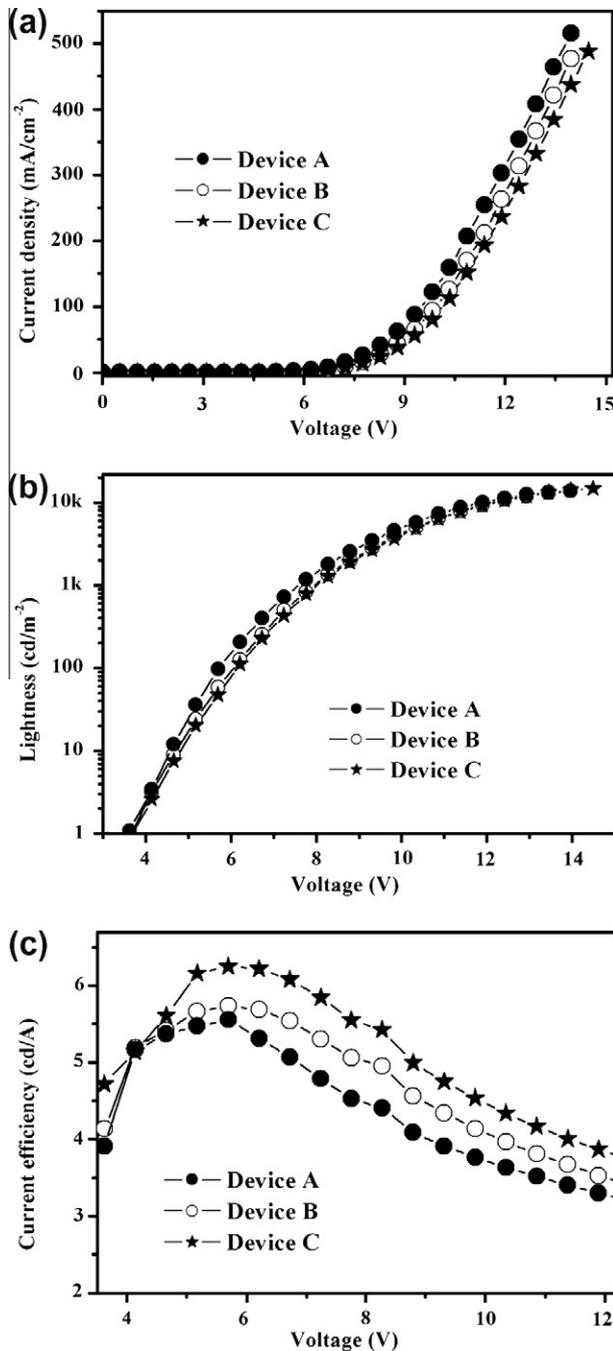


Fig. 4. (a) The current density-voltage, (b) luminance-voltage, and (c) current efficiency-voltage characteristics of the devices A–C.

WOLED with a maximum current efficiency of 5.6 cd/A at 200 mA/cm² [36]. Jiang et al. obtained 2,5,8,11-tetra-butylperylene (TBPe) and DCJTb co-doped single EML WOLED with efficiencies of 6.0 cd/A and 3.1 lm/W [37]. In addition, the performances of our devices were better than that of solution-processed WOLEDs with MH structure based on the DPAVBi and Rubrene as dopants (3.85 cd/A) [38].

These results demonstrate that WOLEDs can be realized through solution-processed small molecular emitting layer, 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.

4. Conclusion

We fabricated a white light-emitting device with a solution-processed single emission layer composing a small molecular MH of NPB and DPVBi by co-doping DPAVBi and DCJTb into the MH. The device exhibited a maximum luminance of 13,638 cd/m² and a current efficiency of 5.7 cd/A. This work provided an alternative route to the fabrication of small-molecular WOLEDs, reducing the cost of devices and avoiding the complicated co-evaporation of multiple dopants and host materials in the vacuum deposition.

Acknowledgements

This work was supported by the Scientific Research Foundation of Nanjing University of Posts and Telecommunications (No. NY211025), and the Project Funded by the Priority Academic Program Development (PAPD) of Jiangsu Higher Education Institutions.

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