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Letter

All-small-molecule efficient white organic light-emitting diodes by multi-layer blade coating

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ABSTRACT

Blue and white small-molecule organic light-emitting diodes are fabricated by multi-layer blade coating on hot plate at 80 °C with hot wind. Uniform multi-layer structures are made without dissolution due to rapid drying. Only small molecules originally developed for vacuum deposition are used. For hole transport layer of, 4′,4″-tris(carbazol-9-yl)triphenylamine (TCTA), electron transport layer of 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TBPI), emissive layer host of, 6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine (26DCzPPy), triplet emitters of bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium(III) (FIrpic), and cathode of LiF/Al, the peak current efficiency for blue emission is 25.1 cd/A (10.8% and 9.3 lm/W). Orange emitter iridium(III)bis (4-(4-t-butylphenyl) thieno[3,2-c]pyridinato-N,C2′)acetylacetonate (PO-01-TB) is added to obtain white emission with CIE coordinate of (0.39, 0.46) [1]. The current efficiency is 34.2 cd/A (11.6% and 12 lm/W) at maximum, 32.4 cd/A at 1000 cd/m^2, and 31 cd/A at 10,000 cd/m^2.

1. Introduction

Vacuum-deposited small-molecule white organic light-emitting diode (OLED) with multi-layer structures shows very high efficiency and is considered as an emerging technology for general solid-state lighting. Using a high-mobility electron transport layer, white OLED with a current efficiency of 53 cd/A and a power efficiency of 44 lm/W at the luminance of 1000 cd/m^2 was recently demonstrated [2]. With enhanced out-coupling by optical design white OLED with power efficiency over 100 lm/W is reached [3]. The obstacle for the general application of OLED lighting is no longer the efficiency but the high cost of the vacuum deposition process itself. There is a great effort to replace the vacuum deposition by the low-cost solution process for efficient white OLED. However, in most of the related works only the emission layer was solution processed, and the electron transport layer was still deposited by vacuum evaporation. This is mainly because of the difficulty of dissolution in solution deposition. In particular, efficiency over 20 cd/A is obtained by evaporating the common electron transport molecule 2,2′,2″-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBI) on top of the emissive layer [4,5]. The white emission layer is usually consisted of a high-triplet-energy host for exciton confinement and two iridium complexes as dopant emitters. The TPBI evaporation becomes the bottleneck for the fabrication cost. All-solution processed white OLED using polymer host without electron transport layer has been reported to show efficiency of 41.7 cd/A and 16.8 lm/W [6]. The relatively unstable barium cathode is used in order to enable sufficient electron injection without the electron transport layer. In general highly water-absorbing materials like CsF or Li salt doping are necessary for easy electron injection into the

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emission layer for efficient blue OLED with polymer host without electron transport layer [7,8]. Compared with the stable LiF/Al cathode commonly used for vacuum-deposited OLED, such reactive cathodes pose a stability problem. Furthermore, small molecules have the intrinsic advantage over polymer of easy purification and absence of variation due to molecular weight distribution. So far there is no report on efficient all solution-processed white OLED using only small molecules.

Unlike vacuum deposition, multi-layer fabrication has been a challenge for solution deposition [9–11]. In this work we use blade coating to deposit multi-layer OLED structure with hole-transport, emissive, as well as electron transport layers.

Dissolution problem between the layers is avoided in blade coating by rapid blade motion and short drying time [12,13]. Only small molecules are used for the entire structure. Due to the lack of molecular entanglement many small molecules do not form uniform film by spin coating. Blade coating gives uniform film for most of the small molecular semiconductors with almost no material waste. Because of the presence of electron-transport layer, stable LiF/Al cathode can be used.

Using a small molecule host with bi-polar carrier transport and high triplet exciton level [14], blue emission with peak current efficiency of 25.1 cd/A is obtained. By adding an orange emitter white emission with peak current efficiency of 34.2 cd/A corresponding to 12 lm/W is reached [1]. The current efficiency remains over 30 cd/A for luminance up to 10,000 cd/m^2. The hole transport and electron transport molecules are both common ones for vacuum deposition. This result demonstrates that the high-performance white and blue OLED can be made entirely of common small molecules, originally designed for vacuum evaporation, based on the multi-layer blade coating method.

2. Experimental

The OLED devices are fabricated on the glass substrates with patterned indium-tin oxide (ITO) layer. The ITO glass is cleaned in acetone and then exposed to UV–ozone for 15 min. The 40 nm hole injection layer of poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate) (PEDOT:PSS CLEVIOS™ P VP AI 4083) is spin coated and annealed at 200 °C for 15 min. The substrates are then taken into a nitrogen glove-box. We use the TCTA as the hole transporting layer. TCTA is dissolved in toluene then blade-spin coated at 2000 rpm [15] on the PEDOT:PSS layer, followed by annealing at 100 °C for 10 min in vacuum environment (10^{-3} torr) to remove the residual solvent. The resulting TCTA film thickness is 40 nm. We also use the di-[4-(N,N-ditolyl-amino)-phenyl] cyclohexane (TAPC) as the hole transport material. TAPC is dissolved in toluene then blade-spin coated at 2000 rpm on the PEDOT:PSS layer, followed by annealing at 80 °C for 10 min in vacuum environment (10^{-3} torr) to remove the residual solvent. The resulting TAPC film thickness is 40 nm. The subsequent emission and electron transport layers are deposited by blade coating on hot plate without spinning. The hot plate is at 80 °C for rapid drying [12,16]. The blade has a gap of 60 μm. The solution of 30 μl is delivered in front of the blade by a pipette, the blade is then moved by hand at about 40 cm/s to cover the 4 mm^2 active area of the device by the wet film. Hot wind from a hair dryer is applied to enhance the drying and uniformity. Dry films forms in about a second before dissolution could happen. The multi-layer structure can be simply verified by the sharp edge of the first layer after the blade coating of the second layer. If the film was not dried quickly enough the edge would be blurred. To fabricate the blue devices, poly(N-vinylcarbazole) (PVK) and 2,6-bis(3-(9H-carbazol-9-yl)phenyl)pyridine (26DCzPPy) were used as host with bis(3,5-difluoro-2-(2-pyridyl)phenyl-(2-carboxypyridyl)iridium(III) (FIrpic) as the blue dopant for the EML. The weight blending ratios of the materials are 26DCzPPy:FIrpic = 89:11 and PVK:OXD-7:FIrpic = 69:21:10. The blend solution in chlorobenzene with total solid concentration of 1.6 wt.% is blade coated with 60 μm gap. Before blade motion 20 μl of solution is delivered by a pipette near the blade gap. The substrate is on a hot plate at 80 °C with hot wind applied from the top. The thickness of the resulting solid EML film is 50–60 nm. The EML film is then annealed at 80 °C for 10 min in nitrogen environment. White OLED can be made by adding a small amount of orange emitter iridium(III)bis (4-(4-t-butylphenyl) thieno[3,2-c]pyridinato-N,C2′)acetylacetonate (PO-01-TB) to the blue emission layer. The white color can be tuned from cold white for the ratio of 40:1 for FIrpic to PO-01-TB to warm white for the ratio of 30:1. The electron transporting layer 2,2′,2″(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBI) dissolved in methanol is blade coated on the emission layer with the thickness of 40 nm. The LiF (0.8 nm)/Al (100 nm) cathode is formed by the thermal evaporation under vacuum at the pressure of 5×10^{-6} torr. The electroluminescence characteristics of the devices are measured with Keithley 2400 and PR650 Spectroscan spectrometer. The Commission internationale de l'éclairage (CIE) coordinates of the white OLEDs are calculated with the PR650 software. All the measurements are carried out in ambient air after packaging. All small molecules are purchased from Luminescence Technology except for PO-01-TB.

3. Results and discussion

The energy levels and chemical structures of the molecules are shown in Fig. 1. The triplet exciton energy for FIrpic, 26DCzppy, and PVK are 2.65 eV, 2.71 eV, and 2.5 eV, respectively [14,17]. Because of the higher triplet energy level than the blue Emitter FIrpic, the host 26DCzppy has triplet exciton confinement which prevents the energy transfer to the host. On the other hand the common polymer host PVK does not have the triplet exciton confinement. OXD-7 is for electron transport in PVK host and has a triplet exciton energy of 2.7 eV [18]. 26DCzppy is reported to have a balanced electron and hole mobility, i.e. bipolar transport [14]. TCTA and TAPC both simultaneously act as the hole transport and electron blocking material. TPBI acts as the electron transport and hole blocking material. PO-01-TB is the orange emitter. Note all the molecules in the tri-layer structure is deposited in solution by blade coating.

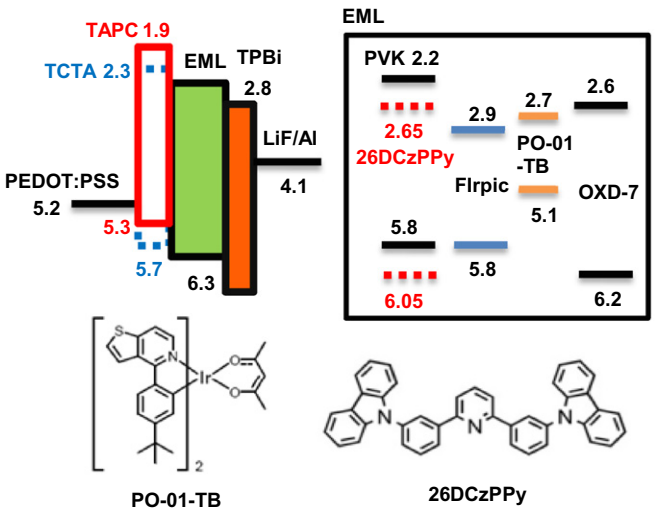

Fig. 1. The energy diagrams in this study and the chemical structures of the used materials.

The results for blue OLED are shown in Fig. 2(a) and (b). The hosts of pure 26DCzppy and PVK blended with OXD-7 are compared. For the same hole transport and electron transport layers of TCTA and TPBI, respectively, device with 26DCzppy have efficiency about three times of the device with PVK host, apparently due to the lack of triplet confinement in PVK. The effect of the emission layer thickness is shown in Fig. 2(c) and (d) in the range of 30–60 nm for 26DCzppy host. As expected the current density and luminance are reduced as the thickness increases. The reduced efficiency in thinner emission layer suggests that the carrier blocking is not complete, therefore as the emission layer is thinner than the recombination zone some recombination takes place in the blocking layers and the energy is wasted. For 60 nm emissive layer the highest current efficiency is 25.1 cd/A, corresponding to external quantum efficiency of 10.8% and power efficiency of 9.3 lm/W. Remarkably the current efficiency remains over 20 cd/A when the luminance is up to 10,000 cd/m^2. Note that in contrary to the reports on solution-processed emis-

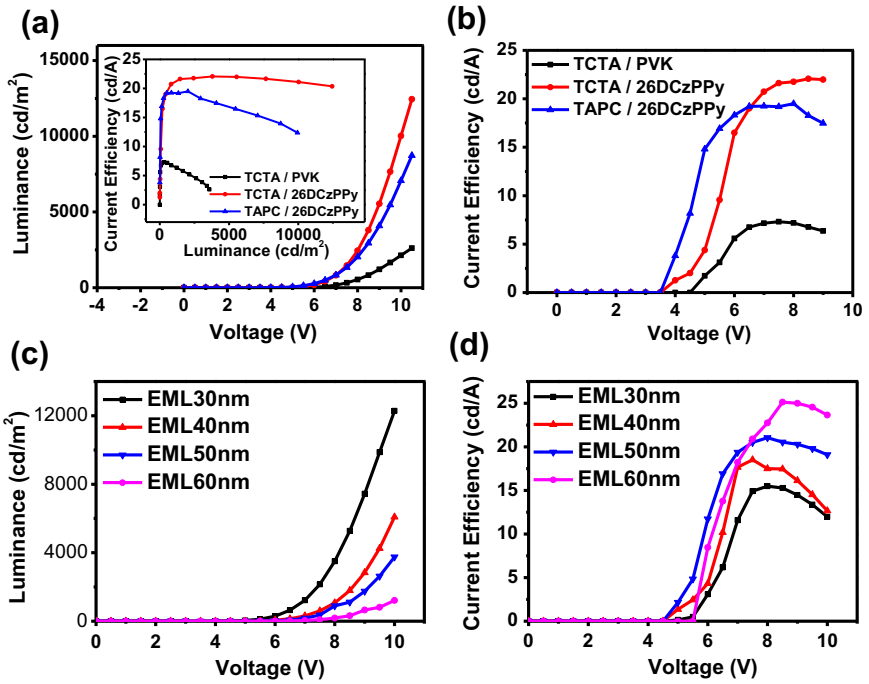

Fig. 2. The (a) luminance and (b) efficiency of the blue emission OLEDs with different hole transport materials and different host materials. The inset of (a) shows the luminance–voltage (*L*–*V*) characteristics of the devices with different hole transport materials and different host materials. The (c) luminance and (d) efficiency of the white emission OLEDs with different emission layer thicknesses.

sion layer with evaporated TPBI [3,4], here the entire structure is fabricated by blade coating including TPBI.

White OLED can be made by adding a small amount of orange emitter to the blue emission layer such that some portion of recombination takes place in the orange emitters. When the weight ratio of the blue emitter FIrpic and orange emitter PO-01-TB is fixed at 40:1, the effect of emission layer host material is shown in Fig. 3(a) and (b). Similar to the case of blue devices, the small molecule host 26DCzppy has a much higher efficiency than the polymer host PVK blended with OXD-7.

This demonstrates the general superiority of small molecules over polymers as long as they can be solution processed. The peak current efficiency of 31.2 cd/A, corresponding to 10.7% and 9.7 lm/W, is achieved. As the case of blue devices, the typical efficiency roll-off is not strong here and the efficiency remains over 30 cd/A up to luminance of 10,000 cd/m^2 as shown in Fig. 4(a). This is probably due to the relatively thick emission layer which give a wide recombination zone and lower average exciton density, as the roll-off mainly results from the triplet–triplet annihilation. The two hole transport layer TCTA and TAPC are compared in Fig. 3(c) and (d). TAPC has slightly lower turn-on voltage and higher peak power efficiency perhaps due to the lower hole injection barrier from PEDOT:PSS as shown in Fig. 1. TAPC has a low glass transition temperature of 78 °C, whereas the glass transition temperature of TCTA is 151 °C [19]. The device variation for TAPC is much larger than TCTA probably due to crystallization in the subsequent annealing process. Finally the color of the white emission can be tuned from cold white for the ratio 40:1 for FIrpic and PO-01-TB to warm white for the ratio of 30:1. The spectra are shown in Fig. 4(b) with CIE color coordinate indicated. For 30:1 device the peak current efficiency is 34.2 cd/A (11.6% and 12 lm/W).

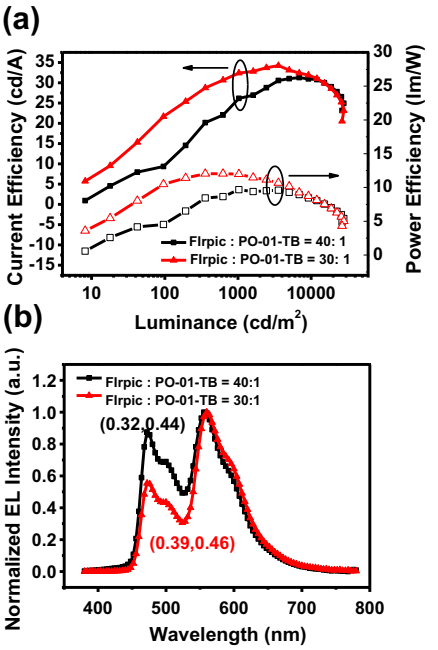

Fig. 4. (a) The performance of the WOLEDs with different ratios of FIrpic and PO-01-TB. (b) The spectrum of the WOLEDs. Cold white for the ratio 40:1 for FIrpic and PO-01-TB. Warm white for the ratio of 30:1. TCTA was used as the hole transport material.

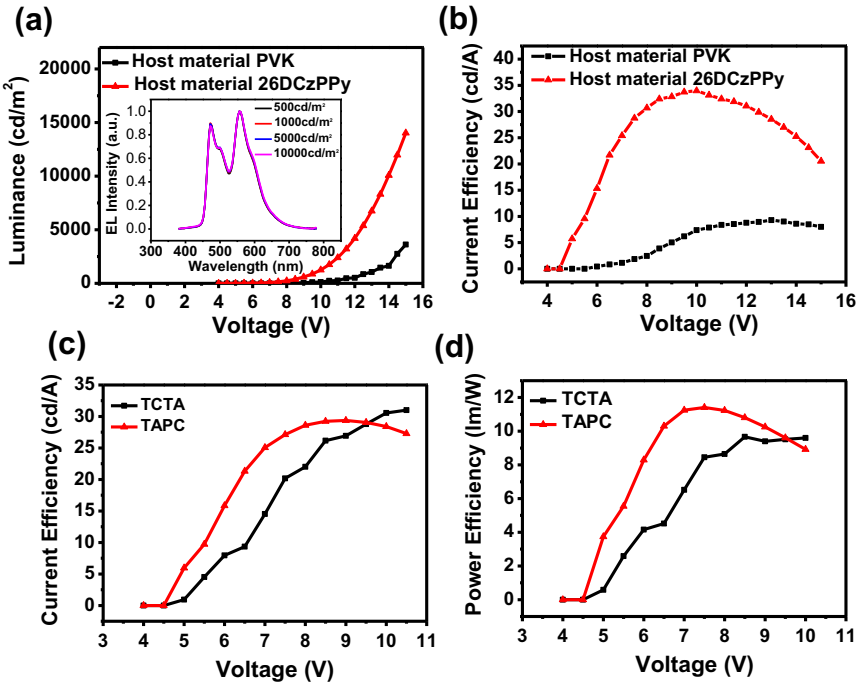

Fig. 3. The (a) luminance and (b) efficiency of the white emission OLEDs with different host materials. The inset of (a) shows the spectrum of the WOLEDs with different luminance. The (c) current efficiency and (d) power efficiency of the WOLEDs with different hole transport materials.

4. Conclusion

In conclusion, blade coating method is used to fabricate multi-layer blue and white phosphorescent OLED using only small molecules originally designed for vacuum evaporation. In particular, the host for the emissive layer has high triplet level for exciton confinement. The hole transport, electron transport, and the cathode materials are all the ones commonly used for evaporation. High current efficiency of 25 cd/A for blue and 34 cd/A for white emission are obtained. The performance is much better than the device with polymer host, demonstrating the superiority of small molecules for solution process to polymers in solid-state lighting once blade coating is employed.

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