

Solution-processed small molecular electron transport layer for multilayer polymer light-emitting diodes

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ARTICLE INFO

Article history:

Received 27 July 2010

Received in revised form

15 December 2010

Accepted 16 December 2010

Available online 15 January 2011

Keywords:

Blade coating

Solution-processed electron transport layers

ABSTRACT

Solution-processed electron transport layers (ETL) have been fabricated by solution process and applied in multilayer polymer light-emitting diodes with tris[2-(p-tolyl)pyridine]iridium(III) blended in poly(vinylcarbazole) as the emissive layer. Three kinds of small molecular electron transport materials, including 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi), 3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (TAZ), and 4,7-diphenyl-1,10-phenanthroline (BPhen), are tested and dissolved in methanol to form electron transport layers by blade coating. Such electron transport layer provides efficient electron injection and electron transport ability in the devices. The efficiency of the devices with the combination of ETL and LiF/Al cathode reaches 21.5 cd/A at 10 V (4050 cd/m²). The efficiency of the devices without ETL are 3.5 cd/A (13 V) for LiF/Al cathode and 17 cd/A (7 V) for CsF/Al cathode at 1000 cd/m². The aggregation of the solution-processed ETL can be controlled by annealing temperature to further optimize the device performance to maximal efficiency of 53 cd/A.

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1. Introduction

Recently the development of polymer light-emitting diodes (PLED) focuses on enhancing the device efficiency and operating lifetime by multilayer device structure [1–4]. In the multilayer PLED, electron transport layer (ETL) plays an important role which can provide efficient electron transport, reduce the potential barrier between the emission layer (EML) and the cathode, and prevent the cathode quenching effect by hole-blocking. Concerning the fabrication of PLED, solution process is low-cost and is more competitive than the high-cost thermal evaporation. Despite of some reports about solution-processed PLED, the dissolution problem between layers still exists in common solution-processed multilayer PLED. Therefore the ETL needs to be deposited by thermal evaporation [5–8]. In addition, if there is no ETL the device needs low work function or unstable cathodes, like Ca, Ba, or CsF/Al. That is one of the reasons why the lifetime of PLED is less than that of small molecular organic light-emitting diodes. The cathode LiF/Al, which is commonly used in small molecular organic light-emitting diodes, is known to be more stable than the low work function cath-

odes in PLED. Up to date there is no polymer electron transport materials for solution-processed PLED. There is no study to apply common small molecular electron transport materials by solution process either [9]. In this report, we demonstrate the performance of solution-processed PLED including the ETL is comparable to the one prepared by conventional vacuum deposition. All solution-processed multilayer PLED in this work is fabricated by blade coating method [10–12]. Three common small molecular electron transport materials, including 2,2',2''-(1,3,5-benzinetriyl)-tris(1-phenyl-1-H-benzimidazole) (TPBi), 3-(4-biphenyl)-4-phenyl-5-(4-tert-butylphenyl)-1,2,4-triazole (TAZ), and 4,7-diphenyl-1,10-phenanthroline (BPhen), are dissolved in methanol, and the ETL can be formed by blade coating method. Methanol is a very weak solvent to the emissive layer and the dissolution problem between ETL and EML is solved. We find that these solution-processed small molecular ETLs would provide efficient electron injection and transport ability although they may have the tendency to form aggregates. The small molecular ETLs can be optimized and the aggregation can be controlled by the annealing temperature and environment. Some ETLs also provide hole-blocking effect with proper energy level compared with the emissive layer and enhance the device performance. As a result, high efficiency of multilayer PLED can be achieved by applying the solution-processed small molecular ETL and LiF/Al cathode.

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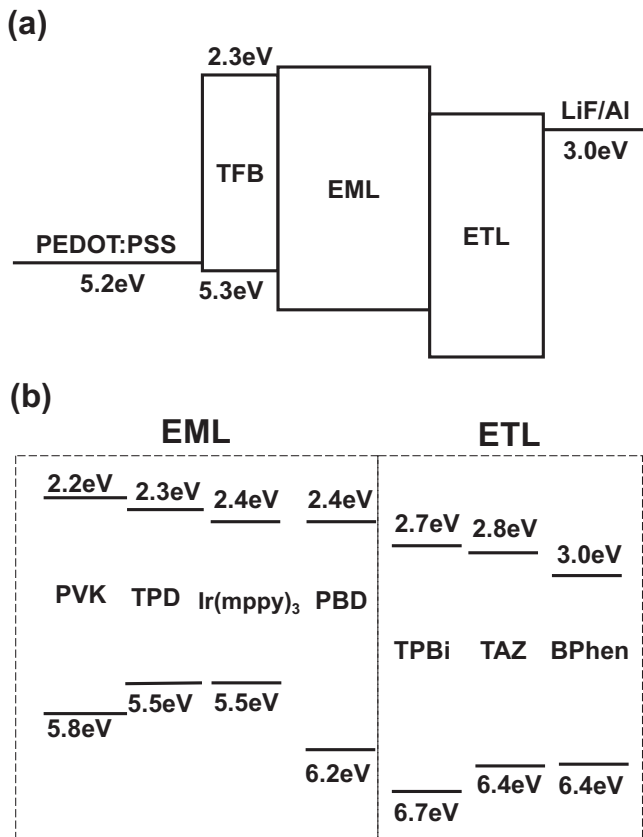


Fig. 1. (a) Schematic energy profile of the multilayer device structure design in this work. (b) Energy level of the materials. The numbers are in eV.

2. Experimental

In this work multilayer devices with three kinds of ETL, including TPBi, TAZ, Bphen, are fabricated. Large indium-tin-oxide (ITO) substrate (7 cm × 8 cm) is used in order to use blade coater. After loading polymer solution in blade coater, the coater is moved in constant speed and a polymer film is formed behind the coater. The ITO substrate is cleaned in the ultrasonic cleaner with detergent for 15 min, then exposed in UV ozone cleaner for 20 min. Poly(3,4-ethylenedioxythiophene):poly(styrenesulfonate) (PEDOT:PSS, CLEVIOS™ P VP Al 4083) is spin-coated on the cleaned ITO substrate as the hole injection layer and annealed in 200 °C for 15 min. Poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-sec-butylphenyl)diphenylamine))] (TFB, purchased from American Dye Source) dissolved in toluene with 1 wt% is blade coated on PEDOT:PSS layer as the hole transport layer and then annealed at 180 °C for 40 min to remove the residual solvent, finally spin-rinsed by toluene to remove dissolvable part [13]. As to the emissive layer, we blend tris[2-(p-tolyl)pyridine]iridium(III) (Ir(mppy)₃, purchased from Luminescence Technology Corp.), N,N'-bis(3-methylphenyl)-N,N'-bis(phenyl)-benzidine (TPD, purchased from Luminescence Technology Corp.), 2-(4-Biphenyl)-5-(4-tert-butylphenyl)-1,3,4-oxadiazole (PBD, purchased from Luminescence Technology Corp.) into poly(vinylcarbazole) (PVK, $M_w = 1,100,000$, purchased from Aldrich) with the ratio 6:9:24:61 in chlorobenzene [14], and form a 60 nm thin film by blade coating. The emissive layer is then annealed at 80 °C for 60 min. For ETL, TPBi, TAZ, and BPhen are dissolved in methanol with 0.5 wt%, and then form a 15 nm thin film by blade coating, and then annealed 50 °C for 10 min. For TPBi layer three anneal temperatures, 25 °C, 100 °C, 150 °C, are also tested to optimize the device performance. The methanol solution of ETL is loaded in blade coater, then the

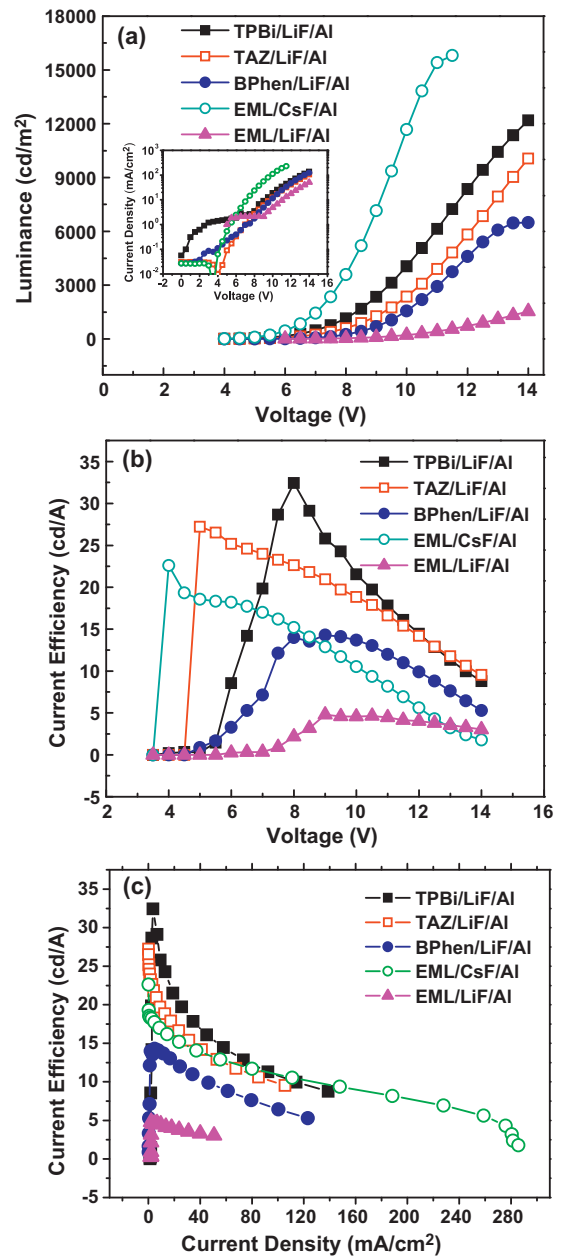


Fig. 2. Device performance of the devices with ETLs, including TPBi (solid square), TAZ (empty square), BPhen (solid circle) with LiF/Al cathode, and device performance without ETL with CsF/Al cathode (empty circle) and LiF/Al (solid triangle). (a) The luminance. Inset is the current density. (b) The current efficiency. (c) The current efficiency vs current density.

coater is moved in constant speed. After the methanol evaporation, ETL is formed behind the coater. Finally, LiF(1 nm)/Al(100 nm) are thermal evaporated on the ETL as the cathode. In order to further discuss the effects of solution-processed ETL, two devices with the cathode of LiF/Al and CsF(2 nm)/Al(100 nm) and without ETL are also made for comparison. Fig. 1(a) shows the schematic energy diagram of the multilayer device. The highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) of materials in this work are listed in Fig. 1(b). All the devices are encapsulated in the glove box with oxygen/humidity level less than 5 ppm. The electroluminescence (EL) spectra and current–luminance–voltage (I–L–V) characteristics are measured by a Photo Research PR650 spectrophotometer integrated with Keithley 2400 multi-meter. In order to study the crystallization

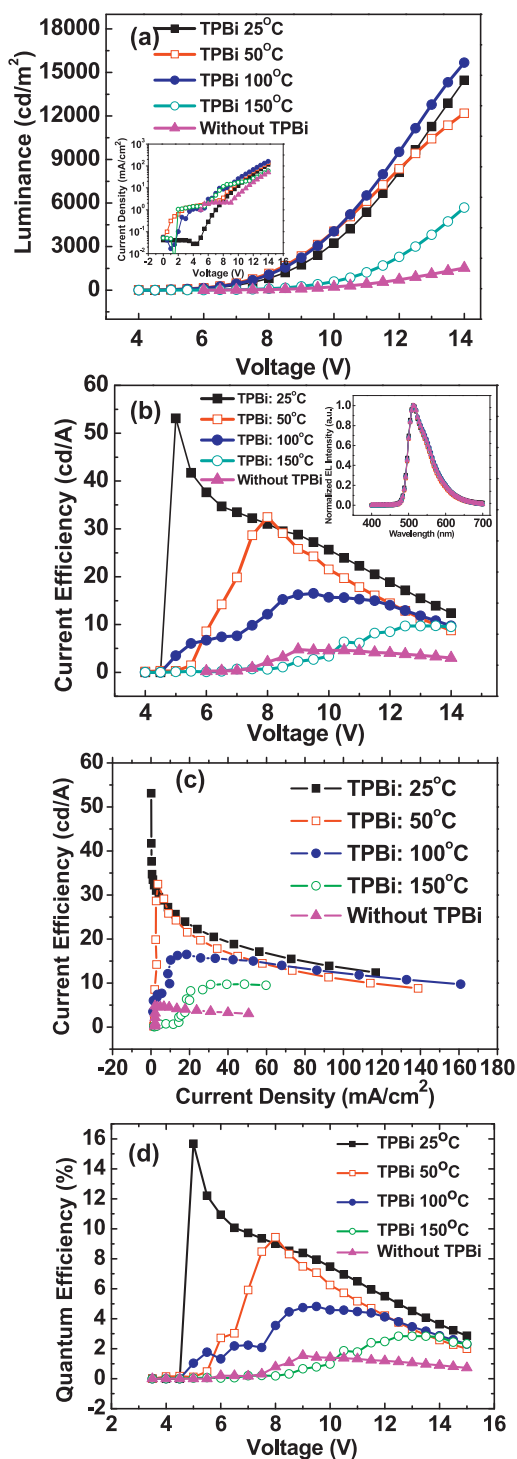


Fig. 3. Device performance of TPBi annealed with different annealing temperatures, 25 °C (solid square), 50 °C (empty square), 100 °C (solid circle), and 150 °C (empty circle). Performance of the device without TPBi is indicated by solid triangle. (a) The luminance. Inset is the current density. (b) The current efficiency. Inset is the electroluminescent spectra. (c) The current efficiency vs current density. (d) Quantum efficiency.

the thin films are observed by grazing incident X-ray diffraction (GI-XRD, MAC Science SRA-M18XHF).

3. Results and discussion

Fig. 2 shows the results of multilayer devices with and without ETL. The current efficiency of the devices with solution-processed

TPBi, TAZ, BPhen reaches values of 21.5 cd/A, 18.8 cd/A, 13.7 cd/A at 10 V respectively. The efficiency of the device without ETL is 10.5 cd/A for CsF/Al and 4.6 cd/A for LiF/Al cathode at 10 V. From the J - V relation of the devices with the same cathode of LiF/Al, the current density of the devices with ETL is larger than that without ETL, indicating the solution-processed ETLs can provide efficient electron injection and electron transport ability. Therefore the device performance, including efficiency, luminance, and current density can be enhanced dramatically. Comparing with the devices with ETL/LiF/Al and CsF/Al, the current density and the luminance of the devices with ETL/LiF/Al are less than that with CsF/Al, but the efficiency of the devices with ETL of TPBi and TAZ are higher. This indicates that the ETL/LiF/Al may not provide as efficient electron injection as CsF/Al does, but the ETL in the devices also have hole-blocking effect, thus enhancing the device efficiency by balancing the electron and hole current. Comparing the current efficiency of the devices with ETL, device with TPBi shows better performance which may results from that TPBi has proper energy level (HOMO: 6.7 eV, LUMO: 2.7 eV) [15]. The HOMO of TAZ and BPhen are only 6.4 eV, which cannot provide enough hole blocking barrier [16,17]. The difference in ETL's LUMO is not much therefore we attribute the enhancement in device efficiency mainly to ETL's hole blocking ability. TPBi can provide not only good electron transport ability but also good hole blocking effect. According to the atomic force microscopy images of TPBi (Fig. 4(b)), TAZ (Fig. 4(f)), and BPhen (Fig. 4(g)), significant morphology difference can be observed between these three electron-transporting layers. Small aggregates can be observed in TAZ film, while pinholes can be observed in BPhen film. These may result from the poor solubilities of TAZ and BPhen in methanol. Film of TPBi is the most uniform one without aggregates and pinholes, and hence TPBi film has the best hole blocking ability among these three electron-transporting materials. Based on this result we further optimize the solution-processed TPBi layer by different annealing temperatures. The devices performances of solution-processed TPBi layer with different annealing temperatures, 25 °C (room temperature), 50 °C for 10 min, 100 °C for 10 min and 150 °C for 10 min, are shown in Fig. 3. As can be seen the current efficiency decreases as the annealing temperature increases larger than 50 °C. The peak efficiency reaches 53 cd/A with the annealing temperature of 25 °C. The efficiencies at 10 V are 25.7 cd/A for 25 °C, 21.5 cd/A for 50 °C, 15.7 cd/A for 100 °C, 3.3 cd/A for 150 °C. From the J - V relation, the current density increases with as the annealing temperature increases, but drops dramatically when the temperature reaches 150 °C, which is higher than the glass temperature of TPBi. For further understanding, the microscopic surface morphologies of solution-processed TPBi with different annealing temperatures are checked by AFM and the crystallization properties are checked by GI-XRD, shown in Fig. 4. The EML and TPBi layer deposited by thermal evaporation are also compared. For thermal evaporated TPBi, the roughness is 1.0 nm which is the same as EML's. For solution-processed TPBi, the roughness are 1.7 nm for annealing at 25 °C, 3.1 nm for 50 °C, 4.5 nm for 100 °C, 30.1 nm for 150 °C. For solution-processed TAZ and BPhen annealed at 50 °C, the roughness are 1.3 nm and 1.7 nm, respectively. The surface of emissive layer prepared by blade coating is flat with roughness about 1.0 nm, and hence the roughness of solution-processed TPBi is not related to the underlayer. Since the solvent of TPBi is methanol which is a weak solvent to EML, the interface between EML and ETL should have minimum dissolution. The roughness of solution-processed TPBi annealed at 25 °C is about the same as the evaporated one. As the annealing temperature increases the roughness increases, indicating the TPBi layer starts to form aggregates. The large aggregates would be formed and the roughness increases dramatically when the annealing temperature is higher than the glass temperature of TPBi (124 °C). Before 100 °C, small aggregates would be formed

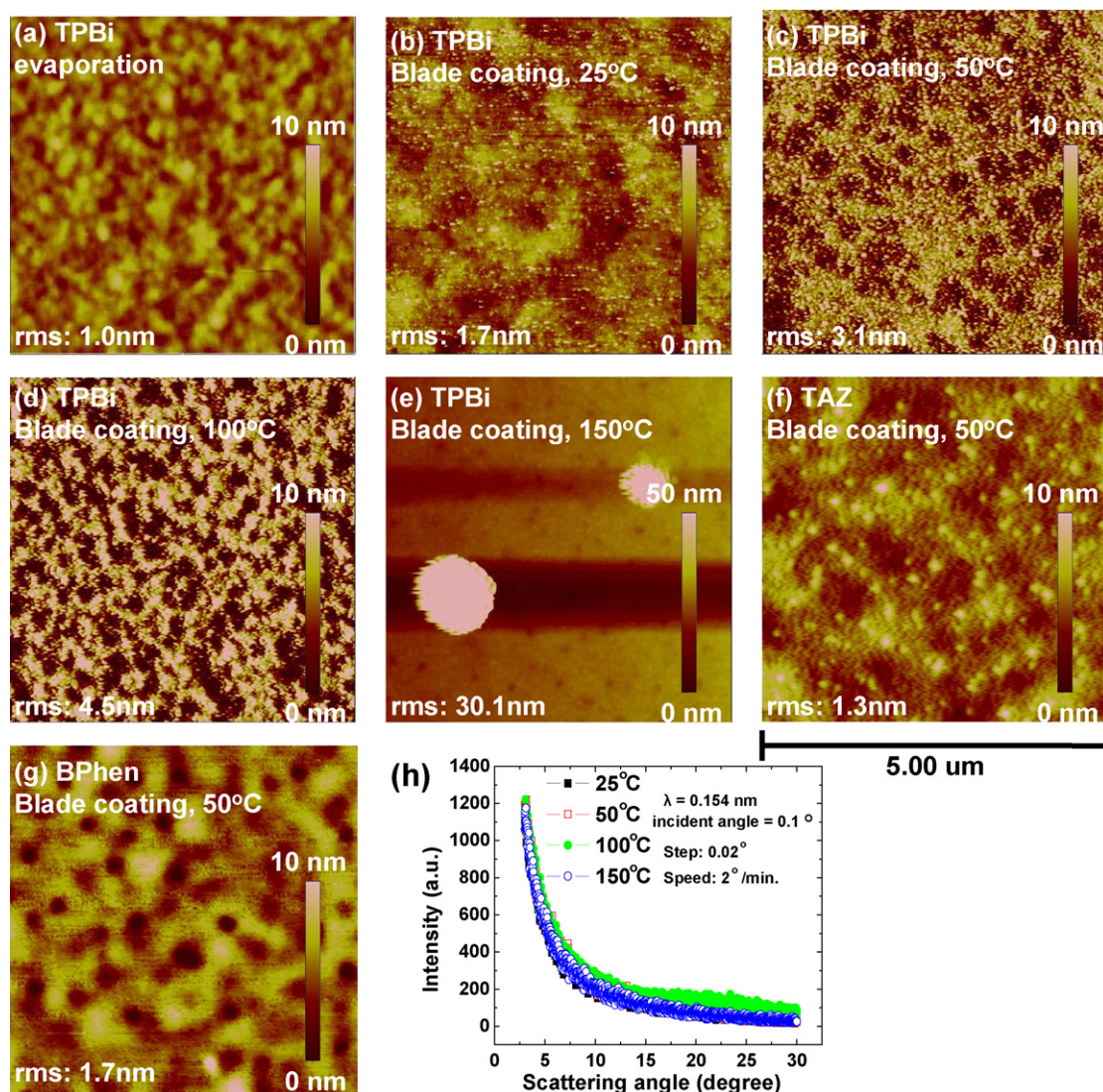


Fig. 4. AFM images of ETLs. The surface morphology of TPBi in different conditions, including (a) thermal vacuum evaporated film of TPBi, (b) solution-processed TPBi annealed at 25 °C (room temperature), (c) solution-processed TPBi annealed at 50 °C for 10 min, (d) solution-processed TPBi annealed at 100 °C for 10 min, (e) solution-processed TPBi annealed at 150 °C (higher than T_g of TPBi) for 10 min. (f) AFM image of solution-processed TAZ annealed at 50 °C. (g) AFM image of solution-processed BPhen annealed at 50 °C. (h) GI-XRD of samples treated with different temperatures.

and the interface between TPBi and the cathode would increase as the annealing temperature increases. This would enhance the amount of electron injection, resulting in high current density. The device efficiency starts to decrease but luminance remains about the same at the annealing temperature of 100 °C, indicating that the TPBi layer provides too much electron current but could not block hole current efficiently. When the annealing temperature reaches 150 °C, we speculate most TPBi molecules start to move and form the large aggregates and leaves other regions only with very thin layers, which cannot provide electron injection. Therefore the performance of the device with TPBi annealed at 150 °C is very close to that of the device without TPBi layer but only LiF/Al cathode. This speculation is confirmed by GI-XRD shown in Fig. 4(h) which demonstrates no crystallization. We believe that only aggregates are formed under the anneal temperature before the glass temperature (124 °C), thus providing efficient electron injection and good device performance.

4. Conclusions

In summary we prove the feasibility of common small molecular ETL by solution process. The electron transport materials can be

dissolved in methanol and form ETL by blade coating. By controlling the annealing temperature, the aggregation of ETL can be prevented and the solution-processed ETL provides efficient electron injection and transport ability. Such method provides an opportunity to fabricate the high-efficiency multilayer organic light-emitting diodes with easy solution process at low cost.

Acknowledgement

This work is supported by the National Science Council of Taiwan under grant number NSC97-3114-M-009-002 and NSC97-2628-M-009-016.

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