Study of All Solution Processed Exciplex Organic Light-Emitting Diode

Juewen Zhao, Youchao Huang, Jing Guo, Ning Zhang, Caijun Zheng, Xiaoyang Du, Hui Lin and Silu Tao*

School of Optoelectronic Science and Engineering, University of Electronic Science and Technology of China (UESTC), Chengdu, China

*Corresponding author e-mail: silutao@uestc.edu.cn

Abstract. Organic light-emitting diodes (OLEDs) are widely used in full-color display panels, fluorescent tubes and solid-state lighting devices. In recent years, due to the material utilization yield of the vacuum deposition method is very low and maintaining a high vacuum further increases the fabrication cost and complexity, solution processing method has become a research hotspot. However, the development of solution-processed OLEDs has a great challenge in multilayer structure formation and nearly all prior reports on solution-processed OLEDs were utilizing a vacuum deposited electron-transport layer (ETL). Therefore, it is of great significance to further research on all solution-processed OLEDs whose ETL were spin-coated. In this paper, spin-coated ETL based OLED with high current efficiency that comparable with vacuum deposited ETL based OLED were successfully achieved.

1. Introduction
Organic light-emitting diodes (OLEDs) are widely used in full-color display panels, fluorescent tubes and solid-state lighting devices [1-3]. In recent years, it has become a research hotspot due to it’s excellent performance. Generally, there are two approaches to fabricate OLEDs devices: for small molecules, the appropriate method is vapor deposition under vacuum; for polymeric materials, solution process is a feasible method [4-6]. The vapor deposition method has excellent performance in manufacturing multilayer OLED devices. However, vacuum deposition has certain disadvantages such as low material utilization, complicated manufacturing process and high cost, which limit its further application. The solution process has the advantages of simple processing, less material consumption and low manufacturing cost whereas the device performances of the solution-processed OLEDs are still inferior to those of vacuum-deposited OLEDs [7-13]. Therefore, it is of great significance to further improve the performance of solution-processed OLEDs to reduce the manufacturing cost of devices and promote the development of OLED.

As an important component of OLED devices, the electron transport layer not only benefits the electron transport, reduces the electron injection barrier, but also effectively blocks the holes, limits the excitons moving to the emitting layer and thus improves the efficiency of devices [14; 15]. However, the development of solution-processed OLEDs has a great challenge in multilayer structure formation because the solvent used to deposit the subsequent layer tends to dissolve the underlying layer. Furthermore, most of electron transport materials own poor solubility. Thus, nearly all prior reports on
solution-processed OLEDs are multilayered structures that include a vacuum deposited electron-transport layer, without realizing the full solution process [16]. Therefore, further research on the all-solution method is of great significance for the development of OLED.

In this paper, in order to solve the two problems abovementioned, the polymer material PVK was selected as a hole transport layer to ensure that it will not be dissolved by the next layer, and a small molecular material PO-T2T with good film forming property and alcohol solubility is selected as an electron transport layer to ensure sufficient solubility. At the same time, PVK and PO-T2T serve as an electron donor and electron acceptor to form an interface exciplex to emit[17-24]. Because of its TADF characteristics, the exciplex can theoretically achieve 100% IQE, and has the advantages of low lighting voltage and low efficiency roll-off[25]. All-solution OLED with device performance almost comparable to that of the vapor deposition method is realized [26; 27]. Thus, an all-solution processed OLED of comparable performance to vapor deposition processed is realized.

2. Experimental Section

Device Fabrication and Characterization: 135 nm-thick indium-tin oxide (ITO)-coated glass substrates with a sheet resistance of 15 Ω sq⁻¹ were washed with detergent, deionized water, acetone, and ethanol in turn. After dried in an oven at 120 °C for over 2 h and then treated with ultraviolet-ozone for 30 min, under ambient atmosphere, filtered (0.45 μm Poly tetra fluoroethylene membrane) PEDOT:PSS (BAYTRON ®P VP CH 4083) was spun coated to make a 30 nm hole-injection layer onto a ITO glass and annealed at 120 °C for 30 min to remove residual water. In a nitrogen atmosphere glove-box containing less than 10 ppm oxygen and moisture, an EML was spun coated from chlorobenzene solution to make a about 30 nm EML on top of the PEDOT:PSS layer and annealed at 95 °C for 20 min to remove residual solvent. For all solution based devices, 50 nm PO-T2T was spun coated from isopropanol solution on top of the EML layer and annealed at 125 °C for 70 min to remove residual solvent. 50 nm of PO-T2T, 1 nm of LiF and 100 nm of aluminium were thermally evaporated in high vacuum (10⁻⁶ mbar) at the rates of 1.0, 0.1 and 10.0 Å s⁻¹, respectively. Through the multiple sensor system in the evaporation device, the evaporation rates of the film of all the materials were surveyed by quartz crystals. The voltage and current were measured by a computer-controlled Keithley 2400 source meter. The luminance characteristics were measured with a Spectrascan PR655 photometer under ambient atmosphere. CE and PE of the devices were calculated using the measured luminance, current, voltage and its lighting area. The EQE of the device was calculated from the current density, luminance, and EL spectrum, assuming a Lambertian distribution.

3. Organization of the Text

In order to prepare an organic electroluminescent device based on the all-solution method with excellent performance, the spin-coating of the electron transport layer material must have good film-forming properties, and the solvent used cannot dissolve the film of the previous layer. Since most light-emitting materials are currently small molecule materials, these materials have a certain solubility in alcohol solvents. Therefore, spin coating on small molecules using an alcohol solvent is not feasible. However, we found that after adding a certain proportion of water to the alcohol solvent, the previous film will not be affected. Through research, we found that PO-T2T can be well dissolved in methanol, ethanol, isopropanol, and their water mixed solutions. As shown in Fig.s 1a-f, we conducted a preliminary study on the film-forming properties of these solvents. It can be found that the film formation characteristics are not very good after adding water. Therefore, although the addition of water will not affect the previous film, the film-forming properties of PO-T2T are not particularly good. Therefore, spin-coated electron transport materials directly on small molecules need further study. In this paper, we selected PVK, a polymer material with poor solubility in alcohol solvents, as the emitting layer (EML), and prepared methanol, ethanol, and isopropanol spin-coated devices and vacuum-evaporated devices. Solution processed OLEDs were investigated with the configuration (Fig. 2) of: indium tin oxide (ITO)/poly(ethyleneoxythiphene):poly(styrenesulfonate) (PEDOT:PSS) (30 nm)/PVK (35 nm)/PO-T2T (55 nm)/lithium fluoride (LiF) (0.8 nm)/aluminum (Al) (80 nm). The maximum current efficiency
(CE) of vacuum-evaporated device is 15 cd A⁻¹. Based on methanol, ethanol, isopropanol aldehyde solution method devices, the maximum CE are below 2 cd A⁻¹.

Figure 1. spin-coated films with (a) methanol; (b) ethanol; (c) isopropanol; (a) methanol:water; (b) ethanol:water; (c) isopropanol:water; as solvents; (g) current efficiency of vacuum deposited PO-T2T device and spin-coated PO-T2T using methanol, ethanol and isopropanol as solvents.

In these three solvents, the all-solution method device based on isopropanol not only exhibited good film-forming characteristics, but also obtained relatively good device efficiency. Therefore, we further optimized the all-solution method based on isopropanol. By adjusting the thickness, annealing temperature and annealing time of the spin-coated PO-T2T, the optimized device efficiency results are shown in Fig. 3. The current density-voltage-luminance (J-V-L) characteristics are shown in Fig. 3c. Devices using spin-coated PO-T2T as ETL shows turn-on voltage (Von, estimated at the brightness of 1 cd m⁻²) of 3.5 V. As shown in Fig. 3d, spin-coated PO-T2T based device exhibits the same green Electroluminescent (EL) emission as vacuum deposited PO-T2T based device with maximum intensity peak at 540 nm, respectively. As shown in Fig. 3 and listed in Table 1, the spin-coated PO-T2T based devices deliver maximum efficiencies of 15.0 cd A⁻¹ for CE, 7.0 lm W⁻¹ for power efficiency (PE) and 4.8% for external quantum efficiency (EQE).

Figure 2. Structure of vacuum deposited and spin-coated PO-T2T based devices.
In general, all-solution devices can achieve the same efficiency and emission wavelength as vacuum evaporation. However, the lighting voltage of the all-solution method device is slightly higher, and there is leakage current at low voltage. This may be because the hole and electron transport of the interfacial exciplex is not well balanced. Therefore, we further doped PO-T2T into PVK to make bulk exciplex device. The device results are shown in Fig. 3 and Table 1. The turn on voltage of the bulk exciplex based device decreased to 2.9 V because the PO-T2T in the EML decreased the hole injection barrier. As shown in Fig. 3b, bulk exciplex based device exhibits the same green EL emission with maximum intensity peak at 540 nm. As shown in Fig. 4 and listed in Table 1, the bulk exciplex based device delivers maximum EQE of 3.1%. It can be seen that the turn-on voltage of the bulk exciplex device has decreased, and the leakage current has disappeared under low voltage. However, the maximum efficiency of the device has decreased, which may be because the small molecular materials in the EML are dissolved by the isopropanol, which affects the film-forming property of the EML.

**Figure 3.** (a) CE and PE; (b) EQE; (c) J-V-L; (d) EL spectrum; of optimized spin-coated PO-T2T based device.

**Table 1.** Summary of device data.

| Device           | \(V_{on}\) [V] | CE [cd A\(^{-1}\)] | PE [lm W\(^{-1}\)] | EQE [%] | \(\lambda_{EL}\) [nm] | Max. luminance [cd m\(^{-2}\)] |
|------------------|-----------------|---------------------|---------------------|---------|-----------------------|-------------------------------|
| Evaporation      | 3.1             | 16.7                | 15.0                | 5.23    | 540                   | 115                           |
| Solution-Processed | 3.5           | 15.0                | 7.00                | 4.75    | 540                   | 2210                          |
| Mixed (5:5)      | 2.9             | 9.95                | 5.22                | 3.09    | 540                   | 5190                          |
Figure 4. (a) CE and PE; (b) EQE; (c) J-V-L; (d) EL spectrum; of optimized spin-coated PO-T2T based device.

4. Conclusion
In conclusion, all solution processed exciplex OLED that using spin coated ETL was achieved. By adjusting the thickness, annealing temperature and annealing time of the spin-coated PO-T2T, the optimized device deliver maximum efficiencies of 15.0 cd A$^{-1}$ for CE, 7.0 lm W$^{-1}$ for PE and 4.8% for EQE. These results are comparable to the vacuum deposited ETL based OLED. The outstanding feature presented here can provide us with a good reference for future design of all solution processed exciplex OLEDs.

Acknowledgments
This work was financially supported by the National Natural Science Foundation of China (NSFC Grant Nos. 61775029 and 51533005), “Science Fund for Distinguished Young Scholars of Sichuan Province (No.2015JQ0006), “the Fundamental Research Funds for the Central Universities (ZYGX2016Z010 and ZYGX2015J048).

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