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High-efficiency blue multilayer polymer light-emitting diode based on poly(9,9-dioctylfluorene)

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A highly efficient blue polymer light-emitting diode based exclusively on commercial poly(9,9-dioctylfluorene) and poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-s-butylphenyl))diphenylamine)] is demonstrated. High electroluminescent efficiency is achieved by enhancing electron currents and making devices in multilayered structures. CsF/Al is used as the efficient electron injection cathode, and the fabrication process is in the glove box to enhance electron mobility by reducing oxygen adsorption. The multilayer structure is prepared by the liquid buffer layer technique. The maximum efficiency is 2.5 cd/A at deep blue with the corresponding external quantum efficiency of 2%. © 2007 American Institute of Physics. [DOI: [10.1063/1.2721830](https://doi.org/10.1063/1.2721830)]

I. INTRODUCTION

Conjugated polymer light-emitting diodes (PLED) have generated a great deal of interest due to their easy solution process, potentially high emission efficiency, and many optoelectronic applications.¹ Therefore, they are viewed as the material of light-weight large-area flat panel display for the next generation. One promising method for display application is using the white PLED combined with color filters. For this purpose highly efficient blue PLED is essential, because one can achieve white PLED through energy transfer by using the blue emitters as the host and red/green emitter as the dopants.^{2,3} Efficient blue PLED still remains a challenge due to their large band gap and difficulty in the charge balance. Much effort has been made to improve PLED efficiency by molecular or device structure designs.⁴⁻⁶ The highest efficiency of deep blue PLED until now is approximately 3 cd/A; however, the materials are of an unusually high molecular weight and purity.^{7,8} In addition, these proprietary blue polymers are either commercially unavailable or with unknown chemical structures. Commercial blue emitter polyfluorene (PF) and its derivatives are of great potential because of their high photoluminescence quantum efficiency at deep blue, excellent chemical and thermal stability, and more importantly the ease to synthesize in large volume with moderate molecular weight and purity.⁹⁻¹² However, they still suffer from low electroluminescence (EL) efficiency and poor color stability attributed to the formation of excimer due to liquid crystalline behavior and ketone defect in the presence of oxygen.^{13,14} Among all the PF derivative poly(9,9-dioctylfluorene) (PFO) is the archetype. The effi-

ciency of PFO-based PLED achieves 1.96 cd/A at low luminance by carefully removing the low molecular weight part of the material, which is not easy to apply.¹⁵ The low EL efficiency of PFO and other commercial PF derivatives indicates the imbalance of charge carriers.¹⁶ The electron current is more critical than hole current because most blue polymers have a higher hole mobility. It will be a great advance for the large-scale application of PLED if a device structure and fabrication procedure can be discovered to realize high-efficiency and high-luminance blue emission based exclusively on commercial PF derivatives by improving the electron current and charge balance. In this work, we significantly enhance the performance of PFO LED using the combination of three approaches to control the charge balance: Cathode with excellent electron injection,¹⁷ improving the electron mobility by reducing the oxygen adsorption in the glove box,¹⁸ and the addition of a hole transport layer by the liquid-buffer method.¹⁹ The resulting deep blue LED has an efficiency of 2.5 cd/A with external quantum efficiency (EQE) at 2%. Such performance is already close to the results using high molecular weight and high purity proprietary polymers. This paper is organized as follows: Section II discusses the device preparation. In Sec. III we discuss the results. Section IV draws the conclusion.

II. DEVICE STRUCTURES

Six bipolar devices and two electron-only devices are fabricated. The hole transport and emissive polymers are spin-coated in air for some devices and in the glove box for other devices. For bipolar devices made in air, A is (ITO/PEDOT:PSS/PFO/LiF/Ca/Al), B is (ITO/PEDOT:PSS/TFB/PFO/LiF/Ca/Al), C is (ITO/PEDOT:PSS/PFO/CsF/Al), and D is (ITO/PEDOT:PSS/TFB/PFO/

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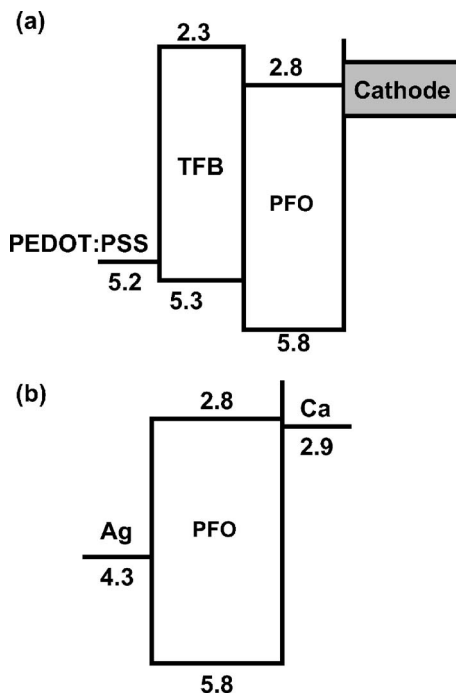


FIG. 1. Schematic electronic energy profile for the (a) double-layer device structure and (b) the electron-only device structure. The numbers are in eV.

CsF/Al). For bipolar devices made in the glove box, E is (ITO/PEDOT:PSS/PFO/CsF/Al), and F is (ITO/PEDOT:PSS/TFB/PFO/CsF/Al). For electron-only devices, G is (Ag/PEDOT:PSS/PFO/Ca/Al) made in the air and H is (Ag/PEDOT:PSS/PFO/Ca/Al) made in the glove box. ITO is indium tin oxide and PEDOT:PSS is poly-(3,4-ethylenedioxythiophene):poly-(styrenesulfonate). PFO is chosen to be the emission material due to its high PL quantum efficiency (40%). TFB is poly[(9,9-dioctylfluorenyl-2,7-diyl)-co-(4,4'-(N-(4-s-butylphenyl))diphenylamine)] used as the hole-transport layer (HTL), as well as the electron-blocking layer (EBL). TFB (Mw=197 000) and PFO (Mw=71 000) are both purchased from American Dye Source and used without further purification. Figure 1(a) shows the electronic energy profiles for the bilayer structure as well as the electron affinity (EA) and ionization potential (IP) of the polymers. The electronic energy profile for the electron-only device is shown in Fig. 1(b). The PEDOT:PSS layer is spin-coated on a patterned ITO substrate and baked at 200 °C in a vacuum (10^{-3} Torr) for 5 min. TFB dissolved in toluene is spin-coated to make a 30 nm thin film and then baked at 180 °C in a vacuum (10^{-3} Torr) for 40 min to remove the solvent. PFO is also dissolved in toluene and then spin-coated to make a 70 nm thin film for bilayer devices (devices B, D, and F) and 90 nm for single layer devices (devices A, C, E, G, and H). To prevent dissolution in the bilayer structure, a liquid buffer 1,2-propylene glycol, is used between TFB and PFO layer.¹⁹ For the bilayer structure, the PFO layer is baked in a vacuum (10^{-3} Torr) at 120 °C for 1 h to remove the residual glycol and organic solvent. For a single layer structure, the PFO layer is baked for 40 min. Two kinds of cathodes are chosen: LiF/Ca/Al and CsF/Al. The thickness is 2 nm for both LiF and CsF, 35 nm for Ca and 100 nm for Al. All the devices are packaged in the glove box. The

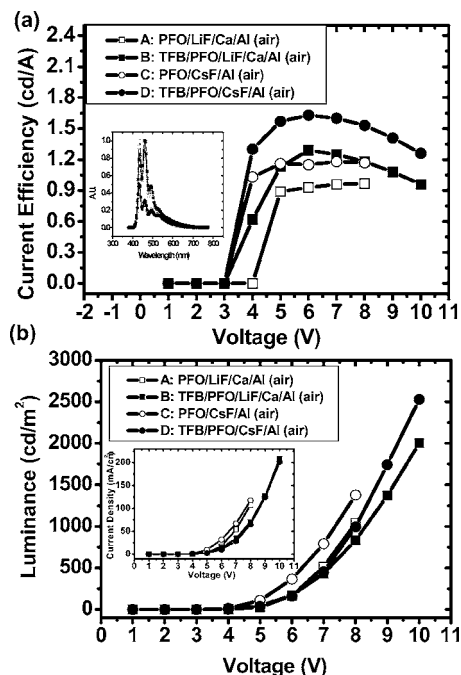


FIG. 2. The performances of blue PLED fabricated in air: Device A (open square), device B (solid square), device C (open circle), and device D (solid circle). (a) The current efficiency. Inset are the EL spectra. (b) The luminance. Inset are the current density.

film thickness is measured by the Kosaka ET4000 Surface Profiler. The EL efficiency is measured by the Photo Research PR650 spectrophotometer integrated with Keithley 2400 multimeter. The PL efficiency is measured by an integrating sphere system. IP is measured by cyclic voltammetry and EA is calculated by the IP plus band gap determined by the ultraviolet absorption spectrum.

III. PLED PERFORMANCES AND DISCUSSION

Figure 2 shows the results of devices A–D, and compares the cathodes LiF/Ca/Al and CsF/Al in single layer and bilayer structures. For single layer devices, the maximum efficiency is 0.96 cd/A for device A with LiF and 1.29 cd/A for device C with CsF. Both Cs and Li are believed to be liberated at the organic-metal interface during evaporation.²⁰ The work function of Cs (2.1 eV) is lower than Li (2.5 eV) and, therefore, more efficient electron injection is provided by the CsF/Al cathode. That is why the efficiency and luminance of device A are higher than those of device C. Despite the small electron mobility, the ohmic contact at the CsF cathode seems to make the single layer devices electron-dominated as the current is largely contributed by the cathode. For TFB/PFO bilayer devices, a better charge balance compared to single layer devices is achieved. The efficiency of the bilayer PLED are 1.29 cd/A for device B with LiF and 1.63 cd/A for device D with CsF. The advantages of adding the TFB layer are fourfold. First, TFB play the role of HTL because of the high hole mobility and the IP of TFB at 5.3 eV between PEDOT:PSS (5.2 eV) and PFO (5.8 eV). Holes can be injected and transported to the PFO layer more easily. Second, TFB is also EBL due to its lower EA (2.3 eV) than PFO (2.8 eV). Electrons injected and

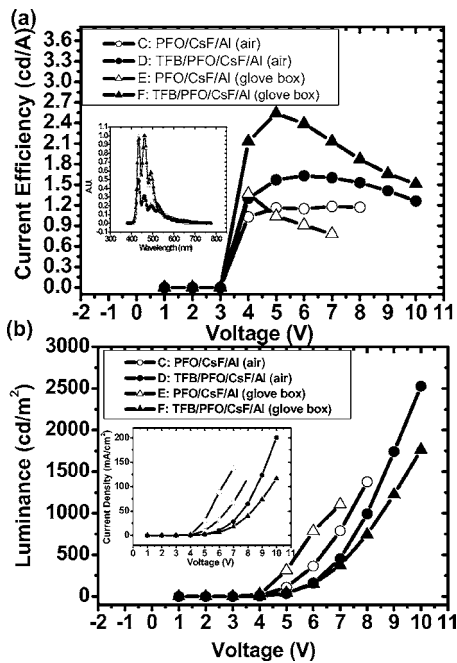


FIG. 3. The performances of blue PLED with CsF/Al cathode: Device C (open circle), device D (solid circle), device E (open triangle), and device F (solid triangle). (a) The current efficiency. Inset are the EL spectra. (b) The luminance. Inset is the current density.

transported in PFO are blocked by the TFB layer instead of reaching the anode. Third, the recombination is shifted away from the cathode and concentrate near the TFB/PFO interface to reduce quenching by liberated Cs atoms. Forth, the TFB layer prevents the degradation of the PFO layer by the acid PEDOT:PSS.²¹ The maximum luminance is 1038 cd/m² (8 V) for device A and 2001 cd/m² (10 V) for device B, 1377 cd/m² (8 V) for device C, and 2528 cd/m² (10 V) for device D. The currents of bilayer devices are smaller than those of single layer devices because the electron current is blocked by the TFB layer. The spectra of the four devices shown in Fig. 2 are similar; a slight difference in the green shoulder may reflect the various recombination zones where the ketone defect levels differ. The CsF/Al cathode is clearly superior to LiF/Ca/Al presumably due to a more efficient electron injection. In addition to injection, electron mobility is also important to the electron current. One way to enhance the electron mobility is to reduce the oxygen adsorption by polymer because oxygen would cause electron traps.^{16,18} For this purpose, we compare the polymer spin-coated in air and in the glove box with the oxygen level about 1 ppm. Figure 3 shows the results of devices C–F, to compare single layer and bilayer structures with a CsF/Al cathode. Compared with the single-layer device C in air, the maximum efficiency of the device E in the glove box is slightly enhanced from 1.18 cd/A (7 V) to 1.37 cd/A (4 V). However, the efficiency decreases rapidly at higher voltages, probably because without oxygen adsorption the electron current rises too much. Due to the HTL, the bilayer devices are likely to be hole dominated so the enhancement of electron mobility by coating the glove box is expected to have a more pronounced effect than single-layer devices. The current of bilayer device F is smaller than that of single-layer device E, indicating that

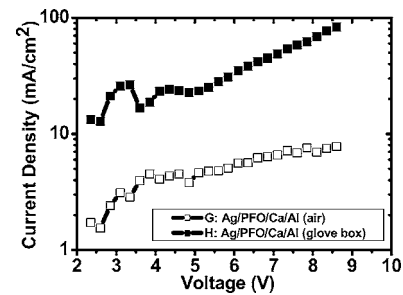


FIG. 4. Comparison of electron currents of devices fabricated in air and in the glove box for device G (air, open square) and device H (glove box, solid square).

electron blocking by TFB. Oxygen reduces the current in single-layer devices (C vs E) but enhances the bilayer devices (D vs F). This might be due to another competing effect of electron traps near the anode which cause a dipole layer and help the hole injection through the large barrier.^{22,23} The spectra for the devices made in the glove box are similar to those made in the air, also shown in Fig. 3. Among all devices, the best is F with both bilayer structure and spin-coating in the glove box. Its peak luminance of 1760 cd/m² and peak current efficiency 2.5 cd/A, corresponding to EQE of 2% at deep blue with Commission Internationale de L'Eclairage (CIE) coordinate at (0.15, 0.14). The efficiency is not far from the best proprietary polymers^{7,8} and is quite remarkable for polyfluorene with low molecular weight ($M_w=71\,000$) and moderate purity (metal purity=14.2 ppm). In fact, such polymers are usually considered as models for scientific inquiry rather than practical applications. These results demonstrate that with the proper design of the device structure and fabrication procedure, large-scale application can be realized using commonly available polymers which are easy to synthesize and does not need to satisfy strict material specifications.

Finally, in order to confirm the effect of oxygen on electron mobility, two electron-only devices are made, device G in air and device H in the glove box. The result is shown in Fig. 4. The electron current of device H is about one order of magnitude higher than that of device G, which is consistent with our assumption of electron trapping effect of oxygen. Electron mobility is fitted using the space-charge-limited current voltage-current relation $J_{SCLC} = \frac{9}{8} \epsilon \mu_e [(V - V_{bi})^2 / L^3]$. J is the current density, ϵ is the permittivity of the polymer, μ_e is the electron mobility, V is driving voltage, V_{bi} is the built-in voltage, and L is the polymer thickness. The fitted electron mobility is 5×10^{-7} cm²/V s in air and 5×10^{-6} cm²/V s in the glove box, both of them smaller than the hole mobility of around 10^{-5} cm²/V s.^{24,25}

IV. CONCLUSION

In conclusion, we demonstrate a highly efficient PLED based on commercial easy-to-synthesize PFO in a bilayer structure using the general liquid buffer method. CsF/Al is used to be the cathode for efficient electron injection. The polymer is spin-coated in the glove box to enhance the electron mobility. The efficiency reaches 2.5 cd/A (EQE 2%) for CIE coordinate (0.15, 0.14) in the deep blue. This perfor-

mance is approaching the high-molecular and high-purity proprietary polymers which are difficult to synthesize. Our result suggests that the material cost problem can be solved in large-scale PLED applications.

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