

Enhanced Performance in Polymer Light-Emitting Diodes (PLEDs) by Using Water Soluble Conjugation Polymer

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Organic and polymeric materials have generated interest in recent year for their potential applications in flat panel displays, such as TVs, monitors, and mobile displays, due to their wide viewing angle, fast response time, and low operating voltage with high external quantum efficiency. A well-balanced charge injection leads to an increase in the external quantum efficiency in polymer-based light-emitting diodes (PLEDs). This can be achieved by forming a multi-layer structure in device fabrication and considering the charge mobility, the ionization potentials and the electron affinities of the organic materials, and the work functions of the metal electrodes.^{1,2} When taking the hole favor property in most conjugated polymers into consideration, it is important to introduce electron injection and transport layers for more balanced charge injection into the emission zone. The electron injection can be enhanced by using a metal cathode with a low work function, such as Ca or ionic compounds like LiF or CsF.^{3,4} However, active metals like Ca are known to diffuse into the organic layer due to the strong electric field inside the device, which forms quenching sites in the emission layer near the cathode.⁵ Brown *et al.*⁶ announced that ionic compounds could also be partially ionized and migrate into the emission layer. In fact, the multilayer structure with selected electron injection and transport layers can enhance the device performance by not only reducing the electron injection barrier and controlling the electron mobility but also preventing the migration of metals or ionic compounds into the emission layer. In general, most conjugated polymers are soluble in common organic solvents, which cause difficulty for fabrication of multilayer polymer films. During the last decade, considerable research efforts have been carried out on multilayer PLEDs to enhance the device performance to make them suitable for practical use. Lee *et al.*⁷ introduced an ionomer layer next to the emitting polymer for electron injection and a hole blocking layer, which lowered the operating voltage by up to 60%. Niu *et al.*⁸ reported that the use of neutral surfactants blended with poly(ethylene glycol) as an electron injection layer with an Al cathode could improve the current efficiency to almost twice that of Ca/Al cathode. Recently, Tseng *et al.*⁹ showed a general method to solution-process multilayer PLEDs by using an intermediate liquid buffer between polymer layers. Several papers have also reported the enhancement of electron injection by using ion-con-

ducting polymer,¹⁰ cross-linkable inter-layers,¹¹ and water/methanol-soluble copolymers.¹² In spite of those improvements in multilayer PLEDs fabrication, however, it is true that we still need more materials for effective hole blocking and electron injection with an easy process. In this study, we synthesized new types of water soluble conjugated polymer and showed enhanced performance on the multi-layered polymer light-emitting diodes (PLEDs) by introducing the water soluble conjugated polymer FPQ as an electron transport layer between the emitting polymer and the cathode metal. The device performances with and without water soluble polymer layer will be compared in terms of the current-voltage characteristics, the luminance, and the external quantum efficiencies.

Materials and Measurement

In this study, the probe-emissive material, MEH-PPV, was purchased from American Dye Source, and the water soluble polymer FPQ were synthesized as described in Figure 1. 2,7-Dibromofluorene, 1,6-dibromohexane, 1,4-benzenediboronic acid bis(pinacol) ester and trimethyl amine were purchased from Aldrich, and used without further purification.

Synthesis of 2,7-Dibromo-9,9-bis(6''-bromohexyl)-fluorene. 9.72 g of 2,7-dibromofluorene and 0.96 g of tetrabutylammoniumbromide were dissolved in 100 mL of 1,6-dibromohexane and 30 mL of a 45% KOH solution was then injected under nitrogen. The solution was stirred at 75 °C for 1 h. The reaction mixture was extracted with 300 mL dichloromethane and the resulting solution was evaporated. The reaction mixture was distilled under vacuum, to remove the 1,6-dibromohexane. The reaction mixture was purified by column chromatography using hexane and dichloromethane. The final product was a white solid, produced in 73% yield. ¹H-NMR (CDCl₃, 400 MHz) δ 7.49-7.43 (m, 6H), 2.18-2.14 (m, 4H), 1.97-1.93 (m, 4H), 1.45-1.40 (m, 4H), 1.26-1.20 (m, 4H), 0.60-0.57 (m, 4H).

Synthesis of Poly(9,9''-bis(6''-bromohexyl)fluorene-co-alt-1,4-phenylene). 2,7-Dibromo-9,9-bis(6''-bromohexyl)-fluorene (325 mg, 0.5 mmol), 1,4-benzenediboronic acid bis(pinacol) ester (165 mg, 0.5 mmol), Pd(PPh₃)₄ (10 mg) were dissolved in 20 mL of toluene under nitrogen and 10 mL 2 M Na₂CO₃ was added. The mixture was refluxed at

85 °C for 24 h, and then precipitated into methanol. The polymer was filtered and washed with methanol and acetone, and then dried under vacuum. ¹H-NMR (CDCl₃, 400 MHz) δ 7.8-7.5 (m, 10H), 3.3 (t, 4H), 2.2 (m, 4H), 1.8 (m, 4H), 1.3-1.2 (m, 8H).

Synthesis of Poly(9,9-bis(6'-N,N,N-trimethylammoniumhexyl)fluorene-alt-phenylene) dibromide (FPQ). 30% aqueous solution of trimethylamine (4 mL) was added dropwise to a solution of the poly(9,9'-bis(6"-bromohexyl)fluorene-co-alt-1,4-phenylene)(60 mg) in THF (10 mL) at room temperature. The mixture was stirred at room temperature for 24 h. After removing most of the solvent, acetone was added to precipitate polymer (FPQ). ¹H-NMR (DMSO, 400 MHz) δ 8.0-7.5 (m, 10H), 3.3 (t, 4H), 2.9 (s, 18H), 1.6-1.0 (br, 20H).

Measurements. The ¹H NMR spectra were recorded on a JNM ECP-400 at 400 MHz. using CDCl₃ and DMSO as the solvent at room temperature. Cyclic voltammetry (CV) experiment was performed using a Perkin Elmer™ Potentiostat/Galvanostat Model 263A. The three-electrode cells were used in all experiments. Platinum wire was used for counter electrodes. Working electrode was made of indium-tin-oxide (ITO) and Ag/AgCl (a saturated 3.5 M KCl-AgCl solution, Princeton, NJ 08540.) was used as a reference electrode. The polymer was coated onto the ITO working electrode by spin coating the ITO into the viscous polymer solution. Electrolyte solutions of 0.1 M Bu₄NClO₄ in DMF were used in our experiments. Cyclic voltammograms were obtained at a scan rate of 50 mV/sec. UV-vis absorbance spectra were recorded on a UV-1601 PC, UV-visible spectrophotometer (SHIMADZU). Approximate relative fluorescence quantum efficiencies of the thin films were determined by using a thin film. The current density-voltage characteristics, the luminance, and the external quantum efficiency were measured with a source meter (Keithley 2400) and a calibrated silicon photodiode attached to a pico-ampere meter (Keithley 195A).

Device Fabrication

Polyethylene dioxythiophene doped with polystyrene

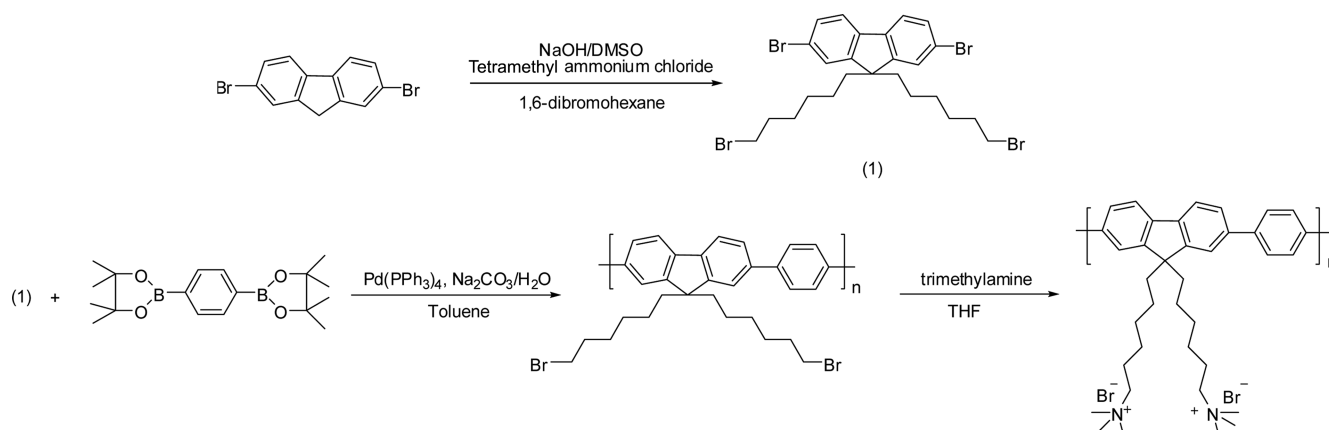


Figure 1. Synthetic scheme for polymer (FPQ).

sulfonate (PEDOT:PSS, Baytron P VP.Al 4083) was used for all devices as a hole injecting buffer. PEDOT was spin coated onto the transparent anode, indium-tin-oxide (ITO), followed by the spin coating of the emitting polymer, MEH-PPV. Layers of the PEDOT and the MEH-PPV were film thicknesses of 40 nm and 50 nm, respectively. For the electron transport layer, we have used our material, FPQ. FPQ was prepared by spin coated with film thicknesses of 10 nm, is methanol solution without dissolving the underlying emitting layer. For all devices, LiF/Al bilayer was used as a cathode with thicknesses of 1 and 120 nm for the LiF and the Al, respectively. Evaporation rate of 0.02 nm/s was maintained during the depositions under vacuum condition of about 1.0×10^{-6} Torr. For Al, after a film thickness of 20 nm, the evaporation rate was increased to 0.1 nm/s. The device structures in this study are summarized as follows:

Device 1 : A / MEH-PPV(50 nm) / C,

Device 2 : A / MEH-PPV(50 nm) / water soluble polymer (FPQ) (10 nm) / C

where, the A and B denote anode (ITO/PEDOT:PSS) and cathode (LiF/Al), respectively

Results

The synthesis of the monomer and polymer (FPQ) is outlined in Figure 1. The polymer typically obtained by the Suzuki type of polymerization reaction and shows good solubility in methanol. Figure 2 shows the UV absorption for FPQ as solid film. The band gap energy of the polymer was estimated from the absorption spectrum and was found to be 434 nm (2.86 eV).

The electrochemical behavior of the polymer was investigated by cyclic voltammetry (CV) and outlined in Figure 3. The onset potential for oxidation was observed to be 1.0 V. On the other hand E_g was estimated from UV_{onset} and calculated from $EA = IP - E_g$. According to the equation, $IP = ([E_{onset}]^{ox} + 4.8)$ eV, where $[E_{onset}]^{ox}$ was the onset potential for the oxidation of polymer, the HOMO and LUMO of the polymer was estimated to be 5.8 and 2.94 eV.

The current density-voltage characteristics are shown in

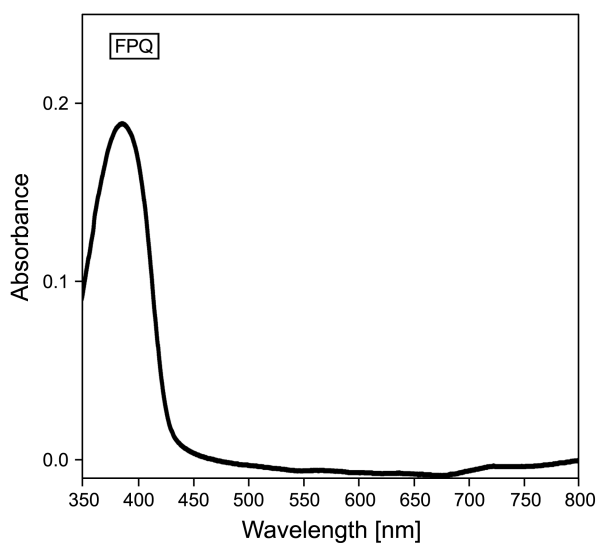


Figure 2. UV-vis absorption spectra of polymer (FPQ).

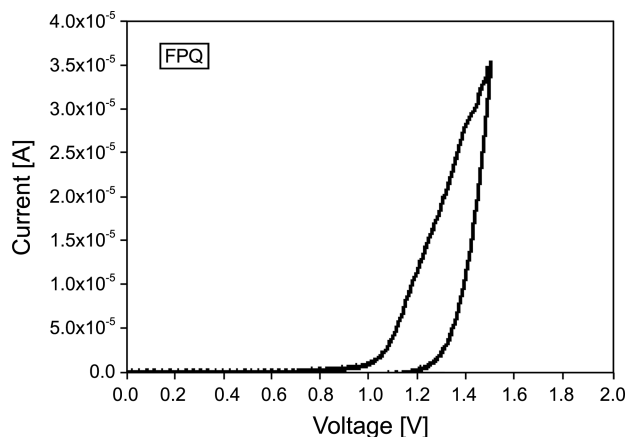


Figure 3. Cyclic voltammogram of Polymer (FPQ).

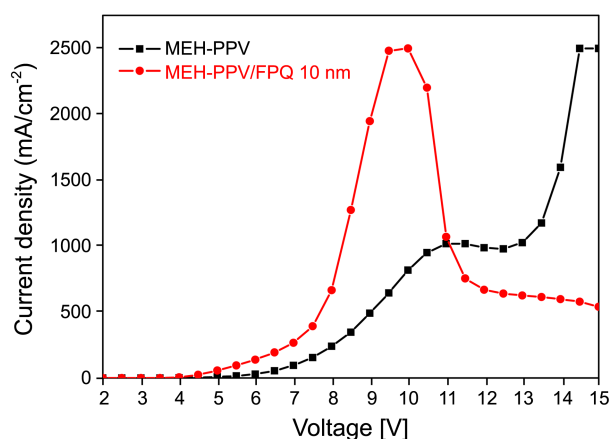


Figure 4. Current density-voltage characteristics of device 1 and 2.

Figure 4. The figure shows slightly lower turn-on voltage from the MEH-PPV/water soluble polymer structure (device 2) than the MEH-PPV (device 1). The turn-on voltages were estimated at a luminance of around 1 cd/m^2 at which the human eyes can detect the light and they were found to be 5 V for the device 1 and 4.5 V for devices 2. Figure 5 shows

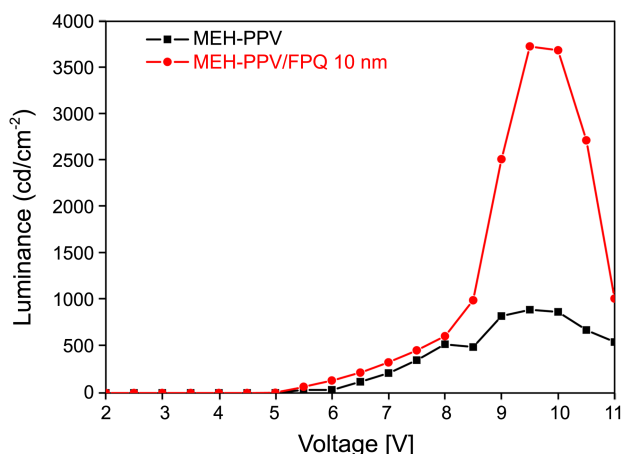


Figure 5. Luminance-voltage relations of device 1 and 2.

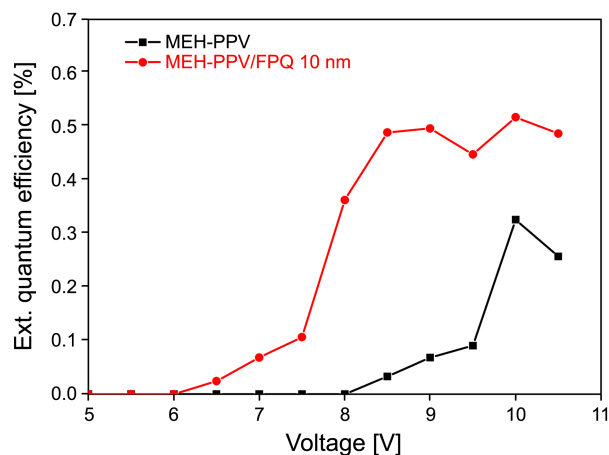


Figure 6. External quantum efficiency relations of device 1 and 2.

the relation of luminance-applied voltage of each device with applied voltages up to 11 V. The figure clearly shows that the MEH-PPV/water soluble polymer structure (device 2) has a better performance than those of devices without the water soluble layer (device 1). Device 2 showed a luminance of 3730 cd/m^2 at an applied voltage of 9.5 V than without water soluble polymer structure (device 1) showed the luminance 897 cd/m^2 at 9.5 V. Also until impressed voltage 7.5 V degree shows the luminance is similar but from impressed voltage of above that case of P-type, Intrinsic, N-type (PIN) junction (device 2) shows the luminance improvement effect which is sudden, this is caused by with p-type polymer and n-type water soluble conjugated polymer the interaction which hole and electron increases attraction. Figure 6 shows the external quantum efficiency of the devices where the maximum value reaches up to 0.5% for the with water soluble polymer layer (device 2) than without water soluble polymer structure (device 1) showed the 0.34% at 10 V.

Conclusion

In conclusion, we have achieved an enhanced luminance in PLED with multi-layered polymer layers by introducing

the water soluble conjugated polymer FPQ as an electron transport layer between the emitting polymer and the cathode metal. The device 2 showed a maximum luminance of 3730 cd/m² at an applied voltage of 9.5 V while the one without FPQ layer showed the luminance 897 cd/m² at the same applied voltage. Also until impressed voltage 7.5 V degree shows the luminance which is similar but from impressed voltage of above that case of MEH-PPV/FPQ layer shows the luminance improvement effect which is sudden, this is caused by with EML(MEH-PPV) polymer and water soluble conjugated polymer the attraction interaction which hole and electron increases attraction. This result implies that further modification of the FPQ or water soluble conjugated polymers could be useful for enhancement of PLED performance.

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References

1. Wang, J. F.; Jabbour, G. E.; Mash, E. A.; Anderson, J.; Zhang, Y.;

- Lee, P.; Armstrong, N. R.; Peygkambarian, N. *Adv. Mater.* **1999**, *11*, 1266.
2. Matsumura, M.; Ito, A.; Miyamae, Y. *Appl. Phys. Lett.* **1999**, *75*, 1042.
3. Hung, L. S.; Tang, C. W.; Mason, M. G. *Appl. Phys. Lett.* **1997**, *70*, 152.
4. Piromerin, P.; Oh, H.; Shen, Y.; Malliaras, G. G.; Scott, J. C.; Brock, P. J. *Appl. Phys. Lett.* **2000**, *77*, 2403.
5. Birgerson, J.; Fahlman, M.; Broms, P.; Salaneck, W. R. *Synth. Met.* **1996**, *80*, 125.
6. Brown, T. M.; Friend, R. H.; Millard, I. S.; Lacey, D. J.; Burroughes, J. H.; Cacialli, F. *Appl. Phys. Lett.* **2004**, *77*, 3096.
7. Lee, H. M.; Choi, K. H.; Hwang, D. H.; Do, L. M.; Zyung, T.; Lee, J. W.; Park, J. K. *Appl. Phys. Lett.* **1998**, *72*, 2382.
8. Niu, Y. H.; Ma, H.; Xu, Q.; Jen, K. Y. *Appl. Phys. Lett.* **2005**, *86*, 083504.
9. Tseng, S. R.; Lin, S. C.; Meng, H. F.; Liao, H. H.; Yeh, C. H.; Lai, H. C.; Horng, S. F.; Hsu, C. S. *Appl. Phys. Lett.* **2006**, *88*, 163501.
10. Lee, T. W.; Park, O. O. *Adv. Mater. (Weinheim, Ger.)* **2001**, *13*, 1274.
11. Liang, Z.; Cabarcos, O. M. *Adv. Mater. (Weinheim, Ger.)* **2004**, *16*, 823.
12. Ma, W.; Iyer, P. K.; Gong, X.; Liu, B.; Moses, D.; Bazan, G. C.; Heeger, A. J. *Adv. Mater. (Weinheim, Ger.)* **2005**, *17*, 274.
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