Improved Efficiency of Polymer LEDs using Electron Transporting Layer

Jong Lae Kim[1], Jai Kyeong Kim[2], Hyun Nam Cho[2], Dong Young Kim[2], Sung Il Hong[1], and Chung Yup Kim[2]
[1] Dept. of Fiber & Polymer Science, Seoul National University, Seoul 151-742, Korea
[2] Polymer Materials Laboratory, Korea Institute of Science and Technology, Seoul 130-650, Korea

Abstract

We report the use of fluorene based copolymers containing quinoline(POF66, P1F66) and pyridine(PFPV) units as electron transporting polymers for multi-layered LEDs. Double-layer device structure combining P1F66 as electron-transporting layer with the emissive MEH-PPV showed a maximum quantum efficiency of 0.03%, which is 30 fold increased compared with ITO/MEHPPV/Al single-layer device. PFPV layer increased the quantum efficiency up to 0.1% in the device structure of ITO/(P-3:PVK)/PFPV/Al. The ETL with the electron deficient moiety improved the LED performance by the characteristics of electron transporting as well as hole blocking between emissive layer and metal cathode.

Introduction

Performance of polymer LEDs have been improved greatly to be comparable to low molecular organic ones, since the first polymer LED was reported in 1990[1]. The light emission in polymer LEDs originates from the radiative decay of exitons which are generated in the emissive layer by the recombination of hole and electron carriers injected from electrodes[2]. The charge injection process is strongly related to the work function of electrode materials and the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) levels of emissive materials. Practically, ITO glass is employed for the anode because of its transparency. The most of light-emissive polymers have the HOMO levels closed to the work function of ITO (-4.8 eV). But the LUMO levels of polymers locate relatively far away from the work function of the air-stable metal for the cathode such as aluminum (-4.2 eV). The hole injection from anode is relatively easier than the electron injection from the cathode due to the small barrier height. The mobility of hole carriers is also faster than that of electrons. The balanced charge injection is one of the most important parameters to improve the quantum efficiency of polymer LED in the viewpoint of device physics [3]. In this work, the copolymers with electron deficient groups such as quinoline or pyridine are used between emissive layer and cathode to improve the electron injection as well as hole blocking characteristics.

Experimental

The electron-transporting materials with electron deficient moiety are listed in Figure 1. Polyquinolines (POF66, P1F66) containing a 9,9'-di-n-hexylfluorene unit in the main chain was synthesized using the Friedländer quinoline synthesis [4]. PFPV containing a pyridine unit were prepared as described in the literature [5]. All the polymers were soluble in common organic solvents as well as formic acid. P-3 and MEH-PPV were used for light-emissive layers. The statistical copolymer with meta:para ratio of 7:3, P-3, was synthesized using the method as reported in the literature [6]. MEH-PPV was used as received from UNIAX Corp. Cyclic voltammetry (CV) was employed to determine the HOMO and LUMO levels of materials with the thin film cast on ITO glass as a working electrode in a 0.1 M acetonitrile solution of tetrabutylammonium tetrafluoroborate with the Ag/AgCl reference electrode. For the fabrication of doubl-layered LED, a MEH-PPV solution was spin-cast on top of ITO glass at first, and the electron-transporting layer was added from the formic acid solution of P1F66. Aluminum cathode was evaporated thermally at the pressure below 10^{-6} torr.

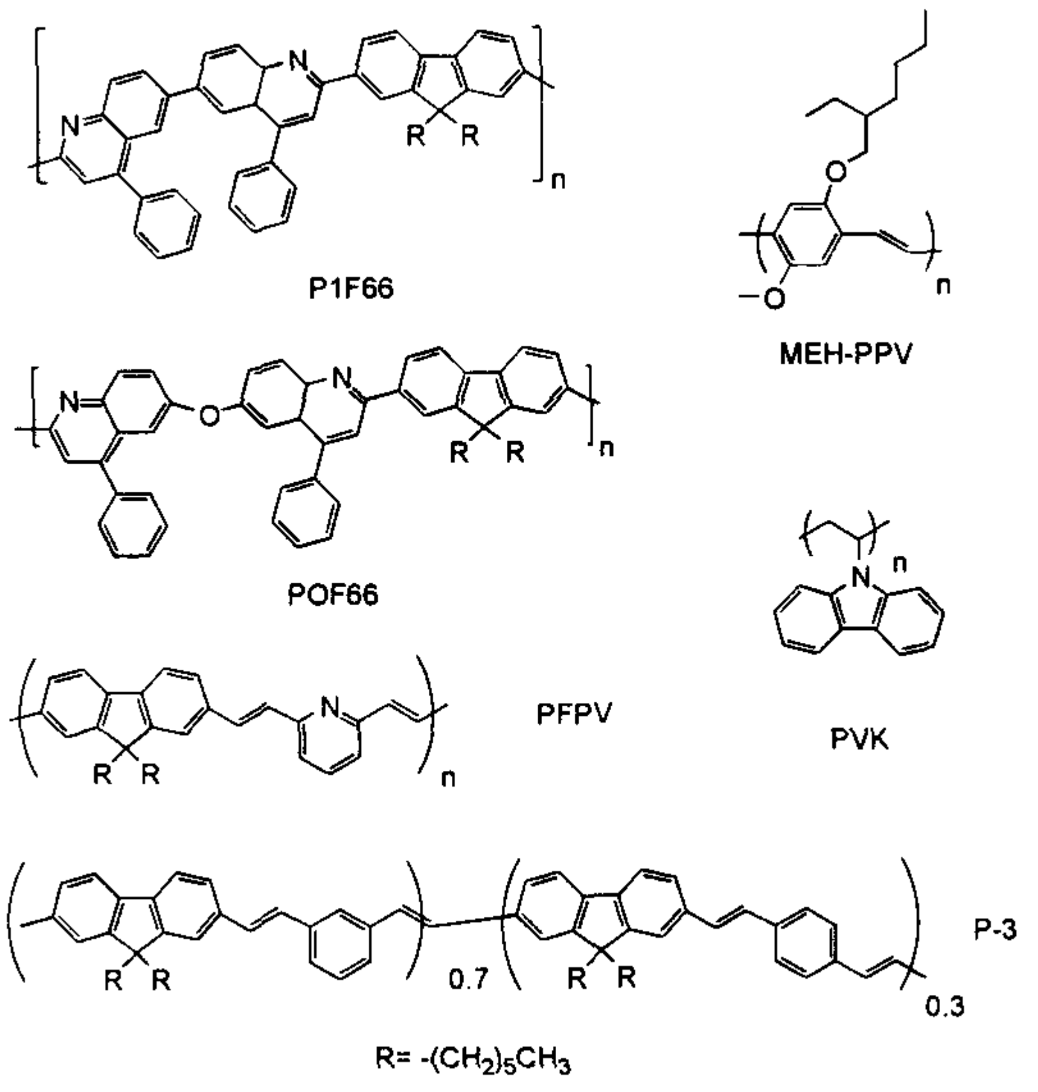

Figure 1. Structures of electron transporting and light-emissive materials.

Result and Discussion

CV of PFPV, POF66 and P1F66 exhibited the irreversible oxidation reaction in anodic sweep. The HOMO level was determined from the oxidation potential against the standard potential of ferrocene/ferrocenium as –4.8eV[7]. The LUMO level was deduced by addition of the optical band-gap energy to the HOMO level. Energy levels and band-gap energy of materials are listed in Table 1.

Table 1. Energy levels and band-gap energy of light-emissive polymers.

Polymer	HOMO(eV)	LUMO(eV)	Band-gap(eV)
MEH-PPV	-5.14	-2.97	2.17
P-3	-5.65	-3.08	2.79
PFPV	-5.67	-2.83	2.84
POF66	-6.10	-3.08	3.02
P1F66	-6.0	-3,21	2.79
PVK	-5.36	-1.92	3.44

The multi-layered LEDs were fabricated ITO/MEH-PPV/ETL/Al by spin-cast method as described. The good solubility of ETL materials in formic acid made the multi-layered devices possible because the light-emissive polymers in this work were very inert to formic acid. The thickness of MEH-PPV and ETL layers was controlled as 170 nm and 30 nm, respectively. Figure 2 shows the I-V characteristics of LEDs with ETL layer. All the devices emitted the light of the peak maximum at 570 nm. The turn-on voltage increased slightly due to the total thickness of the devices by adding ETL compared to the control device with MEH-PPV only.

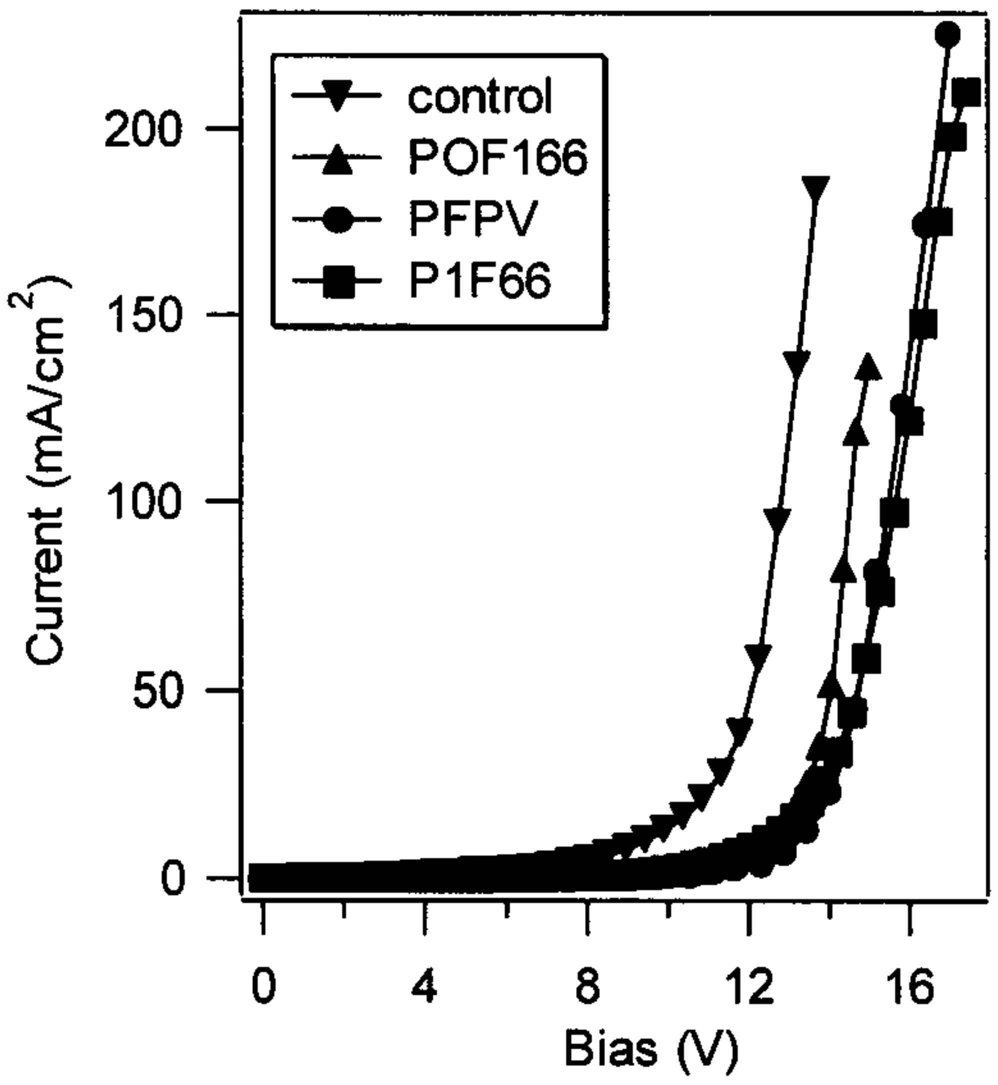

Fig. 2. I-V characteristics of multi-layered LEDs with ETL.

ETL materials have the larger HOMO levels than that of MEH-PPV, and the injected hole carriers are blocked at the interface between MEH-PPV and ETL not to be drained to cathode. The electron injection was also improved in the multi-layered device since the gap between the LUMO of MEH-PPV and the work function of Al cathode reduced. Figure 4 show the I-L characteristics of LEDs with different ETL.

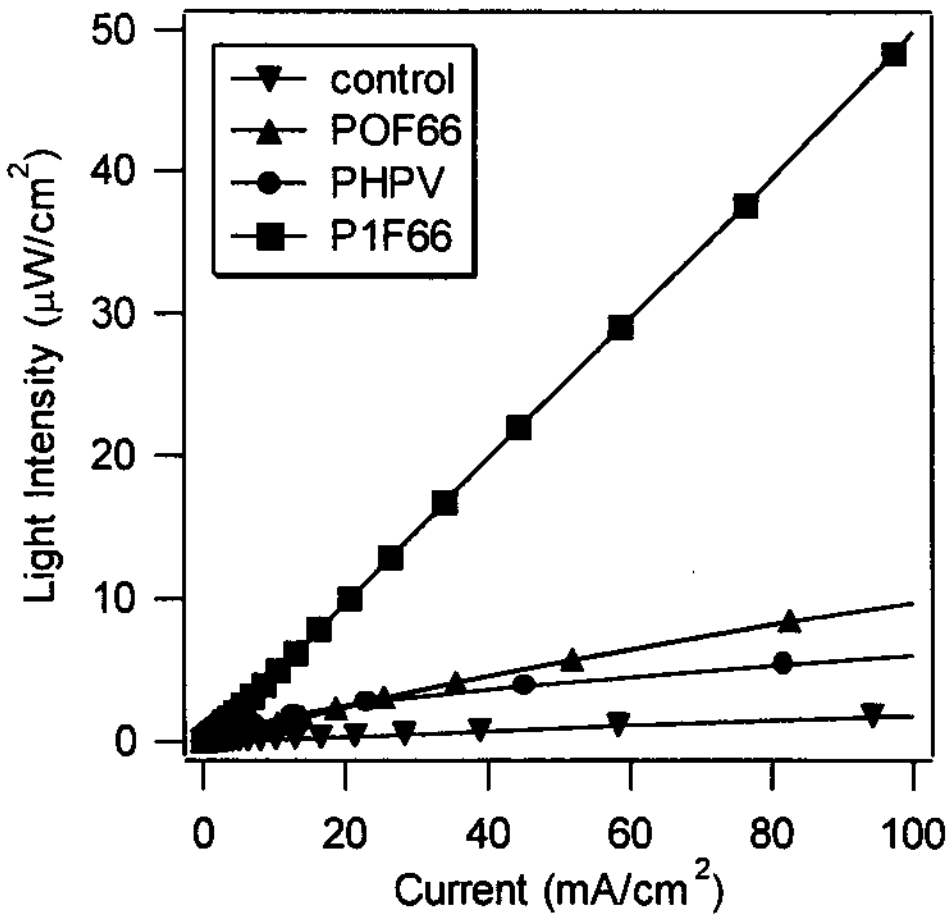

Fig. 4. The I-L characteristics of LED structure of ITO/MEH-PPV/ETL/Al.

The slope in Figure 4 indicated the quantum efficiency of the devices. A single layer device with MEH-PPV only revealed very low quantum efficiency of ~0.001%. The ETL improved the quantum efficiency up to 0.03% with P1F66. The HOMO level of POF66 was lower than that of P1F66, but POF66 did not enhanced the efficiency as much as P1F66 did. In the case of POF66, the electron injection seemed to be improved, however, the oxygen in the structure decreased the charge mobility because of the kink structure in the conjugated π-orbitals.

The LED of ITO/(P-3:PVK)/PFPV/Al emitted the blue light of the peak maximum at 475 nm as shown in Figure 5. PFPV with pyridine unit improved the quantum efficiency up to 0.1% which was five times better than that of the LED without the ETL.

In summary, the fluorene based copolymers with electron deficient units such as quinoline and pyridine revealed the low HOMO and LUMO levels. The ETL between the emitter and cathode improved the quantum efficiency by balancing the charge injection due to the electron transporting and hole blocking functions.

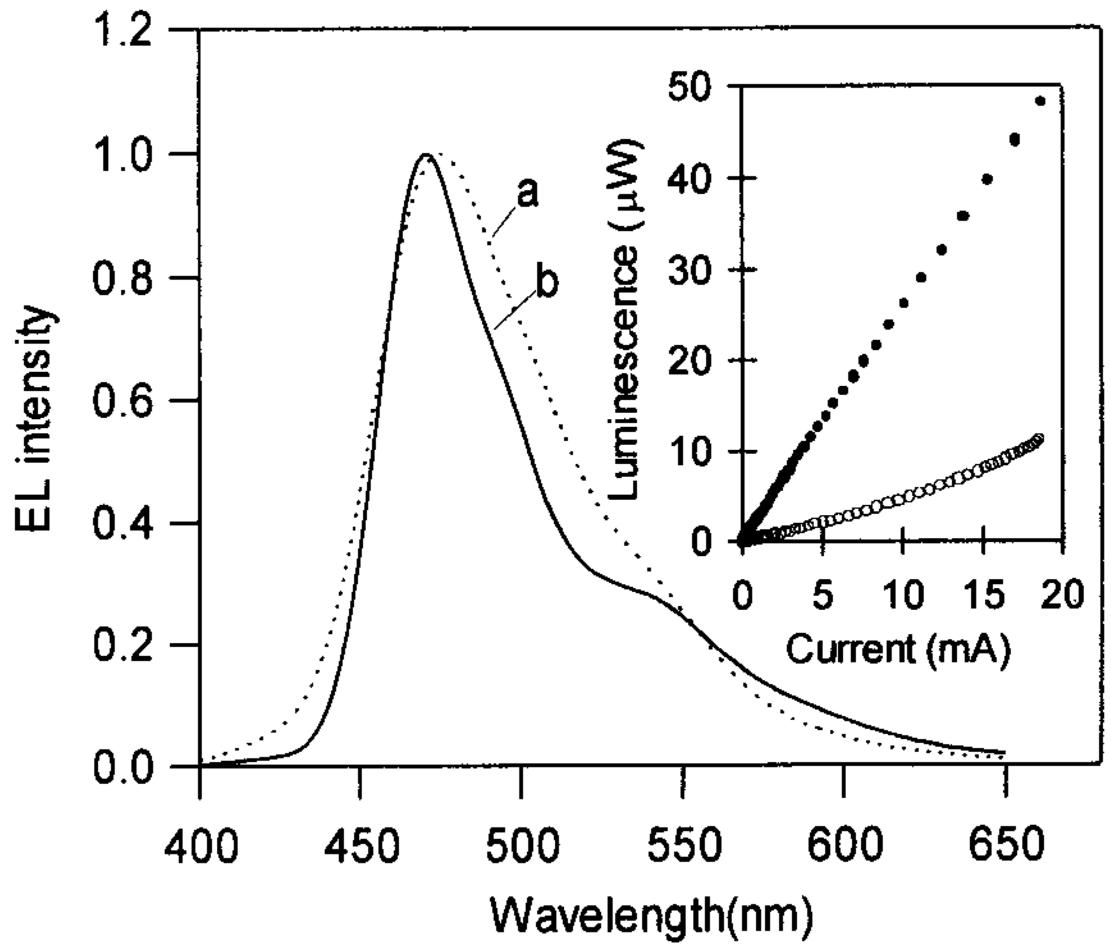

Fig. 5 EL spectra of (P-3)-PVK(2/8) blend without (a) and with (b) PFPV layer between emissive blend and aluminum electrode. Inset shows I-L characteristics of LED without (o) and with(•) PFPV layer

References

[1] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. MacKay, R.H. Friend, P.L. Burn, A.B. Holmes, *Nature*, vol. 347, pp. 539-541, 1990.

[2] L.J. Rothberg and A.J. Lovinger, *J. Mater. Res.*, vol. 11, pp. 3174-3187, 1996.

[3] I.D. Parker, *J. Appl. Phys.*, vol. 75, pp. 1656-1666, 1994.

[4] J.L. Kim, H.N. Cho, J.K. Kim, and S.I. Hong, *Macromolecules*, vol. 32, pp. 2065-2067, 1999.

[5] J.K. Kim, J.W. Yu, J.M. Hong, H.N. Cho, D.Y. Kim, and C.Y. Kim, *J. Mater. Chem.*, vol. 9, pp. 2171-2176, 1999.

[6] H.N. Cho, J.K. Kim, D.Y. Kim, C.Y. Kim, N.W. Song, and D. Kim, *Macromolecules*, vol. 32, pp. 1476-1481, 1999.

[7] G. Gritzner and J. Küta, Pure Appl. Chem., vol. 56, pp. 462-466, 1984.