Synthesis and Light-emitting Properties of Poly (fluorene) Copolymers Containing EDOT Comonomer

Do-Hoon Hwang[*a], Moo-Jin Park[**a], and Ji-Hoon Lee[b]

Abstract

A series of statistical random copolymers of dioctylfluorene (DOF) and 3,4-ethylenedioxythiophene (EDOT) were synthesized by Ni (0) mediated polymerization and their light-emitting properties were compared with poly (9,9-di-n-octylfluorene) (PDOF). The synthesized polymers were characterized using UV-vis spectroscopy, TGA, photoluminescence (PL) & electroluminescence (EL) spectroscopy and by conducting molecular weight studies. The resulting polymers were found to be thermally stable and readily soluble in organic solvents. The UV-visible absorption and PL emission spectra of the copolymers were gradually red-shifted as the fraction of EDOT in copolymers increased. Light-emitting devices were fabricated in an ITO (indium-tin oxide)/PEDOT/polymer/Ca/Al configuration. Interestingly, the EL spectra of these devices were similar to the PL spectra of the corresponding polymer film. However, the EL devices constructed from the copolymer showed more than 10 times higher efficiency level than the devices constructed from the PDOF homopolymer. This higher efficiency is possibly the result of better charge carrier balance in the copolymer systems due to the lower HOMO levels of the copolymers in comparison to that of PDOF homopolymer.

Keywords : polyfluorene copolymer; ethylenedioxythiophene; electroluminescence

1. Introduction

In the past few decades, conjugated polymers have attracted great interest in the field of science and technology as semiconductors and electro-active materials for diverse applications such as transistors [1-2], photovoltaic devices [3], nonlinear optical devices [4], and polymer light-emitting diodes (PLEDs) [5-9]. Among these, LEDs fabricated from conjugated polymers has drawn the greatest increased as its properties are well-suited for flat panel displays – good processibility, low operating voltages, fast response times and facile color tunability over the full visible range.

For the development of a full color PLED, it is essential to development develop new materials that can display proper color. PPV derivatives and polyfluorene derivatives (PFs) are known to be promising materials for practical application. PPV and its derivatives [10-11] have attracted much attention because of their optical and physical properties, and many efforts have been made to improve the performance of electroluminescent (EL) devices. Although all three primary colors (red, green, blue) have been demonstrated in PLEDs, at present, only yellow~orange color emitting devices showed acceptable device performances suited for commercial use.

Recently PFs have drawn more attention as an emissive layer of the light-emitting diodes than PPV derivatives because of their high photoluminescence (PL) quantum efficiency, thermal stability, and also easy color tuning through the introduction of low-band-gap co-monomers. [12-16] The poor efficiency of polyfluorene homopolymer has been improved by blending, copolymerization, or end-capping with charge transporting materials for efficient charge injection.

In this study, we synthesized a series of random copolymers of 2,7-dibromo-9,9-di-n-octylfluorene (DOF) and 2,5-dibromo-ethylenedioxythiophene (EDOT) to tune

[*] Members, KIDS; [**] Student Members, KIDS.
Corresponding Author : Do-Hoon Hwang
a. Department of Applied Chemistry, Kumoh National Institute of Technology, Kumi 730-701, Korea
b. Department of Polymer Science and Engineering, Chungju National University, Chungju 380-702, Korea.
E-mail : dhhwang@kumoh.ac.kr   Tel : +54 467-4369   Fax : +54 467-4477

the emission colors and also to improve device efficiency. The synthetic routes of the PDOF and the copolymers are shown in Schemes 1 and 2.

2. Experimental

2.1 Measurements

NMR spectra were recorded on a Bruker AM 300 MHz spectrometer with tetramethylsilane as the internal reference. The absorption spectra were measured by a Hitachi spectrophotometer model U-3501 and steady-state photoluminescence spectra were recorded on a Spex FL3-11. Cylic-voltammetry (CV) was done on an AUTOLAB/ PG-STAT12 model. The redox properties of the polymer films were investigated by running CV in acetonitrile solution with 0.1 M TBAF at room temperature. A platinum wire electrode coated with a polymer thin film was used as the working electrode. Another platinum wire electrode was used as the counter electrode, and a Ag/Ag$^+$ (AgNO$_3$) reference electrode was calibrated at the beginning of the experiments by running the CV of ferrocene as the internal standard in an identical cell without any polymer on the working electrode. The potential values obtained in reference to Ag/Ag$^+$ electrode were concerted in reference to internal standard of ferrocene/ferrocenium (E^0=0.065 V vs SCE). The polymer film was prepared by spin casting the blend solutions containing 1 % of the polymers by weight in chlorobenzene. Uniform and pinhole free films with a thickness of approximately 80 nm were easily obtained from the polymer solution.

For the double layer device, a modified water dispersion of PEDOT [poly (3,4-ethylenedioxythiophene)], doped with poly (styrene sulfonate)(PSS)(Bayer AG, Germany) was used as a hole-injection/ transport layer. Then, a metal contact (Ca) was deposited on the top of the polymer film through a mask by vacuum evaporation at a pressure of below 4×10^{-6} Torr, yielding active areas of 4 mm^2. In the case of Ca cathode (~ 50 nm), an additional encapsulating layer of Al (~ 200 nm) was thermally eva- porated.

With respect to the measurement of the device characteristics, current-voltage (I-V) changes were mea- sured using a current/voltage source (Keithley 238) and an optical-power meter (Newport 818-SL). Bright and 1931 CIE chromaticity of the EL devices were measured by a PR-650 SpectraScan colorimeter. All processes and mea- surements mentioned above were carried out in air at room temperature.

2.2 Synthesis of PDOF and poly (DOF-*co*-EDOT)s

PDOF and statistical copolymers were synthesized by nickel (0) mediated polymerization. The feed ratio of each monomers was 15 mol% of the total amount of monomer, and the total amount of reactant was 1.8 mmol. Each Schlenk tube containing 5 mL of DMF, bis (1,5-cyclooctadienyl)nickel (0), 2,2'-dipyridyl, and 1,5-cyclo-octadiene (the latter three in a molar ratio of 1:1:1) was kept under argon at 80 °C for 30 minutes. Then, 5 mL of anhydrous toluene was added to the mixture. The polymeri- zation was maintained at 80 °C for 72 hours. Then, 0.1 g of bromobenzene was dissolved in toluene and added to the reaction mixture for end-capping. After the reaction was completed each polymer was precipitated from a mixture of concentrated HCl, methanol, and ace-tone of equal volume. The isolated polymers were then dissolved in chloroform and precipitated in methanol. Finally, the resulting poly- mers were purified by Soxhlet extraction and dried in vacuum.

3. Results and Discussion

3.1 Characterization of the polymers

The synthesized PDOF and poly (DOF-*co*-EDOT)s were found to be soluble in common organic solvents such as THF, chloroform, and toluene without evidence of gel formation. The weight average molecular weights (M$_w$) of PDOF and poly (DOF-*co*-EDOT) copolymers, which were measured by gel permeation chromatography using a polystyrene standard, were found to range from 5,000 to 23,000 with polydispersity indexes ranging from 1.5 to 2.2. The polymer yields were 20 to 60 % after purification. These results for the synthesized polymers are summarized in Table 1.

In addition, the compositions of the copolymers were determined by ^{1}H-NMR spectra by comparing of hydro- gens in ethylene in EDOT with those of octyl groups in fluorene. The feed ratios of 2,5-dibromo-ethylenedioxy- thiophene (EDOT) used in the present work were 5, 10, 25 and 50 mol% of the total amount of monomer, and the resulting ratios of EDOT units in the poly (DOF-*co*-EDOT) copolymers were 4, 6, 16 and 22 mol% respectively. The actual fractions of EDOT in the resulting copolymers were

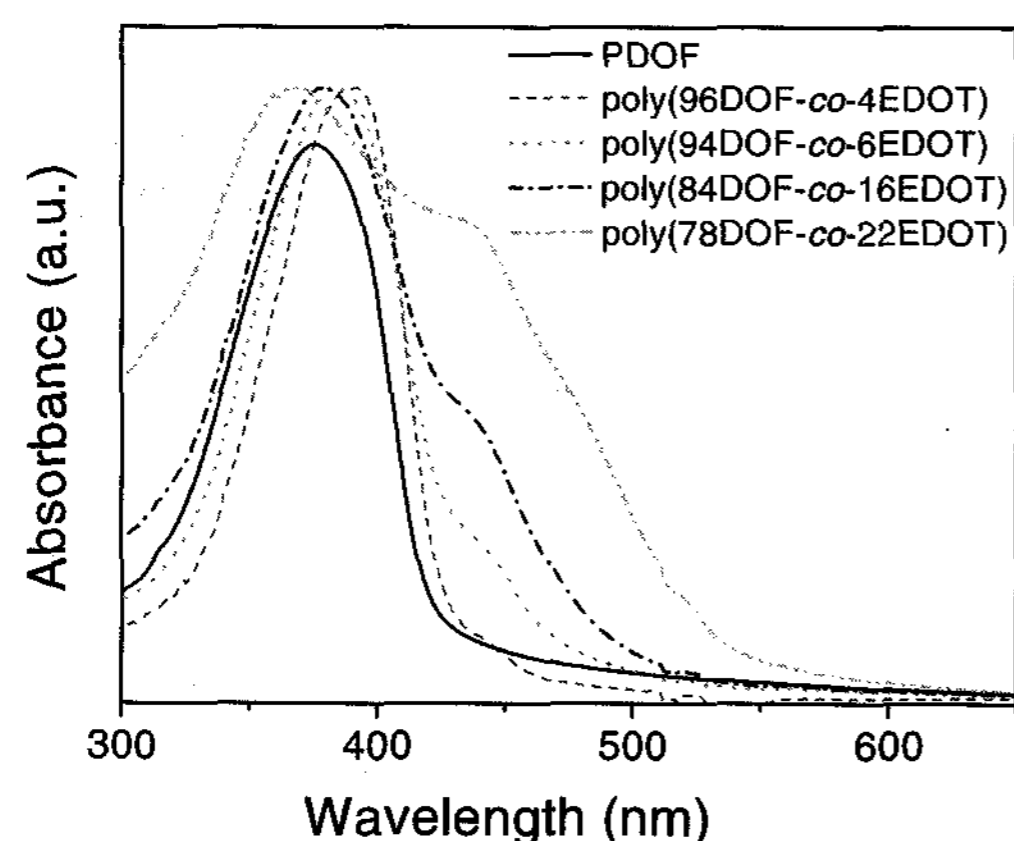found to be slightly lower than the feed ratios. These results

Table 1. Actual compositions, average molecular weights, polydispersity indices and the yields of the synthesized polymers

	Feed EDOT ratio	Actual EDOT ratio[a]	Mw	PDI	Polymer Yield (%)
PDOF	-	-	23,000	1.9	60
poly(96DOF-co-4EDOT)	5	3.9	19,000	2.1	43
poly(94DOF-co-6EDOT)	10	5.9	16,000	2.2	40
poly(84DOF-co-16EDOT)	25	15.5	12,000	2.0	22
poly(78DOF-co-22EDOT)	50	21.6	5,000	5	20

[a]The actual EDOT fractions in the copolymers which were determined by ^{1}H-NMR spectra of the corresponding polymers.
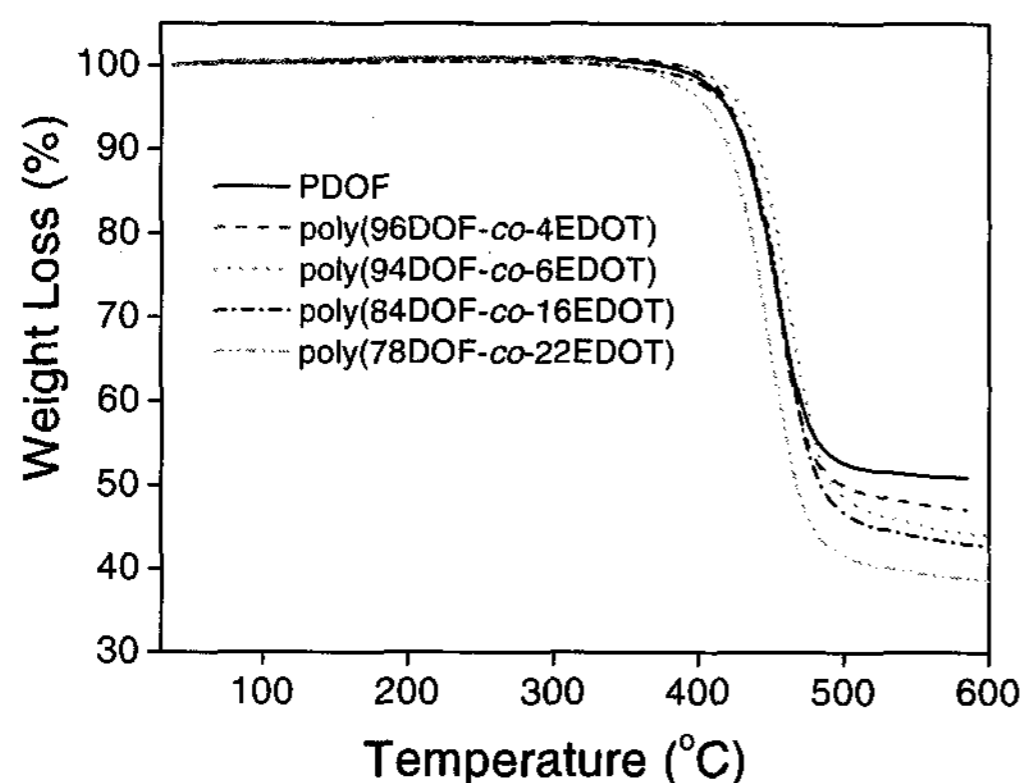
**Fig. 1.** TGA thermograms of the synthesized polymers.

indicate that the EDOT comonomer is less active than the fluorene comonomer in polymerization reactions.

All the polymers exhibited very good thermal stabilities, losing less than 5 % of their weight when heated up to about 400 °C, as determined by TGA under a nitrogen atmosphere. The TGA thermograms of the polymers are shown in Fig. 1.

3.2 Optical and photoluminescence properties

Fig. 2 shows the UV-Vis absorption spectra of thin films of PDOF and poly (DOF-co-EDOT)s coated onto fused quartz plates. The PDOF thin film exhibits maximum UV-visible absorption and absorption onset at 378 nm and426 nm respectively. The UV-visible absorption peaks of the copolymer films become red shifted as the fraction of EDOT in the copolymers increases. The optical band gaps of the polymers were determined from the absorption onset. The optical band gaps of PDOF were found to be 2.91 eV. The band gaps of the copolymer films were found to decrease as the fraction of EDOT in the copolymers increased. The optical band gaps of poly (96DOF-co-4EDOT), poly (94DOF-co-6EDOT), poly (84DOF-co-16EDOT) and poly (78DOF-co-22EDOT) were found to be 2.81, 2.56, 2.42 and 2.25 eV, respectively.

Fig. 3 shows the PL emission spectra of thin films of the polymers coated onto fused quartz plates. The maximum PL of the PDOF film when it is excited at 350 nm with a Xenon lamp appears at 420 nm. The peak PL emissions of the copolymers moved to the longer wavelength region as the fraction of the EDOT unit in

Fig. 2. UV-visible absorption spectra of the polymer films.
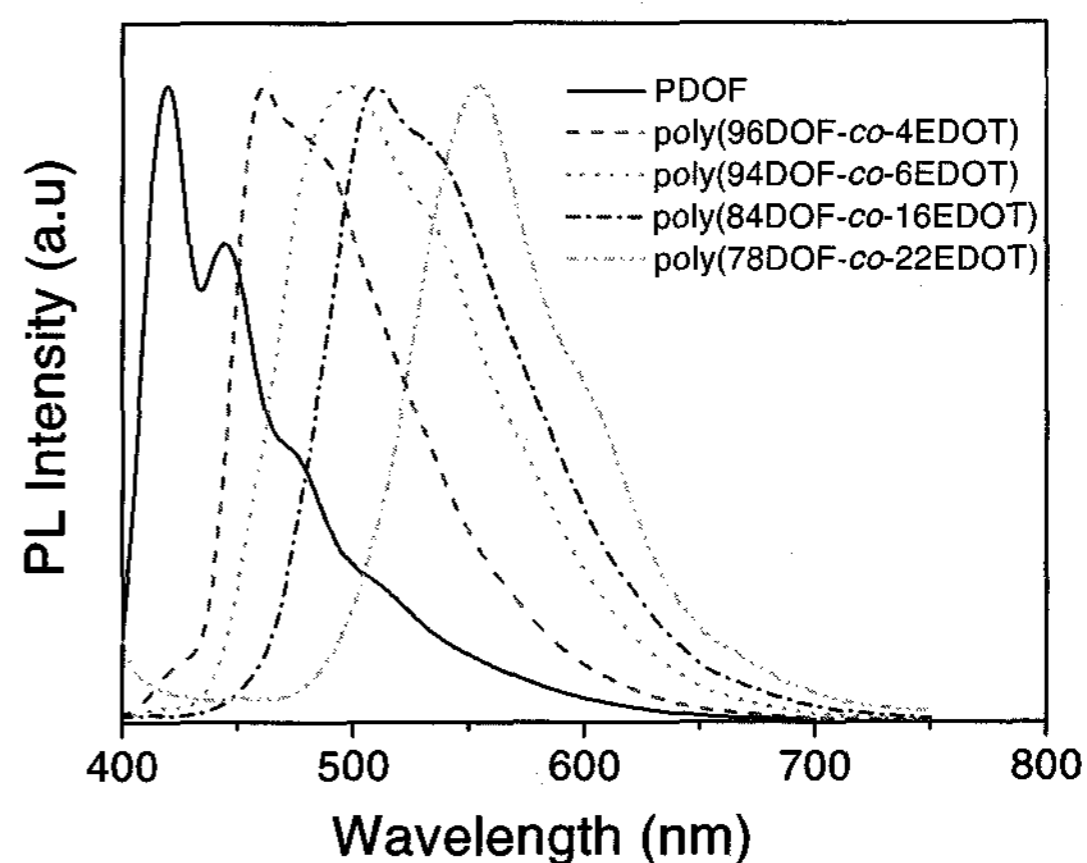
Fig. 3. PL spectra of the polymer films.

copolymers increased.
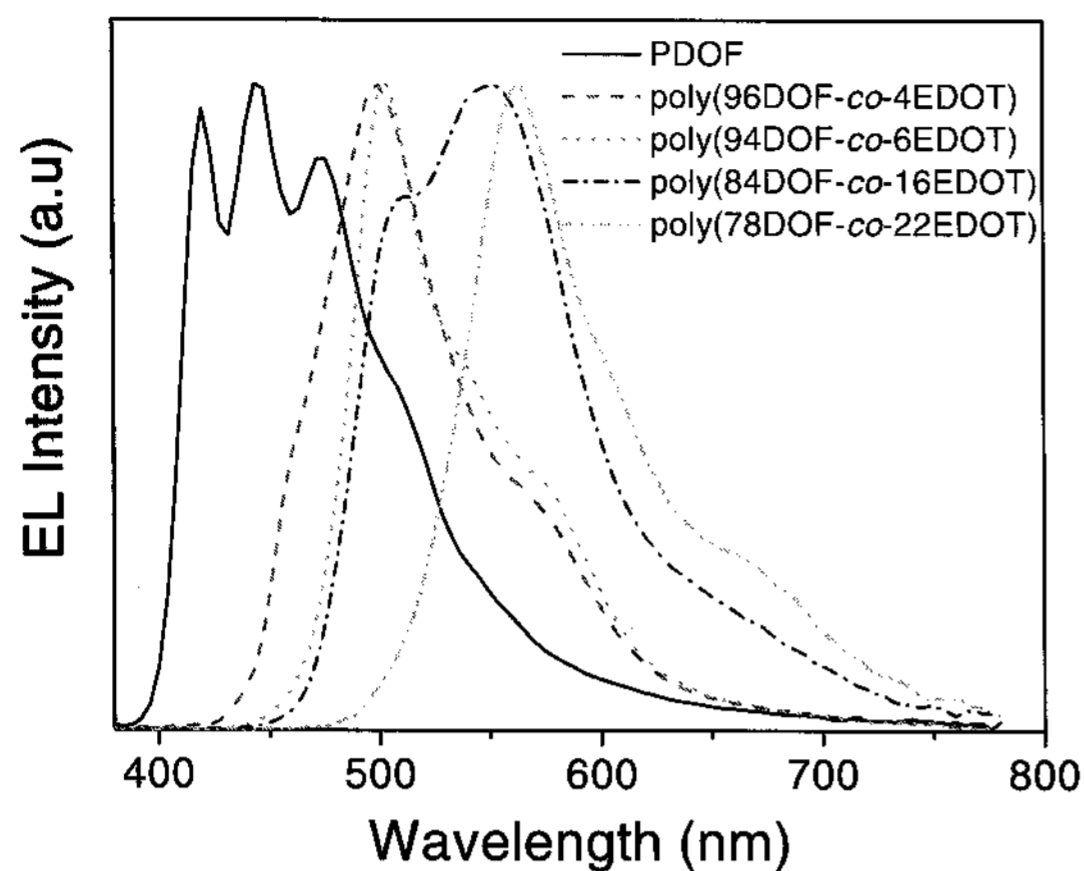
Fig. 4. EL spectra of the EL devices with ITO/PEDOT/Polymer/Ca/Al configuration.

Table 2. Summary of the spectral results of the polymers

|	UV$_{max}$ (nm)[b]	Optical band gap(eV)	PL$_{max}$ (nm)[b]	EL$_{max}$ (nm)
PDOF	378	2.91	420	420
poly(96DOF-co-4EDOT)	388	2.81	461	500
poly(94DOF-co-6EDOT)	382	2.56	498	503
poly(84DOF-co-16EDOT)	379	2.42	510	550
poly(78DOF-co-22EDOT)	367	2.25	554	563

[b]Measured in the thin film onto fused quartz plates.

3.3 Electroluminescence properties and voltage-luminance (V-L) characteristics

EL devices were fabricated in the ITO/PEDOT:PSS (50 nm)/polymers (80 nm)/Ca (50 nm)/Al (200 nm) configuration and characterized as a function of applied voltage. The EL spectra of the devices are shown in Fig. 4. The EL spectra of the PDOF and copolymer devices show little differences with PL spectra of the corresponding polymer films. One possible interpretation of the spectral difference between PL and EL is that the vibronic peak intensity is transferred to lower energy in EL compared to

PL. For the PL cases of all copolymer systems the 0-0 vibronic transitions showed the highest intensity. But, for the EL cases only poly (94DOF-co-6EDOT) and poly (78DOF-co-22EDOT) cases showed good agreement with the PL spectra. Meanwhile, in the cases of poly (96DOF-co-4EDOT) and poly (84DOF-co-16EDOT), the 0-1 vibronic transitions were more pronounced. All the results from the UV-visible, PL, and EL spectra are summarized in Table 2.

Figs. 5 and 6 show the current-voltage and luminance-voltage characteristics of the EL devices, respectivley. In the EL device constructed from the PDOF homopolymer, the forward current increases with increasing forward bias voltage, and the curve has a shape that is typical of a diode. Light emission from the PDOF homopolymer device could be observed at voltages greater than 3.8 V (@1
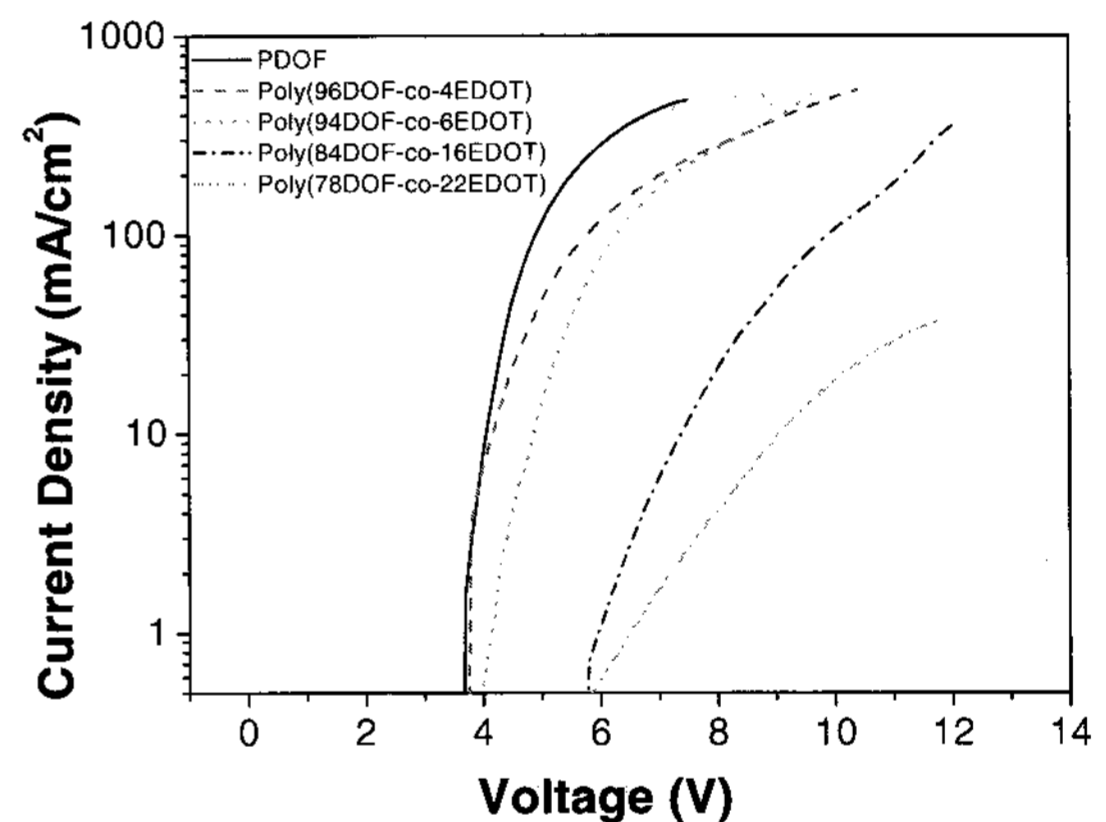
Fig. 5. I-V curves of the EL devices with ITO/PEDOT/Polymer/Ca/Al configuration.
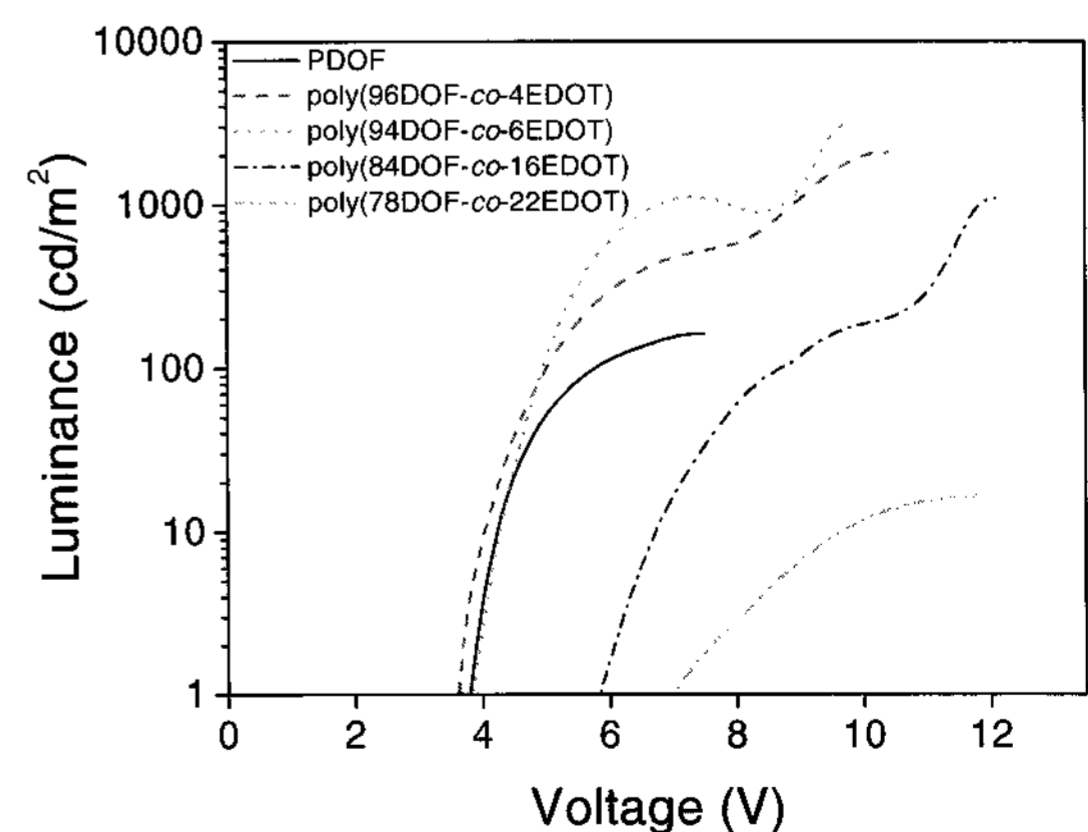
Fig. 6. L-V curves of the EL devices with ITO/PEDOT/Polymer/Ca/Al configuration.

cd/m^2). The maximum brightness of this device was 160 cd/m^2 with a power efficiency of 0.04 cd/A. Interestingly, the EL devices constructed from the copolymers exhibited significantly better device performances than the devices constructed from the PDOF.

Among the EL devices constructed using the co-polymers, the poly (94DOF-co-6EDOT) device exhibited the highest efficiency. The EL device constructed from poly (94DOF-co-6EDOT) exhibited a maximum brightness of 3,060 cd/m^2 and a maximum power efficiency of 0.59 cd/A. One explanation for the dramatic improvement in EL device performance achieved by using the copolymers is that the introduction of EDOT units which have lower HOMO levels facilitates hole injection, resultings in more efficient charge carrier balance. In general, a high barrier to hole injection between ITO and a light emitting polymer results in poor light emitting efficiency for polymers with high work functions, such as polyalkylfluorenes (~5.8 eV).
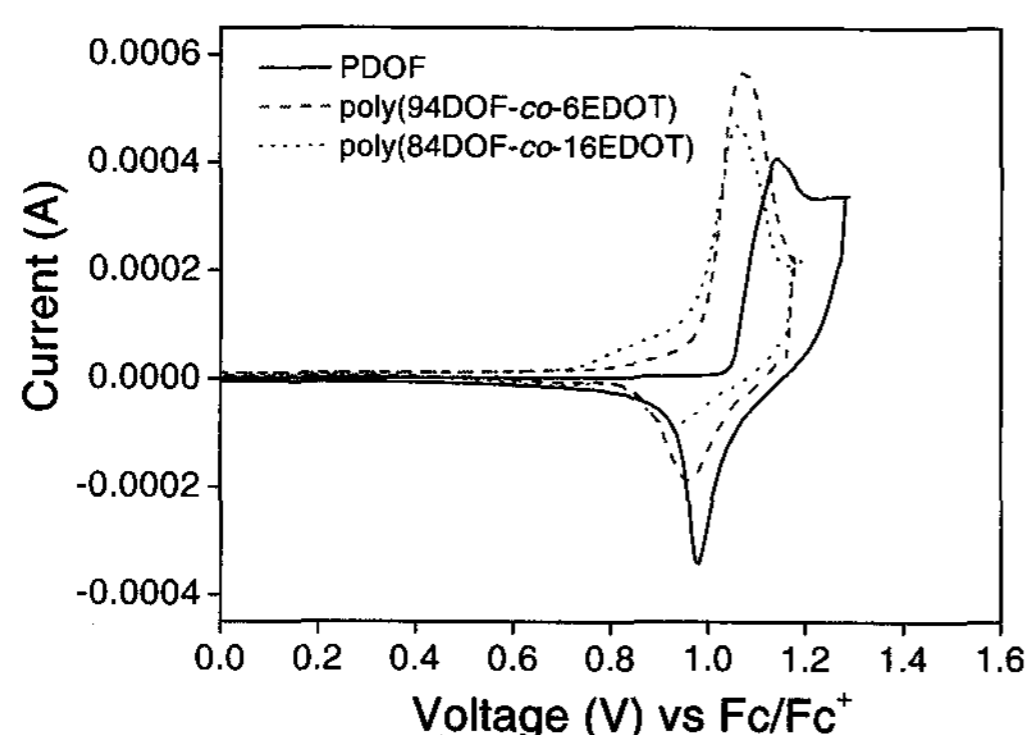
To confirm this hypothesis, we determined the HOMO levels of the PDOF, poly (94DOF-co-6EDOT) and poly (84DOF-co-16EDOT) using cyclic-voltammetry (CV). The ionization potentials of the polymers were determined by oxidation onset of the cyclovoltammograms as shown in Fig. 7. The measured ionization potentials of the PDOF, poly (94DOF-co-6EDOT) and poly (84DOF-co-16EDOT) were 5.80, 5.67 and 5.43 eV, respectively. Given that the optical band gaps of the PDOF, poly (94DOF-co-6EDOT) and poly (84DOF-co-16EDOT) were measured to be 2.91, 2.56 and 2.42 eV from the absorption onset, we can conclude that the LUMO levels of the PDOF, poly (94DOF-co-6EDOT) and poly (84DOF-co-16EDOT) are 2.89, 3.11 and 3.01 eV, respectively. The HOMO level of the PEDOT layer is known to be ~5.2 eV. Thus, hole injection and transportation from PEDOT to the copoly-mers are easier than those to the PDOF (5.80 eV). Accordingly, in the devices constructed from the copoly-mers show greater charge carrier balacnce. The relative band diagram of ITO, PEDOT, the polymers, and the Ca electrode are shown in Fig. 8, and the characteristics of the EL devices are summarized in Table 3.

Fig. 7. Cyclovoltammograms of the PDOF, poly(94DOF-co-6EDOT) and poly(84DOF-co-16EDOT).
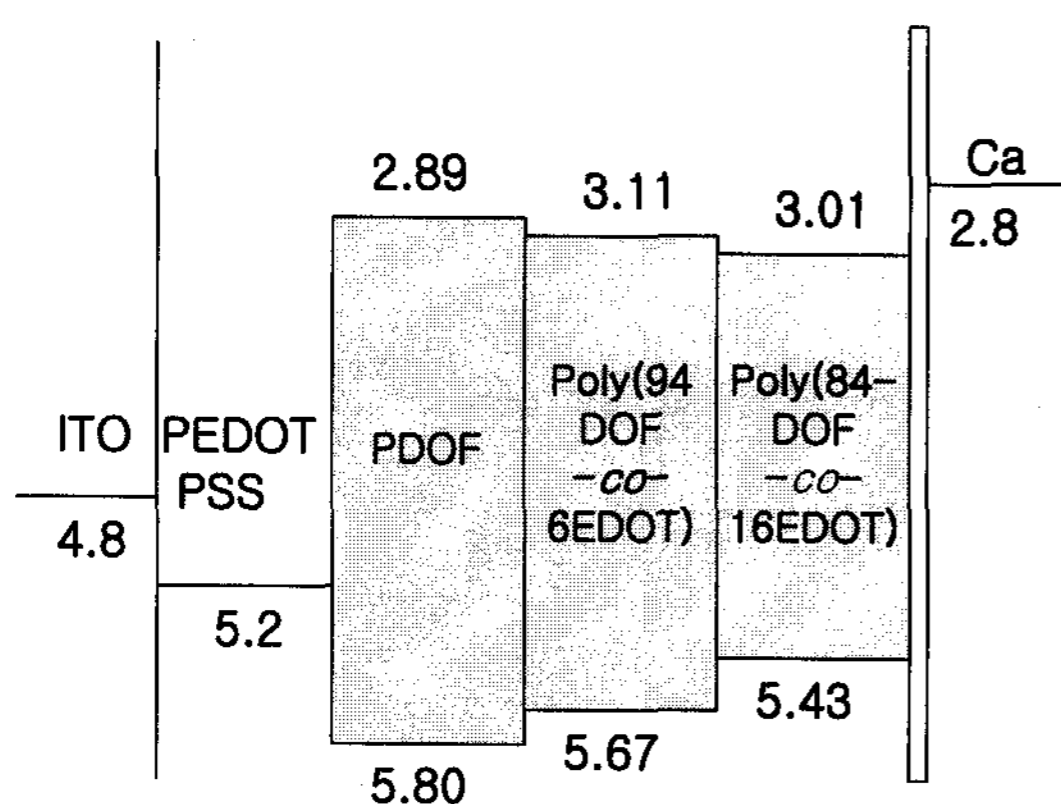
Fig. 8. Band diagram of the PDOF, poly(DOF-co-EDOT)s, PEDOT and Ca electode.

Table 3. Summary of the EL device performances.

	$V_{trun-on}$ (V)	Maximum Brightness (cd/m^2)	Efficiency (cd/A)	CIE 1931 $(x,y)^c$
PDOF	3.8	160	0.04	(0.18,0.14)
poly(96DOF-co-4EDOT)	3.7	2,080	0.40	(0.24,0.43)
poly(94DOF-co-6EDOT)	3.9	3,060	0.59	(0.27,0.53)
poly(84DOF-co-16EDOT)	5.7	1,090	0.29	(0.36,0.55)
poly(78DOF-co-22EDOT)	7.0	17	0.07	(0.46,0.53)

^{c}The CIE coordinates were measured at 100 cd/m^2 brightness.

4. Conclusion

PDOF and poly (DOF-co-EDOT)s were successfully

synthesized through the Yamamoto coupling reaction, and the light emission properties of these polymers were compared. The peak PL and EL emissions of the copolymers were found to become highly red-shifted from that of the PDOF homopolymer as the fraction of EDOT unit in copolymer increases. While the EL device fabricated using the PDOF homopolymer exhibited poor device efficiency and brightness, the devices fabricated using the copolymers exhibited significantly improved device performances in terms of both efficiency and brightness because of their enhanced hole injection and charge carrier balance.

References

[1] A. Dodabalopur, L. Torsi, and H.E. Katz, *Science*, **268**, 270 (1995).

[2] H.E. Katz, Z. Bao, and S.L. Gilat, *Acc. Chem. Res.*, **34**, 359 (2001).

[3] J.J. Halls, C.A. Walsh, N.C. Greenham, E.A. Marseglia, R.H. Friend, S.C. Moratti, and A.B. Holmes, *Nature*, **376**, 498 (1995).

[4] P.N. Prasad and D.J. Williams, Introduction to Nonlinear Effects in Monomers and Polymers, John Wiley & Sons: New York, 1991.

[5] J.H. Burroughes, D.D.C. Bradley, A.R. Brown, R.N. Marks, K. Mackay, R.H. Friend, P.L. Burn, and A.B. Holmes, *Nature*, **347**, 539 (1990).

[6] A. Kraft, A. C. Grimsdale, and A. B. Holmes, Angew. Chem. Int. Ed., **37**, 403 (1998).

[7] G. Gustafsson, Y. Cao, G.M. Treacy, F. Klavetter, N. Colaneri, and A.J. Heeger, *Nature*, **357**, 477 (1992).

[8] P.L. Burn, A.B. Holmes, A. Kraft, D.D.C. Bradley, A.R. Brown, R.H. Friend, and R.W. Gymer, *Nature*, **356**, 47 (1992).

[9] R. H. Friend, R. W. Gymer, A. B. Holmes, J. H. Burroughes, R. N. Marks, C. Taliani, D. D. C. Bradley, D. A. Dos Santos, J. L. Brédas, M. Lögdlund, and W. R. Salaneck, *Nature*, **397**, 121 (1999).

[10] D.H. Hwang, H.K. Shim, J.I. Lee, and K.S. Lee, *J. Chem. Soc. Chem. Commun.*, 2461 (1994).

[11] H. Becker, H. Spreitzer, W. Kreuder, E. Kluge, H. Schenk, I. Parker, and Y. Cao, *Adv. Mater.*, **12**, 43 (2000).

[12] J.I. Lee, G. Klaerner, M. H. Davey, and Robert D. Miller, *Synth. Met.*, **103**, 1087 (1999).

[13] D. Neher, *Macromol. Rapid. Commun.*, **22**, 1365 (2001).

[14] N.S. Cho, D.H. Hwang, J.I. Lee, B.J. Jung, and H.K. Shim, *Macromolecules*, **35**, 1224 (2002).

[15] J.H. Lee and D.H. Hwang, *Chem. Comm.*, 2836 (2003).

[16] D.H. Hwang, S.K. Kim, M.J. Park, J.H. Lee, B.W. Koo, I.N. Kang, S.H. Kim, and T. Zyung, *Chem. Mater.*, **16**, 1298 (2004).