

# Synthesis and Light-Emitting Properties of New Polyfluorene Copolymers Containing 2,3-Diphenylfumaronitrile

DONGBO MI,<sup>1</sup> HEE UN KIM,<sup>1</sup> SEON YOUNG LEE,<sup>1</sup>  
JONGHEE LEE,<sup>2</sup> SUNG-CHUL HONG,<sup>3</sup>  
SUNGMOON PYO,<sup>4</sup> AND DO-HOON HWANG<sup>1</sup>

<sup>1</sup>Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan, Republic of Korea

<sup>2</sup>Convergence Component & Materials Laboratory, Electronics and Telecommunications Research Institute, Daejeon, Republic of Korea

<sup>3</sup>Department of Nano Science and Technology, Sejong University, Gwangjin-gu, Seoul, Republic of Korea

<sup>4</sup>Department of Chemistry, Konkuk University, Gwangjin-Gu, Seoul, Republic of Korea

*A series of polyfluorene copolymers composed of 9,9-dioctylfluorene (DOF) and 2,3-diphenylfumaronitrile (DPFN), poly(DOF-co-DPFN)s, have been synthesized through a palladium (0)-catalyzed Suzuki coupling reaction, and their light-emitting properties have been investigated. The synthesized copolymers were soluble in common organic solvents such as chloroform, toluene, etc and formed a uniform thin film after spin coating. As the contents of 2,3-diphenylfumaronitrile in the copolymers increases, the optical band gaps of the copolymers decreased and HOMO energy levels were also slightly lowered. The absorption and PL emission spectra of the copolymers containing DPFN units shifted to longer wavelength region than those of poly(9,9-dioctylfluorene). Light-emitting devices were fabricated using these polymers as the emissive layers in an ITO/PEDOT:PSS/Polymer/Balq/LiF/Al configuration.*

**Keywords** 2, 3-Diphenylfumaronitrile; electroluminescence; light-emitting diode; polyfluorene copolymer

## Introduction

In the past few decades,  $\pi$ -conjugated polymers have attracted much scientific and technological research interest because of their potential use as semiconductors and electro-active materials in diverse applications such as organic thin-film

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Address correspondence to Prof. Do-Hoon Hwang, Department of Chemistry and Chemistry Institute for Functional Materials, Pusan National University, Busan 609-735, Republic of Korea. Tel.: 82 51 510 2232; Fax: 52 51 516 7421; E-mail: dohoonhwang@pusan.ac.kr

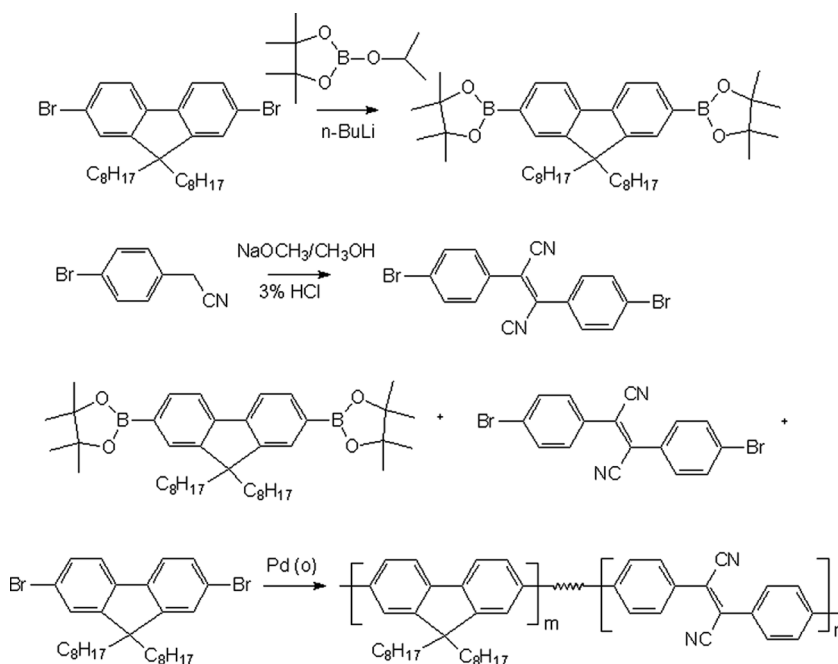
transistors [1], non-linear optical devices [2], photovoltaic cells [3], and polymeric light-emitting diodes (PLEDs) [4].

In particular, interest in PLEDs fabricated from conjugated polymers [5,6] has increased because such PLEDs have properties that are well-suited to flat panel displays: good processability, low operating voltages, fast response times, and facile color tenability over the full visible range. To date, many PLEDs capable of emitting the three primary colors have been developed, although only a few of these PLEDs have adequate efficiencies to be of commercial value [7,8]. Thus, the synthesis and investigation of new conjugated polymers are essential to improve the electronic and optoelectronic properties of these materials and, in turn, to achieving improvements in device performance, particularly the realization of a full-color PLEDs.

PPV derivatives and polyfluorene derivatives (PFs) [9–12] are well-known as promising materials suitable for practical applications. PFs have excellent thermal and chemical stability, good solubility, and high fluorescence quantum yield [13,14]. However, PF homopolymer has hampered their application for commercial use because of their poor electroluminescence (EL) efficiency.

2,3-Diphenylfumaronitrile (DPFN) has two electron-withdrawing nitrile groups in the vinyl group of stilbene structure so that this kind of molecule could have high electron affinity. If the 2,3-diphenylfumaronitrile is introduced to polyfluorene as a comonomer, EL efficiency of the PF copolymers could be improved due to the improved electron-transporting properties.

In this article, we synthesized a series of PF copolymers containing DOP and DPFN, poly(DOP-*co*-DPFN)s, through Suzuki coupling polymerization by controlling the feed monomer ratios. The chemical structure and synthetic route of the poly (DOP-*co*-DPFN)s are shown in Scheme 1.



**Scheme 1.** Synthetic route for the polyfluorene copolymers containing 2,3-diphenylfumaronitrile.

## Experimental

### *Fabrication and Measurement of Organic EL Devices*

A modified water dispersion of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrene sulfonate) (PSS) (Bayer AG, Germany) was used as the hole-injection/transport layer. Each polymer film was prepared by spin casting a solution containing 1% of the polymer by weight in chlorobenzene. Uniform and pinhole-free films with a thickness of 40 nm were easily obtained on the top of the PEDOT:PSS layer. Bis(2-methyl-8-quinolineolate)-4-(phenylphenolata)aluminum (BALq) was used as an electron transporting and also as an hole blocking layer with a thickness of 40 nm. Very thin lithium fluoride (1 nm) was deposited as an electron injecting layer and aluminum was deposited on top of the polymer film through a mask by vacuum evaporation at a pressure below  $4 \times 10^{-6}$  Torr, yielding active areas of 4 mm<sup>2</sup>.

### *Physical Measurements*

NMR spectra were recorded using a Bruker AM 400 MHz spectrometer with tetramethylsilane as an internal reference. Elemental analysis was performed using an EA 1110 Fisons analyzer. UV-vis and PL spectra were recorded using Jasco V-530 and Spex Fluorolog-3 spectrofluorometers. The number- and weight- average molecular weights of polymers were determined by gel permeation chromatography (GPC) on Viscotek T60A instrument, using tetrahydrofuran (THF) as eluent and polystyrene as standard. Cyclic voltammetry measurement was performed on an AUTOLAB/PGSTAT12 at room temperature with a three-electrode cell in a solution of TBABF<sub>4</sub> (0.10 M) in acetonitrile at a scan rate of 50 mV/s. Polymer films were prepared by dipping platinum working electrodes into the polymer solutions and then air-drying. A platinum wire was used as a counter electrode and Ag/Ag<sup>+</sup> electrode as a reference electrode. Film thickness was measured with a TENCOR alphastep 500 surface profiler. LED devices were fabricated on glass substrates coated with indium-tin oxide (ITO). EL spectra of the devices were obtained using a Minolta CS-1000. Current-voltage-luminance (*I-V-L*) characteristics were recorded simultaneously with the measurement of the EL intensity by attaching the photospectrometer to a Keithley 238 and a Minolta LS-100 as the luminance detector. All measurements were carried out at room temperature under ambient atmosphere.

### *Materials*

Tetrahydrofuran, tert-butyl lithium (1.7 M in hexane), 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, sodium carbocation, Aliquat 336, bromobenzene, phenylboronic acid were purchased from Aldrich. Tetrakis (triphenylphosphine) palladium (0) was purchased from DNF Solution Co. All chemicals and solvents (analytical grade) were used without further purification.

*Synthesis of 2,7-bis (4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-dioctylfluorene.* To a solution of 2,7-dibromo-9,9'-dioctylfluorene (8.0 g, 14.6 mmol) in refined THF (120 mL) at  $-78^{\circ}\text{C}$  was added, by syringe, 34.32 mL (58.3 mmol) of tert-butyllithium (1.7 M in hexane). The mixture was stirred at  $-78^{\circ}\text{C}$  for 2 h. Then the solution was warmed to room temperature about 2 h. 2-Isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane (6.55 mL, 29.2 mmol) was added to the

solution dropwise through syringe and the resulting mixture was stirred at  $-78^{\circ}\text{C}$  for 1 h, warmed to room temperature, and stirred for 40 h. The solution was quenched by methanol for 30 min then extracted with dichloromethane and brine, and dried over  $\text{MgSO}_4$ . The solvent was removed by solvent evaporation, and the residue was purified by several precipitations onto mixture of ethylacetate and methanol. The yield was 4.51 g (52.7%):  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  7.77(d, 2H), 7.72(d, 2H), 7.69 (s, 2H), 1.99~1.95 (m, 4H), 1.37 (s, 24H), 1.09~1.21(m, 20H), 0.78(t, 6H), 0.53(m, 4H).  $^{13}\text{C}$  NMR (400 MHz,  $\text{CDCl}_3$ )  $\delta$  150.71, 144.14, 133.87, 129.16, 119.58, 83.93, 55.40, 40.30, 32.00, 30.15, 29.41, 29.36, 25.16, 23.83, 22.80, 14.27.

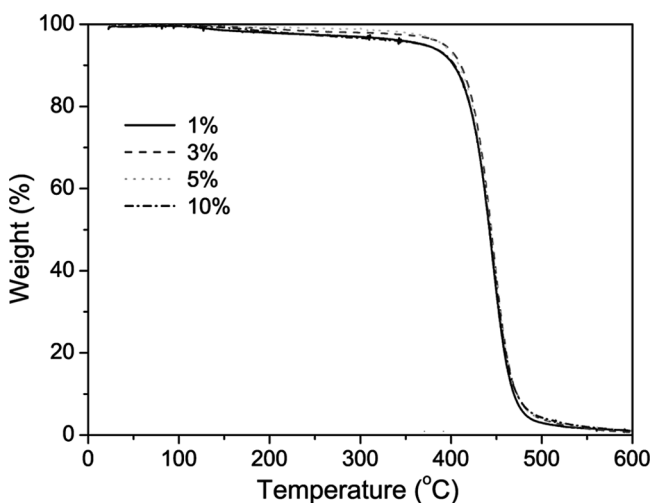
*Synthesis of 2,3-bis(4-bromophenyl)fumaronitrile.* 4-Bromobenzylcyanide (19.61 g, 0.1 mol) and iodine (25.38 g, 0.1 mol) were dissolved in dry diethyl ether (400 mL). Sodium methoxide methanol solution, which was prepared by adding sodium (4.83 g, 0.21 mol) to dry methanol (ca. 70 mL), was added slowly (over a period of 30 min) into the reaction solution at a dry-ice temperature under a nitrogen atmosphere. The reaction solution was allowed to warm up by replacing the dry-ice bath with an ice–water bath before the temperature rose above  $0^{\circ}\text{C}$ . During this time, more and more precipitation was formed in the solution. The reaction solution was further stirred for another 3–4 h and then the reaction was quenched with 3–6% hydrochloric acid at less than  $10^{\circ}\text{C}$ . The solution was filtered to isolate the solid, which was rinsed with cold methanol–water solution to wash away ionic substances. A white solid was obtained. The yield was 17.5 g (90%).  $^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ ):  $\delta$  7.63–7.72 (m, 8H).  $^{13}\text{C}$  NMR( $\text{CDCl}_3$ , ppm):  $\delta$  126.27, 124.27, 123.78, 120.65, 118.65, 110.55. Anal. Calcd for  $\text{C}_{16}\text{H}_8\text{Br}_2\text{N}_2$ : C, 49.52; H, 2.08; N, 7.22. Found: C, 49.57, H, 1.91, N, 7.27.

*Synthesis of poly (99DOP-co-IDPFN).* A mixture of 2,7-dibromo-9,9'-dioctylfluorene (2.0 g, 3.1 mmol), 2, 7-bis (4, 4, 5, 5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9'-dioctylfluorene (1.67 g, 3.05 mmol) and 2,3-bis(4-bromophenyl)fumaronitrile (0.024 g, 0.06 mmol) were dissolved in 20 mL of anhydrous toluene. The Pd (0) complex, tetrakis (triphenylphosphine) palladium (0.215 g, 0.186 mmol), was added into the mixture in glove box. 2.0 M aqueous sodium carbocate (14.55 mL, 29.14 mmol) that had been deaerated for 30 min and a phase transfer catalyst, Aliquat 336 (0.25 g, 0.62 mmol), purged in toluene under nitrogen for 1 h, were transferred to the mixture and was stirred for 48 h. An excess of bromobenzene (1.0 mL) and phenylbolic (0.1 g) that dissolved in 1 mL of anhydrous toluene was added as an end capper. After further stirring for 24 h, the reaction mixture was cooled to about  $50^{\circ}\text{C}$  and added slowly to a vigorously stirred methanol and collected by filtration. After purification, a white polymer was obtained. The polymer yield was 2.1 g (56.8%).

*Synthesis of other poly (DOP-co-DPFN) s.* Poly (97DOP-co-3DPFN), poly (95DOP-co-5DPFN), and poly (90DOP-co-10DPFN) are synthesized similarly as poly (99DOP-co-IDPFN).

## Results and Discussion

The synthesized poly(DOP-co-DPFN)s were soluble in common organic solvents such as chloroform, toluene, chlorobenzene, etc. The number average molecular weights ( $M_w$ ) of poly(DOP-co-DPFN)s were determined by gel permeation



**Figure 1.** TGA thermograms of the polymers.

chromatography using a polystyrene standard, and were found to range from 12,000 to 20,000 with polydispersity indexes ranging from 2.0 to 2.4.

The compositions of the copolymers were determined by elemental analysis of their nitrogen contents as a standard. The feed ratios of 2,3-bis(4-bromophenyl)-fumaronitrile used in the present work were 1, 3, 5 and 10 mol% of the total amount of monomer, and the resulting ratios of DPFN units in the poly(DOP-*co*-DPFN) copolymers were 0.15, 1.53, 3.30, and 5.50 mol% respectively. The actual fractions of DPFN in the resulting copolymers were found to be lower than the feed ratios.

The thermal stabilities of the polymers were investigated by thermogravimetric analysis (TGA). All the polymers were found to exhibit good thermal stability, losing less than 5% of their weight on heating to approximately 370°C as shown in Figure 1. The molecular weight, actual compositions and thermal properties of the synthesized copolymers are summarized in Table 1.

**Table 1.** Physical Properties of poly(DOP-*co*-DPFN)s

Polymers	$M_n^a$	PDI <sup>a</sup>	$T_d$ (°C) <sup>b</sup>	Ratio (DPFN mol %)	
				Feed ratio	Actual ratio <sup>c</sup>
poly(99DOP- <i>co</i> -1DPFN) <sup>d</sup>	20,000	2.4	370	1.0	0.15
poly(97DOP- <i>co</i> -3DPFN)	15,000	2.3	392	3.0	1.53
poly(95DOP- <i>co</i> -5DPFN)	13,000	2.1	392	5.0	3.30
poly(90DOP- <i>co</i> -10DPFN)	12,000	2.0	370	10.0	5.50

<sup>a</sup> $M_n$  and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards.

<sup>b</sup>Temperature resulting in 5% weight loss based on initial weight.

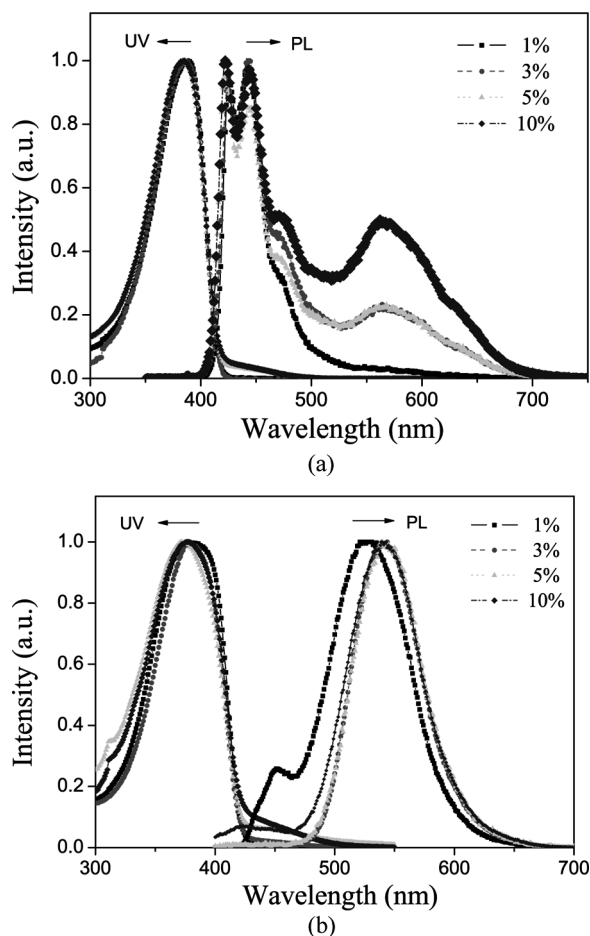
<sup>c</sup>Calculated by elemental analysis through calculation of the amount of nitrogen contained in copolymers.

<sup>d</sup>The number represents feed mole ratio of each monomers.

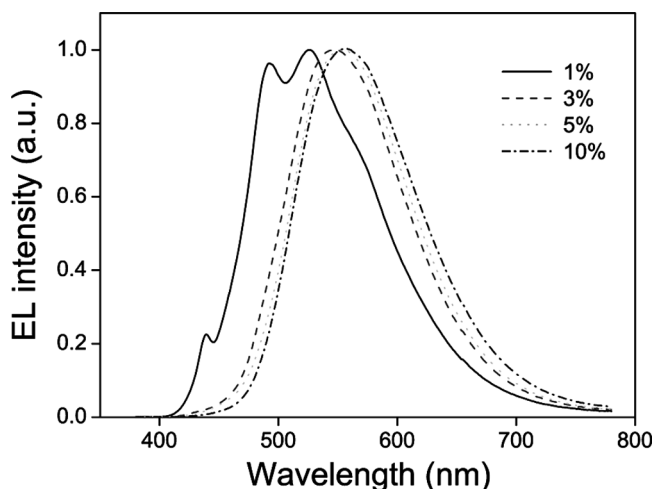
Figure 2 showed UV-visible absorption and photoluminescence (PL) spectra of the copolymers in solution (Fig. 2(a)) and thin films (Fig. 2(b)) coated onto fused quartz plates. The peak absorptions of the copolymer solutions showed at 385 nm regardless the fraction of DFPN in the copolymers. The polymers in chloroform solution showed three major emission peaks at 422 nm, 443 nm and 564 nm respectively. The PL emission peak at 564 nm would be caused by the 2,3- diphenylfumaronitrile segments. As the ratio of 2,3-diphenylfumaronitrile in the copolymer increases, the PL emission intensity at 564 nm increased.

Interestingly the PL emission of the copolymer thin films showed quite different absorption shapes compared to those of solutions. The peak emission moved to 543 nm from 422 and 443 nm suggesting that the energy transfer from fluorene to DPFN is much more efficient in solid state than solution. Even less than 1% DPFN containing poly (99DOP-co-1DPFN) showed peak emission at 527 nm.

The optical band gaps of the polymers were determined from the absorption onset of the copolymer thin films. As the contents of DPFN in the copolymers increases, the optical band gaps of the copolymers slightly decreased. The obtained



**Figure 2.** UV-visible absorption and photoluminescence spectra of the copolymers in solution (a) and thin solid films (b).

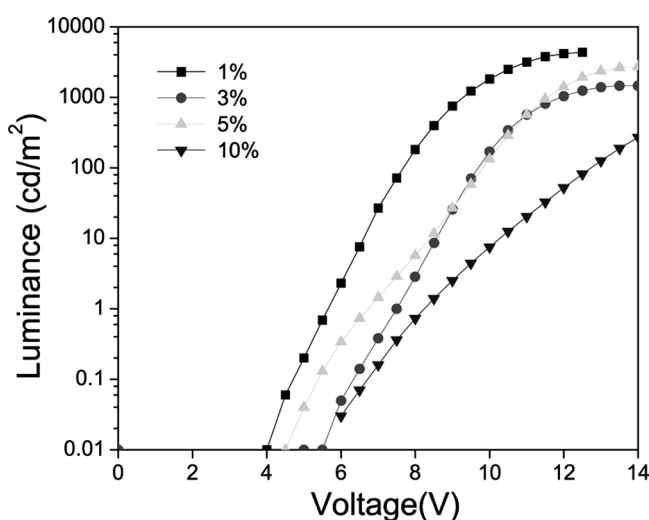


**Figure 3.** EL emission spectra of polymer films.

optical band gaps of poly(99DOP-*co*-1DPFN), poly(97DOP-*co*-3DPFN), poly(95DOP-*co*-5DPFN) and poly(90BEHF-*co*-10PTZ) were found to be 2.85, 2.75, 2.71 and 2.61 eV respectively.

EL devices were fabricated with ITO/PEDOT:PSS/polymers/Balq/LiF/Al structure. PEDOT: PSS was used as buffer layer, Balq as the electron transporting layer, LiF and aluminum were used as the cathode. Figure 3 showed the EL spectra of the devices. The EL spectra of the devices using the copolymers were similar to those PL spectra and showed completely energy transferred emission. Only poly(99DOP-*co*-1DPFN) showed small emission peak at 439 nm.

Figure 4 showed the voltage-luminance characteristics of the devices. All the devices showed excellent luminance. The device fabricated with ITO/PEDOT:



**Figure 4.** Voltage-luminance and voltage-current density characteristics of the devices.

PSS/poly(95DOP-co-5DPFN)/Balq/LiF/Al showed highest luminance at 14 V with very low threshold voltage (so called voltage onset) at 9.8 V. The thresholds of other devices were 7.8 V for the device fabricated by poly (99DOP-co-1DPFN) and 9.7 V for poly (97DOP-co-3DPFN), 11.8 V for poly (90DOP-co-10DPFN). The device using poly (95DOP-co-5DPFN) showed the highest quantum efficiency and brightness among the devices (0.79% and 3,600 cd/m<sup>2</sup> respectively).

Cyclic voltammetry (CV) is an efficient method to check the relative ionization and reduction potentials. Figure 5 showed the cyclic voltammogram (CV) of the polymer thin films on platinum and ferrocene. During the scan of the anode direction, the polymers exhibited strong quasi-reversible p-doping behavior. The oxidation peak appeared about at 1.29 V for poly (99DOP-co-1DPFN), at 1.35 V for poly (97DOP-co-3DPFN), at 1.33 V for poly (95DOP-co-5DPFN) and at 1.34 V for poly (90DOP-co-10DPFN) (all the data were tested vs Ag/AgCl). These polymers also exited very strong reduction peak when the voltage scanned backward. The reduction peaks of the polymers were at 1.41 V for poly (99DOP-co-1DPFN), at 1.13 V for poly (97DOP-co-3DPFN), at 1.28 V for both of the remained polymers.

The HOMO levels could be calculated from the onset oxidation potential ( $E_{OX}$  (onset)) based on the reference energy level of ferrocene (4.8 eV below the vacuum level, which is defined as zero) through the formula below:  $E_{HOMO} = -[(E_{OX}$  (onset)- $E_{Foc}$ ) + 4.8], where the  $E_{Foc}$  is the potential of the external standard, the ferrocene/ ferricinium ion ( $Foc/Foc^+$ ) couple. The value of  $E_{Foc}$ , determined under the same condition as for polymers is about 0.275 V vs Ag/AgCl.

LUMO energy levels of the polymers reduced with the increase of the ratio of 2, 3- diphenylfumaronitrile in polymers, which caused by the electron withdraw effect of the cyano group leading the more efficient electron injection from the compound cathode and higher efficiency of the ext QE of the devices fabricated with these polymers (the device using poly (95DOP-co-5DPFN) as emitters, for example). However, the chance of aggregation might increase when the ratio of the cyanostilbene was too high, leading the quench of fluorescence which might be the reason of the low efficiency of the device configured with poly (90DOP-co-10DPFN). The optical properties and HOMO energy levels of the copolymers were summarized in Table 2, and EL device results were listed in Table 3.

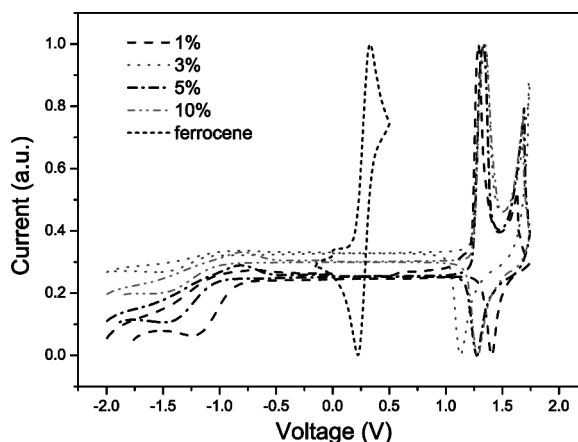


Figure 5. Cyclic voltammograms of the polymers.



**Table 2.** Optical properties and HOMO energy levels of poly(DOP-co-DPFN)s

	Solution, $\lambda_{\max}$ (nm) <sup>a</sup>				Film, $\lambda_{\max}$ (nm) <sup>b</sup>		Band gap (eV)	E <sub>HOMO</sub> <sup>c</sup> (eV)
	Abs.	Ems.	Abs.	Ems.	Abs.	Ems.		
poly(99DOP-co-1DPFN)	385	422 443 544	380	527	380	527	2.85	5.75
poly(97DOP-co-3DPFN)	385	422 443 544	380	543	380	543	2.75	5.76
poly(95DOP-co-5DPFN)	385	422 443 544	380	543	380	543	2.71	5.77
poly(90DOP-co-10DPFN)	385	422 443 544	380	543	380	543	2.61	5.77

<sup>a</sup>Measured in chloroform solution.<sup>b</sup>Measured as thin films on fused quartz plates.<sup>c</sup>Determined from the onset voltage of the first oxidation potential with reference to ferrocene at 4.8 eV.**Table 3.** Summary of the device characteristics

Polymers	$\lambda_{\max}$ (nm)	Luminance (cd/m <sup>2</sup> )	Power efficiency (lm/W)	Luminance efficiency (cd/A)	EQE (%)
poly(99DOP-co-1DPFN)	525	4,300	0.623	1.65	0.64
poly(97DOP-co-3DPFN)	546	1,500	0.574	1.76	0.65
poly(95DOP-co-5DPFN)	555	3,600	0.672	2.13	0.79
poly(90DOP-co-10DPFN)	559	700	0.282	1.12	0.43

## Conclusions

A series of copolymers composed of 9, 9'-dioctylfluorene and 2,3-diphenylfumaronitrile units were successfully synthesized by Suzuki coupling reaction. The synthesized polymers were soluble in organic solvents and showed high thermal stability. The electron withdrawing DPFN units decreased the optical band gaps, and lowered HOMO and LUMO energy levels of the copolymers compared with poly(dioctylfluorene) homopolymer. Efficient energy transfer was also observed between the fluorene and the 2,3-diphenylfumaronitrile units. Only 1% DPFN containing PF copolymer showed its maximum EL emission at 527 nm by intra- or intermolecular energy transfer. The device fabricated using poly (95DOP-co-5DPFN) as the emissive layer showed the best performance with a maximum luminescence of 3,600 cd/m<sup>2</sup> and external quantum efficiency of 0.79%.

## Acknowledgments

This research was financially supported by New University for Regional Innovation (NURI) program, and the National Research Foundation of Korea (NRF) grant funded by the Korean government (MEST) (No. R01-2007-000-20508-0).

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