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Sang Kyu Lee [a] , Young Kwan Jung [b] , Won Suk Shin [a] , Hong-Ku Shim [c] & Sang-Jin Moon [a]

[a] Energy Materials Research Center, Korea Research Institute of Chemical Technology, Yuseong, Dae-jeon, Korea

[b] OLED Technology Development Team3, LG Display Co, Gongdan-dong, Gumi-si, Gyungsangbuk-do, Korea

[c] Department of Chemistry and School of Molecular Science, Korea Advanced Institute of Science and Technology, Dae-jeon, Korea

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Synthesis and Characterization of Fluorene-Based Conjugated Polymers Containing Thiophene Derivatives in Main Chain

SANG KYU LEE,[1] YOUNG KWAN JUNG,[2]
WON SUK SHIN,[1] HONG-KU SHIM,[3]
AND SANG-JIN MOON[1]

[1]Energy Materials Research Center, Korea Research Institute of Chemical Technology, Yuseong, Dae-jeon, Korea
[2]OLED Technology Development Team3, LG Display Co, Gongdan-dong, Gumi-si, Gyungsangbuk-do, Korea
[3]Department of Chemistry and School of Molecular Science, Korea Advanced Institute of Science and Technology, Dae-jeon, Korea

*Three novel alternating copolymers containing 9,9-dioctylfluorene and thiophene derivatives, poly[(9,9-dioctylfluorene-2,7-diyl)-alt-(4,4′-bis(3″-hexyl-2″thienyl)-biphenyl-5”,5″-diyl)] (**P1**), poly[(9,9-dioctylfluorene-2,7-diyl)-alt-(5,5′-bis(3″-hexyl-2”thienyl)-2,2′-bithiophenyl-5”,5″-diyl)] (**P2**), and poly[(9,9-dioctylfluorene-2,7-diyl)-alt-(5,5′-bis(3″-hexyl-2″thienyl)-2,2′-biselenophenyl-5”,5″-diyl)] (**P3**) were synthesized by a palladium-catalyzed Suzuki polymerization. The synthesis, thermal stability, as well as the optical and electrochemical properties of these polymers are systematically investigated. The polymers were thermally stable up to 400°C, and readily soluble in common organic solvent. The absorption and emission maxima of the copolymers varied according to the type of incorporated aromatic group (thiophene, selenophene, or phenylene).*

Keywords Electroluminescence; polyfluorene; thiophene

Introduction

Over the last decade, polymer light emitting diodes (PLEDs) have attracted much scientific and technological research interest because of their potential utility in a wide variety of applications such as flat-panel displays and light-emitting diodes (LEDs) [1–3]. In particular, among all the known π-conjugated polymers for PLEDs, poly(9,9-di-n-octylfluorene) (PFO) are the most promising candidates as blue-light-emitting polymers because of their highly efficient photoluminescence (PL), their

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Address correspondence to Hong-Ku Shim, Department of Chemistry and School of Molecular Science, Korea Advanced Institute of Science and Technology, Dae-jeon, 305-701, Republic of Korea. E-mail: hkshim@kaist.ac.kr; Sang-Jin Moon, Energy Materials Research Center, Korea Research Institute of Chemical Technology, Sinseongno 19, Yuseong, Dae-jeon 305-600, Republic of Korea. E-mail: moonsj@krict.re.kr good thermal, chemical, and electrochemical stability, and their convenient solubility in common organic solvents [4–8]. Moreover, many research groups have studied various electroluminescent fluorene-based polymers emitting in the region of the three elementary colors of light (red, green, and blue). The optical and electroluminescent properties of the polymer may be tuned by introducing into PF of comonomers with a lower band-gap than fluorene monomer [9–11].

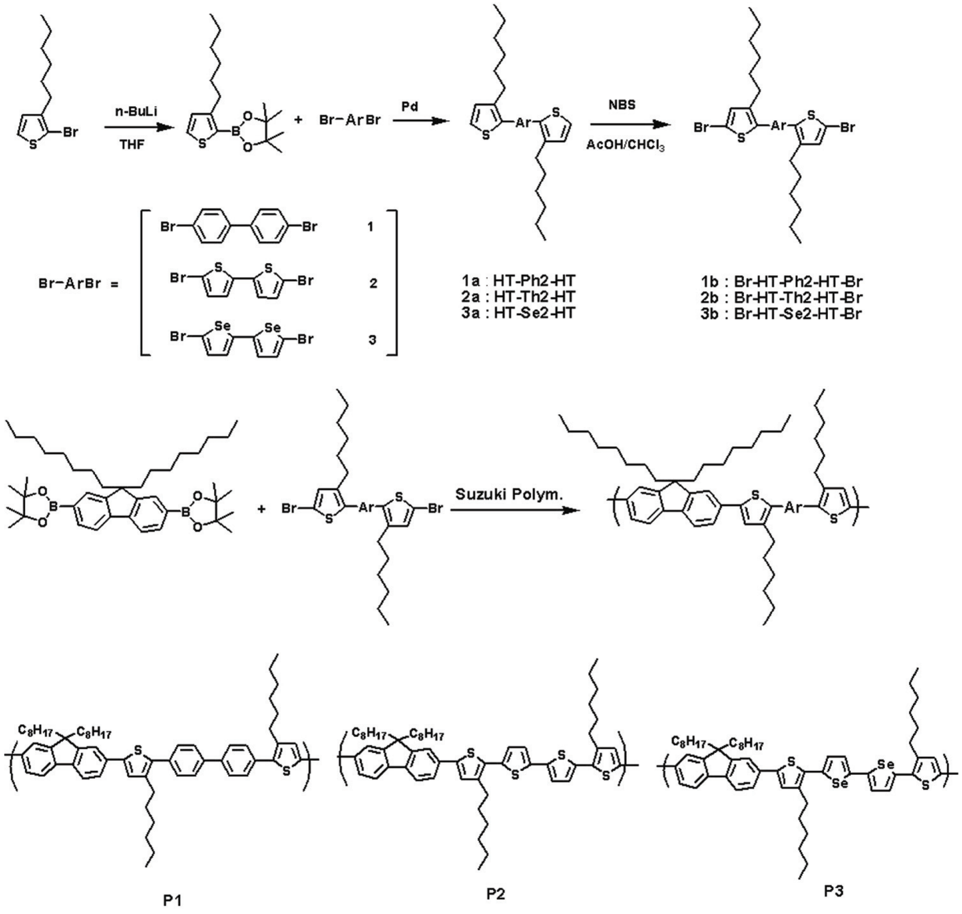
A serious problem associated with PFOs is an imbalance in charge carriers due to large hole injection barriers and different charge carrier mobilities [12]. Several approaches have been tried in efforts to improve the injection of charges from the electrode [13–15]. To promote the charge-transporting properties, it is necessary to design and synthesize conjugated polymers that possess a hole-transporting unit. Here we report the synthesis and characterization of new fluorene-based copolymers containing thiophene derivatives in the main chain. To tune the optical and EL properties of the polymer, the type of incorporated aromatic group (thiophene, selenophene, or phenylene) into thiophene derivative was modified. In this study, three novel alternating copolymers containing 9,9-dioctylfluorene and thiophene derivatives, poly[(9,9-dioctylfluorene-2,7-diyl)-alt-(4,4′-bis(3″-hexyl-2″thienyl)-biphenyl-5”,5″-diyl)] (**P1**), poly[(9,9-dioctylfluorene-2,7-diyl)-alt-(5,5′-bis(3″-hexyl-2″thienyl)-2,2′-bithiophenyl-5”,5″-diyl)] (**P2**), and poly[(9,9-dioctylfluorene-2,7-diyl)-alt-(5,5′-bis(3″-hexyl-2″thienyl)-2,2′-biselenophenyl-5”,5″-diyl)] (**P3**) were synthesized by a palladium-catalyzed Suzuki polymerization. We systematically investigated the synthesis, thermal stability, as well as the optical and electrochemical properties of these polymers.

Experimental

The monomers and 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-di-n-octylfluorene were prepared according to a literature procedure [16,17]. All copolymers were synthesized by a polycondensation of 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-di-n-octylfluorene and corresponding dibromonated dihexylthiophene units through Pd-catalyzed Suzuki coupling reactions (Scheme 1) [18].

The chemical structures of the polymers were verified with ^{1}H NMR and elemental analysis. UV-visible analysis was performed with a Shimadzu Jasco V-530 UV/vis spectrometer. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument, using tetrahydrofuran (THF) as the eluent and polystyrene as the standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) were performed under a nitrogen atmosphere at a heating rate of 10°C/min with a Dupont 9900 analyzer. The thicknesses of the polymer films were measured using an Alpha step 200 profilometer. Photoluminescence (PL) spectra of the polymers were obtained with a Spex Fluolog-3 (Model FL3-11) spectrofluorometer. Electroluminescence spectra were obtained with a Minolta CS-1000. The current-voltage (I-V) and luminescence-voltage (L-V) characteristics of the devices were measured with a Keithley 238 as the voltage and current source and a Minolta LS-100 as the luminance detector. All the measurements were performed in air at room temperature.

In this study, the devices were fabricated with ITO/PEDOT:PSS/polymer/Ca/Al structures. The procedure for cleaning the ITO surface included sonication and rinsing in deionized water, methanol, and acetone. The hole-transporting



Scheme 1. Synthetic scheme for the monomers and copolymers.

PEDOT:PSS layer was spin-coated onto each ITO anode from a solution purchased from Bayer Co. Each polymer solution was then spin-coated onto the PEDOT:PSS layer. The polymer solution for spin-coating was prepared by dissolving the polymer (1 wt%) in chlorobenzene. Ca and aluminum contacts were formed by vacuum deposition at pressures below 10^{-6} Torr, giving an active area of 0.04 cm^2.

Results and Discussion

The synthesized copolymers are soluble in common organic solvent such as tetrahydrofuran (THF), chloroform, or toluene. The molecular weight were determined by GPC against polystyrene standards in THF eluent and were found to be in the range of 11,000–45,000 with a polydispersity index of 2.2–2.3. As shown in Figure 1, the copolymers have good thermal stability up to ca. 400°C. The physical properties of the polymers are summarized in Table 1.

The UV-vis absorption spectra of the polymers in chloroform solution and thin films are shown in Figures 2 and 3, respectively, and the corresponding absorption and emission properties are summarized in Table 2. The absorption and emission

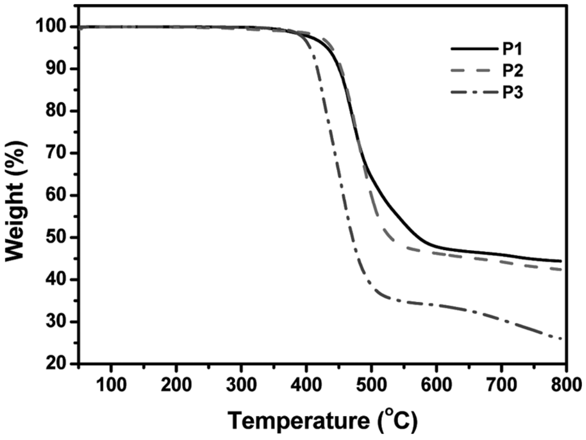


Figure 1. TGA thermograms of the copolymers.

maxima of the copolymers varied according to the type of incorporated aromatic group (thiophene, selenophene, or phenylene). The polymers, P3 containing biselenophene units in solution exhibited red shifted spectra compared to the thiophene-based polymer, P2. The optical band gap obtained from the extrapolation of absorption edges of film are in the order of P3 (2.08 eV) < P2 (2.16 eV) < P1 (2.70 eV). The band-gap of selenophene-based copolymer showed a decrease of ca. 0.1 eV compared to that of thiophene-based copolymer. Such a decrease in the band gap can be explained by the fact that the ease of π-electron delocalization for selenophene unit is greater than that for thiophene, and that the bandwidth of the selenophene unit is larger than that of thiophene unit, which may contribute to the observed red shift [19].

To investigate the redox behavior of the copolymers and determined the energy levels of their highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), the electrochemical properties of the polymers were investigated by using cyclic voltammetry (CV). All measurements were calibrated using ferrocene as a standard. In the anodic scan, the onset of oxidation of P1, P2, and P3 was found to occur at 0.91, 0.58, and 0.50 V (vs. SCE), respectively, corresponding to the ionization potential values of −5.61, −5.28, and −5.24 eV, respectively (Figure 4). Unfortunately, it was difficult to obtain the LUMO energies

Table 1. Physical properties of the polymers

	$M_n{}^a$	$M_w{}^a$	PDI^a	T_g (°C)^b
P1	14,000	32,000	2.3	65
P2	45,000	101,000	2.2	60
P3	11,000	24,000	2.2	61

[a] M_n, M_w, and *PDI* of the polymers were determined by gel permeation chromatography using polystyrene standards.

[b] Glass transition temperature determined by differential scanning calorimetry (DSC).

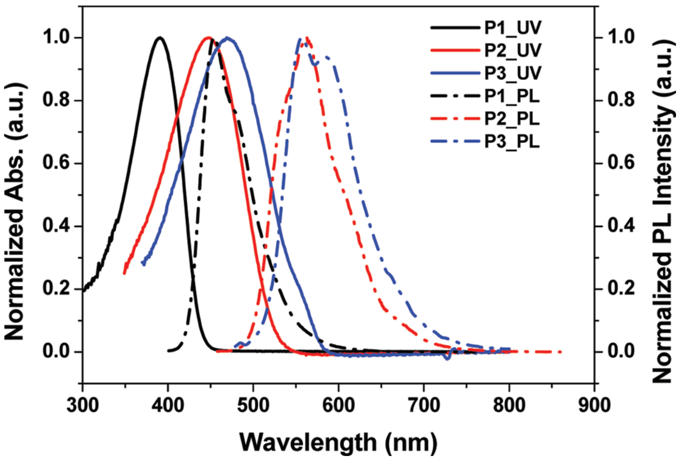


Figure 2. UV-vis absorption and PL spectra of the copolymers in the chloroform solution.

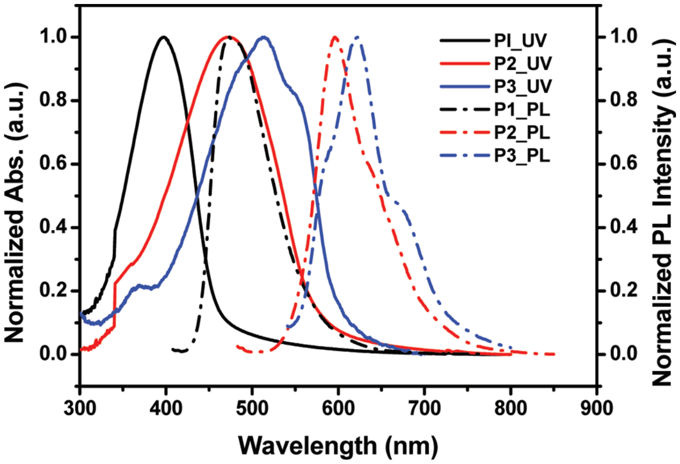


Figure 3. UV-vis absorption and PL spectra of P1, P2, and P3 as films.

Table 2. Spectral data and energy levels of the polymers

	Film, λ_{max} (nm)				
	Absorption	Emission	$\Phi_{PL}{}^{a}$	HOMO^{b}/LUMO^{c} (eV)	E_g^{opt} (eV)^{d}
P1	398	474	1.00	−5.61/−2.91	2.70
P2	473	596	0.41	−5.28/−3.12	2.16
P3	514	623	0.20	−5.24/−3.16	2.08

[a] The film fluorescence quantum yields measured on quartz plates relative to P1 assuming 1.00 for comparison.

[b] Calculated from $E_{1/2}$ (energy level of ferrocene of 4.8 eV under vacuum).

[c] Calculated from the HOMO level and optical band gap.

[d] The optical band gap was determined from the UV-vis. absorption onset in the solid state.

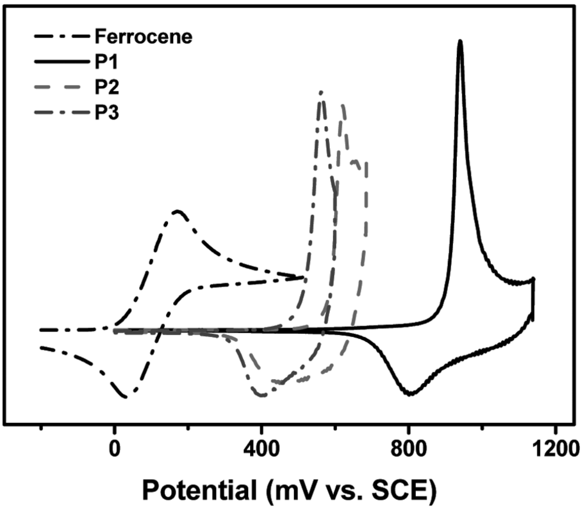


Figure 4. Cyclic voltammograms of the copolymers.

for the copolymers using this technique, so these values were estimated from the optical band gap and the HOMO energies. The energies of the LUMO levels of P1, P2, and P3 are listed in Table 2.

To investigate the EL properties of the polymers, we fabricated devices with the configuration: ITO/PEDOT:PSS (50 nm)/polymers (80 nm)/Ca (50 nm)/Al (100 nm) and characterized them as a function of the applied voltage. The resulting polymer was spin-coated from a 1.0 wt% solution in chlorobenzene onto an ITO substrate coated with PEDOT. As shown in Figure 5, the EL spectra of the copolymers are nearly identical to the PL spectra of the spin-coated films,

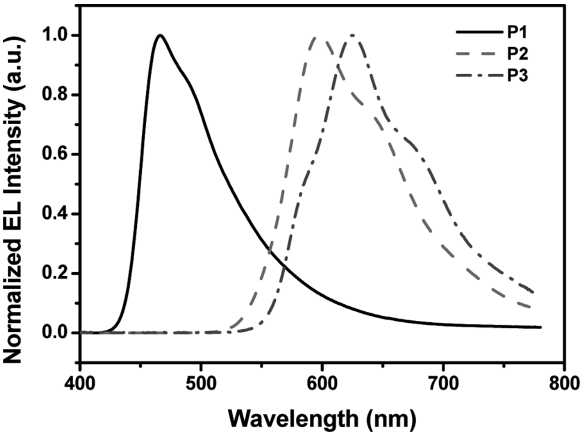


Figure 5. EL spectra of the copolymers devices with the configuration of ITO/PEDOT:PSS/polymer/Ca/Al under 10 V.

Table 3. Summary of the device characteristics

	λmax (nm)[a]	CIE coordinates (x,y)[b]	Maximum luminance (cd/m^2)	Turn-on voltage (V)[c]
P1	466	(0.20, 0.30)	700	4.5
P2	596	(0.59, 0.41)	1100	3.0
P3	625	(0.63, 0.37)	340	3.0

[a] Maximum of the EL spectrum at a voltage of 10 V.
[b] Determined from EL spectrum (Figure 5).
[c] Voltage needed for brightness of 1 cd/m^2.

and this indicates that the energy transfer involved in EL is similar to that in PL. P1, P2, and P3 emitted blue, orange, and red light with a maximum emission at 466, 596, and 625 nm, respectively. Thiophene or selenophene has a narrower band gap energy than phenylene, and hence the emission from copolymers (P2 or P3) containing thiophene or selenophene is red-shifted with respect to that of the copolymer (P1) containing phenylene. In particular, P3 (which contains biselenophene units) showed almost pure red emission with Commission Internationale de l'Eclairage (CIE) coordinates of (0.63, 0.37) as shown in Table 3. Figure 6 shows the characteristics of the voltage-luminance (V-L) and

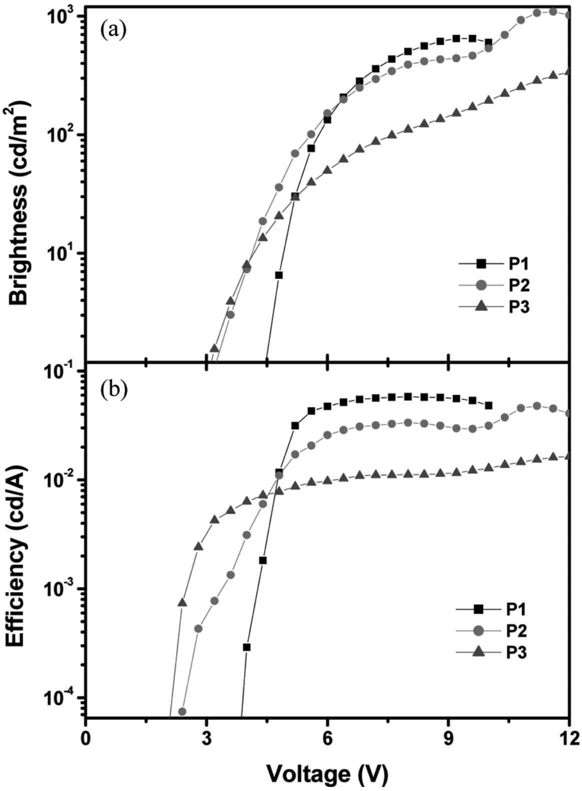


Figure 6. (a) V-L and (b) V-current efficiency characteristics of the copolymers.

the voltage-current efficiency, and Table 3 summarized the EL spectra and related performance data. The turn-on voltages of the polymers ranged from about 3.0 to 4.5 V. The luminance reached 700 cd/m^2 at 9.6 V in P1, 1100 cd/m^2 at 11.6 V in P2, and 340 cd/m^2 at 12 V in P3. We are currently endeavoring to further improve the performance of PLEDs by incorporating a third monomer into the polymer backbone. A detailed study aimed at improving the efficiency of these devices and further research into the new applications in organic photovoltaic cells (OPVs) of these narrow energy band gap polymers are currently underway.

Conclusion

We synthesized new conjugated fluorene-based copolymer containing thiophene derivatives with a variety of aromatic group through palladium-catalyzed Suzuki polymerization. The absorption and emission maxima of the copolymers varied according to the type of incorporated aromatic group (thiophene, selenophene, or phenylene). P1 (which contains biphenylene units), P2 (which contains bithiophene units), and P3 (which contains biselenophene units) emitted blue, orange, and red light with a maximum emission at 466, 596, and 625 nm, respectively. Further modification of the polymer structure and further research into the new application in OPV of these materials are currently underway.

Acknowledgments

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