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Saturated and Efficient Red Light-Emitting Fluorene-Based Alternating Polymers Containing Phenothiazine Derivatives

Nam Sung Cho, Jong-Hwa Park, Sang-Kyu Lee, Jonghee Lee, and Hong-Ku Shim*

Department of Chemistry (BK21) & CAFPoly, Korea Advanced Institute of Science and Technology (KAIST), 373-1 Guseong-dong, Yuseong-gu, Daejeon 305-701, Korea

Moo-Jin Park and Do-Hoon Hwang

Department of Applied Chemistry, Kumoh National Institute of Technology, Kumi 730-701, Korea

Byung-Jun Jung

Corporate R&D Center, Samsung SDI

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ABSTRACT: A series of novel organic semiconducting polymers composed of fluorene and bis(2-phenyl-2-cyanovinyl)-10-hexylphenothiazine) (PZB) comonomer were synthesized and characterized. These polymers were found to be thermally stable and readily soluble in common organic solvents. Our results showed that the color of the light emitted by the homopolymer, poly(9,9-dioctylfluorene-2,7-diyl) (PDOF), could be easily tuned by incorporating PZB comonomer, which has a narrower band gap. The photoluminescence (PL) emission spectra of the copolymers were highly red-shifted as the fraction of PZB in the copolymer was increased. Light-emitting devices were fabricated in the ITO/PEDOT:PSS/polymer/Ca/Al configuration using the polymers as the emitting layer. The electroluminescence (EL) device based on PF−PZB50 showed almost pure red emission [CIE coordinate values $(x, y) - (0.63, 0.36)$] that was very close to the standard red (0.66, 0.34) demanded by the National Television System Committee. In addition, bulk heterojunction polymeric photovoltaic cells (PPVCs) fabricated from a thin film composed of a blend of PF−PZB50 and the fullerene derivative [6,6]-phenyl C61 butyric acid methyl ester (PCBM), in a ITO/PEDOT:PSS/(PF−PZB50:PCBM = 1:3)/LiF/Al configuration, showed promising performance. Specifically, under 100 mW/cm^2 of AM 1.5 white light illumination, the device produced an open-circuit voltage of 0.78 V and a short-circuit current of 2.38 mA/m^2. The fill factor of the device was 0.29, and the power conversion efficiency was 0.53%.

Introduction

The use of electroluminescent polymers as the active materials in polymer light-emitting diodes (PLEDs) has attracted considerable academic and commercial interest due to the potential of these materials in flat-panel display and lighting applications.[1−3] A large number of electroactive and photoactive conjugated polymers have been introduced in recent decades, such as poly(*p*-phenylenevinylene) (PPV),[4] polythiophene (PT),[5] and polyfluorene (PF).[6] Among these polymers, PF and its derivatives have emerged as emitting materials suitable for use in PLEDs because of their high photoluminescence (PL) quantum efficiency, good thermal stability, and amenability to introduction of various functional groups at the 9-position of fluorene. A variety of PFs have been developed by introducing various comonomers, and their properties have been investigated with a view to obtaining stable high-efficiency red, green, and blue emitters.[7−9] As a result of these investigations, PFs have emerged as the most promising candidates for PLEDs. The study of these polymers is ongoing, with numerous attempts having been made to synthesize fluorene-based RGB emitting materials.[10]

Despite many attempts to tune the color of blue-emitting PFs, appropriate red- and green-emitting materials that meet the requirements of display applications have yet to be obtained.[11,12] Among the various methods for color tuning, covalently attaching a chromophore to the polymer has been most widely used because aggregation and excimer formation is prevented and efficient energy transfer from the polymer chromophores to the dye chromophores easily confines the singlet excitons. If two chromophores with different energy band gaps are mixed, energy transfer occurs from the dye with the larger band gap to that with the smaller band gap, and emission from the latter dominates.[13,14] To date, the most widely used narrow energy band gap comonomers have been those containing aromatic heterocycles such as thiophene, bithiophene, benzothiazole, and benzodithiazole derivatives.[15−18]

Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Polymers and organic molecules[19] containing phenothiazine or its derivatives have recently attracted considerable research interest on account of their unique electrooptical properties, which make these molecules potential candidate materials for diverse applications such as light-emitting diodes,[7,20] photovoltaic devices, and chemiluminescence.[16] It has been suggested that inclusion of phenothiazine or its derivatives into PF should improve the hole-transporting ability of the PF and thus improve the EL efficiency.[8,21] Additionally, the nonplanar structure of the phenothiazine ring should impede stacking aggregation and intermolecular excimer formation in the polymer main chain.[8]

On these grounds, we initiated a research project aimed at synthesizing a new class of phenothiazine-based fluorescent polymers with pure and efficient red emission. Our strategy was to first build the basic phenothiazine-based structure and then

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* To whom correspondence should be addressed. E-mail: hkshim@kaist.ac.kr.

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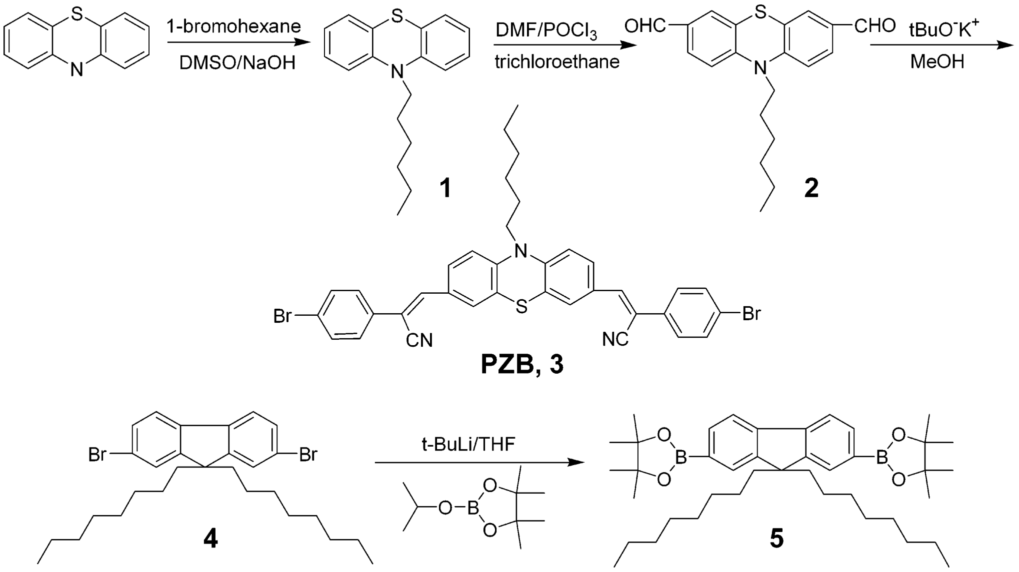
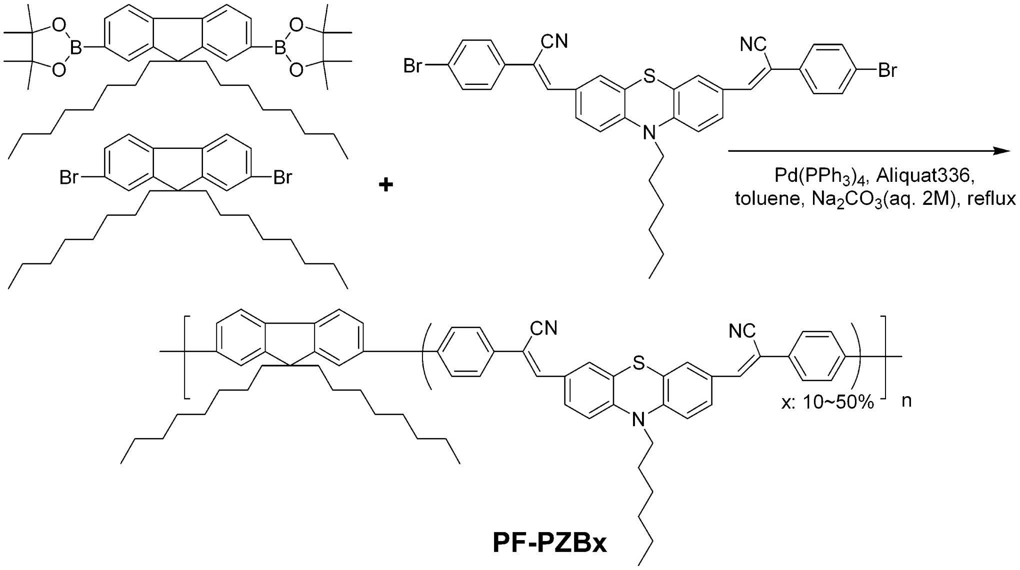
Scheme 1. Synthetic Scheme of 3,7-Bis{2-(4′-bromophenyl)-2-cyanovinyl}-10-hexylphenothiazine (PZB)



Scheme 2. Synthetic Scheme of Poly{9,9-dioctylfluorene-2,7-diyl-*co*-3,7-bis(2-phenyl-2-cyanovinyl)-10-hexylphenothiazine-4′,4′-diyl} (PF−PZBs)



to extend the conjugation length by inserting phenylene and cyanovinylene functionalities capable of imparting red-emitting properties to the polymer.[6a,18] These experiments led to the discovery of the narrow energy band-gap comonomer, bis(2-phenyl-2-cyanovinyl)-10-hexylphenothiazine) (PZB), and to a series of PZB and fluorene-based alternating and statistical copolymers that exhibit pure red emission: poly{9,9-dioctylfluorene-2,7-diyl-*co*-3,7-bis(2-phenyl-2-cyanovinyl)-10-hexylphenothiazine-4′,4′-diyl} (PF−PZB10, PF−PZB30, PF−PZB40, and PF−PZB50). Here we show that the electron-rich phenothiazine ring is an excellent molecular building block for achieving better hole-injection/transport in polymer electronic devices. In addition, we successfully demonstrate that the cyanovinylene group easily tunes the blue-emitting PF to pure red-emitting polymer materials.

In addition to the advantages of PF−PZBs as red-emitting materials, the incorporation of phenothiazine derivatives into PF is expected to result in polymers with narrow energy band gaps suitable for use in organic photovoltaic cells,[22,23] especially in copolymers containing large amounts of PZB such as in PF−PZB50. Photovoltaic cells (PVCs) made from thin films of a composite of PF−PZB50 and the fullerene derivative [6,6]-phenyl C61 butyric acid methyl ester (PCBM) as an active layer show promising performance: its energy conversion efficiency (ECE) is up to 0.54% under AM1.5 solar simulator. In the present study we successfully synthesized a series of new copolymers by changing the ratio of phenothiazine derivative (PZB), and then we applied these copolymers to EL and photovoltaic devices. The synthetic routes and structures of the monomers and polymers are shown in Schemes 1 and 2.

Experimental Section

Measurements. NMR spectra were recorded on a Bruker AVANCE 400 spectrometer with tertramethylsilane as an internal reference. Mass spectra were obtained using AUTOSPEC ULTIMA spectrometer. Elemental analysis was performed using EA-1110-FISONS elemental analyzer. The number- and weight-average molecular weight of the polymer was determined by gel permeation chromatography (GPC) on Waters GPC-150C instrument using tetrahydrofuran (THF) as eluent and monodisperse polystyrene as standard. Thermogravimetric analysis (TGA) and differential scanning calorimetry (DSC) of the polymer were performed under a nitrogen atmosphere at a heating rate of 10 °C/min with a Dupont

9900 analyzer. UV−vis spectra were measured by using a Jasco V-530 UV/vis spectrometer. PL spectra were measured by using Spex Fluorolog-3 spectrofluorometer. Cyclic voltammetry measurement was performed on an AUTOLAB/PGSTAT12 at room temperature with a three-electrode cell in a solution of Bu_4NBF_4 (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^+ electrode as a reference electrode. Film thickness was measured with a TENCOR alpha-step 500 surface profiler.

Device Fabrication and Characterization. A hole injection layer of poly(3,4-ethylenedioxythiophene) (PEDOT) doped with poly(styrenesulfonic acid) (PSS) (PEDOT:PSS, Bayer Al 4083) was spin-coated onto the prepatterned ITO anode and dried. Polymer solution was then spin-coated onto the PEDOT:PSS layer and dried. Ca/Al (100 nm/100 nm) cathode was vacuum-deposited onto the polymer film through shadow mask at a pressure below 1×10^{-6} Torr, yielding an active area of 0.04 cm^2. For PLED measurements, EL spectra were obtained with a Minolta CS-1000. The current−voltage−luminance characteristics were measured with a current−voltage source (Keithley 238) and a luminescence detector (Minolta LS-100). Photocurrent−voltage measurements were performed under AM 1.5, 100 mW/cm^2 irradiation (1 sun) of WXS-105H Solar Simulator made by WACOM Co. Ltd. using the HP4140B, HP3456A digital voltmeter.

Materials. Phenothiazine, 4-bromophenylacetonitrile, 1-bromohexane, 2,7-dibromofluorene, toluene (99.8%, anhydrous), DMSO, and Aliquat 336 were purchased from Aldrich. All chemicals were used without further purification. 2,7-Dibromo-9,9-dioctylfluorene were synthesized according to procedures outlined in the literature.[7,24] Tetrakis(triphenylphosphine)palladium(0) was purchased from DNF Solution Co. Solvents with analytical-grade were used during the whole experiments, and all chemicals were used without further purification.

Synthesis of 10-*n*-Hexylphenothiazine (1). 1-Bromohexane (16.56 g, 100.36 mmol), phenothiazine (10 g, 50.18 mmol), sodium hydroxide (20.0 g, 500 mmol), and dimethyl sulfoxide (DMSO) (100 mL) was placed in a 250 mL two-neck round-bottom flask, and then this mixture was stirred for 2 days at room temperature. The mixture was extracted with EA/brine and then dried with $MgSO_4$. The resulting liquid was purified by column chromatography. The product yield was 67% (9.53 g). ^1H NMR (DMSO-d_6, ppm): δ 7.12 (m, 4H), 6.88 (m, 4H), 3.75 (t, 2H), 1.57 (m, 2H), 1.30−1.13 (m, 6H), 0.74 (t, 3H). ^{13}C NMR (DMSO-d_6, ppm): δ 145.05, 127.97, 127.51, 122.81, 116.24, 48.20, 31.78, 27.45, 26.94, 23.48, 16.08. Anal. Calcd for C_{18}H21NS: C, 76.28; H, 7.47; N, 4.94; S, 11.31. Found: C, 76.90; H, 7.65; N, 6.02; S, 10.11.

Synthesis of 10-*n*-Hexylphenothiazine-3,7-dicarbaldehyde (2). A 500 mL three-necked flask containing 16.7 mL (220 mmol) of anhydrous DMF was cooled in an ice bath. To this solution, 16.8 mL (180 mmol) of phosphorus oxychloride was added dropwisely for 30 min. Compound **1** (5 g, 17.64 mmol) in 30 mL of 1,1,2-trichloroethane was added to the above solution and heated to ca. 90 °C for 2 days. This solution was cooled to room temperature, poured into ice water, and neutralized to pH 6−7 by dropwise addition of saturated aqueous sodium hydroxide solution. The mixture was extracted with EA/water. The organic layer was dried with anhydrous $MgSO_4$ and then concentrated under reduced pressure. The crude product was purified by column chromatography. A bright yellow solid was obtained (4.3 g, 71%). ^1H NMR ($CDCl_3$, ppm): δ 9.78 (s, 2H), 7.63 (q, 2H), 7.54 (2, 2H), 6.91 (d, 2H), 3.89 (t, 2H), 1.79 (q, 2H), 1.43 (m, 2H), 1.28 (m, 4H), 0.85 (m, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 189.79, 148.84, 131.93, 130.10, 128.35, 124.36, 115.51, 48.46, 31.24, 26.56, 26.33, 22.47, 13.89. Anal. Calcd for $C_{20}H_{21}NO_2S$: C, 70.77; H, 6.24; N, 4.13; S, 9.45. Found: C, 69.38; H, 6.22; N, 3.95; S, 9.46.

3,7-Bis(2-(4′-bromophenyl)-2-cyanovinyl-10-hexylphenothiazine (3). Compound **2** (2 g, 5.89 mmol), 1-bromophenylacetonitrile (4.6 g, 23.56 mmol), and methanol (100 mL) were placed in a 250 mL two-neck round-bottom flask at room temperature. A catalytic amount of potassium *tert*-butoxide in methanol was added into this mixture. After 24 h, the bright red solid was filtered and dried. The resulting solid was recrystallized in methylene chloride and methanol, and then the solid was dried in vacuo. The resulting product yield was 65% (2.7 g). Mp: 107 °C ^1H NMR (DMSO-d_6, ppm): δ 7.93 (s, 2H), 7.85 (d, 2H), 7.72−7.64 (m, 10H), 7.20 (d, 2H), 3.97 (t, 2H), 1.70 (m, 2H), 1.41 (m, 2H), 1.27 (m, 4H), 0.83 (m, 3H). ^{13}C NMR (DMSO-*d*,[6] ppm): δ 145.12, 141.45, 133.20, 132.00, 129.43, 128.29, 127.69, 127.40, 122.07, 122.03, 117.86, 115.94, 1.6.35, 47.04, 30.75, 25.89, 25.65, 22.05, 13.79. Anal. Calcd for $C_{36}H_{29}Br_2N_3S$: C, 62.17; H, 4.20; N, 6.04; S, 4.61. Found: C, 61.82; H, 4.34; N, 6.01; S, 4.88.

Synthesis of 2,7-Bis(4,4,5,5,-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-dioctylfluorene (4). To a solution of 2,7-dibromo-9,9′-dioctylfluorene (7.0 g, 12.8 mmol) in THF (120 mL) at −78 °C was added, by syringe, 33.79 mL (57.42 mmol) of *tert*-butyllithium (1.7 M in hexane). The mixture was stirred at −78 °C for 2 h. 2-Isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane (7.97 mL, 38.4 mmol) was added to the solution, and the resulting mixture was stirred at −78 °C for 1 h and warmed to room temperature and stirred for 40 h. The mixture was poured into water, extracted with dichloromethane, and dried over $MgSO_4$. The solvent was removed by solvent evaporation, and the residue was purified by several reprecipitations in hexane to provide 4.82 g (59%) of the product as a white solid. ^1H NMR ($CDCl_3$, ppm): δ 7.78 (d, 2H), 7.72 (s, 2H), 7.70 (d, 2H), 1.97 (m, 4H), 1.37 (s, 24H), 1.18−0.99 (m, 20H), 0.79 (t, 6H), 0.53 (m, 4H). ^{13}C NMR ($CDCl_3$, ppm): δ 150.45, 143.89, 133.62, 128.89, 119.35, 83.69, 55.16, 40.07, 31.76, 29.91, 29.18, 29.13, 24.92, 23.57, 22.57, 14.05. Anal. Calcd for $C_{41}H_{64}B_2O_4$: C, 76.64; H, 10.04. Found: C, 77.00; H, 10.17.

General Polymerization Procedure.[7,18] Into 100 mL two-neck flask were added 2.28 mmol of dibromo compounds (2,7-dibromo-9,9-dioctylfluorene (**4**) and PZB (**3**)) and 2.28 mmol of 2,7-bis-(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene in 25 mL of anhydrous toluene. Water-soluble Pd(0) complex, tetrakis-(triphenylphosphine)palladium (1 mol %), was transferred into the mixture in a drybox. Subsequently, 2 M aqueous sodium carbonate deaerated for 30 min and the phase transfer catalyst, Aliquat 336 (several drops), in toluene purged under nitrogen for 1 h was transferred via cannula. The reaction mixture was stirred at 80 °C for 3 days, and then the excess amount of bromobenzene, the end-capper, dissolved in 1 mL of anhydrous toluene was added and stirring continued for 12 h. The reaction mixture is cooled to about 50 °C and added slowly to a vigorously stirred mixture of 200 mL of methanol. The polymer fibers are collected by filtration and reprecipitation from methanol and acetone. The polymers are purified further by washing for 2 days in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues and column chromatographed with a chloroform solution of the polymer. The reprecipitation procedure in chloroform/methanol is then repeated a several times. The resulting polymers were soluble in common organic solvents. Yield: 63−81%.

Poly{9,9-dioctylfluorene-2,7-diyl-*co*-3,7-bis(2-phenyl-2-cyanovinyl)-10-hexylphenothiazine-4′,4′-diyl} (PF−PZB10). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**5**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**4**) (0.40 equiv), and PZB (**3**) (0.10 equiv) were used in this polymerization. ^1H NMR ($CDCl_3$, ppm): δ aromatic and vinylene; 8.85−7.40 (22H), aliphatic; 4.10−3.77 (2H), 2.02−0.76 (∼47H). Element Anal. Found: C, 81.10%; H, 11.17%; N, 0.79%; S, 1.11%.

Poly{9,9-dioctylfluorene-2,7-diyl-*co*-3,7-bis(2-phenyl-2-cyanovinyl)-10-hexylphenothiazine-4′,4′-diyl} (PF−PZB30). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**5**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**4**) (0.20 equiv), and PZB (**3**) (0.30 equiv) were used in this polymerization. ^1H NMR ($CDCl_3$, ppm): δ aromatic and vinylene; 8.80−7.43 (22H), aliphatic; 4.13−3.80 (2H), 2.10−0.76 (∼47H). Element Anal. Found: C, 86.08%; H, 9.54%; N, 0.93%; S, 2.56%.

Poly{9,9-dioctylfluorene-2,7-diyl-*co*-3,7-bis(2-phenyl-2-cyanovinyl)-10-hexylphenothiazine-4′,4′-diyl} (PF−PZB40). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluo-

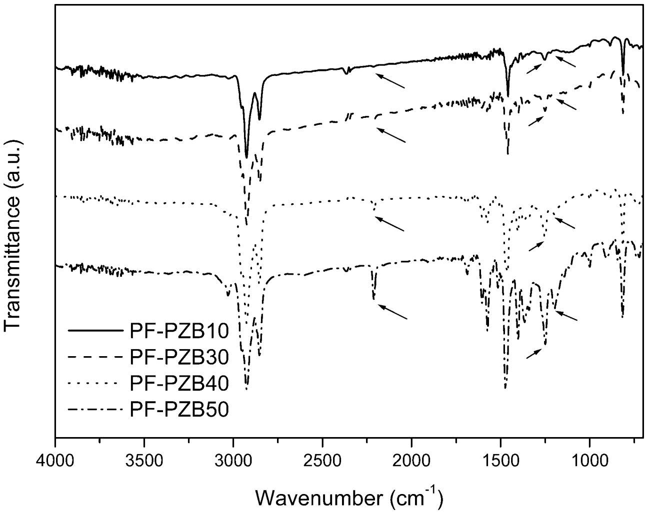


Figure 1. Infrared spectra of the polymers.

Table 1. Polymerization Results

copolymers	PF−PZB10	PF−PZB30	PF−PZB40	PF−PZB50
M_w	49000	38000	45000	65000
M_n	21000	13000	19000	24000
PDI (M_w/M_n)	2.3	2.9	2.4	2.7
polymer yield (%)	69	63	78	81

rene (**5**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**4**) (0.10 equiv), and PZB (**3**) (0.40 equiv) were used in this polymerization. ^{1}H NMR (CDCl$_3$, ppm): δ aromatic and vinylene; 8.83−7.47 (22H), aliphatic; 4.11−3.69 (2H), 2.13−0.80 (~47H). Element Anal. Found: C, 84.93; H, 10.98; N, 2.26; S, 1.38.

Poly{9,9-dioctylfluorene-2,7-diyl-*co*-3,7-bis(2-phenyl-2-cyanovinyl)-10-hexylphenothiazine-4′,4′-diyl} (PF−PZB50). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-dioctylfluorene (**5**) (0.50 equiv), 2,7-dibromo-9,9-dioctylfluorene (**4**) (0.00 equiv), and PZB (**3**) (0.50 equiv) were used in this polymerization. ^{1}H NMR (CDCl$_3$, ppm): δ aromatic and vinylene; 8.80−7.30 (22H), aliphatic; 4.17−3.67 (2H), 2.12−0.76 (~47H). Element Anal. Found: C, 82.98%; H, 7.80; N, 3.80; S, 4.78.

Results and Discussion

Synthesis and Characterization of the Polymers. All the copolymers were found to be soluble in common organic solvents. Each copolymer was spin-coated onto an ITO substrate and was found to produce transparent and homogeneous thin films. The number-average molecular weight (M_n) and the weight-average molecular weight (M_w) of the copolymers, as determined by gel permeation chromatography using polystyrene standards, ranged from 13 000 to 24 000 (M_n) and from 38 000 to 65 000 (M_w), respectively, with polydispersity indices ranging from 2.3 to 3.9. The yields of the copolymers ranged from 63% to 81%. All the copolymers were end-capped with bromobenzene by Suzuki copolymerization. The polymerization results for the synthesized copolymers are summarized in Table 1. The thermal properties of the polymers were determined by thermal gravimetric analysis (TGA). All the polymers were found to exhibit very good thermal stability, losing less than 5% of their weight on heating to ~400 °C in TGA runs under nitrogen.

Optical and Photoluminescence Properties. Representative FT-IR spectra of the polymers are shown in Figure 1. The cyano group produces a medium-intensity, sharp band in the triple-bond region of the spectrum (2270−2210 cm^{-1}), and conjugation with double bonds or aromatic rings moves this absorption to lower frequency. As a result, the absorption band due to stretching of cyano groups in the polymers typically appears at 2210 cm^{-1}, and the intensity of this band increases with increasing fraction of PZB in the polymer. In addition, the phenyl alkyl ether groups in the polymers result in two strong bands at 1215 and 1040 cm^{-1}.

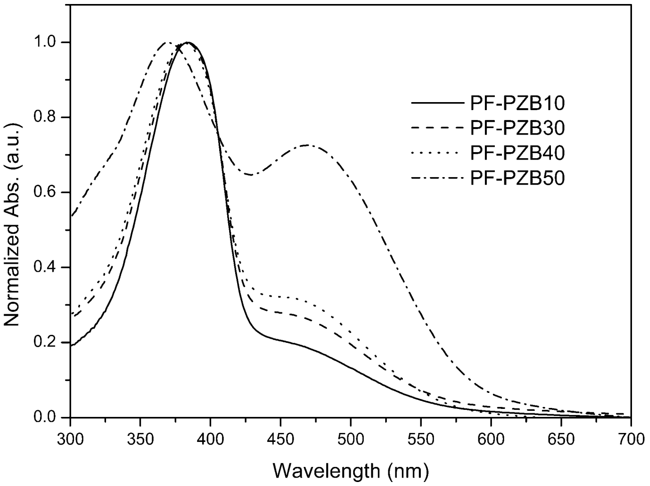


Figure 2. UV−vis absorption spectra of the polymer films.

Table 2. Spectrum Data

	λ_{max}(nm)			
copolymers	UV absorption[a]	PL emission[a]	EL emission	CIE (*x*, *y*)
PBEHF	380	420	419	(0.17, 0.09)
PF−PZB10	383	590	572	(0.57, 0.43)
PF−PZB30	383	597	592	(0.59, 0.41)
PF−PZB40	380	600	598	(0.61, 0.39)
PF−PZB50	369, 469	614	614	(0.63, 0.36)

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

The UV−vis absorption spectra of the copolymers are shown in Figure 2, and the results are summarized in Table 2. All of the polymers exhibit absorption maxima at about 380 nm. However, a slight blue shift in the absorption maximum is observed as the fraction of PZB is increased because increasing the fraction of PZB in the polymer main chain induces a decrease in the effective conjugation length of the fluorene units.[6a,25] In addition, the absorption between 430 and 630 nm increases as the fraction of PZB is increased. The increased absorption in this region is caused by the incorporation of the PZB unit into PF. Of particular note is the spectrum of PF−PZB50, which shows strong absorption between 300 and 400 nm and maxima at 369 and 469 nm. If we consider that the related homopolyfluorene has a strong absorption centered at 380 nm, these spectral characteristics of the alternating copolymer, PF−PZB50, strongly suggest that its ground state is completely different from those of the related homopolymers.[8]

Although the film of the PDOF homopolymer exhibits PL emission maxima at 420 and 440 nm, these two strong and sharp peaks are markedly smaller or nonexistent in the PL spectra of the copolymers, as shown in Figure 3. In contrast, the emission peaks due to the PZB units dominate the PL spectra of the copolymers, indicating that inclusion of these units quenches the emission of PF. These large shifts in the PL maxima are caused by the longer conjugation lengths of the copolymers compared to PDOF, which results in a red shift of the PL emission maxima.

Electroluminescence Properties of LED Devices. To test the performance of the copolymers in real devices, we fabricated double-layer LED devices based on the copolymers with configuration ITO/PEDOT-PSS/polymer/Ca/Al. The EL spectra

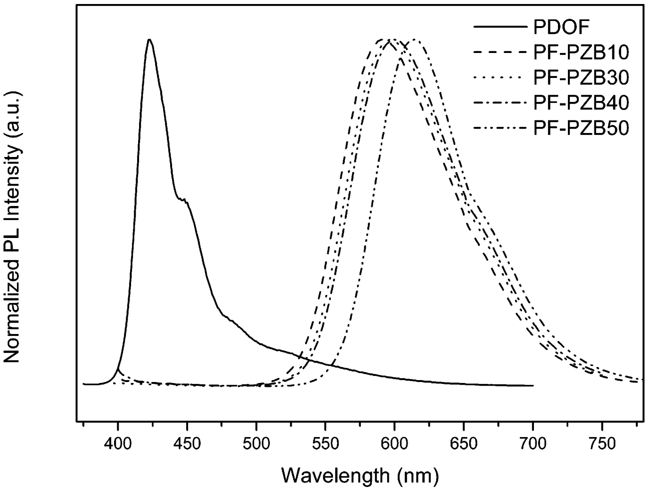


Figure 3. Photoluminescence (PL) spectra of the polymer films.

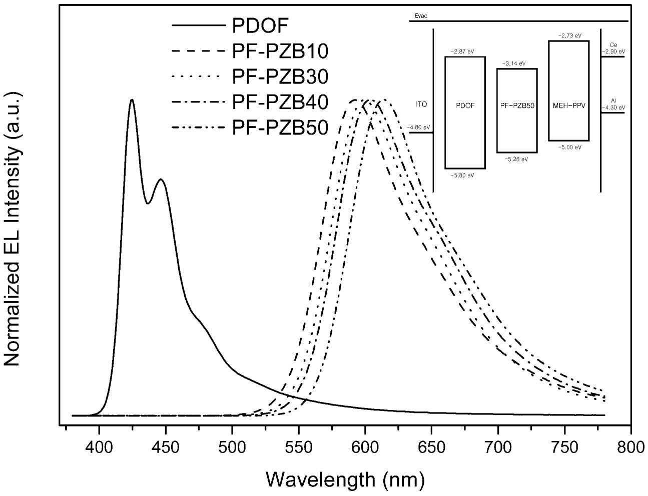


Figure 4. Electroluminescence (EL) spectra and energy band diagram (inset) of the polymers.

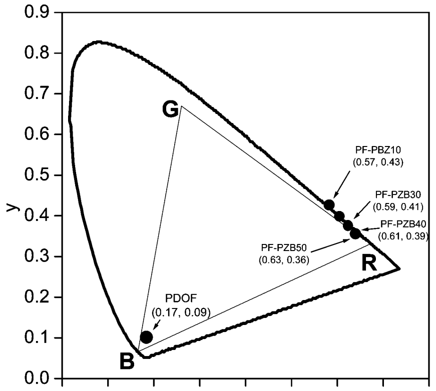


Figure 5. CIE coordinates (*x*, *y*) of polymers (NTSC: solid line).

of the various copolymers are similar to their corresponding PL spectra, as shown in Figure 4. The EL emission maximum is red-shifted to the greatest extent for PF−PZB50. Moreover, as shown in Figure 5, all of the PF−PZBs exhibit almost pure red emission close to the standard red (0.66, 0.33) demanded by the National Television System Committee (NTSC).[26] In particular, the chromaticity value of PF−PZB50 is (0.63, 0.36), which is almost identical to the NTSC standard red. Furthermore, the polymer LED devices all had low turn-on voltages (<4 V).

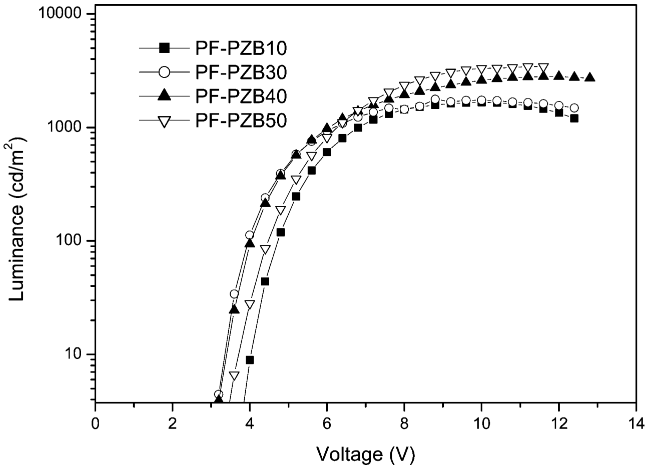


Figure 6. Voltage−luminance curves of the devices.

Table 3. PLED Device Characteristics of the Polymers

polymers	V_{on} (V)[a]	L_{max} (cd/m^2)	luminance efficiency (cd/A, voltage)	ex quantum efficiency (%, voltage)
PF−PZB10	3.8	2800	(0.17,5.6)	(0.30, 5.6)
PF−PZB30	3.1	1660	(0.16, 5.2)	(0.28, 5.2)
PF−PZB40	3.1	1770	(0.48, 6.0)	(0.33, 6.0)
PF−PZB50	3.5	3440	(0.37, 6.4)	(0.43, 6.4)

[a] Turn-on voltage needed for 0.1 cd/m^2.

Figure 6 shows voltage−luminance plots for the copolymer-based devices. The turn-on voltages of the devices ranged from about 3.20 to 3.85 V, and the maximum brightness of all the devices was in the range of 1660−3440 cd/m^2. Although all the devices showed good EL performance, the device based on PF−PZB50 exhibited the highest performance, with a maximum brightness of 3440 cd/m^2 at 11 V. Most of the copolymer devices had good external quantum and luminance efficiencies, reaching values of up to 0.43% and 0.48 cd/A, respectively. On the basis of the above results, we conclude that PF−PZBs are good candidates for use as the red-emitting layer in polymer LED devices. The device properties are summarized in Table 3.

Electrochemical Properties and Polymeric Photovoltaic Cell Characteristics of PF−PZB50. Cyclic voltametry (CV) was employed to investigate the HOMO and LUMO energy levels of PF−PZB50. In the anodic scan, the onset of oxidation of PF−PZB50 occurred at 0.87 V (vs SCE), which corresponds to the ionization potential (I_p) −5.26 eV, according to the empirical relationships proposed by Leeuw et al.: I_p(HOMO) $= -(E_{onset,ox} + 4.39)$ (eV). E_g (LUMO) $= -(E_{onset,red} + 4.39)$ (eV), where $E_{onset,ox}$ and $E_{onset,red}$ are the onset potentials of oxidation and reduction, respectively.[27,28] Because the energy of the HOMO level of PF−PZB50 is −5.26 eV which is closer than PDOF due to the PZB moiety, hole injection is easier in the copolymer than in PDOF. The LUMO energy of PF−PZB50 was estimated from the optical band gap (taken as the onset of absorption in the UV−vis spectrum of the film) and the HOMO energy. Following this approach, we estimate the energy band gap of PF−PZB50 to be 2.14 eV. This energy band gap is narrower than that of the red-orange-emitting copolymer MEH−PPV (2.27 eV), which confirms that PF−PZB50 is a pure red-emitting material. These data are represented in diagrammatic form in Figure 4.

The configuration of typical organic solar cell devices is very similar to that of a PLED, except that a blend of a conjugated polymer and PCBM (phenyl-C_{61} butyric acid) is used as the active layer. To date, various photovoltaic device structures have

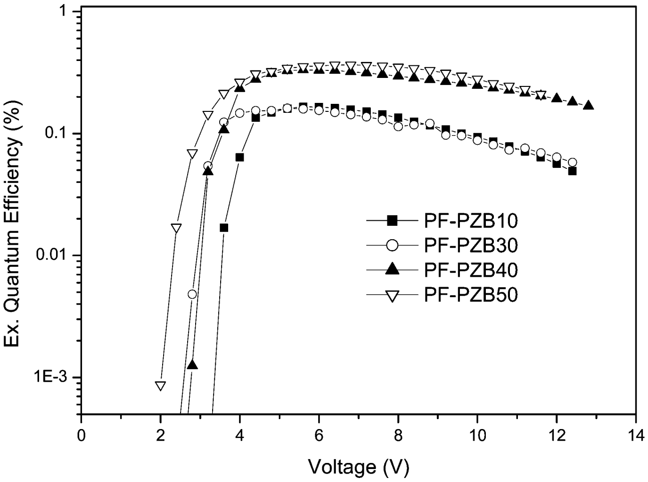


Figure 7. Voltage−external quantum efficiency characteristics of the devices.

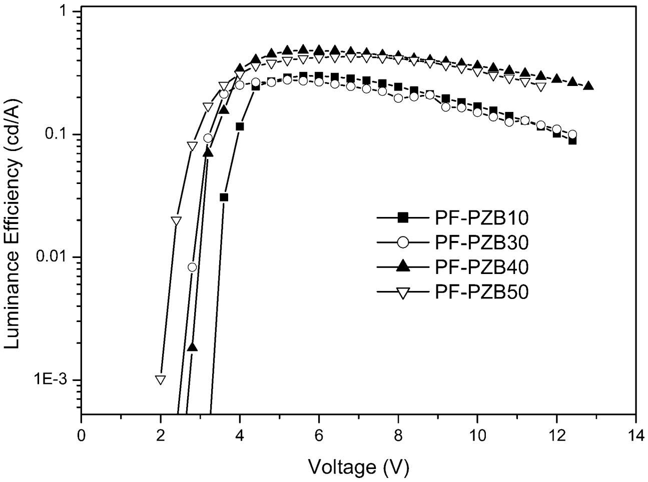


Figure 8. Voltage−luminance efficiency characteristics of the devices.

been reported; however, their performances and lifetimes have yet to meet the requirements of commercial applications. In the present work, we fabricated a photovoltaic cell with the configuration ITO/PEDOT-PSS/PF−PZB50:PCBM = 1:3/LiF/Al. Also, for comparison, an MDMO−PPV photovoltaic cell was fabricated with the same structure (MDMO−PPV:PCBM = 1:4); this cell has been reported to have a power conversion efficiency (PCE) of up to 2.5%.[29]

To achieve efficient charge-carrier generation in light-absorbing polymers, we blended them with suitable acceptors and fabricated bulk heterojunction PVCs based on the resulting composite materials. For example, in polymer−fullerene composites, the conjugated polymers act as donors and the fullerene molecules as acceptors.[30] It is well-known that low-band-gap polymers are better materials for organic solar cell devices because their absorption spectra overlap to a greater extent with the solar spectrum. However, only a limited number of conjugated polymers, such as dialkoxy-PPV derivatives[31] and some thiophene-containing polymers,[32] have been used in organic solar cell devices, and the development of new polymers for these devices is one of the most active areas in this research field.

PF−PZB50 is particularly suitable for use in PVCs because of its relatively low energy band gap (2.14 eV). To test whether a PF−PZB50:PCBM device can show PVC properties, a composite thin film was prepared by spin-coating a 1:3 wt % solution of PF−PZB50 and PCBM in chlorobenzene onto a quartz plate, and its PL spectrum was recorded, as shown in Figure 9. Comparison of the PL spectrum of PF−PZB50 and that of the composite of PF−PZB50 and PCBM shows complete PL quenching in the latter spectrum, which can be attributed to the different kinetics of charge transfer (∼10^{-14} s) and recombination (∼10^{-3} s).[33] These results therefore indicate that PF−PZB50 is suitable for use as an electron-donor in PVCs.

Thus, a PVC based on a composite of PF−PZB50 and PCBM was fabricated with the configuration ITO/PEDOT−PSS/(polymer:PCBM)/LiF/Al. For comparison, the PVC based on MDMO−PPV was also fabricated. Table 4 lists the PVC device performance for the PF−PZB and MDMO−PPV devices under white-light illumination at 100 mW/cm^2. The best performance was obtained for the PF−PZB50:PCBM (1:3) device, which reached J_{sc} (short-circuit current) = 2.38 mA/cm^2, V_{oc} (open-circuit voltage) = 0.78 V, fill factor = 0.29, and PCE = 0.53%, as shown in Figure 10. We note that Voc and FF for the PF−PZB50:PCBM (1:3) device are around 0.78 V and 0.29, respectively, which are approaching those of MDMO−PPV:PCBM cells. In MOMO−PPV, if we consider its ECE has obtained 1.60% as reference that is 65% to the best data reported by Brabec et al.,[29] PF−PZB50 can be a good candidate electron-donor material. We believe that these PVC characteristics could be further improved in future work by varying the ratio of electron donors to acceptors, testing other electron acceptors, and optimizing the film morphology, layer thickness, and postproduction treatment conditions.

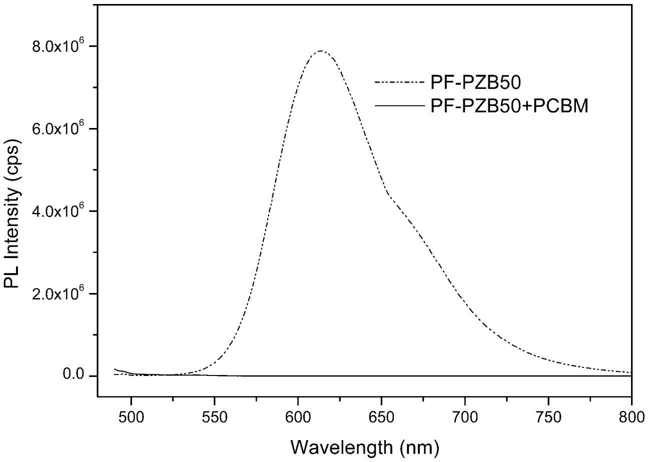


Figure 9. PL spectra of PF−PZB50 film and a blend film (1:3 wt %) of PTHBTzTF and PCBM.

Table 4. Photovoltaic Cell Device Characteristics of MDMO−PPV and PF−PZB50

polymers	V_{oc} (V)	I_{sc} (mA/m^2)	FF	PCE (%)
MDMO−PPV	0.84	3.55	0.54	1.60
PF−PZB50	0.78	2.38	0.29	0.53

Summary

We have synthesized a series of novel fluorene-based copolymers (PF−PZBs) with various molar ratios of the narrow energy band-gap comonomer, PZB. These polymers were synthesized with the aim of creating pure red-light-emitting materials for use in OLEDs as well as polymers that can form the basis of efficient PVCs. The PL and EL emission maxima of the PF−PZBs were gradually red-shifted with respect to those of the homopolymer, poly(9,9-dioctylfluorene-2,7-diyl) (PDOF), as the fraction of PZB in the copolymer was increased. Conventional polymeric LED devices were fabricated in the configuration ITO/PEDOT:PSS/polymer/Ca/Al using the poly-

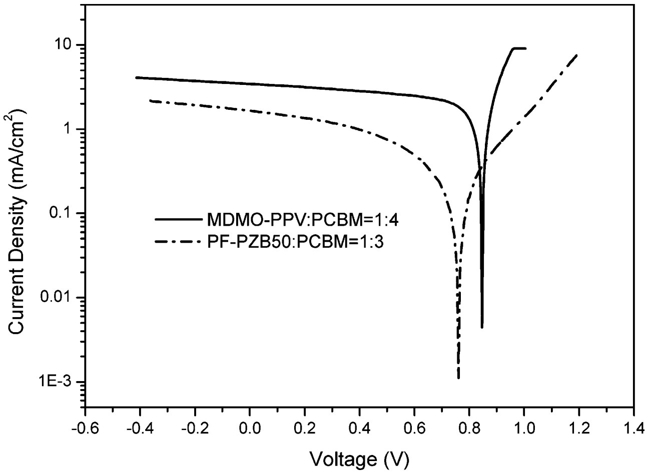


Figure 10. *I*−*V* characteristics of the ITO/PEDOT/PF−PZB:PCBM-(1:3) or MDMO−PPV:PCBM(1:4)/LiF/Al device under 100 mW/cm^2.

mers as emitting layers. The maxima of the EL spectra of PF−PZB10, PF−PZB30, PF−PZB40, and PF−PZB50 were 592, 598, 603, and 614 nm, respectively. Similar features were observed in the corresponding PL spectra. In particular, PF−PZB50 showed almost pure red emission [CIE coordinate values $(x, y) - (0.63, 0.36)$] that was very close to the standard red (0.66, 0.34) demanded by the NTSC and additionally showed the best performance characteristics: maximum brightness, 3440 cd/m^2 (at 11.2 V) and external quantum efficiency, 0.45%. Bulk heterojunction PPVCs fabricated from a thin film composed of a blend of PF−PZB50 and the fullerene derivative PCBM, in the configuration ITO/PEDOT:PSS/(PF−PZB50:PCBM = 1:3)/LiF/Al, showed promising performance. Specifically, under 100 mW/cm^2 of AM 1.5 white light illumination, the device produced an open-circuit voltage of 0.78 V and a short-circuit current of 2.38 mA/m^2. The fill factor of the device was 0.29, and the ECE was 0.53%.

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