Synthesis and Electroluminescence of New Polyfluorene Copolymers with Phenothiazine Derivative. Their Application in White-Light-Emitting Diodes

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ABSTRACT: New alternating polymers based on 2,7-dibromo-9,9-bis(4-octyloxy-phenyl) fluorene (BOPF), poly{9,9-bis-(4-octyloxy-phenyl)-fluorene-2,7-diyl-*co*-3,7-bis(1-cyanovinyl-3-phenothienyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-3′,7′-diyl} (PFPCVBs), have been designed, synthesized, and characterized. The PFPCVBs were synthesized through palladium-catalyzed Suzuki coupling reactions. BOPF and 3′,7-bis[3-(7′-bromo-phenothienyl)-1-cyanovinyl]-1-(2′-ethyl-hexyloxy)-4-methoxy-benzene (BPCVB) were used as the blue- and orange-light-emitting chromophores, respectively. These polymers were found to be thermally stable and readily soluble in common organic solvents. The photoluminescence (PL) spectra of the synthesized polymers contain both blue and orange emissions from these two chromophores. Moreover, by adjusting the BOPF and BPCVB contents, white-light emission can be obtained from a single PFPCVB polymer. EL devices with ITO/PEDOT:PSS/polymer/Balq/LiF/Al configurations using these polymers were found to produce blue and orange emissions. The EL emissions of PFPCVB 025 and PCPCVB 050 were found to result in white electroluminescence with Commission Internationale de L'Eclairage (CIE) coordinates of (0.30, 0.36) and (0.33, 0.39), respectively. The EL emissions of PFPCVB 025 are stable with respect to variation in the voltage, and were found to have the coordinates (0.30, 0.36), (0.29, 0.35), and (0.28, 0.34) at various device driving voltages. The device using PFPCVB 050 exhibits a maximum brightness of 1740 cd/m^2, a maximum current efficiency of 1.95 cd/A, and a maximum external quantum efficiency of 0.9%.

Introduction

Since the initial report of the fabrication of polymer light-emitting diodes (PLEDs) based on poly(*p*-phenylenevinylene) (PPV) by the Cambridge group,[1] luminescent conjugated polymers have been found to be of considerable importance as active materials in new technology fields, because their luminescence properties can be adjusted by the manipulation of their chemical structures. In addition, their physical properties make them suitable for use in the spin coating and printing processes required to create large-area flat-panel displays.[2–5] In particular, white polymeric light-emitting diodes have recently attracted significant research interest because of their potential applications in low-cost backlights for liquid-crystal displays (LCDs), full-color displays, and other lighting sources.[6–8] To realize full-color displays with white PLEDs, their electroluminescence (EL) spectra must be composed of the three primary colors red, green, and blue (RGB), and cover the whole visible range from 400 to 700 nm. A variety of approaches have been used to realize white light PLEDs. Most reported devices have been fabricated by dispersing a small amount of a red- or orange-light-emitting fluorescent or phosphorescent dopant in a host polymer.[9,10] However, there can be problems with these devices, such as poor color stability due to the phase separation of the components, the dependence of their color on the driving voltage, and difficulties in controlling the doping level to achieve balanced white-light emission.[11]

Single chain white-light-emitting polymers remain of great interest in the field of PLEDs because they offer several distinct advantages, such as their simple fabrication processes, ease of scaling up, and the absence of any problems associated with phase separation or the dependence of electroluminescence on the driving voltage. Chen and co-workers reported the fabrication of a white-light-emitting diode using an oxadiazole-containing phenylene vinylene ether linkage copolymer with long wavelength emission from an aggregate state.[12] Wang and co-workers fabricated single polymeric LEDs based on PFs by introducing a small number of orange-emitting units.[13] Cao and co-workers reported white-light emission from a fluorescent polymer with phosphorescent units based on a polyfluorene-containing iridium complex.[14] In our previous study, we developed a new strategy for realizing white-light emission that uses a single polymer incorporating small amounts of green- and red-emitting units in the polymer backbone.[15]

A number of polyfluorenes and their derivatives have been studied as blue-light-emitting polymers.[16] The interest in these polymers arose because they exhibit high photoluminescence quantum yields and excellent chemical and thermal stability as well as photostability, good solubility, and film-forming properties, and can readily be prepared via high-yielding synthetic routes that produce well-defined high-molecular-weight polymers.[17] Hwang et al. have reported that fluorene derivatives with bulky alkoxyphenyl substituents at the 9-position exhibit more

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stable blue emission and better device performance than alkyl-substituted fluorenes.[18] Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Polymers and organic molecules[19a] containing phenothiazine or its derivatives have recently attracted considerable research interest on account of their unique electro-optic properties, which make these molecules potentially useful in diverse applications such as light-emitting diodes,[19b] photovoltaic devices,[19c] and chemiluminescence.[19d–f]

In this Article, we report the electroluminescence properties of a single chain polymer obtained by introducing the phenothiazine derivative 3′,7-bis[3-(7′-bromomo-phenothienyl)-1-cyano-vinyl]-1-(2′-ethyl-hexyloxy)-4-methoxy-benzene (BPCVB) into the main chain of the poly-2,7-dibromo-9,9-bis(4-octyloxy-phenyl) fluorene (PBOPF) homopolymer, which exhibits white-light emission when the BOPF and BPCVB contents are adjusted. We systematically investigated the synthesis, thermal stability, and optical properties of the resulting polymers, as well as the energy-transfer processes between the blue and orange units, by carrying out photoluminescence (PL) and electroluminescence (EL) experiments.

Experimental Details

Measurements. NMR spectra were recorded using a Bruker AM 300 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. Thermogravimetric analysis (TGA) was carried out using a TA Q500 analyzer with a heating rate of 10 °C/min under a nitrogen atmosphere. The number- and weight-average molecular weights of polymers were determined by gel permeation chromatography (GPC) on a Viscotek T60A instrument, using tetrahydrofuran (THF) as eluent and polystyrene as standard. LED devices were fabricated on glass substrates coated with indium−tin oxide (ITO). The device configuration was ITO/PEDOT:PSS/polymer/Balq/LiF/Al structures. The procedure for cleaning the ITO surface included sonication and rinsing in deionized water, methanol, and acetone. The hole-transporting PEDOT:PSS layer was spin-coated onto each TIO anode from a solution purchased from Bayer. Each polymer solution in chlorobenzene was then spin-coated onto the PEDOT:PSS layer. The spin-casting yielded uniform polymer films with thicknesses of approximately 40 nm. A 40 nm thick bis(2-methyl-8-quinolinolate)-4-(phenylphenolata)aluminum (Balq) electron-transporting layer was deposited, and a 1 nm thick lithium fluoride layer and a 70 nm thick aluminum layer were subsequently deposited at pressures below 10–6 Torr. 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. Phenothiazine, 1-bromohexnae, 2,7-dibromofluorenone, toluene (99.8%, anhydrous), *N*,*N*-dimethylformamide (99.8%, anhydrous), 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane, *N*-bromosuccinimide, 2-ethylhexyl bromide, sodium cyanate, and Aliquat336 were purchased from Aldrich. All chemicals were used without further purification. 2,7-Dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**9**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**), 2-(2′-ethylhexyloxy)-5-methoxybenzene (**1**), and 1,4-bis(chloro-methyl)-2-(2′-ethylhexyloxy)-5-methoxybenzene(**2**) were synthesized according to procedures outlined in the literature.[18,20] Tetrakis(triphenylphosphine)palladium(0) was purchased from DNF Solution Co. Solvents of analytical grade were used during the whole experiments, and all chemicals were used without further purification.

Synthesis of 1,4-Bis(cyanomethyl)-2-(2′-ethylhexyloxy)-5-methoxybenzene (3). A mixture of 20.0 g (60 mmol) of compound 3 and 8.8 g (180 mmol) of sodium cyanate in *N*,*N*-dimethylformamide was stirred at 45 °C for 72 h. The resulting mixture was extracted with methylene chloride and brine and then dried with $MgSO_4$. The extract was filtered and evaporated in vacuo. The resulting liquid was poured into water, yielding a pale yellow precipitate that was separated by filtering. The precipitate was recrystallized in dichloromethane and hexane two times. The product yield was 79% (15 g).

^{1}H NMR ($CDCl_3$, ppm) 6.90 (d, 2H), 3.85 (d, 2H), 3.83 (s, 3H), 3.68(s, 4H), 1.72 (m, 1H), 1.55–1.29 (m, 8H), 0.91 (q, 6H). ^{13}C NMR ($CDCl_3$, ppm) 150.43, 150.30, 119.10, 119.00, 119.00, 117.73, 112.48, 111.82, 71.13, 56.12, 39.48, 30.59, 29.07, 23.98, 22.99, 18.63, 18.58, 14.03, 11.16. Anal. Calcd for $C_{19}H_{26}N_2O_2$: C, 72.58; H, 8.33; N, 8.91. Found: C, 72.52; H, 8.11; N, 8.67.

Synthesis of 10-*n*-Hexylphenothiazine (4). 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) were placed in a 500 mL two-neck round-bottom flask, and then, this mixture was stirred for 1 day at room temperature. The mixture was extracted with dichloromethane/brine and then dried with $MgSO_4$. The resulting liquid was purified by column chromatography. The product yield was 67% (9.53 g).

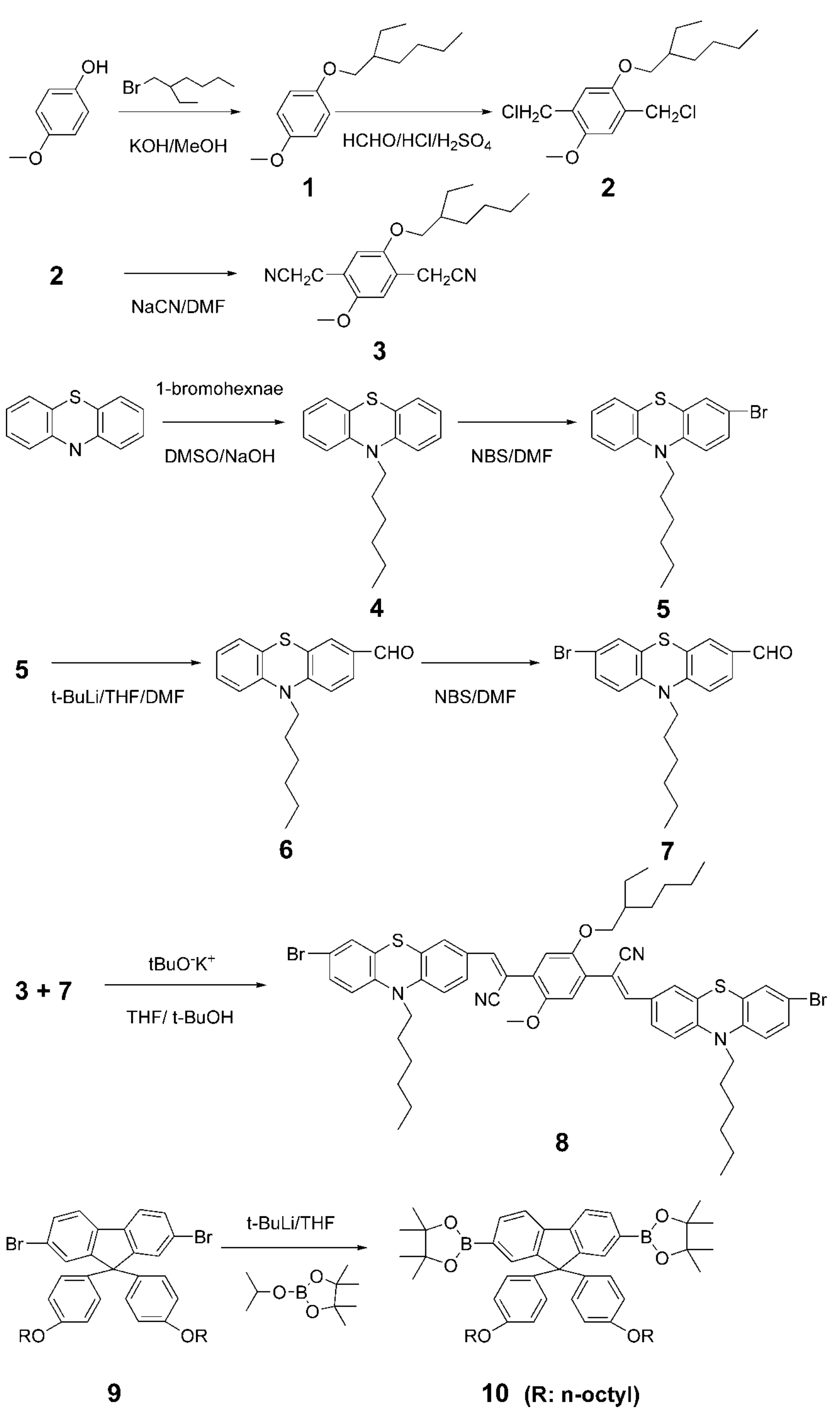
^{1}H NMR (DMSO-d_6, ppm) 7.12 (m, 4H), 6.88 (m, 4H), 3.75 (t, 2H), 1.57 (m, 2H), 1.30–1.13 (m, 6H), 0.74 (t, 3H). ^{13}C NMR (DMSO-d_6, ppm) 145.05, 127.97, 127.51, 122.81, 116.24, 48.20, 31.78, 24.45, 26.94, 23.48, 16.08. Anal. Calcd for $C_{18}H_{21}NS$: C, 76.28; H, 7.47; N, 4.94; S, 11.31. Found: C, 76.90; H, 7.65; N, 6.02; S, 10.11.

Synthesis of 7-Bromo-10-*n*-hexylphenothiazine-3-carbaldehyde (7). Compound (**4**) (7.5 g, 24 mmol) was dissolved in 50 mL of dichloromethane, and then, bromine (8.0 g, 24 mmol) was injected into the solution using a syringe and stirred for 4 h at room temperature. Dilute aqueous sodium hydroxide was added to the reaction mixture and stood for 30 min. The reaction mixture was extracted three times using dichloromethane/brine, and then, the organic layer was separated and concentrated. The crude product was purified using column chromatography using hexane as the eluent. The product (**5**) yield was 79% (9.0 g). The obtained compound (**5**) (9.0 g, 24.8 mmol) was dissolved in THF (150 mL) at −78 °C. To a solution was added, by syringe, 22 mL (37.2 mmol) of *tert*-butyllithium (1.7 M in hexane). The mixture was stirred at −78 °C for 2 h. *N*,*N*-dimethylformamide (2.8 mL, 37.2 mmol) was added to the solution, and the resulting mixture was stirred at −78 °C for 1 h, 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 column chromatography using ethylacetate/hexane (2:8) as the eluent. The product (**6**) yield was 77.6% (6.0 g). A solution of compound (**6**) (6.0 g, 19.3 mmol) in 50 mL of *N*,*N*-dimethylformamide was stirred and cooled with an ice bath while *N*-bromosuccinimide (3.43 g, 19.3 mmol) was added in portionwise. The mixture was then stirred for 1 day at room temperature. The mixture was extracted with dichloromethane and dried over $MgSO_4$. The solvent was removed by solvent evaporation, and the residue was purified by column chromatography using *n*-hexane as the eluent. The product was obtained with a yield of 70.5% (5.3 g).

^{1}H NMR (DMSO-d_6, ppm) 9.77 (s, 1H), 7.68 (d, 1H), 7.54 (s, 1H), 7.28 (m, 2H), 7.10 (d, 1H), 6.92 (d, 1H), 3.89 (t, 2H), 1.79 (q, 2H), 1.43 (m, 2H), 1.28 (m, 4H), 0.85 (m, 3H). ^{13}C NMR (DMSO-d_6, ppm) 189.79, 148.84, 131.93, 130.10, 128.35, 124.36, 115.51, 48.46, 31.24, 26.56, 26.33, 22.37, 13.89. Anal. Calcd for $C_{19}H_{20}NOS$: C, 58.46; H, 5.16; N, 3.59; S, 8.21. Found: C, 59.43; H, 5.43; N, 3.50; S, 8.25.

Synthesis of 3′,7-Bis[3-(7′-brmomophenothienyl)-1-cyanovinyl]-1-(2′-ethyl-hexyloxy)-4-methoxybenzene (8). Compound (**3**) (2 g, 6.36 mmol), compound (**7**) (4.96 g, 12.7 mmol), THF (30 mL), and *tert*-butanol (15 mL) were placed in a 250 mL two-neck round-bottom flask. A catalytic amount of potassium *tert*-butoxide in methanol was added into this mixture. The reaction mixture was then stirred at reflux temperature. After 24 h, the reaction mixture was extracted using dichloromethane/brine, and then, the organic layer was separated and concentrated. The resulting solid was

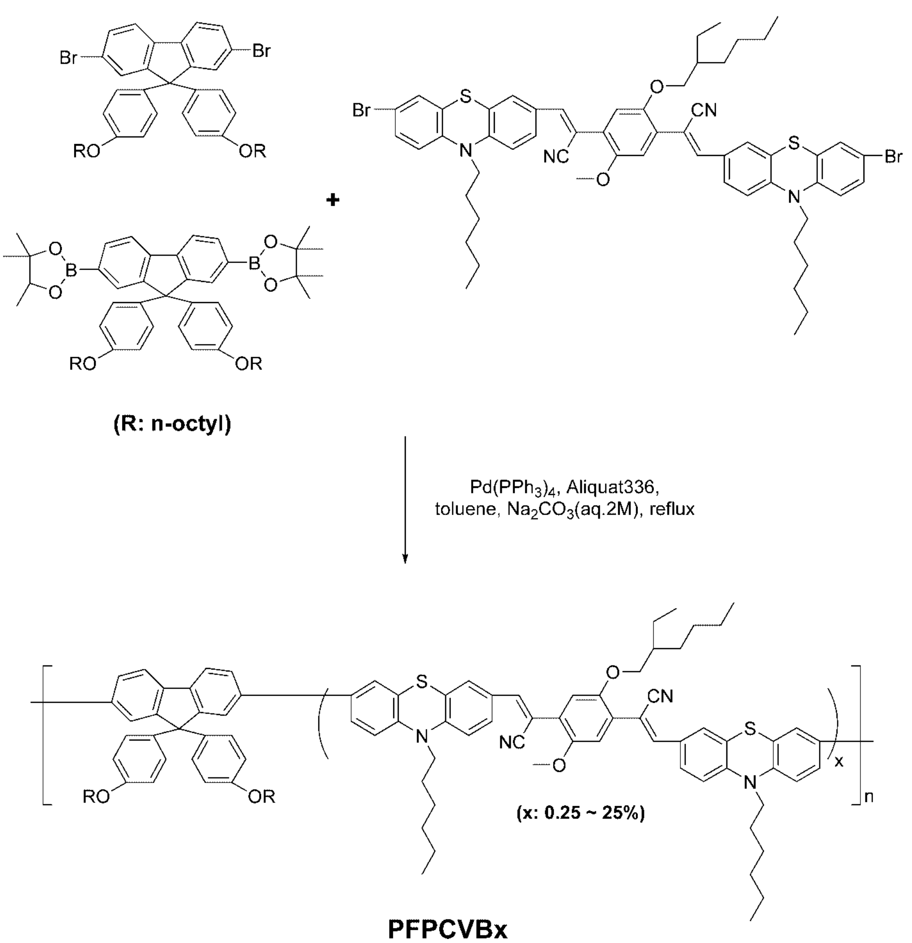
Scheme 1. Synthetic Routes of the Two Comonomers BOPF and BPCVB



recrystallized in dichloromethane and methanol, and then, the solid was dried in vacuo. The resulting product yield was 40% (2.7 g). ^{1}H NMR ($CDCl_3$, ppm) 7.83 (m, 2H), 7.49 (m, 4H), 7.21 (m, 4H), 7.04 (d, 2H), 6.85 (m, 2H), 6.68 (d, 2H), 3.93 (m, 5H), 3.73 (m, 4H), 1.76 (m, 3H), 1.30 (m, 24H), 0.88 (m, 10H). ^{13}C NMR ($CDCl_3$, ppm) 150.78, 146.55, 145.14, 144.98, 143.10, 130.01, 129.56, 128.65, 128.60, 126.01, 125.26, 123.92, 118.25, 118.22, 116.60, 115.18, 115.07, 113.96, 113.44, 105.37, 105.24, 56.51, 47.75, 39.55, 31.30, 30.67, 29.08, 26.53, 26.42, 23.92, 22.99, 22.51, 14.04, 13.92, 11.15. Anal. Calcd for $C_{57}H_{62}Br_2N_4O_2S_2$: C, 64.64; H, 5.90; N, 5.29; S, 6.06. Found: C, 65.01; H, 6.01; N, 5.55; S, 6.51. $m/z = 1059$ (M^+).

General Polymerization Procedure. Into a 100 mL two-neck flask were added dibromo compounds and diborolan compound 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, Aliquat336 (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 was cooled to about 50 °C and added slowly to a vigorously stirred mixture of 200 mL of methanol. The polymer fibers were collected by filtration and reprecipitation from methanol and acetone. The polymers were purified further by washing for 2 days in a Soxhlet apparatus with acetone to remove oligomers and catalyst residues, and column chromatographied with a chloroform solution of the polymer. The reprecipitation

Scheme 2. Synthetic Routes of the Copolymers PFPCVBx



PFPCVBx

procedure in chloroform/methanol is then repeated several times. The resulting polymers were soluble in common organic solvents. Yield: 65–80%.

Poly{9,9-bis-(4-octyloxy-phenyl)-fluorene-2,7-diyl-*co*-3,7-bis(1-cyanovinyl-3-pheno-thienyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-3′,7′-diyl} (PFPCVB 025). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**9**) (0.9975 equiv), and 3′,7-bis[3-(7′-brmomophenothienyl)-1-cyanovinyl]-1-(2′-ethylhexyloxy)-4-methoxybenzene (**8**) (0.0025 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–7.74 (30H), aliphatic; 3.92–3.76 (13H), 1.75–0.86 (~67H). Element Anal. Found: C, 85.57; H, 8.87; N, 0.09.

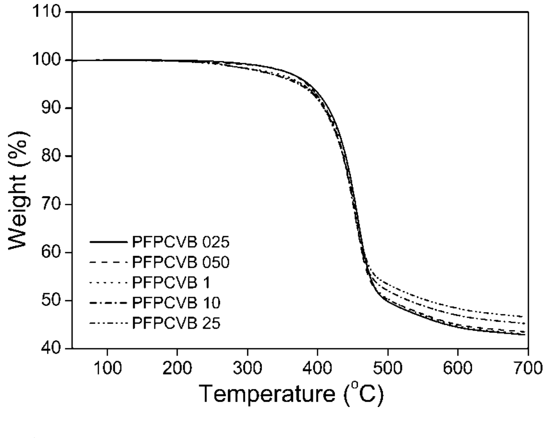


Figure 1. TGA traces of the synthesized PFPCVB polymers.

Table 1. Physical Properties of the Synthesized PFPCVB Polymers

				ratio (BOPF:BPCVB)	
polymer	M_n[a]	PDI[a]	T_d[b] (°C)	in the feed composition	in the copolymers[c]
PFPCVB 025	14 200	1.9	390	99.75:0.25	99.05:0.95
PFPCVB 050	15 000	2.3	385	99.5:0.5	98.3:1.7
PFPCVB 1	13 300	1.7	383	99:1	97.7:2.3
PFPCVB 10	15 100	2.1	376	90:10	94.6:5.4
PFPCVB 25	12 000	1.5	380	75:25	92.1:7.9

[a] M_n and PDI of the polymers were determined by gel permeation chromatography using polystyrene standards. [b] Temperature resulting in 5% weight loss based on initial weight. [c] Calculated by elemental analysis through calculation of the amount of nitrogen contained in copolymers.

Poly{9,9-bis-(4-octyloxy-phenyl)-fluorene-2,7-diyl-*co*-3,7-bis(1-cyanovinyl-3-pheno-thienyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-3′,7′-diyl} (PFPCVB 050). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**9**) (0.995 equiv), and 3′,7-bis[3-(7′-brmomophenothienyl)-1-cyanovinyl]-1-(2′-ethylhexyloxy)-4-methoxybenzene (**8**) (0.005 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–7.74 (30H), aliphatic; 3.92–3.76 (13H), 1.75–0.86 (~67H). Element Anal. Found: C, 85.73; H, 8.91; N, 0.16.

Poly{9,9-bis-(4-octyloxy-phenyl)-fluorene-2,7-diyl-*co*-3,7-bis(1-cyanovinyl-3-pheno-thienyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-3′,7′-diyl} (PFPCVB 1). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**9**) (0.99 equiv) and 3′,7-bis[3-(7′-brmomophenothienyl)-1-cyanovinyl]-1-(2′-ethyl-

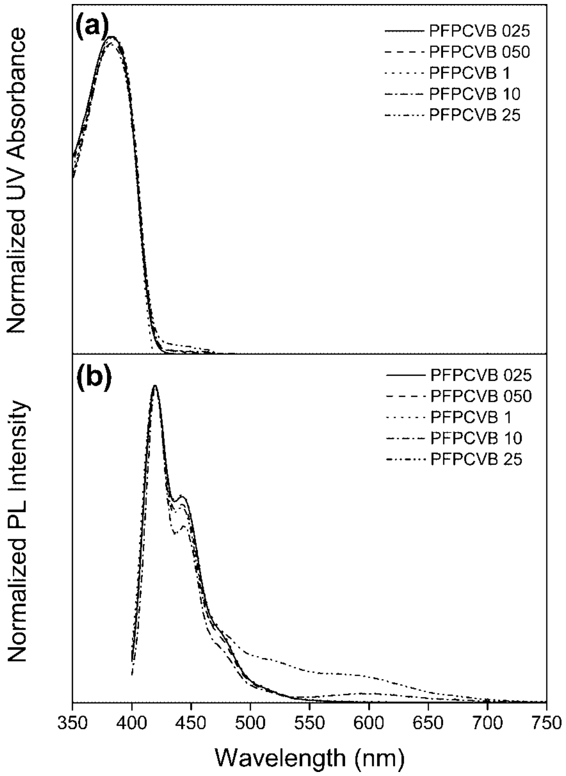


Figure 2. UV–vis absorption (a) and PL emission (b) spectra of the synthesized polymers in chloroform.

hexyloxy)-4-methoxybenzene (**8**) (0.01 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–7.74 (30H), aliphatic; 3.92–3.76 (13H), 1.75–0.86 (~67H). Element Anal. Found: C, 85.07; H, 8.81; N, 0.22.

Poly{9,9-bis-(4-octyloxy-phenyl)-fluorene-2,7-diyl-*co*-3,7-bis(1-cyanovinyl-3-pheno-thienyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-3′,7′-diyl} (PFPCVB 10). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**9**) (0.90 equiv), and 3′,7-bis[3-(7′-brmomophenothienyl)-1-cyanovinyl]-1-(2′-ethylhexyloxy)-4-methoxybenzene (**8**) (0.10 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–7.74 (30H), aliphatic; 3.92–3.76 (13H), 1.75–0.86 (~67H). Element Anal. Found: C, 84.30; H, 8.77; N, 0.51.

Poly{9,9-bis-(4-octyloxy-phenyl)-fluorene-2,7-diyl-*co*-3,7-bis(1-cyanovinyl-3-pheno-thienyl)-1-(2′-ethylhexyloxy)-4-methoxybenzene-3′,7′-diyl} (PFPCVB 25). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxy-phenyl)-fluorene (**10**) (1 equiv), 2,7-dibromo-9,9-bis-(4-octyloxy-phenyl)-fluorene (**9**) (0.75 equiv), and 3′,7-bis[3-(7′-brmomophenothienyl)-1-cyanovinyl]-1-(2′-ethylhexyloxy)-4-methoxybenzene (**8**) (0.25 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm) aromatic and vinylene; 7.76–7.74 (30H), aliphatic; 3.92–3.76 (13H), 1.75–0.86 (~67H). Element Anal. Found: C, 83.61; H, 8.78; N, 0.73.

Results and Discussion

Synthesis and Characterization of the Polymers. The synthetic routes and structures of the polymers are shown in Schemes 1 and 2. The series of conjugated copolymers were synthesized through palladium-catalyzed Suzuki coupling reactions.[19c] All of the PFPCVB copolymers were end-capped with bromobenzene. The actual compositions of the polymers were determined with elemental analysis.[19c] The feed ratios of BPCVB were 0.25, 0.5, 1.0, 10, and 25 mol % of the total amount of monomer, and the resulting ratios of BPCVB units in the PFPCVBs were 0.95, 1.7, 2.3, 5.4, and 7.9%, respectively. The actual ratios of BPCVB in the copolymers are different from the feed monomer ratios, which is possibly due to the reduced reactivity of the bulky BPCVB units in the polymerization. All of the copolymers were found to be soluble in common organic solvents such as tetrahydrofuran (THF), chloroform, and toluene, with no evidence of gel formation. Each copolymer was spin-coated onto an ITO substrate and found to produce transparent and homogeneous thin films. The number-average molecular weights (M_n) of the copolymers, as determined with gel permeation chromatography using a polystyrene standard, were found to range from 12 000 to 15 000 with polydispersity indices ranging from 1.5 to 2.3. The yields of the copolymers were from 65 to

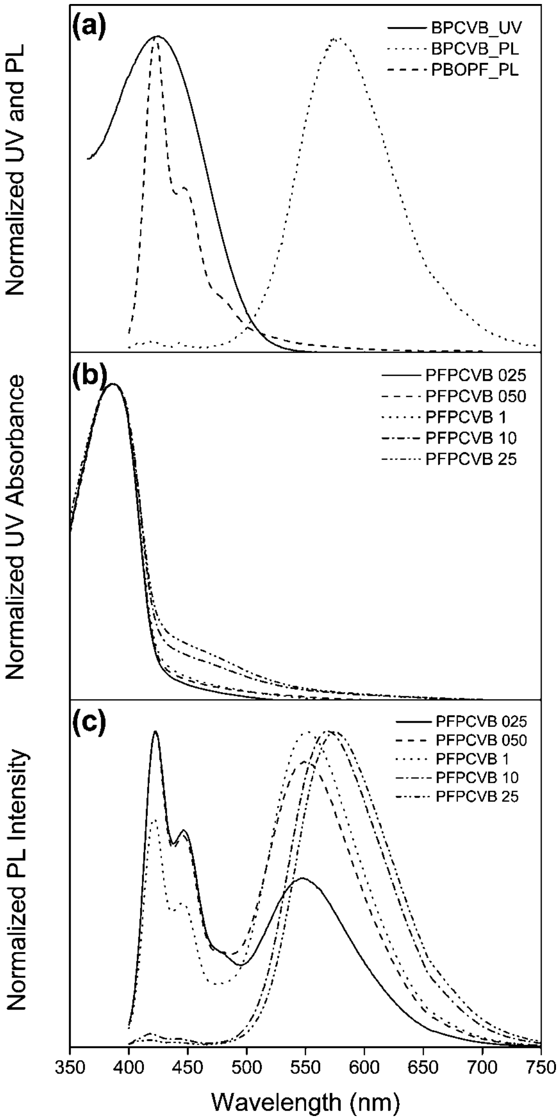


Figure 3. UV–vis absorption and PL emission spectra of BPCVB and PBOPF (a); UV–vis absorption (b) and PL emission (c) spectra of thin films of the synthesized polymers.

Table 2. Summary of the Optical Properties of the Synthesized PFPCVB Polymers

	solution, λ_{max} (nm)		film, λ_{max} (nm)	
polymer	absorption	emission	absorption	emission
PFPCVB 025	382	420	386	423, 546
PFPCVB 050	383	420	386	422, 551
PFPCVB 1	384	419	386	421, 552
PFPCVB 10	384	419	388	570
PFPCVB 25	383	419	384	576

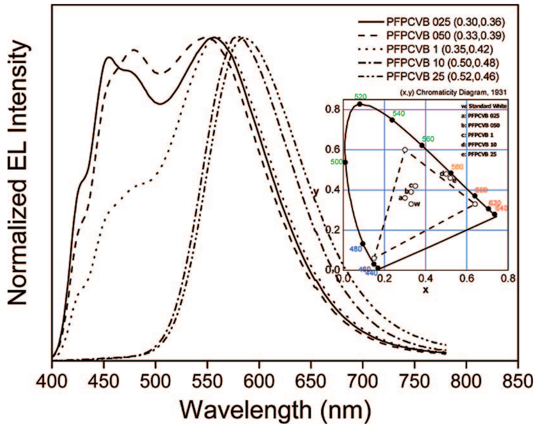


Figure 4. Electroluminescence spectra of PFPCVB devices with ITO/PEDOT:PSS/polymer/Balq/LiF/Al configurations at 10 V and their CIE coordinates.

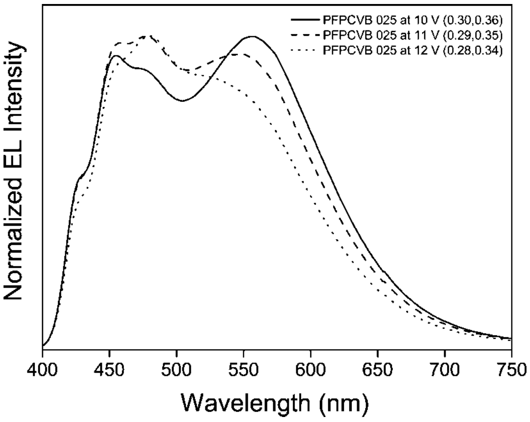


Figure 5. Electroluminescence spectra of the PFPCVB 025 device, which has a ITO/PEDOT:PSS/polymer/Balq/LiF/Al configuration, for various driving voltages.

80%. The thermal properties of the polymers were determined with thermal gravimetric analysis (TGA). All of the polymers were found to exhibit good thermal stability, losing less than 5% of their weight on heating to approximately 400 °C in TGA runs under a nitrogen atmosphere, as shown in Figure 1. The results of the polymerizations of the synthesized copolymers are summarized in Table 1.

Optical and Photoluminescence Properties. The normalized UV–vis absorption and PL emission spectra of the polymers in chloroform solution are shown in Figure 2. PFPCVBs exhibit absorption maxima at about 384 nm. These UV–vis absorption maxima are at wavelengths less than that of the PBOPF homopolymer[18] by approximately 10 nm. This effect is due to the cyano groups in the vinylene linkages with the α-position, which produce a strong steric interaction with the alkoxy chains of the inner phenylene ring that shortens the conjugation length of the molecules, resulting in a blue-shift in the absorption.[21] Another absorption peak of the PFPCVBs is present at about 450 nm, a value that increases as the fraction of BPCVB increases. The increased absorption intensity in this region is caused by the incorporation of the low-band-gap BPCVB units. The PL spectra of all of the polymers contain emission maxima at about 420 nm. The PL emissions of the PFPCVBs are similar to those of PBOPF homopolymers.[18] These PL emission spectra indicate that the energy transfer from the BOPF segments to the BPCVB units in the polymer chain is not strong in the solution state, which suggests that in this state the BPCVB units are not involved with the polymer main-chain processes and possess their own independent π-systems.

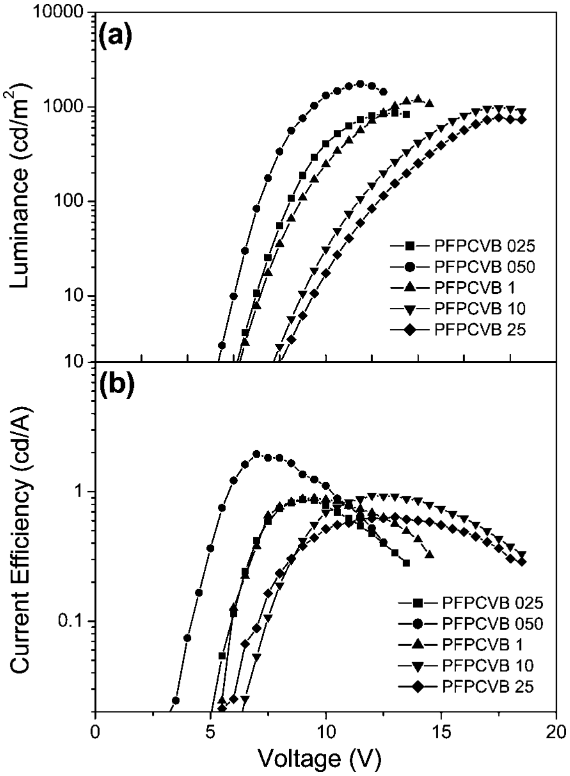


Figure 6. Voltage−luminance (*V*−*L*) (a) and voltage−current efficiency (b) characteristics of the synthesized PFPCVB polymers.

The normalized UV–vis absorption and PL emission spectra of BPCVB in chloroform solution are shown in Figure 3a. The maximum in the UV–vis absorption of the BPCVB monomer arises at about 424 nm. As mentioned above, the maximum in the PL emission spectra of the PBOPF is near 420 nm, and thus, these emissions have significant overlap with the absorption spectrum of BPCVB, which indicates that efficient energy transfer from the BOPF segments to the BPCVB units is possible. The absorption spectra of the polymers in the solid state are shown in Figure 3b. Absorption peaks are present at about 385 nm, which is consistent with those reported for the PBOPF homopolymer;[18] the only long wavelength absorption peak due to the comonomer is near 450 nm, suggesting that most of the absorption is due to the BOPF units. Figure 3c shows the PL spectra of thin films of the polymers. The maxima in the PL emission spectra of the polymers arise at about 422 nm due to the BOPF segments, and orange-light emission is present in the range 546−576 nm due to the BPCVB units. The PL emission maxima of the polymers shift to longer wavelengths with increases in the number of BPCVB units in the copolymers. These red-shifts in PL emission are probably due to intra- and intermolecular energy transfer from the BOPF segments to the lower band gap BPCVB units, which results in emission occurring mainly from the latter. PFPCVB 025 to PFPCVB 1 exhibit white-light emission behaviors. On the basis of the white-light emissions of these polymers, the appearance of both blue and orange emissions in the PL spectrum results from partial energy transfer from the polymer backbone to the BPCVB units. The optical properties of the synthesized polymers are summarized in Table 2.

Electroluminescence Properties and Current–Voltage−Luminance Characteristics. To investigate the electrical properties and performances of the copolymers in real devices, polymer EL devices with the configuration ITO/PEDOT:PSS (40 nm)/polymer (40 nm)/Balq (40 nm)/LiF (1 nm)/Al (70 nm) were fabricated. The EL emission spectra

Table 3. Summary of the EL Device Performances of the Synthesized PFPCVB Polymers

polymer	λ_{max} (nm)	luminance$_{max}$ (cd/m^2)	current efficiency (cd/A)	luminance efficiency (lm/W)	EQE (%)	CIE coordinates (*x*,*y*)[a]
PFPCVB 025	456, 557	860	0.87	0.34	0.41	(0.30,0.36)
PFPCVB 050	478, 549	1750	1.95	0.97	0.90	(0.33,0.39)
PFPCVB 1	558	1200	0.89	0.34	0.37	(0.35,0.42)
PFPCVB 10	580	980	0.93	0.27	0.40	(0.50,0.48)
PFPCVB 25	584	770	0.64	0.19	0.30	(0.52,0.46)

[a] Determined from EL spectra (Figure 4).

of the synthesized polymers are different from the corresponding PL emission spectra for low feed ratios, as shown in Figure 4. The blue emission of the BOPF segments is broader than the bluish green emission. The EL spectra of the synthesized polymers are different from the PL emission spectra due to energy transfer from the higher energy state of the BOPF segments to the lower energy state of the BPCVB units. Such results are common for organic host–guest systems, in which the low-energy-state units act as charge-trapping sites.[22] The EL emission spectra of PFPCVB 025 to PFPCVB 1 are broad, covering the visible range from 400 to 700 nm. The peaks in the blue region are due to the BOPF segments, and the peak at about 550 nm originates from the PBCVB units. Of these EL spectra, those of PFPCVB 025 and PFPCVB 050 consist of well-balanced blue and orange regions, with Commission Internationale de L'Eclairage (CIE) coordinates at 10 V of (0.30, 0.36) and (0.33, 0.39), respectively, which are close to those of pure white light (0.33, 0.33).

Most importantly, these white-light emissions are stable and the EL spectra are insensitive to the driving voltage. The EL spectrum of PFPCVB 025 is stable with respect to the voltage; the CIE coordinates were found to be (0.30, 0.36), (0.29, 0.35), and (0.28, 0.34) at various driving voltages. These results indicate that the use of this polymer ensures the color purity of the EL device, which makes it of great interest for display applications. The dependence of the EL emission spectrum of PFPCVB 025 on voltage is shown in Figure 5.

The voltage−luminance (*V*−*L*) and voltage−current efficiency characteristics of the devices are shown in Figure 6, and their performances are summarized in Table 3. The turn-on voltages of the PFPCVB devices range from 5 to 7.5 V, and their maximum brightnesses are in the range 770–1740 cd/m^2. The *V*−*L* and voltage−current efficiency curves shift to slightly higher voltages with increases in the number of BPCVB units in the copolymers. This phenomenon is due to charge-trapping and results in differences between the EL and PL spectra.[22] The PFPCVB 050 device has the best performance, with a maximum brightness of 1740 cd/m^2 at 11.5 V, a maximum current efficiency of 1.95 cd/A at 7 V, and a maximum external quantum efficiency of 0.9% at 7 V. We suggest that PFPCVB 050 produces balanced electron and hole injection in the device and that the energy transfer is efficient between the blue-light-emitting BOPF segments and the orange-light-emitting BPCVB units. The measured current efficiency and external quantum efficiency of the PFPCVB 050 device are promising results for a white-light emission polymer based on a single chain. We are endeavoring to further improve the performance of these white polymeric LEDs by incorporating a new comonomer into the polymer backbone.

Conclusions

We have successfully prepared BOPF-based copolymers containing a phenothiazine derivative as a comonomer. White-light emission was obtained from a single polymer chain by incorporating 3′,7-bis[3-(7′-bromophenothienyl)-1-cyanovinyl]-1-(2′-ethyl-hexyloxy)-4-methoxybenzene as the orange unit into a PBOPF main chain as the blue host, which exhibits good device performance. EL devices fabricated with PFPCVB 025 and PFPCVB 050 were found to emit white light consisting of simultaneous blue and orange emissions and CIE coordinates of (0.30, 0.36) and (0.33, 0.39), respectively, which are close to the standard for white-light emission. The PFPCVB 050 device exhibits a maximum brightness of 1740 cd/m^2, a maximum current efficiency of 1.95 cd/A, and a maximum external quantum efficiency of 0.9%, with white-light emission at various driving voltages. These results suggest that white polymeric LEDs that utilize a single polymer chain have potential applications in full-color displays.

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