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Synthesis, Characterization, and Electroluminescence of Polyfluorene Copolymers with Phenothiazine Derivative; Their Applications to High-Efficiency Red and White PLEDs

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ABSTRACT: We have synthesized new light-emitting copolymers by introducing the phenothiazine derivative, 4,7-bis(6-bromo-3-thiophenyl-10-*n*-butylphenothiazine)-2,1,3-benzothiadiazole (BPTR), into the main chain of a homopolymer based on 2,7-dibromo-9,9-bis(4-octyloxy-phenyl) fluorene (BOPF). The polymers, designated as poly{9,9-bis-(4-octyloxyphenyl)-fluorene-2,7-diyl-*co*-4,7-bis(3-thiophenyl-10-*n*-butylphenothiazine-6-yl)-2,1,3-benzothiadiazole} (PFPTRs) were synthesized through palladium-catalyzed Suzuki coupling reactions and were found to be thermally stable and readily soluble in common organic solvents. The photoluminescence (PL) emission spectra of the copolymers were highly red-shifted as the fraction of BPTR units in the copolymer was increased. Light-emitting devices were fabricated using the ITO/PEDOT:PSS/polymer/Balq/LiF/Al configuration with the PFPTR polymers as the emitting layer. The electroluminescence (EL) device based on PFPTR 1 showed nearly pure red emission [CIE coordinate values (*x*, *y*), (0.62, 0.36)] that was very close to the standard red (0.66, 0.34) demanded by the National Television System Committee. Furthermore, its maximum external quantum efficiency and maximum current efficiency were 2.3% and 1.70 cd/A at 10 V, respectively. Our device results for PFPTR 1 are among the highest values yet reported for saturated red polymer emitters. Moreover, the EL emissions of PFPTR 01 and PFPTR 025 afforded white electroluminescence with CIE coordinates of (0.27, 0.40) and (0.41, 0.37) respectively, which appeared to be near-white to the naked eye.

Introduction

The use of electroluminescent polymers as the emitting layers in polymer light-emitting diodes (PLEDs) has attracted considerable academic and commercial interest because of the potential of these materials as components in flat-panel displays and lighting applications.[1−3] A large number of electro- and photoactive conjugated polymers have been introduced in recent decades, such as poly(*p*-phenylenevinylene) (PPV),[4] polythiophene (PT),[5] and polyfluorene (PF).[6] In particular, PF and its derivatives have emerged as suitable PLED materials due to their high photoluminescence (PL) quantum efficiencies, good thermal stabilities, and amenability to functionalization at the 9-position of fluorene. We have reported that fluorene derivatives with bulky alkoxyphenyl substituents at the 9-position exhibit enhanced blue emission stability and superior device performance compared to alkyl-substituted fluorenes.[7] A variety of PFs have been developed by introducing various comonomers, and their properties have been investigated with the goal of obtaining stable high-efficiency red, green, blue and white emitters.[8]

While much effort has been made to tune the color of blue-emitting PFs, appropriate red- and green-emitting materials that meet the requirements for display applications have yet to be developed.[9,10] Among the most widely used methods for color tuning is to covalently attach a chromophore to the polymer. In doing so, aggregation and excimer formation are prevented and efficient energy transfer from the polymer chromophores to the dye chromophores easily confines the singlet excitons resulting in the emission of low energy red photons. 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.[11] 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.[12−15] For example, a red-emitting alternating copolymer of fluorene and 4,7-di-2-ethienyl-2,1,3-benzothiadiazole (DBT) has been reported in the patent literature by the Dow Chemical group.[16] Cao et al. have reported that a PFO copolymer containing DBT comonomers shows significantly enhanced efficiencies of up to 1.4%. Furthermore, copolymers in which fluorene is replaced with 9-silafluorene have demonstrated that a maximum external quantum efficiency of 2.89% and a maximum current efficiency of 2.0 cd/A.[17] Phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms. Recently, polymers and organic molecules[18a] containing phenothiazine or its derivatives have attracted considerable research interest due to their unique electro-optic properties. As a result, these phenothiazine-containing materials are potential good candidates light-emitting diodes,[18b] photovoltaic devices,[18c] and chemiluminescence.[12d,f,18d] In a previous study, we developed a new strategy to achieve white light emission from a single polymer by introduc-

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ing orange-red-emitting, phenothiazine-based moieties onto a poly(fluorene) backbone.[19]

In this article, we report the electroluminescence properties of a single chain polymer obtained by introducing the phenothiazine derivative, 4,7-bis(6-bromo-3-thiophenyl-10-*n*-butylphenothiazine)-2,1,3-benzothiadiazole (BPTR), into the main chain of PBOPF homopolymer, which exhibits nearly pure red emission. Moreover, copolymers having low BPTR contents were found to exhibited white light emission. We systematically investigated the synthesis, thermal stability, and optical properties of the resulting polymers. In addition, we probed the energy transfer processes occurring between PBOPF and BPTR units by performing 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 nitrogen atmosphere. 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 $TBABF_4$ (0.10M) 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 thichness was measured with a TENCOR alphastep 500 surface profiler. 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 ITO 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) as an 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, 2,1,3-benzothiadiazole, 2-bromothiophene, 1-brombutane, 2,7-dibromofluorenone, toluene (99.8%, anhydrous), *N,N*-dimethylformamide (99.8%, anhydrous), 2-isopropoxy-4,4,5,5,-tetramethyl-1,3,2-dioxaborolane, phenol, *N*-bromosuccinimide, Aliquat336, and tetrakis(triphenylphosphine)palladium(0) were purchased from Aldrich. All chemicals were used without further purification. 4,7-bis(5-bromo-thiophene-2-yl)-2,1,3-benzothiadiazole (**1**), 10-*n*-butyl-3-bromophenothiazine (**2**), 2,7-dibromo-9,9-bis-(4-octyloxyphenyl)fluorene (**5**), 2,7-bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxyphenyl)fluorene (**6**) were synthesized according to procedures outlined in the literature.[7,18b,20] Solvents with analytical grade were used during the whole experiments, and all chemicals were used without further purification.

Synthesis of 3-(4,4,5,5-Tetramethyl-1,3,2-dioxaborolan-2-yl)-10-*n*-butylphenothiazine (3). Compound **2** (5.0 g, 15.0 mmol) was dissolved in THF (150 mL) at −78 °C. To a solution was added, by syringe, 17.6 mL (30.0 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 (4.5 mL, 22.4 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(1/10) as the eluent. The product was obtained with a yield of 70% (4.0 g).

^{1}H NMR (DMSO-d_6, ppm): 7.48 (d, 1H), 7.32 (s, 1H), 7.15 (t, 1H), 7.10 (d, 1H), 6.95 (m, 3H), 3.83 (t, 2H), 1.62 (m, 2H), 1.34 (m, 2H), 1.23 (s, 12H), 0.82 (t, 3H). ^{13}C NMR (DMSO-d_6, ppm): 147.45, 144.08, 134.15, 132.89, 127.52, 127.06, 123.37, 122.84, 122.70, 115.90, 115.17, 83.44, 46.11, 28.24, 24.55, 19.29, 13.53. Anal. Calcd for $C_{22}H_{28}BNO_2S$: C, 69.29; H, 7.40; N, 3.67; S, 8.41. Found: C, 69.01; H, 7.35; N, 3.62; S, 8.43.

Synthesis of 4,7-Bis(6-bromo-3-thiophenyl-10-*n*-butylphenothiazine)-2,1,3-benzothiadiazole(BPTR) (4). Into a 100 mL two-neck flask were added 2.42 g (6.35 mmol) of compound **3** and 1.38 g (3.00 mmol) of compound **1** in 30 mL of anhydrous toluene. Water-soluble Pd(0) complex, tetrakis(triphenylphosphine)palladiuim (1.0 mol %), was transferred into the mixture in a glovebox. 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 24 h. The reaction mixture is cooled to about 50 °C and added slowly to a vigorously stirred mixture of 200 mL of methanol. The obtained product was purified by column chromatography. And then, a solution of obtained compound in 100 mL of dichloromethane was stirred and cooled with an ice bath while a two times equivalent of bromine was added portionwise. The mixture was then stirred for 2 h at room temperature. The resulting mixture extracted with dichloromethane and dried over $MgSO_4$. The solvent was removed by solvent evaporation, and the residue was purified by column chromatography. The product was obtained with a yield of 33.3% (1.0 g).

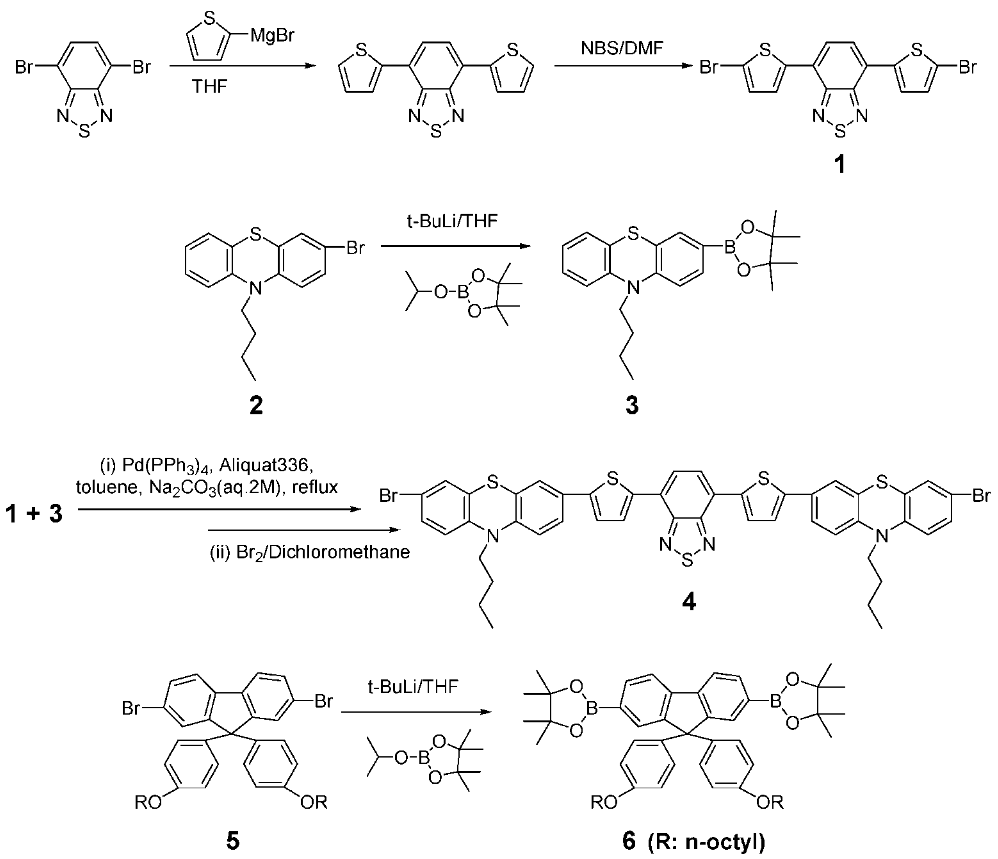
^{1}H NMR (CD_2Cl_2, ppm): 7.48 (s, 2H), 7.29 (m, 4H), 7.12 (m, 6H), 7.02 (d, 2H), 6.83 (d, 2H), 6.71 (d, 2H), 3.78 (m, 4H), 1.74 (m, 4H), 1.45 (m, 4H), 0.95 (t, 9H). ^{13}C NMR (CD_2Cl_2, ppm): 152.47, 145.41, 144.52, 139.72, 138.06, 128.87, 128.72, 128.17, 127.65, 126.97, 125.81, 125.59, 125.31, 125.02, 124.93, 124.26, 123.26, 122.79, 115.71, 47.51, 29.19, 20.48, 13.99. Anal. Calcd for $C_{46}H_{36}Br_2N_4S_5$: C, 57.26; H, 3.76; N, 5.81; S, 16.62. Found: C, 56.96; H, 3.72; N, 5.75; S, 15.54. $m/z = 964$ (M$^+$). $T_m =$ 110 °C.

General Polymerization Procedure. The preparation of polymerization is according to procedure of compound **4**. 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 chromatography 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: 50−72%

Poly{9,9-bis(4-octyloxyphenyl)fluorene-2,7-diyl-*co*-4,7-bis(3-thiophenyl-10-*n*-butylphenothiazine-6-yl)-2,1,3-benzothiadiazole} (PFPTR 01). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxyphenyl)fluorene (**6**) (1.0 equiv), 2,7-dibromo-9,9-bis-(4-octyloxyphenyl)fluorene (**5**) (0.999 equiv) and 4,7-bis(6-bromo-3-thiophenyl-10-*n*-butylphenothiazine)-2,1,3-benzothiadiazole (**4**) (0.001 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm): aromatic, 7.75−6.76 (∼32H); aliphatic, 3.88−3.86 (∼8H), 1.75−0.85 (∼44H). Anal. Found: C, 84.35; H, 8.2; N, 0.014.

Scheme 1. Synthetic Routes of the Two Comonomers, BOPF and BPTR



Poly{9,9-bis(4-octyloxyphenyl)fluorene-2,7-diyl-*co*-4,7-bis(3-thiophenyl-10-*n*-butylphenothiazine-6-yl)-2,1,3-benzothiadiazole} (PFPTR 025). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxyphenyl)fluorene (**6**) (1.0 equiv), 2,7-Dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**5**) (0.9975 equiv), and 4,7-bis(6-bromo-3-thiophenyl-10-*n*-butylphenothiazine)-2,1,3-benzothiadiazole (**4**) (0.0025 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm): aromatic, 7.75−6.76 (~32H); aliphatic, 3.88−3.86 (~8H), 1.75−0.85 (~44H). Anal. Found: C, 82.87; H, 8.16; N, 0.016.

Poly{9,9-bis-(4-octyloxyphenyl)fluorene-2,7-diyl-*co*-4,7-bis(3-thiophenyl-10-*n*-butylphenothiazine-6-yl)-2,1,3-benzothiadiazole} (PFPTR 05). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxyphenyl)fluorene (**6**) (1.0 equiv), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**5**) (0.995 equiv), and 4,7-bis(6-bromo-3-thiophenyl-10-*n*-butylphenothiazine)-2,1,3-benzothiadiazole (**4**) (0.005 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm): aromatic, 7.75−6.76 (~32H); aliphatic, 3.88−3.86 (~8H), 1.75−0.85 (~44H). Anal. Found: C, 83.24; H, 8.07; N, 0.032.

Poly{9,9-bis-(4-octyloxyphenyl)fluorene-2,7-diyl-*co*-4,7-bis(3-thiophenyl-10-*n*-butylphenothiazine-6-yl)-2,1,3-benzothiadiazole} (PFPTR 1). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis-(4-octyloxyphenyl)fluorene (**6**) (1.0 equiv), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**5**) (0.99 equiv), and 4,7-bis(6-bromo-3-thiophenyl-10-*n*-butylphenothiazine)-2,1,3-benzothiadiazole (**4**) (0.01 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm): aromatic, 7.75−6.76 (~32H); aliphatic, 3.88−3.86 (~8H), 1.75−0.85 (~44H). Anal. Found: C, 81.88; H, 7.82; N, 0.07.

Poly{9,9-bis(4-octyloxyphenyl)fluorene-2,7-diyl-*co*-4,7-bis(3-thiophenyl-10-*n*-butylphenothiazine-6-yl)-2,1,3-benzothiadiazole} (PFPTR 25). 2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9-bis(4-octyloxyphenyl)fluorene (**6**) (1.0 equiv), 2,7-dibromo-9,9-bis(4-octyloxyphenyl)fluorene (**5**) (0.75 equiv) and 4,7-bis(6-bromo-3-thiophenyl-10-*n*-butylphenothiazine)-2,1,3-benzothiadiazole (**4**) (0.25 equiv) were used in this polymerization.

^{1}H NMR ($CDCl_3$, ppm): aromatic, 7.75−6.76 (~32H); aliphatic, 3.88−3.86 (~8H), 1.75−0.85 (~44H). Anal. Found: C, 79.40; H, 7.31; N, 1.186; S, 3.61.

Results and Discussion

Synthesis and Characterization of the Polymers. The synthetic routes and structures of the polymers are shown in Scheme 2. The series of conjugated copolymers were synthesized through palladium-catalyzed Suzuki coupling reactions.[18c] All the PFPTR copolymers were end-capped with bromobenzene. The actual compositions of the polymers were determined by elemental analysis.[18c] The feed ratios of BPTR were 0.1, 0.25, 0.5, 1.0, and 25 mol % of the total amount of monomer, and the resulting ratios of BPTR units in the PFPTRs were 0.15, 0.21, 0.33, 0.72, and 12.8%, respectively. The actual ratios of PFPTR in the copolymers are similar to the feed monomer ratios in the first four cases. The lower than expected BPTR content for feed ratio of 25 mol % is tentatively attributed to reduced reactivity of the bulky BPTR units during the polymerization.[19] All 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, determined by gel permeation chromatography using a polystyrene standard, were found to range from 15 400 to 28 000 with polydispersity indices ranging from 2.1 to 3.1. The yields of the copolymers ranged from 50% to 72%. The thermal properties of the polymers were determined by thermal gravimetric analysis (TGA) under a nitrogen atmosphere. All the polymers were found to exhibit good

Scheme 2. Synthetic Routes of the Copolymers, PFPTRx

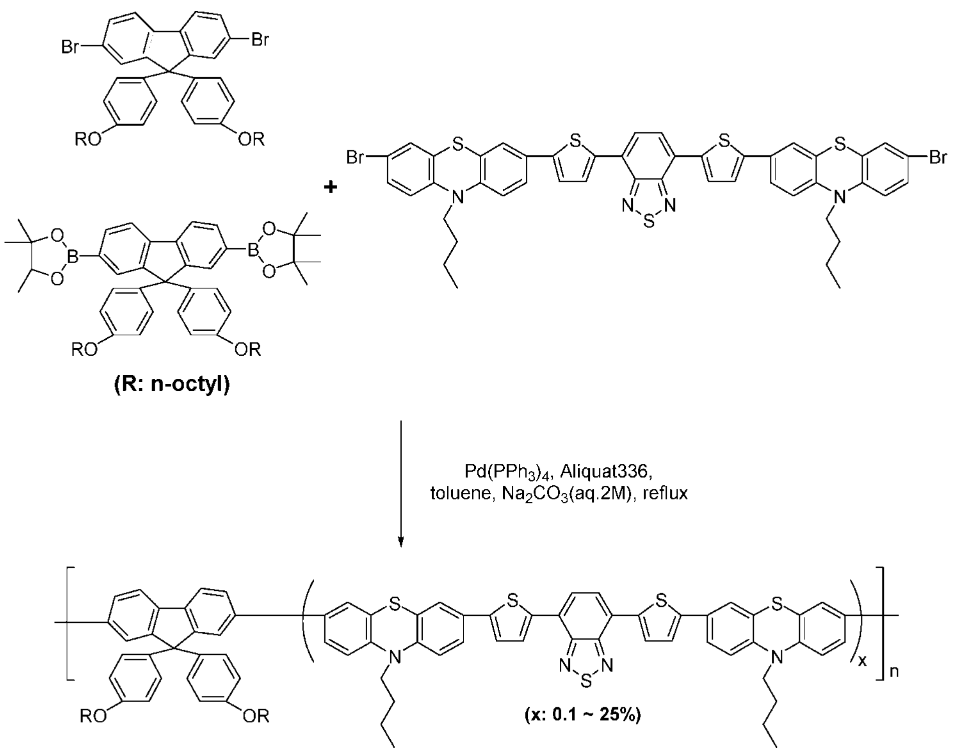


Table 1. Physical Properties of the Synthesized PFPTR Polymers

polymer	M_n[a]	PDI[a]	T_d (°C)[b]	ratio (BPTR mol %) in the feed composition	ratio (BPTR mol %) in the copolymers[c]
PFPTR 01	27 100	2.3	424	0.1	0.15
PFPTR 025	28 000	2.5	427	0.25	0.21
PFPTR 05	26 000	2.4	425	0.5	0.33
PFPTR 1	20 100	2.1	422	1	0.72
PFPTR 25	15 400	3.1	402	25	12.8

[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.

thermal stability, losing less than 5% of their weight upon heating to approximately 400 °C. The results of the polymerizations of the synthesized copolymers are summarized in Table 1.

Optical, Photoluminescence, and Electrochemical Properties. The normalized UV−vis absorption spectra of the polymers are shown in Figure 1. PFPTRs 01, 025, 05 and 1 exhibit a single absorption maxima at ~390 nm. The UV−vis absorption spectra of these PFPTRs in the solid state and in chloroform solution are qualitatively similar, indicating the absence of any remarkable conformational changes between the solid and solution state. In contrast, the absorption spectra of PFPTR 25 shows two distinct absorption peaks in the solid state and solution phase. The maximum absorption peak at ~390 nm is attributed to the BOPF units and the absorption peak at ~540 nm in the solid state (~520 nm in solution) is attributed to the BPTR units. The maximum absorption peak at ~390 nm for PFPTR 25 is slightly blue-shifted relative to the other copolymer and the appearance of the absorption band at ~540 nm is consistent with elemental analysis results showing a larger fraction of BPTR in the polymer, and the BPTR units activate effectively in the polymer chain.

The normalized PL emission spectra are shown in Figure 2. In the solution phase, the PL spectra of all of the polymers exhibit emission maxima at ~420 nm. The PL emissions spectra of the PFPTRs are similar to those of PBOPF homopolymers.[7] The PL results indicate that energy transfer from the BOPF segments to the BPTR units in the polymer chain is negligible in solution. Moreover, the results suggest that the BPTR units are not involved with polymer main-chain processes and possess their own independent Π-systems. The PL spectra for the thin films of the polymers are quite different from the solution data. The PL maximum at ~420 nm is attributed to emission by the BOPF segments and the red light emission between 620 and 700 nm is attributed to the BPTR units. The PL emission

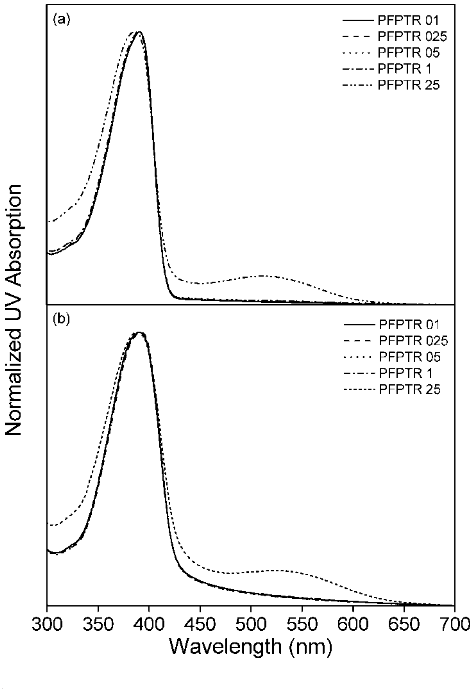


Figure 1. UV−vis absorption spectra of the synthesized PFPTR polymers: (a) solution state in chloroform and (b) film state onto quartz plate.

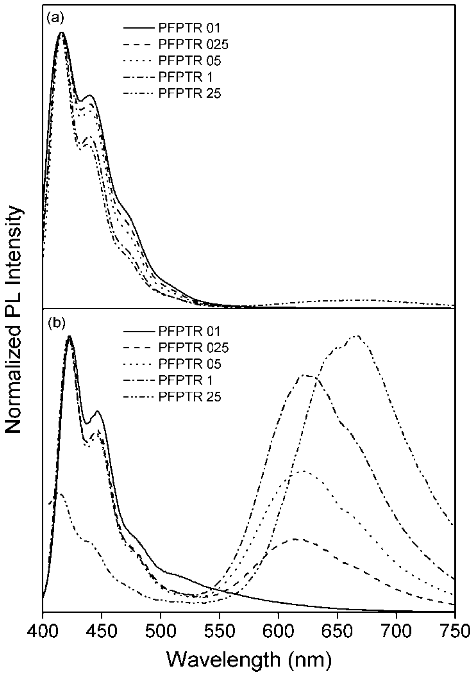


Figure 2. PL emission spectra of the synthesized PFPTR polymers: (a) solution state in chloroform and (b) film state onto quartz plate.

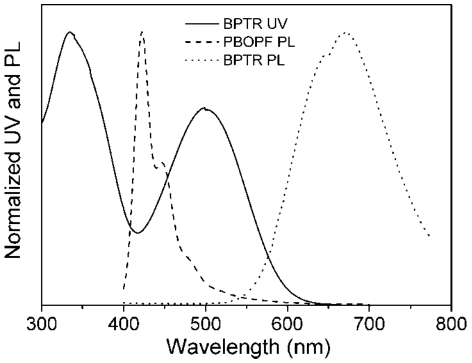


Figure 3. UV−vis absorption and PL emission spectra of BPTR and PBOPF.

maxima of the polymers shift to longer wavelengths as the number of BPTR units in the copolymers increases. The red emission displayed by the copolymers most likely due to intermolecular energy transfer from BOPF segments to the lower band gap BPTR units. We mentioned above that 2,1,3-benzothiadiazole derivative linked with thiophenes is well-known to display good red color (CIE coordinates are (0.70, 0.30)) with high external quantum efficiencies.[17a] Also, the phenothiazine is a well-known heterocyclic compound with electron-rich sulfur and nitrogen heteroatoms.[12−15] In consideration of these factors, we synthesized phenothiazine derivatives with 2,1,3-benzothiadiazole units that are expected exhibit good red color and high efficiency. For realizing white light emission, it demands balance of effective energy transfer from poly(fluorene)s as a host and blue emission unit to BPTR as a red emission unit. Moreover, copolymers containing benzothiadiazole or phenothiazine units in the main chain showed high efficiencies.[17a,18b] Because BPTR unit has these good properties, we expect that PFPTRs introduced BPTR show highly efficient white light emission. As shown in Figure 3, the PL spectrum of the PBOPF homo polymer overlaps significantly with the absorption spectrum of BPTR, indicating that efficient energy transfer from the BOPF segments to the BPTR units is indeed possible. In particular, copolymers with low BPTR content exhibited white light emission behavior. The appearance of both blue and red emissions in the PL spectra results from partial energy transfer from the PBOPF polymer backbone to the BPTR units. The optical properties of the synthesized polymers are summarized in Table 2.

Table 2. Summary of the Optical Properties and Energy Levels of the Synthesized PFPTR Polymers

	solution, λ_{max} (nm)[a]		film, λ_{max} (nm)[b]		$E_{onset,ox}$ (V)	E_{HOMO}[c] (eV)
	abs.	ems.	abs.	ems.		
PFPTR 01	391	416	390	423	1.10	5.82
PFPTR 025	391	416	392	423	1.10	5.82
PFPTR 05	391	416	391	423, 620	1.10	5.82
PFPTR 1	390	416	391	423, 621	1.07	5.78
PFPTR 25	386	416	389	668	1.04	5.76

[a] Measured in chloroform solution [b] Measured as thin films on fused quartz plates [c] Determined from the onset voltage of the first oxidation potential with reference to ferrocene at 4.8 eV

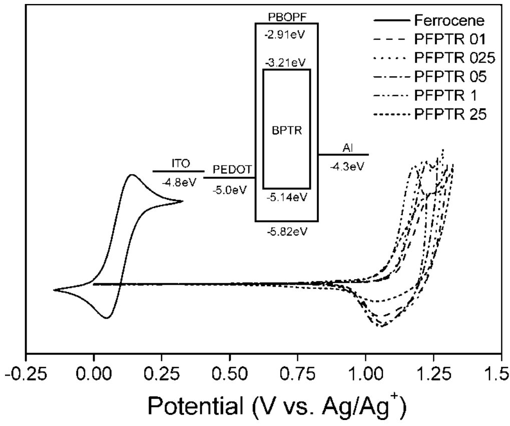


Figure 4. Cyclic voltammograms of the copolymers. Inset: the proposed energy levels of PBOPF and BPTR.

For investigating energy levels of their highest occupied molecular orbitals (HOMO) and lowest unoccupied molecular orbitals (LUMO), the electrochemical properties of PFPTRs were investigated by cyclic voltammetry (CV). A platinum electrode was coated by polymers was used as the working electrode, the counter electrode was a platinum wire, and the reference electrode was a Ag/$AgNO_3$ (0.01M) electrode. The electrochemical properties of the copolymers were investigated in an electrolyte consisting of a solution of 0.1 M tetrabutylammonium tetrafluoroborate ($TBABF_4$) in acetonitrile at room temperature under nitrogen with a scan rate of 50 mV/s. The measurements were calibrated using ferrocene as the standard.[21] Figure 4 shows the oxidation waves and energy levels of the copolymers as result of the p-type doping. As shown figure 4, in the anodic scan and energy diagram, the onsets of oxidation of BPTR and PFPTRs were found to occur at 0.42 to 1.10 V, corresponding to ionization potential values of 5.12 to 5.82 eV respectively. Unfortunately, a reduction wave was hardly obtained. The onsets of oxidation and the energies of the HOMO levels of PFPTRs are listed 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 of the synthesized polymers differ greatly from corresponding PL emission spectra, as shown in Figure 5. The intensities of red emission regions are significantly enhanced under the influence of an electric field. This indicates that the lower energy states of the BPTR units act as charge-trapping sites, and this result are confirmed by

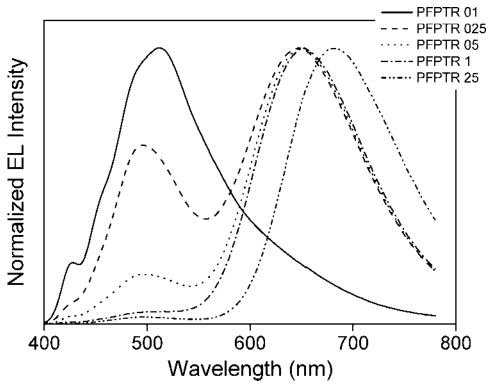


Figure 5. Electroluminescence spectra of PFPTR devices with ITO/PEDOT:PSS/polymer/Balq LiF/Al configurations.

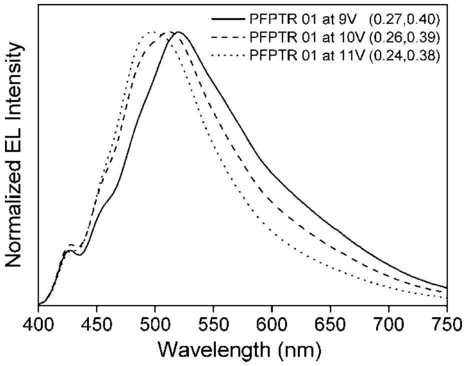


Figure 6. Electroluminescence spectra of PFPTR 01 device with ITO/PEDOT:PSS/polymer/Balq/LiF/Al configurations for various driving voltages.

relative position of their HOMO and LUMOs, as shown by the electrochemical measurements.[22] The EL emission maximum becomes increasingly red-shifted as the fraction of BPTR units increases. In particular, as shown in Figure 5, PFPTR 1 and PFPTR 25 exhibit nearly pure red emission close to the standard red (0.66, 0.34) demanded by the National Television System Committee (NTSC).[23] Their chromaticity values are ($x = 0.62$, $y = 0.36$) and ($x = 0.66$, 0.33), respectively. Moreover, the EL emission spectra of PFPTR 01 and PFPTR 025 are broad, covering the visible range from greenish-blue to red emission regions. The emission in the greenish-blue region originates from the BOPF segments and the red emission is from the BPRT units. Of these EL spectra, their CIE coordinates is shown at 10 V of (0.27, 0.40) and (0.41, 0.37) respectively, which appear near-white to the naked eye.

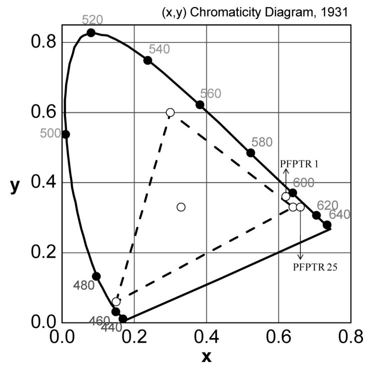


Figure 7. CIE coordinates (x,y) of PFPTR 1 and PFPTR 25 (NTSC-dashed line).

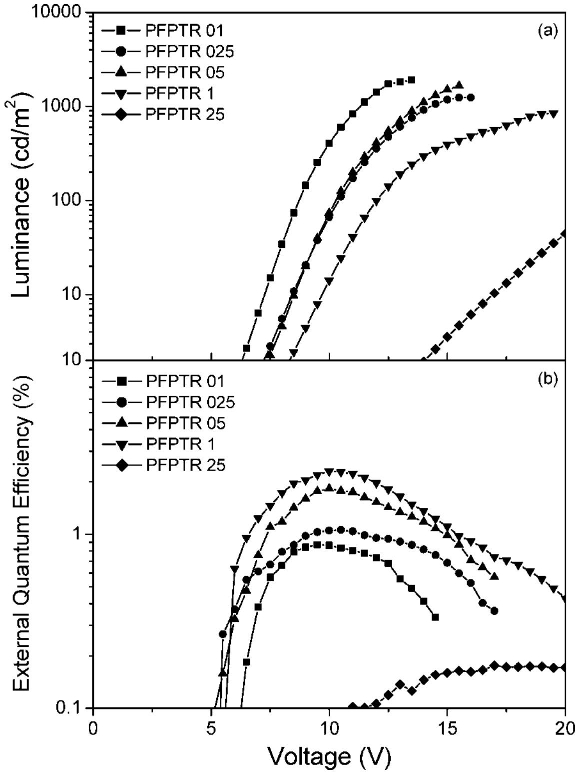


Figure 8. Voltage−luminance (V−L) (a) and external quantum efficiency (b) characteristics of the synthesized PFPTR polymers.

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

polymer	$\lambda_{\max}$ (nm)	luminance$_{\max}$ (cd/m^2)	current efficiency (cd/A)	EQE (%)	CIE coordinates (x,y)[a]
PFPTR 01	510	1910	1.84	0.87	(0.27,0.40)
PFPTR 025	(495), 650	1240	1.21	1.06	(0.41,0.37)
PFPTR 05	650	1650	1.71	1.83	(0.57,0.37)
PFPTR 1	651	850	1.70	2.30	(0.62,0.36)
PFPTR 25	681	100	0.06	0.18	(0.66,0.33)

[a] Determined from EL spectra (Figure 5).

The voltage−luminance (V−L) and external quantum efficiency characteristics of the devices are shown in Figure 7, and their performances are summarized in Table 3. The turn-on voltages of the PFPTR devices range from 6.5 to 14 V and their maximum brightnesses are in the range 100−1900 cd/m^2. The voltage-luminance (V−L) curves shift to slightly higher voltages with increasing BPTR fraction in the copolymers, suggesting the BPTR units dominate the charge-trapping phenomena.[22] All polymers showed promising current efficiency and external quantum efficiency characteristics with the exception of PFPTR 25. In the case of PFPTR 25, the BPTR units presumably operate as charge-trapping sites along the polymer chain, resulting in assumed exciton quenching. Of particular mention, the PFPPTR 1 device showed an impressive maximum external quantum efficiency of 2.3% at 10 V and the maximum current efficiency of 1.70 cd/A at 10V. Cao et al. have reported a fluorene based copolymer containing 2,1,3-benzothiadiazole units that exhibited 2.54% of external quantum efficiency and a current efficiency of 1.45 cd/A. Hence, our device results for PFPTR 1 are among the highest values yet reported in the literature for saturated red polymer emitters.[15,18b]

We mentioned above that copolymers with low BPTR contents exhibited white light emission. In particular, PFPTR 01 and PFPTR 025 displayed white light emission with maximum current efficiencies and external quantum efficiencies of 1.84 and 0.87%, and 1.21 cd/A and 1.06%, respectively. We suggest that PFPTR 01 and PFPTR 025 produce balanced greenish-blue and red emission in the device and measured high efficiencies caused by proper energy transfer. The device properties of PFPTR 01 and PFPTR 025 are promising for the achievement of white light emission based on a single polymer chain. We are currently carrying out experiments to further improve the performance of these white polymeric LEDs by incorporating new comonomers into the polymer backbone.

Conclusions

We have synthesized a series of new fluorene-based copolymers (PFPTRs) with varying molar ratios of the low energy band gap comonomer, BPTR. These polymers were synthesized with the aim of creating pure red-emitting-materials for use in OLEDs as well as polymers that can form the basis of efficient white-light-emitting materials. An EL device fabricated with PFPTR 1 was found to emit nearly pure red light with CIE coordinates of (0.62, 0.36), which are very close to the standard red (0.66, 0.34) demanded by the National Television System Committee. Its maximum external quantum efficiency and maximum current efficiency were 2.3% and 1.70 cd/A at 10V, respectively. Moreover, devices based on PFPTR 01 and PFPTR 025 displayed white electroluminescence with CIE coordinates of (0.27, 0.40) and (0.41, 0.37), their maxima of current efficiency and external quantum efficiency are 1.84 and 1.21 cd/A, 0.87 and 1.06% respectively, which appear near-white to the naked eye. These results suggest that white polymeric LEDs utilizing a single polymer chain have potential applications in full-color displays.

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