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Synthesis and Characterization of a New Light-Emitting Fluorene−Thieno[3,2-*b*]thiophene-Based Conjugated Copolymer

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ABSTRACT: A new alternating polyfluorene copolymer, poly(9,9′-dioctylfluorene-*alt*-thieno[3,2-*b*]-thiophene) (PFTT), containing a thiophene-condensed thieno[3,2-*b*]thiophene moiety has been synthesized via a palladium-catalyzed Suzuki coupling reaction. The synthesized polymer was successfully characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis. It shows good thermal stability and displays unique phase transition behavior between the crystalline and liquid-crystalline states. The ionization potential and electron affinity of PFTT are −5.38 eV and −2.40 eV, respectively, as determined by cyclic voltammetry. Thus, PFTT has an electrochemical band gap of approximately 2.98 eV, which is smaller than that of common polyfluorene (PF) homopolymers. As a film, PFTT exhibits UV−vis and photoluminescence maxima at 471 and 511 nm, respectively. A light-emitting diode device fabricated with an ITO/PEDOT/PFTT/LiF/Al configuration exhibits pure green light emission with the full width at half-maximum (fwhm) of only 57 nm and a low turn-on voltage of 3.3 V. Especially, this emission has the CIE coordinates (0.29, 0.63), which are very close to the standard for green used by the National Television System Committee. In addition, PFTT exhibits better electroluminescence performance than other similar PF homopolymers and than fluorene- and thiophene-based copolymers.

Introduction

In the past decade, fluorene-based π-conjugated polymers (PFs) have emerged as emitting materials suitable for use in polymer light-emitting diodes (PLEDs) because of their highly efficient photoluminescence (PL) and electroluminescence (EL), their thermal and oxidative stability, their good solubility, and their emission of polarized blue light.[1−7] Since the first report of the synthesis of soluble C9-substituted alkyl PFs via the ferric chloride oxidative route by Yoshino et al. in 1989,[8] there have been remarkable advances in the production of high molecular weight and structurally well-defined PF derivatives. In particular, work by researchers at Dow Chemical Corp. has enabled the syntheses via the palladium-catalyzed Suzuki coupling reaction of various 9,9′-dialkylfluorene homopolymers and copolymers that emit the entire visible range of colors.[9,10] The alternating incorporation of various aryl comonomers into the fluorene backbone enables the tuning of the electroluminescence properties, resulting in enhanced stability and high efficiency.[11,12]

At the same time, oligomers and polymers containing thiophene rings as well as polythiophene and poly(alkylthiophene) have attracted considerable attention as candidate materials for use in molecular devices because of their advantageous electrical conductivity. Many research groups have recently carried out syntheses of the polyfluorene derivatives based on thiophene or bithiophene through the Suzuki coupling reaction.[13,14] This approach to thiophene moieties can also be extended to thieno-acenes (e.g., thieno[3,2-*b*]thiophene) and higher homologues of the linear thiophene-condensed π-system. In addition, now that convenient, reproducible methods for the large-scale synthesis of thieno[3,2-*b*]thiophene have been reported by Smith et al.,[15] fluorene- and thieno[3,2-*b*]thiophene-based copolymers can be easily obtained.

In this paper, we outline our strategy for improving the material properties of polyfluorene derivatives, which may eventually be useful in PLED device applications. We have synthesized a new PF derivative, poly(9,9′-dioctylfluorene-*alt*-thieno[3,2-*b*]thiophene) (PFTT), by introducing the thieno[3,2-*b*]thiophene unit alternately into the PF backbone through the Suzuki coupling reaction. The general properties of this derivative, including its thermal, liquid crystalline, electrochemical, and optical properties, are investigated herein. In addition, we discuss the possibility of the use of PFTT as an emissive layer in LEDs.

Experimental Section

Measurements. NMR spectra were recorded on a Bruker Avance 400 spectrometer. Elemental analyses were performed with a CHNS-5 EA1108 elemental analyzer from Carlo ERBA Instruments. The number- and weight-average molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters GPC-150C instrument calibrated using THF as eluent and polystyrene as standard. Differential scanning calorimetry (DSC) and thermal gravimetric analysis (TGA) were performed under a nitrogen atmosphere at a heating rate of 10 °C min^{-1} through the use of a Dupont 9900 analyzer. Polarized light microscopy (PLM) image (magnified 100×) was obtained with a polarizing light microscope (OPTO PHOTO2-POL, Nikon) equipped with a camera attachment. UV−vis spectra were obtained by using a Jasco V-530 UV/vis spectrometer, and PL spectra were obtained by using a Spex Fluorolog-3 spectrofluorometer. The films used in these UV−vis and PL measurements were prepared by spin-coating solutions of the polymers (1 wt % in chloroform). Cyclic voltammograms of the polymer films (dip-coated onto Pt wire) were recorded on an AUTOLAB/PG-STAT12 at room temperature in a solution of tetrabutylammonium tetrafluoroborate (n-Bu$_4$NBF$_4$) (0.10 M) in acetonitrile under nitrogen gas protection at a scan rate of 50 mV/s. A Pt wire was used as the counter electrode and a Ag/Ag$^+$ electrode as the reference electrode. EL spectra were obtained with a

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Table 1. Physical Properties of the Polymers

polymer	M_n[a]	M_w[a]	PDI (M_w/M_n)	T_g (°C)[b]	T_{Cr} (°C)[c]	T_{Cr-LC} (°C)[d]	T_{5d} (°C)[e]
PFTT	13 600	24 500	1.80	112	161	243	419
PFT2	19 000	53 800	2.83	93	160	239	426
PFO	35 600	100 000	2.81				

[a] Determined by GPC, relative to polystyrene standards. [b] The glass transition temperature. [c] Temperature at the crystallization exothermal peak. [d] Temperature at the melting endothermal peak. [e] Temperature resulting in 5% weight loss based on the initial weight measured by TGA analysis.

Minolta CS-1000. The voltage−luminance and voltage−current characteristics were recorded on a current−voltage source (Keithley 238) and a luminescence detector (Minolta LS-100). Films for EL measurement were prepared by spin-coating solutions of the polymers (1 wt % in anhydrous dichlorobenzene (Aldrich)) at 1200 rpm (for PFTT and PFO) or 1500 rpm (for PFT2). Film thicknesses were measured with a TENCOR alpha-step 500 surface profiler.

Materials. Fluorene, 1-bromooctane, tetrabutylammonium bromide (TBAB), toluene, *tert*-butyllithium, 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, copper powder, 3-bromothiophene, lithium diisopropylamide (LDA), *N*-formylpiperidine, quinoline, tetrakis(triphenylphosphine)palladium, Aliquat 336, *N*-bromosuccinimide (NBS), and 2,5-dibromothiophene were purchased from Aldrich. Ethyl 2-sulfanyl acetate and poly(3,4-ethylene dioxythiophene) (PEDOT) were purchased from TCI and Bayer, respectively. All reagents purchased commercially were used without further purification except for tetrahydrofuran (THF), which was dried over sodium/benzophenone. The monomers 2,7-dibromo-9,9′-dioctylfluorene (**2**)[16] and 2,5-dibromothieno[3,2-*b*]thiophene (**8**)[15,17] were prepared with methods in close analogy to those described previously.

2,7-Bis(4,4,5,5-tetramethyl-1,3,2-dioxaborolan-2-yl)-9,9′-dioctylfluorene (3). To a solution of 2,7-dibromo-9,9′-dioctylfluorene (**2**) (7.0 g, 12.8 mmol) in THF (120 mL) at −78 °C was added dropwise 33.79 mL (57.42 mmol) of *tert*-butyllithium (1.7 M in hexane). After the mixture had been 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 then warmed to room temperature and further stirred for 40 h. The mixture was poured into water, extracted with dichloromethane, and then dried over $MgSO_4$. The solvent was removed by rotary evaporation, and the residue was purified by several reprecipitations in hexane, resulting in 4.59 g (56%) of the product as a white solid. ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 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 ($CDCl_3$, 100 MHz): δ (ppm) 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.

2,5-Dibromothieno[3,2-*b*]thiophene (8) was synthesized by a procedure adapted from the literature.[17] ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) 7.15 (s, 2H). ^{13}C NMR ($CDCl_3$, 100 MHz): δ (ppm) 138.26, 121.74, 113.59.

Polymerization. The syntheses of the polymers were carried out using well-known palladium-catalyzed Suzuki couplings between dibromoaryl and diborolanylaryl compounds.[18,19]

Poly(9,9′-dioctylfluorene-*alt*-thieno[3,2-*b*]thiophene) (PFTT). Monomer **8** (0.68 g, 2.28 mmol) and monomer **3** (1.50 g, 2.33 mmol) were dissolved in 25 mL of anhydrous toluene. The air-sensitive Pd(0) complex, tetrakis(triphenylphosphine)-palladium (1 mol %, 0.026 g), was added into the mixture in a drybox. 2 M aqueous sodium carbonate (5.4 mL, 10.7 mmol) that had been deaerated for 30 min and a phase transfer catalyst, Aliquat 336 (0.092 g, 0.23 mmol), purged in toluene under nitrogen for 1 h, were transferred to the mixture via cannula. The reaction mixture was stirred and heated for 60 h until the reaction mixture became viscous. An excess of bromobenzene (0.036 g, 0.23 mmol) dissolved in 1 mL of anhydrous toluene was added as an end-capper. After further stirring and heating for 12 h, the reaction mixture was cooled to about 50 °C and added slowly to a vigorously stirred mixture consisting of 230 mL of methanol and 13 mL of 1 N aqueous HCl. The polymer fibers were collected by filtration and reprecipitation from methanol and acetone. The polymer was purified by a Soxhlet extraction in acetone for 2 days and a column chromatography using chloroform/toluene as the eluent to remove oligomers and catalyst residues. The reprecipitation procedure in toluene/methanol was then repeated several times. The final product, a yellow polymer, was obtained after drying in vacuo at 60 °C, with a yield of 0.52 g (42.0%). ^{1}H NMR ($CDCl_3$, 400 MHz, +50 °C): δ (ppm) aromatic; 7.68−7.54 (m, 8H), aliphatic; 2.05 (br, 4H), 1.22−1.10 (m, 20H), 0.80 (m, 10H). Anal. Calcd for $(C_{37}H_{48}S_2)_n$: C, 79.80; H, 8.69; S, 11.52. Found: C, 79.46; H, 8.62; S, 10.04.

Poly(9,9′-dioctylfluorene-*alt*-bithiophene) (PFT2). PFT2 was synthesized using the same method as used for PFTT, with 0.75 g of 2,5-dibromothiophene (2.28 mmol) and 1.50 g of monomer **3** (2.33 mmol). The final product, an orange polymer, was obtained after drying in vacuo at 60 °C, with a yield of 0.72 g (57.3%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) aromatic; 7.66−6.80 (m, 10H), aliphatic; 2.02 (br, 4H), 1.07 (br, 20H), 0.80 (m, 10H). Anal. Calcd for $(C_{39}H_{50}S_2)_n$: C, 80.35; H, 8.65; S, 11.00. Found: C, 80.14; H, 8.60; S, 10.20.

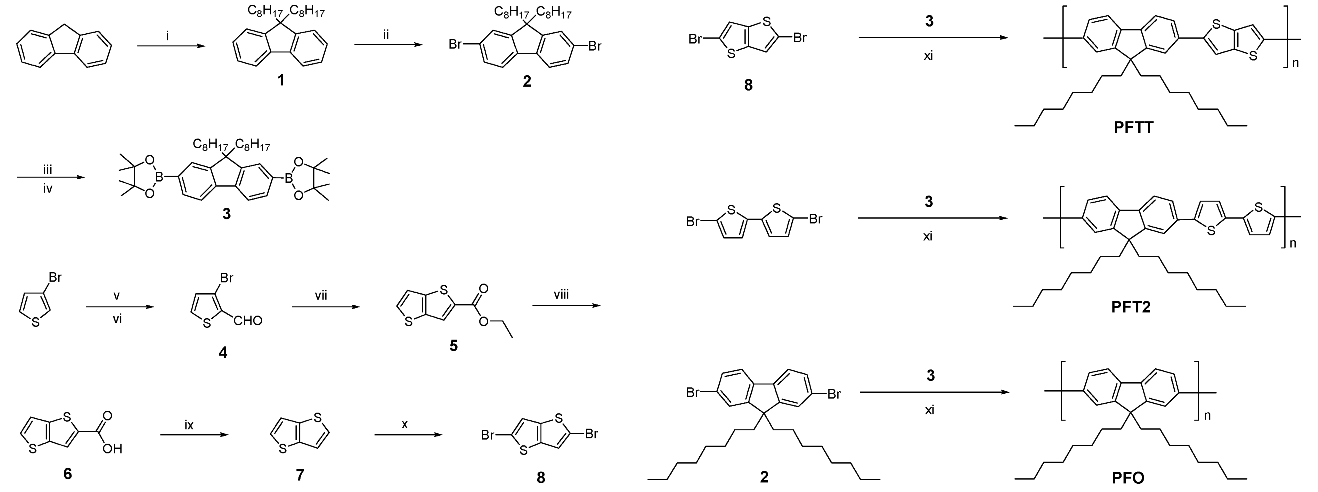
Poly(9,9′-dioctylfluorene) (PFO). PFO was synthesized using the same method as used for PFTT, with 0.88 g of monomer **2** (1.61 mmol) and 1.06 g of monomer **3** (1.65 mmol). The final product, a light-green polymer, was obtained after drying in vacuo, with a yield of 0.85 g (81.0%). ^{1}H NMR ($CDCl_3$, 400 MHz): δ (ppm) aromatic; 7.84−7.82 (d, 2H), 7.68 (br, 4H), aliphatic; 2.09 (br, 4H), 1.13 (br, 20H), 0.77 (m, 10H).

Results and Discussion

Synthesis and Characterization. A new fluorene- and thieno[3,2-*b*]thiophene-based alternating copolymer, PFTT, was synthesized by using the Suzuki coupling reaction. A comparable fluorene- and thiophene-based copolymer, PFT2, and a corresponding well-known and typical polyfluorene homopolymer, poly(9,9′-dioctylfluorene) (PFO), were also prepared under the same conditions for comparison. The syntheses of the monomers and polymers are outlined in Scheme 1. Their chemical structures were verified by ^{1}H NMR, ^{13}C NMR, and elemental analysis. The number-average molecular weights (M_n) of the synthesized polymers, PFTT, PFT2, and PFO, as determined by gel permeation chromatography (GPC) using a polystyrene standard, were 13 600 ($M_w/M_n = 1.8$), 19 000 ($M_w/M_n = 2.8$), and 35 600 ($M_w/M_n = 2.8$), respectively. The relatively low molecular weight of PFTT may be due to the rigidity of the thieno[3,2-*b*]thiophene group. The polymerization results are summarized in Table 1.

The thermal stabilities of the copolymers were evaluated under a nitrogen atmosphere by thermogravimetric analysis (TGA). PFTT shows good thermal stability as weight loss was less than 5% on heating to about 420 °C. The thermally induced phase transition behaviors of the copolymers were investigated with differential scanning calorimetry (DSC) in nitrogen at a heating rate of 10 °C min^{-1} after the samples had been heated to 300 °C and then allowed to slowly cool to room temperature. From the DSC heating scans, PFTT shows a glass transition (T_g) at 112 °C. Moreover, typical liquid-

Scheme 1. Syntheses of the Fluorene- and Thieno[3,2-*b*]thiophene-Based Monomers and Polymers[a]



[a] Reagents and conditions: (i) 1-bromooctane, tetra(*n*-butyl)ammonium bromide, NaOH(aq, 50 wt %), toluene, reflux; (ii) bromine, dichloromethane; (iii) *t*-BuLi, THF, −78 °C for 2 h; (iv) 2-isopropoxy-4,4,5,5-tetramethyl-1,3,2-dioxaborolane, −78 °C for 1 h, then room temperature for 40 h; (v) LDA, THF, 0 °C for 0.5 h; (vi) *N*-formylpiperidine, THF; (vii) ethyl 2-sulfanyl acetate, K_2CO_3, DMF; (viii) NaOH(aq), THF, reflux; (ix) Cu, quinoline, 180 °C; (x) NBS, DMF, 0 °C; (xi) $Pd(PPh_3)_4$, Aliquat 336, toluene, Na_2CO_3(aq, 2 M), reflux.

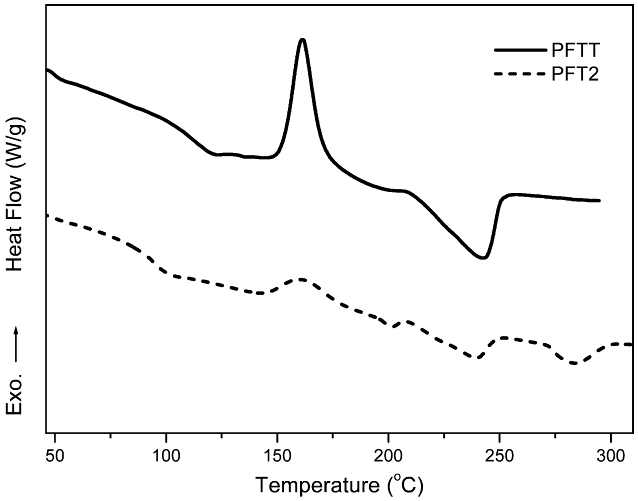


Figure 1. DSC thermograms of PFTT and PFT2.

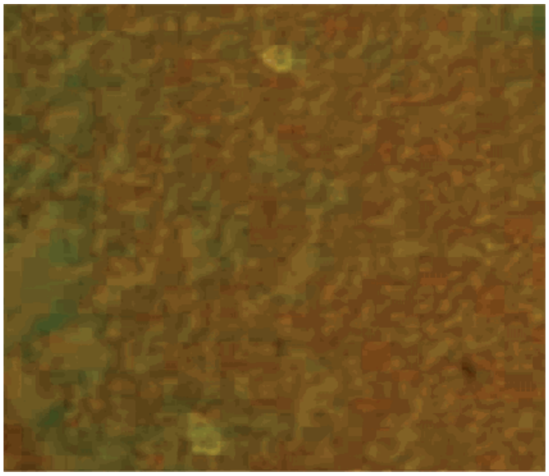


Figure 2. Polarized light microscopy image (magnified 100×) of PFTT.

crystalline (LC) characteristics, i.e., both crystallization and melting processes, were clearly observed in the DSC curve of PFTT, similarly with the previous reported liquid-crystalline fluorene copolymers.[20] A crystallization exothermal peak (T_{Cr}) and a melting endothermal peak ($T_{\mathrm{Cr-LC}}$) appeared at 161 and 243 °C, respectively (see Figure 1). These characteristic temperatures of PFTT are around 100 °C higher than those previously reported for the corresponding PFO homopolymer,[21] probably because of the introduction of the unsubstituted and rigid thieno[3,2-*b*]thiophene moiety. The bulk thermal liquid crystalline properties of polymers can also be determined with polarized light microscopy (PLM). Polymer films with a thickness of 3 μm were prepared on a quartz glass substrate by solution casting of the polymers dissolved in dichlorobenzene. The films were annealed at 285 °C (i.e., just above the $T_{\mathrm{Cr-LC}}$) for 1.5 h and then cooled to room temperature at a rate of −10 to −15 °C min^{-1}. As shown in the PLM image in Figure 2, the annealed film of PFTT exhibits a birefringent fluid phase, indicative of its thermotropic nematic liquid crystallinity. Recently, liquid-crystalline conjugated polymers have been introduced into the fields of organic thin-film transistors (OTFTs) as the active semiconducting layers because of their improved charge-carrier mobility in the LC state.[22] Along with further research into the liquid-crystalline properties of our copolymer, the possible applications of PFTT in polarized EL[6,23,24] and OTFTs[22] are currently under study.

Figures 3 and 4 show the normalized UV−vis absorption and photoluminescence (PL) emission spectra of the polymers in chloroform solution. Both the absorption and emission peaks of the two copolymers, PFTT and PFT2, are clearly red-shifted with respect to those of PFO. This spectral shift can be understood in terms of the more planar backbone and the smaller band gap produced by the introduction of the fused thiophene rings.[13] The UV−vis absorption maxima of PFTT appear at 439 and 457 nm; in PFT2, these transitions are slightly red-shifted to 452 and 470 nm. The PL emission spectra of the two polymer solutions show typical vibronically structured bands comprising a maximum, a shoulder, and a tail, which appear at 478, 510, and 554 nm respectively for PFTT and at 495, 530, and 571 nm respectively for PFT2. These results indicate that the β-substituted bithiophene has a higher effective conjugated length than that of thieno[3,2-*b*]thiophene, the two thiophene-condensed π-system. In addition, both

Table 2. UV−Vis Absorption and PL Emission Spectral Data of the Polymers in Chloroform and as Films

	solution λ_{max} (nm)		film λ_{max} (nm)		PL efficiency (Φ_{fl})		
polymer	absorption	emission	absorption	emission	solution[a]	film[b]	E_g (eV, UV/nm)[c]
PFTT	439, 457	478, 510, 554	448, 471	495, 511, 548	0.32	0.12	2.48 (500)
PFT2	452, 470	495, 530, 571	458, 479	511, 537, 577	0.20	0.12	2.44 (508)
PFO	389	414, 439, 471	394	424, 448	0.81	0.55	2.93 (423)

[a] Solution fluorescence quantum yield measured in chloroform relative to quinine sulfate (approximately 1×10^{-5} M) in 0.10 M H_2SO_4 as standard. [b] Film fluorescence quantum yield estimated by comparison with the fluorescence intensity of the PFO thin film sample ($\Phi_{fl} \approx 0.55$).[4] [c] The optical gap, E_g, taken as the absorption onset (value in parentheses) of the UV−vis spectrum of the polymer film.

Table 3. Electrochemical Properties and Energy Levels of the Polymers[a]

	p-doping (V vs SCE)				n-doping (V vs SCE)					
polymer	$E_{onset,ox}$	E_{pa}	E_{pc}	$E_{1/2}$	$E_{onset,red}$	E_{pc}	E_{pa}	HOMO (eV)[b]	LUMO (eV)[b]	E_g (eV, Echem)
PFTT	0.99	1.09	0.97	1.03	−1.99	−2.12	−1.93	−5.38	−2.40	2.98
PFT2	1.02	1.07	0.88	0.98	−1.91	−2.00	−1.85	−5.41	−2.48	2.93

[a] $E_{onset,ox}$, $E_{onset,red}$, E_{pa}, E_{pc}, and $E_{1/2}$ stand for onset potential of oxidation, onset potential of reduction, anodic peak potential, cathodic peak potential, and the average of the anodic and cathodic peak potentials, respectively (scan rate: 50 mV/s). [b] Calculated using the empirical equation: $I_p(\mathrm{HOMO}) = -(E_{onset,ox} + 4.39)$, $E_a(\mathrm{LUMO}) = -(E_{onset,red} + 4.39)$.[26]

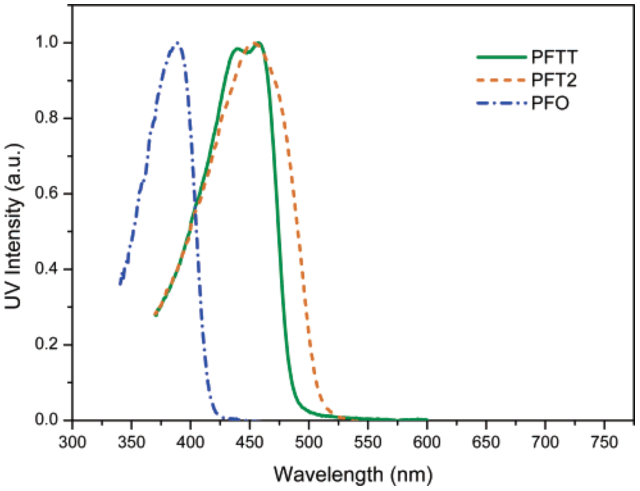


Figure 3. UV−vis spectra of the polymers in chloroform solution.

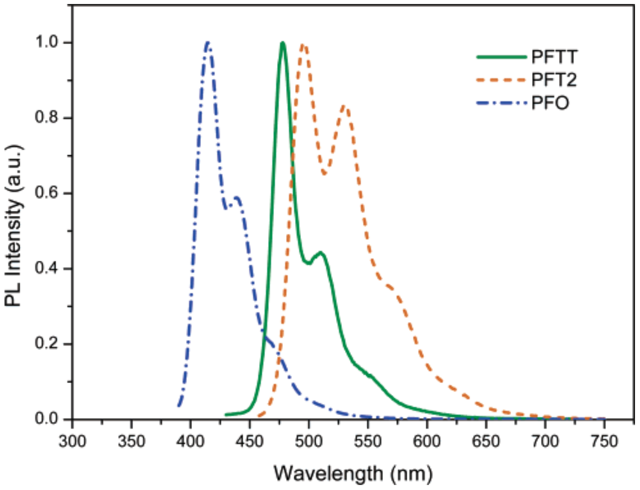


Figure 4. Photoluminescence (PL) spectra of the polymers in chloroform solution.

the absorption and the emission spectra of the film state are more red-shifted and broader than those of the solution state (see Table 2 and Figure 5), probably because of the increased intermolecular interactions between neighboring molecules in the film state. The optical band gaps, E_g, of PFTT and PFT2 are estimated from the absorption onset wavelengths of the UV−vis spectrum of the polymer film. All the UV−vis absorption and PL emission maxima of the polymers are listed in Table 2, together with their optical band gaps and PL quantum efficiencies.

The electrochemical properties of the polymers were investigated in order to gauge their electronic properties. All the electrochemical data for PFTT and PFT2, obtained from the films prepared by dip-coating the polymer solutions onto Pt wire, are listed in Table 3. All measurements were calibrated using ferrocene (Fc) value of −4.8 eV as the standard.[25] In the anodic scan, the onsets of oxidation of PFTT and PFT2 occur at 0.99 and 1.02 V (vs SCE), which correspond to the ionization potential (I_p) values of −5.38 and −5.41 eV, respectively, according to the empirical relationship proposed by Leeuw et al. ($I_p(\mathrm{HOMO}) = -(E_{onset,ox} + 4.39)$ (eV), $E_a(\mathrm{LUMO}) = -(E_{onset,red} + 4.39)$ (eV), where $E_{onset,ox}$ and $E_{onset,red}$ are the onset potentials of oxidation and reduction, respectively).[26] Similarly, the electron affinity (E_a) values of the polymers were determined to be −2.40 eV for PFTT and −2.48 eV for PFT2. From the onset potentials of the oxidation and reduction processes, it can be estimated that the electrochemical band gaps, E_g ($= E_{onset,ox} - E_{onset,red}$),[27,28] of PFTT and PFT2 are 2.98 and 2.93 eV, indicative of green and greenish-yellow light emission, respectively. The electrochemical band gaps are higher than the optically determined ones (see Table 2) due to interface barrier for charge injection.[28,29] The incorporation of the electron-rich thiophene moiety into the polymer backbone leads to higher HOMO and lower LUMO in the two copolymers than those of the PFO homopolymer.[29]

Electroluminescence Properties and Current−Voltage−Luminance (*I*−*V*−*L*) Characteristics. To investigate the electroluminescence properties and the current−voltage−luminance characteristics of the synthesized polymers, devices with the configuration ITO/PEDOT (40 nm)/polymer (80 nm)/LiF (1 nm)/Al (100 nm) were fabricated. The polymer was spin-coated from a 1.0 wt % solution in dichlorobenzene onto an ITO substrate coated with PEDOT. The EL spectra and the CIE coordinates of the polymers are shown in Figure 5, together with the PL spectra of the solid state. The EL spectra of the polymers are nearly identical to the PL spectra of the spin-coated films. PFTT emitted light of a pure green color with a maximum emission at 515 nm, compared with the greenish-yellow emission of PFT2. The quality of emission spectra can be specified by their CIE (Commission Internationale de L'Eclairage) chro-

Table 4. EL Spectral Data and Performance Characteristics of the Devices

polymer	$\lambda_{\max}$ (nm)[a]	fwhm (nm)[b]	CIE coordinates (*x*, *y*)[c]	maximum luminance (cd/m^2)	turn-on voltage (V)[d]
PFTT	515	57	(0.29, 0.63)	970 (at 893 mA/cm^2)	3.3
PFT2	539	80	(0.40, 0.58)	860 (at 1044 mA/cm^2)	3.0
PFO	425, 446	43	(0.17, 0.09)	100 (at 412 mA/cm^2)	5.5

[a] Maximum of the EL spectrum at a voltage of 6 V. [b] The full width at half-maximum. [c] Determined from the EL spectra (Figure 5). [d] Voltage needed for brightness of 1 cd/m^2.

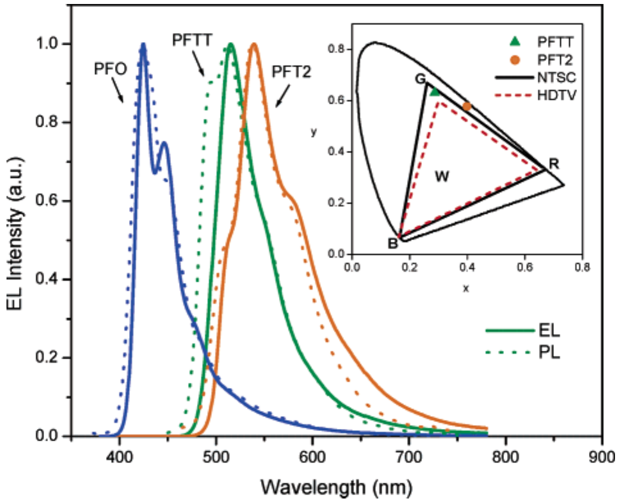


Figure 5. PL (dashed lines) and EL spectra (solid lines) of the polymer films. Inset: CIE coordinates of the emissions from the PFTT (▲) and PFT2 (●) devices. The device structure is ITO/PEDOT/polymer/LiF/Al.

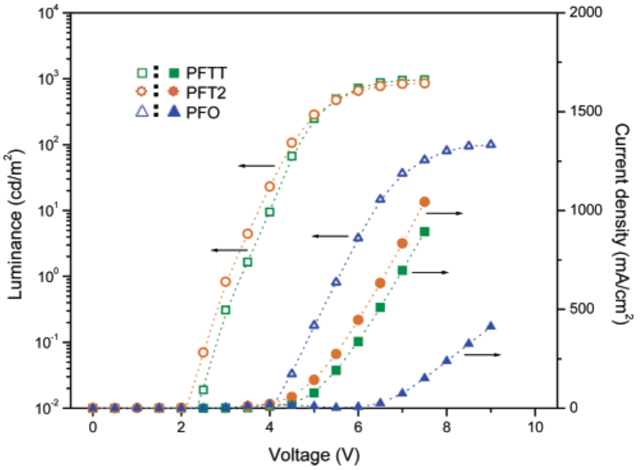


Figure 6. Voltage−luminance (*V*−*L*) and voltage−current density (*V*−*I*) characteristics of PFTT (□, *L*; ■, *I*), PFT2 (○, *L*; ●, *I*), and PFO (△, *L*; ▲, *I*).

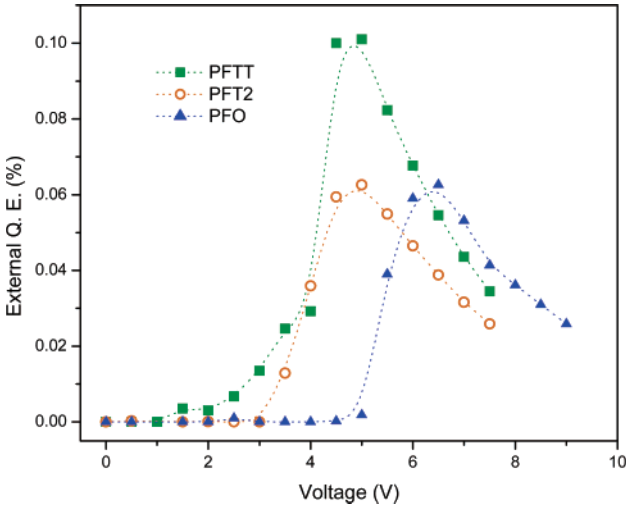


Figure 7. Voltage−external quantum efficiency characteristics of the devices.

maticity coordinates (*x*, *y*) and the full width at half-maximum (fwhm). Interestingly, the color coordinates (0.29, 0.63) of PFTT are closer to those of the standard green (0.26, 0.65) demanded by the National Television System Committee (NTSC) than those of any other previously reported green light-emitting polymers, e.g., (0.39, 0.58) for PF derivatives[9] and (0.33, 0.60) for PPV derivatives.[30] This high spectral quality makes PFTT a good candidate for a green light-emitting polymer. Furthermore, the EL emission spectrum of PFTT has a fwhm of only 57 nm, a resolution that is very important in display applications. In addition, the EL spectrum of PFTT showed stable green emission without any measurable spectral change and/or additional emission peaks with time or driven voltage, contrary to PF homopolymers.[31,32]

The voltage−luminance (*V*−*L*) and voltage−current density (*V*−*I*) characteristics of the devices are shown in Figure 6, and their related performances including their EL spectral data are summarized in Table 4. The devices fabricated with PFTT and PFT2 showed lower turn-on voltages (V_T), around 3.0 V, than that using PFO (5.5 V), as a consequence of the lower energy barriers of the copolymers between the PEDOT work function (−5.0 eV) and the HOMO levels of the polymers (−5.38 eV for PFTT, −5.41 eV for PFT2, and −5.80 eV for PFO[29]). Moreover, as shown in Figure 7, PFTT exhibits an apparently higher EL efficiency, despite its relatively lower PL quantum yield. The EL efficiency of an LED depends not only on the PL efficiency of the active polymer but also on its charge injection balance and its carrier mobility. The maximum current efficiency of PFTT was 0.32 cd/A at 78 mA/cm^2, and under the same conditions PFT2 and PFO had maximum current efficiencies of 0.20 cd/A at 143 mA/cm^2 and 0.06 cd/A at 25 mA/cm^2, respectively. The higher current efficiencies (cd/A) of the two copolymers can be understood because the green light is typically more efficient to the eye than blue or red light.[9] However, in terms of the external quantum efficiency (%) (photons emitted/charge injected), PFTT performed twice as well as PFO, while the performance of PFT2 was about the same as that of PFO (see Figure 7). The incorporation of the thieno[3,2-*b*]thiophene moiety makes PFTT a suitable candidate for use as the emitting layer in polymer LED devices, as it should favor a balanced electron and hole injection. We believe that further improvement of its electroluminescence characteristics could be achieved by incorporating a third comonomer into the polymer backbone in order to enhance and balance the electron and hole transport of the polymer.[33]

The hole-transporting properties of the polymers were investigated using “hole-only” devices consisting of a polymer layer sandwiched between ITO and Al electrodes (ITO/polymer/Al). As shown in Figure 8, the hole

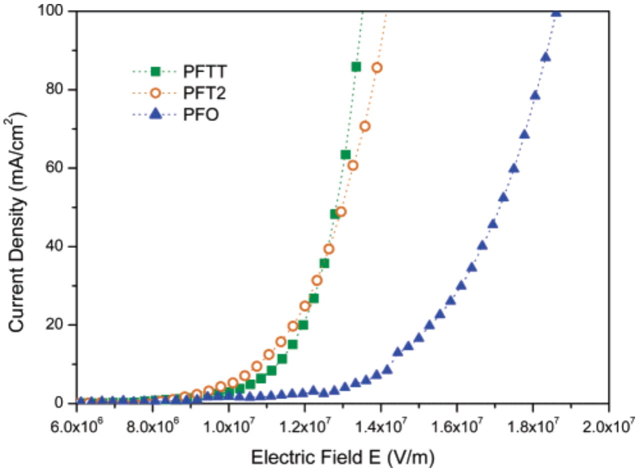


Figure 8. Electric field−current density characteristics in the "hole-only" devices with an ITO/polymer/Al configuration.

current densities of the copolymers are higher than that of PFO at the same electric field. This result is analogous to their HOMO levels as demonstrated by cyclic voltammetry and confirms the improved hole affinity of fluorene- and thiophene-based copolymers.

Conclusions

We synthesized a new conjugated copolymer, PFTT, composed of alternating 9,9′-dioctylfluorene and thieno[3,2-*b*]thiophene, via a palladium-catalyzed Suzuki coupling reaction. An LED device based on PFTT exhibited a pure green emission with a maximum peak at 515 nm, and its high spectral quality was defined by a very small fwhm of 57 nm and CIE coordinates of (0.29, 0.63), which are very close to the standard green required by the NTSC (0.26, 0.65). A device using PFTT exhibited greater efficiency than the devices using PFT2 and PFO. In addition, the study of PFTT using DSC and PLM showed that its liquid-crystalline behavior is comparable to that of poly(9,9′-dialkylfluorene). In future work, we intend to focus on the improvement of PFTT's electroluminescence properties by incorporating a third comonomer into the polymer and to investigate its applications in other organoelectronic devices, such as in polarized EL and thin-film transistors.

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