

# Substituent Effect on the Optoelectronic Properties of Alternating Fluorene-Thiophene Copolymers

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**ABSTRACT:** A novel series of soluble alternating conjugated copolymers, comprised of 9,9-dihexylfluorene and thiophene or substituted thiophene moieties (P1–P5), were synthesized via the palladium-catalyzed Suzuki coupling reaction. Substituents on the thiophene include the electron-donating groups of hexyl and hexyloxymethyl group and the electron-withdrawing groups of hexyl carboxylate and cyano. The steric effects of the bulkier substituents outweigh the electronic effects of the substituents on the observed absorption and photoluminescence properties of the copolymers. Therefore, only the cyano substituted copolymer (P4) exhibits a red shift of the electronic spectra with 1.6 times enhancement in the fluorescence quantum yield as compared with the unsubstituted copolymer (P5). The substituents slightly reduce the values of  $T_g$  and  $T_d$  of P5, but all of the reported copolymers have a  $T_d$  larger than 300 °C.

## Introduction

In the past decade, the design and synthesis of light emitting polymers have received much attention following the discovery of electroluminescence (EL) in conjugated polymers and the development of polymer light emitting diodes (PLEDs) as a display technology.<sup>1,2</sup> A wide range of polymers, poly(*p*-phenylenevinylene) (PPV), polythiophene (PT), poly(*p*-phenylene) (PPP), and polyfluorene (PF),<sup>3</sup> and their derivatives are extensively investigated. Whereas the optoelectronic properties of conjugated copolymers are primarily governed by the chemical structures of the polymer backbone, substituents can fine-tune the band gap (color) and the luminescence quantum efficiency as well as the charge transport behavior of the polymers.<sup>4</sup> For example, introduction of cyano groups into the vinyl group of dialkoxy-substituted PPV (i.e., poly(cyanoterephthalylidene) (CN–PPV)) leads to a high internal quantum efficiency up to 4% in a double-layer device (ITO/PPV/CN–PPV/Al).<sup>4</sup> The improvement was attributed to better electron injection facilitated by the electron-withdrawing cyano groups.

Polyfluorene and its derivatives (PFs) are most widely used in light emitting diodes due to their highly efficient blue emission in both PL and EL.<sup>5–7</sup> However, it is also known that PFs have drawbacks such as excimers formation in the solid state, unsatisfied thermal stability, and high-energy barrier for hole injection, which limit their application in PLEDs.<sup>3,7,8</sup> Structural modification of PFs has proved to be difficult, except for the 9-position. As a result, copolymerization of fluorene with the other arenes becomes an alternative method for tuning the optical, electronic, and thermal properties.<sup>8,9</sup> For example, fluorene- and anthracene-based copolymers are thermally robust and maintain the blue emission even after annealing.<sup>9</sup> In addition, fluorene-triarylamine copolymers possess high charge mobility approaching the hole mobility of the standard glassy films of aryl diamines.<sup>10,11</sup> Copolymers of fluorene and heterocyclic arenes such as thiophene were also reported.<sup>12</sup> The

incorporation of thiophene unit on polymer chain is attractive, because polythiophenes have good stability in both neutral and doped states.<sup>13</sup> One of the most striking features for thiophene-based polymers is the easy and wide electronic tunability by changing the side chains. Therefore, fluorene-thiophene copolymers are potential materials for optoelectronic devices.<sup>14–19</sup>

In this context, we have designed and synthesized four new fluorene-thiophene alternating copolymers P1–P5 to investigate the substituent effects on their thermal, optical and electrochemical properties. The substituents include the electron-donating groups of hexyl and hexyloxymethyl and the electron-withdrawing groups of hexyl carboxylate<sup>20,21</sup> and cyano. The results indicate that the steric influence plays a more important role than the electronic effect in determining the optical and electronic properties of these copolymers.

## Experimental Section

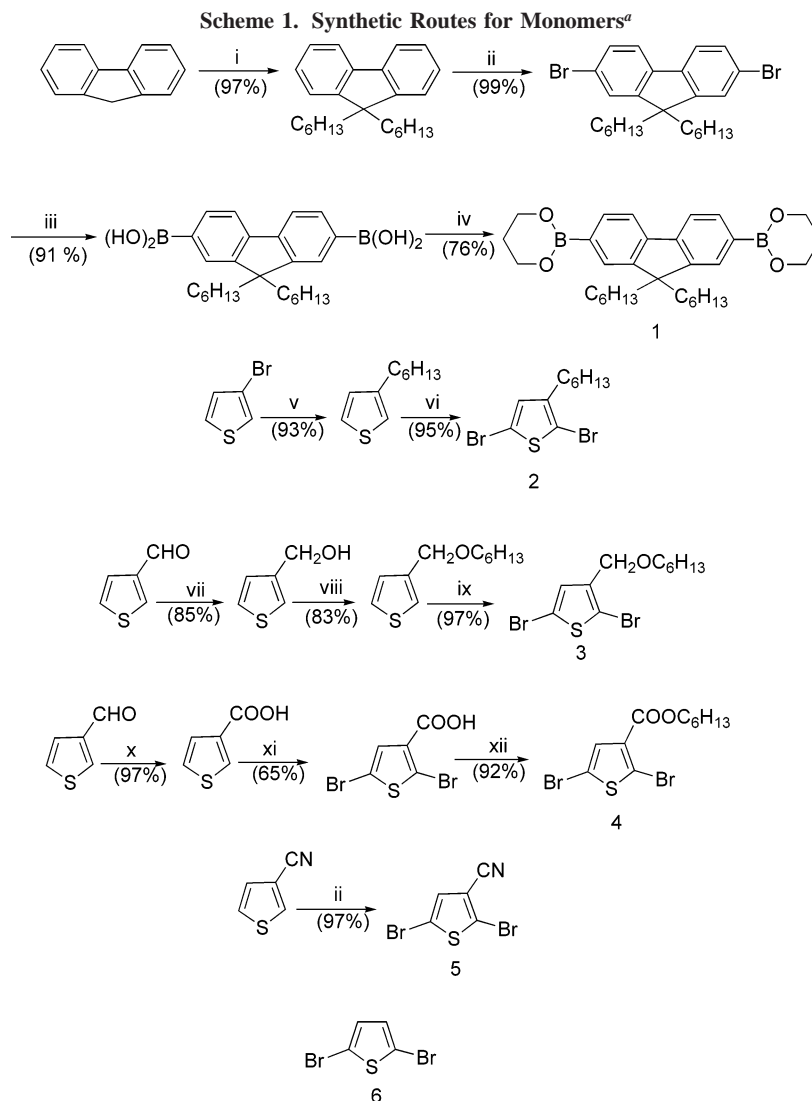
**General.** All of the new compounds were characterized by <sup>1</sup>H NMR, <sup>13</sup>C NMR, and mass spectra. NMR spectra were collected on a Bruker Avance 400 and Varian FT-NMR 400 spectrometers with CDCl<sub>3</sub> and DMSO-d<sub>6</sub> as solvent and tetramethyl silane as internal standard. Melting points (M.P.) were measured on a MEL-TEMP II melting point apparatus. Molecular weights of the polymers were determined by gel permeation chromatography (GPC) on a Waters 1525 Binary HPLC Pump with polystyrene as the standards and tetrahydrofuran (THF) as the solvent. Thermogravimetric analysis (TGA) was conducted on a DuPont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer under a heating rate of 20°C/min and a nitrogen flow rate of 20 mL/min. Differential scanning calorimetry (DSC) was run on a Diamond DSC/Perkin-Elmer at a heating rate of 10°C/min. UV–visible spectra were recorded on a Perkin-Elmer Lambda 35 UV/vis Spectrometer. The photoluminescence (PL) spectra were measured by exciting the polymer samples at 350 nm, and the emission was measured with a Perkin-Elmer LS 55 Luminescence Spectrometer. An integrating sphere made by Labsphere was used to measure the PL efficiencies. Solutions used to detect UV–vis spectra and PL spectra were prepared from the polymer dissolved in THF. UV–vis spectra and PL spectra in the solid state were carried out on films spin-coated onto quartz from chloroform solution. Cyclic voltammetry (CV) was performed on a CH Instruments 611B potentiostat/galvanostat system with a three-electrode cell in a solution of Bu<sub>4</sub>NPF<sub>6</sub> (0.05 M) in dichloromethane (DCM)

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<sup>a</sup> Reagents and Conditions: i. THF, n-BuLi, C<sub>6</sub>H<sub>13</sub>Br, -50 °C, ii. CHCl<sub>3</sub>, FeCl<sub>3</sub>, Br<sub>2</sub>, iii. THF, n-BuLi, B(OBu)<sub>3</sub>, -78 °C, 1 M HCl, iv. Toluene, 1, 3-propanediol, Reflux, v. Mg, Ether, Ni[dppp]Cl<sub>2</sub>, C<sub>6</sub>H<sub>13</sub>Br, vi. THF, NBS, vii. THF, LiAlH<sub>4</sub>, Reflux, viii. DMSO, KOH, C<sub>6</sub>H<sub>13</sub>Br, ix. DMF, NBS, x. AgNO<sub>3</sub>, NaOH soln, xi. Br<sub>2</sub>, CH<sub>3</sub>COOH, xii. SOCl<sub>2</sub>, Reflux, Pyridine, C<sub>6</sub>H<sub>13</sub>OH.

with reversible or partly reversible oxidations and in tetrahydrofuran (THF) with reversible or partly reversible reductions at a scan rate of 300 mV/s.

**Materials.** Fluorene, thiophene, 3-thiophenecarboxaldehyde, 3-cyanothiophene and 2,5-dibromothiophene (6) were obtained from Aldrich Chemical Co. Detailed procedures for the monomer synthesis and spectral data are shown in the Supporting Information.

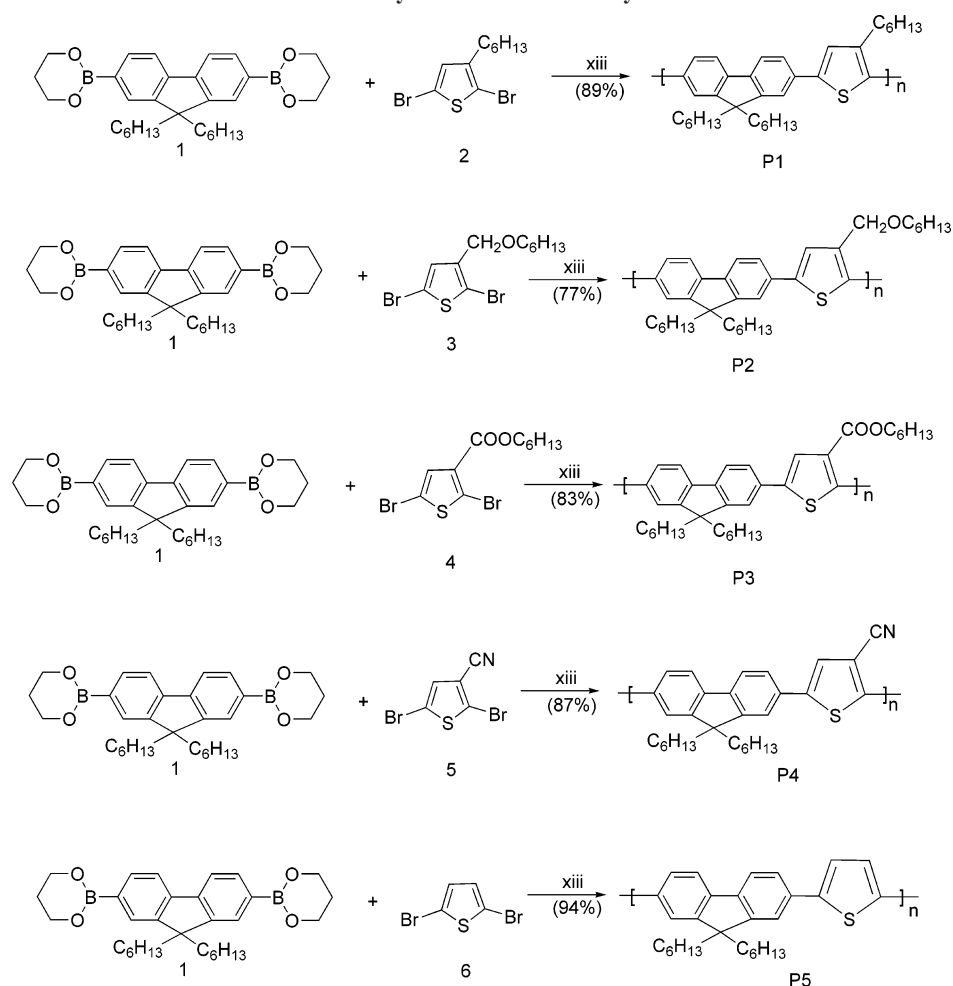
**General Procedure of Polymerization through the Suzuki Coupling Reaction.** To a 1:1 mixture of 9,9-dihexylfluorene-2,7-bis(trimethylene boronate) was added a dibrominated compound of thiophene derivatives and tetrakis(triphenyl-phosphine)palladium(0) [Pd(PPh<sub>3</sub>)<sub>4</sub>] (1 mol %) into a degassed mixture of toluene [(monomer) = 0.1 M] and 2 M potassium carbonate aqueous solution (3:2 in volume). The mixture was vigorously stirred and refluxed at 115–120 °C for 48 h under the protection of nitrogen. After cooling, the mixture was poured into the stirred mixture of methanol and deionized water (10:1). A fibrous solid was obtained by filtration. The solid was redissolved in CHCl<sub>3</sub>, washed with water three times to remove total alkali solution, dried over anhydrous MgSO<sub>4</sub>, and evaporated. The residue was dissolved in a minimum volume of CHCl<sub>3</sub> and poured into 10 times volume of stirred methanol. The mixture was stirred at room temperature for 2 h, filtered, and dried under reduced pressure at room temperature. Yields: 77–94%.

**Poly-{(3-hexyl-2,5-thiophene)-2,7-(9,9-dihexylfluorene)}, P1.** Deep yellow solid (yield 89%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz,

ppm): δ 7.72–7.55 (m, 4H), 7.44 (brd, 2H), 7.29 (brs, 1H), 2.72 (brt, 2H), 2.00 (brt, 4H), 1.70–1.55 (m, 6H), 1.30–1.20 (m, 6H), 1.10–0.89 (m, 12H), 0.86 (brt, 3H), 0.74 (brt, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): δ 151.71, 151.63, 143.15, 140.07 (2XC), 132.19 (2XC), 128.05, 124.37, 123.48 (2XC), 120.06 (2XC), 119.78, 119.65, 119.65, 55.26, 40.41 (2XC), 31.70, 31.63, 31.48, 31.15, 29.73, 29.69, 29.65, 29.36, 29.23, 28.96, 23.76, 22.60, 22.57, 14.11, 14.07, 14.00.

**Poly-{(3-hexoxymethyl-2,5-thiophene)-2,7-(9,9-dihexylfluorene)}, P2.** Yellow solid (yield 77%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.78 (s, 2H), 7.72 (brd, 2H), 7.64–7.56 (brd, 2H), 7.50 (brs, 1H), 4.71 (s, 2H), 4.16 (brt, 2H), 2.01 (brt, 4H), 1.67–1.54 (m, 6H), 1.22–1.03 (m, 18H), 0.81 (brt, 3H), 0.73 (t, J = 7.1 Hz, 6H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): δ 151.87, 151.72, 140.95, 132.13, 132.00, 131.52, 128.93, 128.58, 128.45, 128.04, 126.07, 123.55, 121.43, 120.44, 120.13, 119.77, 69.66, 58.67, 55.37, 40.22 (2XC), 31.46 (2XC), 29.70 (2XC), 29.64 (2XC), 23.84 (2XC), 22.70 (2XC), 22.55 (2XC), 14.02 (3XC).

**Poly-{(hexyl-2,5-thiophene-3-carboxylate)-2,7-(9,9-dihexylfluorene)}, P3.** Bright yellow solid (yield 83%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm): δ 7.78 (s, 2H), 7.70 (brd, 2H), 7.57 (s, 1H), 7.51 (brd, 2H), 4.20 (brt, 2H), 2.02 (brt, 4H), 1.67–1.53 (m, 4H), 1.24–1.05 (m, 18H), 0.85–0.70 (m, 11H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm): δ 171.17, 163.68, 162.27, 152.14, 150.96, 141.29, 132.33, 129.08, 128.81, 128.73, 125.44, 124.76, 124.30, 124.23, 120.44, 119.93, 119.43, 64.92, 55.36, 40.25, 40.10, 31.45, 31.39, 29.67,

Scheme 2. Synthetic Routes for Polymers<sup>a</sup>

<sup>a</sup> Reagents and Conditions :xiii. [(PPh<sub>3</sub>)<sub>4</sub>]Pd(0) (1.0 Mol %), Toluene/2 M K<sub>2</sub>CO<sub>3</sub> sol<sup>n</sup> (3:2), Reflux.

Table 1. Thiophene Chemical Shift of <sup>1</sup>H NMR and <sup>13</sup>C NMR of Fluorene Thiophene Copolymers

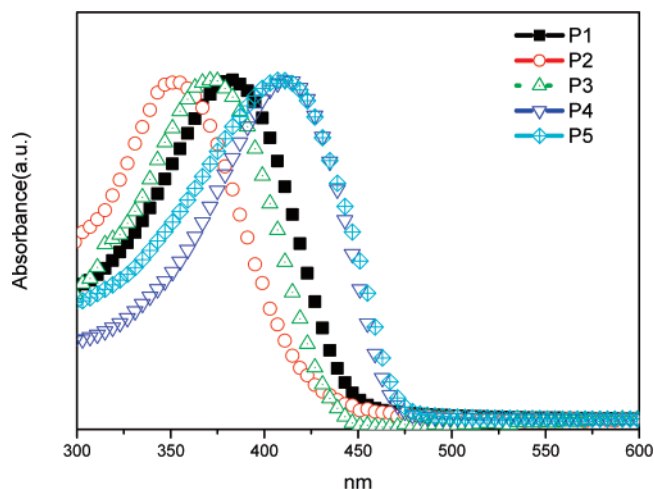
polymer	<sup>1</sup> H NMR ( $\delta_{\text{aromatic}}$ )	<sup>13</sup> C NMR ( $\delta_{\text{aromatic}}$ )
P1, PF-PT(C <sub>6</sub> H <sub>13</sub> )	7.29	119.78
P2, PF-PT(CH <sub>2</sub> OC <sub>6</sub> H <sub>13</sub> )	7.50	121.43
P3, PF-PT(COOC <sub>6</sub> H <sub>13</sub> )	7.57	124.76
P4, PF-PT(CN)	7.63	125.57
P5, PF-PT	7.38	122.88

Table 2. Number-Average (*M<sub>n</sub>*), Weight-Average (*M<sub>w</sub>*) Molecular Weight, Polydispersity Index, and Thermal Properties of Fluorene Thiophene Copolymers

polymer	<i>M<sub>n</sub></i>	<i>M<sub>w</sub></i>	PDI ( <i>M<sub>w</sub>/M<sub>n</sub></i> )	<i>T<sub>g</sub></i> (°C)	<i>T<sub>d</sub></i> (°C)
P1 PF-PT(C <sub>6</sub> H <sub>13</sub> )	4244	6522	1.53	56	303
P2 PF-PT(CH <sub>2</sub> OC <sub>6</sub> H <sub>13</sub> )	4481	6643	1.48	59	300
P3 PF-PT(COOC <sub>6</sub> H <sub>13</sub> )	3482	6119	1.75	75	315
P4 PF-PT(CN)	3760	6221	1.65	not observed	309
P5 PF-PT	2898	4879	1.68	83	326

29.50, 28.54, 28.48, 25.59, 23.76, 22.58, 22.55, 22.48, 21.02, 14.16, 14.02, 13.98.

**Poly-{(3-cyano-2,5-thiophene)-2,7-(9,9-dihexylfluorene)}, P4.** Greenish yellow solid (yield 87%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  7.86–7.72 (m, 4H), 7.63 (brs, 1H), 7.56 (brd, 2H), 2.08 (brt, 4H), 1.10–1.06 (m, 12H), 0.74 (t, *J* = 6.3 Hz, 6H), 0.73–0.67 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  157.78, 152.40, 152.11, 144.30 (2XC), 140.86, 126.70 (2XC), 125.57, 125.07 (2XC), 121.84, 120.89, 120.68, 120.36, 120.00, 106.45, 55.68,



**Figure 1.** UV-visible absorption spectra of P1–P5 in THF solution (ca.  $1.67 \times 10^{-5}$  wt %) at room temperature.

40.24, 40.14, 31.42 (2XC), 29.59 (2XC), 23.79 (2XC), 22.53 (2XC), 13.99 (2XC).

**Poly-{(2,5-thiophene)-2,7-(9,9-dihexylfluorene)}, P5.** Brownish Yellow solid (Yield 94%). <sup>1</sup>H NMR (CDCl<sub>3</sub>, 400 MHz, ppm):  $\delta$  7.67 (brs, 2H), 7.65 (brd, 2H), 7.58 (brd, 2H), 7.38 (s, 2H), 2.03 (brt, 4H), 1.10–1.04 (m, 12H), 0.74 (t, *J* = 5.7 Hz, 6H), 0.73–0.66 (m, 4H). <sup>13</sup>C NMR (CDCl<sub>3</sub>, 100 MHz, ppm):  $\delta$  151.75 (2XC), 144.11 (2XC), 140.25, 133.26, 128.06 (2XC), 124.98 (2XC), 124.62, 123.89 (2XC), 122.88, 120.13, 119.79, 55.32, 40.45 (2XC), 31.92, 31.45, 29.69, 29.35, 23.73 (2XC), 22.68, 22.56, 14.12, 13.99.

Table 3. Optical Properties of Fluorene Thiophene Copolymers

polymer	UV-vis in	PL in	$\Phi_{\text{pl}}$	UV-vis	PL in	$\Phi_{\text{fs}}$	$E_{\text{g}}$ (eV)
	THF soln	THF soln		in films	films $\lambda_{\text{max}}$		
	$\lambda_{\text{max}}$ (nm)	$\lambda_{\text{max}}$ (nm)		$\lambda_{\text{max}}$ (nm)	(nm)		
P1 PF-PT(C <sub>6</sub> H <sub>13</sub> )	383	465	0.40	390	470	0.04	2.79
P2 PF-PT(CH <sub>2</sub> OC <sub>6</sub> H <sub>13</sub> )	353	463	0.14	356	465	0.08	3.01
P3 PF-PT(COOC <sub>6</sub> H <sub>13</sub> )	372	465	0.32	386	468	0.11	2.80
P4 PF-PT(CN)	412	483	0.70	416	498, 510	0.15	2.66
P5 PF-PT	409	468	0.43	412	480, 499	0.10	2.69

## Results and Discussion

**Synthesis and Characterization.** The general synthetic routes toward the monomers and polymers are outlined in Schemes 1 and 2, respectively. The monomer **1**, 9,9-dihexylfluorene-2,7-bis(trimethylene boronate), was synthesized using fluorene as the starting material by following the literature method.<sup>22–24</sup> 3-Hexylthiophene was synthesized from 3-bromothiophene through the Grignard coupling reaction with hexylmagnesium-bromide catalyzed by [1,3-bis(diphenyl-phosphino)propane] dichloronickel(II).<sup>25</sup> Direct bromination of the 3-hexylthiophene with NBS afforded the monomer 2,5-dibromo-3-hexylthiophene<sup>26</sup> (**2**) in 95% yield. Thiophene-3-carboxaldehyde again was reduced by dry THF and LiAlH<sub>4</sub> to form 3-hydroxymethylthiophene in 85% yield. Alkylation of the alcohol was carried out with DMSO, KOH, and 1-bromohexane to afford the 3-hexoxymethylthiophene in 83% yield. Direct bromination of 3-hexoxymethylthiophene with DMF and NBS synthesized the monomer 2,5-dibromo-3-hexoxymethylthiophene<sup>27</sup> (**3**) in 97% yield. Thiophene-3 carboxylic acid<sup>28</sup> was synthesized from thiophene-3 carboxaldehyde by the Tollen's reagent oxidation using AgNO<sub>3</sub> and NaOH in 97% yield. The bromination of thiophene-3-carboxylic acid with acetic acid and bromine formed 2,5-dibromothiophene-3-carboxylic acid in 52% yield and esterified with SOCl<sub>2</sub>, pyridine, and 1-hexanol to afford the monomer hexyl-2,5-dibromothiophene-3-carboxylate<sup>29</sup> (**4**) in 92% yield. Catalytic bromination of 3-cyanothiophene with CHCl<sub>3</sub>, Br<sub>2</sub>, and FeCl<sub>3</sub> afforded the monomer 2,5-dibromo-3-cyanothiophene (**5**) in 98% yield.

The polymerization reaction in Scheme 2 was based on the palladium catalyzed Suzuki coupling reaction (77–94%). The Suzuki coupling methodology is tolerant of a large variety of functional groups on the thiophene ring, insensitive to the presence of water and easy to make high molecular weight polymers.<sup>30</sup> Polymers P1–P5 were synthesized by coupling the fluorene boronate esters with 9,9-dihexylfluorene, 3-hexylthiophene, 3-hexoxymethylthiophene, hexyl-3-thiophenecarboxylate, 3-cyanothiophene, and thiophene dibromides, respectively. The structures of the monomers and polymers were confirmed by <sup>1</sup>H NMR and <sup>13</sup>C NMR spectra, and Table 1 summarizes the chemical shifts of the thiophene group. Compared to that in P5, the chemical shifts are smaller in P1 and P2 but larger in P3 and P4 due to the electron-donating and electron-withdrawing nature of the substituents, respectively. All five polymers readily dissolved in common organic solvents such as chloroform, THF, xylene, and toluene. The color of P1–P5 in the powder form is deep yellow, yellow, bright yellow, greenish yellow, and brownish yellow, respectively. The average molecular weight ( $M_n$ ) of P1–P5 determined by gel permeation chromatography (GPC) using polystyrene as the standards lies in between 2800 and 4500 with the polydispersity index of 1.4–1.8 (Table 2).

**Thermal Stability.** The thermal stability of the copolymers under nitrogen was determined by thermogravimetry analysis (TGA), and their phase transition behavior was evaluated with differential scanning calorimetry (DSC). These data are reported in Table 2. All five polymers showed excellent thermal stability

with decomposition temperature (onset of weight loss, measured by TGA analysis, 20°C/min) at or higher than 300°C. The presence of substituents in the thiophene moiety slightly decreases the  $T_d$  value. Except for P4, the glass transition temperatures ( $T_g$ ) are lower than 100°C (Table 1), which can be attributed to the flexible long alkyl chains in the fluorene moiety. When alkyl chains are also present in the thiophene groups (i.e., P1–P3), the  $T_g$  values become even lower, as shown by comparison to P5. The relatively larger  $T_g$  value observed for P3 vs P1 and P2 can be attributed to the relatively rigid carboxylate group. There is no observation of  $T_g$  for the cyano substituted P4, consistent to the short, rigid, and polar nature of the CN group.

**Optical Properties.** Figure 1 shows the UV-visible absorption spectra of P1–P5 in THF. In principle, either electron donating or electron withdrawing substituents on  $\pi$ -electron ring system results in a lower band gap due to the ease of

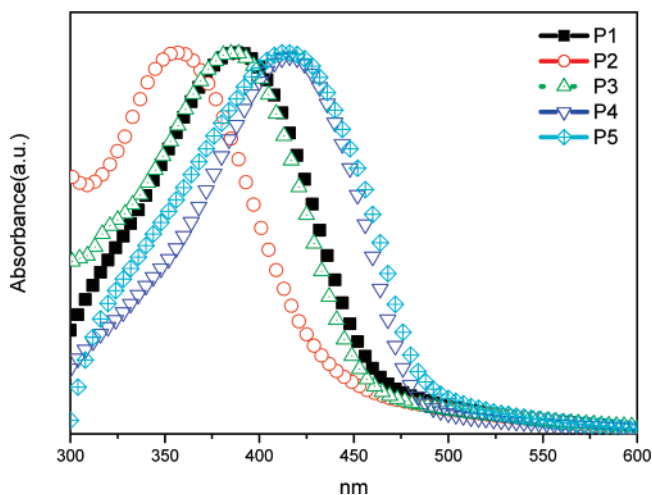


Figure 2. UV-visible absorption spectra of the thin film of P1–P5 coated onto fused quartz plate.

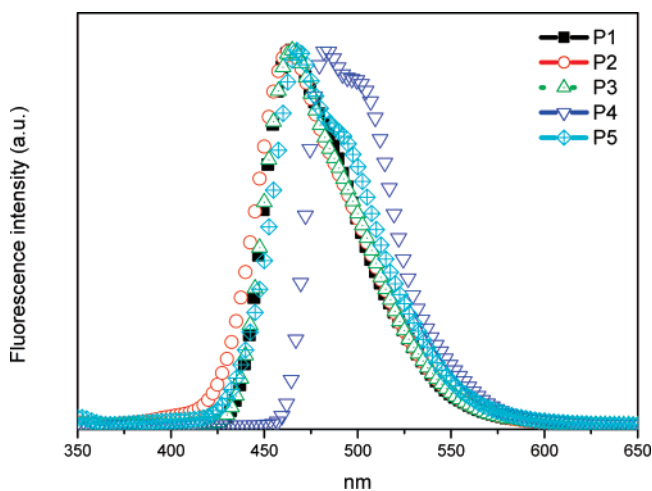
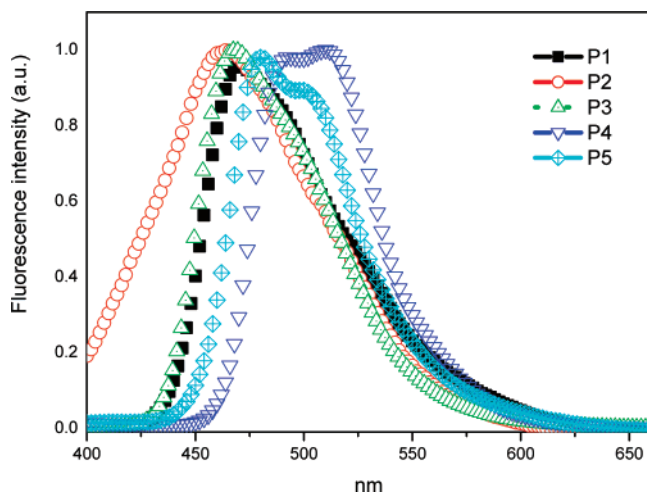
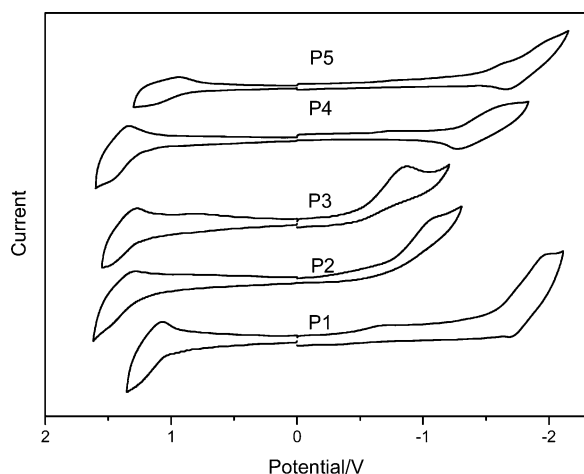


Figure 3. PL spectra of P1–P5 in THF solution (ca.  $1.67 \times 10^{-5}$  wt %) at room temperature.



**Figure 4.** PL spectra of the thin film of P1–P5 coated onto fused quartz plate.



**Figure 5.** Cyclic voltammograms of the electrochemical oxidation and reduction of copolymers P1–P5 in 0.05 M TBAPF<sub>6</sub> in CH<sub>2</sub>Cl<sub>2</sub> and THF at a sweep rate of 300 mV/s.

$\pi$ -electron delocalization. However, the band gap of the polymer is not only dependent on the electronic effect of the side chain but also on other parameters, such as coplanarity and twisting of the bulky substituents of the polymer backbone. As compared to P5, a blue shift was observed for polymers P1–P3 (Table 3). Evidently, the introduction of the substituents on the thiophene induces a twisting of the polymer backbone as a result of the steric repulsion between the substituents on the neighboring thiophene and the fluorene rings. In contrast, the cyano groups in P4 are too small to cause such a steric demand so that the spectrum is red-shifted as compared with that of P5. The absorption spectra undergo small red shifts for P1–P5 on going from the THF solutions to thin solid films (Figure 2), but their relative order of the values of absorption maxima ( $\lambda_{\max}$ ) retain the same as observed in solutions (Table 3). The presence of intermolecular  $\pi$ - $\pi$  interactions or planarization of the polymer backbones in the thin film might account for the spectral shifts.<sup>31,32</sup>

Figures 3 and 4 show the fluorescence spectra of P1–P5 in THF and in thin solid films respectively, recorded upon excitation at 350 nm. In THF, the peak maxima are nearly the same for P1–P3 and P5, whereas it is red-shifted for P4 (Table 3). These results indicate that the polymer backbones in P1–P3 become more planar in the excited-state so that the steric influence of the substituents is reduced. The red shift of fluorescence for P4 vs P5 is as expected due to the elongation

**Table 4. Electrochemical Properties and Energy Levels of Fluorene Thiophene Copolymers**

polymer	$E_{\text{Onset.Oxd}}$ (eV)	$E_{\text{Onset.Red}}$ (eV)	HOMO (eV)	LUMO (eV)	$E_g$ (eV)
P1 PF–PT(C <sub>6</sub> H <sub>13</sub> )	1.05	–1.76	5.44	2.63	2.81
P2 PF–PT(CH <sub>2</sub> OC <sub>6</sub> H <sub>13</sub> )	1.32	–1.20	5.71	3.19	2.52
P3 PF–PT(COOC <sub>6</sub> H <sub>13</sub> )	1.31	–0.99	5.70	3.40	2.30
P4 PF–PT(CN)	1.34	–1.33	5.73	3.06	2.67
P5 PF–PT	0.90	–1.81	5.29	2.58	2.71

of the conjugation length and the increased charge-transfer character induced by the cyano groups. The  $\lambda_{\max}$  of PL in the film is larger than that of in the solution, which is due to a high extent of  $\pi$ - $\pi$  interaction in the condensed matter. The fluorescence quantum yield ( $\Phi_f$ ) of the copolymers in solution was estimated by comparing with the standard of 9,10-diphenylanthracene in THF and in thin films. It is interesting to note that P4 possesses the highest fluorescence quantum yield in both solution and thin films. This might be explained by higher fluorescence rates. In addition, the  $\Phi_f$  values are much lower in the films versus solutions, which can be attributed to interchain dipole–dipole interactions.<sup>33</sup> The absorption onset for P1–P5 in thin films could be used to estimate the band gap ( $E_g$ ) of the polymers. P1–P3 exhibit a higher band gap than that of P5 due to the steric effect of bulky substituents. P4 has a lower band gap than that of P5 because of the electronic withdrawing effect of the cyano group (Table 3). Since the differences between the solution and film spectra of both absorption and emission are rather small for all five polymers, both the intrachain conformational changes and the interchain  $\pi$ - $\pi$  interactions are small for these fluorene-thiophene copolymers.

**Electrochemical Properties.** The electrochemical properties of P1–P5 have been investigated by cyclic voltammetry. The voltammograms and the onset potentials of oxidation ( $E_{\text{onset,ox}}$ ) and reduction ( $E_{\text{onset,red}}$ ) are shown in Figure 5 and Table 4, respectively. All measurements were calibrated using the ferrocene (Fc) value of +0.32 eV as the standard.<sup>34</sup> The HOMO and LUMO and thus the electrochemical band gaps,  $E_g = (E_{\text{LUMO}} - E_{\text{HOMO}})$ ,<sup>35,36</sup> could be estimated (Table 4) according to the empirical relationship proposed by de Leeuw et al. (eq 1)<sup>37</sup>

$$I_p(\text{HOMO}) = -(E_{\text{onset,ox}} + 4.39) \text{ (eV)}, \quad E_a(\text{LUMO}) = -(E_{\text{onset,red}} + 4.39) \text{ (eV)} \quad (1)$$

The resulting band gaps are higher than the optical band gap (see Table 3) for P1, P4, and P5 due to interface barrier for charge injection.<sup>38</sup> However, the measured electrochemical band gaps of polymers P2 and P3 are smaller than that derived from the UV–vis spectrum, because these two polymers reduction potentials could not be measured exactly. It should be noted that incorporation of the electron-rich thiophene groups into the polyfluorene backbone increases the energy level of HOMO but decreases that of LUMO, leading to a smaller band gap in the copolymers versus the PF homopolymer.<sup>39</sup>

## Conclusion

The substituent effect on the optoelectronic properties of alternating fluorene-thiophene copolymers has been investigated on the basis of polymers P1–P5. These polymers were synthesized via the palladium-catalyzed Suzuki coupling reaction. Our results suggest that the steric effects of the bulkier substituents dominate the electronic effects so that absorption spectra are blue-shifted. In contrast, small substituent such as

the cyano group can effectively reduce the band gap and enhance the photoluminescence quantum efficiency. These results should be valuable for the design of new fluorene-thiophene copolymers.

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**Supporting Information Available:** Monomers synthesis and TGA, DSC spectra are available here. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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