Synthesis, Characterization, and Structure−Property Relationship of Novel Fluorene−Thiophene-Based Conjugated Copolymers

Bin Liu,[‡] Wang-Lin Yu,[†] Yee-Hing Lai,*[,‡] and Wei Huang*[,†]

Institute of Materials Research and Engineering (IMRE), National University of Singapore,
3 Research Link, Singapore 117602, Republic of Singapore, and Department of Chemistry,
National University of Singapore, 10 Kent Ridge Crescent, Singapore 119260, Republic of Singapore

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ABSTRACT: A novel series of soluble alternating conjugated copolymers comprised of 9,9-dihexylfluorene and substituted bithiophene or thiophene moieties were synthesized by palladium-catalyzed Suzuki coupling reaction. In the backbone structure of the polymers, the thiophene rings in the bithiophene moieties are β-substituted with decyl chains, and the bithiophene moieties are in two different coupling configurations of head-to-head and tail-to-tail regioregularities. For the thiophene moieties, they are either mono- or disubstituted with decyl chains. By means of the controllable structure modifications, the electronic properties of the polymers were tuned. In addition, the structure−property relationship of the backbone structure was studied. All of the polymers demonstrate efficient blue-to-green light emission, good thermal stability, and relatively high glass transition temperatures ($T_g \sim 78$ °C). For the green-light-emitting polymers comprised of bithiophene moieties, their optical and electrochemical properties are independent of the coupling configurations of the substituted bithiophene moieties, whereas the head-to-head regularity demonstrates higher glass transition temperature and better environmental stability. As for the polymers composed of thiophene moieties, the monosubstitution of a decyl chain on the β-position of thiophene ring produces bluish green emission with high fluorescence quantum efficiency (0.65 in solution). The second attachment of a decyl chain on another β-position of thiophene ring pushes the emission to the blue region with reduced fluorescence quantum efficiency (0.39 in solution). The effort of synthesizing the polymers with the bithiophene moieties through $FeCl_3$ oxidative polymerization is also reported.

Introduction

In the past decade great efforts have been devoted to the design and synthesis of light-emitting polymers (LEPs) for applications in light-emitting diodes (LEDs) in which three primary colors are essential for full color diplays.[1,2] A number of conjugated backbone structures such as poly(*p*-phenylenevinylene) (PPV),[3−6] poly(*p*-phenylene) (PPP),[7−9] polythiophene (PT),[10−12] and polyfluorene (PF)[13−15] have been shown to be of importance in realizing various emissive colors. To provide LEPs with good processability in their final conjugated forms and to achieve different electronic properties, a variety of functional groups have been introduced to the polymers as side chains. Consequently, photoluminescence (PL) and electroluminescence (EL) over the entire visible spectrum have been demonstrated with impressive efficiency and brightness.[16,17] Alternatively, the copolymerization approach, which is widely used in the preparation of traditional polymers, has also been employed in achieving specific electronic and/or physical properties of LEPs. This approach is particularly interesting for the polymers, such as PFs, whose electronic properties are not easy to be tuned by conventional chemical modifications.

Polyfluorene and its derivatives (PFs) are one of the most widely investigated LEPs due to their high efficient blue emission in both PL and EL.[18−20] However, the drawbacks of PFs, such as aggregation and/or excimers formation in the solid state, insufficient stability, and high energy barrier for hole injection, limit their application in polymer LEDs.[13,19,21,22] In the attempt of tuning the physical properties of PFs by molecular structure modification, one has to face the problem that the only available possibility of remote functionalization is at the C-9 position, and any other position of the fluorene unit is very difficult for performing functional chemical reactions. It was found that copolymerization of fluorene with various aryls allows for tunability of electronic properties and enhanced thermal stability.[21,23] In particular, copolymers of fluorene and anthracene are thermally very robust and still maintain their blue emission even after thermal annealing.[23] In addition to light emission, fluorene−triarylamine copolymers demonstrate high charge carrier mobilities that approach hole mobilities of the standard glassy films of aryl diamines.[24,25] Recently, the synthesis of some fluorene−heterocycle hybrid polymers including the copolymers of fluorene and thiophene or bithiophene through Stille coupling reaction was reported.[26] The utilization of thiophene units is attractive because PTs have good stability in both neutral and doped states.[27] In their synthesis, however, thiophene and bithiophene are unsubstituted, and the molecular weights of the polymers were relatively low (M_n < 9000 g mol^{-1}). For thiophene-based polymers, one of the most striking features is the easy and wide electronic tunability by side chain modification.[11] Moreover, different structural regioregularities arising from side chain substitutions in PTs offer additional opportunities for tuning electronic properties by controlling the coupling configurations.[28−30] In this contribution we present the synthesis of alternating copolymers of 9,9-dihexylfluorene with substituted thiophenes and bithiophenes through

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[†] Institute of Materials Research and Engineering (IMRE).
[‡] Department of Chemistry.
* To whom correspondence should be addressed. Tel (65) 874 8592; Fax (65) 872 0785; E-mail wei-huang@imre.org.sg.

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the Suzuki coupling reaction.[31] Different substitutions for thiophene unit and different structural regioregularities for substituted bithiophene unit are attained so that we can study the structure−property relationship of the polymers arising from different substitutions on the thiophene rings.

Experimental Section

General. Reagents and chemicals were purchased from Aldrich Chemical Co. unless otherwise stated. All new compounds were characterized by ^{1}H NMR, ^{13}C NMR, and elemental analysis. NMR spectra were collected on a Bruker ACF 300 spectrometer with chloroform-*d* as solvent and tetramethylsilane as internal standard. FT-IR spectra were recorded on a Bio-Rad FTS 165 spectrometer by dispersing samples in KBr. Melting points (mp) were measured on an Electrothermal IA 9300 digital melting point apparatus. Thermogravimetric analyses (TGA) were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer under a heating rate of 20 °C/min and a nitrogen flow rate of 70 mL/min. Differential scanning calorimetry (DSC) was run on a Du Pont DSC 2910 module in conjunction with the Du Pont Thermal Analyst system at a heating rate of 20 °C/min. Elemental microanalyses were carried out by the Microanalysis Laboratory of the National University of Singapore. Cyclic voltammetry (CV) was performed on an EG&G Parc model 273A potentiostat/galvanostat system with a three-electrode cell in a solution of Bu_4NClO_4 (0.10 M) in acetonitrile at a scan rate of 50 mV/s. GPC analysis was conducted with a Waters 2696 separation module equipped with a Waters 410 differential refractometer HPLC system and Waters Styragel HR 4E columns using polystyrene as standard and THF as eluant.

Synthesis. 2,7-Dibromo-9,9-dihexylfluorene,[15] 3-decylthiophene,[32] 2-bromo-3-decylthiophene,[33] 3,3′-didecyl-2,2′-bithiophene,[33] 4,4′-didecyl-2,2′-bithiophene,[34] and 3,4-didecylthiophene[35] were prepared according to the procedures reported in the literature.

2,7-Bis[2′-(4′-decylthienyl)]-9,9-dihexylfluorene. A solution of *n*-butyllithium (10 mmol) in hexane was added slowly to a solution of diisopropylamine (11 mmol) in 5 mL of dry THF. After the reaction mixture was stirred at 0 °C for 0.5 h, the mixture was cooled to − 78 °C. A solution of 3-decylthiophene (8 mmol) in 10 mL of dry THF was added under a nitrogen atmosphere. The mixture was stirred for another 2 h at −78 °C and transferred into a solution of anhydrous zinc chloride (10 mmol) in 10 mL of dry THF. The mixture was allowed to stir at − 78 °C for 2 h and then slowly warmed to room temperature. The resulting 3-decyl-2-thienylzinc chloride was then slowly added to a solution of 2,7-dibromo-9,9-dihexylfluorene with $Pd(PPh_3)_4$ in 20 mL of dry THF. The resulting mixture was stirred at room temperature overnight and then heated at 50 °C for 5 h. It was cooled and quenched by pouring the reaction mixture into a 1 M HCl solution. The aqueous solution was extracted with ether. The organic layer was collected and washed with saturated $NaHCO_3$ solution and then with brine. After removing the solvent, the product was purified by silica gel column chromatography and eluted by hexane to afford the product as a pale yellow oil (yield: 72%). ^{1}H NMR (300 MHz, $CDCl_3$, ppm): δ 7.64 (d, 2H), 7.54 (m, 4H), 7.22 (s, 2H), 6.88 (s, 2H), 2.64 (t, 4H, $J = 6.92$ Hz), 2.05 (t, 4H, $J = 4.19$ Hz), 1.72 (m, 4H), 1.50−0.75 (m, 56 H). Anal. Calcd for $C_{53}H_{78}S_2$: C, 81.75; H, 10.02; S, 8.23. Found: C, 81.74; H, 9.69; S, 8.19.

9,9-Dihexylfluorene-2,7-bis(trimethylene boronate), 1.[36] A solution of 2,7-dibromo-9,9-dihexylfluorene (16.27 g, 33 mmol) in dry THF was added slowly to a stirred mixture of magnesium turnings (1.90 g, 80 mmol) in dry THF containing a catalytic amount of iodine under argon to form the Grignard reagent. The Grignard reagent solution was slowly dropped into a stirred solution of trimethyl borate (38 mL, 330 mmol) in dry THF at −78 °C over a period of 2 h and then slowly warmed to room temperature. The reaction mixture was stirred at room temperature for 2 days and then was poured into crushed ice containing sulfuric acid (5%) while stirring. The mixture was extracted with ether, and the combined extracts were evaporated to give a white solid. Recrystallization of the crude acid from hexane−acetone (1:2) afforded pure 9,9-dihexylfluorene-2,7-diboronic acid (6.31 g, 44%) as white crystals. The diboronic acid (6.31 g) was then refluxed with 1,3-propandiol (2.04 g, 33 mmol) in toluene for 10 h. After working up, the crude product was recrystallized from hexane to afford (5.50 g, 73%) **1** as white crystals. Mp: 123−4 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 7.77 (d, 2H, $J = 7.55$ Hz), 7.72 (s, 2H), 7.69 (d, 2H, $J = 7.48$ Hz), 4.25−4.16 (t, 8H, $J = 5.36$ Hz), 2.07 (m, 4H, $J = 5.33$ Hz), 1.98 (m, 4H, $J = 4.09$ Hz), 1.20−0.90 (m, 12H), 0.76 (t, 6H, $J = 6.83$ Hz), 0.56 (m, 4H). ^{13}C NMR ($CDCl_3$, 75 MHz, ppm): δ 151.17, 140.03, 139.18, 132.44, 128.10, 123.53, 119.83, 109.94, 55.09, 40.28, 31.53, 31.43, 30.82, 29.62, 29.04, 28.71, 23.76, 22.48, 13.94, 13.88. Anal. Calcd for $C_{31}H_{44}O_4B_2$: C, 74.13; H, 8.83. Found: C, 74.02; H, 8.35.

2,5-Dibromo-3-decylthiophene, 2.[33] A solution of *N*-bromosuccinimide (NBS) (4.44 g, 25 mmol) in 20 mL of DMF was slowly added dropwise to a solution of 3-decylthiophene (2.24 g, 10 mmol) in 20 mL of DMF which is exclusive to light, and the mixture was stirred overnight. The mixture was poured onto ice and extracted several times with ether. The combined organic solution was washed with water and then dried over magnesium sulfate. Evaporation of the solvent and purification by column flushing on silica gel with hexane as the eluant afford **2** as a colorless oil (3.25 g, 85%). ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.77 (s, 1H), 2.53−2.48 (t, 2H, $J = 7.62$ Hz), 1.52−1.25 (m, 16H), 0.88 (t, 3H, $J = 6.44$ Hz). Anal. Calcd for $C_{24}H_{43}BrS$: C, 44.00; H, 5.80. Found: C, 44.62; H, 5.88.

2,5-Dibromo-3,4-didecylthiophene, 3.[33] 3,4-Didecylthiophene (3.62 g, 10 mmol) and NBS (4.44 g, 25 mmol) in 40 mL of DMF were allowed to react as described for the synthesis of **2**. After the usual workup, the dibrominated compound was purified by chromatography on silica gel (eluant: hexane), to afford **3** (4.15 g, 80%) as a colorless oil. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 2.52−2.47 (t, 4H, $J = 7.83$ Hz), 1.45−1.40 (m, 4H), 1.33−1.20 (m, 28H), 0.89−0.85 (t, 6H, $J = 6.42$ Hz). Anal. Calcd for $C_{24}H_{42}Br_2S$: C, 55.17; H, 8.10. Found: C, 55.07; H, 8.07.

5,5′-Dibromo-4,4′-didecyl-2,2′-bithiophene, 4.[33] 4,4′-Didecyl-2,2′-bithiophene (4.47 g, 10 mmol) and NBS (3.73 g, 21 mmol) in 50 mL of DMF were allowed to react under the conditions given for the synthesis of **2**. After the usual workup, the dibrominated compound was purified by chromatography on silica gel (eluant: hexane), to afford **4** (3.32, 55%) as a light yellow solid. Mp: 48−9 °C. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.77 (s, 2H), 2.54−2.49 (t, 4H, $J = 7.64$ Hz), 1.58−1.56 (m, 4H), 1.36−1.22 (m, 28H), 0.90−0.86 (t, 6H, $J = 6.58$ Hz). Anal. Calcd for $C_{28}H_{44}Br_2S_2$: C, 55.63; H, 7.34. Found: C, 55.54; H, 7.83.

5,5′-Dibromo-3,3′-didecyl-2,2′-bithiophene, 5.[33] 3,3′-Didecyl-2,2′-bithiophene (4.47 g, 10 mmol) and NBS (3.73 g, 21 mmol) in 50 mL of DMF were allowed to react under the conditions given for the synthesis of **2**. After the usual workup, the dibrominated compound was purified by chromatography on silica gel (eluant: hexane), to afford **5** (2.42 g, 40%) as a light yellow oil. ^{1}H NMR ($CDCl_3$, 300 MHz, ppm): δ 6.91 (s, 2H), 2.45−2.40 (t, 4H, $J = 7.64$ Hz), 1.53−1.47 (m, 4H), 1.32−1.22 (m, 28H), 0.90−0.86 (t, 6H, $J = 6.63$ Hz). Anal. Calcd for $C_{28}H_{44}Br_2S_2$: C, 55.63; H, 7.34. Found: C, 55.60; H, 7.71.

General Procedure of Polymerization through the Suzuki Reaction. To a 1:1 mixture of 9,9-dihexylfluorene-2,7-bis(trimethylene boronate), a dibrominated compound of thiophene derivatives, and tetrakis(triphenylphosphine)-palladium [$Pd(PPh_3)_4$] (1.0 mol %) was added a degassed mixture of toluene ([monomer] = 0.25 M) and 2 M potassium carbonate aqueous solution (3:2 in volume). The mixture was vigorously stirred at 85−90 °C for 48 h under the protection of nitrogen. After the mixture was cooled to room temperature, it was poured into the stirred mixture of methanol and deionized water (10:1). A fibrous solid was obtained by filtration. The solid was washed with methanol, water, and then methanol. The polymer was further purified by washing with acetone in a Soxhlet apparatus for 24 h to remove oligomers and catalyst residues and was dried under reduced pressure at room temperature. Yields: ∼ 75−85%.

Poly[2,7-(9,9-dihexylfluorene)-*co*-alt-5,5′-(4,4′-didecyl-2,2′-bithiophene)], P1. Brownish yellow solid (yield: 75%). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ 7.76−7.73 (br, 2H), 7.44 (br, 4H), 7.12 (s, 2H), 2.70 (br, 4H), 2.03 (br, 4H), 1.68 (br, 4H), 1.35−0.77 (m, 56H). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ 151.16, 139.88, 139.40, 137.25, 135.25, 133.12, 127.97, 126.03, 123.38, 119.76, 63.44, 55.10, 40.56, 31.82, 31.49, 30.94, 29.71, 29.42, 29.28, 29.08, 23.82, 22.61, 22.55, 14.04, 13.94. FT-IR (KBr, cm^{-1}): 3055, 2953, 2923, 2852, 1890, 1655, 1606, 1541, 1465, 1376, 1260, 1182, 1100, 889, 820, 748, 722. Anal. Calcd for $C_{53}H_{76}S_2$: C, 81.68; H, 10.09; S, 8.23. Found: C, 80.23; H, 9.74; S, 8.82.

Poly[2,7-(9,9-dihexylfluorene)-*co*-alt-5,5′-(3,3′-didecyl-2,2′-bithiophene)], P2. Light yellow solid (yield: 82%). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ 7.71−7.58 (m, 6H), 7.30 (s, 2H), 2.63 (br, 4H), 2.06 (br, 4H), 1.69 (br, 4H), 1.35−0.76 (m, 56H). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ 151.63, 144.35, 143.46, 140.23, 133.03, 127.99, 124.55, 124.42, 119.99, 119.52, 55.25, 40.42, 31.84, 31.42, 30.75, 29.50, 29.44, 29.28, 23.66, 22.61, 14.03, 11.94. FT-IR (KBr, cm^{-1}): 3058, 2953, 2926, 2853, 1890, 1655, 1608, 1578, 1539, 1465, 1377, 1260, 1225, 1195, 1135, 881, 836, 816, 754, 723. Anal. Calcd for $C_{53}H_{76}S_2$: C, 81.68; H, 10.09; S, 8.23. Found: C, 80.74; H, 10.24; S, 8.51.

Poly[2,7-(9,9-dihexylfluorene)-*co*-alt-2,5-(decylthiophene)], P3. Bright yellow solid (yield: 85%). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ 7.71−7.57 (m, 6H), 7.31 (s, 1H), 2.67 (br, 2 H), 2.05 (br, 4H), 1.68 (br, 2H), 1.32−0.73 (m, 39H). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ 151.16, 139.88, 139.41, 137.25, 135.25, 133.12, 127.97, 126.03, 123.39, 119.76, 63.44, 55.10, 40.85, 31.82, 31.49, 30.94,29.71, 29.42, 29.28, 29.08, 23.82, 22.61, 22.55, 14.04, 13.94. FT-IR (KBr, cm^{-1}): 3053, 3020, 2953, 2923, 2851, 1897, 1607, 1577, 1544, 1462, 1376, 1258, 1134, 1102, 881, 818, 748, 722. Anal. Calcd for $C_{39}H_{54}S$: C, 84.11; H, 10.13; S, 5.76. Found: C, 83.68; H, 10.02; S, 5.96.

Poly[2,7-(9,9-dihexylfluorene)-*co*-alt-2,5-(3,4-didecylthiophene)], P4. Greenish yellow solid (yield: 79%). ^{1}H NMR (CDCl$_3$, 300 MHz, ppm): δ 7.77−7.75 (br, 2H), 7.50 (br, 4H), 2.71 (br, 4H), 2.04 (br, 4H), 1.57 (br, 4H), 1.32−0.76 (m, 56H). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ 150.99, 139.88, 138.86, 137.72, 133.92, 128.15, 123.52, 119.63, 55.10, 31.84, 31.55, 31.11, 29.95, 29.78, 29.56, 29.38, 29.29, 27.92, 23.82, 22.59, 22.56, 14.03, 13.93. FT-IR (KBr, cm^{-1}): 2955, 2925, 2854, 2730, 2624, 1903, 1656, 1607, 1578, 1543, 1463, 1377, 1273, 1250, 1134, 1082, 1005, 891, 823, 757, 722. Anal. Calcd for $C_{49}H_{74}S$: C, 84.41; H, 10.99; S, 4.60. Found: C, 83.76; H, 10.70; S, 4.80.

Poly[2,7-(9,9-dihexylfluorene)-*co*-alt-5,5′-(3,3′-didecyl-2,2′-bithiophene)], P2′. Ferric chloride (4 mmol) in 70 mL of dry chloroform was added slowly to a stirred solution of 2,7-bis[2′-(4′-decylthienyl)]-9,9-dihexylfluorene (1 mmol) in 20 mL of dry chloroform at 0 °C. The mixture was stirred in an ice−water bath for 24 h under a slow flow of nitrogen. The mixture was poured into 300 mL of methanol, and the crude polymer was collected by filtration and washed with excessive portions of methanol and water and then methanol. The crude polymer was dedoped by stirring in concentrated ammonia ($NH_3{\cdot}H_2O$) for 12 h. The resulting yellow material was isolated by filtration and washed thoroughly with methanol and acetone. The polymer was dried in vacuo overnight (yield: 65%). ^{1}H NMR (300 MHz, CDCl$_3$, ppm): δ 7.69−7.57 (br, 6H), 7.29 (br, 2H), 2.61 (br, 4H), 2.03 (br, 4H), 1.66 (br, 4H), 1.30−0.80 (br, 56H). ^{13}C NMR (CDCl$_3$, 75 MHz, ppm): δ 151.62, 144.35, 143.41, 140.21, 133.03, 127.98, 124.36, 124.18, 119.97, 119.53, 55.21, 40.34, 31.68, 31.58, 30.68, 29.90, 29.30, 29.10, 23.66, 22.49, 13.95, 11.80. FT-IR (KBr, cm^{-1}): 3055, 2952, 2924, 2852, 1890, 1655, 1607, 1578, 1539, 1462, 1375, 1257, 1222, 1194, 1133, 880, 835, 814, 751, 723. Anal. Calcd for $C_{53}H_{76}S_2$: C, 81.68; H, 10.09; S, 8.23. Found: C, 81.65; H, 9.71; S, 8.49.

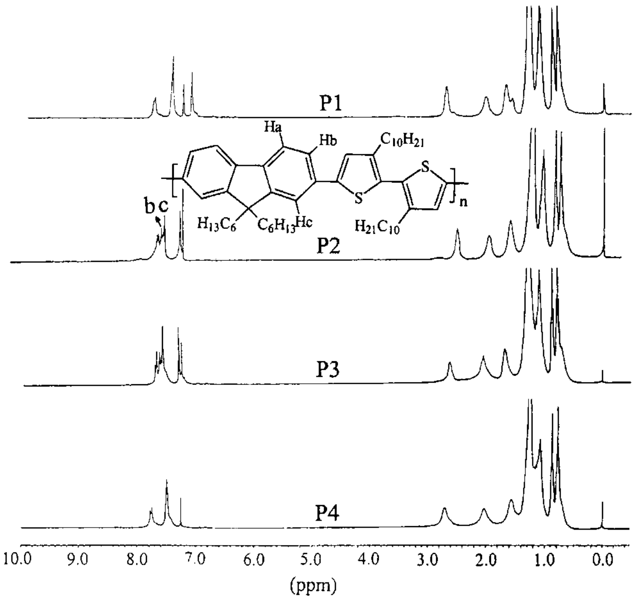
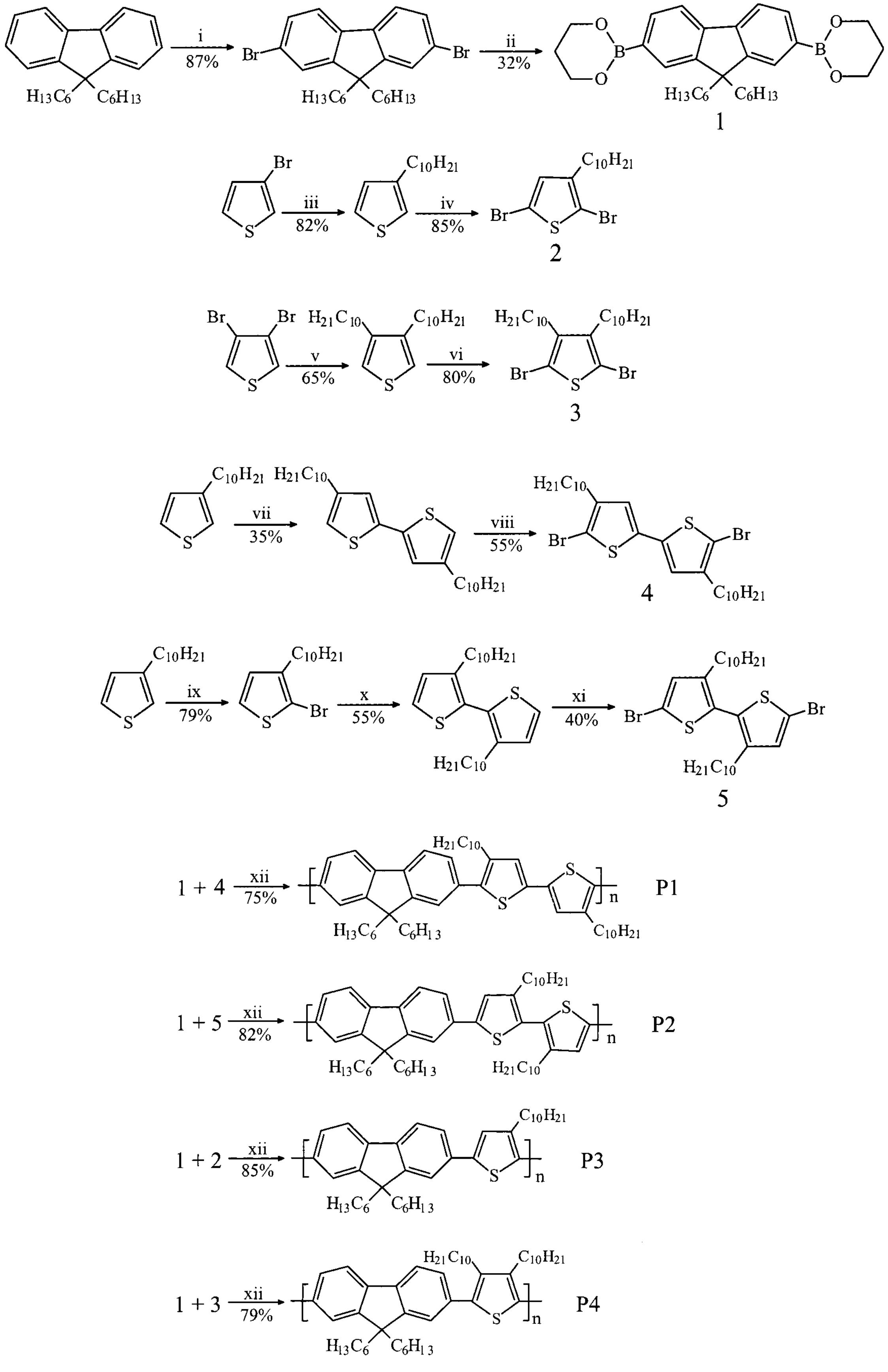


Figure 1. ^{1}H NMR spectra of **P1**−**P4**.

Results and Discussion

Synthesis and Characterization. The general synthetic routes toward the monomers and polymers are outlined in Scheme 1. The monomer **1**, 9,9-dihexylfluorene-2,7-bis(trimethylene boronate), was synthesized using 2,7-dibromofluorene as the starting material following the literature method.[36] 3-Substituted and 3,4-disubstituted thiophenes were synthesized from 3-bromothiophene and 3,4-dibromothiophene, respectively, through the Grignard coupling reaction with decylmagnesium bromide catalyzed by [1,3-bis(diphenylphosphino)propane]dichloronickel(II). 4,4′-Didecyl-2,2′-bithiophene was synthesized from the corresponding 3-decylthiophene by lithiation with butyllithium and followed by oxidative coupling with copper chloride.[34] 3,3′-Didecyl-2,2′-bithiophene was synthesized from 2-bromo-3-decylthiophene through the Grignard coupling reaction with its magnesium bromide. Direct bromination of the thiophene derivatives with NBS afforded the monomers **2**−**5** in 40−85% yield, after purification. The polymerization depicted in Scheme 1 is based on the Suzuki coupling reaction, which was carried out in a mixture of toluene and aqueous potassium carbonate solution (2 M) containing 1 mol % Pd(PPh$_3$)$_4$ under vigorous stirring at 85−90 °C for 2 days. Poly[2,7-(9,9-dihexylfluorene)-*co*-alt-5,5′-(4,4′-didecyl-2,2′-bithiophene)] (**P1**), poly[2,7-(9,9-dihexylfluorene)-*co*-alt-5,5′-(3,3′-didecyl-2,2′-bithiophene)] (**P2**), poly[2,7-(9,9-dihexylfluorene)-*co*-alt-2,5-(decylthiophene)] (**P3**), and poly-[2,7-(9,9-dihexylfluorene)-*co*-alt-2,5-(3,4-didecylthiophene)] (**P4**) were prepared in good yields. After purification and drying, polymers **P1**, **P2**, **P3**, and **P4** were obtained as brown, light yellow, bright yellow, and greenish yellow powders, respectively. All these polymers readily dissolve in common organic solvents, such as chloroform, THF, toluene, and xylene. The number-average molecular weights (M_n) of the polymers were determined by gel permeation chromatography (GPC) using the polystyrene as the standards to be ∼15 000 to ∼23 000 with the polydispersity index of 1.4−1.9 (see Table 1). The chemical structures of the polymers were verified by ^{1}H NMR, ^{13}C NMR, FT-IR, and elemental analyses.

Scheme 1. Synthetic Routes for the Monomers and Polymers. Reagents and Conditions: (i) Br_2, $FeCl_3$, $CHCl_3$, 0 °C; (ii) Mg, THF; $B(OCH_3)_3$, −78 °C; 1,3-Propandiol, Toluene, Reflux; (iii) $C_{10}H_{21}Br$, Mg, Ether, $Ni(dppp)Cl_2$; (iv) 2NBS, DMF; (v) Mg, Ether, $Ni(dppp)Cl_2$; (vi) 2NBS, DMF; (vii) TMEDA, BuLi, $CuCl_2$; (viii) 2NBS, DMF; (ix) NBS, DMF; (x) $C_{10}H_{21}Br$, Mg, Ether, $Ni(dppp)Cl_2$; (xi) 2NBS, DMF; (xii) $[(PPh_3)_4]Pd(0)$ (1.0 Mol %), Toluene/2 M K_2CO_3 (3:2), Reflux



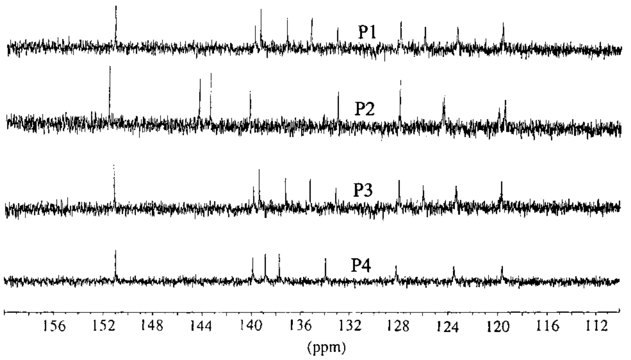


Figure 2. ^{13}C NMR spectra of **P1**−**P4**.

Table 1. Number-Average (M_n) and Weight-Average (M_w) Molecular Weight of Polymers

polymer	M_n	M_w	PD (M_w/M_n)
P1	15 200	29 100	1.9
P2	22 600	39 400	1.7
P2′	26 500	50 200	1.9
P3	18 700	26 600	1.4
P4	18 600	29 300	1.6

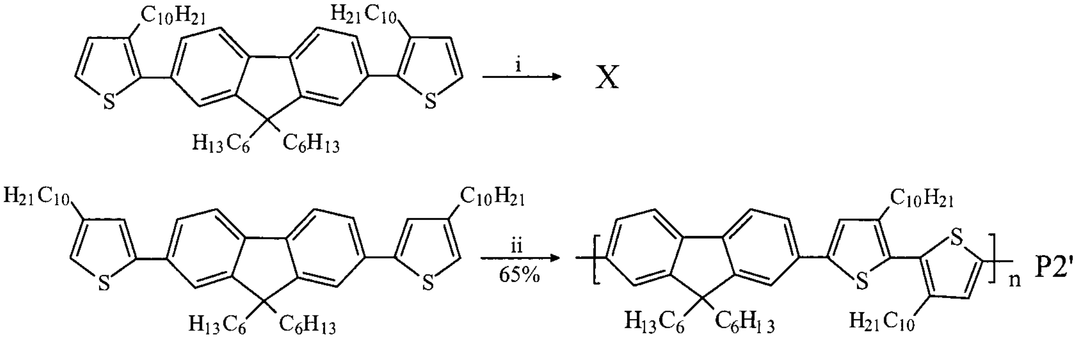
Figure 1 shows the ^{1}H NMR spectra of **P1**−**P4** and the assignment of protons in **P2**. **P1** and **P2** have the same backbone structure, but the adjacent 3-substituted thiophene rings are in different connection patterns in the two polymers. In **P1**, the two adjacent 3-substituted thiophene rings are in a tail-to-tail (TT) configuration, whereas they are in a head-to-head (HH) configuration in **P2**. It has been well demonstrated in poly(3-alkylthiophenes) that the chemical shifts of the β-proton of the thiophene ring and the protons of the methylene adjacent to thiophene ring are different corresponding to different coupling configurations.[37] The similar NMR spectral difference resulted from the different coupling configurations is also reflected in **P1** and **P2**. The resonance signal of thiophene β-H in **P1** appears at 7.12 ppm. It shifts to 7.30 ppm in **P2**. Correspondingly, the resonance signal of the methylene adjacent to the thiophene ring shifts from 2.70 ppm in **P1** to 2.63 ppm in **P2**. It is noted that the chemical shifts of the Hb and Hc on the fluorene ring are also affected by the connection patterns of the bithiophene moiety. In **P1**, the resonance signals of both of the two protons appear around 7.44 ppm. The signals of Hb and Hc in **P2** appear at 7.63 and 7.58 ppm, respectively. The spectra of **P3** and **P2** are very similar although **P3** has only one 3-substituted thiophene ring in its repeating unit. As for **P4**, the characteristic peak of the β-proton of thiophene in the aromatic region disappears due to the disubstitution on the thiophene ring.

The ^{13}C NMR spectra of the four polymers are shown in Figure 2. There are 10 well-resolved signals in the aromatic region for **P1** and **P2,** and eight peaks in the aromatic region for **P4**, which correspond to the 10 aromatic carbons in **P1** and **P2**, and eight aromatic carbons in **P4**. The ^{1}H NMR and ^{13}C NMR spectra certainly demonstrate that the polymers have well-defined structures. For **P3**, due to the monosubstitution at the β-position of the thiophene ring, there should be two different coupling configurations between the thiophene ring and the fluorene ring, which should result in two sets of carbon signals corresponding to the carbons of the fluorene ring. However, only 10 clear and well-resolved peaks were observed in the aromatic region of the ^{13}C NMR spectrum of **P3**. It seems that the difference of the coupling configurations between the β-substituted thiophene and the fluorene unit does not noticeably influence the chemical environments of the fluorene carbons.

Our efforts were also devoted to the synthesis of **P1** and **P2** through $FeCl_3$ oxidative polymerization, a method that has been widely used in the polymerization of 3-substituted thiophenes and variously substituted bithiophenes, from the corresponding monomers of (2,7-bis(2-(3′-decylthienyl)-9,9-dihexylfluorene (for **P1**) and 2,7-bis(2-(4′-decylthienyl)-9,9-dihexylfluorene (for **P2**), as depicted in Scheme 2. **P2** was obtained as expected as a yellow powder after being dedoped and purified (the polymer is denoted as **P2′**). The molecular weights of **P2′** are a little higher than those of **P2** (see Table 1). **P2′** exhibits exactly the same NMR spectra (^{1}H and ^{13}C) as **P2**, which demonstrates that the well structure-defined alternating copolymers of fluorene and bithiophene having the structural feature of **P2** may be prepared through the facile $FeCl_3$ oxidation approach. However, synthesizing **P1** with the same $FeCl_3$ oxidation approach failed. Instead of a polymer powder, only a small amount of methanol-insoluble oil was obtained after the polymerization. This observation is in accordance with the literature reports about the $FeCl_3$ oxidative polymerization of substituted bithiophenes, in which HH bithiophenes is more difficult to polymerize than the TT ones.[28,38]

The thermal stability of the polymers in nitrogen was evaluated by thermogravimetric analysis (TGA). The thermograms are depicted in Figure 3. The polymers showed weight loss starting at 394 °C for **P1**, 390 °C for **P2**, 381 °C for **P3**, and 374 °C for **P4,** indicative of good thermal stability. Thermally induced phase transition behavior of the polymers was investigated with differential scanning calorimetry (DSC) in a nitrogen atmosphere. The DSC traces are shown in Figure 4. **P1**

Scheme 2. Synthetic Routes to P1′ and P2′ Using $FeCl_3$ as Oxidizing Reagent. Reagents and Conditions: (i) $FeCl_3$, $CHCl_3$, 40 °C, 2 days; (ii) $FeCl_3$, $CHCl_3$, 0 °C, 24 h



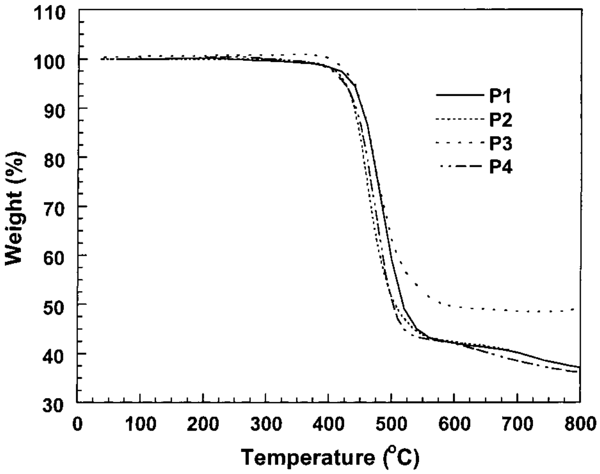


Figure 3. Thermograms of **P1**−**P4** measured in a nitrogen atmosphere.

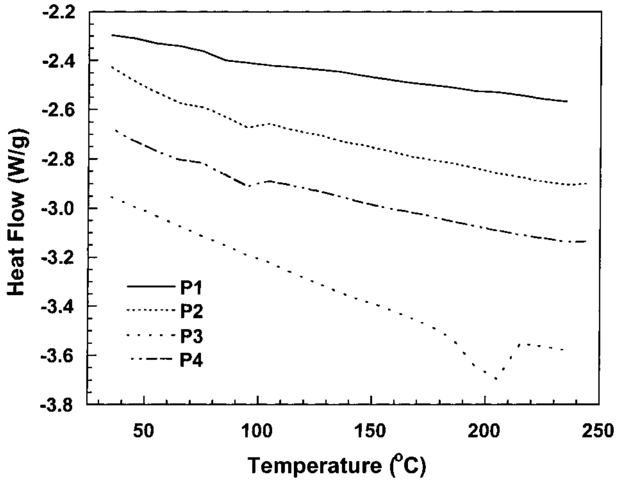


Figure 4. DSC traces of **P1**−**P4** measured in a nitrogen atmosphere.

exhibits a clear glass transition starting at ~63 °C. In comparison with **P1**, the glass transition temperature, T_g, of **P2** increased by ~14 °C to 77 °C. However, at this stage it is not clear whether the increase of T_g is due to the structural difference between **P1** and **P2** or is caused by the difference of their molecular weights because the molecular weight of **P2** is about 50% higher than that of **P1**. When the bithiophene moieties are replaced by β-substituted thiophenes (**P3)**, a phase transition was observed at 203 °C, which may be attributed to the melt of the polymer. When the thiophene moiety is disubstituted (**P4**), a clear glass transition was determined at about 78 °C. The determined glass transition temperatures of **P2** and **P4** are comparable with those of 9,9-dialkyl polyfluorenes.[39] The relatively high glass transition temperatures are essential for many applications such as in light-emitting diodes as emissive materials.[40]

Optical Properties. The spectroscopic properties of polymers **P1**−**P4** were measured both in solution ($CHCl_3$) and as thin films. The UV−vis absorption and PL spectra of **P1**−**P4** in chloroform (ca. 1×10^{-5} M) are shown in Figure 5. **P1** exhibits the absorption maximum at 401 nm. Its PL spectrum peaks at 482 nm with a shoulder around 515 nm. Interestingly, **P2** gives almost identical absorption and PL spectra with **P1**. In comparison with **P1**, the coplanarity between the two adjacent thiophene rings in **P2** is poorer because of the steric hindrance of the decyl chains, which should result in a reduction in conjugation of the backbone. On the other hand, however, the coplanarity between the fluorene ring and the thiophene ring is better in **P2** than that in **P1**. Under the effect of the two opposite factors, the net result is that **P1** and **P2** have similar effective conjugation. Another interesting phenomenon we noted is that the color of the **P1** solution changed from yellow to deep brown upon storing the solution overnight in ambient conditions. With the color change, the emissive intensity of the solution also decreased dramatically. When the solution was further kept under this condition for several days, its UV−vis absorption spectrum showed a slight blue shift. On the contrary, the solution of **P2** maintained its color and spectra (both in shape and in intensity) even after being stored under the same conditions for over 1 month. It is evident that **P2** has better stability than **P1** in ambient conditions. This implies that the difference of coupling configuration between thiophene rings in the alternating copolymers of fluorene and bithiophene may influence the stability of the resulting polymers, and the head-to-head coupling configuration corresponds to better stability, although the origin of this phenomenon is not understood as yet.

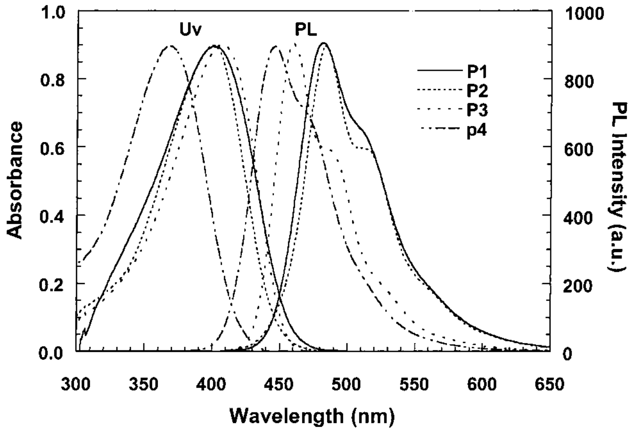


Figure 5. UV−vis absorption spectra and photoluminescence spectra of **P1**−**P4** measured from the solutions (~1×10^{-5} M) in chloroform at room temperature.

The UV−vis absorption of **P3** in chloroform bears a resemblance to **P2** and **P1** with the maximum at 403 nm. The results indicate that the extension of β-substituted thiophene to β-substituted bithiophenes in the repeat unit of the alternative copolymers does not increase the effective conjugated length of the resulting polymers. However, the PL spectrum of **P3** blue-shifted by about 20 nm compared to those of **P1** and **P2**. The PL difference may be attributed to the different radiative decay processes of excitons in the polymers. In comparison with **P3**, **P4** shows an obvious spectral blue shift both in absorption ($\Delta\lambda = 36$ nm) and in emission ($\Delta\lambda = 14$ nm). The spectral difference between **P3** and **P4** could be understood in terms of the enhanced steric effect of the second alkyl group attached to the thiophene ring. It increases the torsion angle between the fluorene and the thiophene units so as to reduce the effective conjugated length along the polymer main chain, which, in turn, leads to the spectral blue shift.

The fluorescence quantum yields (Φ_{fl}) of the polymers in chloroform were estimated by comparing with the standard of quinine sulfate (ca. 1×10^{-5} M solution in 0.1 M H_2SO_4, having a fluorescence quantum yield of

Table 2. Optical and Electrochemical Data and the Fluorescence Quantum Yields (in Chloroform Solution) of P1–P4

	λ_{max} (solution)^a (nm)			λ_{max} (films)^a (nm)			p-doping^c (V)			n-doping^c (V)		
polymer	abs	em	Φ_{FL}	abs	em	$E_g{}^b$ (eV)	E_{pa}	E_{pc}	$E^{1/2}$	E_{pc}	E_{pa}	$E^{1/2}$
P1	401	482 (515)	0.31	403	490 (520)	2.49	1.30	0.92	1.11		−2.11	
P2	398	483 (520)	0.28	401	493 (520)	2.58	1.28	0.93	1.10	−2.50	−2.07	−2.28
P3	403	461 (490)	0.65	412	492 (477)	2.50	1.27	1.02	1.15	−2.31	−2.09	−2.20
P4	367	447	0.39	378	458 (475)	2.76	1.49	1.18	1.34	−2.48	−2.23	−2.36

^{a} The data in the parentheses are the wavelengths of shoulders and subpeaks. ^{b} E_g stands for the band gap energy estimated from the onset wavelength of the optical absorption. ^{c} E_{pa} and E_{pc} stand for anodic peak potential and cathodic peak potential, respectively.

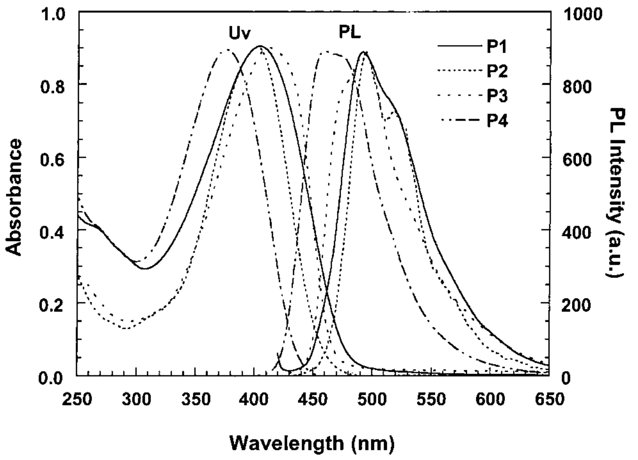


Figure 6. UV–vis absorption spectra and photoluminescence spectra of **P1**–**P4** measured from the spin-coated films on quartz plates at room temperature.

55%).[41] The results are listed in Table 2. In general, the polymers copolymerized with monothiophenes (**P3** and **P4**) have higher Φ_{fl} than those copolymerized with bithiophenes (**P1** and **P2**). The Φ_{fl} of **P3** (0.65) was measured to be more than twice higher than those measured from **P1** and **P2**. The fluorescence quantum yields of **P1** (0.31) and **P2** (0.28) are very close, indicating that the variation in the configuration of the β-substituted bithiophene has little effect on the PL quantum efficiency of the polymers based on the backbone structure. On the other hand, however, the introduction of the second decyl chain onto the thiophene ring in **P3** reduced the Φ_{fl} from 0.65 of **P3** to 0.39 of **P4**. This observation is consistent with the finding for the substituted polythiophenes, in which the fluorescence quantum yields of disubstituted polythiophenes (0.01–0.04) are usually much lower than those of the monosubstituted polythiophenes (0.18–0.27).[42]

Transparent and uniform films of the polymers were prepared on quartz plates by spin-casting their solutions in toluene at room temperature. The films of **P1** and **P2** emit intensive green light by the excitation of UV light. **P3** film emits bluish green light, while the emissive color of **P4** film is blue. The UV–vis and PL spectra of **P1**–**P4** as films are displayed in Figure 6. The absorption of the **P1** film onsets at 498 nm, which can be used to estimate the band gap (E_g) of the polymer (2.49 eV), and gives the peak at 403 nm. The absorption spectrum of **P2** film onsets at 480 nm (E_g, 2.58 eV) and peaks at 401 nm. The emission of **P1** peaks at 490 nm with a shoulder around 520 nm. **P2** gives an emissive maximum at 493 nm and a subpeak at 520 nm. Both the absorption and the PL spectra of **P1** and **P2** are only very slightly red-shifted with respect to their corresponding spectra in solution, an indication that there is no noticeable molecular conformation change from solution to solid film states. The spectroscopic parameters of **P3** and **P4** in film states are summarized in Table 2.

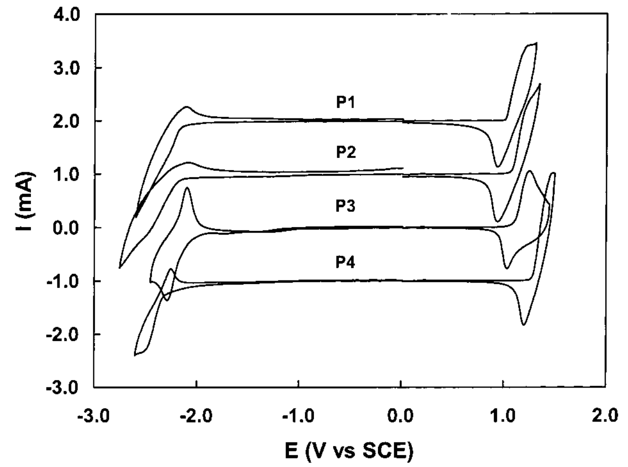


Figure 7. Cyclic voltammograms of **P1**–**P4** films coated on platinum plate electrodes in acetonitrile containing 0.1 M Bu_4NClO_4. Counter electrode: platinum wire. Reference electrode: $Ag/AgNO_3$ (0.10 M in acetonitrile). Scan rate: 50 mV/s.

Electrochemical Properties. The electrochemical behavior of the polymers was investigated by cyclic voltammetry (CV). The CV was performed in a solution of Bu_4NClO_4 (0.10 M) in acetonitrile at a scan rate of 50 mV/s at room temperature under the protection of argon. A platinum electrode (~0.08 cm^2) was coated with a thin polymer film and was used as the working electrode. A Pt wire was used as the counter electrode, and a $Ag/AgNO_3$ electrode was used as the reference electrode.

As shown by the cyclic voltammograms in Figure 7, all the polymers (**P1**–**P4**) exhibit partial reversibility in both n-doping and p-doping processes. Take **P3** for example, we may find that, on sweeping the polymer cathodically, the reduction peak was measured to be −2.31 V with a corresponding reoxidation peak appearing at −2.09 V. The n-doping potential $E_{red}{}^{1/2}$ was thus calculated to be −2.20 V. In the anodic scan, the oxidation (p-doping) process gave a sharp peak at 1.27 V with the re-reduction peak appearing at 1.02 V. Accordingly, the p-doping potential $E_{ox}{}^{1/2}$ was determined to be 1.14 V. The clear redox behavior and the good doping reversibility not only prove that the polymers may be good candidates of electroluminescent materials for applications in polymer light-emitting diodes but also allow us to study the electronic properties of the polymers. The electrochemical data of all the four polymers are summarized in Table 2.

The electrochemical properties of **P1** and **P2** are very similar. These results, once again, demonstrate that the conformational difference in **P1** and **P2** does not cause a noticeable electronic difference between the two polymers. Comparison of the electrochemical data of **P3** with those of **P1** and **P2** could find a minute decrease in the reduction potential and a slight increase in the oxidation potential for **P3**. This reveals that, due to the addition of one more thiophene ring, a strong π-excessive group, into the repeat unit, **P1** and **P2** are more electropositive than **P3** although **P1** and **P3** have the same band gap. In comparison with **P3**, **P4** exhibits both a higher oxidation potential (by 0.19 V) and a higher reduction potential (by 0.16 V). This is evident due to the decrease in effective conjugation of the polymer main chain caused by the enhanced steric hindrance of the second decyl chain on the thiophene ring.

Conclusions

A new series of fluorene-based hybrid conjugated polymers comprised of alternating 9,9-dialkylfluorene and substituted thiophene or bithiophene were synthesized through a palladium-catalyzed Suzuki coupling reaction. Efficient blue-to-green light emission, good solubility in common organic solvents, good thermal stability, and relatively high glass transition temperatures were demonstrated with these backbone structures, which makes them promising candidates of emissive materials for light-emitting diodes. The defined structures of the polymers allow us to study the structure–property relationship of the polymers based on the hybrid backbones, especially by controlling the substitution of thiophene rings and the coupling configuration between the two adjacent thiophene rings. The optical, electrochemical, and thermal properties are all sensitive to the changes of the thiophene ring number in the repeat unit and the substitution on the thiophene ring. In the case that substituted bithiophene are incorporated, different from the observation in poly(3-alkylthiophenes), the structural regioregularity of head-to-head or tail-to-tail between the two substituted thiophene rings does not affect the optical and electrochemical properties of the resulting polymers. However, the glass transition temperatures and the environmental stability of the polymers depend on the structural regioregularity, and head-to-head coupling configuration corresponds to a higher glass transition temperature and better stability. More meaningfully, the polymer with the head-to-head structural regularity can also be prepared by the facile $FeCl_3$ oxidative polymerization in even higher molecular weights. Disubstitution of alkyl group on the thiophene ring of the polymers may enlarge the band gap and realize blue emission, but the fluorescence quantum efficiency is significantly reduced because of the second attachment of an alkyl group compared to the corresponding monosubstituted polymer.

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