# A Novel Series of p−n Diblock Light-Emitting Copolymers Based on Oligothiophenes and 1,4-Bis(oxadiazolyl)-2,5-dialkyloxybenzene

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ABSTRACT: A new series of p−n diblock conjugated copolymers consisting of alternate 1,4-bis(oxadiazolyl)-2,5-dialkyloxybenzene and oligothiophenes with one to three thiophene rings (**P1**−**P3**) have been synthesized. The polymers have well-defined structures and exhibit good thermal stability with the onset decomposition temperatures in nitrogen at around 300 °C. The glass transition temperature ($T_g$) of the polymers decreases with increasing the length of oligothiophene blocks. Both the absorption spectra and photoluminescence spectra shift to longer wavelength with increase in the length of oligothiophene blocks. The emissive color of the polymers could be tuned from blue to green to orange just by increasing the number of thiophene rings in the oilgothiophene blocks from one to three. No obvious change in reduction potential is found for the polymers with variation in the length of oligothiophene blocks. The reduction potential $E^{1/2}$ of the polymers is measured by cyclic voltammetry to be around −1.7 V vs SCE, comparable to those of poly(cyanoterephthalyidene) (CN-PPV) and other good electron-transporting materials. The oxidation potential of the polymers can be reduced remarkably by increasing the length of oligothiophene blocks. The oxidation potential $E^{1/2}$ of **P3** is measured to be 1.25 V with the onset potential at 1.0 V vs SCE. These values are comparable to those of some hole-injection favorable electroluminescent polymers. The results prove that the p−n diblock structure may be a promising molecular design for synthetically tuning the HOMO and LUMO of conjugated polymers.

## Introduction

Since the initial report in 1990 of electroluminescence of conjugated polymers in films of poly(*p*-phenylenevinylene) (PPV) sandwiched between an anode and a cathode of appropriate work functions,[1] enormous efforts have been devoted to the synthesis of light-emitting polymers[2,3] because of their important properties with potential applications to conjugated polymer photoluminescence and electroluminescence. Polymer processability, band gap tunability, and mechanical flexibility make conjugated polymers excellent candidates for low-cost, large-area flat-panel display applications.[1−4] Many conjugated polymers, such as PPV,[1] poly(2-methoxy-5,2′-ethylhexyloxy)-1,4-phenylenevinylene) (MEH-PPV),[4] poly(*p*-phenylene)s (PPPs),[5,6] polyfluorenes (PFs),[7,8] and polythiophenes (PTs),[9−11] have been synthesized for application as emissive and/or charge-transporting materials in polymer light-emitting diodes (PLEDs). However, some important issues such as stability and color tunability remain to be addressed.[2]

The emissive light of a PLED arises from the capture of electrons and holes, which are injected from the two opposite electrodes, in an emissive polymer layer.[2,12] To achieve high electroluminescence efficiency, it is necessary to balance the rates of injection of electrons and holes from the opposite contacts into the polymer layer.[13] For most of the conjugated polymers investigated so far, the barrier between the LUMO of polymer and the work function of aluminum, which is normally used as cathode in PLEDs, is much larger than that between the HOMO of polymer and the work function of indium tin oxide (ITO), a normal anode material. This results in an imbalance of the injection between electrons and holes.[13−15] To overcome this problem, two approaches have been developed. One is to use metals with low work functions (such as calcium and magnesium) as cathode materials.[16] Such metals, however, are highly susceptible to atmospheric degradation and are difficult to encapsulate, that the resulting devices suffer from poor stability. The other approach is to insert an additional electron-transporting layer between the emissive layer and cathode.[17,18] Although this has been proven to be an effective way of achieving improved efficiency, in practical fabrication of devices one has to face additional technical difficulties, and the emissive spectrum may be shifted. Therefore, it would be attractive for PLEDs if we could afford light-emitting polymers with suitable levels of the HOMO and LUMO, which could match well the work functions of cathode and anode simultaneously. To realize this tentative idea, the key is to develop an effective synthetic approach to adjust the HOMO and LUMO of conjugated polymers. Accordingly, we have developed a p−n diblock structure of conjugated polymers,[19,20] in which typical p-dopable and n-dopable segments are incorporated into one backbone of conjugated polymer to adjust the HOMO and LUMO of conjugated polymers.

A series of conjugated polymers comprised of substituted thiophene and 1,4-di(oxadiazole) show typical n-dope type characteristics,[21,22] while the polymer composed of alternating 3,3′-didecyl-2,2′-bithiophene and 2,6-bis(1,3,4-oxadiazolyl)toluene exhibits balanced p-dope and n-dope tendency.[19,20] These preliminary results indicate that the p−n diblock structure may be a promising approach of adjusting the HOMO and LUMO levels of conjugated polymers. In this contribution we present the synthesis and characterization of another series of p−n diblock conjugated copolymers, which have the chemical structures as shown in Chart 1 (**P1**, **P2**, and **P3**). **P4** was also synthesized for comparison.

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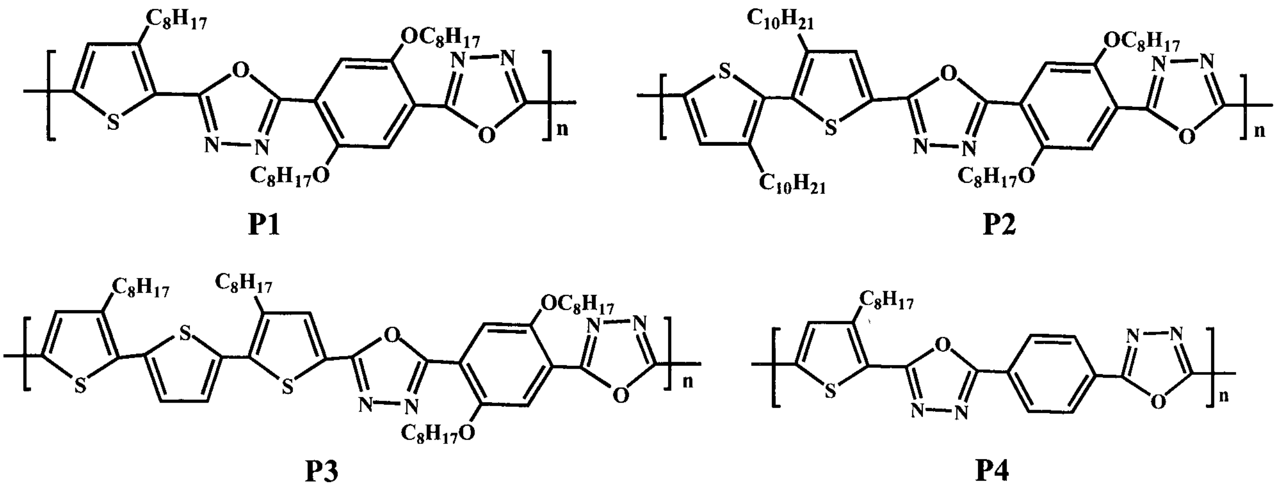
**Chart 1**



**P1** **P2** **P3** **P4**

## Experimental Section

**General Methods.** Reagent chemicals were purchased from Aldrich Chemical Co. unless otherwise stated. All new compounds were characterized by $^{1}$H NMR, $^{13}$C NMR, MS, and elemental analysis (Microanalytical Laboratory at the National University of Singapore). Nuclear magnetic resonance (NMR) spectra were taken on a Bruker ACF 300 spectrometer. All chemical shifts were reported relative to tetramethylsilane (TMS) at 0.0 ppm. FTIR spectra were recorded on a Bio-Rad TFS 156 spectrometer by dispersing samples in KBr disks. UV–vis and fluorescence spectra were obtained on a Shimadzu UV–vis–NIR 3101 scanning spectrophotometer and on a Perkin-Elmer LS 50B luminescence spectrometer, respectively. Thermogravimetric analysis (TGA) was carried out on a DuPont thermal analyst 2100 system with a TGA 2950 thermogravimetric analyzer at a heating rate of 10 °C min$^{-1}$ and at an air or nitrogen flow rate of 75 cm$^{3}$ min$^{-1}$. Differential scanning calorimetry (DSC) was run on a DuPont DSC 2910 module in conjunction with the DuPont thermal analyst system. Cyclic voltammetry (CV) was performed on an EG&G 273A potentiostat/galvanostat system with a three-electrode cell in a solution of $Bu_4NClO_4$ (0.1 M) in acetonitrile at a scan rate of 50 mV s$^{-1}$. The polymer films were coated on a square Pt electrode (1.0 cm$^{2}$) by dipping the electrode into the corresponding solutions and then drying in air. A Pt wire was used as the counter electrode, and an Ag/$AgNO_3$ (0.1 M) electrode was used as the reference electrode. Gel permeation chromatography (GPC) analysis was conducted with a Perkin-Elmer 200 HPLC system equipped with Phenogel MXL and MXM columns using polystyrenes as standards and THF as the eluant.

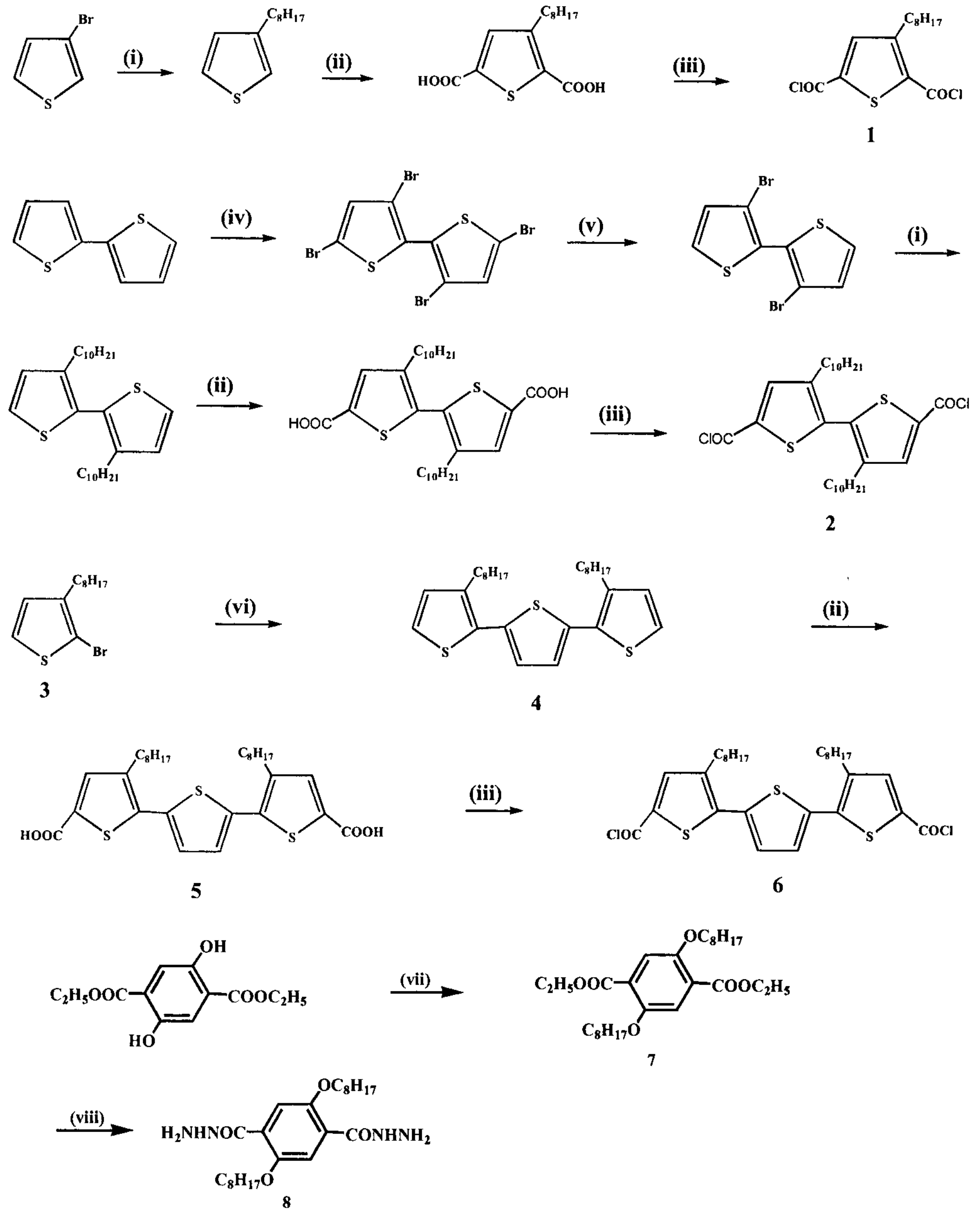
**Preparation of Monomers.** The syntheses of 2,5-bis(chlorocarbonyl)-3-octylthiophene (**1**) and 3,3′-didecyl-5,5′-bis(chlorocarbonyl)-2,2′-bithiophene (**2**) have been described in our previously published papers.[19,21,22]

**2-Bromo-3-octylthiophene (3).** Into a dried round-bottom flask was charged 200 cm$^{3}$ of 1:1 mixture of chloroform and acetic acid. The mixed solvent was then purged with pure nitrogen for 10 min. A 19.6 g (0.1 mol) sample of freshly distilled 3-octylthiophene, which was obtained by the coupling reaction between 3-bromothiophene and 1-bromooctane in diethyl ether in the presence of [1,3-bis(diphenylphosphino)propane]dichloronickel(II) ($Ni(dppp)_2Cl_2$) was added in one portion. After the mixture was cooled to 5 °C, 17.0 g (0.095 mol) of *N*-bromosuccinimide (NBS) was added in portions over a period of 2 h. During that period, the temperature of the reaction mixture was maintained at 5–10 °C. The mixture was further stirred at room temperature overnight and then extracted with chloroform. The extract was washed with dilute NaOH solution followed by water until it gave a pH of 6–7 and finally was dried over anhydrous $MgSO_4$. The solvent was removed by rotary evaporation, and the residue was distilled under reduced pressure (90–92 °C/0.5 mbar) to yield 21.5 g (82%) of a colorless oil. $^{1}$H NMR ($CDCl_3$, ppm): $\delta$ 7.17 (d, $J$ = 5.6 Hz, 1H), 6.79 (d, $J$ = 5.6 Hz, 1H), 2.58 (t, $J$ = 7.5 Hz, 2 H), 1.59–1.54 (m, 2 H), 1.31–1.26 (m, 10 H), 0.89 (t, $J$ = 4.5 Hz, 3H). MS *m*/*z* 275. Anal. Calcd for $C_{12}H_{19}BrS$: C, 52.36; H, 6.96; S, 11.64; Br, 29.09. Found: C, 52.43; H, 7.29; S, 12.00; Br, 28.80.

**3,3″-Dioctyl-2,2′:5′,2″-terthiophene (4).** A Grignard reagent of 3-*n*-octylthienyl-2 magnesium bromide (0.05 mol), prepared from the reaction of 15.1 g (0.055 mol) of 2-bromo-3-octylthiophene with 1.5 g (0.062 mol) of Mg in 200 cm$^{3}$ of diethyl ether, was added dropwise into a solution of 2,5-dibromothiophene (6.05 g, 0.025 mol) in 250 cm$^{3}$ of ether containing 216 mg of $Ni(dppp)_2Cl_2$ (0.8 mmol) as catalyst over a period of 1.5 h. After refluxing for 20 h, the reaction mixture was quenched with 0.2 M HCl and extracted with ether. The extract was washed with $H_2O$ three times and with brine once and then dried over anhydrous $Na_2SO_4$. After removal of solvent, a dark-brown liquid was obtained. It was dissolved in hexane, and the solution was decolorized with charcoal. After removal of the hexane, the residue was subjected to purification by column chromatography on silica gel using hexane as eluant. An 8.0 g (yield 68%) aliquot of a yellow liquid was obtained after two chromatographic separations. MS *m*/*z* 472. HRMS calcd mass for $C_{28}H_{40}S_3$: 472.22922. Found mass: 472.22910. $^{1}$H NMR ($CDCl_3$, ppm): $\delta$ 7.17 (d, $J$ = 5.6 Hz, 1H), 6.79 (d, $J$ = 5.6 Hz, 1H), 2.58 (t, $J$ = 7.5 Hz, 2H), 1.59–1.54 (m, 2H), 1.31–1.26 (m, 10H), 0.89 (t, $J$ = 4.5 Hz, 3H). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ 139.98, 136.22, 130.48, 130.06, 126.09, 123.73, 31.89, 30.73, 29.65, 29.55, 29.34, 29.22, 22.79, 14.20. Anal. Calcd for $C_{28}H_{40}S_3$: C, 71.19; H, 8.47; S, 20.34. Found: C, 71.22; H, 8.11; S, 20.87.

**3,3″-Dioctyl-5,5″-dicarboxy-2,2′:5′,2″-terthiophene (5).** To a $N_2$-flushed flask initially containing a solution of TMEDA (3.0 g, 26 mmol) and *n*-BuLi (1.6 M solution in hexane, 16.2 cm$^{3}$, 26 mmol) in 10 cm$^{3}$ of hexane was added 3.5 g (7.42 mmol) of 3,3″-dioctyl-2,2′:5′,2″-terthiophene under nitrogen atmosphere at room temperature. After stirring at room temperature for 1 h, the mixture was refluxed for 30 min. The reaction mixture was cooled to −70 °C and then slowly poured into a 500 cm$^{3}$ flask half filled with crushed dry ice under the protection of $N_2$. The mixture was warmed to room temperature overnight and then poured into 100 cm$^{3}$ of 10 M HCl solution with ice. The aqueous solution was extracted with ether (two portions of 100 cm$^{3}$). The combined ether solutions were then extracted with 10% NaOH aqueous solution (100 cm$^{3}$), and the aqueous extract was acidified with a 10 M HCl solution. The mixture was extracted with ether (two portions of 50 cm$^{3}$), and the ether extract was washed with water and brine and dried over anhydrous $MgSO_4$. Evaporation of the ether and recrystallization from ethanol afforded 3.4 g (yield 83%) of a yellow powder. MS: *m*/*z* 560. $^{1}$H NMR (acetone-*d*, ppm): $\delta$ 7.68 (s, 2H), 7.35 (s, 2H), 2.89–2.84 (t, $J$ = 7.6 Hz,

**Scheme 1. Synthetic Routes for Monomers**[a]



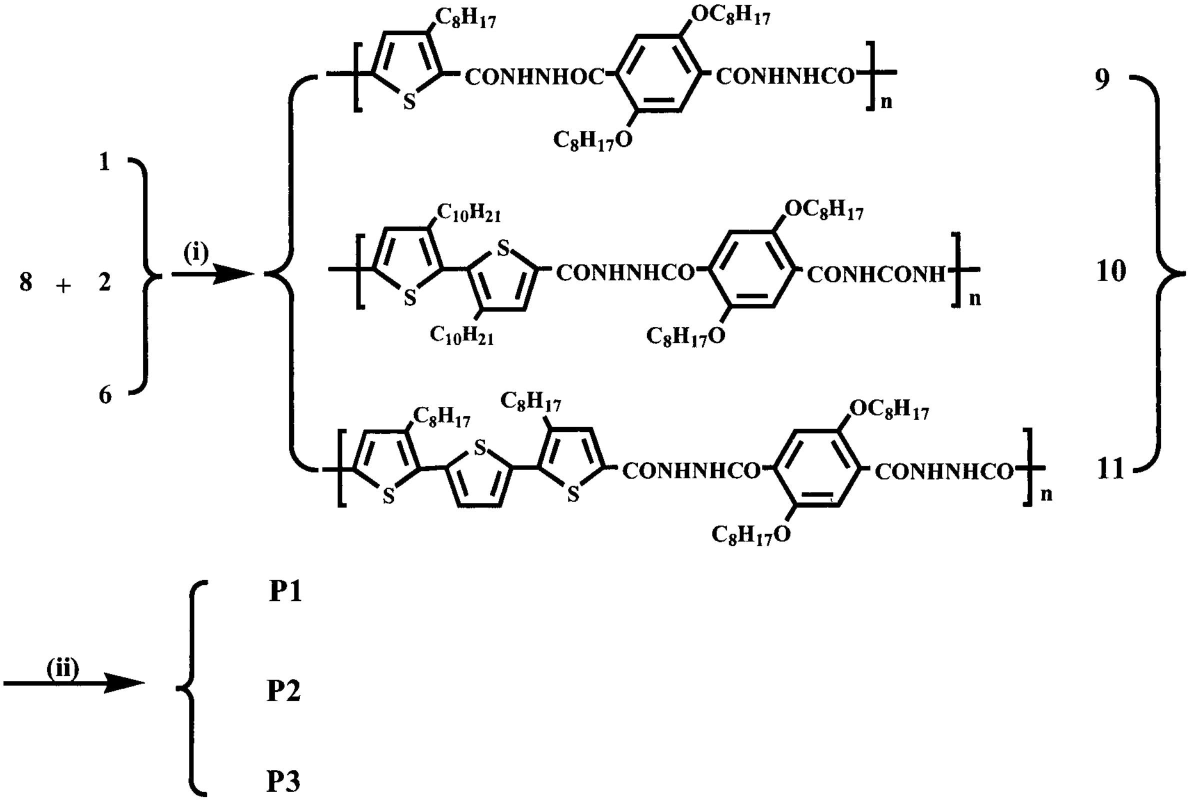
[a] Reagents and conditions: (i) 1-bromooctane or 1-bromodecane, Mg, Ni(dppp)$_2$Cl$_2$, diethyl ether; (ii) *n*-BuLi, TMEDA, dry ice, −70 °C to room temperature; (iii) $SOCl_2$; (iv) bromine, AcOH/$CHCl_3$; (v) Zn, EtOH/AcOH/HCl; (vi) Mg, 2,5-dibromothiophene, Ni(dppp)$_2$Cl$_2$, diethyl ether; (vii) 1-bromooctane, $K_2CO_3$, acetone; (viii) $NH_2NH_2{\cdot}H_2O$, MeOH.

4H), 1.76−1.74 (m, 4H), 1.42−1.27 (m, 24H), 0.89−0.84 (t, *J* = 6.5 Hz, 6H). $^{13}$C NMR (acetone-*d*, ppm): *δ* 166.97, 145.85, 141.67, 141.29, 141.04, 136.82, 132.86, 37.18, 35.90, 35.55, 35.28, 35.14, 35.05, 28.40, 18.79. Anal. Calcd for $C_{30}H_{40}O_4S_3$: C, 64.25; H, 7.19; S, 17.15. Found: C, 64.53; H, 7.29; S, 17.54.

**3,3″-Dioctyl-5,5″-bis(chlorocarbonyl)-2,2′:5′,2″-terthiophene (6).** Freshly distilled thionyl chloride (25 cm$^3$) was added to a flask containing 2.6 g (1.60 mmol) of 3,3″-dioctyl-5,5″-dicarboxy-2,2′:5′,2″-terthiophene. The mixture was refluxed for 5 h. The excess thionyl chloride was removed by distillation under reduced pressure. The residue was washed with hexane to give 2.4 g (97%) of an orange powder. MS: *m*/*z* 596. $^1$H NMR ($CDCl_3$, ppm): *δ* 7.80 (s, 2H), 7.29 (s, 2H), 2.83−2.78 (t, *J* = 7.9 Hz, 4H), 1.71−1.58 (m, 4H), 1.46−1.20 (m, 24H), 0.88−0.86 (t, *J* = 7.0 Hz, 6H). $^{13}$C NMR ($CDCl_3$, ppm): *δ* 159.13, 142.40, 141.48, 140.17, 136.28, 133.93, 128.28, 31.73, 30.15, 29.39, 29.33, 29.23, 29.10, 22.54, 13.98. Anal. Calcd for $C_{30}H_{38}O_2Cl_2S_3$: C, 60.28; H, 6.41; S, 16.09. Found: C, 59.98; H, 7.19; S, 17.21.

**Diethyl 2,5-Dioctyloxyterephthalate (7).** A mixture of 15.3 g (0.060 mol) of diethyl 2,5-dihydroxyterephthalate and 33.0 g (0.240 mol) of potassium carbonate in 200 cm$^3$ of acetone was refluxed for 0.5 h, and then 46.5 g (0.240 mol) of 1-bromooctane was added dropwise over a period of 1 h. The mixture was further refluxed for 2 days. After cooling to room temperature, the mixture was filtered and the filtered residue was washed with acetone three times. The solvent of the combined filtrate was removed by evaporation. The residue was redissolved in ether, and the solution was washed three times with 5% KOH, followed by water, and dried over magnesium sulfate. The ether was removed by rotary evaporation, and the residue was distilled to remove the excess 1-bromooctane. Recrystallization from ethanol afforded white crystals of diethyl 2,5-dioctyloxyterephthalate (19.8 g, yield 69%). MS: *m*/*z* 478. $^1$H NMR ($CDCl_3$, ppm): *δ* 7.34 (s, 2H), 4.38−4.35 (q, *J* = 6.9, 4H), 3.94−4.00 (q, *J* = 6.8, 4H), 1.81−1.73 (m, 4H), 1.61−1.33 (m, 26H), 0.95−0.83 (t, *J* = 6.8, 6H).$^{13}$C NMR ($CDCl_3$, ppm): *δ* 166.05, 151.63, 124.63, 116.50, 69.80, 61.17, 31.71, 29.22, 29.20, 29.14, 25.88, 22.55, 14.17, 13.98.

**Scheme 2. Synthetic Route for Polymers**[a]



[a] Reagents and conditions: (i) LiCl, pyridine, NMP, 80 °C; (ii) $POCl_3$, reflux.

Anal. Calcd for $C_{28}H_{46}O_6$: C, 70.26; H, 9.69. Found: C, 69.73; H, 9.85.

**2,5-Dioctyloxyterephthalic Dihydrazide (8).** A 7.2 g (0.015 mol) sample of diethyl 2,5-dioctyloxyterephthate was added into a solution of 10 cm$^3$ hydrazine monohydrate (99%) in 60 cm$^3$ of $CH_3OH$. The reaction mixture was refluxed for 24 h. The mixture was cooled and filtered to give a white precipitate. The precipitate was recrystallized from ethanol and dried in vacuum at 60 °C to yield 6.4 g (95%) of white crystals. MS: *m*/*z* 450. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 9.19 (broad, 2 H, NH), d 7.84 (s, 2H), 4.19−4.16 (t, *J* = 6.7, 4H), 1.92−1.82 (m, 4H), 1.48−1.28 (m, 20H), 0.88−0.86 (t, *J* = 6.8, 6H).$^{13}$C NMR ($CDCl_3$, ppm): $\delta$ 165.24, 150.70, 122.97, 115.66, 69.80, 31.61, 29.08, 29.02, 28.97, 25.88, 22.50, 13.95. Anal. Calcd for $C_{24}H_{42}N_4O_4$: C, 63.97; H, 9.39; N, 12.43. Found: C, 63.78; H, 9.29; N, 12.22.

**Preparation of Precursor Polymers, Polyhydrazides (9−11).** To a stirred solution of monomer **8** (0.424 mmol as a representative) in *N*-methylpyrrolidinone (NMP) (20 cm$^3$) containing LiCl (0.1 g) and 1−2 drops of pyridine was added another monomer of **1** or **2** or **6** at room temperature. The reaction mixture was then heated to 80 °C and stirred at this temperature for 3 h. After cooling to room temperature, precipitation in $CH_3OH$ and washing with water and ethanol afforded a high yield (90−95%) of a polyhydrazide. Because of the poor solubility in common solvents, the polyhydrazides were not further purified and characterized.

**Preparation of Polymers (P1−P3).** Generally, ~0.2 g of a polyhydrazide (**9** or **10** or **11**) was dispersed in 20 cm$^3$ of $POCl_3$ at room temperature. The mixture was refluxed for 6−12 h. After cooling to room temperature, the reaction mixture was poured into water. The precipitate was collected by filtration and was washed with water, ethanol, followed by ether and finally dried under vacuum at room temperature. The yield was in the range 85−90%.

**P1**. $^1$H NMR ($CDCl_3$:TFA-*d* = 20:1, ppm): $\delta$ 7.93 (s, 1H), 7.74 (d, 2H), 4.23 (s, 4H), 3.20 (t, 2H), 2.00−1.60 (b, 6H), 1.60−1.15 (b, 30H), 0.83 (m, 9H). Anal. Calcd for $C_{38}H_{54}N_4SO_4$: C, 68.85; H, 8.21; N, 8.46; S, 4.84. Found: C, 68.01; H, 8.20; N, 8.94; S, 4.33.

**P2**. $^1$H NMR ($CDCl_3$, ppm): $\delta$ 7.84 (s, 2H), 7.75 (s, 2H), 4.19 (t, 4H), 2.62 (t, 4H), 1.93 (b, 4H), 1.59 (b, 8H), 1.23 (b, 44H), 0.84 (t, 12). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ 162.71, 160.99, 150.84, 144.39, 132.19, 131.09, 125.30, 116.36, 114.57, 69.65, 31.78, 30.50, 29.52, 29.48, 29.30, 29.23, 28.88, 26.05, 22.56, 13.99. Anal. Calcd for $C_{54}H_{80}N_4S_2O_4$: C, 71.01; H, 8.83; N, 6.13; S, 7.02. Found: C, 70.46; H, 9.14; N, 6.11; S, 7.13.

**P3**. $^1$H NMR ($CDCl_3$:TFA-*d* = 20:1, ppm): $\delta$ 7.92 (s, 2H), 7.76 (s, 2H), 7.38 (s, 2H), 4.28 (t, 4H), 2.94 (b, 4H), 1.97 (b, 4H), 1.78 (b, 4H), 1.65−1.00 (b, 34H), 0.87 (b, 12 H). $^{13}$C NMR ($CDCl_3$, ppm): $\delta$ 162.42, 160.92, 150.84, 140.86, 135.82, 135.14, 132.38, 127.20, 122.49, 116.40, 114.56, 69.72, 31.79, 30.37, 29.60, 29.38, 29.21, 26.11, 22.58, 14.00. Anal. Calcd for $C_{54}H_{74}N_4S_3O_4$: C, 69.04; H, 7.94; N, 5.96; S, 10.24. Found: C, 67.54; H, 8.83; N, 6.08; S, 10.29.

## Results and Discussion

**Synthesis and Characterization of Polymers.** The polymers were synthesized through precursor polymers of polyhydrazides,[23] which were prepared by polycondensation of $\alpha,\omega$-dicarbonyl chlorides of alkyl-substituted oligothiophenes with 2,5-dioctyloxyterephthalic dihydrazide in NMP in the presence of LiCl and pyridine.[24,25] The $\alpha,\omega$-dicarbonyl chlorides of alkyl-substituted oligothiophenes and dioctyloxyterephthalic dihydrazide were synthesized following the routes depicted in Scheme 1. For the synthesis of the dicarbonyl chlorides, the $\alpha$-oligomers of alkyl-substituted thiophene were synthesized first, and then the carboxylation at the $\alpha$-positions of thiophene rings with *n*-BuLi and dry ice and a following reaction with $SOCl_2$ were performed.[26] The dioctyloxyterephthalic dihydrazide (**8**) was obtained by the reaction of diethyl 2,5-dioctyloxyterephthalate (**7**), prepared from diethyl 2,5-dihydroxy-

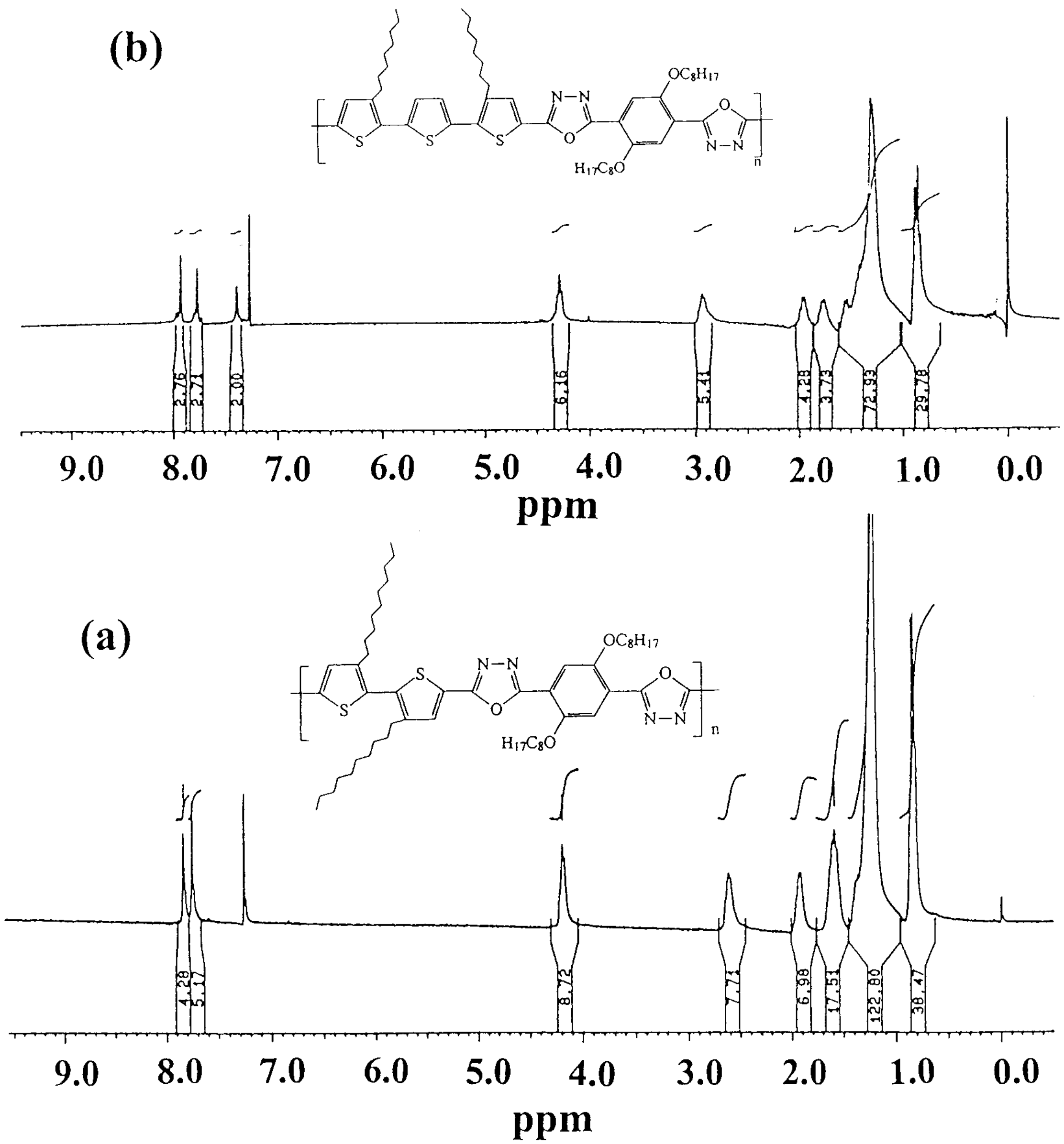


**Figure 1.** $^1$H NMR spectra of **P2** (a) and **P3** (b).

terephthalate and 1-bromooctane, with excess hydrazine monohydrate (Scheme 1). The polyhydrazides **9–11** were obtained as light-yellow powders. They are insoluble in common organic solvents but completely dissolve in NMP. As shown in Scheme 2, the polyhydrazides were converted to the final polymers **P1–P3** via a cyclodehydration reaction by refluxing in $POCl_3$, which was used as both dehydrating reagent and solvent. The successful cyclodehydration could be confirmed by FTIR spectra, in which two intensive absorption bands around 1660 and 3246 cm$^{-1}$ in the polyhydrazides, assigned to the stretching of the carbonyl groups and N–H stretching, respectively, disappeared after the treatment with $POCl_3$, while two new peaks around 1586 and 1081 cm$^{-1}$ attributed to 1,3,4-oxadiazole ring stretching appeared.[19] The synthesis of **P4** has been reported previously.[21]

Polymers **P1**, **P2**, and **P3** were obtained as gray, yellow, and orange powders, respectively. **P1** and **P3** are partially soluble in both chloroform and THF. Polymer **P2** is completely soluble in chloroform and partially soluble in THF. However, all of the three polymers readily dissolve in chloroform with a little amount of trifluoroacetic acid (TFA) to give clear solutions. The chemical structures of the polymers were confirmed by $^1$H and $^{13}$C NMR as well as elemental analysis. Figure 1 displays the $^1$H NMR spectra of **P2** and **P3**. In the spectrum of **P2**, there are two clear singlet peaks in the aromatic region, which correspond to the $\beta$-proton on the thiophene ring at $\delta$ 7.75 ppm and the protons on the benzene ring at $\delta$ 7.84 ppm. The signals at $\delta$ 4.19 and 2.62 ppm arise from the $-OCH_2-$ groups on the benzene ring and the methylenes attached on the thiophene rings, respectively. For **P3**, there are three signals in the aromatic region, which are assigned to two kinds of protons on thiophene rings ($\delta$ 7.76 and 7.38 ppm) and one kind of proton on benzene ($\delta$ 7.92 ppm). The peaks corresponding to the $-OCH_2-$ on the benzene ring and the methylene groups adjacent to thiophene rings in **P3** appear at $\delta$ 4.28 and 2.96 ppm, respectively. The $^{13}$C NMR spectra of **P2** and that of **P3** in the aromatic region are shown in Figure 2. There are nine well-resolved signals in the aromatic region for **P2** and 11 peaks in the aromatic region for **P3**, which correspond to the nine aromatic carbons in **P2** and 11 aromatic carbons in **P3**. It could be concluded from the

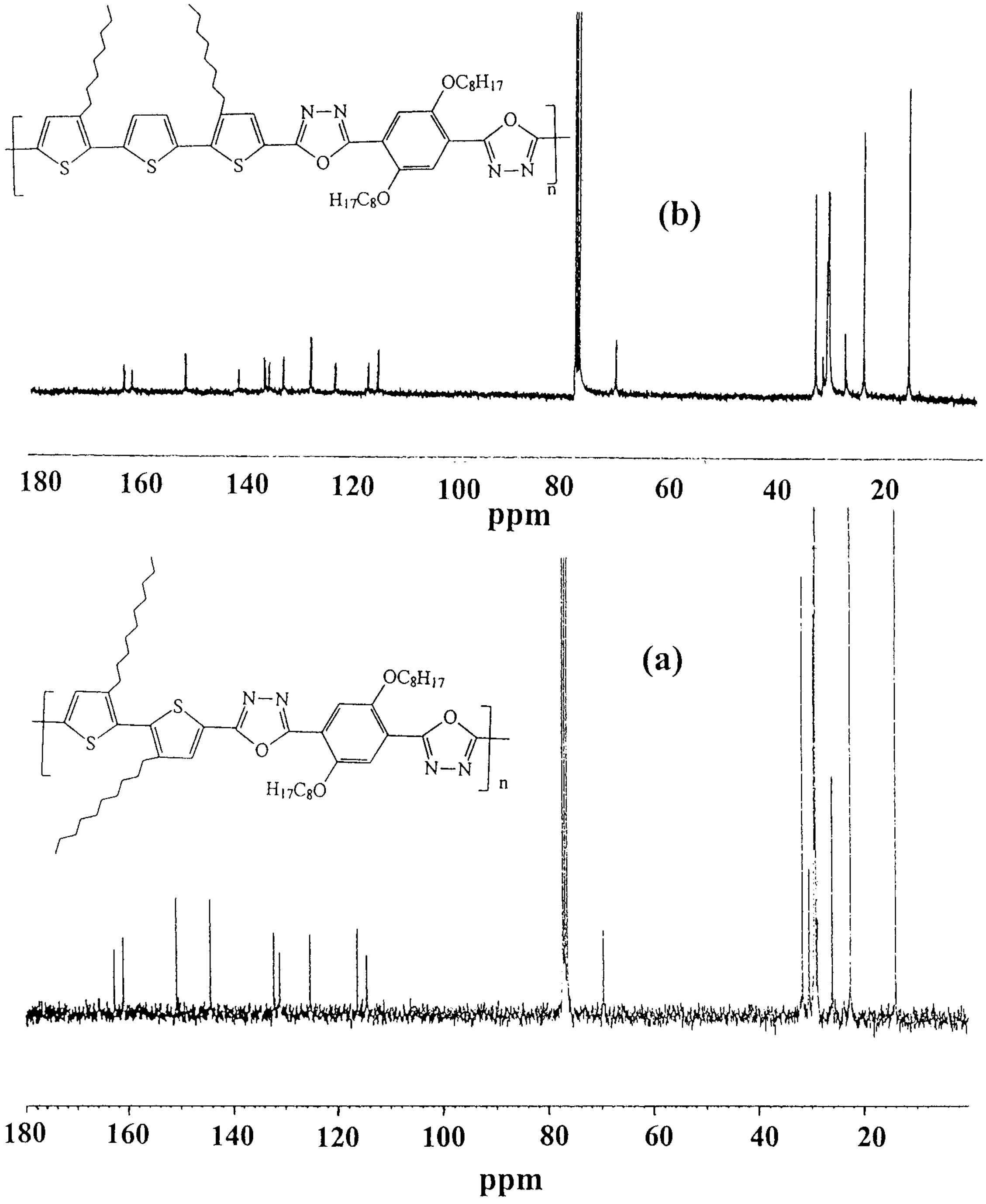


**Figure 2.** $^{13}$C NMR spectra of **P2** (a) and **P3** (b).

NMR spectra that the polymers have well-defined structures.

Because the polymers are partially soluble in THF, only the molecular weights of the THF-soluble parts of the polymers were measured by means of GPC using THF as eluant against polystyrene standards. The molecular weights of the THF soluble parts were measured as $M_n = 5419$ ($M_w/M_n = 1.9$) for polymer **1**, 7574 (2.0) for polymer **2**, and 2814 (1.4) for polymer **3**. The actual molecular weights of the polymers should be higher than these measured values because of the insolubility of the parts with higher molecular weights. Although the results cannot give accurate information on molecular weights of the polymers, they convince us of the polymeric structure of the obtained products.

Thermogravimetric analysis (TGA) reveals that the polymers have good thermal stability with the onset decomposition temperatures around 300 °C in nitrogen. One representative TGA plot is given in Figure 3. It is quite similar to that of our previously synthesized polymer, poly[3,3′-didecyl-2,2′-bithiophene)-*co*-(2,6-bis-(oxadiazolyl)toluene]. The glass transition temperatures ($T_g$) of the polymers were measured to be 124.3 °C for **P1**, 53.8 °C for **P2**, and 34.1 °C for **P3**. It is evident that the chain mobility of the polymers increases with the length of oligothiophene blocks in the polymers.

**Optical Properties: Tuning the Emissive Wavelength.** The absorption and fluorescence spectra of polymers **P1**−**P3** as films are shown in Figures 4 and 5, respectively. The spectra of P4 are also exhibited for comparison. The films were prepared by spin-coating

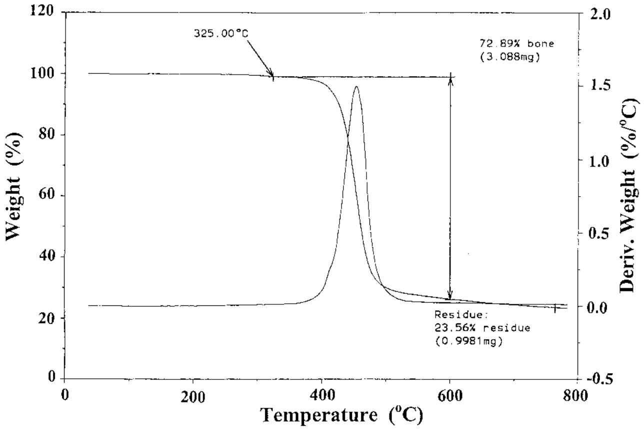


**Figure 3.** Representative TGA (in nitrogen) plot (**P3**).

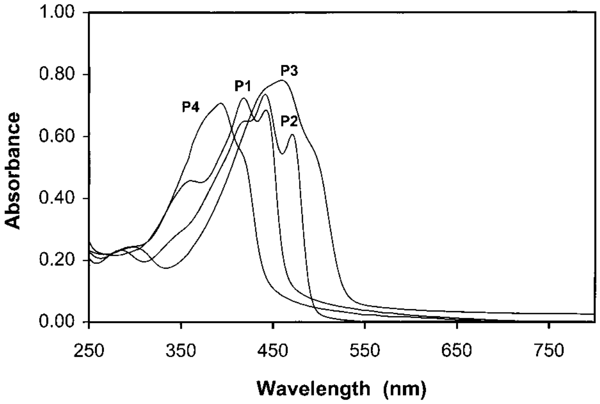


**Figure 4.** UV–vis absorption spectra of **P1** (a), **P2** (b), **P3** (c), and **P4** (d) in film states at room temperature.

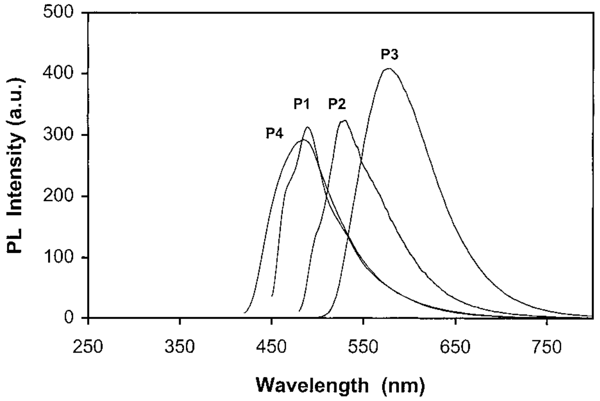


**Figure 5.** Fluorescence spectra of **P1** (a), **P2** (b), **P3** (c), and **P4** (d) in film states at room temperature.

on quartz plates from the solutions of the polymers in chloroform with a small amount of TFA. An expected gradual bathochromic shift of absorption spectra is exhibited with increasing the length of oligothiophenes in the polymers. The absorption maximum increases from **P1** ($\lambda_{max}$ = 420 nm) to **P2** ($\lambda_{max}$ = 441 nm) to **P3** ($\lambda_{max}$ = 461 nm). The absorption spectra of all of the three polymers are structured, indicated by the well-defined subpeaks or shoulders at 360 and 443 nm for **P1**, 419 and 471 nm for **P2**, and 439 and 494 nm for **P3**. It is worth noticing that the resolution of a well-defined structure in the spectra decreases on going from **P1** to **P3**. This phenomenon implies that the polymers with shorter oligothiophenes have higher regular structure in the solid state. Polymers **P1**–**P3** emit intense blue, green, and orange light, respectively, upon UV–vis excitation ($\lambda > 350$ nm) in the solid state. As shown in Figure 6, the emissive maxima are 489 nm for **P1**, 530nm for **P2**, and 579 nm for **P3**. The emissive spectra are much less structured than the absorption spectra. The Stokes shift can be determined to be 69 nm for **P1**, 89 nm for **P2**, and 118 nm for **P3**. The spectral difference among the three polymers could be further ascribed to differences in the internal charge transfer along the backbones of the polymers in their excited states.

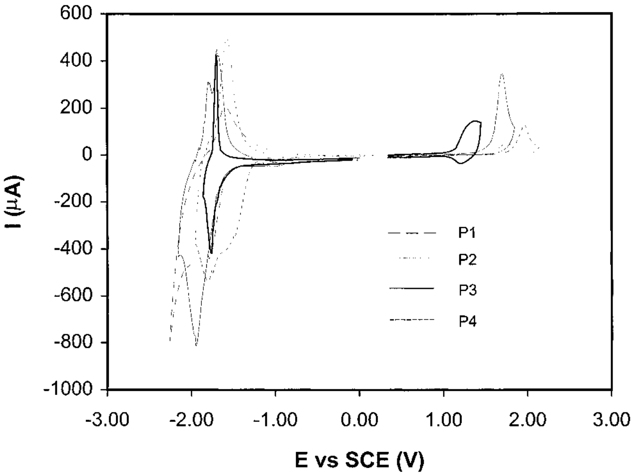


**Figure 6.** Cyclic voltammograms of polymers **P1**–**P4** in films on Pt electrode in $CH_3CN$ solution of $Bu_4NClO_4$ (0.1 M) at a scan rate of 50 mV $s^{-1}$.

The effective tuning of the emissive wavelength of the new series of polymers could be attributed to the remarkable difference of the band gaps between oligothiophenes and 1,4-bis(oxadiazolyl)-2,5-dialkoxybenzene, the two blocks constructing the polymers alternately. As demonstrated by head-to-tail regioregular poly(3-alkylthiophenes),[27] oligothiophenes may have low band gaps, while most of 1,3,4-oxadiazole-containing conjugated polymers and molecular materials exhibit quite large band gaps (larger than 3.0 eV).[28,29] The new polymers could be seen as the derivatives of polythiophene, in which the 1,4-bis(oxadiazolyl)-2,5-dialkoxybenzene block is inserted. The extension of conjugation along the backbone of polythiophene is limited or changed due to this insertion, and the total conjugated properties of the resultant polymers will be varied with the change of the length of oligothiophene blocks. Comparing the spectral data to those of alkyl-substituted oligothiophenes and conjugation-interrupted polymers based on oligothiophenes,[30–38] polymers **P1**, **P2**, and **P3** correspond to the effective conjugated length of about 3, 4–5, and 5–6 extended thiophene rings, respectively. It is evident that 1,4-bis(1,3,4-oxadiazole)-benzene does not serve as a conjugation-interrupting block in the polymers; rather, it is a part of the whole conjugated structures, and its contribution to conjugation is equivalent to about two to three extended thiophene rings. Spectral comparison between polymers **P1** and **P4** indicates spectral red shift because of the attachment of alkoxy chains on the benzene ring, so the electronic properties of the polymers could be finely tuned by attaching different functional groups on the benzene ring. It could be concluded that the p–n diblock structure is an effective approach to tune the emissive color of conjugated polymers.

**Electrochemical Properties: Tuning Redox Behavior.** The CV traces of the polymers are shown in

**Table 1. Properties of the p−n Diblock Conjugated Copolymers**

| polymer | mol wt[a] ($M_n$) | $T_g$ (°C) | abs $\lambda_{max}$[b] (nm) | fluor $\lambda_{max}$[b] (nm) | oxidative $E_{pa}/E_{pc}$[c] (V) | reduction $E_{pc}/E_{pa}$[c] (V) |
|---|---|---|---|---|---|---|
| **P1** | 5419 (1.9) | 124.3 | 420 (360, 443) | 489 | 1.75/− | −1.83/−1.60 |
| **P2** | 7574 (2.0) | 53.8 | 441 (419, 471) | 530 | 1.70/− | −1.95/−1.70 |
| **P3** | 2814 (1.4) | 34.1 | 461 (439, 494) | 580 | 1.30/1.20 | −1.79/−1.70 |

[a] Number-average molecular weight determined by GPC against polystyrene standards. The data in parentheses are polydispersity indexes ($M_n/M_w$). [b] Obtained from solid films on quartz plates; data in parentheses are wavelengths of subpeaks or shoulders. [c] Peak potential of anodic ($E_{pa}$) and cathodic ($E_{pc}$) peak (vs SCE) measured between neutral and oxidized (oxidative) or reduced (reductive) states on a square platinum electrode (1.0 cm$^2$) in 0.1 M $Bu_4NClO_4$ solution in acetonitrile at a scan rate of 50 mV s$^{-1}$.

Figure 6, and the corresponding electrochemical data are summarized in Table 1. All the polymers (**P1**−**P3**) exhibit reversible n-doping process (reduction). The reduction peaks are measured to be −1.83 V for **P1**, −1.95 V for **P2**, and −1.79 V for **P3** with corresponding reoxidation peaks at −1.60, −1.70, and −1.70 V, respectively. Thus, the n-doping potentials $E^{1/2}$ are −1.72 V for **P1**, −1.82 V for **P2**, and −1.74 V for **P3**. Generally the reduction potential of the polymers is not changed remarkably with the variation of thiophene ring number in the oligothiophene blocks. This implies that the reduction properties of the polymers are dominated by the 2,6-bis(1,3,4-oxadiazolyl)phenylene segments. These reduction potentials are lower than those of 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (−1.95 to −1.94 V vs SCE),[18,39] one of the most widely used electron-transporting/hole-blocking materials, and other 1,3,4-oxadiazole-containing materials,[40−42] and are comparable with those of some good electron-transporting materials.[18] The reduction onset potentials of the polymers were measured to be −1.20 to −1.40 V. These values are comparable to that of poly(cyanoterephthalyidene) (CN-PPV) (−1.6 V vs Ag/Ag$^+$ (0.1 M)),[43] which shows good electron transport ability in PLED devices.[13] Cyclic voltammetric reduction potential values could be used as a surrogate for LUMO energy levels.[18] The results suggest that the LUMO energy levels of the polymers may be lower than those of conventional p-dope type electroluminescent polymers, and PBD and may be comparable to that of CN-PPV. Such energy levels may provide a closer match to the work function of Al when they are used as active materials in PLEDs.

A more interesting electrochemical phenomenon was found when we scanned the polymer films anodically. **P1** showed an irreversible oxidation peak at 1.75 V. A similar irreversible oxidation peak was obtained at 1.70 V for **P2**. A partially reversible oxidation peak was observed at 1.30 V with a re-reduction peak at 1.20 for **P3**. The oxidation potentials of the polymers decrease with increasing length of oligothiophene blocks in the polymers. For **P3**, the oxidation potential $E^{1/2}$ is thus calculated to be 1.25 V with the onset potential at 1.0 V. These values are lower than that of PPV and are close to those of electroluminescent substituted polythiophenes, which are hole-injection favorable electroluminescent materials. The results indicate that the HOMO of the p−n diblock copolymers can be adjusted by changing the length of oligothiophene blocks to a suitable level for hole injections when the polymers are used as electroluminescent materials in PLEDs. The comparison of electrochemical properties between **P1** and **P4** reveals the function of alkoxy groups attached on benzene ring on the redox behavior of the polymers. It leads to a slight increase of reduction potential and a decrease of oxidation potential. This is easily understood from the electron-donating character of alkoxy groups.

## Conclusions

A new series of p−n diblock conjugated copolymers composed of oligothiophenes and 1,4-bis(oxadiazolyl)-2,5-dialkyloxybenzenes were synthesized. These polymers have well-defined structures and exhibit high thermal stability. The p−n diblock structure may be a useful molecular design for tuning emissive wavelength of conjugated polymers. The emissive color of the polymers presented in this article can be tuned from blue to green to orange simply by increasing the number of the thiophene rings in oligothiophene blocks from one to three. The redox behavior of the p−n diblock conjugated copolymers can be adjusted effectively. This provides a promising approach to balance the barrier between the LUMO of an electroluminescent material and the work function of ITO and the barrier between the HOMO of the electroluminescent material and the work functions of stable metal electrodes (such as Al) in PLEDs. This balance is essential for achieving high quantum efficiency of PLEDs.

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