

Novel Photoluminescent Polymers Containing Oligothiophene and *m*-Phenylene-1,3,4-oxadiazole Moieties: Synthesis and Spectroscopic and Electrochemical Studies

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Three conjugated polymers containing oligothiophene units (from one to three thiophene rings) and aromatic 1,3,4-oxadiazole moieties have been successfully synthesized. The polymer structures were characterized and confirmed by ^1H and ^{13}C NMR, FT-IR, and elemental analysis. Thermogravimetric analysis demonstrated that the polymers are highly thermal stable. Tunable absorption (from 342 to 428 nm) and fluorescence (from 411 to 558 nm) properties of polymers were observed. The electrochemical investigation indicated that the LUMO and HOMO energy levels of the new polymers could be adjusted. It was also revealed by the electrochemical analysis that the polymers have good charge injection properties for both *p*-type and *n*-type charge carriers, as well as good color tunable luminescence and film-forming properties, which makes them potentially useful for fabricating efficient light-emitting devices.

Introduction

Polythiophenes (PTs) occupy a prominent position in polymer electronics because of their unique electronic and optical properties.^{1,2} Their amenability to chemical modifications and reversible redox properties offer additional reasons for further investigation of this class of materials.^{3,4} Recent research of conjugated polymers has been devoted to their application of light-emitting diodes (LEDs) and other optoelectronic devices.^{5–7} Among conjugated polymers used as electroluminescent materials, PTs and poly(*p*-phenylene vinylene)s (PPVs) have been most widely investigated.^{8–10} Substituted PTs permit color tuning by means of controlling the conjugation length of thiophene rings, which has been widely exploited.¹¹ However, because of their relatively low fluorescent quantum yields, their application toward this goal is limited.¹² Also, conjugated polymers such as PPV, PT, and their derivatives tend to be *p*-type (that is, prefer

transporting holes) and mainly conduct holes.¹³ Poor electron injection has been recognized to limit device efficiency.^{14,15} There are few known polymers with good electron-injection capability because of the difficulty in synthesis approaches. In the past few years, a number of polymers with oxadiazole units as side groups or as part of the polymer main chain have fit this position as efficient materials for electron transport and emission layers.^{16–18} Aromatic oxadiazole compounds such as 1,3,4-oxadiazoles have been investigated as electron-transporting materials within multilayered devices.¹⁹ Our initial work has also proven that good results could be achieved if substituted thiophene and 1,4-benzene-1,3,4-oxadiazole moiety (PRTOBO) (Figure 1) are combined as function materials used in the fabrication of blue LEDs.²⁰ Therefore, further development and exploitation of this kind of new materials with a wide range of color emission as well as a better charge balance for polymer LEDs is very interesting.

It is well established that various conjugation lengths can be obtained in the polythiophene system by judicious design of the polymer geometry.²¹ The oligothiophene blocks exhibit high π -electron density, while the aromatic oxadiazole blocks show high electron affinity. The length of the oligothiophene block leaves a possibility of tuning the luminescence of the polymers, whereas the aromatic oxadiazole block facilitates the electron-transfer proper-

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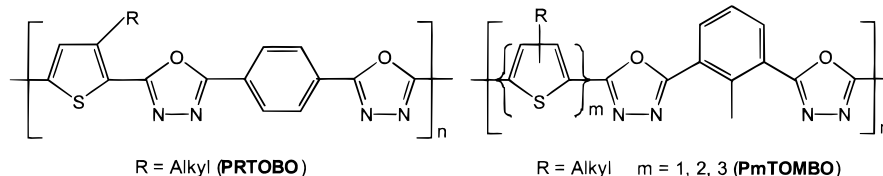


Figure 1. Novel polymers containing oligothiophenes and aryl-1,3,4-oxadiazole.

ties of the polymers when used in LEDs. Materials composed of a hole-conducting block and an electron-transporting segment may combine properties of both components to produce new properties that are not possible with either one separately. PLED devices based on such materials can be expected to have high quantum efficiencies because the limitation of low electron affinity of normal emissive polymeric materials used could be improved by introducing the oxadiazole segment into the polymer backbone. In addition, it is expected that single layer devices can be fabricated with a satisfactory efficiency performance, and such an approach can simplify the device configuration and diminish problems in multilayer devices such as the space-charge and tunneling of accumulated holes.

Herein we are further extending our effort toward these novel materials. We have successfully obtained three new polymers (PmTOMBO) (see Figure 1) with different emission colors. Such a design strategy provides a feasible way for the wavelength tuning of new emissive polymers. With the use of *m*-phenylene in the polymer main chain, the repulsive interaction between the adjacent aromatic rings results in a distortion of the π -conjugated backbone.²² The emitting colors of such polymers, from blue to orange, were achieved by varying the conjugation length of oligothiophene moiety.

Experimental Section

The synthetic procedures for the polymers are depicted in Schemes 1 and 2.

Measurements. 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 disks. UV-visible and fluorescence spectra were obtained on a Shimadzu UV 3101PC UV-Vis-NIR spectrophotometer and Perkin-Elmer LS 50B luminescence spectrometer with a Xenon lamp as light source, respectively. 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 an air or nitrogen flow rate of 75 cm³/min. Differential scanning calorimetry (DSC) was run on a DuPont DSC 2910 module in conjunction with the DuPont Thermal Analyst system. Elemental analysis was performed on a Perkin-Elmer 240C elemental analyzer for C, H, N, and S determinations. Cyclic voltammograms were obtained using an EG&G model 273A potentiostat/galvanostat under argon atmosphere. All potentials were measured against a Ag/AgNO₃ 0.10 mol/dm³ (acetonitrile) electrode (0.34 V vs SCE), and all experimental values in this report were corrected with respect to SCE. GPC analysis was conducted with a Perkin-Elmer model 200 HPLC system equipped with Phenogel MXL and MXM columns, using polystyrene as standard and THF as eluant.

Materials. Diethyl ether was distilled over sodium/benzophenone, and hexane was distilled over calcium hydride. *N*-Methylpyrrolidone (NMP), *N,N,N,N*-tetramethylethylene-

diamine (TMEDA), and pyridine (purchased from Aldrich, A.R. grade) were redistilled prior to use. 2,2'-Bithiophene, 1-bromodecane, dichloro-[1,3-bis(diphenylphosphino)propane]nickel(II) (Ni(dppp)Cl₂), magnesium turnings, thionyl chloride, and phosphorus oxychloride were used as received (Fluka or Aldrich chemicals).

Synthesis of Monomers. 3-Octylthiophene.²³ Into a three-necked flask containing Ni(dppp)Cl₂ (193 mg, 0.36 mmol) was injected through a syringe 3-bromothiophene (20.0 g, 0.122 mol) in 100 mL of diethyl ether. The reaction mixture cooled to 0 °C and was placed under N₂ and 1-octylmagnesium bromide prepared from 0.158 mol of 1-bromooctane and 4.10 g (0.174 mol) of Mg in 28 mL of dry ether was added dropwise into the mixture over 1.5 h. After refluxing for an additional 24 h, the reaction mixture was quenched with 0.2 mol/dm³ HCl and extracted with diethyl ether. The organic phase was washed three times with H₂O and once with saturated NaCl and then dried over anhydrous Na₂SO₄. After removal of the solvent, the crude product was distilled (80–81 °C/0.2 mmHg) to give 17.1 g (73%) of the product. MS *m/z*: 196. ¹H NMR (CDCl₃, ppm): δ 7.23 (d, *J* = 4.5 Hz, 1H), 6.93 (m, 2H), 2.62–2.58 (t, *J* = 7.3 Hz, 2H), 1.64–1.56 (m, 2H), 1.38–1.20 (m, 10H), 0.88–0.85 (t, *J* = 5.7 Hz, 3H).

3,3',5,5'-Tetrabromo-2,2'-bithiophene.²⁴ Bromine (190 g, 0.59 mol) was added dropwise over 1.5 h to a solution of 2,2'-bithiophene (46.2 g, 0.278 mol) in the mixed solvent of glacial acetic acid (200 mL) and chloroform (450 mL) at a temperature of 5–15 °C. The mixture was stirred at room temperature for 5 h and then under reflux for 24 h. After the mixture was cooled to room temperature, 500 mL of 10% KOH aqueous solution was added. The mixture was extracted with CHCl₃ twice; the combined chloroform layer was washed with water, dried over anhydrous MgSO₄, and filtered; and the solvent was removed by rotary evaporation. Recrystallization from ethanol afforded a light yellow crystal in a yield of 89%. Mp: 139–141 °C (lit. 139–140 °C). MS *m/z*: 482. ¹H NMR (CDCl₃, ppm): δ 7.05 (s, 2H).

3,3'-Dibromo-2,2'-bithiophene.²⁵ 3,3',5,5'-Tetrabromo-2,2'-bithiophene (48.2 g, 0.10 mol) is added in portions within 0.5 h to a refluxing zinc powder (25.2 g, 0.40 mol) dispersion in 500 mL of ethanol containing 50 mL of water, 120 mL of acetic acid, and 10 mL of 2 mol/dm³ HCl. After refluxing for additional 2 h and then cooling to room temperature, the mixture was filtered and washed three times with ethanol, and the filtrate was collected. The solvent was removed by evaporation, and then 250 mL of H₂O was added. The mixture was extracted with ether, and the combined ether was washed with water, dried over anhydrous MgSO₄, and filtered. Removal of the solvent and recrystallization from hexane gave a light green crystal (yield 79%). Mp: 98–99 °C. MS *m/z*: 324. ¹H NMR (CDCl₃, ppm): δ 7.41 (d, *J* = 5.3 Hz, 2H), 7.08 (d, *J* = 5.3 Hz, 2H).

3,3'-Didecyl-2,2'-bithiophene.²⁶ A Grignard reagent prepared from 1-bromodecane (44.2 g, 0.20 mol) and Mg turnings (5.0 g, 0.21 mol) in 60 mL of diethyl ether was added dropwise to a solution of 3,3'-dibromo-2,2'-bithiophene (22.7 g, 0.070 mol) and Ni(dppp)Cl₂ (622 mg, 1.19 mmol) in 100 mL of diethyl ether at 0 °C. After the addition was complete, stirring was

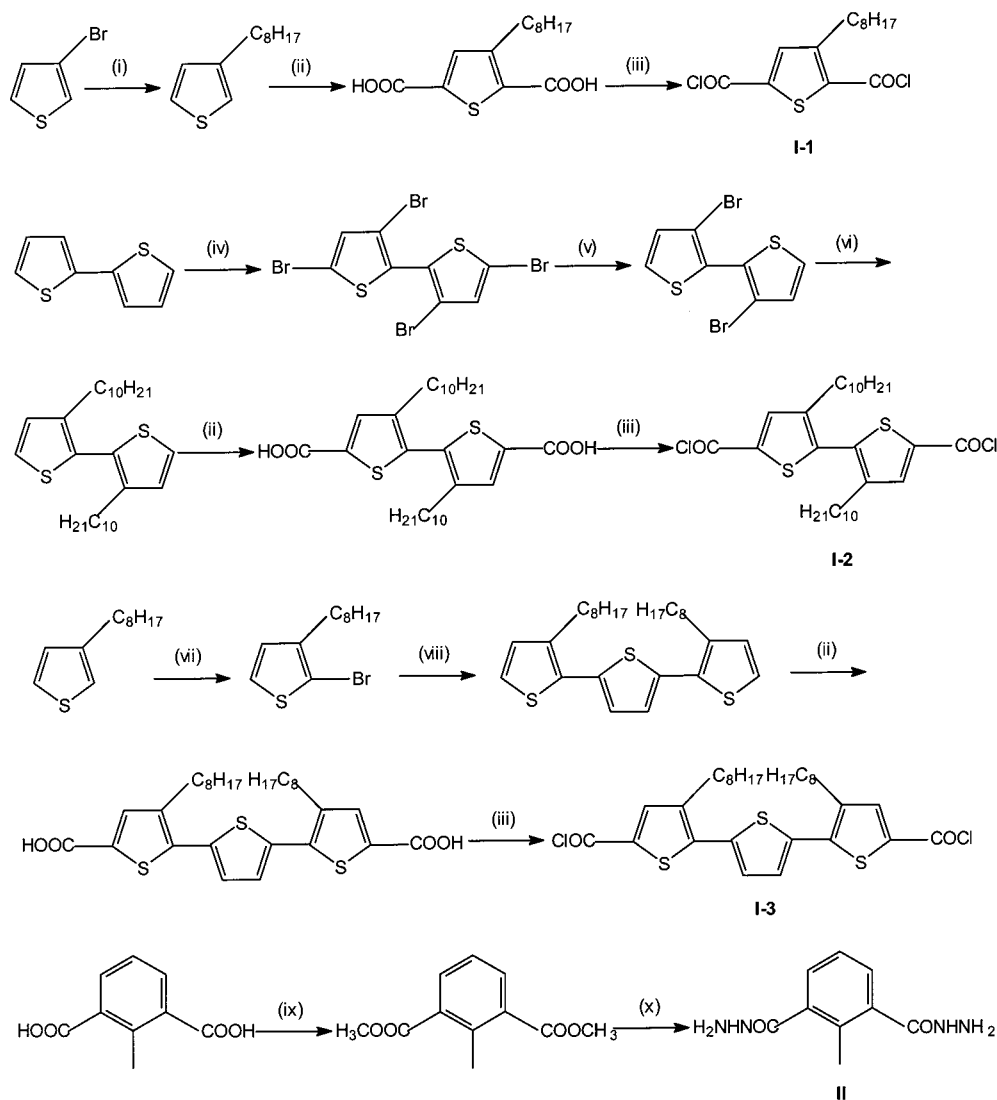
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Scheme 1. Synthetic Route to Monomers^a

^aReagents and conditions: (i) 1-bromooctane, Mg, Ni(dppp)Cl₂, diethyl ether; (ii) *n*-BuLi, TMEDA, dry ice, -70 °C to rt; (iii) SOCl₂; (iv) bromine, AcOH/CHCl₃; (v) Zn, EtOH/AcOH/HCl; (vi) 1-bromodecane, Mg, Ni(dppp)Cl₂, diethyl ether; (vii) NBS, CHCl₃/AcOH; (viii) Mg/THF, 2,5-dibromothiophene, Ni(dppp)Cl₂, diethyl ether; (ix) CH₃OH/H₂SO₄; (x) NH₂NH₂·H₂O, MeOH.

continued for 24 h under refluxing, and then the reaction was quenched with 0.2 mol/dm³ of HCl and extracted with diethyl ether. The combined diethyl ether solution was dried over anhydrous Na₂SO₄ and filtered, and the solvent was removed by rotary evaporation. Vacuum distillation (130–132 °C/0.05 mbar) provided 22.2 g (71%) pure product. ¹H NMR (CDCl₃, ppm): δ 7.29 (d, *J* = 5.4 Hz, 2H), 6.98 (d, *J* = 5.4 Hz, 2H), 2.65–2.53 (t, *J* = 7.5 Hz, 4H), 1.65–1.57 (m, 4H), 1.46–1.26 (m, 28H), 0.93–0.88 (t, *J* = 6.2 Hz, 6H). Anal. Calcd for C₂₈H₄₆S₂: C, 75.34; H, 10.31; S, 14.35. Found: C, 75.42; H, 9.76; S, 14.09.

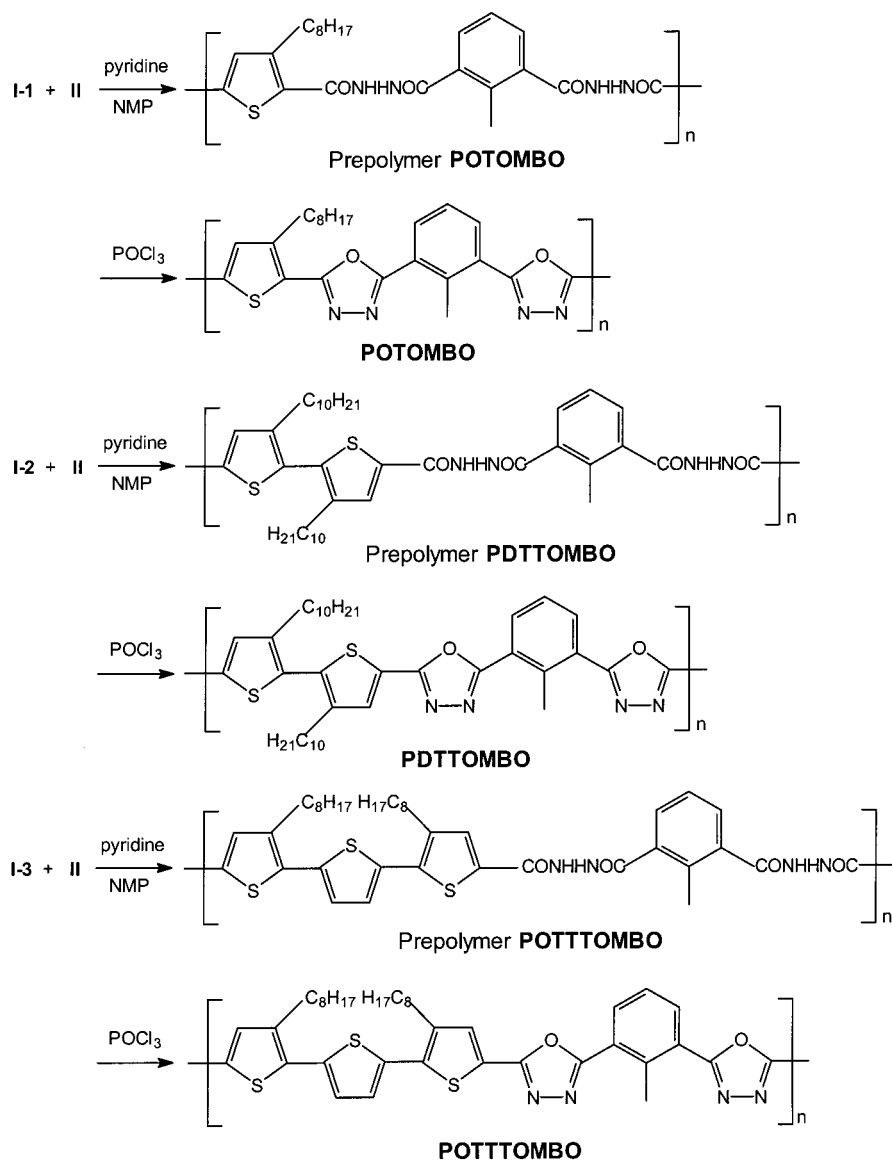
2-Bromo-3-octylthiophene.²⁷ Into a dry round-bottom flask was placed 100 mL of acetic acid and 100 mL of CHCl₃, and the flask was then purged with nitrogen for 10 min. Then 19.6 g (0.10 mol) of freshly distilled 3-octylthiophene was added. The mixture was cooled to 5 °C, whereupon 17.0 g (0.095 mol) of NBS was added over a period of 2 h while the temperature was maintained at 5–10 °C. The mixture was stirred overnight and cooled in an ice bath, followed by the addition of 100 mL of 0.1 mol/dm³ HCl. The mixture was extracted with CHCl₃. The CHCl₃ layer was washed with water several times until it reached a pH of ~6 and dried over

anhydrous MgSO₄. The solvent was removed by rotary evaporation. The residue was reduced-distilled (90–92 °C/0.5 mmHg) to yield 21.5 g (82%) of product. ¹H NMR (CDCl₃, ppm): δ 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). MS *m/z*: 275. Anal. Calcd for C₁₂H₁₉BrS: 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'-Diocetyl-2,2';5',2''-terthiophene.²⁸ The Grignard reagent of 3-octylthienyl-2-magnesium bromide, obtained from the reaction of 15.1 g (0.055 mol) 2-bromo-3-octylthiophene in 200 mL of ether with 1.5 g (0.062 mol) of Mg, was added dropwise into a mixture of 2,5-dibromothiophene 6.05 g (0.025 mol) and 216 mg of Ni(dppp)Cl₂ (0.8 mol %) catalyst in ether over 1.5 h. After refluxing for additional 20 h, the reaction mixture was quenched with 0.2 mol/dm³ HCl and extracted with ether. The organic phase was washed with H₂O three times and once with NaCl and then was dried over Na₂SO₄. After removal of solvent, a dark brown liquid was obtained. It was diluted with hexane, decolorized with active charcoal, and then chromatographed on silica gel using hexane as eluant. The yield of the final compound (8.0 g, yellow liquid) after flash chromatography is 68%. MS *m/z*: 472; HRMS C₂₈H₄₀S₃: calcd

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Scheme 2. Synthetic Route to Prepolymers and Final Polymers^a

^a Reagents and conditions: (i) LiCl, pyridine, NMP, 80 °C; (ii) POCl₃, reflux.

472.22922; found mass 472.22910; formula C₂₈H₄₀S₃. ¹H NMR (CDCl₃, ppm): δ 7.17 (d, *J* = 5.6 Hz, 2H), 7.04 (s, 2H), 6.93 (d, *J* = 5.6 Hz, 2H), 2.58 (t, *J* = 7.5 Hz, 4H), 1.70–1.59 (m, 4H), 1.31–1.26 (m, 20H), 0.89–0.85 (t, *J* = 4.5 Hz, 6H). ¹³C NMR (CDCl₃, ppm): δ 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 C₂₈H₄₀S₃: C, 71.19; H, 8.47; S, 20.34. Found: C, 71.22; H, 8.11; S, 20.87.

3-Octylthiophene-2,5-dicarboxylic Acid.²⁹ To a N₂-flushed flask initially containing TMEDA (18.3 g, 0.158 mol) in 30 mL of hexane and a solution of *n*-BuLi (1.6 mol/dm³ solution in hexane, 98 mL, 0.158 mol) under a nitrogen atmosphere was added 12.4 g (0.0633 mol) of 3-octylthiophene at room temperature. After stirring at room temperature for 1 h, the mixture was refluxed for a further 30 min, cooled to –70 °C, and slowly poured under N₂ into a 500 mL flask half-filled with crushed dry ice. The mixture was warmed to room temperature overnight and then poured into 10 mol/dm³ HCl and ice. The aqueous layer was extracted with ether (two 100 mL portions). The ether extract was extracted with 10% NaOH (100 mL), and the aqueous layer was acidified with 10 mol/dm³ HCl. The mixture was extracted with ether (two 50 mL portions), and the ether extract was washed with water and

saturated NaCl and dried using MgSO₄. Evaporation of the ether and recrystallization of the white powder from ethanol–water afforded 14.0 g (78%) of product. MS *m/z*: 284. ¹H NMR (CDCl₃, ppm): δ 7.69 (s, 1H), 2.62–2.57 (t, *J* = 7.5 Hz, 2H), 1.60–1.28 (m, 12H), 0.87–0.82 (t, *J* = 6.5 Hz, 3H). Anal. Calcd for C₁₄H₂₀O₄S: C, 59.15; H, 7.04; S, 11.27. Found: C, 58.53; H, 7.18; S, 11.49.

3,3'-Didecyl-2,2'-bithiophene-5,5'-dicarboxylic Acid. The compound was prepared as described above under the same condition using TMEDA (2.9 g, 0.025 mol) and a solution of *n*-BuLi (1.5 mol/dm³ solution in hexane, 17 mL, 0.025 mol) in 30 mL of hexane. 3,3'-Didecyl-2,2'-bithiophene (4.46 g, 0.010 mol) was added under the protection of nitrogen at room temperature. Recrystallization from ethanol–water yielded 4.1 g (76%) of a pure light yellow powder product. ¹H NMR (CDCl₃, ppm): δ 7.76 (s, 2H), 2.55–2.50 (t, *J* = 7.7 Hz, 4H), 1.64–1.56 (m, 4H), 1.38–1.23 (m, 28H), 0.89–0.85 (t, *J* = 5.5 Hz, 6H). Anal. Calcd for C₃₀H₄₆O₄S₂: C, 67.42; H, 8.61; S, 11.98. Found: C, 67.70; H, 8.75; S, 12.14.

3,3'-Dioctyl-2,2';5',2''-terthiophene-5,5''-dicarboxylic Acid. The compound was prepared as described above under the same condition using 3.5 g (7.4 mmol) 3,3''-dioctyl-2,2';5',2''-terthiophene, TMEDA, hexane, and *n*-BuLi. A yellow powder was obtained upon recrystallization from ethanol. Yield: 83%. MS *m/z*: 560. HRMS C₃₀H₄₀O₄S₃: calcd 560.20886;

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found mass 560.21109; formula $C_{30}H_{40}O_4S_3$. 1H NMR (acetone- d_6 , ppm): δ 7.68 (s, 2H), 7.35 (s, 2H), 2.89–2.84 (t, $J = 7.6$ Hz, 4H), 1.76–1.74 (m, 4H), 1.42–1.27 (m, 20H), 0.89–0.84 (t, $J = 6.5$ Hz, 6H). ^{13}C NMR (acetone- d_6 , 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, 64.43; H, 7.14; S, 17.14. Found: C, 64.53; H, 7.29; S, 17.54.

3-Octylthiophene-2,5-dicarbonyl Chloride (I-1). A 25 mL portion of distilled thionyl chloride was added to 5 g of 3-octylthiophene-2,5-dicarboxylic acid. The mixture was heated at reflux for 5 h, and the excess thionyl chloride was removed under reduced pressure. The residue was distilled under vacuum to give a light yellow oil at 132–134 °C/0.1 mbar, 5.0 g (89%). MS m/z : 321. 1H NMR ($CDCl_3$, ppm): δ 7.78 (s, 1H), 2.95–2.90 (t, $J = 7.6$ Hz, 2H), 1.66–1.56 (m, 2H), 1.38–1.27 (m, 10H), 0.90–0.85 (t, $J = 7.0$ Hz, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 159.70, 158.61, 154.35, 142.90, 139.79, 138.84, 31.70, 30.28, 29.51, 29.24, 29.13, 29.02, 22.53, 13.95. Anal. Calcd for $C_{14}H_{18}Cl_2O_2S$: C, 52.34; H, 5.65; S, 9.98; Cl, 22.07. Found: C, 52.47; H, 5.78; S, 10.03; Cl, 22.18.

3,3'-Didecyl-2,2'-bithiophene-5,5'-dicarbonyl Chloride (I-2). A 15 mL portion of thionyl chloride was added to 3.0 g (5.62 mmol) of 3,3'-didecyl-2,2'-bithiophene-5,5'-dicarboxylic acid. The mixture was heated at reflux for 5 h, and then the excess thionyl chloride was removed under reduced pressure. The residue was recrystallized from hexane to give 2.9 g (92%) of a yellow powder. Mp: 68–69 °C. 1H NMR ($CDCl_3$, ppm): δ 7.85 (s, 2H), 2.56–2.51 (t, $J = 7.6$ Hz, 4H), 1.57–1.54 (m, 4H), 1.23 (m, 28H), 0.89–0.85 (t, $J = 6.6$ Hz, 6H). ^{13}C NMR ($CDCl_3$, ppm): δ 159.32, 145.06, 138.96, 138.68, 137.18, 31.77, 30.32, 29.45, 29.36, 29.18, 29.16, 29.10, 28.81, 22.56, 13.98. Anal. Calcd for $C_{30}H_{44}Cl_2O_2S_2$: C, 63.03; H, 7.76; S, 11.22. Found: C, 62.38; H, 8.01; S, 11.54.

3,3'-Diocetyl-2,2';5,5''-terthiophene-5,5''-dicarbonyl Chloride (I-3). The compound was prepared as described above under the same condition using 2.6 g (4.64 mmol) of 3,3''-diocetyl-2,2';5,5''-terthiophene-5,5''-dicarboxylic acid reacted with 25 mL of thionyl chloride for 8 h. MS m/z : 596. HRMS $C_{30}H_{38}Cl_2O_2S_3$: calcd 596.14111; found mass 596.14220; formula $C_{30}H_{38}Cl_2O_2S_3$. 1H NMR ($CDCl_3$, ppm): δ 7.80 (s, 2H), 7.29 (s, 2H), 2.83–2.78 (t, $J = 7.9$ Hz, 4H), 1.71–1.64 (m, 4H), 1.46–1.20 (m, 20H), 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 $C_{30}H_{38}Cl_2O_2S_3$: C, 60.28; H, 6.41; S, 16.09. Found: C, 59.98; H, 7.19; S, 17.21.

2,6-Dicarbonylhydrazide-toluene (II). A 7.0 g (0.034 mol) portion of dimethyl 2-methylisophthalate was added into a solution of 10 mL of monohydrazine hydrate (99%) in 70 mL of CH_3OH . The reaction mixture was refluxed for 24 h. After cooling and filtering, a white precipitate was obtained. The precipitate was washed with chloroform and dried under vacuum to give the product as a white powder. Mp: 108.0–109.5 °C. MS m/z : 208. 1H NMR (DMSO- d_6 , ppm): δ 9.45 (s, 2H), 7.31–7.23 (d, $J = 8.8$ Hz, 3H), 4.46 (s, 4H), 2.28 (s, 3H). ^{13}C NMR ($CDCl_3$, ppm): δ 168.17, 136.95, 133.02, 127.86, 125.11, 16.19. Anal. Calcd for $C_9H_{12}N_4O_2$: C, 51.92; H, 5.77; N, 26.92. Found: C, 52.19; H, 5.68; N, 26.52.

Synthesis of Polymers. Prepolymer of POTOMBO. Poly(3-octylthiophene-2,5-dihydrazide-co-toluene-2,6-dihydrazide).³⁰ A 3.2 g (0.010 mol) portion of 3-octylthiophene-2,5-dicarbonyl chloride (I-1) was added with stirring into a solution containing 2.08 g (0.010 mol) of II, 20 mL of NMP, 0.10 g of LiCl, and 0.02 mol of pyridine at room temperature for 3 h. The viscous solution was then poured into 200 mL of water, and the precipitated polymer was collected, washed with water and ethanol, and then dried in a vacuum at 60 °C to give a white powder (4.0 g, 90%). Anal. Calcd for $C_{23}H_{28}N_4O_2S$: C, 60.51; H, 6.18; N, 12.27; S, 7.02. Found: C, 58.89; H, 6.07; N, 11.44; S, 6.82.

Prepolymer of PDDTOMBO. Poly(3,3'-didecyl-2,2'-bithiophene-5,5'-dihydrazide-co-toluene-2,6-dihydrazide). A 0.242 g (0.424 mmol) portion of 3,3'-didecyl-2,2'-bithiophene-5,5'-dicarbonyl chloride (I-2) was added into a stirred solution of 2,6-dicarbonylhydrazide-toluene (II) (88.2 mg, 0.424 mmol) in 20 mL of NMP containing 0.10 g of LiCl and 0.01 mol of pyridine at room temperature. After heating at 80 °C for 3 h, the brown viscous solution was cooled to 50 °C and then poured into 100 mL of deionized water. The precipitated polymer was filtered, washed with water and then ethanol, and finally was dried under vacuum at 60 °C to give 0.288 g of a light yellow powder. Yield: 95%. Anal. Calcd for $C_{39}H_{54}N_4O_4S_2$: C, 66.25; H, 7.70; N, 7.92; S, 9.07. Found: C, 64.46; H, 7.84; N, 8.18; S, 9.02.

Prepolymer of POTTOMBO. Poly(3,3''-diocetyl-2,2';5,5''-terthiophene-5,5''-dihydrazide-co-toluene-2,6-dihydrazide). A 0.500 g (0.837 mmol) portion of 3,3''-diocetyl-2,2';5,5''-terthiophene-5,5''-dicarbonyl chloride was added with stirring into a solution containing 0.174 g (0.837 mmol) of II, 15 mL of NMP, 0.05 g of LiCl, and 1 drop of pyridine at room temperature for 5 h. The viscous solution was then poured into 100 mL of deionized water. The polymer was filtered, washed with water and ethanol, and then dried in a vacuum at 60 °C to give a light yellow powder (0.54 g, 90%). Anal. Calcd for $C_{39}H_{48}N_4O_4S_3$: C, 63.90; H, 6.60; N, 7.64; S, 13.12. Found: C, 62.97; H, 6.89; N, 7.56; S, 13.31.

Poly(3-octylthiophene-2,5-diyl-1,3,4-oxadiazole-2,5-diyl-toluene-2,6-diyl-1,3,4-oxadiazole-2,5-diyl) (POTOMBO).³¹ A 0.457 g portion of the prepolymer of POTOMBO and 15 mL of $POCl_3$ were refluxed for about 10 h and then poured into water. The filtered precipitate was washed with water, ethanol, and ether and then dried under vacuum to afford a light yellow powder polymer (0.368 g, 87%). 1H NMR (TFA- $d/CDCl_3$, ppm): δ 8.21 (d, br, 2H), 7.97 (s, br, 1H), 7.69 (m, br, 1H), 3.18–3.15 (t, br, 2H), 3.01 (s, 3H), 1.81–1.77 (br, 2H), 1.44–1.27 (br, 10H), 0.88–0.84 (t, br, 3H). Anal. Calcd for $C_{23}H_{24}N_4O_2S$: C, 65.69; H, 5.75; N, 13.32; S, 7.62. Found: C, 64.34; H, 5.48; N, 12.54; S, 7.46.

Poly(3,3'-didecyl-2,2'-bithiophene-5,5'-diyl-1,3,4-oxadiazole-2,5-diyl-toluene-2,6-diyl-1,3,4-oxadiazole-2,5-diyl) (PDDTOMBO). A mixture of 200 mg of the prepolymer of PDDTOMBO and 25 mL of $POCl_3$ was refluxed for 6 h. After cooling, the reaction mixture was poured into water. The precipitate was collected by filtration, washed with water, ethanol, and then ether, and finally dried under vacuum. A brown powder was obtained (180 mg, 93%). 1H NMR ($CDCl_3$, ppm): δ 8.17 (br, 2H), 7.77 (s, br, 2H), 7.57 (br, 1H), 3.12 (s, br, 3H), 2.64 (s, br, 4H), 1.84–1.47 (s, br, 4H), 1.47–1.23 (br, 28H), 0.90–0.84 (br, 6H). ^{13}C NMR ($CDCl_3$), δ 163.6, 160.5, 144.6, 138.9, 132.4, 131.4, 126.5, 126.4, 125.2, 124.9, 31.8, 30.5, 29.5, 29.4, 29.2, 29.1, 29.0, 28.9, 22.6, 19.3, 14.0 ppm. Anal. Calcd for $C_{39}H_{50}N_4O_2S_2$: C, 69.81; H, 7.51; N, 8.35; S, 9.56. Found: C, 68.34; H, 7.25; N, 7.98; S, 9.30.

Poly(3,3''-diocetyl-2,2';5,5''-terthiophene-5,5''-diyl-1,3,4-oxadiazole-2,5-diyl-toluene-2,6-diyl-1,3,4-oxadiazole-2,5-diyl) (POTTOMBO). A mixture of 400 mg of prepolymer POTTOMBO and 20 mL of $POCl_3$ was refluxed for 12 h. After cooling, the reaction mixture was poured into water. The precipitate was collected by filtration, washed with water, ethanol, and then ether, and finally dried under vacuum. An orange powder was obtained (320 mg, 84%). 1H NMR ($CDCl_3/TFA-d$, ppm): δ 8.19–8.17 (d, $J = 6.2$ Hz, 2H), 7.85 (s, 2H), 7.73–7.66 (m, 1H), 7.33 (s, 2H), 2.97 (s, 3H), 2.92–2.87 (t, $J = 7.5$ Hz, 4H), 1.74–1.72 (m, br, 4H), 1.43–1.28 (m, br, 20H), 0.87–0.85 (t, br, $J = 6.0$ Hz, 6H). Anal. Calcd for $C_{39}H_{44}N_4O_2S_3$: C, 67.21; H, 6.36; N, 8.04; S, 13.80. Found: C, 65.91; H, 6.59; N, 7.86; S, 13.90.

Results and Discussion

The polymers were synthesized through precursor polymers of polyhydrazides that were prepared by polycondensation of α,ω -dicarbonyl chlorides of alkyl-substi-

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tuted oligothiophenes with 2,6-dihydrazide-toluene in NMP in the presence of LiCl and pyridine.³² The dicarbonyl chlorides of alkyl-substituted oligothiophenes and 2,6-dihydrazide-toluene were synthesized following the routes depicted in Scheme 1. For the synthesis of the dicarbonyl chlorides, the oligomers of alkyl-substituted thiophene were synthesized first, and then the carboxylation at the α -positions of the thiophene rings through *n*-BuLi and dry ice and a following reaction with SOCl₂ were performed.³³ The 2,6-dihydrazide-toluene (**II**) was obtained by the reaction of dimethyl-2-methylisophthalate with excess hydrazine monohydrate. The prepolymers-polyhydrazides were obtained as white or light yellow powders. They are not soluble in common organic solvents but dissolve completely in NMP. As shown in Scheme 2, the polyhydrazides were converted to the final polymers via a cyclodehydration reaction by refluxing in POCl₃, which was used as both dehydrating reagent and solvent. Polymers **POTOMBO**, **PDTTOMBO**, and **POTTOMBO** were obtained as light yellow, yellow, and orange powders, respectively. **POTOMBO** and **POTTOMBO** are partially soluble in chloroform and THF. Polymer **PDTTOMBO** is completely soluble in these two solvents. However, all three polymers readily dissolve in chloroform with a little amount of trifluoroacetic acid (TFA) to give clear solutions. Further purification of the polymers was carried out by reprecipitation in which the polymer was dissolved in CHCl₃ or CHCl₃ with a little amount of TFA and then precipitated in methanol.

Structural Elucidation. The successful cyclodehydration could be confirmed by the FT-IR spectra. Two intensive absorption bands at 1660 and 3246 cm⁻¹ assigned to the stretching vibration of the carbonyl groups and N-H in the polyhydrazides, respectively, disappeared after the treatment with POCl₃. In the meantime, two new peaks at around 1586 and 1081 cm⁻¹ attributed to the 1,3,4-oxadiazole ring stretching appeared in the final polymers.³⁴ The weak peaks at 1650 cm⁻¹ and the negligible absorption in the range of 3200–3400 cm⁻¹ may be caused by the end groups of the polymers' chains. This result also agrees well with the report by Pei et al.¹⁷

The chemical structures of the polymers were further confirmed by ¹H and ¹³C NMR and elemental analysis. The ¹H and ¹³C NMR spectra were obtained either in CDCl₃ or in CDCl₃/TFA-*d*. All of the chemical shift values are referenced to tetramethylsilane (TMS, 0 ppm). Since the resonance of the polymers is broadened, the coupling constants could not be obtained. In the spectrum of **POTOMBO**, there are three clear single broad peaks in the aromatic region, which correspond to the β -proton on the thiophene ring at δ 7.97 ppm (1H) and the protons on the benzene ring at δ 8.21 (br, 2H) and 7.67 (m, 1H) ppm, respectively. The aliphatic protons of methylenes attaching on the thiophene rings are assigned with less information regarding the resonance constants as a result of the broad peaks as mentioned above. The NMR spectra of polymer **PDTTOMBO** shows a little difference from that of polymer **POTOMBO**. For polymer **POTTOMBO**, there are four signals in the aromatic region, which are assigned to two kinds of protons on the thiophene

rings and benzene rings. The chemical shift at δ 7.85 ppm was assigned to the substituted thiophene ring, and that at δ 7.33 ppm was assigned to the unsubstituted bithiophene rings. The other two protons at δ 8.19 ppm (d, *J* = 6.6, 1H) and 7.66 ppm (m, 2H) are assigned to the benzene rings. The peaks at around δ 3.00 ppm corresponding to the aliphatic chains are assigned to the methyl group on benzene ring and the methylene groups adjacent to the thiophene rings. Comparing the asymmetrically substituted polymer **POTOMBO** to the symmetrically substituted polymers **PDTTOMBO** and **POTTOMBO**, it is interesting to note that the ¹H NMR spectra are not more complicated. The phenomena are observed in the random polymerization of asymmetric monomers of thiophenes, which leads to both head-to-head and head-to-tail linkages. Since the adjacent thiophene rings are separated by two oxadiazole rings and one benzene ring in **POTOMBO**, the interactions between the side chains on the thiophene rings with head-to-head and/or head-to-tail linkages diminish dramatically. Therefore, the effects of such structural defects on the optoelectronic properties are negligible. In the ¹³C NMR spectrum of **PDTTOMBO**, there are 10 well-resolved signals in the aromatic region that correspond to the 10 aromatic carbons in the polymer. The 10 aliphatic signals are assigned to the alkyl long chains on the thiophene rings. The ¹³C NMR spectra of the other two polymers have not been obtained because of the low signals of the samples. The NMR spectra supported the conclusion that the polymers have well-defined structures and the conversion from prepolymers to final polymers is almost complete. The elemental compositions of the polymers also confirmed the structures of the polymers. The results are summarized in the Experimental Section.

Molecular Weights and Thermal Properties. The molecular weights of the polymers were measured by means of GPC using THF as eluant against polystyrene standards. Because polymers **POTOMBO** and **POTTOMBO** are partially soluble in THF, only the molecular weights of the THF-soluble parts of the polymers were measured. The molecular weights of the THF-soluble parts of polymers **POTOMBO** and **POTTOMBO** were measured as $M_w = 6890$ ($M_w/M_n = 1.8$) and 5734 ($M_w/M_n = 2.0$), respectively. Polymer **PDTTOMBO** is completely soluble in THF; thus M_w is 35105 with a polydispersity of 1.41. The actual molecular weights of the partially soluble polymers should be higher than these measured values because of the insoluble parts with higher molecular weights.

The thermal stability of the polymers was determined by thermogravimetric analysis (TGA) under nitrogen. All of the polymers exhibited an onset degradation temperature higher than 300 °C under nitrogen. All of the degradation patterns for the three polymers are quite similar, with a main weight loss step in the range of 380–450 °C. The result reveals that the polymers have good thermal stability. The glass transition temperatures (T_g) of the polymers were measured by DSC. T_g is 127.8 °C for **POTOMBO**, 60.2 °C for **PDTTOMBO**, and 122.4 °C for **POTTOMBO**. The relatively lower T_g for **PDTTOMBO** might be owing to the bithiophene segment in the polymer main chain with a head-to-head linkage.

Optical Properties. The absorption and fluorescence spectra of spin-coated films of the polymers are shown in Figure 2. The absorption spectra of the polymers show a broad main peak with a couple of the minor shoulders

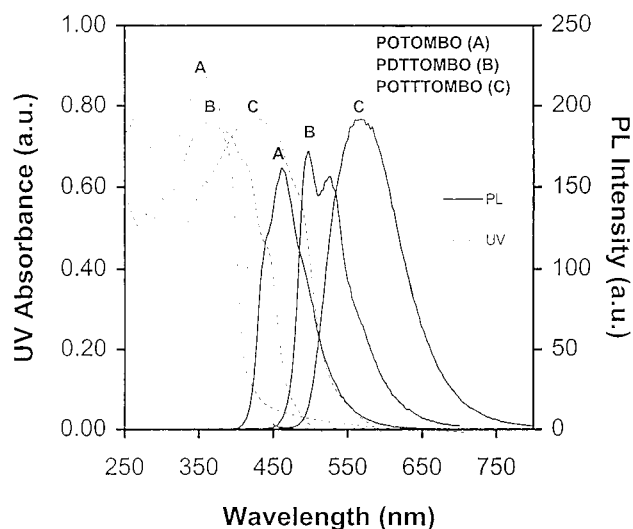
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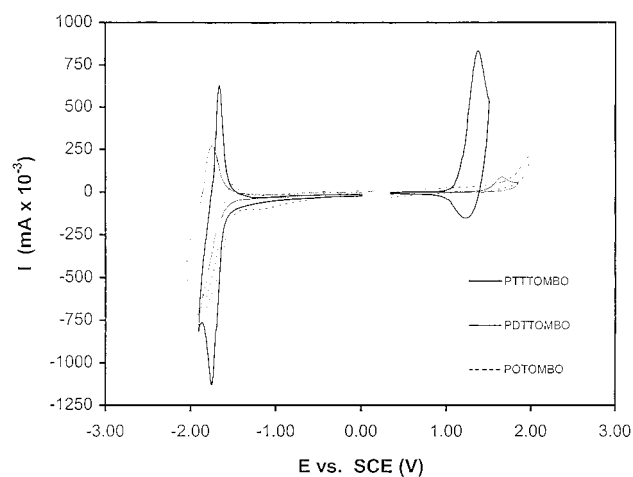
Table 1. Characteristics and Physical Properties of New Polymers

polymer	T_g (°C)	M_w (g/mol)	λ_{max} (nm/abs)	λ_{max} (nm/abs)	λ_{max} (nm/PL)	λ_{max} (nm/PL)
POTOMBO	127.8	6890		358 (film)		462 (film)
PDTTOMBO	60.2	35105	342 (CHCl ₃)	376 (film)	444/462 (CHCl ₃)	498/526 (film)
POTTOMBO	122.4	5734		430 (film)		568 (film)

**Figure 2.** The UV-vis absorption and fluorescent spectra of polymer films spin-coated on quartz plates.

at the low energy side. As expected, gradual bathochromic shift of absorption spectra is exhibited with increase in the length of oligothiophenes in the polymers. The absorption maximum increases from **POTOMBO** ($\lambda_{max} = 358$ nm) to **PDTTOMBO** ($\lambda_{max} = 376$ nm) to **POTTOMBO** ($\lambda_{max} = 430$ nm). The emission spectra of the polymers were obtained under excitation at the main absorption wavelength of each polymer. Polymer **POTOMBO** emits intense blue light, while polymers **PDTTOMBO** and **POTTOMBO** emit green and pale orange light, respectively. The emission spectra of polymers are shown together with their UV spectra in Figure 2. The emissive maximums are 462 nm for **POTOMBO**, 498 nm with a subpeak at 526 nm for **PDTTOMBO**, and 568 nm for **POTTOMBO**. The physical properties of the three polymers are summarized in Table 1.

The effective tuning of the emissive wavelength of the new series of polymers could be attributed to the remarkable difference of band gap between oligothiophenes and 2,6-bis(1,3,4-oxadiazole-2,5-diyl)-toluene, the two blocks constructing the polymers alternatively. As demonstrated by head-to-tail regioregular poly(3-alkylthiophenes),³⁵ oligothiophenes may have low band gap, whereas most of conjugated polymers containing 1,3,4-oxadiazole and molecular materials exhibit quite large band gaps (larger than 3.0 eV).³⁶ The new polymers could be regarded as derivatives of polythiophene in which the 2,6-bis(1,3,4-oxadiazole-2,5-diyl)-toluene is inserted. The extension of conjugation along the backbone of polythiophene is limited or changed as a result of this insertion, and the total conjugated properties of the resultant polymers will be varied with the change of the length of the oligothiophene blocks.

**Figure 3.** Cyclic voltammograms of **POTOMBO**, **PDTTOMBO**, and **POTTOMBO** films on Pt electrodes in acetonitrile supported by Bu₄ClO₄ (0.10 mol/dm³) at a scan rate of 50 mV/s.

Electrochemical Studies. Cyclic voltammetry (CV), a dynamic electrochemical method, is an important technique for measuring band gaps, electron affinities, and work functions of various conjugated polymers. The electrochemical studies of the polymers were carried out in *n*-Bu₄NClO₄ in acetonitrile. The CV spectra are shown in Figure 3. The electrochemical reduction of the thin polymer films (**POTOMBO**, **PDTTOMBO**, and **POTTOMBO**) exhibit reversible *n*-doping processes. The cathodic peaks appear at -1.73 V for **POTOMBO**, -1.86 V for **PDTTOMBO**, and -1.76 V for **POTTOMBO** with corresponding anodic peaks at -1.53, -1.75, and -1.67 V, respectively. Generally speaking, the reduction potential of the polymers is not changed remarkably with variation of the number of thiophene rings in the oligothiophene blocks. This implies that the reduction properties of the polymers are dominated by the 2,6-bis(1,3,4-oxadiazole-2,5-diyl)toluene segments. These reduction potentials are lower than those of 2-(4-biphenyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) (-1.95 to -1.94 V vs SCE), one of the most widely used electron-transporting/hole-blocking materials, and other 1,3,4-oxadiazole-containing polymer materials and are comparable to those of some good electron-transporting materials. The ionization potential (IP) and electron affinity (EA) of the polymers were estimated according to the equations³⁷

$$IP = E_{\text{(onset vs SCE)}^{\text{ox}}} + 4.4 \text{ eV}$$

$$EA = E_{\text{(onset vs SCE)}^{\text{red}}} + 4.4 \text{ eV}$$

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Table 2. Electrochemical and Optical Data of Various Polymers

polymer	IP (eV)	EA (eV)	$E_{\text{ox,pa}}/E_{\text{ox,pc}}$ (V)	$E_{\text{red,pc}}/E_{\text{red,pa}}$ (V)	E_{g} (eV, Echem)	E_{g} (eV, optical)
POTOMBO	6.00	2.98	1.95/.....	-1.73/-1.53	3.02	3.04
PDTTOMBO	5.74	2.90	1.64/.....	-1.86/-1.75	2.84	2.83
POTTOMBO	5.43	2.92	1.38/1.24	-1.76/-1.67	2.51	2.54
Poly3OcT ^a	4.90	2.63			2.33	
PBD ^b	5.90	2.60			3.30	
polyoxadiazole ^c	6.04	2.90			3.14	3.19
PPV ^c	5.35	2.80			2.50	2.55
MEH-PPV ^c	4.87	2.60			2.27	2.29
CN-PPV ^c	5.55	3.02			2.53	2.65

^a Poly3OcT (poly(3-octylthiophene)) data measured under the same conditions as the new polymers. ^bData from ref 37c. ^cSee ref 37a.

where $E_{\text{onset}}^{\text{ox}}$ (vs SCE) and $E_{\text{onset}}^{\text{red}}$ (vs SCE) are the onset potentials for the oxidation and reduction of polymers versus the reference electrode, respectively. The onset potentials were determined from the intersection of the two tangents drawn at the rising current and baseline charging current of the CVs. The electrochemical data and the optical properties of the polymers are summarized in Table 2.

The electron affinities of the polymers are around 2.95 eV. These values are comparable to those materials which show good electron transport ability in PLED devices. Cyclic voltammetric reduction potentials could be used as a surrogate for the LUMO energy levels. The results suggest that the LUMO energy levels of the polymers may be lower than those of conventional *p*-dope-type electroluminescent polymers such as poly(3-octylthiophene), PPV, MEH-PPV, and PBD and may be comparable to that of poly(cyanoterephthalylidene) (CN-PPV) (EA, 3.02 eV) and other oxadiazole polymers. Such energy levels may provide a closer match to the work function of Al when they are used as active materials in PLEDs.

When we scanned the polymer films anodically, an interesting electrochemical phenomenon was observed. Both polymers **POTOMBO** and **PDTTOMBO** showed irreversible oxidation with the anodic peaks at 1.95 and 1.64 V, respectively, while polymer **POTTOMBO** showed a partially reversible anodic peak at 1.38 V with a cathodic peak at 1.24 V. The oxidation potential of the polymers decreases with increasing length of the oligothiophene blocks in the polymers. For polymer **POTTOMBO**, the ionization potential is 5.43 eV. This value is higher than that of MEH-PPV and is close to those of other electroluminescent PPVs that are hole-injection favorable electroluminescent materials. The results indicate that the HOMO energy levels of the *p-n* diblock copolymers might be adjusted by changing the length of the oligothiophene blocks to a suitable level for hole injection when the polymers are used as the electroluminescent materials in PLEDs.

Conclusions

A series of novel *p-n* diblock conjugated copolymers containing oligothiophenes and 2,6-di(1,3,4-oxadiazole-2,5-diyl)-toluene have been prepared by polycondensation reaction. The structures of the polymers are consistent with the ¹H and ¹³C NMR spectra, FT-IR spectra, and elemental analysis results. These polymers have well-defined structures and exhibit highly thermal stability. The *p-n* diblock structure may be a useful molecular design for tuning the emissive wavelength of conjugated polymers. The emissive color of the polymers presented here could be tuned from blue to green to light-orange just by increasing the number of thiophene rings in the oligothiophene blocks from one to three. The electrochemical behavior of the *p-n* diblock conjugated copolymers could be adjusted effectively. Comparison of the electrochemical data to those of the currently used electroluminescence materials suggests that the synthesis of this new series of polymers provide a promising approach to balance the barrier between the HOMO of an electroluminescent material and the work function of ITO and the barrier between the LUMO of the electroluminescent material and the work functions of stable metal electrodes (such as Al) in PLEDs.

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Supporting Information Available: FT-IR spectra of prepolymers and final polymers; ¹H NMR spectra of POTOMBO, PDTTOMBO, and POTTOMBO; ¹³C NMR spectra of PDTTOMBO; thermogravimetric analysis of POTOMBO, PDTTOMBO, and POTTOMBO; and differential scanning calorimetry of POTOMBO, PDTTOMBO, and POTTOMBO. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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