Synthesis and Characterization of a New *p*−*n* Diblock Light-Emitting Copolymer

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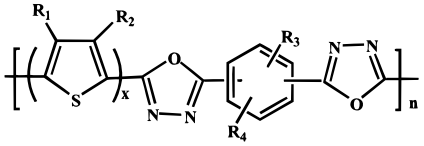
ABSTRACT: In this paper we present the synthesis and characterization of a new light-emitting copolymer constituted of regularly alternating segments of 3,3′-didecyl-2,2′-bithiophene and 2,6-bis(1,3,4-oxadiazolyl)-toluene, which are *p*-dopable and *n*-dopable, respectively. The new polymer emits intense green light under the irradiation of UV light in its film states and shows strong solvatochromism both on absorption and on emission. The *n*-doping potential of the polymer is measured to be similar with that of 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) and other reported oxadiazole-containing polymers, the currently excellent electron-transporting materials, while its *p*-doping potential is much lower than those of other oxadiazole-containing light-emitting polymers and is comparable with that of poly(*p*-phenylenevinylene) (PPV) and polythiophenes (PT), the typical *p*-dope type materials. The presented synthesis reveals a possible approach to balance the rates of injection of electrons and holes from opposite contacts into an emissive layer in polymer light-emitting diodes by controlling the intrinsic properties of light-emitting materials.

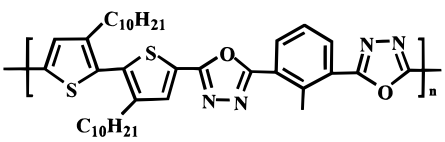
Introduction

As potential patterned light sources and large area displays, polymer light-emitting diodes (PLEDs) that use conjugated polymers as active elements have afforded several appealing advantages over other technologies.[1] In the past several years, the synthesis and properties of light-emitting polymers and their applications in PLEDs have been studied intensively.[2] A lot of such conjugated polymers have been synthesized. Among them, the most important ones include poly(*p*-phenylenevinylene) (PPV),[3−5] polythiophene (PT),[6−8] poly(*p*-phenylene) (PPP),[9,10] polyfluorene (PF),[11] and their derivatives. The electroluminescence from these polymers can sweep the whole range of the visible spectrum. However, all these polymers have π-excessive nature, i.e., they are typical *p*-dope type polymers with much greater tendency for transporting holes than for transporting electrons. Another series of useful electroluminescent polymers are those composed of highly π-deficient heterocycles, such as pyridine and oxadiazole rings.[12,13] These polymers are typical *n*-dopable ones with high electron affinity, showing greater tendency for transporting electrons. All these polymers are unipolar characteristic, which may result in an imbalance of injection of electrons and holes at the opposite contacts in PLED devices. Because the electroluminescent (EL) light in PLEDs arises from the recombination of electrons and holes in active polymer layers,[14] in order to achieve high electroluminescent efficiency, it is necessary to balance the injection and transport of electrons and holes. If light-emitting polymers are endowed with bipolar character, the balance between electrons and holes may be improved. Some efforts have been devoted to this aspect recently. A few π-conjugated donor−acceptor copolymers constituted of π-excessive and π-deficient arylene units were synthesized and showed unique electrochemical and optical properties.[15] Several bipolar EL molecular materials gave quite high external EL quantum efficiency (∼4%) and luminance (higher than 19 000 cd/m^2).[16]

In our laboratory, to develop highly efficient EL polymeric materials, we focus on designing and synthesizing *p*−*n* diblock conjugated copolymers to achieve the bipolar character of the resultant materials. As one of the aspects, a series of diblock copolymers constituted of substituted oligothiophenes and arylene-1,3,4-oxadiazoles are designed (as shown below). The portions of oligothiophenes provide the *p*-doping or hole-transporting ability and the arylene-1,3,4-oxadiazoles act as *n*-dopable or electron-transporting units. In addition, the whole electron affinity and the emission color of the resultant polymers can be adjusted by controlling the repeated units in oligothiophene portions. We present here the synthesis and properties of one of such *p*−*n* diblock conjugated copolymers, PDBTBOT, which has the molecular structure illustrated here.



p-*n* Diblock Copolymers (x = 1 – 8)



PDBTBOT

Results and Discussion

Polymer Synthesis and Characterization. The synthetic approach to PDBTBOT is sketched in Figure

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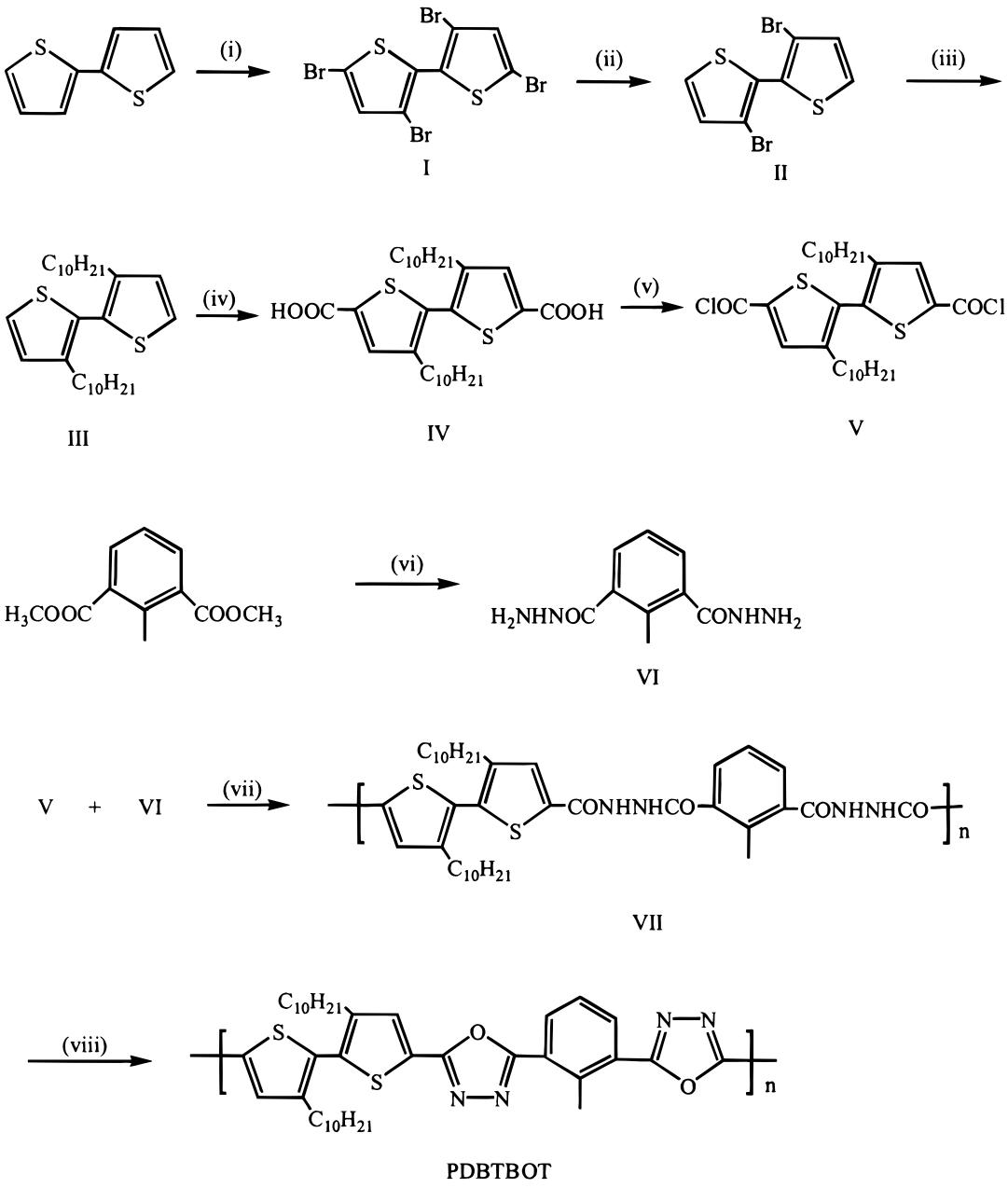

Figure 1. Synthetic scheme of PDBTBOT. Reagents and conditions: (i) bromine, AcOH/$CHCl_3$; (ii) Zn, EtOH/AcOH/HCl; (iii) 1-bromodecane, Mg, Ni(dppp)Cl_2, diethyl ether; (iv) *n*-BuLi, TMEDA, dry ice, −70 °C to room temperature; (v) $SOCl_2$; (vi) NH_2-NH_2·H_2O, MeOH; (vii) LiCl, pyridine, NMP; (viii) PPA, refluxing.

1. The key intermediates in the synthesis are 5,5′-bis-[4-decyl-2-thiophenecarbonyl chloride] (V) and 2-methylisophthalic dihydrazide (VI). Compound V was prepared by the carboxylation of 3,3′-didecyl-2,2′-bithiophene (IV) and the subsequent reaction with $SOCl_2$. The 3,3′-didecyl-2,2′-bithiophene (IV) was obtained from a coupling reaction of 3,3′-dibromo-2,2′-bithiophene with the Grignard reagent of 1-bromodecane in the presence of dichloro-[1,3-bis(diphenylphosphino)propane]nickel(II) (Ni(dppp)$_2Cl_2$). Another key intermediate (compound VI) was synthesized via the reaction of dimethyl 2-methylisophthalate with excess hydrazine monohydrate. Polycondensation between monomers V and VI in *N*-methylpyrrolidinone (NMP) in the presence of LiCl and pyridine afforded the polyhydrazide VII. Polyhydrazides could be converted into corresponding poly(arylene-1,3,4-oxadiazole)s by heating to 300 °C under vacuum or by heating in dehydrating reagents.[17] In this synthesis, polyphosphoric acid (PPA) was used as both dehydrating reagent and solvent.

The FTIR spectra of VII before and after the treatment with PPA are exhibited in Figure 2. The absence of two intensive absorption bands at 1660 and 3246 cm^{-1} arising from the stretching of the carbonyl groups and the N−H in the polyhydrazide respectively, together with the appearance of two new peaks at 1586 and 1081 cm^{-1} attributed to 1,3,4-oxadiazole ring stretching, after the treatment, indicate the successful cyclodehydration of the polyhydrazide VII. The completion of the cyclodehydration reaction by heating in PPA could be further confirmed by elemental analysis. The empirical formula of the final polymer PDBTBOT was determined to be $C_{39.2}H_{49.6}N_{3.9}S_{2.0}O_x$ according to the elemental analysis. It is in good agreement with the expected formula $C_{39}H_{50}N_4S_2O_2$.

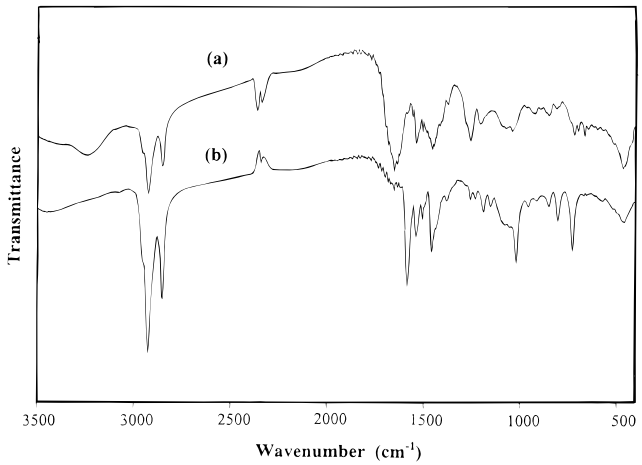

Figure 2. FTIR spectra of the polyhydrazide VII before (a) and after (b) treatment with PPA.

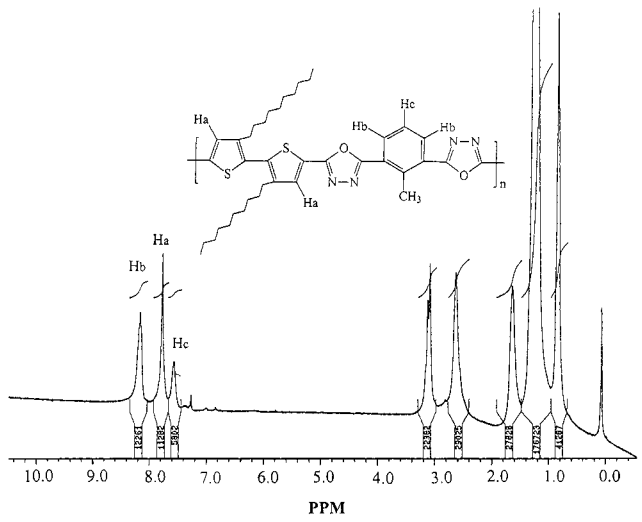

Figure 3. ^{1}H NMR spectrum of PDBTBOT.

NMR spectra of the polymer are globally consistent with the expected repeating unit. The ^{1}H NMR spectrum is given in Figure 3. There are three absorption peaks in the aromatic region. The signal at δ 7.77 ppm arises from the β−H of the thiophene rings. The other two peaks at δ 8.17 and 7.57 ppm are due to the two kinds of protons in the benzene ring. In the ^{13}C NMR spectrum, 10 signals can be identified in the aromatic region from δ 165 to 120 ppm, corresponding to the 10 kinds of aromatic carbons in the polymer.

The final polymer PDBTBOT was obtained as a dark brown solid. It readily dissolves in common solvents such as chloroform, tetrahydrofuran (THF), and xylene to be light yellow solutions. Gel permeation chromatography (GPC) measurement using THF as eluant and polystyrene as standard indicated $M_w = 35\,105$ with the polydispersity of 1.41. The molecular weight of the polymer should be dominated by the step of the polycondensation. The relatively high molecular weight may result from the good solubility of the polyhydrazide VII in NMP, which is used as a solvent in the polycondensation reaction and gives a clear solution in the whole process.

Thermogravimetric analysis (TGA) reveals good thermal stability of the polymer with the starting temperature of decomposition of ~300 °C under nitrogen (Figure 4b). The gradual weight loss beyond 300 °C may

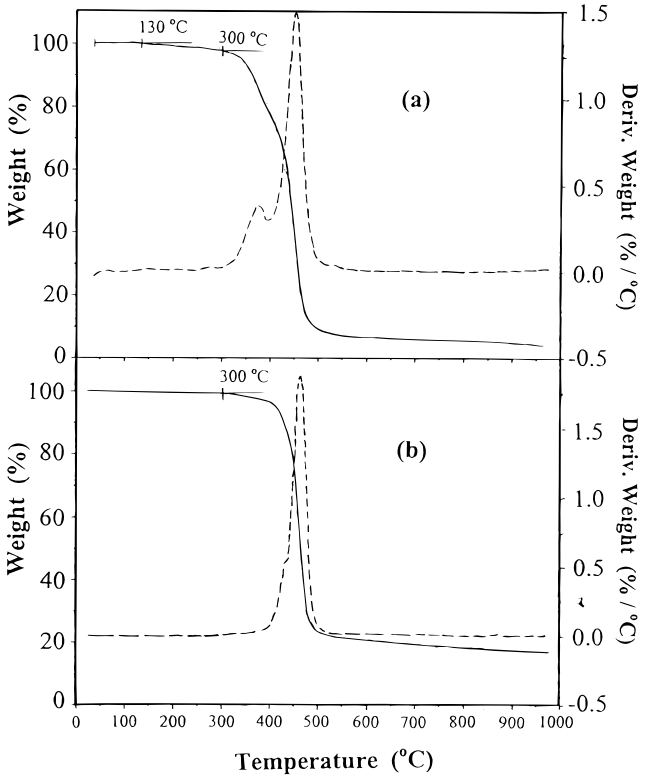

Figure 4. TGA−DTA plots of PDBTBOT (b) and its precursor polymer, polyhydrazide VII (a).

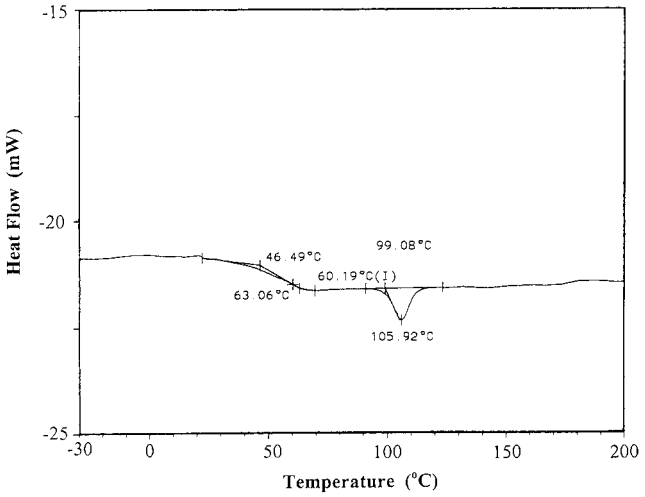

Figure 5. DSC chart of PDBTBOT.

be attributed to the degradation of the attached alkyl chains on the thiophene rings. Similar behavior has been observed for substituted polythiophenes.[18] Subsequently, a rapid weight loss begins at about 400 °C, which corresponds to the decomposition of the backbone of the polymer. The TGA−DTA chart of the precursor polymer, polyhydrazide VII, is also given in Figure 4a for comparison. The small weight loss between 130 and 300 °C (~2.5%) and the faster weight-loss after 300 °C with respect to the situation of the final polymer are attributed to the cyclodehydration of the polyhydrazide. The differential scanning calorimetry (DSC) thermogram of PDBTBOT (Figure 5) shows a clear glass transition at 46.5 °C and a melting point at 105.9 °C.

Optical Properties. The UV−visible absorption spectrum of the new polymer in $CHCl_3$ solution was measured to have a maximum at 342 nm. The solution

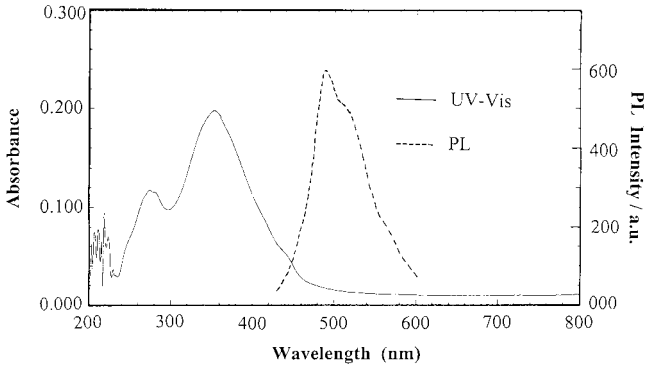

Figure 6. Absorption and photoluminescence (excited at 380 nm) spectra of PDBTBOT thin film.

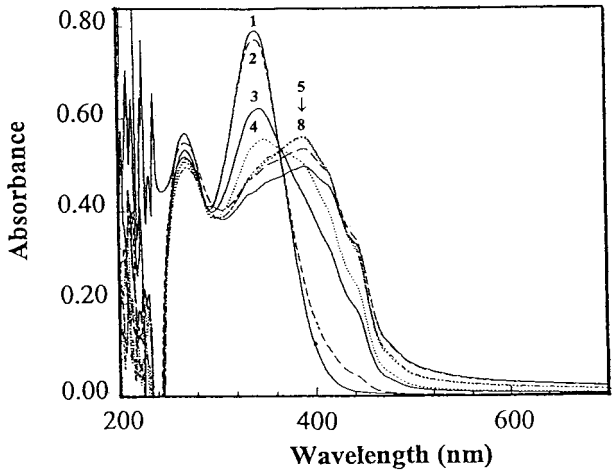

Figure 7. UV−visible absorption spectra of PDBTBOT in the mixture of chloroform and methanol with the volume fractions of methanol α: 0 (1), 0.35 (2), 0.45 (3), 0.50 (4), 0.65 (5), 0.75 (6), 0.85 (7), and 0.90 (8).

showed very intense blue fluorescence with a maximum peak at 462 nm and a shoulder at 444 nm under the irradiation of UV light (380 nm). The UV−visible absorption and fluorescence spectra of the polymer film (spin-coated on quartz plate from its $CHCl_3$ solution) are displayed in Figure 6. The absorption spectrum has a maximum at 351 nm with the onset of 2.6 eV corresponding to the $\pi-\pi^*$ band gap of the polymer. The fluorescence spectrum shows a maximum at 490 nm and a shoulder at 525 nm. The Stokes shift is as large as 140 nm, and the emission spectrum overlaps very little with the absorption spectrum. This implies that the reabsorption of the emitted light by the material itself is negligible when it is used as a light-emitting material.

A strong solvatochromism was observed on both the absorption and the fluorescence spectra. The UV−visible and fluorescence spectra of the polymer in $CHCl_3$/MeOH mixtures with different volume fractions of methanol (α) are given in Figures 7 and 8, respectively. To our knowledge, so far there has not been any report on the solvatochromism of oxadiazole-containing conjugated polymers, although the phenomenon has been widely observed on other soluble conjugated polymers, especially substituted polythiophenes.[20−23] With the increase of α, the maximum absorption of the polymer shifts from 341 nm in pure chloroform to 389 nm with well-defined vibronic shoulders at 340, 418, and 445 nm in MeOH-rich mixed solvents. The spectral change corresponds to the disorder to order transformation of the conjugated polymeric chains, which has been demonstrated for other substituted conjugated polymers.[19−22] It is worth noticing that the absorption spectra of the new polymer in the MeOH-rich mixed solvents even shift to longer wavelengths by 37 nm with respect to that in its film states. This means that the polymer has a more extensive conjugated structure in the MeOH-rich solvents than in its film states. This is an interesting unusual solvatochromic behavior; maybe it is caused by the plasticization of the solvent to the polymer, which allows an extensive crystallization or reorganization of the polymer chains.

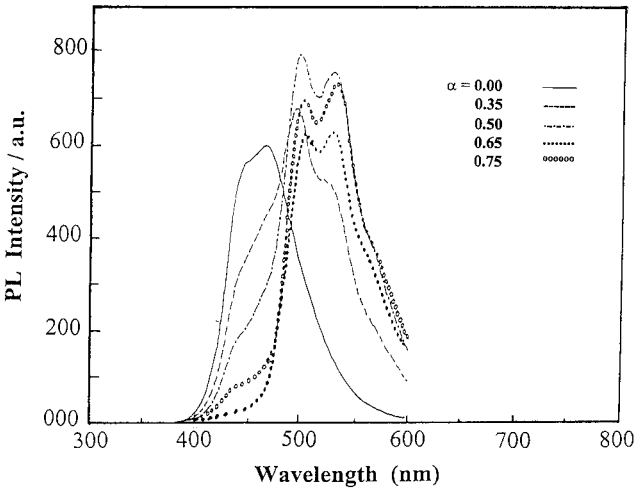

Figure 8. Fluorescence spectra of PDBTBOT in various $CHCl_3$−MeOH mixtures (excited at 350 nm). The volume fractions (α) of methanol are 0 (—), 0.35 (- - -), 0.50 (—·—), 0.65 (···), and 0.75 (ooo).

The solvatochromic nature of the polymer is more manifest in emission properties. The emission properties are more sensitive to the addition of methanol than the absorption properties, indicated by the results that the emission peak red-shifts from 462 to 491 nm with the increase of α from 0 to 0.35, while the absorption spectrum does not show noticeable changes in the same region of α. When α reaches 0.45, the shoulder at 525 nm grows to an emission peak. Further increase of α induces an increase of the relative intensity of the new emission peak. By 0.75 of α, the intensity of the peak at 525 nm has exceeded that at 491 nm. Like the situation in absorption properties, an unusual red shift of emission peak in MeOH-rich solvents with respect to that in film states is also observed in the emission spectra. The results indicate that the emission color of PDBTBOT can be tuned from blue to green by controlling the environmental conditions.

Electrochemical Properties. The cyclic voltammetry of the polymer film (prepared from its solution in xylene) on a golden disk electrode (0.03 cm^2) was measured in a 0.2 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) solution in CH_3CN at a scan rate of 20 mV/s in an argon drybox. A Pt wire was used as the counter electrode and a Ag wire was used as a quasi-reference electrode,[23] which has a close potential with the Ag/AgCl electrode (ca. 0.02 V vs Ag/AgCl).

As shown in Figure 9, the polymer is electroactive either in the cathodic region or in the anodic region. On sweeping the polymer cathodically, the onset of the *n*-doping process (reduction) is at the potential of ca. −1.6 V. The cathodic current quickly increases from −1.7 V, and a cathodic peak appears at −1.94 V. A corresponding reoxidation (*n*-dedoping) peak occurs at

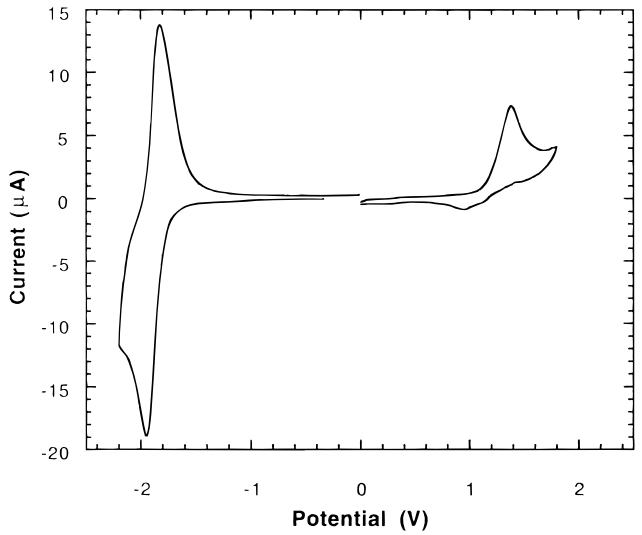

Figure 9. Cyclic voltammograms of a PDBTBOT film on a Au electrode in a CH_3CN solution of $TBAPF_6$ (0.2 M) at a scan rate of 20 mV s^{-1}.

−1.82 V. Thus, the *n*-doping potential $E^{1/2}$ is −1.88 V. This *n*-doping potential is obviously lower than those of other oxadiazole-containing light-emitting polymers[24−26] and is even lower by 50 mV than that of 2-(4-biphenylyl)-5-(4-*tert*-butylphenyl)-1,3,4-oxadiazole PBD),[27] the most widely used electron-transporting material in PLEDs.[28] Therefore, the new polymer is easier to be reduced than PBD and other oxadiazole-containing light-emitting polymers. For the *p*-doping process, the onset potential is ca. 1.0 V and an anodic current peak occurs at 1.38 V. A rereduction (*p*-dedoping) peak can be observed at 0.96 V, although the reversibility of the *p*-doping process is poorer than that of its *n*-doping process. The difference between the *p*-doping and *n*-doping onset potentials is determined to be 2.6 V, this means that the $\pi-\pi^*$ bad gap of the polymer obtained from the electrochemical measurement is 2.6 eV, which is exactly the same as the optically determined one.

The comparison with other reported oxadiazole-containing light-emitting and charge-transporting polymers,[13,24−27] which exhibit strong electron-transporting ability, indicates that the new polymer has comparable reduction and reduction onset potentials but has much lower oxidation and corresponding onset potentials. This implies that our new polymer may have electron-transporting ability similar to theirs but with much better hole-transporting properties. Although the *p*-doping onset potential of the new polymer (1.0 V vs Ag/AgCl) is higher than those of MEH−PPV (0.34 V vs Ag/Ag^+)[24] and poly(3-alkylthiophene)s (∼0.5 V vs Ag/Ag^+),[29] it is lower than that of PPV (0.85 V vs Ag/Ag^+).[24] The polymer may have hole-transporting tendency comparable to that of PPV. In comparison with conventional light-emitting polymers, an improved balance of injection of electrons and holes may be expected when it is used as emissive material in PLEDs. Therefore, the present effort shows a promising synthetic approach to balance the injection of electrons and holes in PLED devices so as to improve the electroluminescent efficiency.

Conclusions

A new *p*−*n* diblock light-emitting copolymer composed of 3,3′-didecyl-2,2′-bithiophene and 2,6-bis(1,3,4-oxadiazolyl)toluene was synthesized and characterized. It is highly soluble and emits green light under the irradiation of UV light. Both of its absorption and its emission properties exhibit a strong and unusual solvatochromism, and this is the first example of solvatochromism of oxadiazole-containing light-emitting polymers. It is electroactive both in the cathodic region and in the anodic region. The electrochemical comparison with other light-emitting polymers indicates the possibility of developing highly efficient electroluminescent polymeric materials with balanced transporting ability for electrons and holes by incorporating *p*-dope type and *n*-dope type segments into conjugated backbones.

Experimental Section

Measurements. NMR spectra were collected on a Bruker ACF 300 spectrometer with chloroform-*d* or D_2O as solvent and tetramethylsilane as the internal standard. FTIR spectra were recorded on a Bio-Rad TFS 156 spectrometer by dispersing samples in KBr disks. UV−visible and fluorescence spectra were obtained on a Shimadzu UV 1601 SCM 3632 spectrophotometer and Perkin-Elmer LS 50B luminescence spectrometer with a xenon lamp as the 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 10 °C min^{-1} and 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. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer for C, H, N, and S determinations. Cyclic voltammetry was carried out on a BAS 100A Electrochemical Workstation. GPC analysis was conducted with a Perkin-Elmer Model 200 HPLC system equipped with Phenogel MXL and MXM columns using polystyrene as the standard and THF as the eluant.

Materials. Diethyl ether was distilled over sodium, and hexane was distilled over calcium hydride. NMP, *N*,*N*,*N*′,*N*′-tetramethylethylenediamine (TMEDA), and pyridine (purchased from Fluka or Aldrich, A.R. grade) were distilled prior to use. 2,2′-Bithiophene, 1-bromodecane, $Ni(dppp)_2Cl_2$, magnesium turnings, thionyl chloride, phosphoric acid, and phosphorus pentoxide were used as received (Fluka or Aldrich chemicals).

Synthesis. 3,3′,5,5′-Tetrabromo-2,2′-bithiophene (I). Bromine (190.2 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 cm^3) and chloroform (450 cm^3) at the temperatures of 5−15 °C. Subsequently, the mixture was stirred at room temperature for 5 h and then under reflux for 24 h. After cooling to room temperature, 500 cm^3 of 10% KOH aqueous solution was added. The mixture was extracted with $CHCl_3$ twice, the combined extracts were washed with water, dried over anhydrous $MgSO_4$, and filtered, and the solvent was removed by evaporation. Recrystallization from ethanol afforded a light-yellow crystal with the yield of 89%. Mp: 139−141 °C (lit. 139−140 °C).[30]

3,3′-Dibromo-2,2′-bithiophene (II).[31] 3,3′,5,5′-Tetrabromo-2,2′-bithiophene (48.2 g, 0.1 mol) was added in portions within 0.5 h to a refluxing dispersion of zinc powder (25.2 g, 0.4 mol) in 500 cm^3 of ethanol containing 50 cm^3 of water, 120 cm^3 of glacial acetic acid, and 10 cm^3 of 3 M HCl. After being refluxed for an additional 2 h and then cooled 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 250 cm^3 of H_2O was added. The mixture was extracted with diethyl ether, and the combined extracts were washed with water, dried over anhydrous $MgSO_4$ and filtered. The solvent was removed by evaporation and the crude product was recrystallized from hexane to give a light-green crystal (yield 79%). Mp: 98−99 °C. ^1H NMR ($CDCl_3$): δ 7.40 (d, J = 5.3 Hz, 2H), 7.07 (d, J = 5.3 Hz, 2H) ppm.

3,3′-Didecyl-2,2′-bithiophene (III).[32] A Grignard regent prepared from 1-bromodecane (44.2 g, 0.2 mol) and Mg turnings (5.0 g, 0.21 mol) in 60 cm^3 diethyl ether was added dropwise to a solution of 3,3′-dibromo-2,2′-bithiophene (22.7 g, 0.07 mol) and Ni(dppp)Cl_2 (622 mg, 1.19 mmol) in 100 cm^3 of diethyl ether at 0 °C. After the addition was complete, stirring was continued for 24 h under refluxing; then the reaction was quenched with 0.2 M HCl, and the mixture was extracted with diethyl ether. The combined extracts were dried over anhydrous Na_2SO_4 and filtered, and the solvent was removed by evaporation. Vacuum distillation (130 °C/0.05 mbar) provided 22.2 g (71%) of pure product. ^{1}H NMR ($CDCl_3$): δ 7.31 (d, J = 5.4 Hz, 1H), 6.99 (d, 2H), 2.55−2.50 (t, J = 7.5 Hz, 4H), 1.59−1.54 (m, 4H), 1.26 (m, 24H), 0.93−0.88 (t, J = 6.2 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ 142.2, 128.7, 128.4, 125.1, 31.9, 30.7, 29.6, 29.5, 29.4, 29.3, 29.2, 28.7 ppm. Anal. Calcd for $C_{28}H_{46}S_2$: C, 75.34; H, 10.31; S, 14.35. Found: C, 75.42; H, 9.76; S, 14.09.

3,3′-Didecyl-5,5′-dicarboxy-2,2′-bithiophene (IV).[33] Into a N_2-flushed flask containing TMEDA (2.9 g, 0.025 mol) and a solution of *n*-BuLi (1.5 M solution in hexane, 17 cm^3, 0.025 mol) in 30 cm^3 of hexane was added 3,3′-didecyl-2,2′-bithiophene (4.46 g, 0.01 mol) under the protection of nitrogen at room temperature. The mixture was stirred at room temperature for 1 h and then refluxed for an additional 0.5 h. Subsequently, the reaction mixture was cooled to −70 °C and slowly poured into a 250 cm^3 flask half-filled with crushed dry ice under the protection of dry nitrogen. The mixture was warmed to room temperature overnight and then poured into 150 cm^3 cooled 1 M HCl solution (with ice). The aqueous solution was extracted twice with chloroform. The combined extracts were washed with water and then with saturated sodium chloride solution, dried over anhydrous $MgSO_4$, and filtered. After removal of the solvent and recrystallization from ethanol−water, 4.1 g (76%) pure product was obtained. ^{1}H NMR ($CDCl_3$): δ 7.76 (s, 2H), 2.55−2.50 (t, J = 7.7Hz, 4H), 1.56 (m, 4H), 1.23 (m, 12H), 0.89−0.85 (t, J = 5.5 Hz, 6.3H) ppm. Anal. Calcd for $C_{30}H_{46}O_4S_2$: C, 67.42; H, 8.61; S, 11.98. Found: C, 67.70; H, 8.75; S, 12.14.

3,3′-Didecyl-5,5′-bis(chlorocarbonyl)-2,2′-bithiophene (V). Thionyl chloride (15 cm^3) was added to the 3,3′-didecyl-5,5′-dicarboxy-2,2′-bithiophene (3.0 g, 5.62 mmol). The mixture was refluxed 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 yellow powder. Mp: 68−69 °C. ^{1}H NMR ($CDCl_3$): 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), 0.89−0.81 (t, J = 6.6 Hz, 6H) ppm. ^{13}C NMR ($CDCl_3$): δ 159.3, 145.1, 139.0, 138.7, 137.2, 31.8, 30.3, 29.4, 29.3, 29.2, 29.1, 29.0, 28.8, 22.6, 14.0 ppm. Anal. Calcd for $C_{30}H_{44}O_2Cl_2S_2$; C, 63.03; H, 7.76; S, 11.22. Found: C, 62.38; H, 8.01; S, 11.54.

2,6-Bis(hydrazinocarbonyl)toluene (VI). Dimethyl 2-methylisophthalate (7.0 g, 0.034 mol) was added into a solution of 10 cm^3 of hydrazine monohydrate (99%) in 70 cm^3 of CH_3OH. The reaction mixture was refluxed for 24 h. Subject to 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: 109 °C. ^{1}H NMR (D_2O): δ 7.43−7.40 (d, J = 7.8 Hz, 2H), 7.35−7.33 (d, J = 7.6 Hz, 1H), 4.74 (s, 6H), 2.26 (s, 3H) ppm. Anal. Calcd for $C_9H_{12}N_4O_2$: C, 51.94; H, 5.81; N, 26.92. Found: C, 52.91; H, 5.68; N, 26.52.

Polyhydrazide (VII).[34,35] 3,3′-didecyl-5,5′-bis(chlorocarbonyl)-2,2′-bithiophene (V) (0.242 g, 0.424 mmol) was added into a stirred solution of 2,6-bis(hydrazinocarbonyl)toluene (VI) (88.2 mg, 0.424 mmol) in 20 cm^3 of NMP containing 0.1 g LiCl and 0.01 mol pyridine at room temperature. After being heated at 80 °C for 3 h, the brown viscous solution was cooled to 50 °C and then poured into 100 cm^3 of deionized water. The precipitated polymer was filtered off and washed with water and then ethanol and finally was dried under vacuum at 60 °C to give a light-yellow powder (0.288 g/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, 64.71; H, 8.00; N, 8.26; S, 9.01.

Poly[(3,3′-didecyl-2,2′-bithiophene)-*co*-(2,6-bis(oxadiazolyl)toluene)] (PDBTBOT).[34] The mixture of 200 mg of VII and 25 cm^3 of PPA prepared from 85% H_3PO_4 and P_2O_5 was refluxed for 6 h. After being cooled, the reaction mixture was poured into water. The precipitate was collected by filtration and was washed with water, ethanol, and then ether and finally dried under vacuum. Brown powder (180 mg/93%) was obtained. ^{1}H NMR ($CDCl_3$): δ 8.17 (2H), 8.16(2H), 7.77 (1H), 3.12 (3H), 2.64 (4H), 1.64−1.23 (28H), 0.9 (6H) ppm. ^{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, 69.15; H, 7.33; N, 8.07; S, 9.45.

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