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New Series of Blue-Light-Emitting Polymers Constituted of 3-Alkylthiophenes and 1,4-Di(1,3,4-oxadiazolyl)phenylene

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A new series of conjugated polymers constituted of 3-alkylthiophenes and 1,4-di(1,3,4-oxadiazolyl)phenylene are synthesized through precursor polymers of polyhydrazides. The solubility of the precursor polymers and the corresponding target polymers is improved by increasing the length of side chains on thiophene rings, which results in a higher degree of the conversion from the precursors to the final polymers and thus results in longer effective conjugated length in the polymers bearing longer side chains. The thermal stability and electrochemical properties of the polymers are studied. The polymers emit blue light under the irradiation of UV light in their film states. The relative fluorescence yield in solutions increases with the increase in length of side chains on thiophene rings in the polymers and reaches up to 79% for the polymer bearing octyl side chains. The possibility of polymers being used as electroluminescent material in polymer light-emitting diodes (PLEDs) is demonstrated by the successful fabrication of a single-layer device of indium tin oxide (ITO)/polymer/Ca, which emits visible blue light above 8 V of forward bias.

Introduction

Conjugated polymers have attracted intensive attention in the past 20 years on account of their unique electrical and optical properties.[1] In 1990, a spectacular advanced technology developed at Cambridge using conjugated polymers as electroluminescent materials in light-emitting diodes (LEDs) ignited a tremendous worldwide research effort on the design and synthesis of novel conjugated polymeric materials for LED application.[2] Poly(*p*-phenylenevinylene) (PPV),[3] polythiophene (PT),[4−6] poly(*p*-phenylene) (PPP),[7] polyfluorene (PF),[8] and their derivatives have been widely studied as light-emitting materials in polymer LEDs. The electroluminescence (EL) from these polymers can sweep the whole range of the visible spectrum.[9] 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. This charge imbalance is one of the key limits for increasing the EL quantum efficiency of polymer light-emitting diodes (PLEDs).[10] Although the EL quantum efficiency of PLEDs may be increased remarkably by using low-work function metals as cathodes[11] or adding electron injection/transporting layers between a light-emitting polymer film and a cathode,[12] the approaches suffer from the high reactivity of the metals and the technical difficulties in fabricating multilayer structures. Therefore, the synthesis of light-emitting polymers with strong electron affinity is necessary for fabricating highly efficient and stable polymer LEDs. Unfortunately, the synthesis of soluble and stable total conjugated n-dope-type polymers with high light-emitting efficiency is still a challenge for chemists.

2-(4-Biphenylyl)-5-(*tert*-butylphenyl)-1,3,4-oxadiazole (PBD) is one of the most widely used electron injection/transport or hole-blocking materials.[12,13] Its function is believed to result from the high electron affinity of the oxadiazole ring in the molecule.[14] Several oxadiazole-containing polymers (copolymers and graft copolymers) have been synthesized as electron-transporting materials;[15] a few light-emitting polymers composed of alternating phenylene and oxadiazole also have

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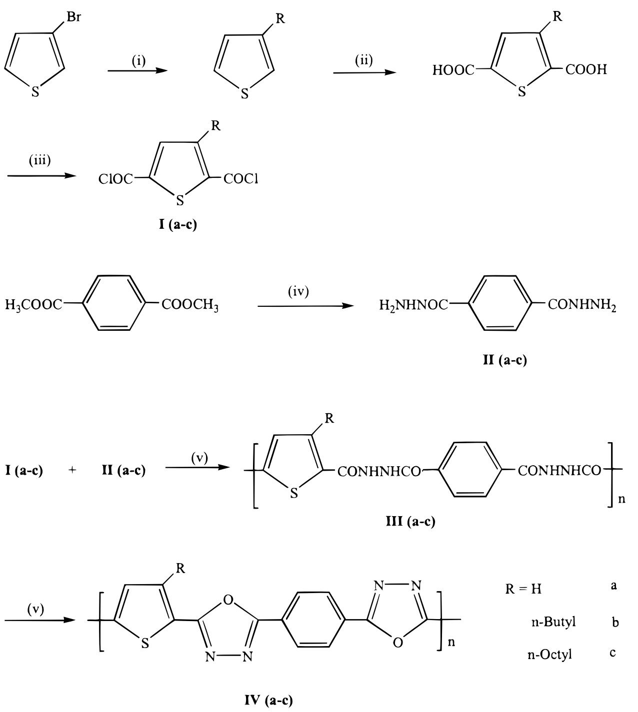
Scheme 1. Synthetic Route[a]



[a] (i) RMgBr, Ni(dppp)Cl_2, Et_2O; (ii) −70 °C, *n*-BuLi (2.5 M), TMEDA, hexane; (iii) $SOCl_2$; (iv) $NH_2NH_2 \cdot H_2O$, MeOH; (v) LiCl, pyridine, NMP; (vi) $POCl_3$, 125 °C, 6 h.

been synthesized in the last several years.[16−19] To our knowledge, no effort has been devoted to the synthesis of total conjugated light-emitting polymers composed of oxadiazole and thiophene rings. In this paper we present the synthesis, characterization, and application in polymer LEDs of a new series of light-emitting polymers constituted of 3-substituted thiophenes and 1,4-di(oxadiazolyl)phenylene. The effects of the length of the substituted chains on the thiophene ring on the synthesis and optical properties of the polymers will also be discussed.

Results and Discussion

Synthesis and Characterization. The polymers were synthesized according to the route depicted in Scheme 1. The synthesis of monomer **I** was started with the preparation of 3-alkylthiophene from 3-bromothiophene by a coupling reaction with alkyl Grignard reagent in the presence of Ni(dppp)Cl_2, followed by the carboxylation[20] at the 2 and 5 positions of thiophene ring, and finally reaction with $SOCl_2$. The reaction of dimethyl terephthalate with hydrazine afforded the monomer **II**. Polycondensation between monomers **I** and **II** in *N*-methylpyrrolidone (NMP) in the presence of LiCl and pyridine at ambient temperature gave the polyhydrazide **III**. The polyhydrazide precursors are not soluble in common organic solvents and just partially dissolve in NMP. Because of the poor solubility, the purification of the polyhydrazide precursors is difficult. This should be responsible for the poor agreement of the results of elemental analysis with the calculated values (as shown in the Experimental Section). **III** was converted to the final polymer **IV** by refluxing in $POCl_3$ for 4 h.

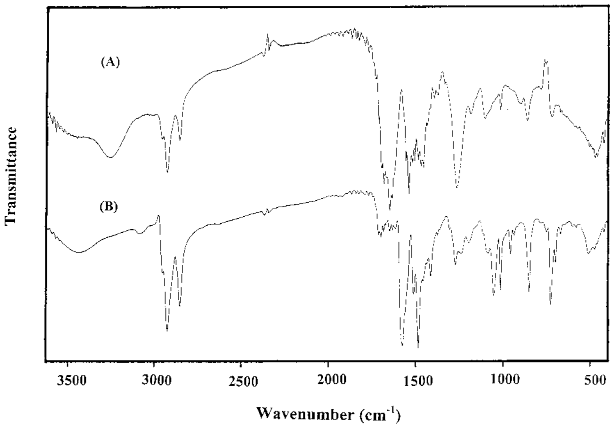


Figure 1. FTIR spectra of the polyhydrazide **IIIc** before (A) and after (B) treament with $POCl_3$.

The synthesis of aromatic poly(1,3,4-oxadiazole) compounds has been reviewed recently.[21] The widespread route involves the preparation of polyhydrazide precursors followed by cyclodehydration. The cyclodehydration can be achieved by heating the precursors under vacuum or by heating in dehydrating solvents. In the present work, $POCl_3$ is employed as dehydrating solvent. The degree of cyclodehydration for the polyhydrazine precursors can be estimated from Fourier transform infrared spectroscopy (FTIR). For polymer **IIIc** (Figure 1), after the treatment with $POCl_3$, two intensive absorption peaks around 1650 and 1543 cm^{-1} arising from the carbonyl groups in polyhydrazine and the absorption in the range of 3200−3300 cm^{-1} due to N−H stretching disappear. Meanwhile, two new peaks at 1578 and 1050 cm^{-1} attributed to oxadiazole ring appear. These results indicate a successful cyclodehydration. However, the completion of cyclodehydration does not happen on polymers **IIIa** and **IIIb**. As shown in Figure 2, the absorption around 1650 cm^{-1} can be identified in the FTIR spectrum of $POCl_3$-treated polymer **IIIb**, while the absorption band is still intensive in the spectrum of $POCl_3$-treated polymer **IIIa**. It is evident that the degree of cyclodehydration decreases with the decrease in length of the substituted chains on thiophene ring. This may be attributed to the lower solubility of the precursor polyhydrazides **IIIa** and **IIIb** and their corresponding final polymers in $POCl_3$. The reaction mixture of **IIIc** in $POCl_3$ is always clear during the whole process of cyclodehydration, while the reaction mixtures of **IIIa** and **IIIb** are turbid and cloudy, respectively. The chemical structures of the polymers can be further confirmed by elemental analysis and NMR. The ^1H NMR spectrum of polymer **IVc** is exhibited in Figure 3. The signals at 8.43 and 8.04 ppm

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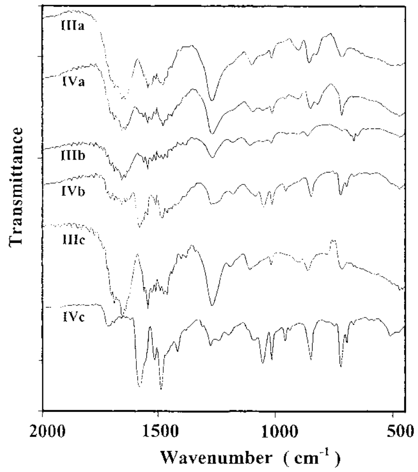

Figure 2. FTIR spectra of polymers **IVa**−**IVc** and their precursor polyhydrazides **IIIa**−**IIIc**.

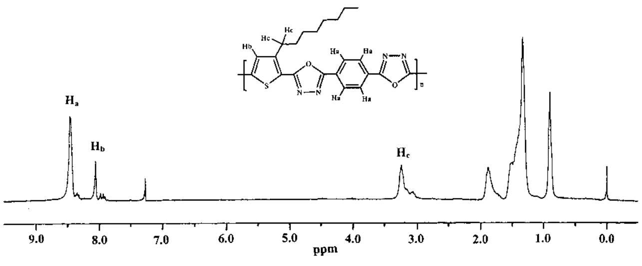

Figure 3. ^{1}H NMR spectrum of polymer **IVc**.

Table 1. Elemental Composition of the Polymers

polymer	empirical formula	expected formula
IVa	$C_{15.0}H_{11.2}N_{4.0}S_{0.9}O_{5.3}$	$C_{14}H_6N_4SO_2$
IVb	$C_{18.4}H_{17.9}N_{4.0}S_{1.0}O_{3.2}$	$C_{18}H_{14}N_4SO_2$
IVc	$C_{21.7}H_{24.1}N_{4.0}S_{0.9}O_{2.5}$	$C_{22}H_{22}N_4SO_2$

are assigned to the aromatic protons on phenylene and thiophene rings, respectively. The resonance for the methylene group adjacent to the thiophene ring appears at 3.23 ppm. The weak signals below the peaks may be attributed to terminal groups, different linkage of 3-octylthiophene with oxadiazole ring, and the existence of trace amounts of noncyclodehydrated hydrazide groups. The calculated empirical formulas of the polymers from the results of elemental analysis are listed in Table 1, which show good agreement with the expected formulas. The higher contents of hydrogen can be attributed to the absorbed water, which is supported by the higher contents of oxygen, as well as the incompleteness of the cyclodehydration.

Polymer **IVa** is insoluble in common solvents, while polymers **IVb** and **IVc** are partially soluble in chloroform and dimethyl sulfoxide (DMSO). In mixtures of chloroform ($CHCl_3$) and trifluoroacetic acid (TFA), polymers **IVb** and **IVc** can dissolve readily to give clear solutions, but polymer **IVa** only partially dissolves. Long alkyl chains on the thiophene ring enhance the solubility of the resultant polymers. Polymers **IVb** and **IVc** are stable up to 250 °C either in air or in nitrogen according to thermogravimetric analysis (TGA) (Figure 4). However, polymer **IVa** shows obvious weight-loss below 300 °C and a faster weight-loss between 300 and 350 °C with respect to the other two polymers. This may be attributed to the noncyclodehydrated hydrazide groups, which are cyclodehydrated during heating.

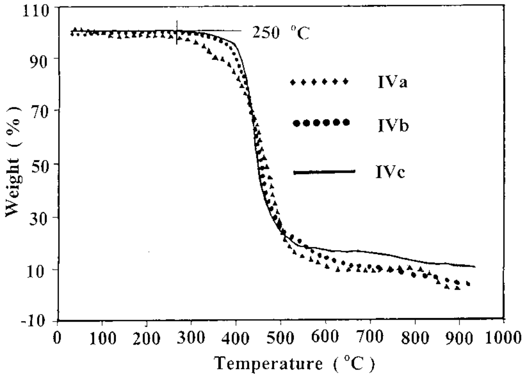

Figure 4. Thermogravimetric analysis (TGA) curves of polymers **IVa**−**IVc**.

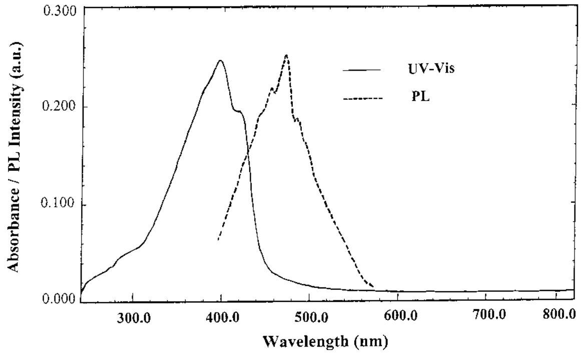

Figure 5. UV−visible absorption and fluorescence spectra of polymer **IVc** cast film.

Optical Properties. Either in the solutions of $CHCl_3$−TFA or in film states, polymers **IVb** and **IVc** emit strong blue fluorescence under ultraviolet irradiation. The UV−visible and fluorescence spectra from the cast film of polymer **IVc** (from $CHCl_3$−TFA solutions) are given in Figure 5. The absorption spectra show a maximum at 396 nm with the onset of 445 nm, which corresponds to a band gap of 2.79 eV. The film of polymer **IVb** exhibits similar absorption and fluorescence spectra. However, the maximum of both absorption and fluorescence of polymer **IVb** appear at shorter wavelengths compared with those of polymer **IVc** either in solutions or in their film states. Detailed spectral data are summarized in Table 2. It can be seen clearly from the data listed in Table 2 that the maxima of absorption and fluorescence of the polymers in solutions shift to longer wavelength with the increase in length of side chains on thiophene rings, while the $\pi-\pi^*$ band gaps determined from the absorption onsets decrease with the increase in the length of side chains. These results indicate that the effective conjugated length of the series of polymers increases with the length of side chains on thiophene rings.

The fluorescence quantum yields of the polymers in $CHCl_3$−TFA solutions (ca. 10^{-6} M) were estimated by employing quinine sulfate (ca. 10^{-5} M) in 0.1 M H_2SO_4 as reference standard.[22,23] The results are listed in Table 2. The relative fluorescence quantum efficiencies are 7.6%, 68%, and 79% for **IVa**, **IVb**, and **IVc**, respectively. The increase in fluorescence quantum

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Table 2. Optical and Electrochemical Data of the Polymers

polymers	λ_{max} (nm) in film and solution[a]	E_g[b] (eV) (HOMO−LUMO)	fluorescence max (nm) in film and solution[a]	relative quantum yield in solution[c] (%)	anodic peak potential[d] (onset) (V)	cathodic peak potential[d] (onset) (V)
IVa	(330)	(2.87)	(425)	7.6		
IVb	*395* (364)	*2.83* (2.85)	*475* (433)	68	1.92 (1.76)	−1.86 (−1.42)
IVc	*396* (375)	2.79 (2.84)	*486* (438)	79	1.93 (1.79)	−1.88 (−1.17)
quinine sulfate	350		450	100		

[a] Film values are shown in italic type; solution values are shown in parentheses. [b] HOMO−LUMO band gap, obtained from the onset of UV absorption. [c] Comparison with the standard of a 10^{-5} mol/L solution of quinine sulfate. [d] vs SCE.

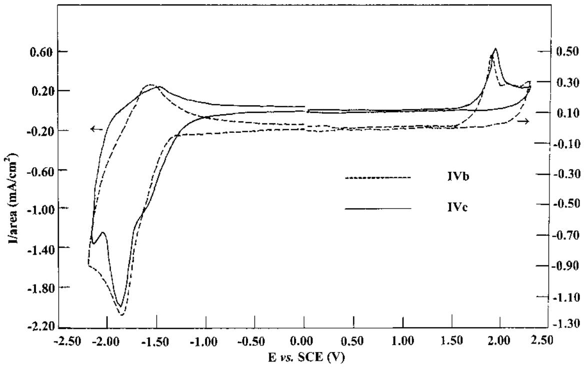

Figure 6. Cyclic voltammograms of **IVb** (- - -, right axis) and **IVc** (—, left axis) films on a Pt electrode in an electrolyte solution of Bu_4NClO_4 (0.1 M) in CH_3CN at a scan rate of 50 $mV{\cdot}s^{-1}$.

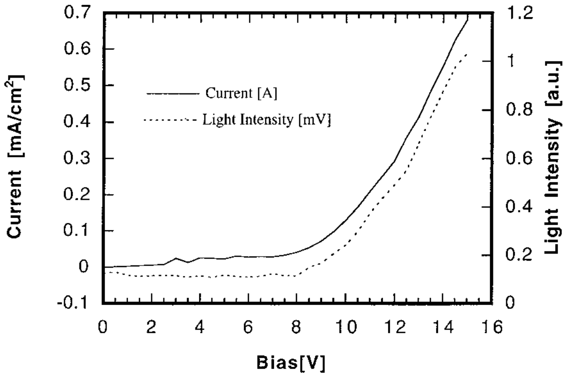

Figure 7. Current vs bias and light vs bias characteristics of an ITO/polymer **IVc**/Ca device.

efficiency with the increase in length of the side chain on thiophene ring can be attributed to the longer effective conjugated length in the polymers bearing longer side chains, which results from higher solubility in the synthetic process.

Cyclic Voltammetry. The electrochemical properties were studied by cyclic voltammetry (*C*−*V*). The polymer films were coated on a working platinum electrode by drying a layer of solution in $CHCl_3$−TFA. The cyclic voltammogram was performed in a one-compartment three-electrode cell with a Pt wire counter electrode and a $Ag/AgNO_3$ (0.1 M) reference at the scan rate of 50 mV/s. The electrolyte was 0.1 M Bu_4NClO_4 in acetonitrile, and the cell was purged with argon.

Figure 6 shows the cyclic voltammogram of polymer **IVc**. When scanning takes place in a negative direction, the n-doping (reduction) process onsets at ca. −1.17 V (vs SCE, same below) and a cathodic peak appears at ca. −1.88 V. A corresponding reoxidation (n-dedoping) peak appears at ca. −1.46 V. Accompanying the reversible n-doping and n-dedoping process, there was an obvious color change in the polymer film: yellow color in the neutral state and dark brown in the doped state. On sweeping anodically, an irreversible p-doping (oxidation) peak occurs at ca. 1.93 V with the onset at ca. 1.79 V. The band gap of the polymer thus can be estimated to be 2.96 eV from the cyclic voltammograms; it is almost the same as the optically determined one. A similar cyclic voltammogram is obtained from the film of polymer **IVb** (as shown in Figure 6). However, its band gap is determined to be 3.18 eV, higher than that of polymer **IVc**. The increase of band gap is caused mainly by the increase in n-doping onset potential, which is −1.42 V for polymer **IVb**. This may be attributed to the lower effective conjugated length in polymer **IVc** due to the incompleteness of the cyclodehydration of hydrazide groups, which has been demonstrated by FTIR. All the electrochemical data are listed in the last two columns in Table 2. The cyclic voltammogram of polymer **IVa** is not obtained because of the poor solubility of the polymer.

LED Device Fabrication. A polymer light-emitting diode was fabricated with polymer **IVc** as active material. To fabricate the device, a film of the polymer was spin-coated on an indium tin oxide (ITO) glass from its solution in $CHCl_3$−TFA and a layer of metal Ca was evaporated as top electrode. All the fabrication and tests were performed in a nitrogen drybox. Under a bias in the forward direction, the single-layer diode begins to emit visible blue light at about 8 V. The current−voltage (*I*−*V*) and light characteristics of the ITO/polymer **IVc**/Ca device are displayed in Figure 7, showing a typical diode character. With the increase of forward bias, both the current and the emitting light intensity increase rapidly after 8 V. The external quantum efficiency was determined to be ~0.0001% photons/electron. These results show the potential of these new materials as emissive material in polymer LEDs, although the optimization of chemical structure of the polymers and structure of device is necessary to improve the performance of the PLED devices based on the new series of materials.

In summary, the synthesis and characterization of a novel series of conjugated polymers constituted of 3-substituted thiophenes and 1,4-di(1,3,4-oxadiazolyl)-phenylene are presented. The polymers are n-dope-type blue-light-emitting polymers and could be potential electroluminescent materials. The alkyl side chains on thiophene rings are essential for both the solubility of the resultant polymers and the successful synthesis of target polymers. A long alkyl side chain results in a higher degree of conversion from precursor polymers of polydrazides to final 1,3,4-oxadiazolyl-containing polymers and thus increases the effective conjugated length in the final polymers. Although we could not measure the molecular weights of the polymers because of their poor solubility in common solvents, it could be inferred that the polymers with longer alkyl side chains should have higher molecular weights.

Experimental Section

General Information. All experiments were carried out under a dry atmosphere of pure nitrogen. Diethyl ether and hexane were distilled over sodium and calcium hydride, respectively. *N*-Methylpyrrolidone (NMP), *N*,*N*,*N'*,*N'*-tetramethylethylenediamine (TMEDA), pyridine, and phosphorus oxychloride ($POCl_3$) were distilled prior to use. Thiophene, 3-bromothiophene, 1-bromobutane, 1-bromooctane, Ni(dppp)-Cl_2, and magnesium turnings were used as received. Elemental analyses were performed on a Perkin-Elmer 240C elemental analyzer for C, H, N, and S determinations. FTIR spectra of polymers dispersed in KBr disks were recorded on a Bio-Rad TFS156 spectrometer. UV−Vis absorption spectra were obtained on a Shimadzu UV 1601 spectrophotometer. Fluorescence measurements were carried out on a Perkin-Elmer LS 50B photoluminescent spectrometer with a xenon lamp as light source. Thermogravimetric analyses (TGA) of polymer powders were conducted on a Du Pont Thermal Analyst 2100 system with a TGA 2950 thermogravimetric analyzer. A heating rate of 20 °C/min with an air and nitrogen flow of 75 $cm^3 \cdot min^{-1}$ was used with the runs being conducted from room temperature to 1000 °C. Cyclic voltammetry experiments were carried out in a three-electrode compartment cell with a total electrolyte (0.1 M $Bu_4N^+ClO_4^-$ in acetonitrile) volume of 2 cm^3, using a Ag/$AgNO_3$ (0.1 M) electrode as reference, a platinum wire as counter electrode and a platinum disk (effective area 1.00 cm^2) as working electrode on which the thin polymers were dipped/grafted. The experiments were performed with an EG&G Model 273A potentiostat/galvanostat under argon atmosphere. All potentials were measured against a Ag/$AgNO_3$ 0.1 $mol \cdot dm^{-3}$ (acetonitrile) electrode (0.307 V vs SCE). In the fabrication of devices, indium tin oxide- (ITO-) coated glass was used as substrate. A uniform film (thickness ∼1000 Å) of polymer **IVc** was obtained by spin-coating from the filtered polymer solution at a rate of 4000 rpm for 15 s. Calcium was vapor-deposited as the top electrode at a pressure below 4×10^{-6} Torr, yielding a 1000 Å layer.

Synthesis: 3-Alkythiophenes. All 3-alkylthiophenes were synthesized according to the procedure of Zimmer et al.[24] All compounds were purified either by distillation or on a silica gel column with hexane as the eluent. The chemical structures were characterized by ^1H NMR, ^{13}C NMR, MS, and elemental analysis.

3-Octylthiophene (73% yield): MS *m*/*z* 196; ^1H NMR ($CDCl_3$) δ 7.23 (d, $J = 4.5$ Hz, 1 H), 6.93 (m, 2 H), 2.63 (t, $J = 7.5$ Hz, 2 H), 1.63 (m, 2 H), 1.38−1.20 (m, 10 H), and 0.88 (t, $J = 5.7$ Hz) ppm.

3-Butylthiophene (65% yield): MS *m*/*z* 140; ^1H NMR ($CDCl_3$) δ 7.23 (d, $J = 4.7$ Hz, 1 H), 6.89 (m, 2 H), 2.62 (t, $J = 7.0$ Hz, 2 H), 1.68−1.23 (m, 4 H), and 0.88 (t, $J = 6.2$ Hz, 3 H) ppm.

3-Alkylthiophene-2,5-dicarbonyl Acid. Into a N_2-flushed flask containing TMEDA (0.158 mol) and a solution of *n*-BuLi (1.6 M solution in hexane, 98 cm^3, 0.158 mol) in 30 cm^3 of hexane was added 3-alkylthiophene (0.0633 mol) at room temperature under nitrogen atmosphere. After being stirred at room temperature for 1 h, the mixture was refluxed for additional 30 min and then cooled to −70 °C. The cold mixture was slowly poured into a 500 cm^3 flask half-filled with crushed dry ice under the protection of dry nitrogen. Subsequently, the mixture was warmed to room temperature overnight and then poured into a cold solution of 10 M HCl with ice. The aqueous layer was extracted with ether (two portions of 100 cm^3). The combined ether extract was extracted with 10% NaOH (100 cm^3), and the aqueous layer was acidified with 10 M HCl. The mixture was extracted with ether (two portions of 50 cm^3), and the ether extract was washed with water and saturated NaCl and then dried over anhydrous $MgSO_4$. Removal of ether by evaporation and recrystallization from the mixed solvent of ethanol−water afforded the final products (yield 70−80%).

3-Butylthiophene-2,5-dicarbonyl acid: MS *m*/*z* 228; ^1H NMR ($CDCl_3$) δ 7.7 (s, 1 H), 4.5 (br s, 2 H), 3.0 (t, $J = 7.6$ Hz, 2 H), 1.6 (m, 2 H), 1.3 (m, 2 H), and 0.9 (t, $J = 7.3$ Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 165.2, 163.7, 151.8, 142.0, 139.1, 138.3, 33.3, 29.6, 23.1, and 14.1 ppm.

3-Octylthiophene-2,5-dicarbonyl acid: MS *m*/*z* 284; ^1H NMR ($CDCl_3$) δ 7.7 (s, 1 H), 4.9 (br s, 2 H), 2.6 (t, $J = 7.3$ Hz, 2 H), 2.4 (br s, 2 H), 1.6−1.3 (m, 12 H), and 0.9 (t, $J = 5.5$ Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 159.7, 158.6, 154.4, 142.9, 139.8, 138.9, 31.7, 30.3, 29.6, 29.3, 29.2, 29.1, 22.6, and 14.0 ppm.

3-Alkylthiophene-2,5-dicarbonyl Chloride (Ib and Ic). Excess thionyl chloride and 3-alkylthiophene-2,5-dicarbonyl acid were mixed in a round-bottom flask. The mixture was refluxed for 5 h and then the excess thionyl chloride was removed under reduced pressure. The residue was distilled under vacuum to give the light-yellow oil (134 °C/0.1 mbar with a yield of 89% for **Ic**).

3-Butylthiophene-2,5-dicarbonyl chloride (Ib): MS *m*/*z* 265; ^1H NMR ($CDCl_3$) δ 7.8 (s, 1 H), 2.9 (t, $J = 7.8$ Hz, 2 H), 1.6−1.5 (m, 2 H), 1.4−1.3 (m, 2 H), and 0.9 (t, $J = 7.2$ Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 160.2, 158.8, 154.3, 142.9, 139.8, 138.8, 31.6, 30.0, 22.4, and 13.6 ppm. Anal. Found: C, 45.60; H, 3.89; Cl, 27.11; S, 12.54. Calcd for $C_{10}H_{10}O_2Cl_2S$: C, 45.30; H, 3.80; Cl, 26.74; S, 12.09.

3-Octylthiophene-2,5-dicarbonyl chloride (Ic): MS *m*/*z* 321; ^1H NMR ($CDCl_3$) δ 7.7 (s, 1 H), 2.9 (t, $J = 7.6$ Hz, 2 H), 1.6−1.3 (m, 12 H), and 0.8 (t, $J = 6.5$ Hz, 3 H) ppm; ^{13}C NMR ($CDCl_3$) δ 159.7, 158.6, 154.4, 142.9, 139.8, 138.9, 31.7, 30.3, 29.6, 29.3, 29.2, 29.1, 22.6, and 14.0 ppm. Anal. Found: C, 52.47; H, 5.78; Cl, 22.18; S, 10.03. Calcd for $C_{14}H_{18}O_2Cl_2S$: C, 52.34; H, 5.65; C, 22.07 S, 9.98.

Thiophene-2,5-dicarbonyl Chloride (Ia). Thiophene-2,5-dicarbonyl chloride was prepared from the starting material of thiophene using the same procedures in synthesizing **Ib** and **Ic**. ^1H NMR ($CDCl_3$) δ 7.93 (s, 2H). Anal. Found: C, 34.73; H, 0.98; S, 15.90; Cl, 34.89. Calcd for $C_6H_2Cl_2O_2S$: C, 34.45; H, 0.97; S, 15.34; Cl, 33.97.

2,5-Terephthalic Dihydrazide (II). The compound was prepared from dimethyl 2,5-terephthalate by reaction with excess hydrazine monohydrate in methanol. ^1H NMR (DMSO-d_6 with little $CDCl_3$) δ 9.9 (s, 2 H), 7.9 (s, 4 H), 4.5 (br s, 4 H). Anal. Found: C, 49.74; H, 5.33; N, 28.82. Calcd for $C_8H_{10}N_4O_2$: C, 49.48; H, 5.19; N, 28.85.

Poly(3-octyl)thiophene-2,5-hydrazide-*p*-phenyl-2,5-hydrazide (IIIc). 3-Octylthiophene-2,5-dicarbonyl chloride (3.2 g, 0.01 mol) was added with stirring into a solution of 1.94 g (0.01 mol) of **II** in 20 cm^3 of NMP containing 0.1 g of LiCl and 0.02 mol of pyridine at room temperature over a period of 3 h. After the reaction, the viscous solution was poured into 200 cm^3 of water and the polymer was precipitated out. The polymer was isolated by filtering and was washed with water and then ethanol and then dried under vacuum at 60 °C to give a white powder polymer (4.0 g, 90%). Anal. Found: C, 58.62; H, 6.15; N, 10.69; S, 7.56. Calcd for $C_{22}H_{26}N_4O_4S$: C, 59.72; H, 5.88, N, 12.67; S, 7.23.

A similar synthetic procedure was performed for the synthesis of **IIIa** and **IIIb**.

Poly(3-butyl)thiophene-2,5-hydrazide-*p*-phenyl-2,5-hydrazide (IIIb): Anal. Found: C, 53.60; H, 4.53; N, 13.00; S, 8.27. Calcd for $C_{18}H_{18}N_4O_4S$: C, 55.95; H, 4.66; N, 14.51; S, 8.29.

Polythiophene-2,5-hydrazide-*p*-phenyl-2,5-hydrazide (IIIa): Anal. Found: C, 49.09; H, 3.79; N, 14.62; S, 9.53. Calcd for $C_{14}H_{10}N_4O_4S$: C, 50.91; H, 3.03; N, 16.97; S, 9.70.

Poly(3-alkyl)thiophene-2,5-oxadiazole-*p*-phenyl-2,5-oxadiazole (IVa−c). Poly(3-alkyl)thiophene-2,5-hydrazide-

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[24] (a) Van Pham, C.; Mark, H. B.; Zimmer, H. *Synth. Commun.* **1986**, *16*, 689. (b) Cunningham, D. D.; Laguren-Davisson, L.; Mark, H. B., Jr.; Van Pham, C.; Zimmer, H. *J. Chem. Soc., Chem. Commun.* **1987**, 1021.

p-phenyl-2,5-hydrazide (2.0 g) was refluxed in 25 cm^3 of $POCl_3$ for 4 h and then the reaction mixture was poured into 200 cm^3 of water. The precipitated polymer was isolated by filtering and was washed with water, ethanol, and ether successively and then was dried under vacuum at room temperature to give yellow powders.

IVc (90% yield): ^{1}H NMR (TFA-*d*/$CDCl_3$) δ 8.5 (br s, 4 H), 8.0 (br s, 1 H), 3.2 (m, 2 H), 1.9−1.3 (m, 12 H), and 0.9 (m, 3 H) ppm. Anal. Found: C, 63.53; H, 5.93; N, 13.46; S, 7.25. Calcd for $C_{22}H_{22}N_4O_2S$: C, 65.02; H, 5.42; N, 13.79; S, 7.88.

IVb: ^{1}H NMR (TFA-*d*/$CDCl_3$) δ 8.5 (s, with two small peaks at 8.39 and 8.26, 4 H), 8.1 (s, with two small peaks at 8.05 and 7.97, 1 H), 3.3 (m, 2 H), 1.9 (m, 2 H), 1.6 (m, 2 H), and 1.1 (m, 3 H) ppm. Anal. Found: C, 58.58; H, 4.78; N, 14.35; S, 8.85. Calcd for $C_{18}H_{14}N_4O_2S$: C, 61.71; H, 4.00; N, 16.00; S, 9.14.

IVa: Anal. Found: C, 49.91; H, 3.13; N, 15.49; S, 8.03. Calcd for $C_{14}H_6N_4O_2S$: C, 57.14; H, 2.04; N, 19.05; S, 10.88.

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