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Poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl). A New Low Band Gap Conducting Polymer

Martin Pomerantz,* Xiaomin Gu, and Simon Xinnong Zhang

Center for Advanced Polymer Research, Department of Chemistry and Biochemistry, Box 19065, The University of Texas at Arlington, Arlington, Texas 76019-0065

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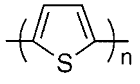
ABSTRACT: A new low band gap conducting polymer, poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl) (**5**), predicted to have nearly equi-energetic aromatic and quinonoidal forms, was synthesized by a multistep sequence involving $FeCl_3$ polymerization of 2-decylthieno[3,4-*b*]thiophene (**7**) and studied. A film of **5** showed a vis−NIR spectral $\lambda_{max} = 925$ nm, a band edge band gap of 0.92 eV, and an $FeCl_3$-doped conductivity of 3.1×10^{-3} S cm^{-1}. A $CHCl_3$ solution showed $\lambda_{max} = 739$ nm and a band-edge band gap of 0.98 eV. GPC (polystyrene standards) gave a number-average molecular weight, $\bar{M}_n$, of 52 000 with a polydispersity $\bar{M}_w/\bar{M}_n$ of 1.7. The band gap of 0.92 eV makes **5** one of the lowest band gap organic polymers known.

Introduction

Electrically conducting polymers represent an important new class of materials and have been under intensive study for about 20 years. Among all approaches, band gap control represents one of the most important ways to improve the performance of conducting polymers in terms of conductive and optical properties. The band gap is the energy gap between the filled valence band and the unfilled conduction band, and in the case of polythiophene it is about 2.1 eV. If the band gap of a conductive polymer could be reduced to zero (or close to zero), inherent organic conductors similar to metals, which have overlapping bands, would be obtained.[1] Also, conducting polymers are generally highly colored in the nonconducting state due to optical transitions of electrons from the valence band to the conduction band. Upon doping, two new states are produced within the energy gap between the valence and conduction bands, and the presence of these gives rise to new low-energy transitions in the doped material. These transitions increase in intensity upon increased doping while the original absorptions, seen in the undoped material, decrease in intensity. Thus, by lowering the band gap (as in low band gap polymers) the optical transition would be in the long wavelength portion of the visible spectrum (the material would be highly colored). Upon oxidative doping, the new absorptions would be at still longer wavelength, in the near-infrared spectral region, and the original absorption which produced the color would be considerably reduced. This, as is the case with a number of low band gap polymers, renders the polymer very lightly colored and essentially transparent.[1]

The band gap of conjugated, conducting polymers, in particular polythiophenes, depends on the extent of aromatic and quinonoid character. In particular, Brédas, Kertesz, Jenehke, and their co-workers have shown that the band gap is more or less proportional to the bond length alternation along the polymer backbone.[1−5] Increased quinonoid contribution in polymers such as polythiophene linearly reduces the band gap.[2,3] Thus, the presence of both aromatic and quinonoid thiophene units in the polymer will reduce the band gap through the relaxation of bond length alternations along the polymer backbone.

While polythiophene is known to exist in the aromatic form **1**, molecules such as poly(benzo[*c*]thiophene-1,3-diyl) [poly(isothianaphthene)][6] and poly(thieno[3,4-*b*]-pyrazin-5,7-diyl) {poly(thieno[3,4-*b*]pyrazine)}[7,8] exist in the quinonoid forms **2** and **3**, respectively, in the undoped state.[1,9−12] Over the past several years materials that are intermediate between the two forms have been sought, and these polymers have generally had methine groups in the backbone. This results in both aromatic and quinonoid thiophene rings being present in the backbone of the polymer main chain as shown, for example, in **4**.[13−17]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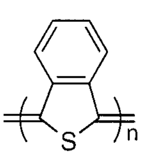
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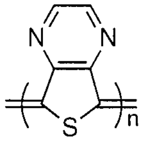
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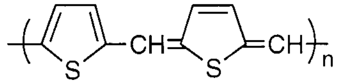
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Three years ago we reported preliminarily on poly-(2-decylthieno[3,4-*b*]thiophene-4,6-diyl) {poly(2-decylthieno[3,4-*b*]thiophene)} (**5**),[18] and we now wish to report a more complete study on the synthesis and properties of this polymer **5**. Polymer **5** has been designed to have the unique property of having the aromatic **5a** and the quinonoid **5q** forms be of nearly equal energy. Near energetic degeneracy is the result of having each repeat unit contain one aromatic and one quinonoid ring. In addition, an alkyl group is used for solubility. Quantum mechanical calculations, using PRDDO optimized geometries, have been carried out by Hong and Marynick, who verified the near energy degeneracy of the two forms with the aromatic form **5a** being very slightly favored by 0.3 kcal/repeat unit (1.3 kJ/repeat unit) over the quinonoid form **5q**.[19] In addition, alkyl (methyl)

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* Corresponding author. E-mail: pomerantz@uta.edu.

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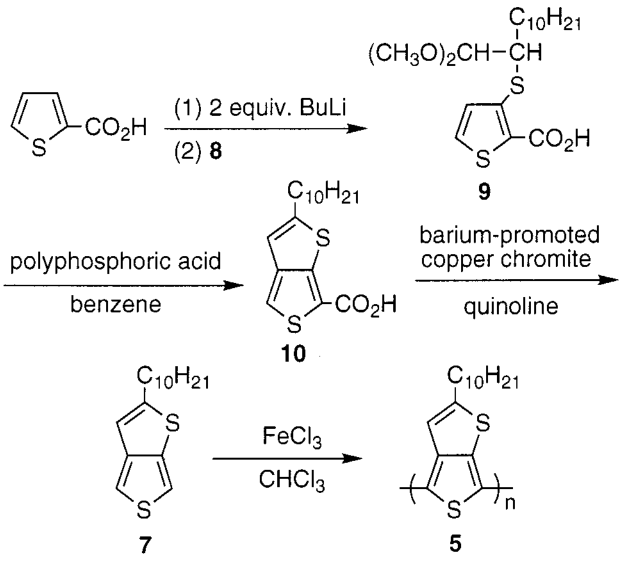
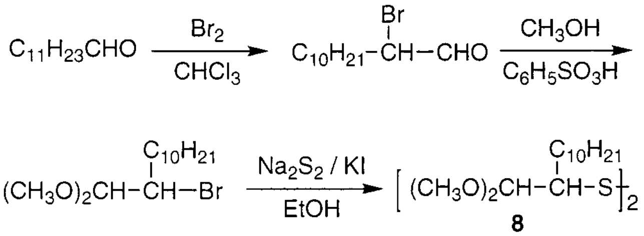
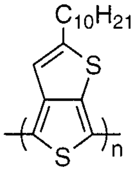
Scheme 1



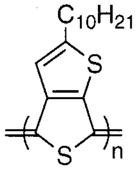
Scheme 2



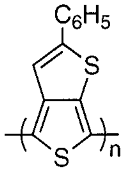
substitution was said to very slightly increase the stability of the aromatic over the quinonoid form.[19] Very recently, a brief report on a related polymer, poly(2-phenylthieno[3,4-*b*]thiophene) (**6**), has appeared.[20]



5a



5q



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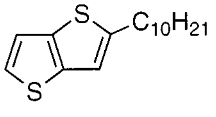
Results and Discussion

The synthesis of poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl) {poly(2-decylthieno[3,4-*b*]thiophene)} (**5**) was by $FeCl_3$-induced oxidative polymerization of the monomer 1-(2-thieno[3,4-*b*]thienyl)decane (2-decylthieno[3,4-*b*]thiophene, **7**). The synthesis of **7** along with its polymerization is shown in Scheme 1. Further, one of the starting materials, bis(1,1-dimethoxy-2-dodecyl) disulfide (**8**), had to first be prepared, and this is shown in Scheme 2.

Dodecanal was brominated in chloroform solution to produce 2-bromo-1-dodecanal (Scheme 2). It is important that the concentration of the reaction mixture be kept dilute since when the reaction was run at higher concentration (chloroform:1-dodecanal = 4:1), 90% of the reaction product was the oxidized compound, dodecanoic acid. The aldehyde group was protected as the dimethylacetal with methanol to give 2-bromo-1,1-dimethoxydodecane. This was heated at reflux in ethanol overnight with a mixture of sulfur and sodium sulfide (Na_2S_2) in the presence of KI[21] to produce bis(1,1-dimethoxy-2-dodecyl) disulfide (**8**), which was used directly in next step without purification (Scheme 1). Interestingly, the two methoxy groups of the bromoacetal showed the identical ^1H NMR chemical shift for the methoxy groups but different ^{13}C NMR chemical shifts. This is because the two methoxy groups are diastereotopic, and the greater dispersion in the ^{13}C NMR spectrum allows for peak separation. Actually there were three peaks at δ 55.4, 55.0, and 54.9. Selective ^1H decoupling experiments showed that the peaks at 55.4 and 54.9 were due to the methoxy groups while the one at 55.0 was due to the carbon bearing the bromine.

As shown in Scheme 1, thiophene-2-carboxylic acid was deprotonated with 2 equiv of *n*-BuLi at -78 °C[22] followed by treatment with the disulfide **8**. The reaction was quenched with water. The basic reaction mixture was gradually neutralized and then adjusted to a pH of 6−7. The solution was extracted with ether while carefully controlling the pH between 6 and 7 in order to prevent hydrolysis of the acetal. By careful control of the work-up conditions, pure (1,1-dimethoxy-2-dodecyl) 2-carboxy-3-thienyl sulfide (**9**) was obtained in 47% yield. The structure was confirmed by both NMR spectroscopy and elemental analysis. Here the two diastereotopic methoxy groups showed separate peaks in both the ^1H and ^{13}C NMR spectra. The acetal group was very sensitive to acid; even a trace impurity of hydrochloric acid in $CDCl_3$ solvent would result in the conversion to the aldehyde. A pure grade of $CDCl_3$ (99.96% deuterium) was used to obtain a good NMR spectrum. The substitution was established as 2,3 since in the ^1H NMR spectrum the ring protons at δ 7.13 and 7.53 were an AB double−doublet with $J = 5.2$ Hz which is in the normal range for 2,3-disubstituted thiophenes. Also, no other disubstituted thiophene isomer shows an H−H coupling constant of greater than 4.4 Hz.[23] Cyclization of **9** with polyphosphoric acid in benzene gave 2-decylthieno[3,4-*b*]thiophene-6-carboxylic acid (**10**) in 44% yield. There was also a fairly major side product produced, namely 1-(2-thieno[3,2-*b*]thienyl)decane (**11**).



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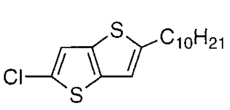
This molecule also was identified on the basis of its ^1H NMR spectrum which showed three aromatic hydrogen atoms. The two peaks at δ 7.16 and 7.24 were an AB pair which showed $J = 5.3$ Hz. This defines one of the thiophenes as a 2,3-disubstituted moiety.[23] The peaks at δ 6.94 (the one on the other thiophene ring) and the one at δ 7.16 both showed a small long-range inter-ring 5-bond coupling of 0.7 Hz. 1-(2-Thieno[3,2-*b*]thienyl)decane (**11**) was also synthesized by another route, namely by dechlorination of 2-chloro-5-decylthieno[3,2-*b*]thiophene (**12**)[24] using butyllithium followed by quenching with water. **12**, in turn, was a side product in the cyclization of (1,1-dimethoxy-2-dodecyl) 2-carboxy-5-chloro-3-thienyl sulfide (**13**) using PPA.[24]



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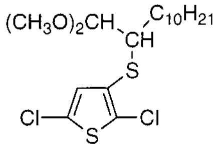

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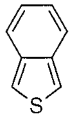

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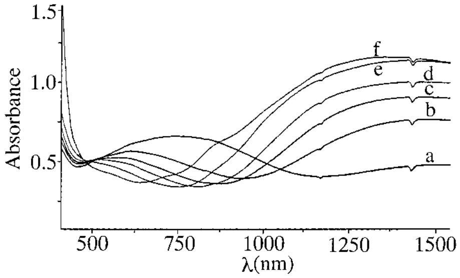


Figure 1. Vis−NIR spectra of **5** in $CHCl_3$ solution (a) before doping and after doping with (b) 2.5% $FeCl_3$, (c) 5.0% $FeCl_3$, (d) 10% $FeCl_3$, (e) 20% $FeCl_3$, and (f) >30% $FeCl_3$.

The decarboxylation of 2-decylthieno[3,4-*b*]thiophene-6-carboxylic acid (**10**) was carried out using barium promoted copper chromite in quinoline at 200 °C[25] to give the monomer 1-(2-thieno[3,4-*b*]thienyl)decane (**7**) in 69% yield. The three aromatic protons appeared at δ 7.11 (2H) and 6.57 (1H) in the ^{1}H NMR spectrum, and the six aromatic carbon atoms appeared between δ 109.9 and 152.9 in the ^{13}C NMR spectrum. It should be pointed out that 1-(2-thieno[3,4-*b*]thienyl)decane (**7**) darkens slowly when exposed to ambient conditions, but it could be kept for many weeks without darkening in a drybox. Thus, **7** is considerably more stable than isothianaphthene (**14**).[6,26]

Polymerization was effected with 1.2 equiv of $FeCl_3$ in chloroform and provided poly(2-decylthieno[3,4-*b*]-thiophene-4,6-diyl) (**5**) in 66% yield as a blue-green material which was soluble in a variety of organic solvents such as chloroform, THF, and chlorobenzene. Any low molecular weight material was removed by extraction with methanol for 2 days. **5** was dedoped by extraction of a chloroform solution with either anhydrous hydrazine or hydrazine hydrate. Upon polymerization, the ring hydrogen at $\delta = 6.57$ in the ^{1}H NMR spectrum of monomer **7** moved to $\delta = 6.64$ in polymer **5**. In the infrared spectrum, the aromatic CH stretch at 3107 cm^{-1} in monomer **7** got very much smaller, leaving only the band at about 3050 cm^{-1}, which appeared in both monomer **7** and polymer **5**. GPC analysis, using polystyrene standards, gave a number-average molecular weight, $\bar{M}_n$, of 52 000 and a weight-average molecular weight, $\bar{M}_w$, of 90 000 with a polydispersity of 1.7.

The vis−NIR spectrum of the polymer solution in chloroform showed a λ_{max} at 739 nm with the band edge at 1260 nm (0.98 eV). Upon doping with ferric chloride at different levels (see Figure 1), the absorption peak at 739 nm gradually diminished and moved to somewhat shorter wavelength while a new peak at 1377 nm began to appear. The absorption peak at 1377 nm reached its maximum when the peak at 739 nm had disappeared. The color of the poly(2-decylthieno[3,4-*b*]-thiophene-4,6-diyl) (**5**) solution changed from brilliant blue to pale gray-brown after doping. The film of polymer **5** showed a red shift in the vis−NIR spectrum (Figure 2) relative to that in solution and displayed a λ_{max} at 925 nm with the band edge at 1350 nm (0.92 eV). Upon doping, the absorption peak at 925 nm disappeared, and a new broad peak at 1450 nm was observed. The color of the film changed from blue-green to a pale blue-gray.

The band gap of 0.92 eV is one of the lowest band gaps observed up to the present[1] but is not quite as low as that reported recently for the phenyl derivative, poly-(2-phenylthieno[3,4-*b*]thiophene) (**6**), of 0.85 eV.[20] The absorption maxima of 739 nm, 1.68 eV, in solution and 925 nm, 1.34 eV, as a film are in reasonably good agreement with the value calculated, using quantum mechanical calculations, of 1.5−1.6 eV[19] and with that reported for the film of **6** of 954 nm.[20]

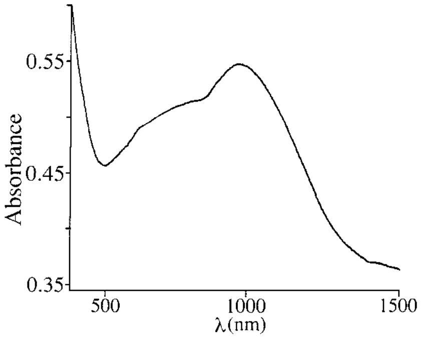
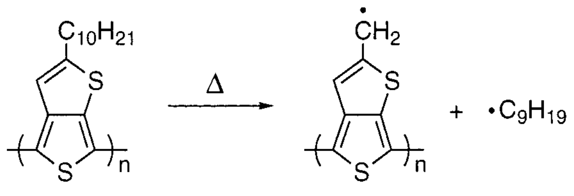


Figure 2. Vis−NIR spectrum of a film of **5**.

Scheme 3



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A film of poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl) (**5**) could be cast onto glass from either chloroform or chlorobenzene solution. The conductivity measured by the standard four-in-line probe method[27,28] for the polymer film was in the range 10^{-6}−10^{-5} S cm^{-1} with 6.8×10^{-5} S cm^{-1} being the highest value observed. The conductivities of the films doped with $FeCl_3$, I_2, and $NOBF_4$ were 3.1×10^{-3}, 1.0×10^{-6}, and 4.2×10^{-6} S cm^{-1}. Thus, only in the case of $FeCl_3$ doping is there a significant increase in the conductivity relative to the undoped material. After doping, the polymer film became free-standing (it peeled away from the glass surface) and very brittle. Unfortunately, conductivity measurements were not carried out for the related polymer poly(2-phenylthieno[3,4-*b*]thiophene) (**6**).[20]

Thermogravimetric analysis (TGA; argon atmosphere) of poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl) (**5**) showed the onset of decomposition to be at about 145 °C with the decomposition, up to 600 °C, occurring in two stages. The first was from about 145 to about 270 °C and showed a weight loss of approximately 44%, and the second was from about 270 to about 460 °C and showed a weight loss of approximately 80%. At 600 °C the weight loss was 86%. It is interesting to note that loss of C_9H_{19} from the side chain, by cleavage of the weakest C−C bond, would result in a weight loss of just under 46%, which corresponds to the first decomposition shown in the TGA. This cleavage would produce a highly resonance stabilized benzylic type radical as shown in Scheme 3.

Experimental Section

General Procedures. ^{1}H NMR spectra were obtained at either 300.13 MHz (Bruker MSL-300 instrument) or 500.16 MHz (JEOL Eclipse 500 instrument) using $CDCl_3$ solvent with TMS ($\delta = 0.00$ ppm) as internal reference. ^{13}C NMR spectra were recorded at either 75.47 or 125.78 MHz in $CDCl_3$ solvent with $^{13}CDCl_3$ ($\delta = 77.0$ ppm) as internal reference. HPLC was conducted using a Waters instrument, an ECONOSIL C18 reverse-phase column (250 mm × 4.6 mm), a UV−vis detector set at 254 nm, and a Maxima 820 chromatography data station. Methanol was used as the eluent with a flow rate of 1.0 mL/min. Gas chromatography was carried out on a Varian 3700 instrument with a DB-5 silica capillary column (30 m long, 0.319 mm diameter, 0.025 μm coating thickness) with an initial temperature of 80 °C for 1 min and a heating rate of 10 °C/min from 80 to 240 °C. Infrared spectra were taken on a Biorad-Digilab FTS-40 Fourier transform infrared spectrometer, using KBr pellets, powdered samples with KBr in a diffuse reflectance unit, or neat liquid samples between NaCl plates. Elemental analysis were obtained on a Perkin-Elmer 2400 CHN analyzer. Gel permeation chromatography (GPC) was carried out on a Waters GPC system, using a UV−vis detector set at 254 nm, Millennium 2010 software, and a serial combination of 10^3, 10^4, and 10^5 Å Ultrastyragel columns. The calibration curve was determined by use of polystyrene standards with a molecular weight of 800−900 000. THF was used as the eluent with a flow rate of 1.0 mL/min. TGA was conducted under argon on a TA Instruments system fitted with a TGA 2050 thermogravimetric analyzer using a heating rate of 10 °C/min. UV−vis−NIR spectra were recorded using a Varian Cary 5E UV−vis−NIR spectrophotometer as solutions in chloroform or hexanes or as polymer thin films cast onto quartz plates. Commercially available *n*-BuLi (1.6 M in hexane), bromine, polyphosphoric acid, 2-thiophenecarboxylic acid, $Na_2S\cdot 9H_2O$, *n*-dodecanal, sulfur, and barium promoted copper chromite were used without further purification. THF was dried over sodium benzophenone ketyl and distilled prior to use. Methanol was distilled from Mg turnings and stored over 4A molecular sieves in sealed bottles. Quinoline was distilled and stored over 4A molecular sieves in a brown container. Chloroform was freshly distilled from $CaCl_2$ prior to use. BuLi solution was titrated with diphenylacetic aced.[29] 0.212 g of diphenylacetic acid (1.00 mmol) was dissolved in 4 mL of dry THF and was placed in a serum-capped 10 mL Erlenmeyer flask under argon. BuLi solution in hexanes was added drop by drop from a syringe under argon until the yellow end point. The concentration of *n*-BuLi is given by $M = 1/X$ (X = volume of *n*-BuLi solution used in milliliters).

2-Bromo-*n*-dodecanal. 20.0 g (109 mmol) of *n*-dodecanal dissolved in 400 mL of chloroform was placed in a one-necked 1 L flask with a dropping funnel. 4.4 mL (13.6 g, 85 mmol) of bromine dissolved in 400 mL of chloroform was dropped into the reaction flask at such a rate that the red brown color of the bromine diminished immediately upon the addition. When the addition was complete (the reaction could be monitored by GC), the reaction mixture was stirred for an additional half hour and then poured into 100 mL of saturated $NaHCO_3$ solution. The chloroform layer was washed twice with 30 mL portions of water, dried (Na_2SO_4), and filtered. The solvent was removed under reduced pressure, and the crude liquid product was distilled under vacuum; bp 83 °C (0.04 mmHg). Yield 17.0 g (75%). ^{1}H NMR: δ 9.43 (d, J = 3 Hz, 1 H), 4.22 (m, 1 H), 1.8−2.1 (m, 2 H), 1.2−1.6 (m, 16 H), 0.88 (t, J = 6 Hz, 3 H). ^{13}C NMR: δ 192.7, 55.5, 31.9, 31.7, 29.5, 29.4, 29.3, 28.9, 26.9, 22.7, 14.1. Anal. Calcd for $C_{12}H_{23}OBr$: C, 54.76; H, 8.81. Found: C, 55.05; H, 8.86.

2-Bromo-1,1-dimethoxydodecane. 15.4 g (58.6 mmol) of 2-bromo-1-dodecanal was combined with 2.26 g (14.3 mmol) of benzenesulfonic acid in 510 mL of dry methanol, and the mixture was refluxed for 4 h under argon. After cooling, the methanol was removed under reduced pressure, and 50 mL of saturated $NaHCO_3$ solution was added. The aqueous layer was then extracted with 3 × 130 mL of ether, and the combined ether phase was washed with 50 mL of saturated $NaHCO_3$ solution and then with 3−5 50 mL portions of water. The product was dried (Na_2SO_4) and filtered, and the solvent was removed under reduced pressure. The crude liquid product was distilled under vacuum; bp 89−90 °C (0.03 mmHg). Yield 14.2 g (78%). ^{1}H NMR: δ 4.38 (d, J = 5 Hz, 1 H), 3.97 (m, 1 H), 3.45 (s, 6 H), 1.90 (m, 1 H), 1.73 (m, 1 H), 1.26 (m, 16 H), 0.88 (t, J = 7 Hz, 3 H). ^{13}C NMR: δ 106.3, 55.4, 55.0, 54.9, 32.8, 31.9, 29.5, 29.4, 29.3, 29.0, 27.3, 22.6, 14.1. Anal. Calcd for $C_{14}H_{29}O_2Br$: C, 54.37; H, 9.45. Found: C, 54.76; H, 9.09.

Bis(1,1-dimethoxy-2-dodecyl) Disulfide (8). The reaction was carried out following a literature procedure.[21] 0.702 g (21.9 mmol) of sulfur was mixed with 60 mL of absolute ethanol in a three-necked flask. 3.51 g (14.6 mmol) of $Na_2S\cdot 9H_2O$ was added, and the mixture was stirred until all the solid was dissolved. 0.165 g (0.994 mmol) of KI and 6.00 g (19.4 mmol) of 2-bromo-1,1-dimethoxydodecane were then added to the flask, and the reaction mixture was refluxed overnight. The ethanol was removed under reduced pressure until about 7 mL remained. Water was added, and the mixture was extracted several times with ether. The etherial solution was dried ($MgSO_4$) and filtered, and the ether was removed under reduced pressure. The dark brown crude product was used directly in the next step.

(1,1-Dimethoxy-2-dodecyl) 2-Carboxy-3-thienyl Sulfide (9). The reaction was conducted following a literature procedure.[22] 1.20 g (9.36 mmol) of 2-thiophenecarboxylic acid and 300 mL of dry THF were placed in a dry one-necked 500 mL flask purged with argon. The solution was cooled to −78 °C, and 20.2 mmol (approximately 13 mL) of *n*-BuLi (1.6 M in hexanes) was very slowly injected into the cold 2-thiophenecarboxylic acid solution with a syringe. After addition, the reaction mixture was stirred at −78 °C for 1 h. The disulfide **8** prepared above from 6.00 g (19.4 mmol) of 2-bromo-1,1-dimethoxydodecane was dissolved in 30 mL of dry THF and very slowly injected into the flask with a syringe. The reaction mixture was stirred at −78 °C for an additional hour and then slowly warmed to ambient temperature. The THF was removed under reduced pressure, and 18 mL of water and 30 mL of ether were added. The basic aqueous phase was slowly neutralized to pH 6−7 with 6 N hydrochloric acid. It was extracted several times with ether while carefully maintaining the pH between 6 and 7. The combined ether extracts were then dried ($MgSO_4$) and filtered, and the ether was removed under reduced pressure. 12 mL of hexanes was added to the residue which was kept for several hours at ambient temperature and then put into a freezer (−15 °C). The solid which crystallized was filtered and washed with 8 mL of cold hexanes. Yield 1.71 g (47%); mp 104−106 °C. ^{1}H NMR: δ 11.34 (br s, 1 H), 7.55 (d, J = 5 Hz, 1 H), 7.13 (d, J = 5 Hz, 1 H), 4.37 (d, J = 5 Hz, 1 H), 3.45 (s, 3 H), 3.42 (s, 3 H), 3.38 (m, 1 H), 1.87 (m, 1H), 1.56 (m, 1H), 1.25 (m, 16 H), 0.87 (t, J = 7 Hz, 3 H). ^{13}C NMR: δ 165.7, 142.6, 131.9, 129.6, 125.8, 107.4, 56.3, 55.7, 52.0, 31.9, 29.7, 29.5, 29.4, 29.3, 27.0, 22.7, 14.1. Anal. Calcd for $C_{19}H_{32}O_4S_2$: C, 58.73; H, 8.30. Found: C, 58.42; H, 8.19.

2-Decylthieno[3,4-*b*]thiophene-6-carboxylic Acid (10). The reaction was carried out according to a literature procedure.[30] 2.00 g (5.14 mmol) of (1,1-dimethoxy-2-dodecyl)-2-carboxy-3-thienyl sulfide **(9)** and 10 mL of benzene were placed in a one-necked 25 mL flask equipped with a condenser. 20.0 g of polyphosphoric acid (PPA) was weighed into the flask, and the mixture was heated at reflux for 4 h. The reaction mixture was cooled to ambient temperature, the benzene solution was poured out, and the residual viscous mixture was washed with benzene, and then 14 mL of water was added. The aqueous mixture was extracted three times with benzene. The combined benzene extracts were washed three times with H_2O and dried ($MgSO_4$), and the solvent was removed under reduced pressure. The product was purified by recrystallization from hexanes. Yield: 0.72 g (44%); mp 89−91 °C. ^{1}H NMR: δ 9.05 (br s, 1 H), 7.49 (s, 1 H), 6.66 (s, 1 H), 2.80 (t, J = 7 Hz, 2 H), 1.72 (quintet, J = 7 Hz, 2 H), 1.2−1.4 (m, 14 H), 0.88 (t, J = 7 Hz, 3 H). ^{13}C NMR: δ 167.6, 154.8, 147.9, 147.4, 119.8, 116.4, 113.2, 31.9, 31.7, 30.3, 29.6, 29.5, 29.3, 29.1, 22.7, 14.1. Anal. Calcd for $C_{17}H_{24}S_2O_2$: C, 62.92; H, 7.45. Found: C, 63.12; H, 7.75.

The reaction was run again and worked up using the same procedure as above, but after the benzene was evaporated, the crude product was purified using column chromatography (silica gel) with hexanes/ethyl acetate (4/1) as the eluent. In addition to 2-decylthieno[3,4-*b*]thiophene-6-carboxylic acid (**10**), 2-decylthieno[3,2-*b*]thiophene (**11**; 0.30 g, 21%) was obtained. This was then compared to the independently synthesized **11** (see below). ^{1}H NMR: δ 7.26 (d, J = 5.0 Hz, 1

H), 7.17 (dd, $J = 5.1$ Hz, $J = 0.6$ Hz, 1 H), 6.95 (d, $J = 0.7$ Hz, 1 H), 2.87 (t, $J = 7.8$ Hz, 2 H), 1.71 (quintet, $J = 7.6$ Hz, 2 H)), 1.26 (m, 14 H), 0.88 (t, $J = 6.9$ Hz, 3 H). ^{13}C NMR: δ 148.6, 138.7, 137.3, 125.2, 119.4, 116.1, 31.9, 31.6, 31.2, 29.6, 29.5, 29.4, 29.3, 29.1, 22.7, 14.1.

1-(2-Thieno[3,2-*b*]thienyl)decane (11). 100 mg (0.32 mmol) of 2-chloro-5-decylthieno[3,2-*b*]thiophene[24] and 4 mL of freshly distilled THF were put in a 10 mL three-necked flask fitted with a N_2 inlet. 1.0 mL (1.6 mmol) of *n*-BuLi was added dropwise while the reaction mixture was cooled to 0 °C (ice bath). The reaction mixture was warmed to ambient temperature and stirred for 1 h. It was then quenched with 2 mL of water and extracted with 10 mL of ether. The ether layer was dried ($MgSO_4$), and the ether was removed under reduced pressure. The residue was run through a silica gel column with hexane as an eluent to yield 80 mg (89%) of 1-(2-thieno[3,2-*b*]thienyl)decane (**11**). ^{1}H NMR and ^{13}C NMR spectra as above. Anal. Calcd for $C_{16}H_{24}S_2$: C, 68.52; H, 8.62. Found: C, 68.87; H, 8.89.

2-Decylthieno[3,4-*b*]thiophene (7). The decarboxylation reaction was carried out, following literature procedures.[25,31] 0.20 g (0.62 mmol) of 2-decylthieno[3,4-*b*]thiophene-6-carboxylic acid (**10**) and 2 mL of quinoline were placed in a one-necked 10 mL flask equipped with a condenser. 0.10 g of barium-promoted copper chromite was added to the solution, and the reaction mixture was kept under argon. It was heated to 200 °C (oil bath) for 25 min and cooled, 15 mL of benzene was added, and the catalyst was removed by filtration. The organic phase was washed 3 times with 15 mL of 1 N hydrochloric acid, 3 times with saturated $NaHCO_3$ solution, 3 times with water, dried ($MgSO_4$), and filtered. The benzene was removed under reduced pressure, and the product, 2-decylthieno[3,4-*b*]thiophene (**7**), was isolated by chromatography on silica gel with hexanes as eluent. Yield: 0.12 g (69%) of a colorless liquid. Purity (HPLC) >99.5%. ^{1}H NMR: δ 7.09 (s, 2 H), 6.57 (t, $J = 0.9$ Hz, 1 H), 2.72 (dt, $J = 0.9$ Hz, $J = 7.7$ Hz, 2 H), 1.68 (quintet, $J = 7.6$ Hz, 2 H), 1.2−1.4 (m, 14 H), 0.88 (t, $J = 6.4$ Hz, 3 H). ^{13}C NMR: δ 153.0, 147.6, 138.8, 113.2, 110.2, 110.0, 31.9, 30.3, 29.6, 29.3, 29.1, 22.7, 14.1. IR (neat) $\bar{\nu}$: 3106, 3056, 2952, 2925, 2852, 1571, 1524, 1465, 1435, 1377, 1347, 1171, 1086, 1023, 837, 814, 744, 691, 503 cm^{-1}. Anal. Calcd for $C_{16}H_{24}S_2$: C, 68.52; H, 8.62. Found: C, 68.56; H, 8.30. UV−vis (hexanes): λ_{max} 293 nm ($\epsilon = 3.1 \times 10^3$), 278 nm ($\epsilon = 3.1 \times 10^3$), 240 nm ($\epsilon = 1.1 \times 10^4$), and 271 nm (shoulder; $\epsilon = 3.1 \times 10^3$).

Poly(2-decylthieno[3,4-*b*]thiophene) (5). The reaction was conducted, following the literature procedures.[24,36,37] 100 mg (0.357 mmol) of 2-decylthieno[3,4-*b*]thiophene (**15**) was dissolved in 2 mL of dry $CHCl_3$. The solution was placed in a dry and argon-prepurged three-necked flask equipped with an argon inlet and an addition funnel. 69.0 mg (0.425 mmol) of $FeCl_3$ suspended in 2 mL of $CHCl_3$ was dropped into the flask over half an hour. The reaction mixture turned purple upon the addition of the first drop of $FeCl_3$. It was kept stirring at ambient temperature for another hour and poured into 200 mL of methanol. The mixture which formed was kept in a freezer overnight and then filtered under argon. The polymer solid was dissolved in $CHCl_3$ and reprecipitated with methanol. Then a 2 day Soxhlet extraction with methanol was conducted on the green-blue precipitate. The polymer was dried under vacuum overnight. Yield: 66 mg (66%). The polymer was very unstable at ambient conditions. It turned to dark gray upon standing. The dedoping was carried out by extraction of the polymer solution ($CHCl_3$) 3 times with anhydrous hydrazine or hydrazine hydrate. After dedoping the polymer was dried under vacuum overnight. ^{1}H NMR: δ 6.24 (br 1 H), 2.64 (br 2 H), 1.57 (br 2 H), 1.26 (br 14 H), 0.88 (t, $J = 7$ Hz, 3 H). ^{13}C NMR: δ 160−115 (very br), 31.9, 31.5, 31.0, 29.7, 29.4, 22.7, 29.0 14.1. IR (KBr): $\bar{\nu}$ 3109, 2955, 2923, 2852,1458, 1382, 1265, 1187, 1117, 908, 839, 720 cm^{-1}. Vis−NIR: $CHCl_3$ solution: $\lambda_{max} = 739$ nm (dedoped), $\lambda_{max} = 1377$ nm (doped with $FeCl_3$); film: $\lambda_{max} = 925$ nm (dedoped), $\lambda_{max} = 1450$ nm (doped with $FeCl_3$); conductivity (dedoped): 6.8×10^{-5} S cm^{-1}; (doped with $FeCl_3$): 3.09×10^{-3} S cm^{-1}; (doped with I_2): 1.0×10^{-6} S cm^{-1}; (doped with $NOBF_4$): 4.2×10^{-6} S cm^{-1}. Molecular weight of the polymer determined by GPC showed the polymer had $\bar{M}_n = 52\,000$ and $\bar{M}_w = 90\,000$ with a polydispersity of 1.7.

Doping and Conductivity Measurements. The polymer in chloroform solution was doped with a solution of 1.0 g/L of anhydrous $FeCl_3$ in chloroform. Vis−NIR spectra were obtained on the polymer solution containing 0.0%, 2.5%, 5.0%, 10%, 15%, 20%, and over 30% ferric chloride as dopant. This percentage was the weight ratio of the ferric chloride based on the amount of the $FeCl_3$ solution used to the weight of the polymer. The polymer films were doped with solutions of $FeCl_3$ in methanol and solutions of $NOBF_4$ in nitromethane or gaseous I_2. For $FeCl_3$ and $NOBF_4$ doping, the polymer samples were soaked in a 1% solution of the dopant at room temperature for 1 min. The doped films were washed with fresh methanol or nitromethane and dried before the electrical conductivity measurement. For I_2 doping, the polymer films were exposed to iodine vapor at room temperature for 24 h, and then excess iodine was pumped off under vacuum for 24 h. The electrical conductivity of doped or undoped polymer films was measured using the standard four-in-line probe method.[27,28] The thickness of polymer film was measured with a digital micrometer with an accuracy of ±1 μm.

Summary and Conclusions

A new low band gap conducting polymer, poly(2-decylthieno[3,4-*b*]thiophene-4,6-diyl) (**5**), which was predicted to have nearly equi-energetic aromatic and quinonoidal forms,[19] has been prepared by a multistep synthetic sequence employing $FeCl_3$ polymerization of the monomer, 1-(2-thieno[3,4-*b*]thienyl)decane (2-decylthieno[3,4-*b*]thiophene, **7**). A film showed a vis−NIR spectral $\lambda_{max} = 925$ nm, a band edge band gap of 0.92 eV, and an $FeCl_3$-doped conductivity of 3.1×10^{-3} S cm^{-1}. A $CHCl_3$ solution showed $\lambda_{max} = 739$ nm and a band-edge band gap of 0.98 eV. GPC (polystyrene standards) gave a number-average molecular weight of $\bar{M}_n = 52\,000$ with a polydispersity $\bar{M}_w/\bar{M}_n$ of 1.7. In solution the polymer went from a bright blue when undoped to a pale gray-brown upon doping while the film went from a blue-green when undoped to a pale blue-gray when doped.

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