Alkyl-Substituted Thieno[3,2-*b*]thiophene Polymers and Their Dimeric Subunits

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ABSTRACT: A series of alkyl-substituted polythieno[3,2-*b*]thiophenes were synthesized by cross-coupling and oxidative coupling reactions. Their electronic properties were studied by UV−vis absorption and fluorescence spectroscopies. The poly(3-nonylthieno[3,2-*b*]thiophene) prepared via Stille coupling of a differentially functionalized monomer displayed a longer λ_{max} of absorption and a corresponding lower optical band gap when compared to those of regiorandom polymers prepared by the $FeCl_3$ method or through Kumada coupling. Employing a dialkyl-substituted monomer to produce poly(3,6-dinonylthieno-[3,2-*b*]thiophene) leads to dramatic shifting of both the absorption and emission spectra to shorter wavelength. The electrochemistry of these polymers were studied by cyclic voltammetry and revealed that mono alkyl-substituted polymers have relatively lower oxidation potentials compared to that of the dialkyl-substituted polymer. To study the conformation of monomers in the polymer backbone, dimeric subunits of these polymers were prepared. Both UV−vis spectroscopy and computations indicate that the head-to-tail linkage causes a small distortion of adjacent ring units, and head-to-head linkage results in a large decrease of conjugation.

Introduction

Conjugated polymers have received considerable attention as a novel class of organic semiconducting materials, owing to their remarkable electronic and optical properties.[1] In particular, polythiophene and derivatives are of great interest[2−4] due to their relatively small band gaps,[5,6] environmental stability, and good processability.[7] Extensive studies on poly(3-alkylthiophene)s (P3ATs) have demonstrated the importance of monomer connectivity in controlling properties including solid-state packing.[8,9] From a device standpoint, regioregular P3ATs (Figure 1) are superior and have been successfully employed as an active layer in organic field-effect transistors (OFETs) where high field-effect mobilities have been achieved.[7,10,11]

Although many studies involving small molecules have focused on fused-ring organic conjugated materials such as pentacene,[12−14] fully fused polymers are generally too insoluble for device fabrication. However, incorporating partially planarized units into a polymer backbone is a strategy that is recently enjoying increased activity. For example, fluorene-based materials contain planarized biphenyl units and are the basis for several commercial polymers employed in organic light-emitting diodes (OLEDs).[15−18] Recently, the special properties of fused thiophene rings have been explored in the context of polymers. A thieno[3,2-*b*]thiophene-based copolymer exhibits better electroluminescence performance than the corresponding fluorene−bithiophene copolymer,[19] and a polythieno[3,4-*b*]thiophene synthesized by electropolymerization exhibits an extremely low (<1.0 eV) band gap.[20]

We have recently synthesized a series of planarized thiophene oligomers in which two or more of the thiophene units are replaced by fused rings.[21] These compounds display generally low solubility at room temperature, and indeed polymers of thieno[3,2-*b*]thiophenes[22−24] and dithieno[3,2-*b*:2′,3′-*d*]thiophenes[23,25] have been reported to be sufficiently insoluble to preclude full characterization and utilization in devices. Here, we report the syntheses and characterization of poly-(3-alkylthieno[3,2-*b*]thiophene)s and poly(3,6-dialkylthieno[3,2-*b*]thiophene) (Figure 1) and compare the properties of these polymers to those of the extensively studied P3ATs. Because of the higher degree of unsaturation in the fused rings, relatively long nonyl chains were used to increase the solubility of the thieno[3,2-*b*]thiophene-based polymers. The effect of regioregularity on the polymer properties was explored by employing three different polymerization mechanisms. To support these studies, by providing well-defined models for comparison, dimeric subunits of these polymers were synthesized in order to determine the conformation of monomer units in the polymer backbone.

Preparation and Characterization

The monomer 3-nonylthieno[3,2-*b*]thiophene (**4**) was prepared as described in Scheme 1. 1-(3-Bromo-thiophen-2-yl)-decan-1-one (**1**) was synthesized by Friedel−Crafts acylation of 3-bromothiophene with decanoyl chloride. When compound **1** was treated with ethyl thioglycolate and a catalytic amount of NaOH in ethanol, 3-nonylthieno[3,2-*b*]thiophene-2-carboxylate (**2**) was obtained in 70% yield. Hydrolysis with NaOH in ethanol gave the corresponding acid (**3**). Thermal decarboxylation of **3** was carried out in quinoline in the presence of Cu to yield monomer **4** (Scheme 1).

The poly(3-nonylthieno[3,2-*b*]thiophene)s were made by three different methods (Scheme 2). Regiorandom poly(3-nonylthieno[3,2-*b*]thiophene) (**5**) was prepared by an oxidative coupling with $FeCl_3$ in $CHCl_3$ directly from **4**. GPC analysis of **5** indicates the molecular weight of the THF soluble portion is low ($M_n = 1895$, $M_w = 5514$). The large PDI (2.91) is consistent with some cross-linking taking place. Analysis by MALDI−TOF MS reveals that **5** has three types of chains: those with no

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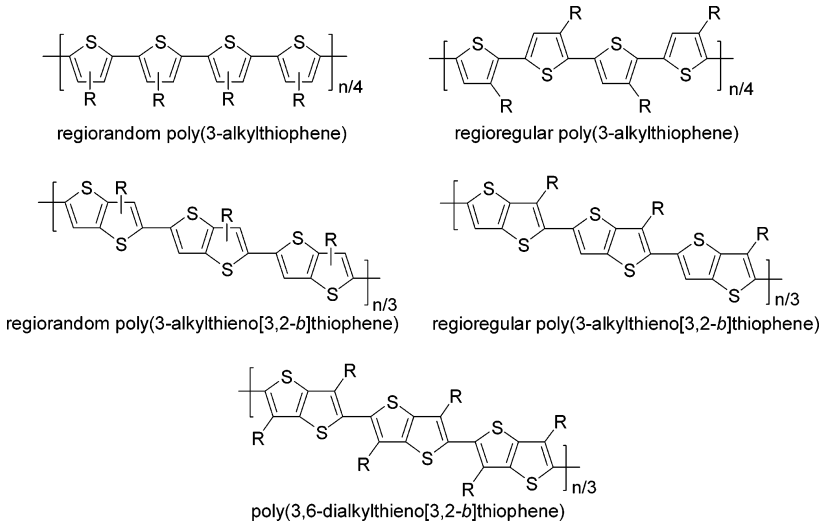
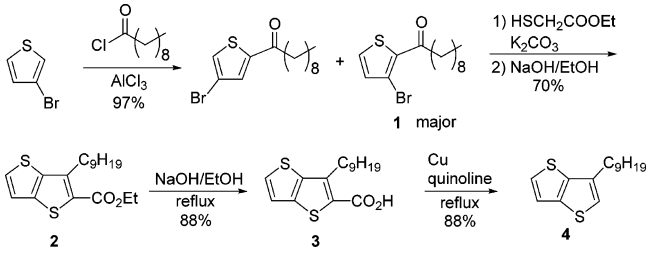


Figure 1. Chemical structures of poly(3-alkylthiophene)s, poly(3-alkylthieno[3,2-*b*]thiophene)s, and poly(3,6-dialkylthieno[3,2-*b*]thiophene). A thieno[3,2-*b*]thiophene ring of regiorandom poly(3-alkylthieno[3,2-*b*]thiophene) can be substituted on either β position.

Scheme 1. Synthesis of 3-Nonylthieno[3,2-*b*]thiophene

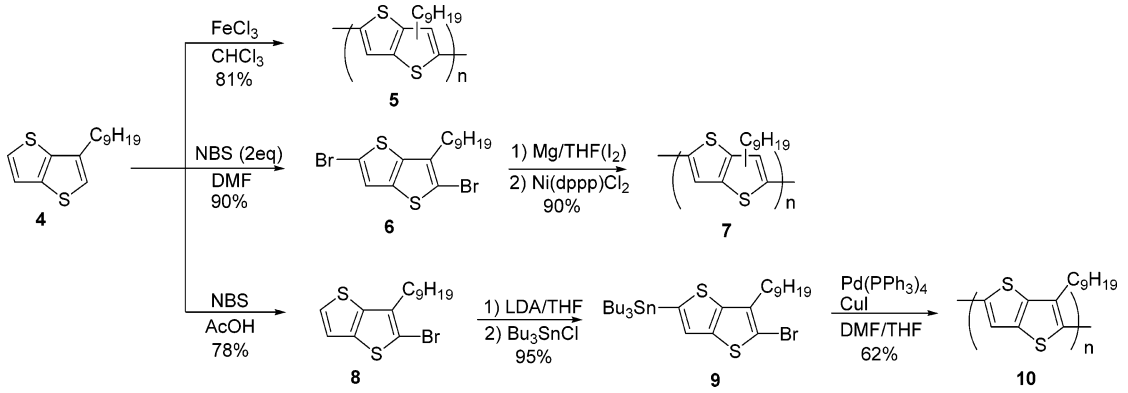


chlorine atoms, monochlorinated chains, and dichlorinated chains. The relative ratio of these types of chains varies substantially from reaction to reaction and very little between different oligomer lengths from a given batch. This latter observation suggests that the chlorines correspond to end groups of the polymers. The small peak at $m/z = 1954$ (7 repeat units + 3Cl) in the mass spectrum suggests that some of the chains contain Cl in the backbone[26] or that branching is occurring accompanied by Cl termination. Both of these effects will lead to a decrease of the coplanarity of adjacent ring units in the polymer chain. Because oxidative polymerization with $FeCl_3$ introduces Cl and a mixture of α- and β-linkages, causing disruption of conjugation,[1,27] regiorandom poly(3-nonylthieno[3,2-*b*]thiophene) (**7**) was produced through a Kumada coupling. Monomer **6** was prepared by bromination of **4** with 2 equiv of NBS in DMF. The polymerization of **6** was accomplished via Kumada coupling catalyzed by $Ni(dppp)Cl_2$. The low measured molecular weight ($M_n = 2184$, $M_w = 2672$, GPC) is due in part to the limited solubility of the polymer in THF. The MALDI mass spectrum reveals, as expected from competing hydrodebromination reactions, that **7** contains three types of end groups: H/H, H/Br, and Br/Br.

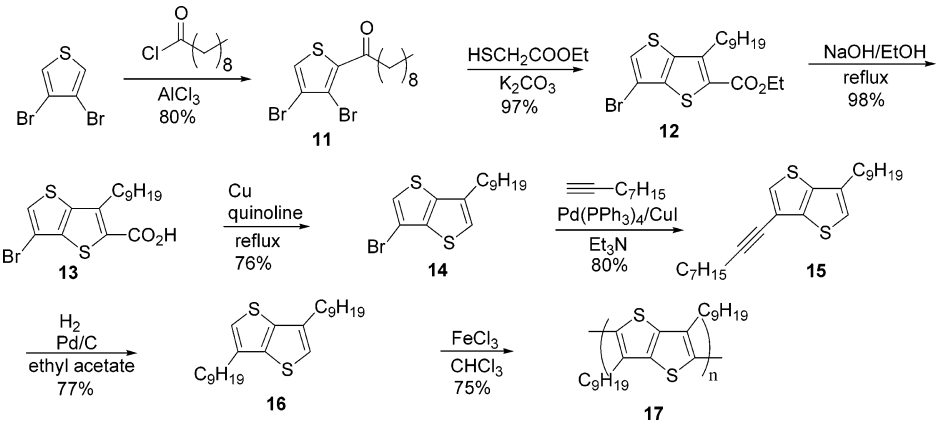
To synthesize a regioregular polymer, a differentially functionalized monomer is required. To pursue a Stille coupling route, monomer **9** was synthesized by deprotonation of monobromide **8** with LDA and quenching with Bu_3SnCl. Poly(3-nonylthieno[3,2-*b*]thiophene) (**10**) was prepared by $Pd(PPh_3)_4$ and CuI catalysis (Scheme 2). The red dark polymer has very limited solubility in THF, and the molecular weight of this soluble fraction is $M_n = 2714$, $M_w = 3119$. The MALDI mass spectrum of **10** reveals a mixture of H/H, H/Br, and Br/Br end groups, favoring H/Br chains. Hydrogen termination likely results from destannylation of the terminal tributylstannyl groups after quenching the polymerization with methanol or during isolation. The formation of H/H and Br/Br chains arises from homocoupling of bromo and tributylstannyl functionalities, common side reactions in Pd-catalyzed couplings. The mass spectra of all poly(3-nonylthieno[3,2-*b*]thiophene)s (**5**, **7**, and **10**) exhibit prominent 264 Da spacings between peaks corresponding to the mass of the repeat unit: 3-nonylthieno[3,2-*b*]thiophenediyl.

Although the poly(3-nonylthieno[3,2-*b*]thiophene)s have alkyl chains on each monomer unit, the solubility of the polymers was generally poor. Because poly(3-hexylthiophene), which has same ratio of aliphatic to aromatic carbons as poly(3-nonylthieno[3,2-*b*]thiophene), is much more soluble in common organic solvents[7] than the fused-ring polymer, it suggests that the increased rigidity of the latter is causing a substantial change in properties. Molecular modeling (vide infra) suggests that, in contrast to the alternation observed in regioregular polythiophene,[28−31] the substituents in the lowest energy conformation of **10** are directed to one side of the polymer. This allows for close approach between the thiophene rings in the solid state, and this, coupled with the greater rigidity of the poly(3-nonylthieno[3,2-*b*]thiophene) backbone, leads to substantially decreased solubility. To prevent this mode of aggregation, a dialkyl-substituted polymer was targeted. The requisite monomer was prepared as shown in Scheme 3. The key intermediate 3-bromo-6-nonylthieno[3,2-*b*]thiophene (**14**) was prepared by a similar procedure to that used in the production of **4** but starting with 3,4-dibromothiophene (see Experimental Section). Dinonylthieno[3,2-*b*]thiophene (**16**) was prepared by a Pd-catalyzed coupling of **14** with 1-nonyne followed by hydrogenation of alkyne **15**. The alternative strategy of directly coupling of nonylmagnesium bromide through a Kumada coupling led to a substantial amount of debrominated compound (**4**) as a byproduct. The polymerization of monomer **16** was carried out by $FeCl_3$ oxidation in $CHCl_3$. The absence of β-hydrogens in monomer **16** leads to the exclusive formation of α-linkages in the polymer chain. Unlike poly(3-nonylthieno[3,2-*b*]thiophene)s (**5**, **7**, and

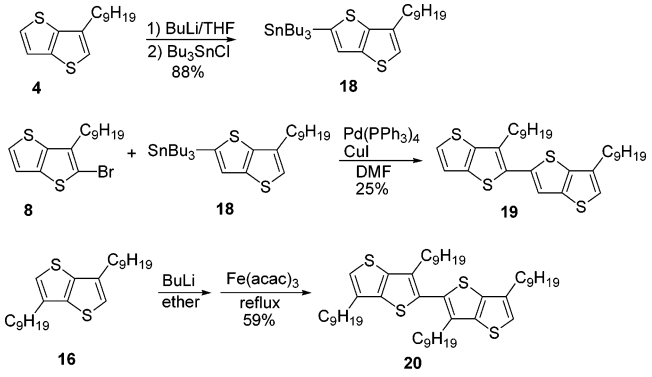
Scheme 2. Syntheses of Poly(3-nonylthieno[3,2-*b*]thiophene)s



Scheme 3. Syntheses of 3,6-Dinonylthieno[3,2-*b*]thiophene and Poly(3,6-dinonylthieno[3,2-*b*]thiophene)



Scheme 4. Syntheses of the HT Dimer of 3-Nonylthieno[3,2-*b*]thiophene (19) and the Dimer of 3,6-Dinonylthieno[3,2-*b*]thiophene (20)



10), the yellow polymer **17** was soluble in THF, $CHCl_3$, and toluene and was easily purified by precipitation from CH_2Cl_2 into MeOH. The molecular weight of polymer **17**, determined by GPC, is considerably higher (M_n = 54 372, M_w = 70 210) than the polymers derived from **4**. However, characterization of **17** by MALDI−TOF MS was not successful, perhaps due its high molecular weight.[32]

To investigate the planarity and conformation of monomer units in the backbone of the polythieno[3,2-*b*]thiophene polymer chains, the head-to-tail (HT) dimer of 3-nonylthieno[3,2-*b*]thiophene (**19**) and the dimer of 3,6-dinonylthieno[3,2-*b*]thiophene (**20**) were synthesized (Scheme 4). Syntheses of these dimers were achieved by cross-coupling and oxidative coupling reactions as shown in Scheme 4. Compound **19** was prepared by the Stille coupling of **8** with tin compound **18**, which was prepared by deprotonation of **4** with BuLi and quenching with Bu_3SnCl. Homocoupling of the stannyl and bromo compounds occurred as side reactions to give head-to-head (HH) and tail-to-tail (TT) dimers as minor byproducts. Compound **20** was prepared by oxidative coupling of lithiated **16**. Both compounds **19** and **20** were purified by zone sublimation. Comparison of the α-methylene regions in the ^{1}H NMR spectra of dimers **19** and **20** to polymers **5**, **7**, **10**, and **17** allows the regiochemistry of the latter to be determined. In particular, the chemical shifts of the HT-α-methylene, HH-α-methylene, and end-group α-methylene (chain on terminal ring) were determined from the ^{1}H NMR spectra of **19** and **20**; the HT-α-methylene peak occurs at 2.93 ppm, HH-α-methylene peak at 2.68 ppm, and end-group α-methylene peak at ∼2.72 ppm. The NMR spectra of the polymers, taken at 70° in $CDCl_3$ due to their poor solubility, showed resonances in both of these chemical shift regions. The relative integration ratios of HT to HH (or end group) α-methylene protons of polymers **5** and **7** are 5:3 and 5:4, respectively, which indicates these two polymers are essentially regiorandom. In polymer **10**, prepared via Stille coupling, the corresponding ratio is 5:2, indicating at least 71% regioregular HT content.[33] End-group contributions, which appear in the same region as HH linkages, and the poorer solubility of regioregular polymer chains both act to reduce the regioregularity measured by NMR spectroscopy. As expected, polymer **17** shows only HH α-methylenes in its ^{1}H NMR spectrum.

Optical Properties

The optical properties of P3ATs have been studied in depth by UV−vis absorption[8,29,34,35] and fluorescence spectroscopies.[8] Regioregular P3ATs exhibit lower optical band gaps (1.7−1.8 eV) and better ordering in the

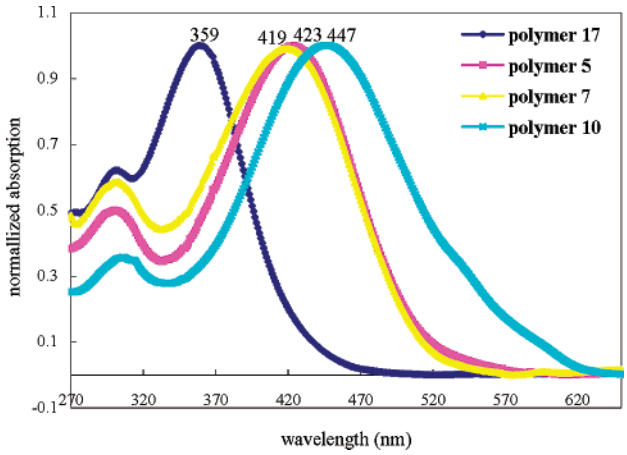


Figure 2. UV−vis absorption spectra of polymer **5**, **7**, **10**, and **17** in $CHCl_3$ solution.

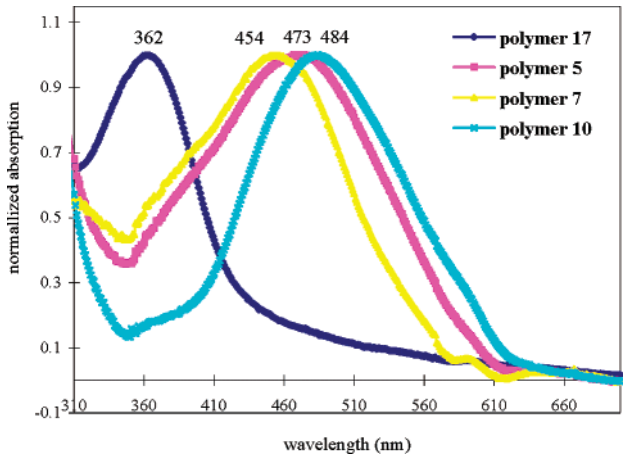


Figure 3. UV−vis absorption spectra of polymer **5**, **7**, **10**, and **17** as thin films.

solid state when compared to regiorandom P3ATs.[8] A similar trend is evident in the electronic absorption spectra of solutions and solid films of the poly(3-nonylthieno[3,2-*b*]thiophene)s (Figures 2 and 3).

In $CHCl_3$ solution, polymers **5** and **7** display similar λ_{max} values (423 and 419 nm, respectively) and onset values: 513 nm (2.41 eV) and 512 nm (2.42 eV), respectively (Figure 2). A ca. 25 nm bathochromic shift of the absorption maximum is observed comparing regiorandom polymers **5** and **7** to polymer **10**. This red shift indicates that polymer **10**, which is prepared by a Stille coupling, is more regioregular and therefore has a longer effective conjugation length and lower energy π-to-π^* transition compared to those of the regiorandom polymers. A corresponding longer wavelength of absorption onset value of polymer **10** is also observed (586 nm, 2.12 eV). Such a red shift has been reported in the case of P3ATs; regioregular poly(3-octylthiophene) displays a longer λ_{max} of absorption (446 nm)[29] compared to the regiorandom polymer (428 nm).[8] By contrast, polymer **17** displays a relatively short λ_{max} value (359 nm) and an onset of 425 nm (2.92 eV). This likely results from the steric repulsion between β-alkyl chains, preventing the coplanarity of ring units and causing a decrease in the effective conjugation length of the polymer chain (vide infra). The spectra of all these polymers have an absorption peak at approximately 300 nm, which is close in energy to the longest λ_{max} of thieno[3,2-*b*]thiophene.

The maximum absorption wavelength of conjugated polymers commonly shows a red shift upon transformation from solution to the solid state.[8,36] This is generally explained by noting that the better structural ordering and increased planarity of the polymer chains in the solid state leads to an increased conjugation length and correspondingly longer wavelength absorption. The spectra of drop-cast films of polymers **5**, **7**, **10**, and **17** are displayed in Figure 3. Thin films of **5** displayed a maximum wavelength of absorption at 473 nm and a band edge at 600 nm (2.07 eV), corresponding to a bathochromic shift of 50 nm of the absorption maximum in the solid state as compared to solution. Polymer **7** shows an absorption peak at 419 nm in solution, which broadens and shifts to 454 nm in the solid state. The onset value of polymer **7** is 567 nm (2.19 eV). For polymer **10** a maximum wavelength of absorption occurs at 484 nm in the solid state, a 37 nm red shift compared to its solution spectrum. The optical band gap (623 nm, 1.99 eV) of **10** is similar to the band gap of unsubstituted polythieno[3,2-*b*]thiophene (2.0 eV) reported previously for polymer produced by an electrochemical route.[23] By contrast to polymers constructed from monoalkyl-substituted monomers, the λ_{max} of polymer **17** shows a very small shift (3 nm) between the solution and solid-state electronic absorption spectra. This suggests that the chain conformation is nearly identical under both conditions. The band edge of this polymer is at relatively higher energy (436 nm, 2.85 eV) compared to the less substituted polymers. In both solution and the solid state, polymer **10** displays a longer maximum wavelength of absorption than regiorandom polymers **5** and **7**, and polymer **17** shows the shortest λ_{max} of absorption in this series. These effects can be understood as resulting primarily from differences in the number of head-to-head (HH) linkages in the series.

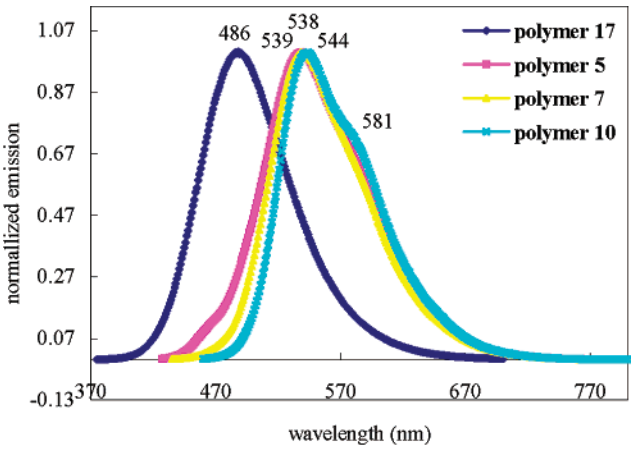
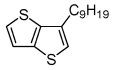
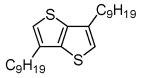
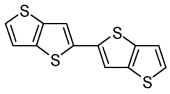
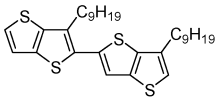
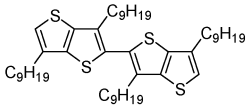


Figure 4. Fluorescence spectra of polymers **5**, **7**, **10**, and **17** in $CHCl_3$ solution.

Fluorescence spectra of polymers in $CHCl_3$ solution are shown in Figure 4. The fluorescence spectra are independent of the excitation wavelength in the region between 400 and 500 nm for polymers **5**, **7**, and **10**, and between 300 and 400 nm for polymer **17**. Polymers **5** and **7** display similar emission maxima at 539 and 538 nm, respectively. Polymer **10** has a λ_{max} of emission at 544 nm and a shoulder at 581 nm. Polymers **5**, **7**, and **10** display similar λ_{max} of emission, which is consistent with the notion of energy migration and emission from planar regions of the polymer. Introduction of more alkyl chains in the polymer backbone leads to shifting of the λ_{max} of emission in **17** to shorter wavelengths (486 nm).

UV−vis absorption spectra and computations of dimeric subunits provide a picture of the conformational

Table 1. Longest Wavelength Electronic Absorption Maxima of 19, 20, 21, and Corresponding Monomeric Subunits in $CHCl_3$

		λ_{max} (solution) (nm)
		280
	**4**	283
	**16**	287
	**21**	350
	**19**	337
	**20**	296

consequences of each type of linkage that occurs in the polymer chain. The λ_{max} of dimers **19**, **20**, 2,2′-bithieno[3,2-*b*]thiophene[21] (**21**), and the corresponding monomers are summarized in Table 1. Monomers thieno[3,2-*b*]thiophene,[37] **4**, and **16** show vibronic bands in their UV−vis absorption spectra (Figure 5), which is characteristic of fused-ring aromatic systems absorbing predominantly from a single conformation. Thieno[3,2-*b*]thiophene displays the longest λ_{max} at 280 nm. Substitution of a nonyl chain on the β-position of the thieno[3,2-*b*]thiophene ring leads to a ~3 nm red shift of the absorption spectrum. As expected, the λ_{max} and molar extinction coefficient (see Experimental Section) increase on going from monomers to dimers (Figure 6). The λ_{max} of **21** is 350 nm.[21] The introduction of a HT nonyl chain between the adjacent monomer units results in a 13 nm blue shift, which is opposite to what is expected from alkyl substitution alone. This blue shift indicates that substitution yields a slightly nonplanar geometry for the conjugated system (vide infra). Such a blue shift, although somewhat less pronounced, is also found in alkyl-substituted bithiophenes; the absorption λ_{max} of 3-octyl-2,2′-bithiophene (293 nm) is blue-shifted compared to that of 2,2′-bithiophene (302 nm).[38] Dramatically, introducing two more nonyl chains causes an additional 41 nm blue shift in the absorption spectrum (compound **20**). This observation indicates that the HH linkages lead to a dramatic decrease of planarity and conjugation, which is due to the large steric effect introduced by the alkyl chains on adjacent conjugated units. Therefore, regiorandom polymers (**5** and **7**) show a blue shift of absorption λ_{max} relative to **10** because they contain a higher proportion of HH linkages. Polymer **17** displays a shorter absorption λ_{max} compared to that

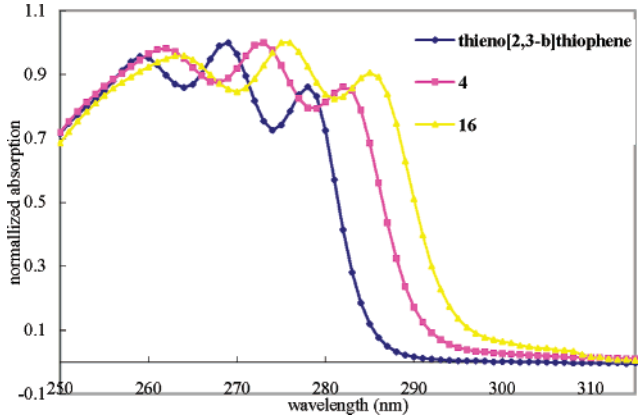


Figure 5. UV−vis absorption spectra of monomers thieno[3,2-*b*]thiophene, **4**, and **16** in $CHCl_3$ solution.

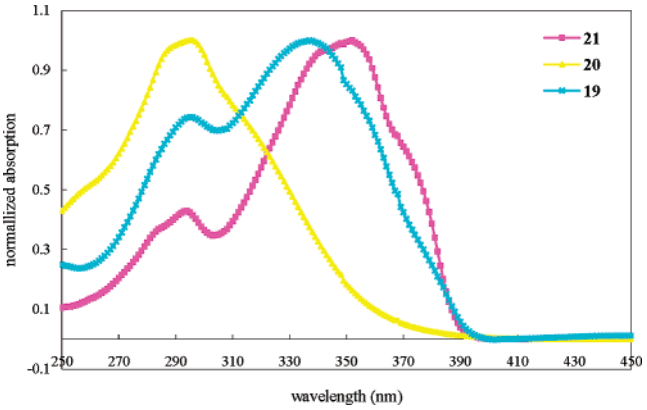


Figure 6. UV−vis absorption spectra of dimers **19**, **20**, and **21** in $CHCl_3$ solution.

of mono-alkyl-substituted polymers, despite its dramatically higher molecular weight, because it has exclusively HH linkages.

The influence of substitution pattern on the trends in the electronic absorption spectra can be appreciated by examining the preferred conformations of models for each of the linkages. Three dimers were examined with density functional theory at the B3LYP/6-31G* level: **21**, **22**, and **23** (Figure 7). In each case the energy was computed for 10 different torsion angles (defined between the carbon atoms linking the two thieno[3,2-*b*]thiophene rings) to determine the minimum-energy geometry and barrier for adopting a planar conformation (Figure 7). The unsubstituted dimer **21** is approximately planar with a very flat energy profile for deformations on the order of 30°. When the rings are orthogonal, the energy rises by more than 3 kcal/mol. The model for a HT linkage with methyl groups is destabilized by 0.7 kcal/mol when planarized from its minimum-energy torsion angle of 140°. Although a larger substituent will likely increase this difference, it is on the order of energies which can be overcome by solid-state packing forces, thus accounting in part for the red shift observed in films of polymers **5**, **7**, and **10** compared to solution. By contrast, **23**, the model for polymer **17**, is destabilized by nearly 3.5 kcal/mol in the planar state when compared to the conformation with orthogonal rings. Therefore, a relatively low level of conjugation through the polymer backbone is seen in both solution and the solid state.

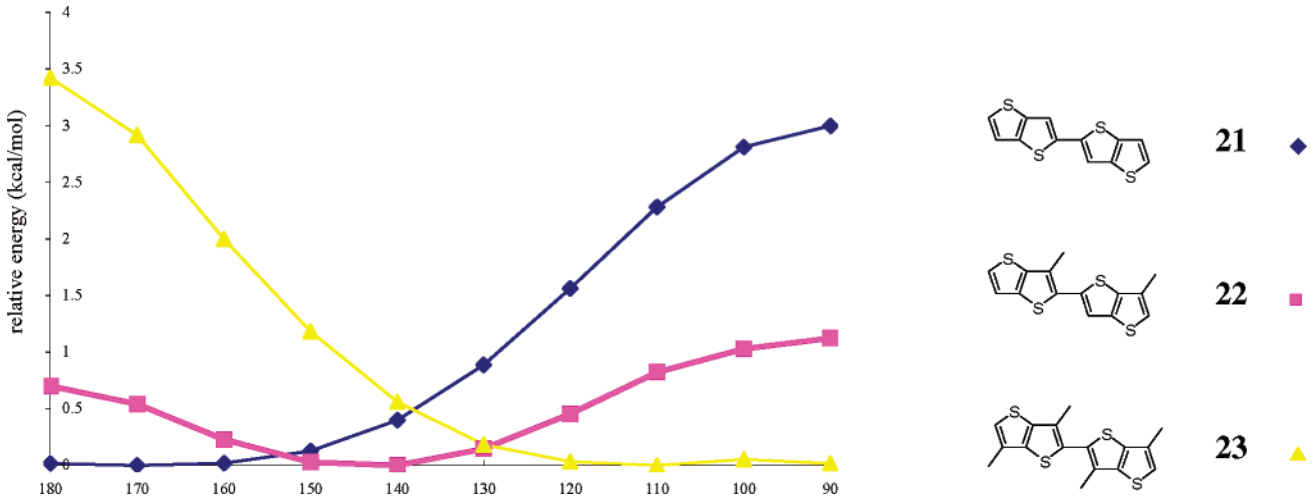


Figure 7. Calculated energies comparison of dimers **21**, **22**, and **23** at different torsion angles.

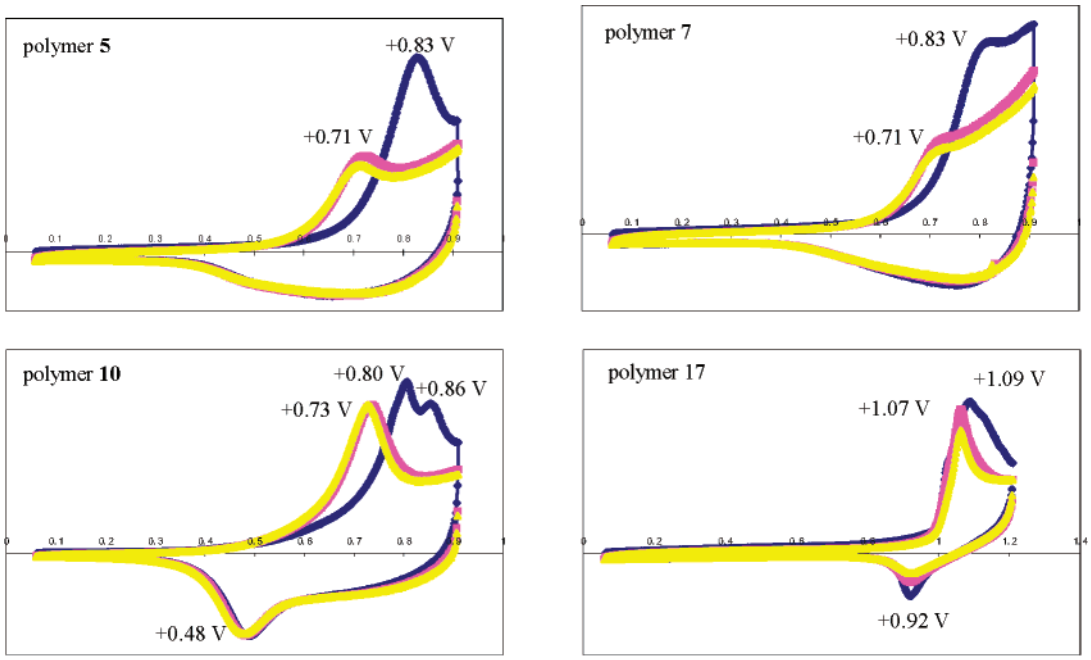


Figure 8. Cyclic voltammetry of films of polymers **5**, **7**, **10**, and **17** at scan rate of 100 mV/s: cycle one, blue; cycle two, red; cycle three, yellow.

Electrochemistry

Cyclic voltammetry of polymers prepared in this study was carried out to determine the possibility of n- or p-doping processes. The cyclic voltammograms were recorded from thin films of the polymers solvent cast onto a Pt electrode (Figure 8). Regiorandom polymers **5** and **7** show similar oxidation peaks at +0.83 V vs Ag/Ag$^+$. After three scans cycling through the oxidation process, the peaks of both these polymers shift to lower potential (+0.71 V), indicating that a more conjugated system formed on the electrode after the first oxidation cycle. Relatively high potential reduction peaks were observed for polymer **5** and **7** at −2.3 and −2.4 V, respectively (see Supporting Information). Both the oxidation and reduction processes of these polymers are irreversible. In the case of polymer **10**, two quasi-reversible oxidation peaks at +0.80 and +0.86 V and an irreversible reduction peak at −2.34 V were observed. The oxidation peak shifts to lower potential (+0.73 V) after cycling for three scans and remains quasi-reversible. As expected, the film of polymer **17** shows a higher oxidation potential at 1.09 V. The higher oxidation potential of **17** can be explained by noting that introducing HH linkages leads to a decrease of conjugation and orbital overlap and is therefore less efficient at stabilizing charged states. After cycling for several scans, the oxidation peak shifts to slightly to lower potential, 1.07 V. All four of these polymers display relatively low oxidation potentials, indicating that they are suitable to be used as p-type materials. Comparison of the electrochemistry and electronic spectra presents a clear picture: the poly(3,6-dinonylthieno[3,2-*b*]thiophene) (**17**) has a significantly larger band gap than poly(3-nonylthieno[3,2-*b*]thiophene)s (**5**, **7**, and **10**), indicating that HH linkages seriously disrupt planarity in thieno[3,2-*b*]thiophene-based polymers.

Conclusion

A series of alkyl-substituted polythieno[3,2-*b*]thiophenes were synthesized through a variety of polymerization methods. Although the solubility of poly(3-nonylthieno[3,2-*b*]thiophene)s is low compared to that

of P3ATs, similar trends in spectroscopic and electrochemical properties were observed. For example, polymer **10** has a longer λ_{max} of absorption in both solution and solid-state spectra compared to those of regiorandom polymers (**5** and **7**). Introducing the second alkyl chain into the monomer leads to substantially decreased conjugation as observed in both electronic spectra and electrochemistry of polymer **17**. Furthermore, the study of dimeric subunits of these polymers indicates that the HT linkage causes a small distortion of adjacent ring units and HH linkage results in a large decrease of coplanarity and conjugation.

Experimental Section

General. All polymerization and deprotonation reactions were performed under a dry N_2 atmosphere using oven-dried glassware. THF and ether were dried by passage through a column packed with activated alumina. Thieno[3,2-*b*]thiophene was prepared according to the literature procedure.[37]

UV−vis absorption spectroscopy was performed on a CARY 300 Bio UV−vis spectrophotometer in $CHCl_3$ solution ($<10^{-4}$ wt %) and on thin films drop-cast from the same solution. Fluorescence spectra were collected on a FluoroMax-2 spectrophotometer using the longest λ_{max} from the absorption spectra as the excitation wavelength. Cyclic voltammetry experiments of polymer films were performed using a Princeton Applied Research potentiostat/galvanostat model 263A with platinum as the working electrode, a platinum wire counter electrode, and Ag/Ag^+ reference electrode in 0.1 M tetrabutylammonium hexafluorophosphate ($TBAPF_6$) in CH_3CN. The polymer films were prepared by drop casting on the working electrode from a solution of the polymer (∼0.1 wt %) in $CHCl_3$. Polymer molecular weights were determined by gel permeation chromatography (GPC) using THF as eluent and polystyrene standards (n.b.: for rigid polymers use of these standards will tend to overestimate molecular weight) on Waters Styragel HT 3 columns (500−30 000 molecular weight range). MALDI spectra of polymers were collected using a Micromass Tof Spec 2E equipped with a 337 nm nitrogen laser (funded with NSF Grant DBI 99874). The samples for MALDI were prepared by depositing 1.0 μL of a mixture of an equal volume of matrix (10 mg/mL in toluene) and analyte (∼1 mg/mL in $CHCl_3$) onto a target plate.

1-(3-Bromo-thiophen-2-yl)-decan-1-one (1). $AlCl_3$ (13.3 g, 100 mmol) was added in portions over 30 min to a stirring solution of 3-bromothiophene (17.4 g, 107 mmol) and decanoyl chloride (20.4 g, 107 mmol) in CH_2Cl_2 (100 mL). The resulting mixture was stirred for 3 h at ambient temperature. The reaction was then quenched by the slow addition of cold water (100 mL). Additional CH_2Cl_2 (100 mL) was added to extract the product from the aqueous layer, and the combined organic layers were washed with 1 M NaOH (3 × 200 mL). The organic layer was dried over anhydrous Na_2SO_4, and the solvent was removed in vacuo to give a mixture (30.9 g, 97%) of **1** and its 4-bromo isomer (10:1 as determined by ^{1}H NMR). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.89 (t, J = 6.8 Hz, 3H), 1.22−1.45 (br, 12H), 1.73 (tt, J = 7.6, 7.1 Hz, 2H), 3.02 (t, J = 7.6 Hz, 2H), 7.10 (d, J = 5.2 Hz, 1H), 7.49 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.91, 22.48, 23.95, 29.04, 29.09, 29.26, 29.28, 31.69, 41.34, 131.6, 133.5, 138.5, 144.7, 192.6. Anal. Calcd for $C_{14}H_{21}SBr$: C, 53.00; H, 6.67. Found: C, 52.74; H, 6.58. IR (thin film): 3105 (m), 2952 (s), 2923 (s), 2852 (s), 1659 (s), 1492 (s), 1465 (m), 1408 (s), 1350 (m), 1182 (m), 871 (m), 730 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 318 (2), 316 (2, M^+), 237 (18), 219 (12), 217 (10), 207 (8), 206 (100), 205 (9), 204 (94), 191 (42), 189 (41), 138 (18), 97 (12).

3-Nonylthieno[3,2-*b*]thiophene-2-carboxylic Acid Ethyl Ester (2). Ethyl thioglycolate (9.86 mL, 82.1 mmol) was added to a mixture of compound **1** (27.3 g, 91% pure, 77.5 mmol), K_2CO_3 (20.0 g, 145 mmol), and DMF (150 mL) at ambient temperature. After the resulting mixture was stirred for 24 h, a solution of NaOH (0.60 g, 15 mmol) in EtOH (30 mL) was added, and stirring was continued for an additional 24 h. The mixture was poured into water (150 mL) and extracted with ethyl acetate (250 mL). The organic layer was washed with water (4 × 200 mL) and dried over anhydrous Na_2SO_4. Pure **2** was obtained after vacuum distillation (120 °C, 6 mTorr): 18.4 g, 70%. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.89 (t, J = 6.8 Hz, 3H), 1.21−1.32 (br, 12H), 1.40 (t, J = 7.2 Hz, 3H), 1.74 (tt, J = 7.7, 7.5 Hz, 2H), 3.17 (t, J = 7.6 Hz, 2H), 4.36 (q, J = 6.8 Hz, 2H), 7.21 (d, J = 5.2 Hz, 1H), 7.51 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 13.94, 14.16, 22.52, 29.14, 29.16, 29.28, 29.31, 29.38, 29.57, 31.74, 60.71, 120.0, 127.7, 130.6, 140.7, 141.3, 143.1, 163.1. Anal. Calcd for $C_{18}H_{26}O_2S_2$: C, 63.86; H, 7.74. Found: C, 63.66; H, 7.74. IR (thin film): 3084 (w), 2954 (s), 2924 (s), 2853 (s), 1705 (s), 1514 (m), 1432 (m), 1366 (m), 1283 (m), 1250 (s), 1103 (s), 1023 (m), 913 (m), 795 (m), 764 (m), 723 (m), 674 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 338 (34, M^+), 239 (11), 228 (13), 227 (14), 226 (100), 198 (10), 197 (22), 193 (15), 180 (34), 153 (30).

3-Nonylthieno[3,2-*b*]thiophene-2-carboxylic Acid (3). A mixture of ester **2** (13.4 g, 39.6 mmol) and NaOH (3.30 g, 82.5 mmol) in EtOH (125 mL) was heated to reflux for 3 h. After TLC indicated the absence of starting material, the solvent was removed in vacuo. Water (100 mL) was added to the residue, and the pH was adjusted to 1 with 12 M hydrochloric acid. The precipitate was collected by filtration and recrystallized from hexanes to yield acid **3** (10.8 g, 88%); mp 115−116 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 0.84 (t, J = 6.6 Hz, 3H), 1.15−1.34 (br, 12H), 1.65 (tt, J = 7.5, 7.3 Hz 2H), 3.10 (t, J = 7.5, 2H), 7.46 (d, J = 5.1 Hz, 1H), 7.90 (d, J = 5.1 Hz, 1H), 13.1 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 13.83, 22.01, 28.31, 28.59, 28.59, 28.64, 28.78, 28.79, 31.20, 120.7, 128.7, 132.0, 140.2, 140.8, 141.8, 164.0. Anal. Calcd for $C_{16}H_{22}O_2S_2$: C, 61.90; H, 7.14. Found: C, 62.07; H, 7.35. IR (KBr): 3092 (m), 2955 (s), 2921 (s), 2851 (s), 2523 (m), 1662 (s), 1511 (s), 1429 (s), 1299 (s), 1269 (s), 1126 (m), 911 (m), 723 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 310 (31, M^+), 265 (3.5), 199 (17), 198 (100), 197 (21), 153 (32), 97 (12).

3-Nonylthieno[3,2-*b*]thiophene (4). A mixture of acid **3** (15.0 g, 48.3 mmol), copper (∼45 μm powder, 8.50 g, 134 mmol), and quinoline (70 mL) was heated to reflux for 1 h. The solvent volume was reduced to 5 mL by distillation at 25 Torr. Ethyl acetate (200 mL) was added to the mixture, and the organic layer was washed with 1 M HCl (3 × 200 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the residue was chromatographed on silica gel eluting with hexanes to yield **4** (11.3 g, 88%). UV−vis ($CHCl_3$) λ_{max} (log ϵ): 264 (4.00), 274 (4.01), 283 (3.93). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.88 (t, J = 6.7 Hz, 3H), 1.21−1.42 (br, 12H), 1.75 (tt, J = 7.5, 7.3 Hz, 2H), 2.73 (t, J = 7.4 Hz, 2H), 7.00 (d, J = 1.0 Hz, 1H), 7.24 (d, J = 5.2 Hz, 1H), 7.36 (dd, J = 5.2, 1.0 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.07, 22.62, 28.51, 29.28, 29.31, 29.36, 29.49, 29.85, 31.85, 119.8, 121.7, 126.4, 134.7, 138.7, 139.9. Anal. Calcd for $C_{15}H_{22}S_2$: C, 67.61; H, 8.32. Found: C, 67.56; H, 8.62. IR (thin film): 3085 (w), 2954 (s), 2924 (s), 2853 (s), 1465 (m), 1375 (w), 1365 (w), 1188 (w), 1087 (w), 905 (m), 792 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 266 (18, M^+), 167 (18), 156 (8), 155 (13), 154 (100), 153 (56), 134 (7), 109 (6).

2,5-Dibromo-3-nonylthieno[3,2-*b*]thiophene (6). *N*-Bromosuccinimide (730 mg, 4.10 mmol) was added in portions over 20 min to a solution of **4** (583 mg, 2.02 mmol) in DMF (15 mL) at 0 °C. After stirring the solution for 3 h at ambient temperature, water (50 mL) was added, and the aqueous layer was extracted with ethyl acetate (50 mL). The organic layer was dried (anhydrous Na_2SO_4) and the solvent removed in vacuo. The residue was purified by chromatography on silica gel eluting with hexanes to give **6** (1.31 g, 90%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.92 (t, J = 6.8 Hz, 3H), 1.22−1.42 (br, 12H), 1.39 (tt, J = 7.3, 7.2 Hz, 2H), 2.69 (t, J = 7.4 Hz, 2H), 7.13 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.05, 22.61, 27.89, 28.94, 29.16, 29.23, 29.27, 29.40, 31.79, 110.3, 112.8, 122.1, 133.9, 135.9, 138.5. Anal. Calcd for $C_{15}H_{20}Br_2S_2$: C, 42.46; H, 4.75. Found: C, 42.45; H, 4.79. IR (thin film): 3096 (w), 2953 (s), 2924 (s), 2853 (s), 1467 (s), 1352 (m), 1153 (m), 979 (m), 849 (s), 808 cm^{-1} (s). MS (EI, 70 eV) *m*/*z* (relative intensity): 426

(10), 424 (20), 422 (8, M^+), 345 (36), 343 (39), 314 (11), 313 (12), 312 (19), 311 (20), 310 (11), 310 (10), 264 (46), 234 (25), 233 (100), 232 (43), 231 (99), 230 (19).

2-Bromo-3-nonylthieno[3,2-*b*]thiophene (8). *N*-Bromosuccinimide (1.07 g, 6.01 mmol) was added in portions over 20 min to a solution of **4** (1.65 g, 6.20 mmol) in AcOH (15 mL) at room temperature. After stirring the solution for 3 h at 60 °C, water (30 mL) was added and the aqueous layer was extracted with ethyl acetate (50 mL). The organic layer was washed with saturated $NaHCO_3$ (50 mL) and brine (50 mL) and dried over anhydrous Na_2SO_4. The solvent was removed in vacuo, and the residue was purified by chromatography on silica gel eluting with hexanes to give **8** (1.61 g, 78%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.89 (t, J = 6.8 Hz, 3H), 1.18−1.44 (br, 12H), 1.72 (tt, J = 7.5, 7.3 Hz, 2H), 2.75 (t, J = 7.6 Hz, 2H), 7.16 (d, J = 5.2 Hz, 1H), 7.38 (d, J = 5.2 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.10, 22.62, 27.98, 29.15, 29.26, 29.29, 29.34, 29.47, 31.88, 110.1, 119.4, 125.7, 134.1, 136.8, 138.3. Anal. Calcd for $C_{15}H_{21}BrS_2$: C, 52.17; H, 6.13. Found: C, 52.02; H, 6.12. IR (thin film): 2953 (m), 2924 (s), 2853 (s), 1463 (m), 1355 (w), 1080 (w), 903 (m), 796 (w), 710 (m), 665 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 346 (5), 344 (7, M^+), 254 (34), 231 (10), 155 (10), 154 (22), 153 (100), 152 (15).

(5-Bromo-6-nonylthieno[3,2-*b*]thiophen-2-yl)-tributylstannane (9). To a stirring solution of LDA (2.0 M in THF/*n*-heptane, 0.30 mL, 0.60 mmol) in THF (5.0 mL) at −40 °C was added **8** (127 mg, 0.500 mmol) over 10 min. After stirring for 40 min at this temperature, chrorotributyltin (0.200 mL, 0.750 mmol) was added dropwise. The reaction solution was allowed to warm to room temperature slowly and stirred for 12 h. After removing the solvent in vacuo, the reaction was quenched with saturated NH_4Cl (20 mL) and extracted with hexanes (30 mL). After washing with brine (30 mL), the organic layer was dried over anhydrous Na_2SO_4 and evaporated to give crude product **9** (621 mg, 95%), which was used directly for polymerization. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.90 (t, J = 7.3, 12H), 1.12 (m, 6H), 1.22−1.40 (br, 13H), 1.34 (m, 6H), 1.58 (m, 6H), 1.70 (m, 2H), 2.73 (tt, J = 7.7, 7.2 Hz, 2H), 7.15 (s, 1H).

1-(3,4-Dibromothiophen-2-yl)-decan-1-one (11). Compound **11** was obtained from 3,4-dibromothiophene (12.2 g, 51.0 mmol) and decanoyl chloride (10.0 g, 50.0 mmol) following a similar procedure described for **1** (yield: 15.8 g, 80%); mp 46−47 °C. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.88 (t, J = 6.6 Hz, 3H), 1.18−1.43 (br, 12H), 1.73 (tt, J = 7.4, 7.2 Hz, 2H), 3.03 (t, J = 7.2 Hz, 2H), 7.60 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.00, 22.55, 23.92, 29.07, 29.16, 29.32, 29.33, 31.76, 41.13, 116.9, 117.0, 129.2, 139.8, 192.0. Anal. Calcd for $C_{14}H_{20}SBr_2$: C, 42.44; H, 5.09. Found: C, 42.47; H, 5.17. IR (KBr): 3111 (m), 2921 (s), 2849 (s), 1663 (s), 1468 (m), 1407 (s), 1367 (m), 1314 (s), 1290 (m), 1252 (m), 1213 (m), 1179 (s), 1134 (m), 876 (m), 762 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 399 (4), 397 (6), 395 (4, $[M + 1]^+$), 317 (11), 315 (10), 299 (6), 297 (11), 294 (6), 286 (54), 285 (10), 284 (100), 282 (52), 271 (18), 269 (30), 267 (17).

6-Bromo-3-nonylthieno[3,2-*b*]thiophene-2-carboxylic Acid Ethyl Ester (12). Compound **12** was obtained from **11** (15.9 g, 40.3 mmol) and ethyl thioglycolate (4.5 mL, 40.3 mmol) following a similar procedure described for **2** (yield: 16.2 g, 97%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.87 (t, J = 7.0 Hz, 3H), 1.20−1.35 (br, 12H), 1.40 (t, J = 7.1 Hz, 3H), 1.70 (tt, J = 7.5, 7.5 Hz, 2H), 3.12 (t, J = 7.4 Hz, 2H), 4.36 (q, J = 7.1 Hz, 2H), 7.41 (s, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.06, 14.25, 22.60, 29.00, 29.23, 29.24, 29.33, 29.44, 29.60, 31.81, 61.06, 123.7, 127.2, 128.5, 140.1, 141.7, 143.8, 162.5. Anal. Calcd for $C_{18}H_{25}S_2O_2Br$: C, 51.79; H, 6.04. Found: C, 51.80; H, 6.10. IR (thin film): 3105 (w), 2954 (m), 2924 (s), 2853 (s), 1711 (s), 1514 (m), 1366 (m), 1282 (m), 1250 (s), 1104 (s), 945 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 418 (49), 416 (41, M^+), 319 (15), 317 (16), 306 (100), 304 (95), 299 (21), 281 (30), 277 (25), 271 (17), 267 (19), 260 (24), 258 (26), 225 (45), 211 (20), 209 (50), 207 (50), 193 (16), 140 (15), 73 (18).

6-Bromo-3-nonylthieno[3,2-*b*]thiophene-2-carboxylic Acid (13). Compound **13** was prepared by the hydrolysis of **12** (14.3 g, 34.4 mmol) with NaOH (2.75 g, 68.8 mmol) in EtOH (170 mL) following the procedure given for **3** (yield: 11.1 g, 98%); mp 81−82 °C. ^{1}H NMR (400 MHz, DMSO-d_6, δ): 0.82 (t, J = 6.8 Hz, 3H), 1.13−1.32 (br, 12H), 1.63 (tt, J = 7.2, 7.0 Hz, 2H), 3.09 (t, J = 7.4 Hz, 2 H), 8.05 (s, 1H), 13.4 (br, 1H). ^{13}C NMR (100 MHz, DMSO-d_6, δ): 13.84, 22.01, 27.95, 28.57, 28.59, 28.61, 28.74, 28.75, 31.18, 102.1, 129.1, 129.6, 139.8, 140.5, 142.5, 163.4. Anal. Calcd for $C_{16}H_{21}BrO_2S_2$: C, 49.35; H, 5.44. Found: C, 49.75; H, 5.77. IR (KBr): 3114 (w), 2965 (m), 2949 (m), 2917 (s), 2853 (m), 2516 (w), 1664 (s), 1653 (s), 1517 (s), 1438 (m), 1362 (m), 1304 (s), 1290 (s), 1276 (s), 1127 (m), 943 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 390 (34), 388 (32, M^+), 291 (15), 289 (15), 279 (14), 278 (100), 277 (28), 276 (94), 275 (17), 234 (15), 233 (31), 232 (15), 231 (29), 198 (10), 166 (10), 140 (15).

3-Bromo-6-nonylthieno[3,2-*b*]thiophene (14). Compound **14** was prepared by decarboxylation of **13** (4.10 g, 10.6 mmol) with Cu (∼45 μm powder, 360 mg, 5.56 mmol) in quinoline (20 mL) as described for **4** (2.77 g, 76%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.91 (t, J = 6.8 Hz, 3H), 1.23−1.42 (br, 12H), 1.74 (tt, J = 7.5, 7.3 Hz, 2H), 2.71 (t, J = 7.5 Hz, 2H), 7.04 (d, J = 1.5 Hz, 1H), 7.25 (d, J = 1.5 Hz, 1H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.11, 22.66, 28.60,29.29, 29.30, 29.36, 29.49, 29.64, 31.87, 102.9, 122.6, 123.3, 135.8, 139.0, 139.9. Anal. Calcd for $C_{15}H_{21}BrS_2$: C, 52.17; H, 6.13. Found: C, 52.12; H, 6.29. IR (thin film): 3105 (w), 2952 (s), 2923 (s), 2852 (s), 1463 (m), 1362 (m), 941 (m), 822 (m), 722 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 346 (100), 345 (17), 343 (90, M^+), 234 (40), 233 (16), 232 (42), 166 (18), 153 (24), 152 (38), 69 (16).

3-Nonyl-6-non-1-ynylthieno[3,2-*b*]thiophene (15). Compound **14** (384 mg, 1.17 mmol) was added to a mixture of 1-nonyne (378 mg, 3.05 mmol), $Pd(PPh_3)_4$ (27.0 mg, 23.4 mmol), and CuI (8.9 mg, 47 mmol) in Et_3N (4 mL) under a nitrogen atmosphere. The solution was stirred for 12 h at 130 °C in a 15 mL pressure vessel. After addition of hexanes (20 mL), the solution was filtered to remove precipitated salts. The organic layer was washed with 1 M hydrochloric acid (20 mL) and brine (20 mL) and dried over anhydrous Na_2SO_4. Then the solvent was removed in vacuo, and the residue was purified by chromatography on silica gel eluting with hexanes to give **15** (363 mg, 80%). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.88 (t, J = 7.0 Hz, 3H), 0.90 (t, J = 7.0 Hz, 3H), 1.22−1.39 (br, 18H), 1.47 (tt, J = 7.5 7.2 Hz, 2H), 1.63 (tt, J = 7.3, 7.2 Hz, 2H), 1.73 (tt, J = 7.6, 7.2 Hz, 2H), 2.44 (t, J = 7.1 Hz, 2H), 2.70 (t, J = 7.4, 2H), 7.00 (d, J = 1.2 Hz, 1H), 7.35 (d, J = 1.4 Hz, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.01, 14.02, 19.42, 22.57, 22.60, 28.60, 28.61, 28.77, 28.78, 29.25, 29.25, 29.33, 29.46, 29.64, 31.71, 31.83, 73.70, 92.86, 116.4, 122.1, 128.3, 135.3, 138.5, 140.8. Anal. Calcd for $C_{24}H_{36}S_2$: C, 74.16; H, 9.34. Found: C, 73.92; H, 9.30. IR (thin film): 2924 (s), 2852 (s), 1456 (m), 1354 (w), 833 (w), 735 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 389 (12), 388 (69, M^+), 299 (18), 289 (11), 277 (17), 276 (100), 225 (34), 227 (18), 211 (18), 209 (26), 207 (15), 193 (12), 191 (12).

3,6-Dinonylthieno[3,2-*b*]thiophene (16). To a solution of compound **15** (582 mg, 1.50 mmol) in ethyl acetate (10 mL) was added 5% Pd/C (159 mg). The mixture was stirred under a H_2 atmosphere for 24 h. The solution was filtered through Celite, and an additional 20 mL of ethyl acetate was used to elute the product. After removal of the solvent in vacuo, the residue was recrystallized from absolute EtOH to give **16** (448 mg, 77%); mp 49−50 °C. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 266 (3.98), 277 (4.00), 287 (3.95). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.89 (t, J = 6.9 Hz, 6H), 1.21−1.43 (br, 22H), 1.75 (tt, J = 7.7, 7.3 Hz, 4H), 2.71 (t, J = 7.7 Hz, 4H), 6.95 (s, 2H). ^{13}C NMR (100 MHz, $CDCl_3$, δ): 14.03, 22.60, 28.65, 29.25, 29.33, 29.34, 29.46, 29.71, 31.83, 120.9, 135.5, 139.3. Anal. Calcd for $C_{24}H_{40}S_2$: C, 73.40; H, 10.27. Found: C, 73.58; H, 10.45. IR (KBr): 2956 (m), 2921 (s), 2846 (m), 1466 (s), 839 (m), 722 (m), 709 cm^{-1} (m). MS (EI, 70 eV) *m*/*z* (relative intensity): 393 (19), 392 (72, M^+), 298 (22), 281 (34), 280 (100), 227 (26), 225 (65), 211 (23), 209 (53), 207 (17), 169 (16), 168 (71).

Tributyl-(6-nonylthieno[3,2-*b*]thiophen-2-yl)-stannane (18). Butyllithium (1.6 M in hexanes, 0.625 mL, 1.00 mmol) was added dropwise to a solution of **4** (325 mg, 1.22 mmol) in THF (5 mL) at 0 °C. After stirring for 1 h, chrorotributyltin

(325 mg, 1.00 mmol) was added dropwise, and the mixture was allowed to warm to room temperature. The solution was stirred for another 2 h, quenched with saturated NH_4Cl (20 mL), and extracted with hexanes (30 mL). The organic layer was washed with brine (30 mL) and dried over anhydrous Na_2SO_4. The crude product **18** (623 mg, 88%) was obtained after removing the solvent in vacuo and used directly in the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.91 (t, J = 7.3 Hz, 12H), 1.13 (m, 6H), 1.22−1.41 (br, 13H), 1.35 (m, 6H), 1.59 (m, 6H), 1.75 (tt, J = 7.5, 7.2 Hz, 2H), 2.72 (t, J = 7.7 Hz, 2H), 6.95 (s, 1H), 7.23 (s, 1H).

3,6′-Dinonyl-2,2′-bi[thieno[3,2-*b*]thiophenyl] (19). Crude tributyl-(6-nonylthieno[3,2-*b*]thiophen-2-yl)-stannane (**18**) from the above reaction was added to a stirring mixture of 2-bromo-3-nonylthieno[3,2-*b*]thiophene (**8**) (275 mg, 0.799 mmol), $Pd(PPh_3)_4$ (23.1 mg, 0.0200 mmol), and CuI (7.6 mg, 0.040 mmol) in DMF (10 mL). After the solution was stirred for 12 h at 80 °C, CH_2Cl_2 (200 mL) was added to the solution. The organic layer was washed with water (3 × 200 mL) and dried over anhydrous Na_2SO_4. After removing the solvent in vacuo, the residue was purified by column chromatography on silica gel (hexanes) and zone sublimation (180 °C, 8 mTorr) to yield **19** (106 mg, 25%); mp 37−38 °C. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 294 (4.14), 337 (4.25). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.87 (t, J = 6.9 Hz, 3H), 0.88 (t, J = 6.9 Hz, 3H), 1.19−1.43 (br, 24H), 1.77 (m, 4H), 2.74 (t, J = 7.9 Hz, 2H), 2.93 (t, J = 7.9 Hz, 2H), 7.00 (s, 1H), 7.23 (d, J = 5.2 Hz, 1H), 7.29 (s, 1H), 7.37 (d, J = 5.2 Hz, 1H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 14.10, 14.10, 22.68, 22.68, 28.63, 28.93, 29.03, 29.31, 29.32, 29.36, 29.37, 29.41, 29.51, 29.54, 29.62, 29.92, 31.88, 31.89, 119.1, 119.6, 121.6, 126.7, 132.1, 132.5, 135.0, 136.7, 137.5, 138.6, 139.9, 141.4. Anal. Calcd for $C_{30}H_{42}S_4$: C, 67.87; H, 7.97. Found: C, 67.77; H, 7.77. IR (KBr): 2954 (m), 2919 (s), 2851 (s), 1469 (m), 1450 (w), 806 (w), 722 (m), 704 (m), 671 cm^{-1} (w). MS (EI, 70 eV) m/z (relative intensity): 533 (10), 532 (30), 531 (42), 530 (100, M^+), 431 (12), 419 (13), 418 (33), 417 (15), 305 (19).

3,6,3′,6′-Tetranonyl-2,2′-bi[thieno[3,2-*b*]thiophenyl] (20). Butyllithium (1.6 M in hexanes, 0.500 mL, 0.800 mmol) was added dropwise to a stirring solution of 3,6-dinonylthieno[3,2-*b*]thiophene (**16**) (313 mg, 0.800 mmol) in ether (5.0 mL) at 0 °C. The solution was warmed to room temperature and stirred for an additional 30 min followed by addition of $Fe(acac)_3$ (564 mg, 1.60 mmol). After refluxing for 3 h, the mixture was poured into hexanes (50 mL). The solution was filtered through silica gel, and an additional 20 mL of hexanes was added to rinse the silica gel. After removing the solvent in vacuo, the residue was purified by zone sublimation (170 °C, 2 mTorr) to yield **20** (184 mg, 59%); mp 31−32 °C. UV−vis ($CHCl_3$) λ_{max} (log ϵ): 296 (4.35). ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.87 (t, J = 7.0, 6H), 0.88 (t, J = 7.0 Hz, 6H), 1.17−1.42 (br, 48H), 1.72 (m, 8H), 2.68 (t, J = 7.6 Hz, 4H), 2.71 (t, J = 7.6 Hz, 4H), 7.00 (s, 2H). ^{13}C NMR (125 MHz, $CDCl_3$, δ): 14.10, 14.12, 22.68, 22.69, 28.55, 28.74, 28.84, 29.31, 29.33, 29.36, 29.41, 29.43, 29.47, 29.53, 29.54, 29.83, 31.88, 31.90, 120.9, 130.2, 135.3, 135.3, 138.9, 139.2. Anal. Calcd for $C_{48}H_{78}S_4$: C, 73.59; H, 10.04. Found: C, 73.39; H, 10.38. IR (KBr): 2953 (m), 2921 (s), 2850 (s), 1468 (w), 1466 (m), 1376 (w), 834 (w), 717 cm^{-1} (w). MS (EI, 70 eV) m/z (relative intensity): 786 (15), 785 (35), 784 (57), 783 (100, M^+), 671 (10), 557 (5), 84 (12).

Polymerization. Poly(3-nonylthieno[3,2-*b*]thiophene) Prepared by Oxidative Coupling (5). $FeCl_3$ (648 mg, 4.00 mmol) was added to a stirring solution of **4** (266 mg, 1.00 mmol) in $CHCl_3$ (10 mL). After stirring for 5 h at room temperature, the reaction solution was poured into MeOH (100 mL). The red powder was collected by filtration, and the impurities were removed by Soxhlet extraction with MeOH (150 mL) to yield polymer **5** (216 mg, 81%). GPC (THF soluble fraction): M_n = 1895, M_w = 5514. The polymer was fractionated by Soxhlet extraction with hexanes (150 mL) to give 41.0 mg (16%) and with $CHCl_3$ (150 mL) to give 42.7 mg (17%). UV−vis: λ_{max} (hexanes fraction) = 286, 380 nm, λ_{max} ($CHCl_3$ fraction) = 298, 424 nm, λ_{max} (film, $CHCl_3$ fraction) = 473 nm. ^{1}H NMR of $CHCl_3$ fraction (400 MHz, $CDCl_3$, 70 °C, δ): 0.90 (CH_3), 1.12−1.54 ($C_6H_{12}CH_3$), 1.80 (ring-CH_2CH_2), 2.76 (ring-CH_2, HH linkage), 2.99 (ring-CH_2, HT linkage), 7.00 (ring proton, end group), 7.20−7.43 (ring proton). IR (KBr): 2923 (s), 2852 (s), 1457 (m), 1375 (w), 1153 (w), 805 (m) cm^{-1}. MS of $CHCl_3$ fraction (MALDI, dithranol) m/z (relative intensity): 794 (98), 795 (58), 796 (43), 797 (12), 828 (66), 829 (35), 830 (47), 831 (19), 862 (16), 863 (6), 864 (19), 865 (4), 1058 (62), 1059 (50), 1060 (41), 1061 (21), 1092 (23), 1093 (16), 1094 (20), 1095 (10), 1126 (20), 1127 (15), 1128 (26), 1129 (13), 1586 (11), 1587 (11), 1588 (11), 1589 (8), 1621 (7), 1622 (8), 1623 (13), 1624 (7), 1656 (11), 1657 (17), 1658 (12), 1659 (9), 1670 (6), 1850 (17), 1851 (16), 1852 (19), 1853 (12), 1854 (8), 1886 (6), 1887 (11), 1888 (9), 1889 (6), 1918 (8), 1919 (12), 1920 (15), 1921 (16), 1922 (12), 1923 (8), 1954 (5), 1955 (3), 1956 (3), 2114 (3), 2115 (3), 2116 (4), 2117 (3).

Poly(3-nonylthieno[3,2-*b*]thiophene) Prepared by Kumada Coupling (7). A solution of 2,5-dibromo-3-nonylthieno-[3,2-*b*]thiophene (**6**) (1.54 g, 3.64 mmol) in ether (2.5 mL) was added dropwise to a stirred mixture of Mg (87.4 mg, 3.64 mmol) and ether (2.5 mL). The reaction solution was then heated to reflux for 3 h until all Mg reacted. After the flask was cooled to 0 °C, Ni(dppp)Cl_2 (19.7 mg, 0.0363 mmol) was added at this temperature. The solution was heated to reflux for another 17 h. The reaction mixture was then poured into MeOH (100 mL) and the precipitate collected by filtration. Impurities were removed by Soxhlet extraction with MeOH (150 mL) to give polymer **7** (865 mg, 90%). GPC (THF-soluble fraction): M_n = 2184, M_w = 2672. The polymer was fractionated by Soxhlet extraction with hexanes (150 mL) to give 43.3 mg (4.5%) and with $CHCl_3$ (150 mL) to give 163 mg (17%). UV−vis: λ_{max} (hexanes fraction) = 292, 390 nm, λ_{max} ($CHCl_3$ fraction) = 301, 419 nm, λ_{max} (film, $CHCl_3$ fraction) = 454 nm. ^{1}H NMR of $CHCl_3$ fraction (400 MHz, $CDCl_3$, 70 °C, δ): 0.90 (CH_3), 1.15−1.56 ($C_6H_{12}CH_3$), 1.78 (ring-CH_2CH_2), 2.74 (ring-CH_2, HH linkage), 2.99 (ring-CH_2, HT linkage), 7.00 (ring proton, end group), 7.20−7.42 (ring proton). IR (KBr): 2921 (s), 2850 (s), 1630 (w), 1455 (m), 1363 (w), 1155 (w), 1109 (w), 804 (m), 719 cm^{-1} (w). MS of $CHCl_3$ fraction (MALDI, dithranol) m/z (relative intensity): 794 (100), 795 (45), 796 (26), 872 (33), 874 (57), 875 (21), 1058 (45), 1059 (26), 1060 (23), 1136 (35), 1137 (17), 1138 (59), 1139 (21), 1140 (17), 1216 (33), 1217 (14), 1218 (25), 1219 (9), 1322 (13), 1323 (9), 1324 (9), 1402 (18), 1403 (10), 1404 (7), 1480 (6), 1481 (6), 1482 (7), 1586 (3), 1587 (5), 1588 (3). 1666 (10), 1667 (3), 1668 (3).

Poly(3-nonylthieno[3,2-*b*]thiophene) Prepared by Stille Coupling (10). (5-Bromo-6-nonylthieno[3,2-*b*]thiophen-2-yl)-tributylstannane (**9**) (620 mg, 0.500 mmol) was added dropwise into mixture of $Pd(PPh_3)_4$ (12.0 mg, 0.0104 mmol) and CuI (4.0 mg, 0.021 mmol) in DMF (5.0 mL) and THF (5.0 mL). The solution was stirred for 3 days at 60 °C, cooled to room temperature, and poured into MeOH (50 mL). The red precipitate was collected by filtration, and the impurities were removed by Soxhlet extraction with MeOH (150 mL) to give polymer **10** (81.1 mg, 62%). GPC (THF soluble fraction) M_n = 2714, M_w = 3119. The polymer was fractionated by Soxhlet extraction with hexanes (150 mL) to give 16.0 mg (12%) and with $CHCl_3$ (150 mL) to give 50 mg (37%). UV−vis: λ_{max} (hexanes fraction) = 288, 407 nm, λ_{max} ($CHCl_3$ fraction) = 303, 447 nm, λ_{max} (film) = 484 nm. ^{1}H NMR of $CHCl_3$ fraction (400 MHz, $CDCl_3$, 70 °C, δ): 0.90 (CH_3), 1.06−1.60 ($C_6H_{12}CH_3$), 1.84 (ring-CH_2CH_2), 2.77 (ring-CH_2, HH linkage), 3.00 (ring-CH_2, HT linkage), 6.97 (ring proton, end group), 7.22 (ring proton, HH linkage), 7.30 (ring proton, HT linkage). IR (KBr): 2923 (s), 2852 (s), 1463 (m), 1375 (w), 1154 (w), 804 (m), 721 cm^{-1} (w). MS of $CHCl_3$ fraction (MALDI, dithranol) m/z (relative intensity): 1323 (5), 1324 (4), 1325 (2), 1400 (46), 1401 (40), 1402 (70), 1403 (51), 1404 (34), 1478 (44), 1479 (36), 1480 (82), 1481 (73), 1482 (78), 1483 (45), 1484 (14), 1586 (4), 1587 (5), 1588 (3), 1664 (52), 1665 (56), 1666 (85), 1667 (74), 1668 (56), 1669 (14), 1742 (46), 1743 (48), 1744 (91), 1745 (87), 1746 (92), 1747 (75), 1748 (35), 1930 (23), 1931 (17), 1932 (10), 2194 (4), 2195 (5), 2196 (3), 2457 (2), 2459 (5), 2460 (6), 2461 (5), 2538 (2), 2539 (3), 2722 (5), 2723 (5), 2724 (6), 2725 (7), 2801 (3), 2802 (3), 2803 (3), 2986 (2), 2987 (3), 2988 (4), 2989 (4), 3065 (1.84), 3066 (3), 3067 (3), 3252 (3), 3253 (2), 3254 (2), 3331 (2), 3332 (3), 3333 (2), 3594 (2), 3595 (3), 3596 (3), 3597 (3), 3598 (2).

Poly(3,6-dinonylthieno[3,2-*b*]thiophene) (17). $FeCl_3$ (83.0 mg, 0.512 mmol) was added to a stirring solution of **16** (49.4 mg, 0.130 mmol) in $CHCl_3$ (2.0 mL). After 5 h at room temperature, the reaction solution was poured into MeOH (20 mL). The yellow precipitate was collected by filtration, and the polymer was purified by reprecipitation from CH_2Cl_2 (10 mL) into MeOH (50 mL) twice. The precipitate was then collected washed with MeOH to yield polymer **17** (37.0 mg, 75%). GPC $M_n = 54\,372$, $M_w = 70\,210$. UV−vis: λ_{max} ($CHCl_3$) = 300, 359 nm, λ_{max} (film) = 362 nm. ^{1}H NMR (400 MHz, $CDCl_3$, δ): 0.87 (t, J = 7.3 Hz, CH_3), 1.14−1.42 (br, C_6H_{12}-CH_3), 1.77 (br, ring-CH_2CH_2), 2.78 (br, ring-CH_2). IR (KBr): 2923 (s), 2852 (s), 1635 (w), 1465 (m), 1377 (w), 1107 (w), 1053 (w), 812 (w), 720 cm^{-1} (w).

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Supporting Information Available: Cyclic voltammetry traces showing reduction cycles of polymers **5**, **7**, **10**, and **17**. This material is available free of charge via the Internet at http://pubs.acs.org.

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