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Dialkyl-Substituted Thieno[3,2-*b*]thiophene-Based Polymers Containing 2,2′-Bithiophene, Thieno[3,2-*b*]thiophene, and Ethynylene Spacers

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ABSTRACT: A series of 3,6-dinonylthieno[3,2-*b*]thiophene-based polymers containing either 2,2′-bithiophene, thieno[3,2-*b*]thiophene, or ethynylene spacer units were synthesized by Stille and oxidative coupling reactions. Their electronic properties were studied by UV−vis absorption and fluorescence spectroscopies in solution and in the solid state and compared to poly(3,6-dinonylthieno[3,2-*b*]thiophene). The introduction of these spacers led to a substantial red shift in the longest wavelength of absorption, indicating that these modifications restore, to a significant extent, the planarity of the system resulting in increased conjugation. Model compounds representing the basic structural unit of each polymer were synthesized, and computations were performed to understand the role of the spacer in dictating the conformation of the polymer backbone.

Introduction

Semiconducting organic polymers have been extensively studied due to their remarkable optical and electrical properties.[1] Thiophene-based polymers[2−6] hold particular interest owing to their good environmental stability, processability,[7] and small band gaps.[8,9] In particular, poly(3-alkylthiophene)s, (P3AT)s, have been successfully employed as the active layer in organic field effect transistors (OTFT).[7,10−13] Although P3ATs have displayed good properties, these materials possess low barriers to deplanarization that could result in a decrease in conjugation and solid-state ordering.[14] The incorporation of partially planarized fused thiophene-based units into the polymer backbone represents a promising approach toward improving conjugation and optimizing solid-state properties. For example, the polymerization of dithieno[3,2-*b*:2′,3′-*d*]pyrroles (Figure 1) results in highly fluorescent polymers with reduced band gaps.[15,16] Polythiophenes containing thieno[2,3-*b*]thiophene units display good charge carrier mobility,[17] and the polymerization of thieno[3,4-*b*]thiophene results in stable low band gap conducting polymers.[18−20] In addition, polymers and copolymers based on thieno[3,2-*b*]thiophene have been studied, but the inclusion of these fused units into a polymer backbone results in poor solubility which hinders characterization and processability.[21−23]

The introduction of alkyl chains into a polymer generally increases solubility which facilitates purification and characterization; however, in some cases steric interactions with alkyl substituents have a negative impact on conjugation due to decreased backbone planarity. We previously described the syntheses of thieno[3,2-*b*]thiophene-based polymers in which alkyl substituents were appended to the polymer backbone.[24] The incorporation of one or two nonyl chains into the β-position of thieno[3,2-*b*]thiophene units to produce poly(3-nonylthieno[3,2-*b*]thiophene) (**1**) and poly(3,6-dinonylthieno[3,2-*b*]thiophene) (**2**), respectively (Figure 2), results in polymers that drastically differ in solubility and conjugation. Polymer **2** has excellent solubility compared to polymer **1**, but the conjugation of **2** is limited due to the increase in repulsive interactions caused by the incorporation of an additional alkyl chain to the polymer backbone. The strategy explored here is to introduce 2,2′-bithiophene, thieno[3,2-*b*]thiophene, and ethynylene spacers to reduce the steric interactions between adjacent 3,6-dialkylthieno[3,2-*b*]thiophene units, thus restoring planarity and conjugation of the polymer backbone. Indeed, alternating copolymers of thieno[3,2-*b*]thiophene and 2,2′-bithiophene have recently been reported incorporating side chains on either the fused[25] or

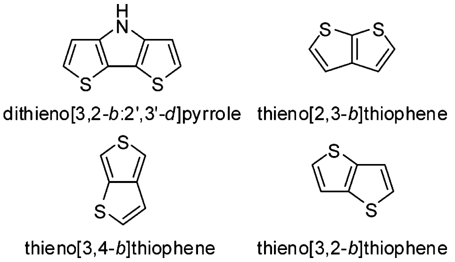

Figure 1. Partially planarized thiophene-based building blocks for conjugated polymers.

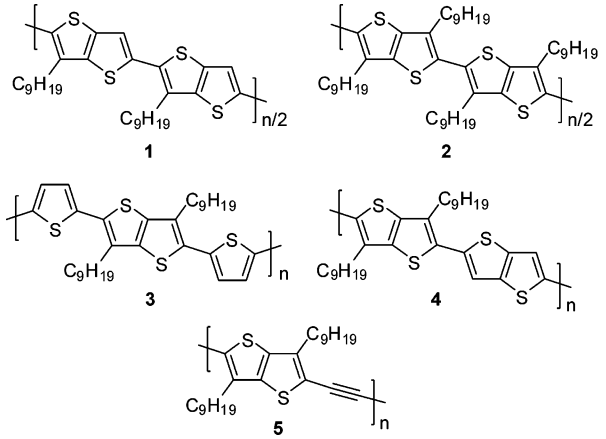

Figure 2. Chemical structures of poly(3-nonylthieno[3,2-*b*]thiophene)[24] (**1**), poly(3,6-dinonylthieno[3,2-*b*]thiophene)[24] (**2**), poly(2-[2,2′]bithiophen-5-yl-3,6-dinonylthieno[3,2-*b*]thiophene) (**3**), poly(3,6-dinonyl-[2,2′]bi-[thieno[3,2-*b*]thiophene]) (**4**), and poly(3,6-dinonylthieno[3,2-*b*]thiophen-2,5-diylethynylene) (**5**).

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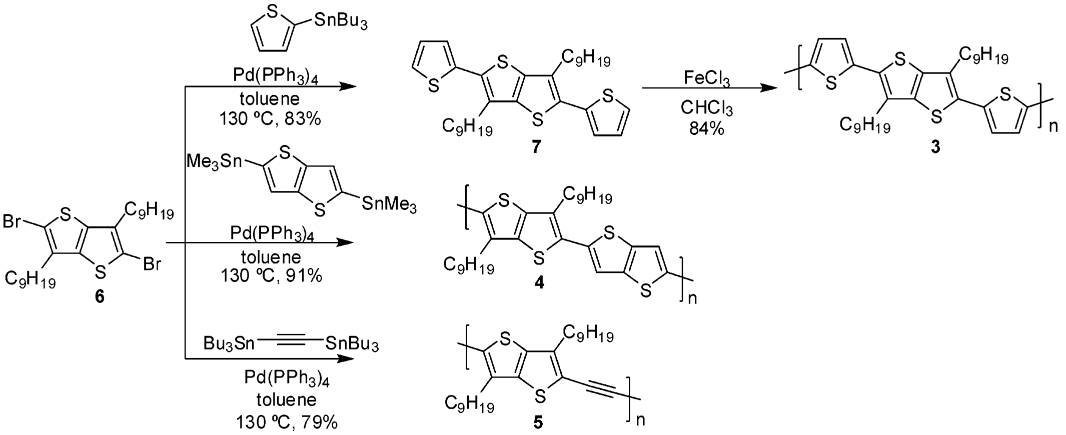
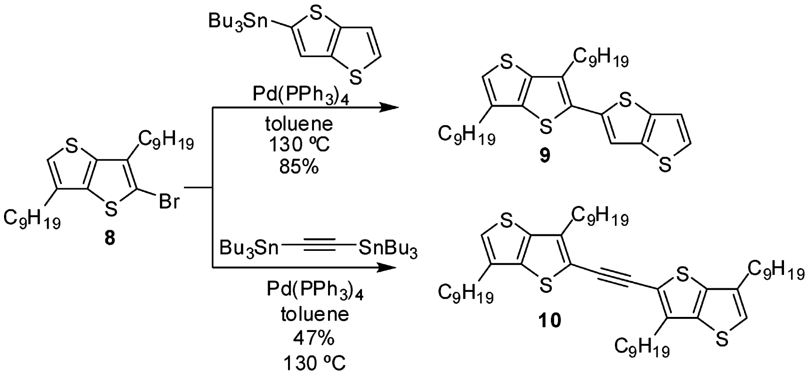
Scheme 1. Syntheses of Polymers 3−5



Scheme 2. Syntheses of the Model Subunits for Polymers 4 and 5



nonfused unit.[26] In both cases, good conjugation and charge transport characteristics were observed. Considering the current interest in OTFTs based on fused thiophene units and their remarkable device performance, the continued study of the fundamental properties of these types of polymers is warranted.

Here we report the syntheses and characterization of 3,6-dinonylthieno[3,2-*b*]thiophene-based polymers containing 2,2′-bithiophene, thieno[3,2-*b*]thiophene, and ethynylene spacers (Figure 2). The effect of the introduction of each spacer between dialkylated thieno[3,2-*b*]thiophene in the polymer backbone is studied in order to understand their role in determining the electronic properties of these materials. The optical properties of these polymers were studied in solution and in the solid-state and compared to polymer **2**. In addition, model subunits of these polymers were synthesized and used, in conjunction with computations, as well-defined models to gauge the extent of conjugation and planarity of the monomer units in the polymer backbone.

Preparation and Characterization

The synthesis of polymer **3** was targeted from the oxidative coupling of 3,6-dinonyl-2,5-bithiophen-2-yl-thieno[3,2-*b*]thiophene (**7**) (Scheme 1). To produce this monomer, 2,5-dibromo-3,6-dinonylthieno[3,2-*b*]thiophene (**6**), prepared by the bromination of 3,6-dinonylthieno[3,2-*b*]thiophene,[24] was coupled to 2-(tributylstannyl)thiophene under Stille conditions. Polymer **3** was obtained as a red solid with good solubility in hot toluene, allowing purification by Soxhlet extraction; however, the solubility of this polymer in THF at room temperature is limited leading to an underestimation of the molecular weight by GPC analysis (M_n = 3430, M_w = 4210).[27]

Polymers **4** and **5** were prepared by Stille coupling of **6** with the appropriate stannyl compounds (Scheme 1). The cross-coupling of **6** and 2,5-bis(trimethylstannyl)thieno[3,2-*b*]thiophene[26] in the presence of catalytic $Pd(PPh_3)_4$ in toluene yields polymer **4**. The dark red product obtained during the synthesis of **4** has limited solubility in THF, and the molecular weight of this soluble fraction is M_n = 5482, M_w = 6709. Polymer **5** was obtained from the reaction of **6** with bis(tributylstannyl)acetylene under Stille conditions as described for polymer **4**. The molecular weight of polymer **5** determined by GPC is M_n = 57 955, M_w = 121 950, indicating improved solubility relative to polymers **3** and **4**.

To explore the planarity and conformation of the monomer units in the backbone of polymers **3**−**5**, the corresponding model subunits were synthesized by Stille coupling (Scheme 2). Dimer **9**, which serves as the model compound for polymer **4**, was synthesized from compound **8** and 2-(tributylstannyl)thieno[3,2-*b*]thiophene[28] under Stille conditions. Compound **8** was obtained from the lithium−halogen exchange of **6** followed by the addition of methanol (see Supporting Information). Model compound **10** was prepared by cross-coupling **8** with bis(tributylstannyl)acetylene.

Optical Properties

The electronic properties of polymers **3**−**5** were studied by UV−vis and fluorescence spectroscopies and compared to **1** and **2**; these data are listed in Table 1. Polymer **2** has a longest wavelength absorption maximum (λ_{max}) at 359 nm, which is 88 nm blue-shifted relative to polymer **1** (447 nm). This blue shift in λ_{max} of absorption is a direct consequence of the introduction of the second alkyl chain into the polymer backbone, leading to increased steric repulsion between alkyl substituents and sulfurs on adjacent rings.[24] These repulsive interactions are also present in polymer **1**, but they are reinforced in polymer **2** by the introduction of the additional alkyl chain causing a more dramatic deplanarization of the polymer backbone. The introduction of conjugated spacers into the polymer backbone reduces these unfavorable interactions as illustrated here for 2,2′-bithiophene, thieno[3,2-*b*]thiophene, and ethynylene units.

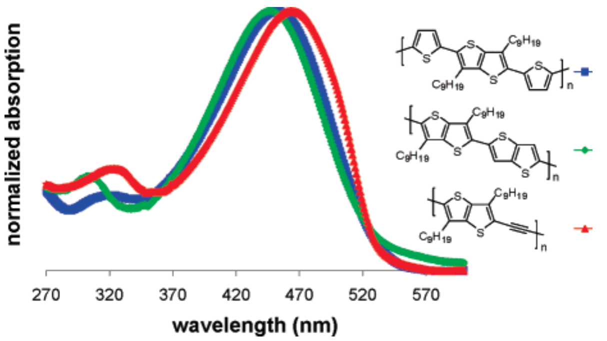


Figure 3. UV−vis absorption spectra of polymers **3**−**5** in $CHCl_3$ solution.

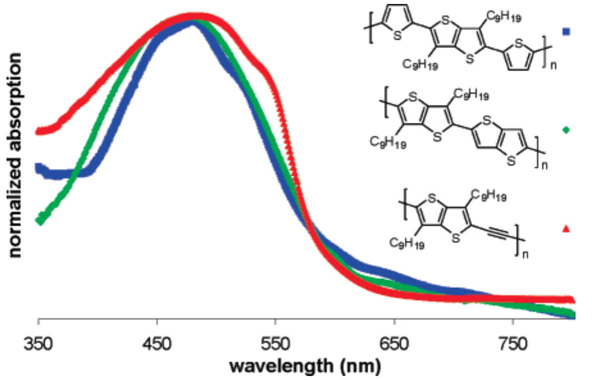


Figure 4. UV−vis absorption spectra of polymers **3**−**5** as thin films.

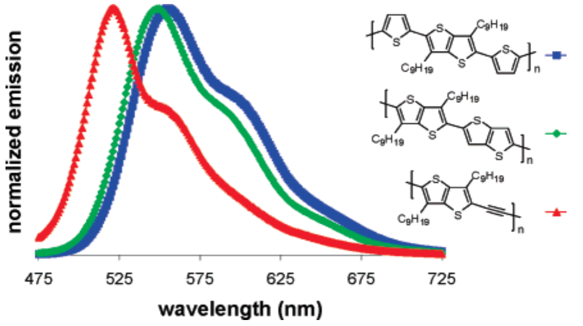
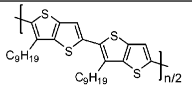
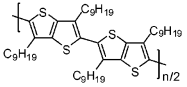
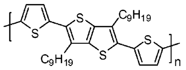
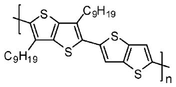
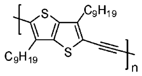
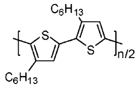


Figure 5. Fluorescence spectra of polymers **3**−**5** in $CHCl_3$ solution.

Table 1. Longest Wavelength of Absorption and Emission Maxima of Polymers 3−5 and Reference Compounds in $CHCl_3$ Solution and Thin Film

	polymer structure	λ_{max} absorption (nm)		λ_{max} emission (nm)
		solution	thin film	solution
1		447^{24}	484^{24}	544^{24} 581 (sh)
2		359^{24}	362^{24}	486^{24}
3		453	481 524 (sh)	556 599 (sh)
4		446	478	550 591 (sh)
5		463	492 544 (sh)	522 558 (sh)
		456^{29}	526^{29}	570^{29}

Polymer **3**, with a 2,2′-bithiophene spacer, has a λ_{max} of absorption of 453 nm (Figure 3), corresponding to a 94 nm red shift relative to **2**. A further red shift in λ_{max} of absorption of 28 nm is observed upon a transformation from solution to the solid state (Figure 4). The fluorescence spectrum for polymer **3** shows an emission peak at 556 nm and a shoulder at 599 nm (Figure 5). However, when a more rigid and planar thieno[3,2-*b*]thiophene spacer unit is integrated in polymer **4**, the λ_{max} of absorption is 446 nm in solution and 478 nm in the solid state, corresponding to a bathochromic shift of 87 nm in solution and 116 nm in solid state relative to polymer **2**. The fluorescence spectrum of **4** features an emission peak at 550 nm and a shoulder at 591 nm. Despite having a lower molecular weight, polymer **3** has a slightly smaller optical band gap than polymer **4**, suggesting that the 2,2′-bithiophene spacer unit leads to a more conjugated polymer than the corresponding thieno[3,2-*b*]thiophene spacer unit in polymer **4**. It should be noted that polymers **4** and **1**, isomers that vary only in the position of the alkyl chains, show similar λ_{max} of absorption in solution of 446 and 447 nm, respectively. This indicates that in these systems the conjugation of both polymers is dictated by the deviation from planarity caused by the interactions between alkyl chains and sulfurs on the adjacent thieno[3,2-*b*]thiophene ring; these interactions are the same in **4** and **1**. When an ethynylene unit is incorporated between dialkylated thieno[3,2-*b*]thiophene units (polymer **5**), the result is a red shift of the λ_{max} of absorption of 104 nm relative to polymer **2**. In the solid state polymer **5** displays an absorption peak at 492 nm and a shoulder at 544 nm. The fluorescence spectrum shows an emission peak at 522 nm and a shoulder at 558 nm. Polymer **5** has the smallest Stokes shift in the series which can be attributed to the less sterically hindered spacer unit that leads to a more planar conformation (vide infra) of the polymer in solution relative to polymers **3** and **4** with a correspondingly smaller change in conformation between ground and excited state. On the basis of these data, the introduction of all spacer units into the target polymer backbone results in greatly superior conjugation compared to **2**. This is mainly attributed to the fact that in polymers **3**−**5** the steric interactions between alkyl chains and the spacer cause a smaller deviation from planarity than the steric interactions between adjacent dialkylated rings in polymer **2**.

To further elucidate the effect of each spacer on the optical properties of these materials, UV−vis and computational studies of model subunits were performed. The λ_{max} of absorption of compounds **7**, **9**, and **10** and appropriate reference compounds are summarized in Table 2. The longest wavelength of absorption is greatly influenced by the number of π-bonds in conjugation; therefore, these model subunits are divided into two groups according to the number of conjugated π-bonds present in the system. The model subunits of polymers **4** and **2**, compounds **9** and **11**, respectively, have six π-bonds in conjugation but differ in λ_{max} of absorption. Compound **11** has the shortest λ_{max} of absorption of this group due to severe deplanarization caused by the repulsive interactions between adjacent dialkylated rings. DFT calculations (B3LYP/6-31G*) of 10 different torsion angles for the methyl analogues of **7**, **9**, **10**, and **11** were examined to determine their minimum-energy geometry and the energy barrier for adopting a planar conformation (Figure 6). The use of methyl groups in place of nonyl chains gives a reasonable approximation of molecular conformation while simplifying the calculations greatly. The use of

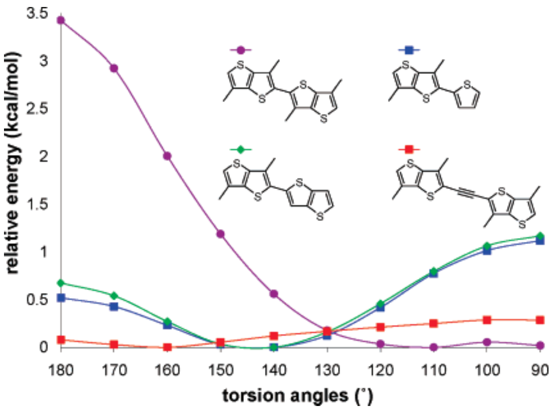
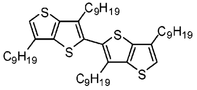
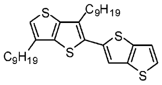
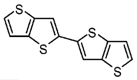
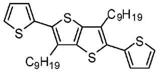
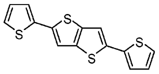
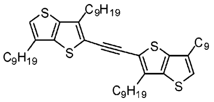


Figure 6. Calculated energies for the methyl analogues of **7** and **9**−**11** at different torsion angles.

Table 2. Longest Wavelength of Absorption of 7, 9, 10, and Reference Compounds in $CHCl_3$ Solution

	model subunit structure	π-bonds in conjugation	λ_{max} absorption (nm) solution
11		6	296[24]
9		6	336
12		6	353
7		7	353
13		7	373[28]
10		7	387

2,2′-bithiophene and thieno[3,2-*b*]thiophene spacers reduces the steric interactions between alkyl chains and sulfurs on adjacent rings, and the use of the ethynylene spacer completely removes these repulsive interactions. Notably, computations predict that decreasing the number of sulfur to alkyl chain steric interactions from two (as in polymer **2**) to one (as in polymers **3** and **4**) reduces the barrier to planarization by significantly more than half. Upon planarization from its minimum-energy conformation, the methyl analogue of **11** is destabilized by more than 5-fold compared to the methyl analogue of **9** (Figure 6). This can be attributed to two major factors: (1) compound **9** has an attractive thienyl C−H···S interaction that is lost upon alkyl chain introduction[30] and (2) in **9** the angle between thieno[3,2-*b*]thiophene rings can be adjusted to accommodate the steric interactions between alkyl chains and sulfurs on adjacent rings (see Supporting Information, Figure S2). Consequently, oligomer **9** has a λ_{max} of 336 nm (Figure 7), which corresponds to a red shift of 40 nm relative to **11**. The unsubstituted dimer of thieno[3,2-*b*]thiophene (**12**) has the longest λ_{max} of absorption (353 nm) of this group, indicating that any alkyl substituent leads to some deplanarization, and this assertion is supported by DFT calculations.[24]

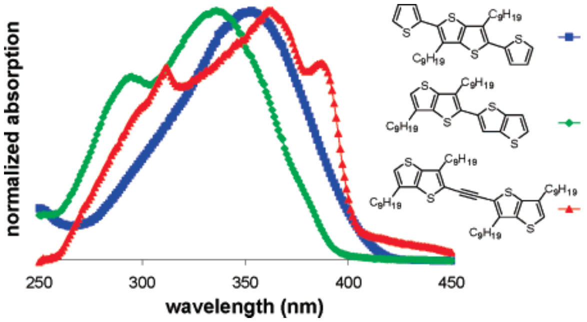


Figure 7. UV−vis absorption spectra of model subunits **7**, **9**, and **10** in $CHCl_3$ solution.

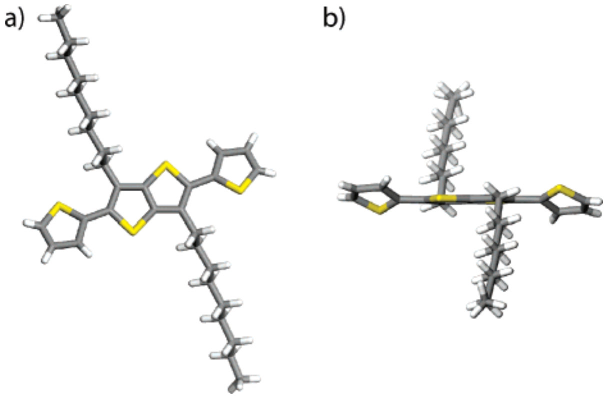


Figure 8. Solid-state structure of compound **7** illustrating two views: (a) parallel and (b) perpendicular to the 3,6-dinonylthieno[3,2-*b*]thiophene plane.

The second group of oligomers contains seven π-bonds in conjugation and is composed of compounds **7** and **10** and reference compound 2,5-di(2-thienyl)thieno[3,2-*b*]thiophene (**13**).[28] The model subunit for polymer **3**, compound **7**, has a λ_{max} that is 20 nm blue-shifted relative to **13**, which is the unsubstituted analogue of **7**. This demonstrates that the incorporation of the alkyl chains in **7** causes some deviation from planarity; support for this notion is found in DFT calculations where the methyl analogue of **7** is destabilized by 0.5 kcal/mol when planarized from its minimum-energy torsion angle of 140°. Moreover, a torsion angle of 161° is observed in the single-crystal structure of **7** determined by X-ray diffraction (Figure 8). The longest λ_{max} observed in this group (seven conjugated π-bonds) corresponds to compound **10**, the model subunit for polymer **5**, which has an absorption peak at 387 nm, and at its planar conformation the analogue of **10** is destabilized by only 0.08 kcal/mol with a minimum-energy torsion angle of 160°. The increased conjugation of compound **10** can be explained by the addition of the ethynylene spacer unit between dialkylated thieno[3,2-*b*]thiophene units. A less sterically demanding ethynylene spacer unit maintains the planarity of the system, resulting in increased conjugation.

Conclusion

A series of dialkyl-substituted thieno[3,2-*b*]thiophene polymers incorporating 2,2′-bithiophene, thieno[3,2-*b*]thiophene, and ethynylene spacer units were synthesized and compared to monoalkylated and dialkylated thieno[3,2-*b*]thiophene polymers. The introduction of these spacing units leads to improved planarity and conjugation as demonstrated by a red shift in λ_{max} relative to poly(3,6-dinonylthieno[3,2-*b*]thiophene). This suggests that dialkylated thieno[3,2-*b*]thiophene can be used as a building block for semiconducting polymers but that a spacer unit is needed to reduce steric interactions between adjacent dialkylated rings in order to obtain a more planar backbone conformation.

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Supporting Information Available: Experimental procedures, UV−vis data for different molecular weight fractions of polymer **4**, equilibrium geometry calculations for the methyl analogues of compounds **9** and **11**, and CIF files for **7**. This material is available free of charge via the Internet at http://pubs.acs.org.

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