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Thiophene/Thieno[3,2-*b*]thiophene Co-oligomers: Fused-Ring Analogues of Sexithiophene

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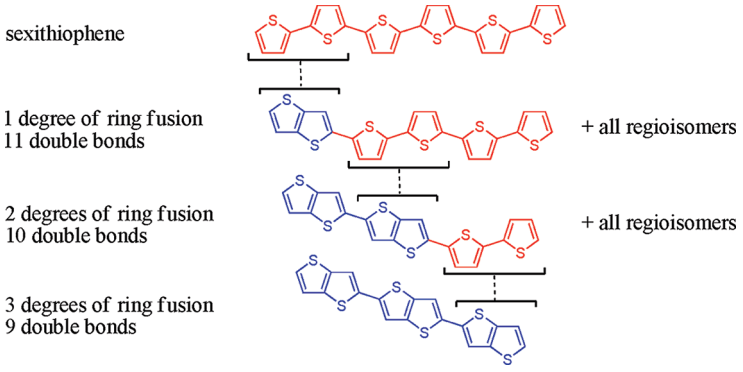

A series of six-ring oligothiophenes containing one to three degrees of ring fusion were assembled by a combination of metal-catalyzed Stille cross-coupling and oxidative homocoupling reactions. The effect of position and extent of ring fusion on the electronic properties was studied by UV−vis absorption and fluorescence spectroscopies, and these data were interpreted in the context of TD-DFT computational analysis. Within each set of regioisomers, a slight red shift is revealed in the onset of the UV−vis absorption spectra when the fused-ring unit is located nearer to the periphery of the oligomer, indicating a narrower HOMO−LUMO gap. Incorporation of the unit of ring fusion toward the interior of the oligomer results in a decrease in the longest wavelength emission maximum and a reduced Stokes shift, and is accompanied by an increase in fluorescence quantum yield.

Introduction

Oligomers and polymers containing thiophene units are among the most extensively studied conjugated materials due to their relatively good environmental stability, excellent optical and electronic properties, and tunability at the molecular level.[1] Incorporating ring fusion as a structural element is a powerful approach to control properties.[2−4] In cases where fused-ring units are employed adjacent to more conventional oligothiophene segments, developing an understanding of the interaction between subunits will facilitate the rational design of future oligo- and polythiophenes. Sexithiophene, the α-linked hexamer of thiophene and its derivatives are among the most extensively investigated oligothiophenes making it an appropriate starting point for exploration of ring fusion effects. Previous work in our group has determined the effect of ring fusion on oligothiophenes with four rings;[3,4] however, only isolated examples of

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(2) Selected examples include: (a) McCulloch, I.; Heeney, M.; Chabinyc, M. L.; DeLongchamp, D.; Kline, R. J.; Coelle, M.; Duffy, W.; Fischer, D.; Cundloch, D.; Hamadani, B.; Hamilton, R.; Richter, L.; Salleo, A.; Shkunov, M.; Sporrowe, D.; Tierney, S.; Zhong, W. *Adv. Mater.* **2009**, *21*, 1091–1109. (b) Litvinov, V. P. *Usp. Khim.* **2005**, *74*, 235–267. (c) Liu, P.; Wu, Y. L.; Pan, H. L.; Li, Y. N.; Gardner, S.; Ong, B. S.; Zhu, S. P. *Chem. Mater.* **2009**, *21*, 2727–2732. (d) Parmer, J. E.; Mayer, A. C.; Hardin, B. E.; Scully, S. R.; McGehee, M. D.; Heeney, M.; McCulloch, I. *Appl. Phys. Lett.* **2008**, 92. (e) Fong, H. H.; Pozdin, V. A.; Amassian, A.; Malliaras, G. G.; Smilgies, D. M.; He, M. Q.; Gasper, S.; Zhang, F.; Sorensen, M. *J. Am. Chem. Soc.* **2008**, *130*, 13202–13203. (f) Tang, W. H.; Ke, L.; Tan, L. W.; Lin, T. T.; Kietzke, T.; Chen, Z. K. *Macromolecules* **2007**, *40*, 6164–6171. (g) Okamoto, T.; Kudoh, K.; Wakamiya, A.; Yamaguchi, S. *Chem.—Eur. J.* **2007**, *13*, 548–556. (h) Miguel, L. S.; Matzger, A. J. *Macromolecules* **2007**, *40*, 9233–9237. (i) He, M. Q.; Zhang, F. X. *J. Org. Chem.* **2007**, *72*, 442–451. (j) Lim, E.; Kim, Y. M.; Lee, J. I.; Jung, B. J.; Cho, N. S.; Lee, J.; Do, L. M.; Shim, H. K. *J. Polym. Sci., Part A: Polym. Chem.* **2006**, *44*, 4709–4721. (k) Li, Y. N.; Wu, Y. L.; Liu, P.; Birau, M.; Pan, H. L.; Ong, B. S. *Adv. Mater.* **2006**, *18*, 3029–3032. (l) Zhang, X. N.; Cote, A. P.; Matzger, A. J. *J. Am. Chem. Soc.* **2005**, *127*, 10502–10503. (m) Zhang, X. N.; Kohler, M.; Matzger, A. J. *Macromolecules* **2004**, *37*, 6306–6315. (n) Lim, E.; Jung, B. J.; Lee, J.; Shim, H. K.; Lee, J. I.; Yang, Y. S.; Do, L. M. *Macromolecules* **2005**, *38*, 4531–4535.

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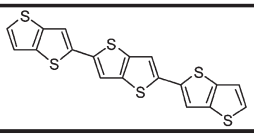
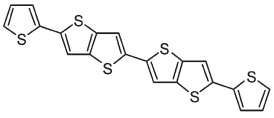
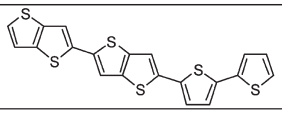
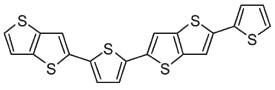
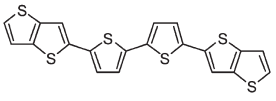
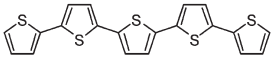
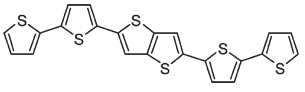
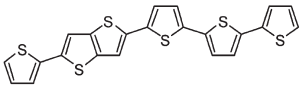
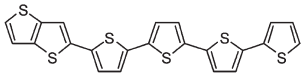
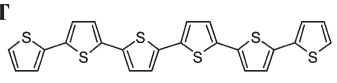
TABLE 1. Experimental and Calculated Electronic Transitions for Oligomers 1−8, Quinquethiophene, and Sexithiophene

	oligomer	double bonds	absorption λ_{max} (nm)[a]	emission λ_{max} (nm)[a]	Stokes shift (nm)	calculated transition (nm)[b]	quantum yield (%)[a,c]
1		9	401	448	47	441	43
2		10	415	463	48	467	56
3		10	415	470	55	471	46
4		10	416	473	57	472	33
5		10	416	478	62	475	26
α-5T		10	417	481	64	482	28
6		11	426	484	58	495	45
7		11	427	490	63	496	36
8		11	427	494	67	499	31
α-6T		12	432[d]	512[d]	80	521	42[d]

[a] CH_2Cl_2 as solvent. [b] Computations performed on the planar conformation, using TD-DFT at the B3LYP/6-31G* level. [c] Percent error in fluorescence quantum yield measurements for **1**−**8** is ±1.0 or less. [d] Literature value (ref 12).

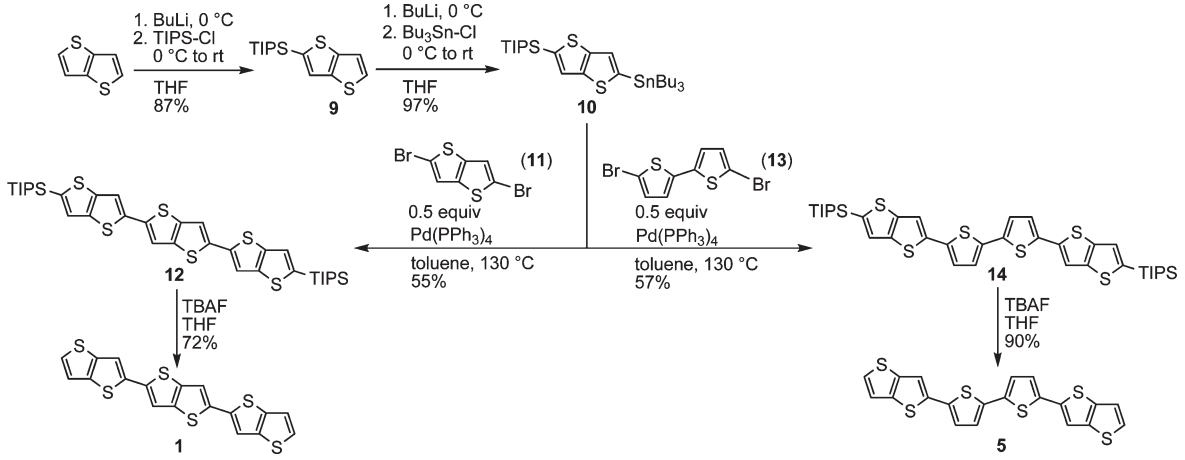
ring fusion in thiophene oligomers with more than four rings have been reported[5] and therefore the optical properties of longer oligothiophenes, where new regiochemical issues arise, have not yet been scrutinized. Here we report the synthesis and optical properties of a series of eight sexithiophene analogues in which one, two, or three 2,2′-bithiophene units are replaced with the same number of thieno[3,2-*b*]thiophene units. This set of six-ring compounds with systematic structural perturbation reveals trends in conjugation and molecular conformation reflecting the effects associated with both the degree and position of ring fusion.

Results and Discussion

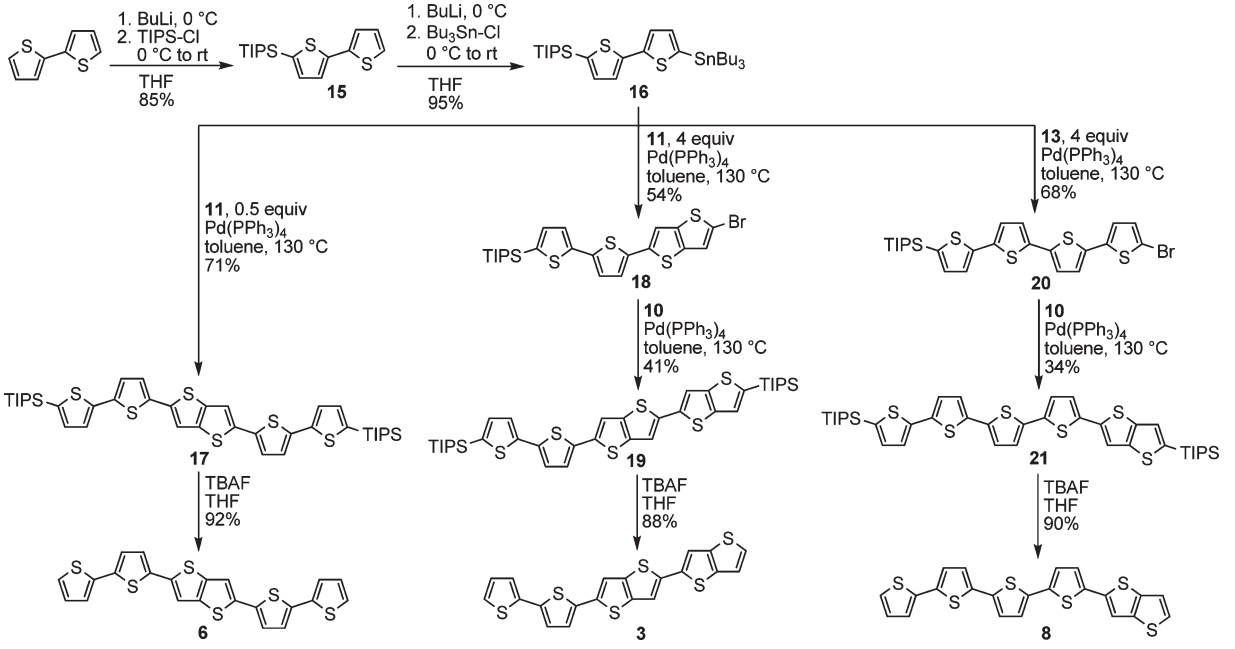
Solubility, potential for oligomer aggregation, and purification efficiency were considered key factors when designing the synthetic route to oligomers **1**−**8** (Table 1). Unsubstituted conjugated oligomers of this size typically suffer from low solubility and this can be exacerbated by increased planarization. Permanent solubilizing groups, such as alkyl chains, were not incorporated so that the inherent properties

(3) Zhang, X. N.; Johnson, J. P.; Kampf, J. W.; Matzger, A. J. *Chem. Mater.* **2006**, *18*, 3470–3476.
(4) Zhang, X. N.; Matzger, A. J. *J. Org. Chem.* **2003**, *68*, 9813–9815.
(5) (a) Kong, H.; Jung, Y. K.; Cho, N. S.; Kang, I. N.; Park, J. H.; Cho, S.; Shim, H. K. *Chem. Mater.* **2009**, *21*, 2650–2660. (b) Medina, B. M.; Van Vooren, A.; Brocorens, P.; Gierschner, J.; Shkunov, M.; Heeney, M.; McCulloch, I.; Lazzaroni, R.; Cornil, J. *Chem. Mater.* **2007**, *19*, 4949–4956. (c) Lim, E.; Jung, B. J.; Shim, H. K.; Taguchi, T.; Noda, B.; Karnbayashi, T.; Mori, T.; Ishikawa, K.; Takezoe, H.; Do, L. M. *Org. Electron.* **2006**, *7*, 121–131. (d) Nakayama, J.; Dong, H. B.; Sawada, K.; Ishii, A.; Kumakura, S. *Tetrahedron* **1996**, *52*, 471–488.

SCHEME 1. Synthetic Route to Oligomers 1 and 5



SCHEME 2. Synthetic Route to Oligomers 6, 3, and 8



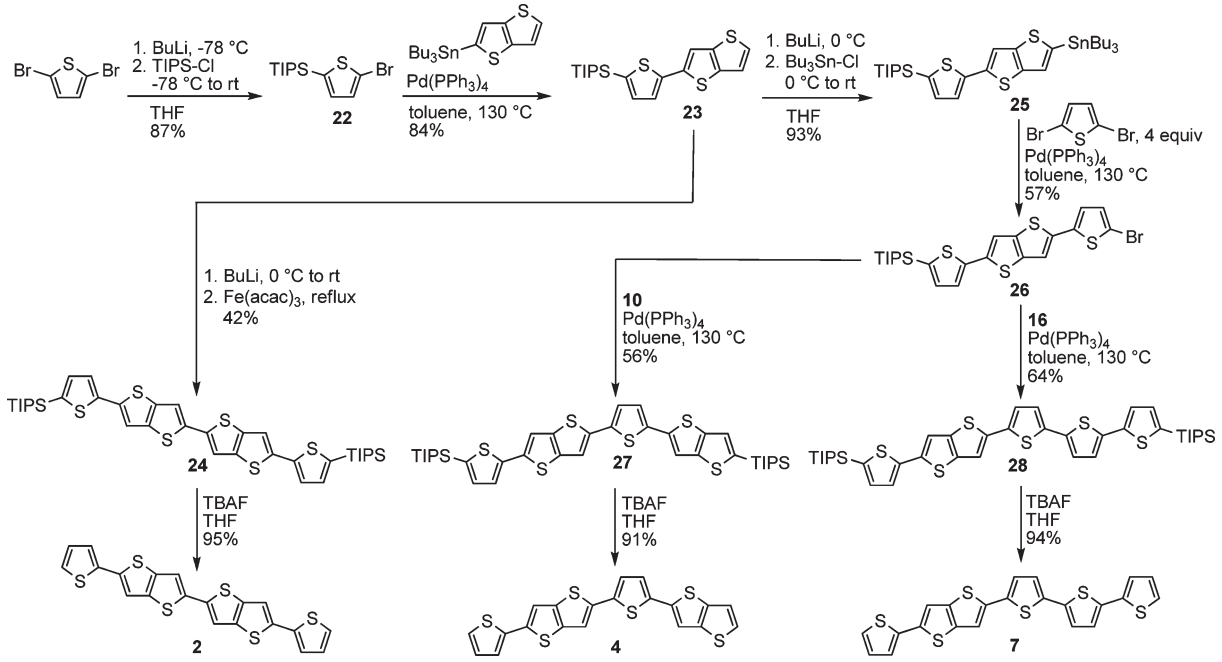
of the oligomers could be probed. Instead, removable triisopropylsilyl (TIPS) groups were introduced at the terminal α-positions of the oligomers which allows for significantly higher solubility, aiding in reaction efficiency and enabling purification by column chromatography.[6] Protecting one terminal α-position with a TIPS group also allows for selective deprotonation and subsequent functionalization at a single α-position during the construction of oligomers. Designing all of the six-ring oligomers to have TIPS groups at *both* terminal positions provides a set of oligomers (**12**, **14**, **17**, **19**, **21**, **24**, **27**, **28**) where the possibility of perturbation of electronic properties resulting from aggregation in solution is minimized. Oligomers were assembled by a combination of metal-catalyzed Stille cross-coupling and oxidative homocoupling techniques. Because Stille cross-coupling reactions generate minor side products of homocoupled stannyl and bromo compounds the synthetic route to each of the bis-TIPS-substituted six-ring oligomers (Schemes 1−3) was designed such that the homocoupled side products would have either four or eight rings thus aiding in purification.[7] The synthetic routes to oligomers **1**−**8** rely heavily on the ring-fused unit thieno[3,2-*b*]thiophene. Utilization of a recently optimized synthetic strategy allows for scalable access to this moiety in high purity via a two-step route starting from 3-bromothiophene.[8]

As illustrated in Scheme 1, the syntheses of oligomers **1** and **5** rely on the common intermediate **10**, which is readily derived from **9** by deprotonation with BuLi and quenching with TIPS-Cl. Compound **9** is synthesized by monolithiation of thieno[3,2-*b*]thiophene[8] upon treatment with BuLi, followed by quenching with TIPS-Cl. Bis-TIPS oligomers **12** and **14** are obtained from the cross-coupling reactions of

(6) For example, TIPS-substituted oligomer **17** is more than 2 orders of magnitude more soluble than unsubstituted oligomer **6** (Supporting Information).

(7) Katz, H. E.; Bao, Z. N.; Gilat, S. L. *Acc. Chem. Res.* **2001**, *34*, 359–369.
(8) Henssler, J. T.; Matzger, A. J. *Org. Lett.* **2009**, *11*, 3144–3147.

SCHEME 3. Synthetic Route to Oligomers 2, 4, and 7



10 with half of an equivalent of 2,5-dibromothieno[3,2-*b*]-thiophene (**11**)[9] and 5,5′-dibromo-2,2′-bithiophene (**13**),[10] respectively. The target six-ring oligomers **1** and **5** are isolated as precipitates in high yield and purity upon removal of the solubilizing groups with tetrabutylammonium fluoride (TBAF).

The construction of oligomers **6**, **3**, and **8** (Scheme 2) requires **16**, which is prepared by a procedure analogous to that used for the assembly of **10**, except employing 2,2′-bithiophene as the starting material (Supporting Information). Oligomer **6** is generated by a cross-coupling reaction of **16** with half of an equivalent of **11**, followed by desilylation of **17**. To obtain oligomers **18** and **20** with a terminal bromide, stannyl compound **16** is reacted under Stille cross-coupling conditions with a 4-fold excess of **11** and **13**, respectively. Both **18** and **20** are coupled with stannyl compound **10** to afford oligomers **19** and **21**, and upon desilylation oligomers **3** and **8**, respectively, are isolated in high yields and purity.

Intermediate **23** is employed in the formation of oligomers **2**, **4**, and **7** (Scheme 3), and is derived from a cross-coupling reaction of **22** and tributyl(thieno[3,2-*b*]thien-2-yl)stannane.[11] Compound **22** is produced through mono Li−Br exchange of 2,5-dibromothiophene with BuLi and quenching with TIPS-Cl. Treatment of **23** with BuLi generates the α-anion, which is oxidatively homocoupled with $Fe(acac)_3$ to afford **24**, and subsequently oligomer **2** upon reaction with TBAF. Stannyl derivative **25** is created by quenching lithiated **23** with tributyltin chloride (Bu_3Sn-Cl). Cross-coupling stannyl compound **25** with a 4-fold excess of 2,5-dibromothiophene gives access to bromide-terminated compound **26**. Bromide **26** is coupled with stannyl compounds **10** and **16** to yield oligomers **27** and **28**, respectively. Removal of the solubilizing TIPS groups precipitates the unsubstituted oligomers **4** and **7** in high purity. Further purification of all six-ring oligomers (**1**−**8**) can be achieved by zone sublimation under high vacuum.

Optical Properties. The experimental and computed optical data for oligomers **1**−**8**, quinquethiophene (α-5T), and sexithiophene (α-6T) are summarized in Table 1. Sets of isomers **2**−**5** and **6**−**8**, which each contain the same number of double bonds and vary only in the position of the thieno-[3,2-*b*]thiophene units, are used to probe the effect of regiochemistry and the extent of ring fusion on the relative conjugation and molecular conformation in solution. Data for quinquethiophene are included because, although it is not isomeric with any of the newly synthesized compounds, it has the same number of double bonds as isomers **2**−**5** and therefore is used to investigate the effect of introducing additional thienyl sulfur linkages. Sexithiophene has six α-linked thiophene rings and is an appropriate reference compound for comparison because it has an equal number of thiophene rings as oligomers **1**−**8**. Substitution of each 2,2′-bithiophene unit in sexithiophene with thieno[3,2-*b*]thiophene introduces one degree of ring fusion and eliminates one double bond in the oligomer, resulting in a predictable blue shift in the longest wavelength absorption maximum (λ_{max}). For example, **1** and sexithiophene each have six rings but incorporation of three degrees of ring fusion in **1** eliminates three double bonds resulting in an increase in the HOMO−LUMO gap, reflected in a 31 nm blue shift in the absorption λ_{max}.

Isomers **6**−**8** vary only in the placement of a single thieno[3,2-*b*]thiophene unit, therefore regiochemical effects of ring fusion can be directly investigated. Remarkably, all of these oligomers display a similar absorption λ_{max} indicating that the conjugation across the molecules in solution

(9) Li, P.; Ahrens, B.; Feeder, N.; Raithby, P. R.; Teat, S. J.; Khan, M. S. *Dalton Trans*. **2005**, 874–883.
(10) Bauerle, P.; Wurthner, F.; Gotz, G.; Effenberger, F. *Synthesis* **1993**, 1099–1103.
(11) Prim, D.; Kirsch, G. *J. Chem. Soc., Perkin Trans. 1* **1994**, 2603–2606.
(12) Garcia, P.; Pernaut, J. M.; Hapiot, P.; Wintgens, V.; Valat, P.; Garnier, F.; Delabouglise, D. *J. Phys. Chem*. **1993**, *97*, 513–516.

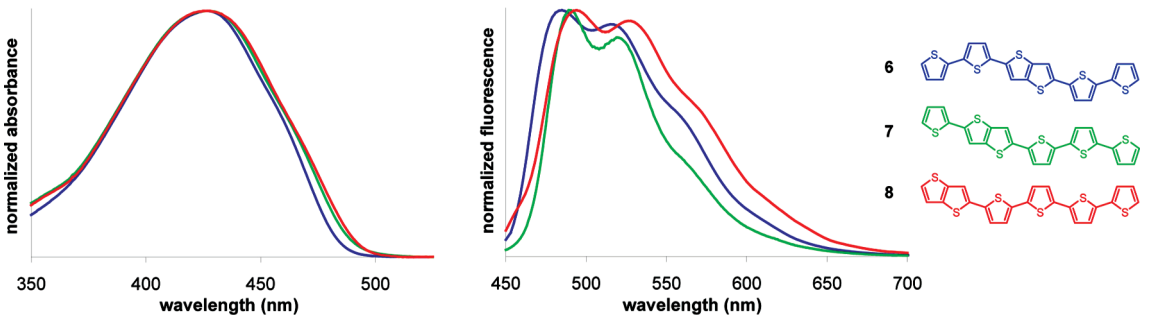


FIGURE 1. Absorption and emission spectra for oligomers **6**−**8** in CH_2Cl_2.

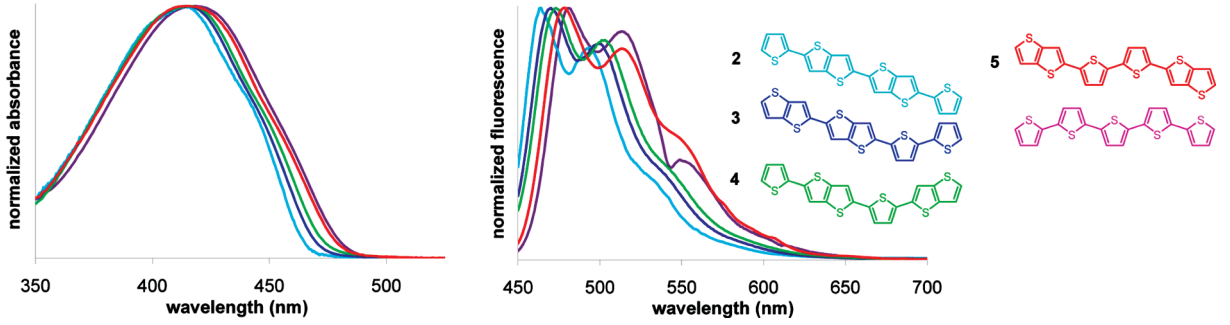


FIGURE 2. Absorption and emission spectra for oligomers **2**−**5** in CH_2Cl_2.

is nearly identical (Table 1). However, the computed electronic transition of the planar structures with time-dependent density functional theory (TD-DFT) at the B3LYP/6-31G* level reveals that migrating the fused-ring unit from the periphery toward the center of the oligomers leads to a small, but discernible, blue shift (Table 1). This apparent discrepancy between experiment and theory arises because the experimental absorption λ_{max} reflects conjugation across the more populated nonplanar conformations in solution,[13] whereas the calculated transition corresponds to the planar conformation. It is the onset region of the absorption spectrum that is indicative of absorption from the oligomers in their planar conformation. Upon close inspection of the low-energy portion of the absorbance spectrum, the onset values are in agreement with the theoretically predicted tends (Figure 1). The longer tails into the red of the absorption spectra observed for **7** and **8** therefore reflect a slightly more conjugated planar conformation relative to **6**. This suggests that the introduction of ring fusion in the center of the molecule is slightly more disruptive to electron delocalization across the planar molecule than positioning thieno[3,2-*b*]thiophene toward the periphery. Although the differences are subtle, the trend is consistent with computational and experimental data across this whole series of oligomers. In fact, the trend is more pronounced in isomers **2**−**5** which have two degrees of ring fusion (Figure 2). The calculated transitions of the planar conformation for **2**−**5** span almost 10 nm across these regioisomers, which is in excellent agreement with the experimental absorption onset region. Oligomer **2**, which has both thieno[3,2-*b*]thiophene units at the innermost positions, displays the shortest wavelength onset and calculated transition in the absorption spectrum. As the thieno[3,2-*b*]thiophene units are moved toward the exterior of the oligomer the absorption onset shifts to longer wavelengths indicating a more conjugated planar conformation. Extending this investigation to include the comparison of **2**−**5** to quinquethiophene, which has the same number of double bonds but one fewer thienyl sulfur linkage, reveals a similar absorption λ_{max} but the absorption onset and computed electronic transition of quinquethiophene indicate it has the most conjugated planar conformation.

Data which further support the notion that introduction of ring fusion at the center of the oligomer, as opposed to the periphery, is more disruptive to the electronic communication across the oligomers in the planar conformation are found in the emission spectra. Oligothiophenes adopt a quinoidal structure in the excited state and consequently emission maxima correspond to relaxation from the planar excited state conformation.[14] Isomers **6**−**8** differ only in the position of ring fusion but have emission λ_{max} spanning 10 nm. Oligomer **8**, which has the longest wavelength absorption onset, also displays the longest emission λ_{max}, corresponding to the most conjugated planar structure, followed by **7** and then **6**. Isomers **2**−**5** display a 15 nm span in the emission λ_{max} and follow an identical trend to **6**−**8** indicating that introduction of ring fusion at the center of the oligomer yields an increase in the HOMO−LUMO gap in the planar conformation. Quinquethiophene, which has the same number of double bonds as isomers **2**−**5**, exhibits the longest emission λ_{max}. These emission data are in agreement with the onset absorption

(13) Zade, S. S.; Bendikov, M. *Chem. Eur.* **2007**, *13*, 3688–3700.

(14) Becker, R. S.; deMelo, J. S.; Macanita, A. L.; Elisei, F. *J. Phys. Chem.* **1996**, *100*, 18683–18695.

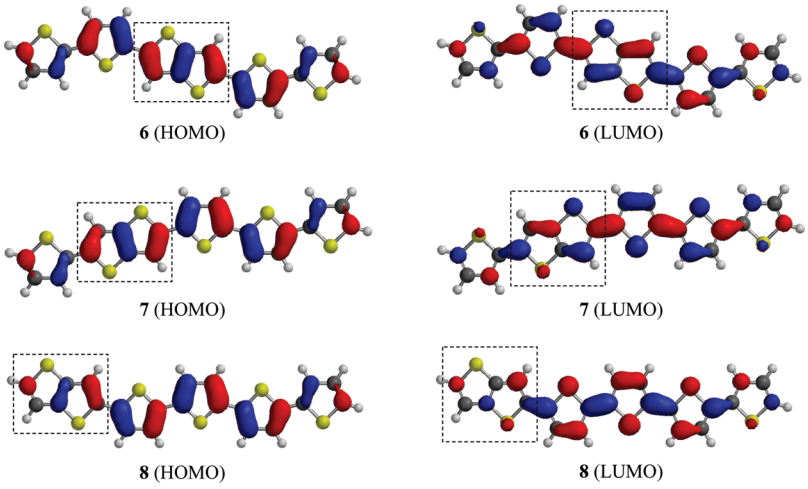


FIGURE 3. Frontier molecular orbitals in **6**−**8** (DFT/B3LYP//6-31G* level).

wavelengths and the computed electronic transitions of the planar oligomers.[15]

Experimental and computational data indicate that introduction of sulfur linkages in oligothiophenes results in a modest widening of the band gap,[4,16] but the effect of regiochemistry of ring fusion on conjugation efficiency has not been previously evaluated. The topologies of the frontier molecular orbitals of regioisomers **6**−**8** are virtually identical and it is notable that the p_z orbitals with the largest orbital coefficients are clustered at the interior of the structure (Figure 3). Apparently when ring fusion is introduced toward the center of the molecule where the p_z orbitals are most prominent, and thus contribute more significantly to electron delocalization across the π-conjugated frame, the result is a greater disruption to conjugation relative to incorporation of ring fusion at the periphery where the orbital coefficients are smaller. As evidenced by experimental studies and predicted by TD/DFT//6-31G* computational analysis of the $\pi-\pi^*$ electronic transitions, conjugation is most efficient in oligomers with nonfused thiophene rings at the center of the structure. The same correlations among frontier molecular orbital coefficients, position of ring fusion, and conjugation are observed for regioisomers **2**−**5** (Supporting Information). These results serve as the basis for a predictive method of tuning the electronic properties of oligothiophenes by strategic positioning of ring fusion.

Insight into the ground state oligomer conformations in solution can be obtained by inspection of the optical data. One approach is quantifying the difference between the absorption and emission λ_{max}, the Stokes shift. A smaller Stokes shift tends to arise when there is less conformational reorganization between the nonplanar ground state and the planar quinoidal excited state, thus corresponding to a more planar molecule in solution. For example, **6**, with ring fusion in the center of the oligomer, has a smaller Stokes shift than **7** or **8** (Table 1), indicating that it undergoes a smaller degree of conformational reorganization when transitioning from the ground to excited state and suggests that this molecule is more planar in its most populated ground state conformation in solution. In the context of molecular conformation in solution it is worth restating that despite the differences in conjugation among the planar structures of **6**−**8**, these oligomers have a similar absorption λ_{max}. This similarity, in accord with the Stokes shift analysis, is attributed to a cancelation of the electronic effects by the ground state conformational variations. That is, **6**, with ring fusion in the center of the molecule, is less conjugated in its planar conformation as compared to **8**, but is more planar in its most populated ground state geometry in solution. Conversely, **8** has a more conjugated planar structure than **6** but is on average less planar in solution and consequently they display similar absorption λ_{max}. For each set of isomers, introduction of ring fusion toward the center of the structure results in increased planarity in solution and this trend is accompanied by an increase in the fluorescence quantum yield (Table 1). In this context it is not surprising that quinquethiophene, with ten double bonds but no ring fusion, presents the largest Stokes shift and the lowest quantum yield when compared with the isomers **2**−**5**.

Conclusion

In summary, a series of sexithiophene analogues was synthesized in order to systematically probe the effects of both regiochemistry and extent of ring fusion on the properties of α-linked oligothiophenes. The synthetic strategies demonstrated allow for efficient production of eight new six-ring oligothiophenes with ring fusion. Relative to nonfused sexithiophene, introduction of up to three degrees of ring fusion results in a range of absorption λ_{max} values that spans 31 nm and emission λ_{max} values that spans 64 nm. Further, regiochemical control of ring fusion allows for fine-tuning of the conjugation and molecular conformation of these sexithiophene analogues in solution.

Experimental Section

General Procedure One (GP1): Preparation of Stannyl Oligomers. In a dry flask, 1.6 M butyllithium in hexanes (1.0 equiv)

(15) Additional studies were conducted in order to ensure that the trends in the optical properties are an accurate representation of the inherent properties of the molecular structure and not influenced by intermolecular interaction in solution. Absorption and emission spectra were recorded for **12**, **14**, **17**, **19**, **21**, **24**, **27**, and **28**, which are the precursors, and bis-TIPS substituted analogues, of **1**−**8**. These oligomers with bulky solubilizing groups exhibit the same trends in absorption and emission properties as the unsubstituted oligomers (Supporting Information).

(16) Osuna, R. M.; Zhang, X. N.; Matzger, A. J.; Hernandez, V.; Navarrete, J. T. L. *J. Phys. Chem. A* **2006**, *110*, 5058–5065.

was added dropwise to a solution of the thiophene oligomer in THF (0.1 M) at 0 °C under a N_2 atmosphere. After 1 h of stirring at this temperature, neat tributylstannyl chloride (1.0 equiv) was added dropwise. The solution was stirred for another 12 h and allowed to warm to room temperature, followed by dilution with hexanes and washing with brine. The organic layer was collected and dried over anhydrous Na_2SO_4. The crude stannyl product (**10**, **16**, and **25**) was obtained after removing the solvent in vacuo and used directly in the next step without further purification.

General Procedure Two (GP2): Preparation of Bromide-Terminated Oligomers via Stille Coupling. The stannyl compound and an excess of the bromide (4.0 equiv) were combined in toluene (0.1 M) and the solution was sparged with N_2 gas. $Pd(PPh_3)_4$ (0.02 equiv) was added to the mixture and the solution was stirred under N_2 for 14 h at 130 °C in a pressure vessel. The reaction mixture was added dropwise to stirring EtOH at rt. The resulting precipitate was collected on a fritted funnel and rinsed with EtOH. The solid was purified by column chromatography on silica gel (5−10% CH_2Cl_2 in hexanes) to give the coupled product (**18**, **20**, and **26**).

General Procedure Three (GP3): Preparation of Oligomers via Stille Coupling. The bromide (1.0 equiv) and the stannyl compound (1.0 equiv per bromine) were combined in toluene (0.1 M) and the solution sparged with N_2 gas. $Pd(PPh_3)_4$ (0.02 equiv per bromine) was added to the mixture and the solution was stirred under N_2 for 14 h at 130 °C in a pressure vessel. The workup conditions (A or B) dictated the solubility of the product in EtOH.

Workup A (GP3-A): The reaction mixture was added dropwise to stirring EtOH at rt. The resulting precipitate was collected on a fritted funnel and rinsed with EtOH. The solid was then purified by column chromatography on silica gel (5−10% CH_2Cl_2 in hexanes) to give the coupled product (**12**, **14**, **17**, **19**, **21**, **24**, **27**, **28**).

Workup B (GP3-B): After solvent was removed in vacuo, the resulting oil was added dropwise to stirring EtOH, then placed in the freezer (−80 °C) for 10 h. The precipitate was collected by cold filtration on a fritted funnel and washed with cold EtOH. The solid was purified by column chromatography on silica gel (hexanes) to yield the coupled product.

General Procedure Four (GP4): Desilylation of Oligomers. Tetrabutylammonium fluoride trihydrate (8 equiv) was added to a solution of the TIPS-substituted oligomer (1 equiv) in THF (0.01 M). The reaction mixture was stirred for 14 h in the absence of light. The precipitate was collected on a fritted funnel and rinsed with THF and CH_2Cl_2 to give the unsubstituted oligomer (**1**−**8**). These oligomers can be further purified by sublimation (200−250 °C, 10^{-6} Torr).

Triisopropyl[5-(tributylstannyl)thieno[3,2-*b*]thien-2-yl]silane (10): The title compound was prepared according to **GP1**, using **9** (1.88 g, 6.40 mmol), 1.6 M butyllithium in hexanes (4.00 mL, 6.40 mmol), and tributylstannyl chloride (1.73 mL, 6.40 mmol), to yield stannyl compound **10** (3.59 g, 97%), which was carried on to the next step without further purification. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 0.5 Hz, 1H), 7.24 (d, J = 0.5 Hz, 1H), 1.58 (m, 6H), 1.85 (m, 6H), 1.36 (sep, J = 7.3 Hz, 3H), 1.09−1.15 (m, 6H), 1.12 (d, J = 7.3 Hz, 18H), 0.91 (t, J = 7.3 Hz, 9H).

[5′-(5-Bromothieno[3,2-*b*]thien-2-yl)-2,2′-bithien-5-yl](triisopropyl)-silane (18): The title compound was prepared according to **GP2**, using 2,5-dibromothieno[3,2-*b*]thiophene (1.40 g, 4.70 mmol), stannyl compound **16** (719 mg, 1.17 mmol), and $Pd(PPh_3)_4$ (27.0 mg, 0.024 mmol), to yield the coupled product **18** (344 mg, 54%) as a yellow solid; mp 123−124 °C. UV−vis (CH_2Cl_2) λ_{max} 387 nm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.27 (d, J = 3.5 Hz, 1H), 7.23 (d, J = 0.5 Hz, 1H), 7.21 (d, J = 0.5 Hz, 1H), 7.17 (d, J = 3.5 Hz, 1H), 7.11 (d, J = 3.8 Hz, 1H), 7.10 (d, J = 3.8 Hz, 1H), 1.35 (sep, J = 7.4 Hz, 3H), 1.13 (d, J = 7.3 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.7, 139.9, 138.4, 137.0, 136.6, 136.4, 135.6, 134.4, 124.9, 124.7, 124.3, 122.1, 115.1, 113.2, 18.6, 11.7. IR (KBr) 3080 (w), 3055 (w), 2941 (vs), 2887 (s), 2864 (vs), 2756 (w), 2723 (w), 2713 (w), 1759 (w), 1601 (w), 1464 (s), 1443 (m), 1411 (m), 1383 (m), 1340 (m), 1319 (m), 1307 (w), 1211 (s), 800 (vs), 743 (m), 683 (s), 654 (s), 515 (s), 492 (s) cm^{-1}. MS (EI, 70 eV) m/z (rel intensity) 542.2 (25.3), 541.2 (34.9), 540.2 (100), 539.2 (29.7), 538.1 (81.3, M^+), 497.1 (54.5), 495.1 (44.9), 455.0 (46.5), 453.0 (39.6), 441.0 (30.0), 439.0 (26.0). Anal. Calcd for $C_{23}H_{27}BrS_4Si$: C, 51.18; H, 5.04. Found: C, 51.33; H, 5.01.

2,2′:5′,2″-Terthieno[3,2-*b*]thiene-5,5″-diylbis(triisopropylsilane) (12): The title compound was prepared according to **GP3-A**, using 2,5-dibromothieno[3,2-*b*]thiophene (147 mg, 0.493 mmol), stannyl compound **10** (647 mg, 1.10 mmol), and $Pd(PPh_3)_4$ (50.9 mg, 0.044 mmol), to yield the coupled product **12** (199 mg, 55%) as a yellow solid; mp 214−215 °C. UV−vis (CH_2Cl_2) λ_{max} 412 nm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (s, 2H), 7.34 (s, 2H), 7.33 (s, 2H), 1.38 (sep, J = 7.5 Hz, 6H), 1.14 (d, J = 7.3 Hz, 36H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 139.9, 139.7, 139.5, 138.7, 138.6, 126.9, 115.8, 115.7, 18.6, 11.8. IR (KBr) 3077 (w), 2942 (s), 2846 (s), 1463 (s), 1435 (m), 1384 (w), 1296 (w), 1172 (m), 1071 (m), 1015 (m), 999 (s), 982 (m), 939 (w), 919 (w), 882 (s), 790 (s), 683 (s), 653 (s), 562 (m), 530 (s), 507 cm^{-1} (s). MS (EI, 70 eV) m/z (rel intensity): 732.3 (13.0), 731.3 (24.8), 730.3 (52.3), 729.3 (59.3), 728.3 (100, M^+), 687.2 (15.2), 686.2 (17.0), 685.3 (30.2), 645.2 (12.6), 644.2 (13.1), 643.2 (24.5), 83.9 (11.2), 59.1 (21.8). Anal. Calcd for $C_{36}H_{48}S_6Si_2$: C, 59.29; H, 6.63. Found: C, 59.46; H, 6.61.

Triisopropyl(5-thieno[3,2-*b*]thien-2-yl-2-thienyl)silane (23): The title compound was prepared according to **GP3-B**, using bromide **22** (6.38 g, 20.0 mmol), 2-(tributylstannyl)thieno[3,2-*b*]thiophene (8.58 g, 20.0 mmol), and $Pd(PPh_3)_4$ (0.462 g, 0.400 mmol), to yield the coupled product **23** (6.38 g, 84%) as a light yellow solid; mp 77−78 °C. UV−vis (CH_2Cl_2) λ_{max} 341 nm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.38 (d, J = 0.5 Hz, 1H), 7.34 (d, J = 5.2 Hz, 1H), 7.29 (d, J = 3.4 Hz, 1H), 7.22 (dd, J = 5.2, 0.5 Hz, 1H), 7.17 (d, J = 3.4 Hz, 1H), 1.35 (sep, J = 7.5 Hz, 3H), 1.13 (d, J = 7.4 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.6, 139.7, 139.2, 138.0, 136.4, 134.3, 126.8, 124.8, 119.4, 115.7, 18.6, 11.8. IR (KBr) 3111 (vw), 3084 (w), 3051 (w), 2939 (vs), 2922 (s), 2887 (s), 2862 (s), 2721 (w), 1458 (s), 1416 (m), 1306 (w), 1217 (m), 1066 (m), 1018 (m), 993 (s), 974 (s), 883 (s), 876 (s), 800 (s), 694 (vs), 681 (s), 654 (s), 627 (s), 565 (m), 517 (s), 501 (s) cm^{-1}. MS (EI, 70 eV) m/z (rel intensity) 380.0 (22.92), 378.9 (38.92), 377.9 (100, M^+), 335.9 (31.96), 334.9 (95.62). Anal. Calcd for $C_{19}H_{26}S_3Si$: C, 60.26; H, 6.92. Found: C, 60.37; H, 6.95.

2,2′:5′,2″-Terthieno[3,2-*b*]thiophene (1): The title compound was prepared according to **GP4**, using tetrabutylammonium fluoride trihydrate (450 mg, 1.43 mmol) and oligomer **12** (141 mg, 0.194 mmol), to yield oligomer **1** (57.1 mg, 72%) as a yellow solid; mp >360 °C. UV−vis (CH_2Cl_2) λ_{max} (log ε) 423 (1.71, sh), 401 (1.88), 294 (1.34), 261 (1.21) nm. IR (KBr) 3059 (w), 1613 (w), 1470 (w), 1451 (w), 1434 (m), 1414 (w), 1346 (m), 1191 (w), 1172 (m), 1153 (w), 1078 (w), 948 (m), 864 (w), 800 (s), 791 (m), 707 (m), 695 (s), 629 (m), 509 cm^{-1} (s). MS (EI, 70 eV) m/z (rel intensity) 418.0 (30.6), 417.0 (26.4), 416.0 (100, M^+), 208.0 (10.9). Anal. Calcd for $C_{18}H_8S_6$: C, 51.89; H, 1.94. Found: C, 51.82; H, 1.61.

Triisopropyl(thieno[3,2-*b*]thien-2-yl)silane (9): In a dry flask 1.6 M butyllithium in hexanes (6.25 mL, 10.0 mmol) was added dropwise to a solution of the thieno[3,2-*b*]thiophene (1.24 g, 10.0 mmol) in THF (100 mL) at 0 °C under a N_2 atmosphere. After 1 h of stirring at this temperature, neat triisopropylchlorosilane (2.46 mL, 11.5 mmol) was added dropwise. The solution was stirred for another 3 h and allowed to warm to rt, followed by dilution with hexanes and washing with water and brine. The organic layer was collected and dried over anhydrous Na_2SO_4. After the solvent was removed in vacuo, the residue was purified by column chromatography on silica gel, eluting with hexanes to yield silyl compound **9** (2.58 g, 87%) as a white solid; mp

33.5−34.0 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.40 (d, J = 5.3 H, 1H), 7.38 (d, J = 0.5 Hz, 1H), 7.25 (dd, J = 5.3, 0.5 Hz, 1H), 1.38 (sep, J = 7.5 Hz, 3H), 1.14 (d, J = 7.5 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 11.8, 18.6, 119.1, 126.9, 127.9, 138.0, 141.2, 144.6. IR (KBr) 3083 (w), 2942 (s), 2864 (s), 1652 (w), 1484 (m), 1463 (s), 1438 (s), 1384 (m), 1366 (m), 1343 (m), 1299 (s), 1253 (w), 1192 (m), 1087 (m), 1072 (m), 1061 (s), 999 (s), 978 (s), 919 (m), 882 (s), 814 (m), 763 (m), 705 (m), 638 (m), 637 (m), 597 cm^{-1} (m). MS (EI, 70 eV) m/z (rel intensity) 297.1 (11.51), 296.0 (51.5, M^+), 253.1 (49.0), 230.1 (16.6), 229.0 (50.9), 225.0 (14.5), 213.1 (14.5), 212.1 (17.4), 211.1 (100), 201.1 (18.6), 197.1 (15.6), 195.0 (19.5), 187.1 (11.4), 183.1 (22.7), 177.1 (17.6), 175.1 (13.6), 171.1 (10.3), 169.1 (23.1), 149.0 (12.7), 135.2 (11.1), 132.0 (12.6), 131.0 (75.3). Anal. Calcd for $C_{15}H_{24}SiS_2$: C, 60.75; H, 8.16. Found: C, 60.72; H, 8.33.

(5-Bromo-2-thienyl)(triisopropyl)silane (22): In a dry flask under a N_2 atmosphere at −78 °C, 1.6 M butyllithium in hexanes (62.5 mL, 100 mmol) was added dropwise to a solution of 2,5-dibromothiophene (24.2 g, 100 mmol) in THF (700 mL). After 20 min of stirring at this temperature, triisopropylchlorosilane (21.4 mL, 100 mmol) was added dropwise. The reaction mixture was allowed to warm to room temperature and then stirred for 2 h, followed by dilution with hexanes and washing with water and brine. The organic layer was dried over Na_2SO_4 and the solvent was removed in vacuo to yield **22** (27.8 g, 87%); bp 307 °C. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.12 (d, J = 3.5 Hz, 1H), 7.01 (d, J = 3.5 Hz, 1H), 1.30 (sep, J = 7.5 Hz, 3H), 1.09 (d, J = 7.4 Hz, 18H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 137.3, 136.0, 130.9, 116.5, 18.5, 11.7. IR (KBr) 3060 (w), 2943 (vs), 2889 (s), 2866 (vs), 2725 (w), 1502 (w), 1462 (s), 1404 (s), 1385 (m), 1367 (w), 1203 (s), 1068 (m), 1016 (m), 999 (m), 947 (s), 883 (s), 795 (s), 654 (s), 683 (s), 517 (vs), 573 (s) cm^{-1}. MS (EI, 70 eV) m/z (rel intensity) 319.7 (10.56), 317.8 (20.53, M^+), 276.8 (91.52), 274.8 (100). Anal. Calcd for $C_{13}H_{23}BrSSi$: C, 48.89; H, 7.26; Found: C, 49.17; H, 7.50.

(2,2′-Bithieno[3,2-*b*]thiene-5,5′-diyldithiene-5,2-diyl)bis(triisopropylsilane) (24): In a dry two-necked flask fitted with a reflux condenser, **23** (300 mg, 0.792 mmol) was dissolved in THF (20 mL) and the solution was sparged with N_2 gas. Butyllithium (1.6 M) in hexanes (0.500 mL, 0.792 mmol) was added to the solution at 0 °C under a N_2 atmosphere. After 30 min at this temperature the reaction mixture was allowed to warm to rt over 15 min. $Fe(acac)_3$ (615 mg, 1.74 mmol) was added to the flask in one portion and the solution was heated to reflux for 12 h. The reaction mixture was poured into stirring EtOH and the resulting precipitate was collected by centrifugation. The solid was purified by column chromatography on silica gel (10% CH_2Cl_2 in hexanes) to yield **24** (126 mg, 42%); mp 248−249 °C. UV−vis (CH_2Cl_2) λ_{max} 424 nm. ^{1}H NMR (400 MHz, $CDCl_3$) δ 7.33 (d, J = 0.5 Hz, 2H), 7.32 (d, J = 0.5 Hz, 2H), 7.30 (d, J = 3.5 Hz, 2H), 7.18 (d, J = 3.5 Hz, 2H), 1.36 (sep, J = 7.5 Hz, 6H), 1.13 (d, J = 7.3 Hz, 32 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 142.4, 139.3, 138.8, 138.7, 138.5, 136.4, 134.6, 124.9, 115.8, 115.7, 18.6, 11.8. IR (KBr) 3064 (w), 2958 (s), 2943 (s), 2924 (s), 2887 (m), 2864 (vs), 2758 (w), 2723 (w), 2713 (w), 1456 (m), 1423 (m), 1207 (w), 1173 (w), 1070 (m), 997 (m), 974 (m), 881 (m), 795 (vs), 673 (s), 654 (m), 592 (m), 515 (m), 505 (m) cm^{-1}. MS (EI, 70 eV) m/z (rel intensity) 757.3 (25.67), 756.3 (53.07), 755.2 (59.96), 754.2 (100, M^+), 669.1 (21.38). Anal. Calcd for $C_{38}H_{50}S_6Si_2$: C, 60.42; H, 6.67; Found: C, 60.14; H, 6.80.

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Supporting Information Available: Experimental procedures, NMR spectra, normalized UV−vis absorption and emission spectra of **1**, **12**, **14**, **17**, **19**, **21**, **24**, **27**, and **28**, and FMOs for **1**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.