Rapid Syntheses of Oligo(2,5-thiophene ethynylene)s with Thioester Termini: Potential Molecular Scale Wires with Alligator Clips

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The syntheses of soluble oligo(3-ethyl-2,5-thiophene ethynylene)s via an iterative divergent/convergent approach starting from 3-ethyl-2-(trimethylsilylethynyl)thiophene are described. The monomer, dimer, tetramer, octamer, and 16-mer were synthesized. The 16-mer is 100 Å long in its minimized extended zigzag conformation. At each stage in the iteration, the length of the framework doubles. Only three sets of reaction conditions are needed for the entire iterative synthetic sequence: an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. The oligomers were characterized spectroscopically and by mass spectrometry. The optical properties are presented which show that at the octamer stage, the optical absorbance maximum is nearly saturated. The size exclusion chromatography values for the number average weights, relative to polystyrene, illustrate the tremendous differences in the hydrodynamic volume of these rigid rod oligomers verses the random coils of polystyrene. These differences become quite apparent at the octamer stage. Attachment of thiol end groups, protected as the thioacetyl moieties, was achieved. These serve as binding sites for adhesion to gold surfaces. In some cases, one end of the oligomeric chains were capped with a thiol group so that the surface attachments to gold could be studied. In other cases, thiol groups were affixed to both ends of the molecular chains so that future conduction studies could be done between proximal metallic probes. The rigid rod conjugated oligomers may act as molecular wires in molecular scale electronic devices, and they also serve as useful models for understanding analogous bulk polymers.

Introduction

Future computational systems will likely consist of logic devices that are ultradense, ultrafast, and molecular-sized.[1−3] The slow step in existing computational architectures is not usually the switching time, but the time it takes for an electron to travel between devices. By using molecular scale electronic interconnects,[4] the transmit times could be minimized, resulting in computational systems that operate at far greater speeds than is presently attainable from conventional patterned architectural arrays.[1] There is another technical advantage that might also be gained from molecular scale devices. A powerful computational system presently utilizes ca. 10^{10} silicon-based devices. If devices were to be based upon single molecules,[3r] using routine chemical syntheses, one could prepare ca. 10^{23} devices in a single reaction flask. Of course, the task of addressing large arrays of ordered molecular scale devices is presently unattainable; however, the potential is certainly enough to maintain current and future interests.

Though it is well-documented that bulk conjugated organic materials can be semiconducting or even conducting when doped,[5] we only recently determined how thiol-ended rigid rod conjugated molecules orient themselves on gold surfaces,[6] and how we could record electronic conduction through single undoped conjugated molecules that are end-bound onto a metal probe surface.[7] Here we describe the synthetic details for the formation

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(1) For some recent background work on molecular scale electronics, see: (a) *Molecular Electronics: Science and Technology;* Aviram, A., Ed.; Confer. Proc. No. 262, American Institute of Physics: New York, 1992. (b) Miller, J. S. *Adv. Mater.* **1990**, *2*, 378, 495, 601. (c) *Molecular and Biomolecular Electronics*; Birge, R. R., Ed.; Advances in Chemistry Series 240, American Chemical Society: Washington, DC, 1991. (d) *Nanostructures and Mesoscopic Systems*; Kirk, W. P., Reed, M. A., Eds.; Academic: New York, 1992.

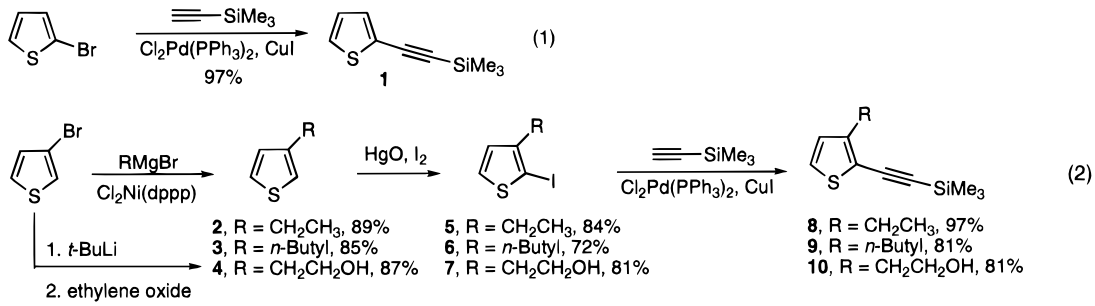
(2) For some theoretical considerations on molecular scale wires, see: (a) Samanta, M. P.; Tian, W.; Datta, S.; Henderson, J. I.; Kubiak, C. P. *Phys. Rev. B* **1996**, *53*, R7626. (b) Mujica, V.; Kemp, M.; Roitberg, A.; Ratner. M. *J. Phys. Chem.* **1996**, *104*, 7296. (c) Joachim, C.; Vinuesa, J. F. *Europhys. Lett.* **1996**, *33*, 635.

(3) For some recent background work on the formation of molecular-based transporters and devices, see: (a) Grosshenny, V.; Harriman, A.; Ziessel R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1100. (b) Langler, L.; Stockman, L.; Heremans, J. P.; Bayor, V.; Olk, C. H.; Van Haesendonck, C.; Bruynseraede, Y.; Issi, J.-P. *Synth. Met.* **1995**, *70*, 1393. (c) Pascual, J. I.; Méndez, J.; Gómez-Herrero, J.; Baró, A. M.; Garcia, N.; Landman, U.; Luedtker, W. D.; Bogachek, E. N.; Cheng, H.-P. *Science* **1995**, *267*, 1793. (d) Purcell, S. T.; Garcia, N.; Binh, V. T.; Jones, L., II; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11985. (e) Martin, C. R. *Science* **1994**, *266*, 1961. (f) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578. (g) Gust, D. *Nature* **1994**, *372*, 133. (h) Wu, C.; Bein, T. *Science* **1994**, *266*, 1013. (i) Wagner, R. W.; Lindsey, J. S.; Seth, J.; Palaniappan, V.; Bocain, D. F. *J. Am. Chem. Soc.* **1996**, *118*, 3996. (j) Sailor, M. J.; Curtis, C. L. *Adv. Mater.* **1994**, *6*, 688. (k) Brigelletti, F.; Flamigni, L.; Balzani, V.; Collin, J.; Sauvage, J.; Sour, A.; Constable, E. C.; Thompson, A. M. W. C. *J. Am. Chem. Soc.* **1994**, *116*, 7692. (l) Wu, C.; Bein, T. *Science* **1994**, *264*, 1757. (m) Moerner, W. E. *Science* **1994**, *265*, 46. (n) Sessler J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618. (o) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram. A. *J. Am. Chem. Soc.* **1990**, *112*, 4206. (p) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7064. (q) Dai, H.; Wong, E. W.; Lieber, C. M. *Science* **1996**, *272*, 523. (r) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906. (s) Ward, M. D. *Chem. Ind.* **1996**, 569.

(4) "Molecular electronics" is a poorly defined term since some authors refer to it as any molecular-based system such as a film or a liquid crystalline array. Other authors, including us, have preferred to reserve the term "molecular electronics" for single molecule tasks, such as single molecule-based devices or single molecular wires. Due to this confusion, we have chosen here to follow the Petty *et al.* (*Introduction to Molecular Electronics*, Petty, M. C., Bryce, M. R., Bloor, D., Eds.; Oxford Univ. Press: New York, 1995) terminology by using two subcategories, namely "molecular materials for electronics" for bulk applications and "molecular scale electronics" for single molecule applications.

(5) *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986.

S0022-3263(96)02335-3 CCC: $14.00



of soluble oligo(3-ethyl-2,5-thiophene ethynylene)s, potential molecular scale wires, by a rapid iterative divergent/convergent doubling approach.[8,9] Additionally, the syntheses and attachments of protected thiol moieties to one or both ends of the oligomers are presented. These thiols serve as molecular scale alligator clips for adhesion of the molecular scale wires to the gold probes.[6,7]

There has been considerable recent effort to prepare large conjugated molecules of precise length and constitution.[10] Our approach to these compounds maintains several key features that make it well-suited for the requisite large molecular architectures for molecular scale electronics studies. Specifically, the route involves (1) a rapid construction method that permits doubling molecular length at each coupling stage to afford an unbranched 100 Å oligomer, the approximate size of present nanopatterned probe gaps,[1] (2) an iterative approach so that the same high yielding reactions can be used throughout the sequence, (3) the syntheses of conjugated compounds that are semiconducting in the bulk, (4) products that are stable to light and air so that subsequent engineering manipulations will not be impeded, (5) products that could easily permit independent functionalization of the ends to serve as molecular alligator clips that are required for surface contacts to metal probes, (6) products that are rigid in their frameworks so as to minimize conformational flexibility yet containing substituents for maintaining solubility and processability, (7) alkynyl units (cylindrically symmetric) separating the aryl units so that ground state contiguous π-overlap will be minimally affected by rotational variations, (8) molecular systems that do not have degenerate ground state resonance forms and are thus not subject to Peierls distortions,[5] and finally, (9) products that serve as useful models for the understanding of bulk polymeric materials.[5]

The iterative divergent/convergent approach is outlined in Figure 1.[10,11] A batch of monomer material M, with inactive end groups X and Y, is divided into two portions. In one portion, the end group X is activated by conversion to X′. In the second portion, Y is activated by conversion

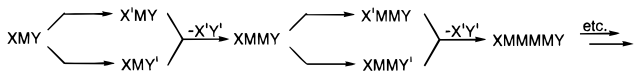


Figure 1. Schematic presentation of the iterative divergent/convergent approach to molecular length doubling.

to Y′. The two portions are then brought back together to form the dimer XMMY with loss of X′Y′. Since the same end groups that were present in the monomer are now present in the dimer, the procedure can be repeated with a doubling of molecular length at each iteration. The advantages of this approach are that the molecular length grows rapidly, at a rate of 2^n were n = the number of iterations, and incomplete reactions yield unreacted material that is half the size of the desired compound. Thus, purification at each step is far simpler since separation involves, for example, an octamer from a 16-mer. This iterative divergent/convergent approach is therefore particularly attractive.[10,11]

Results and Discussion

Monomer Syntheses. The syntheses of several monomers were conducted as shown in eqs 1 and 2. Oligomers derived solely from **1** had minimal solubility. Oligomers derived from **9** were too difficult to purify since the butyl groups promoted excessively rapid migration on silica gel chromatography even with hexane as an eluent. Oligomers that were prepared from **10** or mixtures of **1** and **10** required protection of the hydroxyl moieties as *tert*-butyldimethylsilyl ethers, and they suffered from silyl migration reactions. The use of monomer **8**, however, proved to be optimal; there were no protection/deprotection steps necessary and acceptable R_f values on silica gel could be maintained.

Controlled Oligomer Syntheses. The iterative divergent/convergent synthetic approach is outlined in Scheme 1. The sequence involves partitioning **8** into two portions, iodinating the 5-position in one of the portions to form **11**, and protodesilylating the alkynyl end of the second portion to form **12**. Bringing the two portions back together in the presence of a soluble Pd/Cu catalyst mixture[12] couples the aryl iodide to the terminal alkyne, thus generating the dimer **13**. Iteration of this reaction sequence doubles the length of the dimer **13** to afford the tetramer **16**, and so on to the octamer **19**, and finally the 16-mer **22**. The silylated alkynes showed good oxidative stability; however, upon protodesilylation, the tetramer **18** and octamer **21** were air sensitive and immediate workup and further coupling was necessary to minimize oxidative decomposition of these terminal alkyne intermediates. Similarly, the Pd/Cu coupling reactions to form **19** and **22** required the strict exclusion of oxygen;

(6) (a) Tour, J. M.; Jones, L., II; Pearson, D. L.; Lamba, J. S.; Burgin, T.; Whitesides, G. W.; Allara, D. L.; Parikh, A. N.; Atre, S. *J. Am. Chem. Soc.* **1995**, *117*, 9529. (b) Dhirani, A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P., Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319.

(7) Bumm, L. A.; Arnold, J. J.; Cygan, M. T.; Dunbar, T. D.; Burgin, T. P.; Jones, L., II, Allara, D. L.; Tour, J. M.; Weiss, P. S. *Science* **1996**, *271*, 1705.

(8) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360.

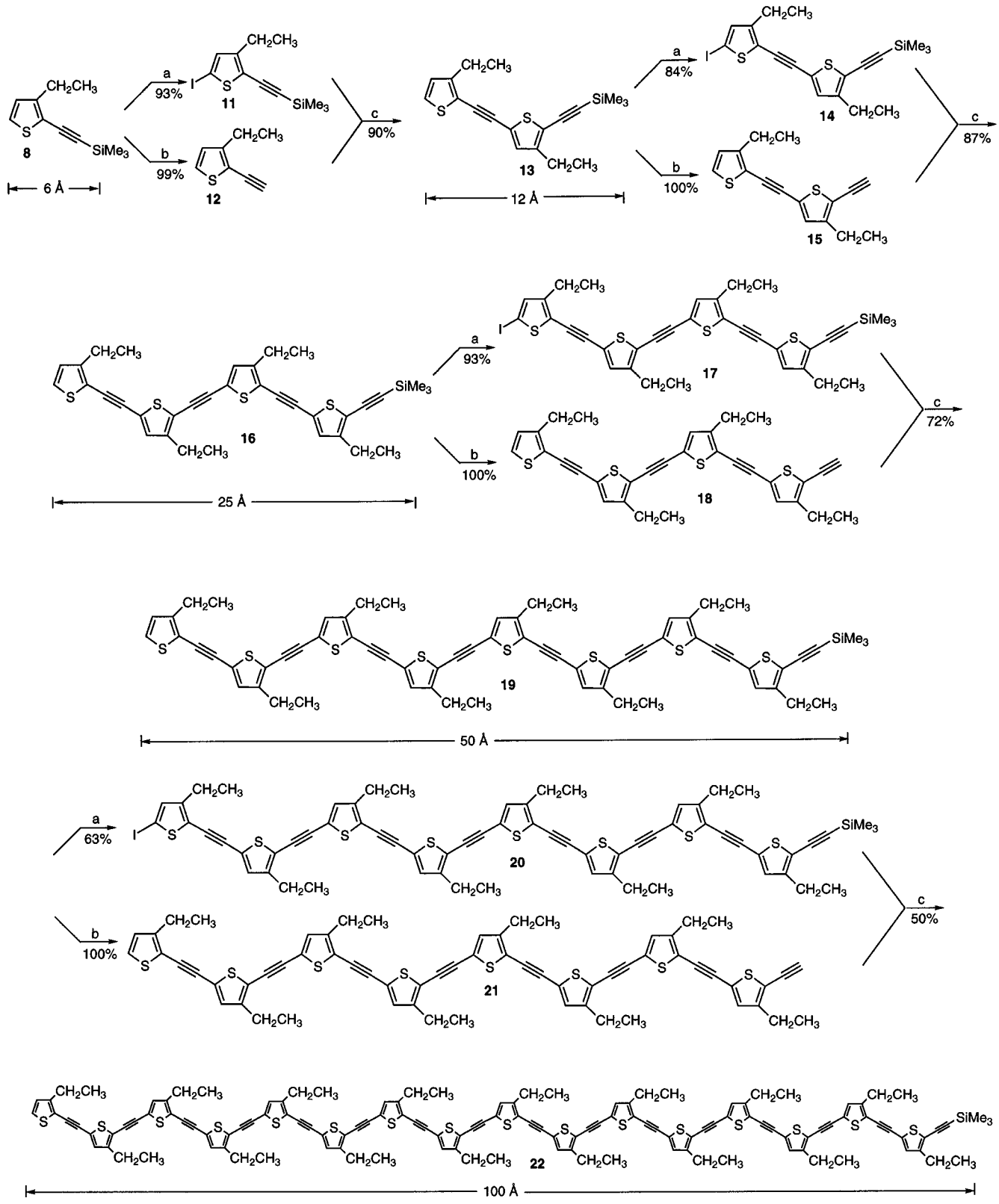
(9) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348.

(10) Tour, J. M. *Chem. Rev.* **1996**, *96*, 537.

(11) (a) Wegner, G. In *Thermoplastic Elastomers, A Comprehensive Review*; Legge, N. R., Holden, G., Schroeder, H. E., Eds.; Hanser: New York, 1987; p 405. (b) Young, J. K.; Nelson, J. C.; Moore, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 10841. (c) Nelson, J. C.; Young, J. K.; Moore, J. S. *J. Org. Chem.* **1996**, *61*, 8160.

(12) Suffert, J.; Ziessel, R. *Tetrahedron Lett.* **1991**, *32*, 757.

Scheme 1



Reagents: (a) LDA, Et_2O, -78° to 0°C then I_2, -78°. (b) K_2CO_3, MeOH, 23°C. (c) $Cl_2Pd(PPh_3)_2$ (2 mol %), CuI (1.5 mol %), THF, *i*-Pr_2NH, 23 °C.

degassing and use of a dry box was required to attain reasonable yields.

The 16-mer, in its minimum-energy extended zigzag conformation, has a molecular length of approximately 100 Å. The zigzag conformation is significantly lower in energy, by molecular mechanics calculations,[13] than other nonextended forms. Once one end of the molecule binds to a gold probe, the other end could affix to the proximal probe with 2 eV stabilization[14] on each end from the Au−S bonds.

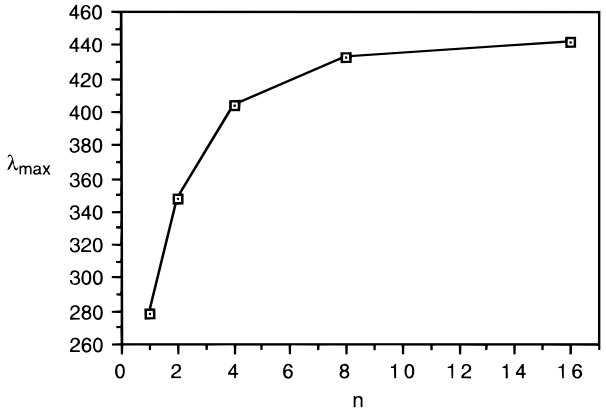


Figure 2. The optical absorbance maximum (λ_{max}) in CH_2Cl_2 versus the number of units in the oligomer (n) for **8**, **13**, **16**, **19**, and **22**.

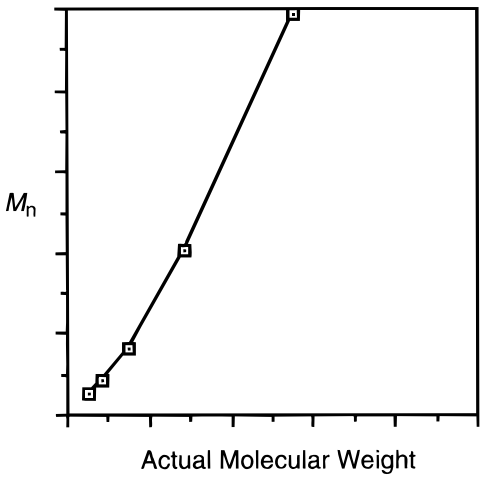


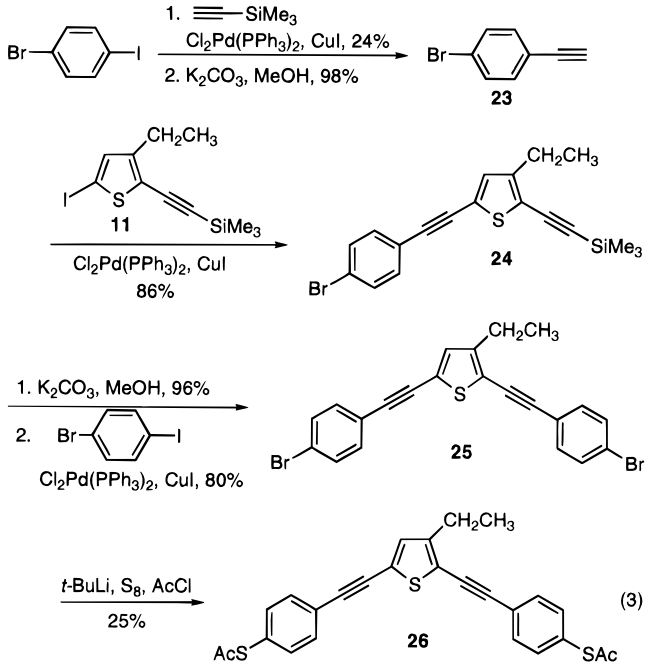
Figure 3. The values of M_n determined by SEC in THF (relative to polystyrene standards) versus the actual molecular weights of the monomer through 16-mer, **8**, **13**, **16**, **19**, and **22**, respectively.

Oligomer Characterization. The monomer through 16-mer, **8**, **13**, **16**, **19**, and **22**, have been characterized spectroscopically. While the tetramer **16** and octamer **19** afforded molecular ions by direct exposure via electron impact mass spectrometry (MS), neither this method nor FAB or electrospray MS sufficed for obtaining a molecular ion of **22**. However, matrix-assisted laser desorption MS (MALDI-MS) did afford an M + 1 peak for **22** (sinapinic acid matrix, positive ion mode).

The optical spectra are interesting in that a near saturation of the systems appears to have occurred by the octamer stage so that doubling the conjugation length to the 16-mer caused little change in the absorbance maximum (Figure 2). We observed a similar near saturation for the third order ($\chi^{(3)}$) nonlinear optical intensities.[15]

The results of the size exclusion chromatography (SEC) are also quite intriguing (Figure 3). SEC is not a direct measure of molecular weight but a measure of the hydrodynamic volume. Thus, by SEC using randomly coiled polystyrene standards, the number average molecular weights (M_n) of rigid rod polymers are usually greatly inflated relative to the actual molecular weights (MW). Accordingly, the SEC-recorded M_n values of the octamer **19** (M_n = 1610, actual MW= 1146) and 16-mer **22** (M_n = 3950, actual MW= 2218) were much greater than the actual MWs. Conversely, the monomer **8** through tetramer **16** had M_n values that were very close to the actual MWs (slope ~1.0 in Figure 3) because they are in the low MW region, prior to significant polystyrene coiling. Therefore Figure 2 could serve as a useful calibration chart for determining the MW of rigid rod polymers. In all cases, the SEC-determined values of M_w/M_n = 1.02−1.05 were within the detectable range limits.

Attachment of Thiol End Groups. We then sought to affix protected thiol moieties to the ends of the oligomers. These thiols were used as molecular alligator clips for adhesion to gold probe surfaces.[6,7] In some cases, we prepared monothiol-terminated systems for adhesion of these oligomers to single gold surfaces. In other cases, we prepared the α,ω-difunctionalized systems for adhesion between two gold probe surfaces. We found that the terminal aromatic thiols were most difficult to manipulate since they were unstable, undergoing disulfide formation in the presence of oxygen, often resulting in insoluble oligomers. However, the acetyl-protected thiols were resilient enough for manipulations in air, yet they could be readily hydrolyzed with NH_4OH, in situ, once exposed to the gold probe surfaces.[6a] Initially, we attached phenylene bromides to the ends of the thiophene-ethynylene oligomers and then converted the halide moieties to protected thiols via a one-pot lithiation−sulfide−acetylation protocol (eq 3).[16] This thioacetyl-generating protocol was low-yielding, and it only worked for the monomeric thiophene case. For instance, we made the corresponding α,ω-dibromoaryl-16-mer **29** that we were unable to transform into the α,ω-dithioacetyl oligomer using the sequence of *t*-BuLi, S_8, AcCl (Scheme 2).



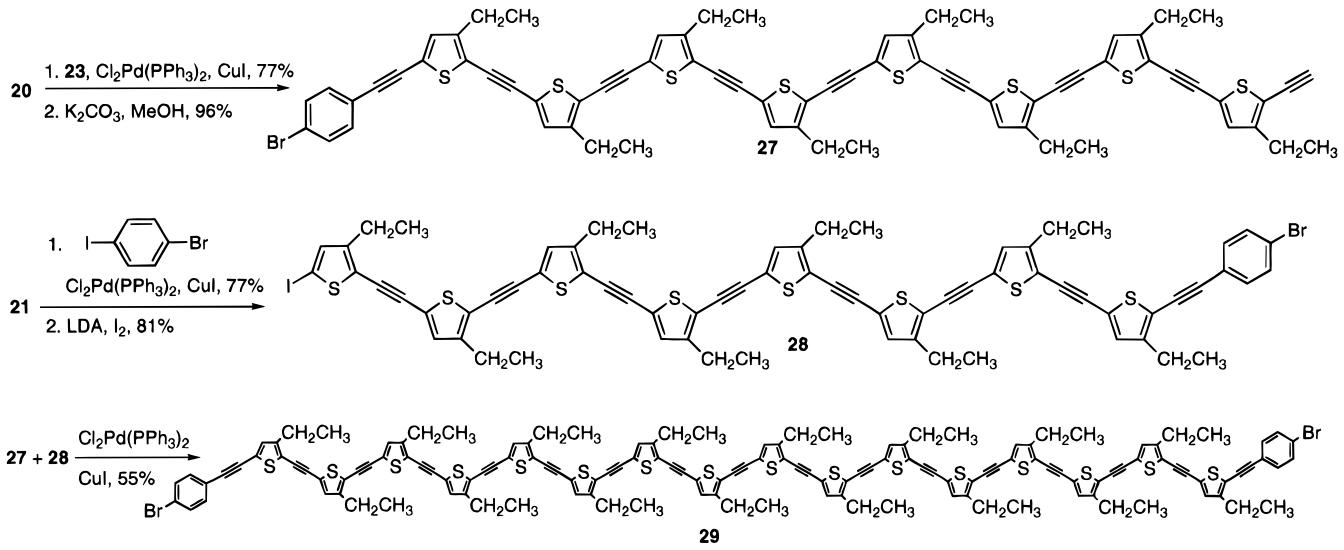
(3)

(13) Oligomer lengths were simulated using standard molecular modeling procedures. All calculations were performed on a Power Macintosh 8100/80 AV using Personal CAChe version 3.7 for both structure drawing and minimization. The CAChe mechanics application implements a standard MM2 force field. All energy calculations were minimized over a large number of iterations to convergence at local minima nearest in energy to the starting compounds' energies.

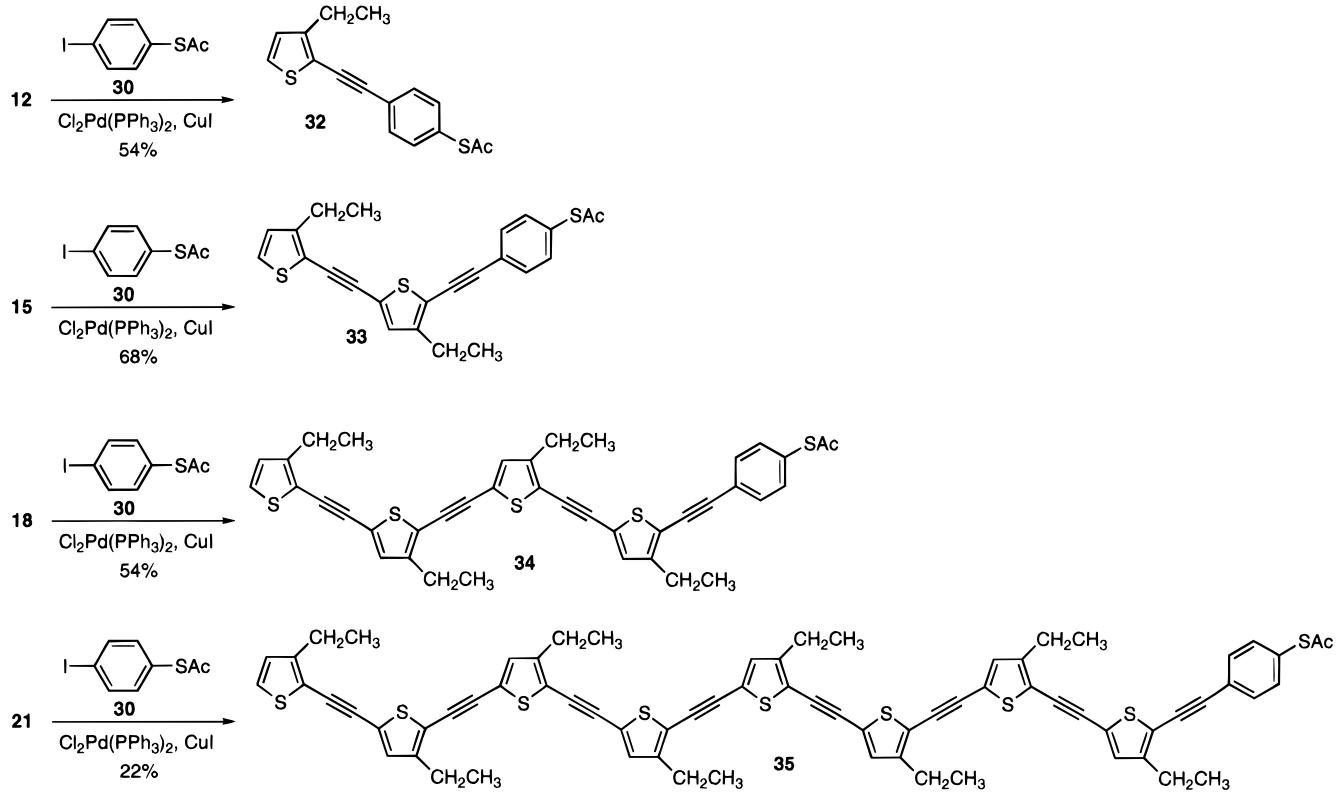
(14) Ulman, A. *An Introduction to Ultrathin Organic Films*; Academic: Boston, 1991.

(15) Samuel, I. D. W.; Ledoux, I.; Delporte, C.; Zyss, J.; Pearson, L.; Tour, J. M. *Chem. Mater.* **1996**, *8*, 819.

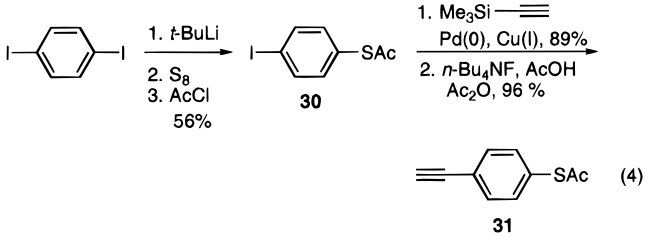
Scheme 2



Scheme 3



We then decided to follow a more convergent approach by synthesizing the two complementary alligator clips, **30** and **31**, from a common intermediate, and then to affix the thioester-containing units directly to the ends of the oligomers (eq 4). During the final protodesilylation for the formation of **31**, if acidic conditions were not used, the fluoride was nucleophilic enough to cause deacylation as well as desilylation. Moreover, addition of acetic anhydride increased the yield of **31**, presumably by reacylating any thiol intermediate that formed. The aryl iodide **30** can be coupled to the alkynyl end (head) of the oligomers while the alkynyl arene **31** can be coupled to the thienyl iodide end (tail) of the oligomers.

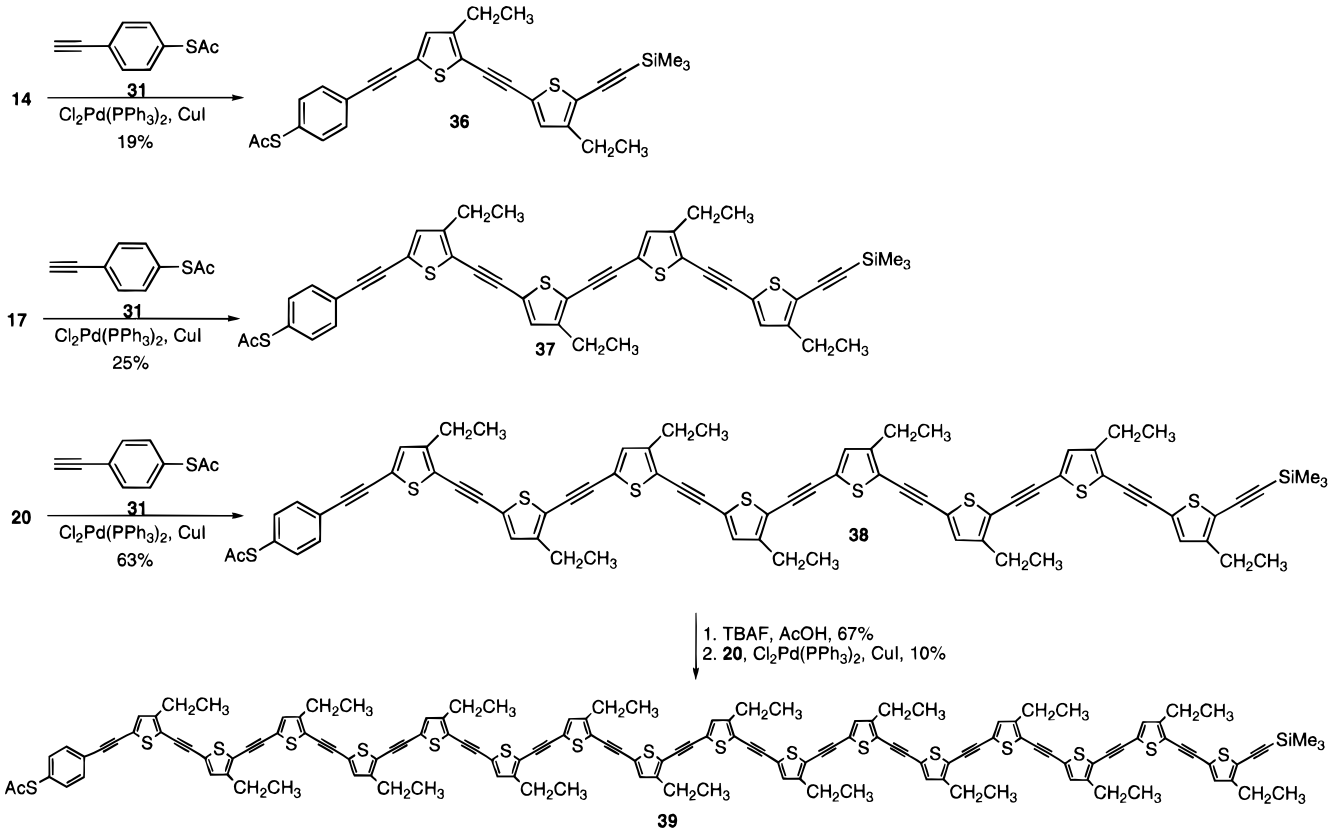


(4)

Scheme 3 shows the attachment of **30** to the heads of the monomer through octamer (**12**, **15**, **18**, and **21**, respectively). The yield for the attachment of **30** to the octamer **21** was low, and we were unable to obtain any desired material when we attempted the same reaction

(16) For sulfur quench without acylation, see: Jones, E.; Moodie, I. M. *Org. Synth.* **1970**, *50*, 104. Note that we also used thienylthiols as alligator clips; however, dimerization reactions via conjugate addition on thiol tautomers ensued. For analogous dimerizations, see: Ponticello, G. S.; Habecker, C. N.; Varga, S. L.; Pitzenbeger, S. M. *J. Org. Chem.* **1989**, *54*, 3223.

Scheme 4



on the corresponding 16-mer, the protodesilylation product of **22**. Again, the sensitivity of the terminal alkynes increases with increased conjugation length.

We then synthesized tail-functionalized dimer through 16-mer, **36**−**39**, respectively, as outlined in Scheme 4. As before, direct functionalization of the iodinated 16-mer was unsuccessful; however, coupling of the protodesilylated product of **38** did afford **39**, albeit in low yield.

We also prepared α,ω-difunctionalized oligomers based on some of our larger conjugated systems. For example, the α,ω-diphenylthioacetyl-octamer **40** has been prepared. Additionally, the phenylthioacetyl-containing tetramer **37**, after protodesilylation, was coupled to the α,ω-diiodo-nonamer **42** to afford the 128 Å long α,ω-diphenylthioacetyl-17-mer **43** (Scheme 5).[13] These are the macromolecules that we are presently using in our attempts to bridge proximal gold probes.

Summary

We outlined the rapid syntheses of oligo(3-ethyl-2,5-thiophene ethynylene)s via an iterative divergent/convergent approach starting from 3-ethyl-2-[(trimethylsilyl)-ethynyl]thiophene (**8**). At each stage in the iteration, the length of the framework doubled. Only three sets of reaction conditions were needed for the entire iterative synthetic sequence: an iodination, a protodesilylation, and a Pd/Cu-catalyzed cross coupling. Convergent attachment of the complementary thiol end groups, protected as thioester moieties, was achieved. These serve as binding units for adhesion to gold surfaces. The rigid rod conjugated oligomers may act as molecular wires in molecular scale electronic devices. Moreover, they also serve as useful models for understanding analogous bulk polymers as judged by the optical spectra and SEC-determined values.

Experimental Procedures

General. Unless otherwise noted, all operations were carried out under a dry, oxygen-free nitrogen atmosphere. Molecular weight analyses were performed using two 30 × 75 cm GPC columns (10^5 Å 10 μm and 500 Å 5 μm) eluted with THF at 60 °C (flow rate 1.0 mL/min). Molecular weight results were based on eight polystyrene standards (M_w = 52000, 30300, 9200, 7000, 5050, 2950, 1060, and 580 with a correlation coefficient > 0.9998) purchased from Polymer Laboratories Ltd. 3-Bromothiophene was purchased from Lancaster Synthesis Ltd. and used without purification. Alkyllithium reagents were obtained from Aldrich Chemical Co. Inc. or FMC. Reagent grade diethyl ether and tetrahydrofuran (THF) were distilled under nitrogen from sodium benzophenone ketyl. Reagent grade benzene and dichloromethane were distilled over calcium hydride. Bulk grade hexane was distilled prior to use. The Pd/Cu couplings were conducted in a manner analogous to that described by Suffert.[12] The 2-halogenations of 3-alkylthiophenes were performed according to the procedure of Uhlenbroek and Reinecke.[17] The terminal alkynes larger than the dimer stage were oxidatively unstable, and they were used immediately after their preparation. The synthetic procedures for the preparation of **1**, **2**, **5**, **8**, **11**−**16**, and **18** have been described previously.[3r] Unless otherwise noted, all compounds were >95% pure as judged by NMR, GC, or combustion analyses. The oligomers' purities can be assessed by their polydispersity indexes M_w/M_n.

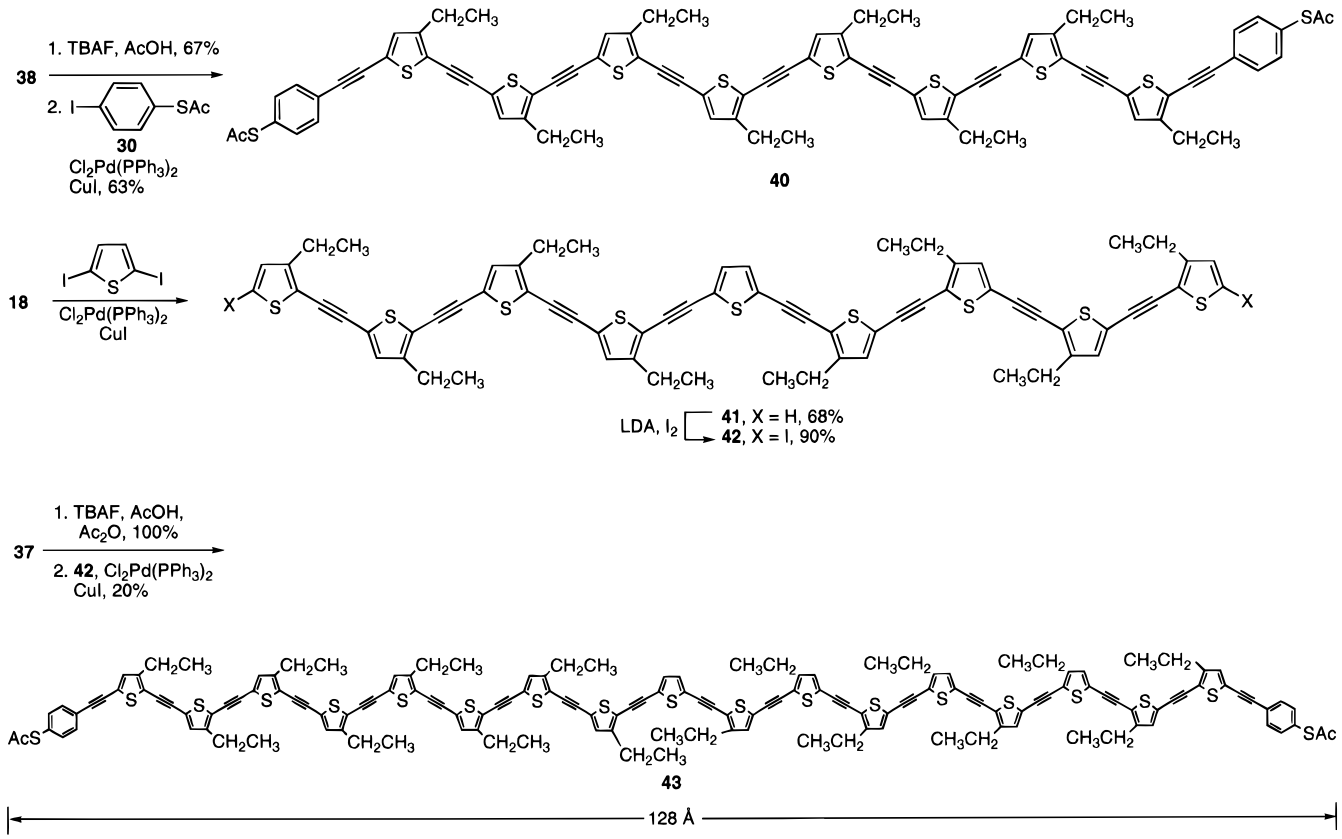
3-*n*-Butylthiophene (3).[18a] A procedure analogous to that of Kumada and co-workers was used as follows.[18b] To magnesium turnings (1.82 g, 75 mmol) in ether (20.0 mL) was added dropwise butyl bromide (10.3 g, 75 mmol) in ether (20.0

(17) (a) Uhlenbroek, J. H.; Bijloo, J. D. *Rec. Trav. Chim.* **1960**, *79*, 1181. (b) Reinecke, M. G.; Adickes, H. W.; Pyrn, C. *J. Org. Chem.* **1971**, *36*, 2690.

(18) (a) Pham, C. V.; Mark, H. B.; Zimmer, H. *Synth. Commun.* **1986**, *16*, 689. (b) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347. (c) Campaigne, E.; Yokley, O. E. *J. Org. Chem.* **1963**, *28*, 914.

(19) Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.

Scheme 5



mL) at room temperature, and an ice bath was used occasionally to maintain a mild reflux. The mixture was stirred at room temperature for 1 h and transferred via cannula to a solution of 3-bromothiophene (8.15 g, 50 mmol) and dichloro-[(diphenylphosphino)propane]nickel(II) (30 mg, 0.055 mmol) in ether (20.0 mL) at 0 °C . The mixture was then allowed to warm to room temperature and stir overnight before being poured into water with a few drops of 3 N hydrochloric acid. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography on silica gel (hexane) to provide 5.93 g (85%) of the title product as colorless liquid. IR (neat) 2929, 2859, 1466, 1079, 857, 834, 768 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 1 H), 6.91 (m, 2 H), 2.62 (t, J = 7.62 Hz, 2 H), 1.60 (pent, J = 7.58 Hz, 2 H), 1.32 (sext, J = 7.38 Hz, 2 H), 0.92 (t, J = 7.32 Hz, 3 H).

3-(Hydroxyethyl)thiophene (4).[18c] To a 1 L flame-dried vessel were added ether (300 mL) and *tert*-butyllithium (212 mL, 467 mmol, 2.2 M in pentane), and the vessel was cooled to −78 °C. To the solution was added 3-bromothiophene (19.5 mL, 208 mmol) dropwise, and the reaction was stirred at −78 °C for 1 h at which time ethylene oxide (45.8 mL, 229 mmol, 5 M in ether) was added. The reaction was allowed to warm to room temperature and stir overnight. The mixture was poured into water and extracted with ether (3 × 20 mL) and the organic layer dried over magnesium sulfate and filtered. The product was purified by flash chromatography (1:1 hexane/ethyl acetate) to afford 23 g (87%) the title compound as a clear colorless liquid. IR (neat) 3356, 2933, 1410, 1047, 909, 835, 774 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.29−7.27 (m, 1 H), 7.04−7.03 (m, 1 H), 6.97−6.96 (m, 1 H), 3.83 (q, J = 6.1 Hz, 2 H), 2.89 (t, J = 6.4 Hz, 2 H), 1.43 (t, J = 5.9 Hz, 1 H).

3-*n*-Butyl-2-iodothiophene (6). To a solution of 3-butylthiophene (5.89 g, 42 mmol) in benzene (10.0 mL) were alternately added mercuric oxide (8.41 g, 38.9 mmol) and iodine (10.93 g, 43.1 mmol) in small portions at 0 °C . The mixture was stirred at room temperature overnight before filtration. The filtrate was poured into water, the aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation and the residue was purified by a column chromatography on silica gel (hexane) to provide 8.06 g (72%) of the title product as colorless liquid. IR (neat) 2929, 2857, 2361, 1464, 1398, 966, 829, 715 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.36 (d, J = 5.51 Hz, 1 H), 6.73 (d, J = 5.46 Hz, 1 H), 2.48 (t, J = 7.63 Hz, 2 H), 1.54 (p, J = 7.70 Hz, 2 H), 1.35 (sext, J = 7.29 Hz, 2 H), 0.93 (t, J = 7.21 Hz, 2 H).

3-(Hydroxyethyl)-2-iodothiophene (7). See the preparation of **6** for the synthetic protocol. Used were 3-(hydroxyethyl)thiophene (10.6 g, 82.8 mmol), benzene (100 mL), mercuric oxide (17.9 g, 82.9 mmol), iodine (21.0 g, 82.8 mmol), and flash chromatography on silica gel (3:2 hexane/ethyl acetate) to afford 17.11 g (81%) of the title product as a clear light yellow liquid. IR (neat) 2929, 2857, 1464, 1397, 965, 829 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, J = 5.5 Hz, 1 H), 6.81 (d, J = 5.5 Hz, 1 H), 3.82 (t, J = 6.6 Hz, 2 H), 2.84 (t, J = 6.6 Hz, 2 H), 1.39 (br s, 1 H).

3-*n*-Butyl-2-[(trimethylsilyl)ethynyl]thiophene (9). To a 100 mL flame-dried vessel containing 3-*n*-butyl-2-iodothiophene (20.93 g, 78.7 mmol), bis(triphenylphosphine)-palladium(II) chloride (1.1 g, 1.57 mmol), copper(I) iodide (0.44 g, 2.3 mmol), and THF (150 mL) was added diisopropylamine (11.9 mL, 85 mmol) at room temperature. The resulting clear brown solution was stirred for 5 min before (trimethylsilyl)-acetylene (12.0 mL, 85 mmol) was added. The nitrogen outlet was removed and the septum capped. The reaction was stirred overnight at room temperature and poured into water, and the aqueous layer was extracted with ether (3 × 20 mL). The organic layer was dried over magnesium sulfate, and the crude product was concentrated *in vacuo*. The product was distilled at 100 °C/1 mmHg to afford 15.0 g (81%) of the title compound as a clear yellow liquid. IR (neat) 2958, 2144, 1458, 1250, 1084 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.10 (d, J = 5.2 Hz, 1 H), 6.81 (d, J = 5.1 Hz, 1 H), 2.67 (t, J = 7.6 Hz, 2 H), 1.58 (p, J = 7.5 Hz, 2 H), 1.32 (sext, J = 7.3 Hz, 2 H), 0.91 (t, J = 7.3 Hz, 3 H), 0.22 (s, 9 H).

2-(Hydroxyethyl)-1-[(trimethylsilyl)ethynyl]thiophene (10). See the preparation of **9** for the synthetic

protocol. Used were 3-(hydroxyethyl)-2-iodothiophene (34.6 g, 136 mmol), bis(triphenylphosphine)palladium(II) chloride (1.9 g, 2.7 mmol), copper(I) iodide (1.3 g, 6.8 mmol), THF (200 mL), diisopropylamine (19.0 mL, 136 mmol), (trimethylsilyl)acetylene (19.2 mL, 136 mmol), and flash chromatography (3:1 hexane/ethyl acetate) to afford 16.37 g (81%) of the title compound as a clear yellow liquid. IR (neat) 3356, 2958, 2898, 2144, 1418, 1250, 1047, 843 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.15 (d, $J = 5.1$ Hz, 1 H), 6.88 (d, $J = 5.1$ Hz, 1 H), 3.86 (q, $J = 6.4$ Hz, 2 H), 2.96 (t, $J = 6.5$ Hz, 2 H), 1.41 (t, $J = 5.9$ Hz, 1 H), 0.23 (s, 9 H).

Iodinated Tetramer 17. To a solution of diisopropylamine (7.89 g, 11 mL, 78 mmol) in ether (40 mL) at −78 °C was added dropwise *n*-butyllithium (44 mL, 65 mmol, 1.49 M in hexanes). The solution was warmed to 0 °C for 30 min and then recooled to −78 °C. **16** (4.35 g, 7.1 mmol) in ether (15 mL) at room temperature was then added to the −78 °C lithium diisopropylamide solution. This solution was warmed from −78 °C to 0 °C for 10 min and then recooled to −78 °C. While at −78 °C, iodine (19.98 g, 78 mmol) in ether (140 mL) was added via cannula, and the solution was allowed to warm to room temperature overnight. The reaction was quenched with water, the aqueous layer was extracted with methylene chloride, and the organic extracts were washed with brine and aqueous sodium thiosulfate. The organic layers were dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography (silica gel, hexane) to provide 4.86 g (93%) of the title product as a fluorescent yellow liquid which darkened upon standing. IR (neat) 2966, 2140, 1459, 1249, 1020, 844 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.05 (s, 1 H), 7.03 (s, 1 H), 7.01 (s, 1 H), 2.69 (11 line m, 8 H), 1.25 (t, $J = 7.60$ Hz, 3 H), 1.24 (t, $J = 7.56$ Hz, 6 H), 1.22 (t, $J = 7.63$ Hz, 3 H), 0.25 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.24, 149.88, 149.59, 149.57, 137.78, 132.58, 132.51, 132.39, 123.43, 123.38, 123.34, 122.54, 120.07, 119.46, 119.35, 102.69, 96.65, 89.98, 89.76, 89.67, 86.61, 86.01, 85.75, 75.03, 23.02, 23.02, 22.86, 22.78, 22.71, 14.62, 14.55, 14.54, 14.32, −0.04. HRMS calcd for $C_{35}H_{33}IS_4Si$: 736.0279. Found: 736.0294.

Octamer 19. To a solution of **17** (0.23 g, 0.32 mmol) in THF (5 mL) were added **18** (0.36 g, 0.67 mmol) and diisopropylamine (0.10 g, 0.10 mL, 0.71 mmol). This solution was allowed to stir under N_2 in a dry box for 1 h. The catalysts bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.02 mmol) and copper iodide (0.002 g, 0.01 mmol) (degassed in vacuo for 1 h) were added, and the reaction was allowed to stir for 3 days. The reaction was quenched with water, the aqueous layer was extracted with ether, and the organic extracts were washed with brine. The ether layers were dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash chromatography by first using hexane then slowly increasing to 9:1 hexane/methylene chloride to provide 0.26 g (72%) of the title product as a yellow-orange solid. IR (neat) 2967, 1511, 1460, 1321, 1264, 1187, 1061, 900, 844, 739 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, $J = 5.15$ Hz, 1 H), 7.06 (s, 4 H), 7.04 (s, 2 H), 7.02 (s, 1 H), 6.90 (d, $J = 5.14$ Hz, 1 H), 2.72 (overlapping q, $J = 7.6$ Hz, 16 H), 1.26 (overlapping t, $J = 7.6$ Hz, 24 H), 0.26 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.30, 150.24, 150.07, 150.03, 150.00, 133.00, 132.94, 132.85, 132.80, 132.63, 128.27, 127.40, 124.44, 124.40, 124.17, 132.95, 123.87, 123.85, 123.83, 123.73, 122.94, 120.47, 119.88, 119.83, 119.82, 119.80, 119.71, 119.29, 119.24, 119.06, 117.67, 117.66, 103.10, 97.04, 90.17, 90.13, 90.08, 89.83, 89.78, 88.69, 88.68, 87.62, 97.60, 87.19, 87.13, 87.10, 87.03, 86.40, 23.57, 23.44, 23.42, 23.26, 15.10, 15.03, 14.94, 14.71, 0.34. UV (CH_2Cl_2) λ_{max} 432 nm, ϵ_{max} 2.5×10^5. LRMS calcd for $C_{67}H_{58}S_8Si$ at statistical isotopic maximum with one ^{13}C: 1147. Found: 1147. SEC: $M_n = 1610$, $M_w = 1660$.

Iodinated Octamer 20. See the preparation of **17** for the synthetic protocol. Used were diisopropylamine (3.18 g, 4.4 mL, 31.4 mmol), ether (20 mL), *n*-butyllithium (16 mL, 23.8 mmol, 1.49 M in hexanes), **19** (1.00 g, 0.87 mmol) in ether (10 mL), iodine (6.48 g, 25.5 mmol) in ether (45 mL), and flash chromatography (silica gel, 9:1 hexane/methylene chloride) to provide 0.70 g (63%) of the title product as a fluorescent yellow liquid which darkened upon standing. IR (film) 2967, 2930, 2872, 2180, 2140, 1698, 1514, 1460, 1384, 1319, 1262, 1249, 1062, 902, 842, 740 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.062 (s, 3 H), 7.058 (s, 2 H), 7.036 (s, 2 H), 7.014 (s, 1 H), 2.71 (overlapping q, $J = 7.6$ Hz, 16 H), 1.26−1.25 (overlapping t, $J = 7.6$ Hz, 24 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.22, 150.78, 150.33, 149.90, 149.64, 149.59, 137.79, 132.93, 132.59, 132.50, 132.40, 123.97, 123.47, 123.40, 122.56, 120.08, 119.50, 119.45, 119.36, 102.74, 96.71, 92.61, 90.49, 90.07, 89.84, 89.77, 86.80, 86.72, 86.09, 85.85, 75.18, 23.28,, 23.08, 22.90, 22.82, 14.82, 14.77, 14.68, 14.60, 14.37, 14.26, 14.01, 0.00. LRMS calcd for $C_{67}H_{57}IS_8Si$: 1272. Found: 1272.

Deprotected Octamer 21. To a solution of **19** (0.77 g, 0.67 mmol) in methanol (5 mL) and dichloromethane (5 mL) was added potassium carbonate (0.69 g, 5.0 mmol). The solution was allowed to stir for 6 h before being poured into water. The aqueous layer was extracted with methylene chloride, and the organic extracts were washed with brine. The combined organic layers were dried over magnesium sulfate. The solvent was removed by rotary evaporation. No further purification was necessary to afford 0.72 g (100%) of the title compound as a yellow-orange solid. IR (film) 3298, 2967, 2932, 2872, 2180, 2097, 1460, 1321, 1262, 1187, 1061, 901, 843, 739, 661 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, $J = 5.17$ Hz, 1 H), 7.064 (s, 3 H), 7.059 (s, 2 H), 7.039 (s, 1 H), 7.030 (s, 1 H), 6.90 (d, $J = 5.15$ Hz, 1 H), 3.489 (s, 1 H), 2.71 (overlapping q, 16 H), 1.25 (overlapping t, $J = 7.6$ Hz, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.40, 150.31, 149.90, 149.84, 149.67, 149.63, 132.87, 132.61, 132.55, 132.45, 132.35, 132.23, 127.89, 127.03, 124.52, 124.05, 124.01, 123.77, 123.56, 123.46, 123.01, 119.42, 119.37, 119.33, 119.11, 118.90, 118.78, 118.68, 117.28, 89.78, 89.55, 89.48, 89.44, 88.33, 87.25, 87.02, 86.84, 86.76, 86.71, 86.08, 84.65, 81.34, 76.08, 23.19, 23.06, 23.04, 22.82, 14.73, 14.65, 14.57, 14.52.

16-mer 22. See the preparation of **19** for the synthetic protocol. Used were **20** (0.68 g, 0.53 mmol), THF (3 mL), **21** (0.70 g, 0.65 mmol), diisopropylamine (0.30 g, 0.42 mL, 3.0 mmol), bis(triphenylphosphine)palladium(II) chloride (0.02 g, 0.02 mmol), copper(I) iodide (0.01 g, 0.03 mmol), and silica gel flash chromatography by first using hexane and then slowly increasing to 9:1 hexane/methylene chloride and finally 7:3 hexane/methylene chloride to provide 0.60 g (50%) of the title product as a red-orange solid. IR (neat) 2968, 2933, 2180, 2140, 1460, 1321, 1249, 1187, 1062, 906, 844, 734 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, $J = 5.15$ Hz, 1 H), 7.064 (s, 7 H), 7.057 (s, 3 H), 7.045 (s, 2 H), 7.035 (s, 3 H), 6.90 (d, $J = 5.17$ Hz, 1 H), 2.71 (overlapping q, $J = 7.6$ Hz, 32 H), 1.25−1.24 (overlapping t, $J = 7.6$ Hz, 48 H), 0.26 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.30, 150.24, 150.08, 150.03, 133.02, 132.95, 132.87, 132.71, 132.63, 128.96, 128.86, 128.27, 127.39, 124.86, 124.37, 124.04, 123.92, 123.83, 119.79, 119.68, 119.56, 119.25, 119.05, 117.64, 90.08, 90.02, 89.79, 88.65, 87.57, 87.09, 23.62, 23.54, 23.41, 23.23, 15.13, 15.08, 15.01, 14.92, 14.68, 14.31, 0.33. UV (CH_2Cl_2) λ_{max} 442 nm, ϵ_{max} 2.1×10^5. Laser desorption MS (sinapic acid matrix) M + 1 calcd for $C_{131}H_{106}S_{16}Si$ + 1 at statistical isotopic maximum with two ^{13}C: 2221.37. Found 2219.98 ± 1.20. SEC: $M_n = 3950$, $M_w = 4160$.

1-Bromo-4-[(trimethylsilyl)ethynyl]benzene. See the preparation of **19** for the synthetic protocol. Used were 1-bromo-4-iodobenzene (2.83 g, 10 mmol) in THF (15 mL), (trimethylsilyl)acetylene (1.47 g, 2.10 mL, 15 mmol), bis(triphenylphosphine)palladium(II) chloride (0.21 g, 0.30 mmol), copper(I) iodide (0.06 g, 0.30 mmol), and diisopropylamine (2.16 g, 3.00 mL, 21.42 mmol) for 1 day. The reaction was passed through a silica gel plug to remove the catalyst using a 1:1 hexane/methylene chloride eluent. The solvent was removed by rotary evaporation, and the residue was purified by gravity chromatography (silica gel) using hexane as the eluent to provide 0.62 g (24%) of the title product as a light yellow-brown solid. IR (KBr) 2960, 2157, 1896, 1581, 1484, 1393, 1247, 1070, 1009, 846 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.41 (d, $J = 8.39$ Hz, 2 H), 7.31 (d, $J = 8.37$ Hz, 2 H), 0.27 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.38, 131.49, 122.79, 122.15, 103.97, 95.56, −0.03. HRMS calcd for $C_{11}H_{13}BrSi$: 251.9970. Found: 251.9966.

1-Bromo-4-ethynylbenzene (23). See the preparation of **21** for the synthetic protocol. Used were 1-bromo-4-[(trimethylsilyl)ethynyl]benzene (1.42 g, 5.61 mmol), methanol (10 mL), and potassium carbonate (2.77 g, 20.04 mmol) for 5 h. No purification was necessary to afford 1.00 g (98%) of the title compound as a brown liquid. IR (film) 3267, 2976, 1902, 1584, 1484, 1069, 821 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.44 (d, J = 8.45 Hz, 2 H), 7.33 (d, J = 8.49 Hz, 2 H), 3.11 (s, 1 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 133.55, 131.60, 123.15, 121.06, 82.59, 78.37.

Monofunctionalized Monomer 24. See the preparation of **19** for the synthetic protocol. Used were **11** (1.02 g, 3.04 mmol), THF (5 mL), **23** (0.64 g, 3.54 mmol), bis(triphenylphosphine)palladium(II) chloride (0.063 g, 0.09 mmol), copper(I) iodide (0.017 g, 0.09 mmol), and *N*,*N*-diisopropylethylamine (0.74 g, 1.0 mL, 5.74 mmol) for 1 day. Gravity chromatography (silica gel) using hexane as the eluent provided 1.01 g (86%) of the title product as a yellow liquid. IR (neat) 2962, 2931, 2872, 2198, 2146, 1489, 1248, 1068, 1007, 842 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.60 Hz, 2 H), 7.33 (d, J = 8.61 Hz, 2 H), 7.01 (s, 1 H), 2.66 (q, J = 7.60 Hz, 2 H), 1.21 (t, J = 7.65 Hz, 3 H), 0.25 (s, 9 H). ^{13}C NMR (100 NMR, $CDCl_3$) δ 149.84, 132.81, 132.46, 131.67, 122.84, 122.60, 121.66, 119.85, 102.44, 96.58, 92.41, 83.81, 22.79, 14.24, −0.11. HRMS calcd for $C_{19}H_{19}BrSSi$: 386.0160. Found: 386.0150. Anal. Calcd for $C_{19}H_{19}BrSSi$: C, 59.07; H, 4.92. Found: C, 58.82; H, 5.01.

2-[(4′-Bromophenyl)ethynyl]-4-ethyl-5-ethynylthiophene. See the preparation of **21** for the synthetic protocol. Used were **24** (1.01 g, 2.61 mmol), methanol (5 mL), methylene chloride (5 mL), and potassium carbonate (1.60 g, 11.58 mmol) for 5 h. No purification was necessary to afford 0.79 g (96%) of the title compound as a brown liquid. IR (neat) 3298, 2968, 2933, 2874, 2204, 2098, 1899, 1487, 1393, 1085, 1068, 1010, 846 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.48 Hz, 2 H), 7.33 (d, J = 8.47, 2 H), 7.03 (s, 1 H), 3.47 (s, 1 H), 2.68 (q, J = 7.60 Hz, 2 H), 1.21 (t, J = 7.60 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.25, 132.83, 132.41, 131.70, 123.10, 122.94, 121.57, 118.53, 92.49, 84.37, 83.58, 76.03, 22.75, 14.43.

Dibromo Difunctionalized Monomer 25. See the preparation of **19** for the synthetic protocol. Used were 2-[(4′-bromophenyl)ethynyl]-4-ethyl-5-ethynylthiophene (0.79 g, 2.51 mmol), THF (5 mL), 1-bromo-4-iodobenzene (1.45 g, 5.13 mmol), bis(triphenylphosphine)palladium(II) chloride (0.056 g, 0.08 mmol), copper(I) iodide (0.015 g, 0.08 mmol), and diisopropylamine (1.08 g, 1.50 mL, 10.71 mmol) for 1 day. Gravity chromatography (silica gel) using hexane as the eluent provided 0.94 g (80%) of the title product as a yellow solid. IR (film) 2960, 2202, 1631, 1530, 1481, 1391, 1064, 1003, 818 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.53 Hz, 2 H), 7.46 (d, J = 8.53 Hz, 2 H), 7.35 (d, J = 8.55 Hz, 2 H), 7.34 (d, J = 8.55 Hz, 2 H), 7.07 (s, 1 H), 2.73 (q, J = 7.60 Hz, 2 H), 1.26 (t, J = 7.60 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.30, 132.82, 132.74, 132.72, 131.71, 123.14, 122.92, 122.78, 121.84, 121.62, 119.49, 95.37, 92.92, 83.81, 83.00, 22.95, 14.53. HRMS calcd for $C_{22}H_{14}Br_2S$: 467.9183. Found: 467.9186.

Dithioester Functionalized Monomer 26. To a solution of **25** (0.04 g, 0.085 mmol) in ether (2 mL) at −78 °C was added dropwise *tert*-butyllithium (1.0 mL, 2.1 mmol, 2.1 M in hexanes). The solution was stirred at −78 °C for 15 min. Sulfur powder (0.08 g, 2.5 mmol) was added as a solid, and the reaction was warmed to 0 °C for 30 min.[16] The solution was recooled to −78 °C, and acetyl chloride (3.31 g, 3.0 mL, 4.22 mmol) was added in one portion. The solution was allowed to warm to room temperature overnight. The mixture was extracted with methylene chloride and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash chromatography using a 9:1 hexane/methylene chloride and finally a 7:3 hexane/methylene chloride eluent to provide 0.01 g (25%) of the title product as a yellow-brown solid. IR (film) 2925, 2860, 1712, 1591, 1198, 1116, 1022, 958, 836 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.35 Hz, 2 H), 7.51 (d, J = 8.42 Hz, 2 H), 7.38 (d, J = 8.37 Hz, 2 H), 7.37 (d, J = 8.41 Hz, 2 H), 7.09 (s, 1 H), 2.73 (q, J = 7.60 Hz, 2 H), 2.42 (s, 6 H), 1.25 (t, J = 7.59 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.40, 149.51, 134.27, 134.24, 132.87, 131.95, 131.89, 128.29, 124.11, 123.87, 123.18, 95.69, 93.80, 84.00, 83.51, 30.31, 22.94, 14.51. HRMS calcd for $C_{26}H_{20}O_2S_3$: 460.0625. Found: 460.0631.

Coupling of 20 with 23. See the preparation of **19** for the synthetic protocol. Used were **20** (0.33 g, 0.26 mmol), THF (5 mL), **23** (0.18 g, 0.99 mmol), bis(triphenylphosphine)palladium(II) chloride (0.022 g, 0.03 mmol), copper(I) iodide (0.006 g, 0.03 mmol), and *N*,*N*-diisopropylethylamine (0.37 g, 0.50 mL, 2.86 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane then slowly increasing to a 9:1 hexane/methylene chloride to provide 0.26 g (77%) of the desired product as a yellow-orange solid. IR (film) 2966, 2933, 2873, 2180, 2140, 1460, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.45 Hz, 2 H), 7.34 (d, J = 8.41 Hz, 2 H), 7.05−7.01 (4 line m, 8 H), 2.72 (overlapping q, J = 7.6 Hz, 16 H), 1.26 (overlapping t, J = 7.6 Hz, 24 H), 0.25 (s, 9 H).

Compound 27. See the preparation of **21** for the synthetic protocol. Used were the **20/23** coupled product (0.22 g, 0.17 mmol), methanol (5 mL), methylene chloride (5 mL), and potassium carbonate (1.42 g, 10.3 mmol) for 5 h. No purification was necessary to afford 0.20 g (96%) of the title compound as a yellow-orange solid which, due to its oxidative instability, was carried on immediately for the preparation of **29**.

Coupling of 21 with 1-Bromo-4-iodobenzene. See the preparation of **19** for the synthetic protocol. Used were **21** (0.18 g, 0.17 mmol), THF (5 mL), 1-bromo-4-iodobenzene (0.04 g, 0.14 mmol), bis(triphenylphosphine)palladium(II) chloride (0.022 g, 0.03 mmol), copper(I) iodide (0.006 g, 0.03 mmol), and *N*,*N*-diisopropylethylamine (0.37 g, 0.50 mL, 2.86 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to a 9:1 hexane/methylene chloride to provide 0.16 g (77%) of the desired product as a yellow-orange solid. IR (film) 3074, 2960, 2932, 2872, 2181, 1460, 1069, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.43 Hz, 2 H), 7.35 (d, J = 8.45 Hz, 2 H), 7.21 (d, J = 5.15 Hz, 1 H), 7.06 (s, 5 H), 7.04 (s, 2 H), 6.90 (d, J = 5.14 Hz, 1 H), 2.72 (overlapping q, J = 7.60 Hz, 16 H), 1.26 (overlapping t, J = 7.60 Hz, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 152.39, 149.89, 149.84, 149.67, 149.63, 149.34, 132.80, 132.72, 132.61, 132.54, 132.45, 132.23, 131.70, 127.87, 126.99, 123.44, 123.04, 122.78, 121.85, 119.70, 119.39, 117.25, 89.70, 89.40, 88.27, 87.17, 86.69, 23.15, 23.02, 22.97, 22.68, 14.68, 14.61, 14.52, 14.15.

Compound 28. See the preparation of **17** for the synthetic protocol. Used were diisopropylamine (1.59 g, 2.2 mL, 15.71 mmol) in THF (2 mL), *n*-butyllithium (8.5 mL, 12.83 mmol, 1.51 M in hexanes), the **21**/1-bromo-4-iodobenzene-coupled product (0.28 g, 0.23 mmol) in ether (10 mL), and iodine (3.50 g, 13.79 mmol) in ether (40 mL). The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to a 9:1 hexane/methylene chloride eluent to provide 0.25 g (81%) of the title product as an reddish-orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.47 (d, J = 8.48 Hz, 2 H), 7.35 (d, J = 8.55 Hz, 2 H), 7.06 (s, 4 H), 7.03 (s, 4 H), 2.71 (overlapping q, J = 7.6 Hz, 16 H), 1.25 (overlapping t, J = 7.6 Hz, 24 H).

Compound 29. See the preparation of **19** for the synthetic protocol. Used were **28** (0.23 g, 0.18 mmol), THF (1.0 mL), **27** (0.08 g, 0.06 mmol), bis(triphenylphosphine)palladium(II) chloride (0.004 g, 0.006 mmol), copper(I) iodide (0.002 g, 0.01 mmol), and *N*,*N*-diisopropylethylamine (0.370 g, 0.40 mL, 2.30 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to a 9:1 hexane/methylene chloride eluent then a 7:3 hexane/methylene chloride eluent to provide 0.01 g (55%) of the title product as a yellow-orange solid. ^1H NMR (400 MHz, $CDCl_3$) δ 7.46 (d, J = 8.41 Hz, 4 H), 7.34 (d, J = 8.42 Hz, 4 H), 7.07 (s, 4 H), 7.06 (s, 10 H), 7.04 (s, 2 H), 2.72 (overlapping q, J = 7.6 Hz, 32 H), 1.26 (overlapping t, J = 7.6 Hz, 48 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.67, 132.95, 132.80, 132.69, 132.61, 131.70, 123.41, 119.39, 89.69, 86.66, 23.20, 23.00, 22.66, 14.72, 14.51, 14.13, 13.90.

1-Iodo-4-thioacetylbenzene (30). To a solution of 1,4-diiodobenzene (4.95 g, 17.5 mmol) in ether (2 mL) at −78 °C

was added dropwise *tert*-butyllithium (16 mL, 33 mmol, 2.10 M in hexanes). The solution was stirred at −78 °C for 5 min. Sulfur powder (0.08 g, 2.5 mmol) in THF (75 mL) at 0 °C was added, and the reaction was warmed to 0 °C for 30 min.[16] The solution was recooled to −78 °C, and acetyl chloride (1.77 g, 1.6 mL, 22.5 mmol) was added in one portion. The solution was allowed to warm to room temperature overnight. The mixture was extracted with methylene chloride and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by silica gel flash chromatography using a 25:1 hexane−ether eluent to provide 2.34 g (56%) of the title product as a yellowish white solid. IR (film) 3080, 1907, 1694, 1466, 1382, 1122, 1005, 811 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.72 (d, J = 8.35 Hz, 2H), 7.11 (d, J = 8.35 Hz, 2 H), 2.40 (s, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.10, 138.36, 135.94, 127.79, 95.93, 30.25. HRMS calcd for C_8H_7IOS: 277.9262. Found: 277.9272. Anal. Calcd for C_8H_7IOS: C, 34.53; H, 2.52. Found: C, 34.67; H: 2.42.

1-Thioacetyl-4-[(trimethylsilyl)ethynyl]benzene. See the preparation of **19** for the synthetic protocol. Used were **30** (1.11 g, 3.99 mmol), THF (5.0 mL), (trimethylsilyl)acetylene (0.58 g, 0.84 mL, 5.90 mmol), bis(triphenylphosphine)palladium(II) chloride (0.14 g, 0.2 mmol), copper iodide (0.04 g, 0.02 mmol), and *N*,*N*-diisopropylethylamine (0.83 g, 1.12 mL, 6.42 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to 9:1 hexane/methylene chloride to provide 0.88 g (89%) of the title product as an off-white solid. IR (neat) 2960, 2159, 1713, 1484, 1250, 864 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 8.10 Hz, 2 H), 7.33 (d, J = 8.07 Hz, 2 H), 2.40 (s, 3 H), 0.23 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.28, 134.04, 132.49, 128.32, 124.36, 104.15, 96.20, 30.24, −0.13. HRMS calcd for $C_{13}H_{16}OSSi$: 248.0691. Found: 248.0694. Anal. Calcd for $C_{13}H_{16}OSSi$: C, 62.90; H, 6.45. Found: C, 62.66; H, 6.19.

4-Ethynyl-1-thioacetylbenzene (31). To a solution of 1-thioacetyl-4-[(trimethylsilyl)ethynyl]benzene (0.17 g, 0.69 mmol) in THF (2 mL) at 0 °C were added acetic acid (0.01 g, 0.01 mL, 0.167 mmol) and acetic anhydride (0.01 g, 0.01 mL, 0.10 mmol) followed by the dropwise addition of tetrabutylammonium fluoride (2.88 g, 3.20 mL, 11.03 mmol). The solution was allowed to warm to room temperature for 5 min. The reaction was run through a silica gel plug to remove the solid impurities. The solvent was removed by rotary evaporation. No further purification was necessary to afford 0.20 g (96%) of the title compound as a yellow-orange solid. IR (film) 3288, 2924, 1708, 1483, 1398, 1353, 1126, 951, 829 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.46 Hz, 2 H), 7.35 (d, J = 8.55 Hz, 2 H), 3.13 (s, 1 H), 2.41 (s, 3 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 193.26, 134.18, 132.73, 128.80, 123.35, 82.84, 78.85, 30.31. LRMS calcd for $C_{10}H_8OS$: 176. Found: 176.

Compound 32. See the preparation of **19** for the synthetic protocol. Used were **12** (0.22 g, 1.61 mmol), THF (2.0 mL), **30** (0.29 g, 1.04 mmol), bis(triphenylphosphine)palladium(II) chloride (0.041 g, 0.06 mmol), copper iodide (0.013 g, 0.07 mmol), and *N*,*N*-diisopropylethylamine (0.374 g, 1.0 mL, 5.74 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to 9:1 hexane/methylene chloride and finally 7:3 hexane/methylene chloride to provide 0.16 g (54%) of the title product as a yellow-orange solid. IR (neat) 3103, 2967, 2932, 2873, 2201, 1709, 1592, 1486, 1459, 1396, 1258, 1117, 1015, 950, 827 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.54 Hz, 2 H), 7.37 (d, J = 8.51 Hz, 2 H), 7.20 (d, J = 5.17 Hz, 1 H), 6.90 (d, J = 5.17 Hz, 1 H), 2.77 (q, J = 7.60 Hz, 2 H), 2.42 (s, 3 H), 1.25 (t, J = 7.60 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.35, 149.63, 134.25, 131.82, 127.99, 127.88, 126.65, 124.57, 117.51, 94.63, 84.14, 30.27, 22.98, 14.70. HRMS calcd for $C_{16}H_{14}OS_2$: 286.0486. Found: 286.0496. Anal. Calcd for $C_{16}H_{14}OS_2$: C, 67.13; H, 4.89. Found: C, 66.87; H: 4.91.

Compound 33. See the preparation of **19** for the synthetic protocol. Used were **15** (0.26 g, 0.196 mmol), THF (0.5 mL), **30** (0.19 g, 0.70 mmol), bis(triphenylphosphine)palladium(II) chloride (0.014 g, 0.02 mmol), copper iodide (0.004 g, 0.02 mmol), and *N*,*N*-diisopropylethylamine (0.21 g, 0.28 mL, 1.62 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to 9:1 hexane/methylene chloride and finally 7:3 hexane/methylene chloride to provide 0.20 g (68%) of the title product as a yellowish-brown liquid. IR (neat) 3103, 2967, 2932, 2193, 1710, 1591, 1120, 827 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.52 (d, J = 8.34 Hz, 2 H), 7.38 (d, J = 8.29 Hz, 2 H), 7.21 (d, J = 5.16 Hz, 1 H), 7.05 (s, 1 H), 6.90 (d, J = 5.16 Hz, 1 H), 2.76 (q, J = 7.57 Hz, 2 H), 2.73 (q, J = 7.53 Hz, 2 H), 1.26 (t, J = 7.56 Hz, 3 H), 1.25 (t, J = 7.61 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.31, 149.81, 149.47, 134.24, 132.24, 131.85, 128.27, 127.85, 126.92, 124.18, 123.64, 119.13, 117.25, 95.59, 88.89, 83.61, 30.27, 22.96, 14.64, 14.50. HRMS calcd for $C_{24}H_{20}OS_3$: 420.0676. Found: 420.0674.

Compound 34. See the preparation of **19** for the synthetic protocol. Used were **18** (0.85 g, 1.58 mmol), THF (1.0 mL), **30** (0.28 g, 1.01 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.02 mmol), copper iodide (0.002 g, 0.01 mmol), and *N*,*N*-diisopropylethylamine (0.37 g, 0.50 mL, 2.87 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane then slowly increasing to 9:1 hexane/methylene chloride and finally 7:3 hexane/methylene chloride to provide 0.37 g (54%) of the title product as a reddish-brown liquid. IR (neat) 2968, 2933, 2874, 2249, 2194, 1709, 1460, 1120, 907, 827 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.21 Hz, 2 H), 7.38 (d, J = 8.19 Hz, 2 H), 7.20 (d, J = 5.12 Hz, 1 H), 7.07 (s, 1 H), 7.06 (s, 1 H), 7.04 (s, 1 H), 6.90 (d, J = 5.13 Hz, 1 H), 2.74 (overlapping q, J = 7.6 Hz, 8 H), 2.42 (s, 3 H), 1.25 (overlapping t, J = 7.6 Hz, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.33, 149.85, 149.64, 149.63, 149.54, 134.26, 132.62, 132.55, 132.23, 131.87, 128.33, 127.86, 126.97, 124.10, 123.94, 123.45, 123.12, 119.29, 118.83, 117.21, 95.86, 89.59, 89.33, 88.21, 87.10, 86.68, 86.42, 83.52, 30.28, 22.98, 22.95, 14.65, 14.50. HRMS calcd for $C_{40}H_{32}OS_5$: 688.1057. Found: 688.1046.

Compound 35. See the preparation of **19** for the synthetic protocol. Used were **21** (0.20 g, 0.19 mmol), THF (0.5 mL), **30** (0.03 g, 0.11 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.02 mmol), copper iodide (0.002 g, 0.01 mmol), and *N*,*N*-diisopropylethylamine (0.37 g, 0.50 mL, 2.87 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to 9:1 hexane/methylene chloride and finally 7:3 hexane/methylene chloride to provide 0.03 g (22%) of the title product as a yellow-orange film. IR (film) 2966, 2931, 2872, 2181, 1709, 1459, 1186, 1118, 903, 842 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.52 (d, J = 8.50 Hz, 2 H), 7.38 (d, J = 8.50 Hz, 2 H), 7.21 (d, J = 5.19 Hz, 1 H), 7.07 (s, 1 H), 7.065 (s, 3 H), 7.058 (s, 1 H), 7.04 (s, 1 H), 6.90 (d, J = 5.16 Hz, 1 H), 2.71 (overlapping q, J = 7.6 Hz, 16 H), 2.42 (s, 3 H), 1.25 (overlapping t, J = 7.6 Hz, 24 H).

Compound 36. See the preparation of **19** for the synthetic protocol. Used were **14** (0.14 g, 0.30 mmol), THF (0.5 mL), **31** (0.06 g, 0.34 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.02 mmol), copper iodide (0.003 g, 0.02 mmol), and *N*,*N*-diisopropylethylamine (0.37 g, 0.50 mL, 2.87 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane then slowly increasing to 9:1 hexane/methylene chloride and finally 7:3 hexane/methylene chloride to provide 0.03 g (19%) of the title product as a yellow liquid. IR (neat) 2966, 2140, 1712, 1488, 1457, 1250, 1121, 1016, 949, 844 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.45 Hz, 2 H), 7.38 (d, J = 8.45 Hz, 2 H), 7.07 (s, 1 H), 7.01 (s, 1 H), 2.70 (q, J = 7.58 Hz, 2 H), 2.66 (q, J = 7.56 Hz, 2 H), 2.42 (s, 3 H), 1.21 (t, J = 7.65 Hz, 3 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.20, 149.89, 149.55, 134.21, 132.84, 132.41, 131.94, 128.53, 123.84, 123.41, 122.51, 120.03, 119.37, 102.65, 96.60, 93.41, 89.56, 85.94, 84.30, 30.28, 22.97, 22.83, 14.49, 14.28, −0.08. HRMS calcd for $C_{29}H_{28}OS_3Si$: 516.1072. Found: 516.1066.

Compound 37. See the preparation of **19** for the synthetic protocol. Used were **17** (1.83 g, 2.49 mmol), THF (3 mL), **31** (0.47 g, 2.67 mmol), bis(triphenylphosphine)palladium(II) chloride (0.07 g, 0.1 mmol), copper(I) iodide (0.02 g, 0.01 mmol), and *N*,*N*-diisopropylethylamine (0.74 g, 1.00 mL, 5.72 mmol) for 2 days. The residue was purified by silica gel flash chromatography by first using hexane then slowly increasing

to a 9:1 hexane/methylene and then a 7:3 hexane/methylene chloride eluent to provide 0.48 g (25%) of the title product as a yellow-brown liquid. IR (film) 2967, 2933, 2874, 2184, 2140, 1712, 1460, 1249, 1121, 845 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.32 Hz, 2 H), 7.38 (d, J = 8.29 Hz, 2 H), 7.082 (s, 1 H), 7.062 (s, 1 H), 7.056 (s, 1 H), 7.010 (s, 1 H), 2.71 (overlapping q, J = 7.6 Hz, 8 H), 2.42 (s, 3 H), 1.25 (overlapping t, J = 7.6 Hz, 12 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.26, 149.90, 149.64, 149.60, 134.22, 132.86, 132.63, 132.40, 131.94, 128.52, 123.83, 123.52, 123.40, 123.29, 122.50, 120.03, 119.44, 119.37, 119.30, 102.67, 96.60, 93.48, 89.73, 89.67, 89.51, 86.65, 86.59, 85.96, 84.30, 30.30, 23.00, 22.83, 22.68, 14.53, 14.30, 14.17, −0.07. HRMS calcd for $C_{45}H_{40}OS_5Si$: 784.1452. Found: 784.1440.

Compound 38. See the preparation of **19** for the synthetic protocol. Used were **20** (0.23 g, 0.18 mmol), THF (0.5 mL), **31** (0.09 g, 0.50 mmol), bis(triphenylphosphine)palladium(II) chloride (0.01 g, 0.02 mmol), copper iodide (0.002 g, 0.01 mmol), and *N*,*N*-diisopropylethylamine (0.37 g, 0.50 mL, 2.87 mmol) for 1 day. The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to 9:1 hexane/methylene chloride and finally 7:3 hexane/methylene chloride to provide 0.15 g (63%) of the title product as a yellow-orange solid. IR (neat) 2967, 2933, 2140, 1711, 1459, 1249, 904, 843 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.50 Hz, 2 H), 7.38 (d, J = 8.54 Hz, 2 H), 7.08 (s, 1 H), 7.06 (s, 5 H), 7.05 (s, 1 H), 7.01 (s, 1 H), 2.69 (overlapping q, J = 7.6 Hz, 16 H), 2.42 (s, 3 H), 1.23 (overlapping t, J = 7.6 Hz, 24 H), 0.25 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.22, 149.89, 149.67, 134.20, 132.84, 132.61, 132.39, 131.94, 128.52, 123.83, 123.41, 119.37, 89.66, 86.64, 30.28, 23.19, 22.99, 22.81, 14.71, 14.49, 14.26, 13.89, −0.10.

Desilylation of 38. To a solution of **38** (0.11 g, 0.08 mmol) in THF (1 mL) at 0 °C was added acetic acid (0.01g, 0.01 mL, 0.18 mmol) followed by tetra-*n*-butylammonium fluoride (0.36 g, 0.40 mL, 1.38 mmol). The solution was allowed to warm to 23 °C for 5 min. The reaction mixture was run through a silica gel plug using 1:1 hexane/methylene chloride eluent. The solvent was removed by rotary evaporation. No further purification was necessary to afford 0.07 g (67%) of the title compound as a yellow-orange solid. IR (film) 3298, 2966, 2932, 2872, 2183, 2096, 1711, 1186, 903, 843 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.51 (d, J = 8.53 Hz, 2 H), 7.38 (d, J = 8.55 Hz, 2 H), 7.08(s, 1 H), 7.06 (s, 6 H), 7.03 (s, 1 H), 3.48 (s, 1 H), 2.71 (overlapping q, J = 7.6 Hz, 16 H), 2.42 (s, 3 H), 1.23 (overlapping t, J = 7.6 Hz, 24 H).

Compound 39. See the preparation of **19** for the synthetic protocol. Used were **20** (0.18 g, 0.14 mmol), THF (1.0 mL), desilylated **38** (0.08 g, 0.06 mmol), bis(triphenylphosphine)-palladium(II) chloride (0.004 g, 0.006 mmol), copper iodide (0.002 g, 0.01 mmol), and *N*,*N*-diisopropylethylamine (0.30 g, 0.40 mL, 2.32 mmol) for 3 days. The residue was purified by silica gel flash chromatography by first using hexane and then slowly increasing to 9:1 hexane/methylene chloride and finally 7:3 hexane/methylene chloride to provide 0.01 g (10%) of the title product as a yellow-orange solid. IR (neat) 2967, 2930, 2181, 2140, 1712, 1634, 1461, 1320, 1250, 1186, 1092, 1015, 948, 902, 844 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.42 Hz, 2 H), 7.38 (d, J = 8.46 Hz, 2 H), 7.08 (s, 3 H), 7.06 (s, 11 H), 7.01 (s, 2 H), 2.71 (overlapping q, J = 7.6 Hz, 32 H), 2.42 (s, 3 H), 1.25−1.23 (overlapping t, J = 7.6 Hz, 48 H), 0.24 (s, 9 H).

Compound 40. See the preparation of **19** for the synthetic protocol. Used were desilylated **38** (0.07 g, 0.06 mmol), THF (0.3 mL), **30** (0.03 g, 0.11 mmol), bis(triphenylphosphine)-palladium(II) chloride (0.01 g, 0.02 mmol), copper iodide (0.002 g, 0.01 mmol), and *N*,*N*-diisopropylethylamine (0.07 g, 0.10 mL, 0.57 mmol) for 3 days. The residue was purified by silica gel flash chromatography by first using hexane then slowly increasing to 9:1 hexane/methylene chloride, followed by 7:3 hexane/methylene chloride and finally 6:4 hexane/methylene chloride to provide 0.05 g (63%) of the title product as a yellow-orange solid. IR (neat) 2966, 2930, 2180, 1712, 1459, 1119, 843 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.518 (d, J = 8.41 Hz, 2 H), 7.512 (d, J = 8.43 Hz, 2 H), 7.384 (d, J = 8.36 Hz, 2 H), 7.380 (d, J = 8.34 Hz, 2 H), 7.08 (s, 1 H), 7.07 (s, 1 H), 7.06 (s, 6 H), 2.71 (overlapping q, J = 7.6 Hz, 16 H), 2.422 (s, 3 H), 2.420 (s, 3 H), 1.25 (overlapping t, J = 7.6 Hz, 24 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 193.68, 193.63, 150.08, 150.04, 149.93, 134.64, 134.60, 133.24, 133.02, 132.34, 132.26, 128.93, 128.76, 124.50, 124.24, 123.92, 123.81, 119.81, 119.77, 119.75, 119.69, 93.83, 90.04, 87.01, 83.91, 30.67, 30.09, 23.38, 23.35, 14.88.

Compound 41. See the preparation of **19** for the synthetic protocol. Used were **18** (1.42, 2.64 mmol), THF (2.5 mL), 2,5-diiodothiophene[18] (0.38 g, 1.1 mmol), bis(triphenylphosphine)-palladium(II) chloride (0.07 g, 0.1 mmol), copper iodide (0.008 g, 0.04 mmol), and diisopropylamine (0.74 g, 1.0 mL, 5.74 mmol) for 1 day. The residue was purified by gravity chromatography (silica gel) using a 9:1 hexane/methylene chloride eluent to provide 0.89 g (68%) of the title product as a yellow-orange solid. IR (film) 3101, 2966, 2930, 2872, 2183, 1459, 1188, 1060, 842 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.21 (d, J = 5.14 Hz, 2 H), 7.15 (s, 2 H), 7.07 (s, 2 H), 7.06 (s, 2 H), 7.05 (s, 2 H), 6.91 (d, J = 5.14 Hz, 2 H), 2.73 (overlapping q, J = 7.6 Hz, 16 H), 1.26 (overlapping t, J = 7.6 Hz, 24 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 149.86, 149.82, 149.71, 149.65, 132.62, 132.56, 132.24, 132.09, 127.88, 127.01, 124.61, 123.98, 123.56, 119.26, 119.23, 118.86, 117.24, 89.61, 89.40, 89.27, 88.27, 87.18, 86.98, 86.77, 23.03, 23.01, 22.70, 14.70, 14.55, 14.18. LRMS calcd for $C_{68}H_{52}S_9$: 1156. Found: 1156.

Compound 42. See the preparation of **17** for the synthetic protocol. Used were *n*-butyllithium (16 mL, 25.0 mmol, 1.56 M in hexanes), diisopropylamine (5.06 g, 7.0 mL, 50.0 mmol) in ether (5.0 mL), **41** (0.90 g, 0.78 mmol) in ether (30 mL), and iodine (12.94 g, 51.0 mmol) in ether (80 mL). The residue was purified by silica gel flash chromatography using a 9:1 hexane/methylene chloride eluent to provide 0.99 g of the title product as a red-orange solid that was 90% pure by spectral analysis. IR (film) 2965, 2929, 2871, 2184, 1459, 1262, 1185, 1061, 902, 841, 801, 739 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.08 (s, 2 H), 7.06 (s, 3 H), 7.04 (s, 5 H), 2.71 (overlapping q, J = 7.6 Hz, 16 H), 1.25 (overlapping t, J = 7.6 Hz, 24 H).

Desilylation of 37. See the desilylation of **38** for the synthetic protocol. Used were acetic acid (0.01 g, 0.01 mL, 0.18 mmol), **37** (0.11 g, 0.14 mmol), THF (5.0 mL), and tetrabutylammonium fluoride (2.71 g, 3.0 mL, 10.36 mmol). The solution was allowed to warm to 23 °C over 8 min. The reaction mixture was passed through a silica gel plug to remove the solid impurities using a 1:1 hexane/methylene chloride eluent. The solvent was removed by rotary evaporation to afford the desired compound (0.10 g, 100%) as a brown liquid. IR (neat) 3298, 2967, 2932, 2874, 2184, 2097, 1710, 1591, 1460, 1396, 1121, 845, 738 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.46 Hz, 2 H), 7.38 (d, J = 8.52 Hz, 2 H), 7.08 (s, 1 H), 7.06 (s, 1 H), 7.05 (s, 1 H), 7.03 (s, 1 H), 3.49 (s, 1 H), 2.70 (overlapping q, J = 7.60 Hz, 8 H), 2.42 (s, 3 H), 1.25 (overlapping t, J = 7.60 Hz, 12 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 193.32, 150.31, 149.68, 149.64, 134.22 (2C), 132.86, 132.63, 132.61, 132.36, 131.94 (2C), 128.51, 123.82, 123.52, 123.41, 123.38, 122.96, 119.34, 119.30, 118.71, 93.48, 89.63, 89.50, 89.46, 86.65, 86.62, 85.99, 84.60, 84.30, 76.02, 30.30, 23.00, 22.77, 14.52, 14.48, 14.16.

Compound 43. See the preparation of **19** for the synthetic protocol. Used were desilylated **37** (0.10 g, 0.14 mmol), **42** (0.09 g, 0.06 mmol), THF (0.5 mL), bis(triphenylphosphine)-palladium(II) chloride (0.084 g, 0.12 mmol), copper iodide (0.089 g, 0.47 mmol), and *N*,*N*-diisopropylethylamine (0.37 g, 0.5 mL, 2.87 mmol) for 2 days. The residue was purified by silica gel flash chromatography. The eluent was initially hexane and then increased to 9:1 hexane/methylene chloride to provide the title product (0.03 g, 20%) as a red-orange solid. IR (film) 2966, 2936, 2880, 2188, 1712, 1466, 1192, 1128, 850 cm^{-1}. ^1H NMR (400 MHz, $CDCl_3$) δ 7.51 (d, J = 8.24 Hz, 4 H), 7.38 (d, J = 8.27 Hz, 4H), 7.08 (s, 5 H), 7.07 (s, 13 H), 2.71 (overlapping q, J = 7.6 Hz, 32 H), 2.42 (s, 6 H), 1.25 (overlapping t, J = 7.6 Hz, 48 H). ^{13}C NMR (300 MHz, $CDCl_3$) δ 193.67, 152.80, 150.31, 150.12, 150.09, 150.05, 134.61, 133.24, 133.02, 132.87, 132.35, 128.91, 124.85, 124.24, 124.03, 123.92, 123.86, 123.81, 119.75, 119.67, 119.54, 119.04, 93.82,

90.02, 89.95, 89.83, 87.24, 87.11, 87.01, 84.65, 30.68, 23.57, 23.51, 23.38, 15.08, 14.97, 14.87, 14.50, 14.27.

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Supporting Information Available: ^{1}H NMR spectra for compounds **6**, **7**, **9**, **10**, **19**−**29**, **33**-**40**, **41**, and **43** (28 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS see any current masthead page for ordering information.

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