Convergent Synthetic Routes to Orthogonally Fused Conjugated Oligomers Directed toward Molecular Scale Electronic Device Applications

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This paper describes the synthetic organic phase of a project directed toward the construction of molecular scale electronic devices. Outlined is a convergent synthetic route to orthogonally fused conjugated organic oligomers. The final systems are to have a potentially conducting chain fused perpendicularly to a second potentially conducting chain via a σ bonded network. One of the core segments synthesized is based on a spirobithiophene moiety with a central silicon atom. It is formed by a zirconium-promoted bis(bicyclization) of a tetrapropargylsilane. The second core is a 9,9′-spirobifluorene system. Terminal halide groups provide the linkage points for further extension of the chains via Pd-catalyzed or Pd/Cu-catalyzed cross coupling methods. All four branching arms are affixed to the core in a single operation, thus making the syntheses highly convergent. In the cases of the larger functionalized systems, alkyl substituents on the thiophenes afford soluble materials. In order to prepare the molecules with >50 Å lengths, an iterative divergent/convergent approach had to be utilized for the construction of oligo(thiophene−ethynylene) branching arms. Organopalladium-catalyzed procedures are used extensively for the syntheses of the orthogonally fused compounds.

Since the time of the first room-filling computers, there has been a tremendous drive to compress the size of computing instruments. In order to bring this desire to its extreme, it was conceived that one may be able to construct single molecules that could each function as a self-contained electronic device,[1] specifically, molecular scale electronic devices.[2] The slow step in existing computational architectures is often the time it takes for an electron to travel between any two points. By moving to very small dimensions, for example, to the molecular scale, the transmit time would be minimized, hence the computational system could possibly operate at a far greater speed than is presently attainable from conventional patterned architectural arrays. There is another technical advantage that might be gained from molecular scale devices. Present computational systems utilize approximately 10^{10} silicon-based devices. If devices were to be based upon single molecules, using routine chemical syntheses, one could prepare over 10^{23} devices in a single reaction flask. Though the task of addressing large arrays of ordered molecular scale devices is presently unattainable, the potential is exciting.

We recently demonstrated the transport of electrons through single linear conjugated molecules.[1cc,3] Linear molecules can be considered two-terminal systems or single molecular wires. The testing of actual molecular devices, for example transistors where three terminals are required, remains to be demonstrated due to the problem of addressing more than two terminals on a molecular-sized structure. However, we show here that the synthetic organic protocol exists for the preparation of the requisite molecular device architectures. The flexible syntheses of two spiro core systems and the

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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) *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1987. (c) Miller, J. S. *Adv. Mater.* **1990**, *2*, 378, 495, 601. (d) *Molecular and Biomolecular Electronics*; Birge, R. R., Ed.; Advances in Chemistry Series 240, American Chemical Society, 1991. (e) *Nanostructure Physics and Fabrication*; Reed, M. A., Kirk, W. P., Eds.; Academic Press: New York, 1989. (f) *Nanostructures and Mesoscopic Systems*; Kirk, W. P., Reed, M. A., Eds.; Academic: New York, 1992. For some background references to molecular wires and devices, see: (g) Waldeck, D. H.; Beratan, D. N. *Science* **1993**, *261*, 576. (h) Grosshenny, V.; Harriman, A.; Ziessel R. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1100. (i) 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. (j) 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. (k) Purcell, S. T.; Garcia, N.; Binh, V. T.; Jones, L., II; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11985. (l) Martin, C. R. *Science* **1994**, *266*, 1961. (m) Seth, J.; Palaniappan, V.; Johnson, T. E.; Prathapan, S.; Lindsey, J. S.; Bocian, D. F. *J. Am. Chem. Soc.* **1994**, *116*, 10578. (n) Gust, D. *Nature* **1994**, *372*, 133. (o) Wu, C.; Bein, T. *Science* **1994**, *266*, 1013. (p) Wagener, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759. (q) Sailor, M. J.; Curtis, C. L. *Adv. Mater.* **1994**, *6*, 688. (r) Jorgensen, M.; Bechgaard, K. *J. Org. Chem.* **1994**, *59*, 5877. (s) 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. (t) Wu, C.; Bein, T. *Science* **1994**, *264*, 1757. (u) Moerner, W. E. *Science* **1994**, *265*, 46. (v) Curtis, C. L.; Ritchie, J. E.; Sailor, M. J. *Science* **1993**, *262*, 2014. (w) Murphy, C. J.; Arkin, M. R.; Jenkins, Y.; Ghatlia, N. D.; Bossmann, S. H.; Turro, N. J.; Barton, J. K. *Science* **1993**, *262*, 1025. (x) O'Neil, M. P.; Niemczyk, M. P.; Svec, W. A.; Gosztola, D.; Gaines, G. L., III; Wasielewski, M. R. *Science* **1992**, *257*, 63. (y) Sessler J. L.; Capuano, V. L.; Harriman, A. *J. Am. Chem. Soc.* **1993**, *115*, 4618. (z) Hush, N. S.; Wong, A. T.; Bacskay, G. B.; Reimers, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 4192. (aa) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram. A. *J. Am. Chem. Soc.* **1990**, *112*, 4206. (bb) 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*, 9529−9534. (cc) Jones, L., II; Pearson, D. L.; Lamba, J. J. S.; Tour, J. M.; Whitesides, G. M.; Muller C. J.; Reed, M. A. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1995**, *36*(1), 564. (dd) Schumm, J. S.; Pearson, D. L.; Tour, J. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1360. (ee) Schumm, J. S.; Jones, L., II; Pearson, D. L.; Hara, R.; Tour, J. M. *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1994**, *35*(2), 687. (ff) Pearson, D. L.; Schumm, J. S.; Tour, J. M. *Macromolecules* **1994**, *27*, 2348. (gg) Tour, J. M.; Wu, R.; Schumm. J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7064. (hh) Tour, J. M.; Wu, R.; Schumm. J. S. *J. Am. Chem. Soc.* **1990**, *112*, 5662.

(2) One of the troublesome issues in the area of molecular electronics is simply the definition of "molecular electronics", 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 transistors. 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.

(3) 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.

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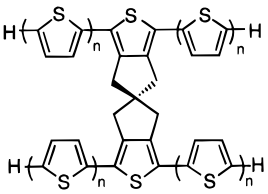
convergent attachment of the branching arms are outlined. The macromolecules, in one case over 50 Å long, are of precise length and constitution; there is no random distribution of chain lengths. Hence, the feasibility of molecular scale electronic devices may soon be experimentally realized.

Aviram, of the IBM Corporation, suggested that molecules ~50 Å long that contain a proconducting (nondoped or nonoxidized system, hence insulating) chain that is fixed at a 90° angle via a nonconjugated σ bonded network to a conducting (doped or oxidized system) chain should exhibit properties that would make them suitable for interconnection into future molecular scale electronic devices. These devices may be useful for the memory, logic, and amplification computing systems.[4] **1**, in undoped form, is an example of a proconducting/σ/conducting molecule. Addressing is proposed by considering a

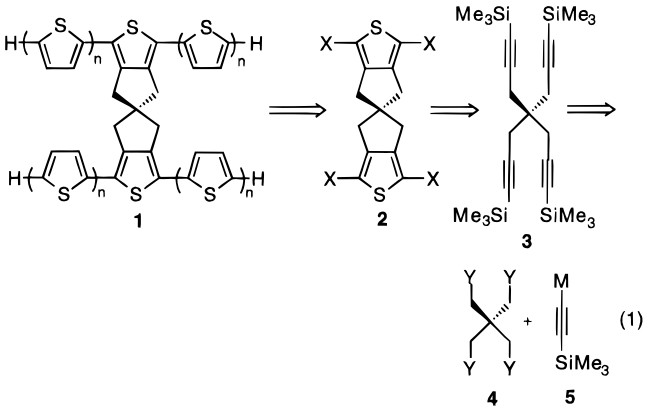


1

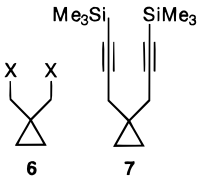
six-probe assembly; a probe at each of the four ends, a probe above the central spiro core moiety, and a probe below the central spiro moiety. Instrument-induced electron removal (doping) from the top branch would permit conduction in the top segment while leaving the bottom segment unchanged, thus insulating (state 1). At a certain threshold potential (perturbation) across the spiro bridge, an electron would tunnel from the lower chain to upper the chain, via the spiro core, to produce a doped (conducting) lower chain and a neutral (insulating) upper chain (state 2).[4–6] Thus the two states would be attainable based on the electrical potential across the spiro bridge, therefore creating a device. In a previous study, we demonstrated that we could, electrochemically, observe the stepwise formation of the mono(radical cation), bis(radical cation), radical-cation(dication), and bis(dication) in some of these orthogonally-fused molecules.[7] These results are in accord with the prerequisite to have no cross-communication between the two arms under unperturbed conditions, thus supporting the proposal that these types of molecules may permit two independent states to exist.[5,6]

From the synthetic standpoint, several aspects are challenging. First, there must be a spiro-fused junction separating two potentially conducting chains with a tetrahedral bonding atom at the center to maintain the 90° angle via a σ bonded network. The 90° angle is essential to minimize the chances of cross-communication between the two arms prior to attainment of the threshold potential across the spiro bridge.[5–7] Secondly, all four conducting chains originating from the central segment must be identical in length so that the two arms are degenerate; only distinguishable once in a device.[4] These requirements, along with the need to have no network polymers formed, prohibit the use of any random polymerization methods.

Our initial approach to these systems involved the synthesis of the key spiro core **2** from which we planned selective attachment of the four branching chains to the target molecule **1**.[1hh] A retrosynthetic analysis is shown in eq 1. Though substitutions on pentaerythrityl tetrahalides involve reactions on a neopentyl system, exhaustive substitution has been accomplished using oxygen, nitrogen, and sulfur nucleophiles.[8] Formation of **3** using 1-metallo-2-(trimethylsilyl)acetylenes **5** and pentaerythrityl systems **4** (Y = Br, I, OTs) proved to be unattainable under numerous coupling procedures (M = MgBr, Li, ZnCl, CuBr, Na with and without Pd and Ni catalysis) in several solvents (THF, diglyme, TMEDA, HMPA, and DMSO).[9] In some cases, we obtained the cyclopropyl systems **6** and/or **7.** Our second proposed route to the

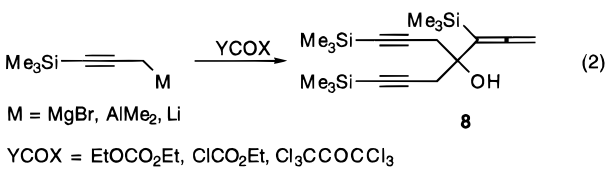


(1)



6 **7**

spiro tetraalkyne involved the formation of a tertiary alcohol, from which we hoped to make the desired tetraalkyne **3**. After investigating numerous reaction conditions,[10] the allenediyne **8** was the only product that we could obtain cleanly (eq 2).



(2)

M = MgBr, $AlMe_2$, Li

8

YCOX = $EtOCO_2Et$, $ClCO_2Et$, $Cl_3CCOCCl_3$

In an effort to bypass these difficulties while maintaining the required σ bonded tetrahedral spiro junction, we turned our attention to the use of silicon as the central

(4) Aviram, A. *J. Am. Chem. Soc.* **1988**, *110*, 5687.

(5) For theoretical studies on electron transfer through σ-bridged compounds, see: (a) McConnell, H. M. *J. Chem. Phys.* **1961**, *35*, 508. (b) Larsson, S.; Volosov, A. *J. Chem. Phys.* **1986**, *85*, 2548. (c) Joachim, C. *Chem. Phys.* **1987**, *116*, 339. (d) Reimers, J. R.; Hush, N. S. *Chem. Phys.* **1989**, *134*, 323. (e) Aviram, A.; Ratner, M. A. *Chem. Phys. Lett.* **1974**, *29*, 277.

(6) For electron transfer studies on related spiro-fused cores, see: (a) Krummel, G.; Huber, W.; Mullen, K. *Angew. Chem., Int. Ed. Engl.* **1987**, *26*, 1290. (b) Maslak, P.; Augustine, M. P.; Burkey, J. D. *J. Am. Chem. Soc.* **1990**, *112*, 5359. (c) Stein, C. A.; Taube, H. *J. Am. Chem. Soc.* **1981**, *103*, 693. (d) Stein, C. A.; Lewis, N. A.; Seitz, G.; Baker, A. D. *Inorg. Chem.* **1983**, *22*, 1124.

(7) (a) Diers, J. R.; DeArmond, M. K.; Guay, J.; Diaz, A. Wu, R.; Schumm, J. S.; Tour, J. M. *Chem. Mater.* **1994**, *6*, 327. (b) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M. *J. Am. Chem. Soc.* **1993**, *115*, 1869.

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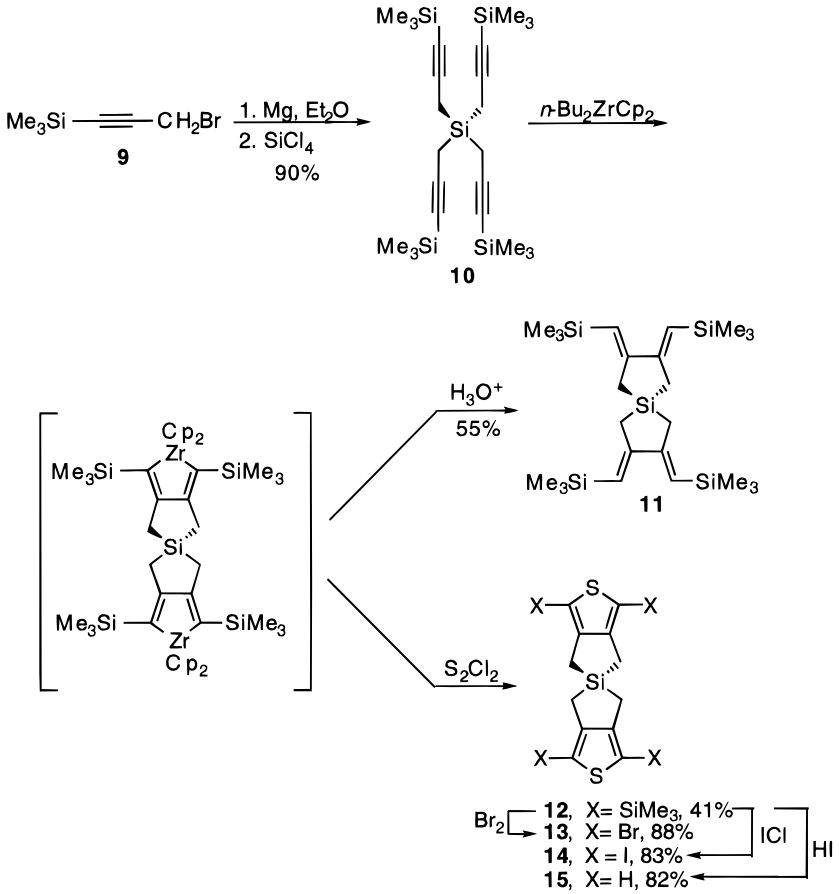
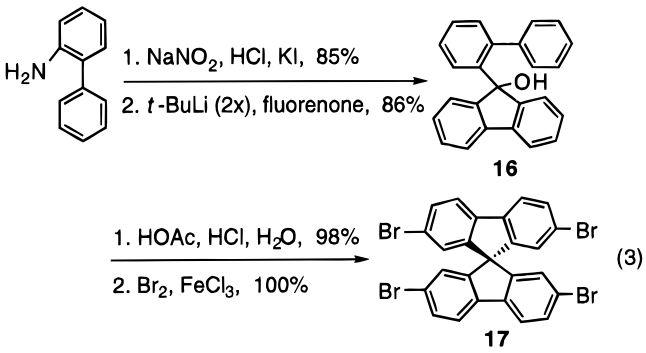
(9) Subsequent to our utilization of this silicon-based approach, a route to tetrapropargylmethane was disclosed. See: Bunz, U.; Vollhardt, K. P. C.; Ho, J. S. *Angew. Chem., Int. Ed. Engl.* **1992**, *31*, 1648.

Scheme 1



atom. Since the primary nature of the central bonding unit is to maintain orthogonality of the two chains thereby limiting electronic migration between the chains, silicon should respond much like the initially proposed carbon analog.[4] Our subsequent studies in solution confirmed this point of interchain isolation.[7] Accordingly, treatment of $SiCl_4$ with the silyl protected propargyl Grignard reagent, cleanly afforded the tetraalkyne **10**. Treatment of **10** with Negishi's reagent (n-Bu_2ZrCp_2),[11] generated *in situ* from zirconocene dichloride and *n*-butyllithium, and quenching with 3 N hydrochloric acid afforded tetraalkene **11**[12] (Scheme 1). When the zirconacycle intermediate was quenched with sulfur monochloride, the desired spiro bithiophene core **12** was formed.[13] The trimethylsilyl-containing core **12** was converted to the tetrabromide **13** or the tetraiodide **14** under electrophilic substitution conditions. We eventually chose to use **13** rather than **14** for the subsequent coupling reactions due to its greater solubility. Additionally, the parent core system **15** could be obtained by treatment with HI (Scheme 1). Remarkably, in all of these substitutions, no attack on the pseudo allylic central silicon atom was observed.

Likewise, we synthesized another key core segment based on a poly(*p*-phenylene)[14] conducting unit which fits the general electronic architectural requirements.[1hh] Conversion of 2-aminobiphenyl to the corresponding iodide under Sandmeyer conditions[15] followed by lithium–halogen exchange and quenching with fluorenone afforded the alcohol **16**. Acid treatment to generate the spiro system[16] followed by reaction with bromine and $FeCl_3$ gave the tetrabromo core **17** in excellent yield (eq 3). Bromination occurred only at the positions *para* to the second ring in the chain as one would expect by



(3)

resonance stabilization of the ionic intermediate. It is imperative that the bromination take place at the *para*-

(10) For the formation of (1-(trimethylsilyl)propargyl)magnesium bromide, see: Hillard, R. L., III.; Parnell, C. A.; Vollhardt, K. P. C. *Tetrahedron* **1983**, *39*, 905. For the formation of (3-(trimethylsilyl)-propargyl)aluminum reagents, see: Sondheimer, F.; Amiel, Y.; Gaoni, Y. *J. Am. Chem. Soc.* **1962**, *84*, 270.

(11) (a) Negishi, E. Holmes, S. J.; Tour, J. M.; Miller, J. A.; Cederbaum, F. E.; Swanson, D. R.; Takahashi, T. *J. Am. Chem. Soc.* **1989**, *111*, 3336. (b) Buchwald, S. L.; Nielsen, R. B. *Chem. Rev.* **1988**, *88*, 1047.

(12) After our initial use of this bicyclization strategy, a synthesis of **11** was reported using this protocol. See: Horn, T.; Müllen, K. *Macromolecules* **1993**, *26*, 3472.

(13) (a) Fagan, P. J.; Nugent, W. A. *J. Am. Chem. Soc.* **1988**, *110*, 2310. (b) Fagan, P. J.; Nugent, W. A.; Calabrese, J. C. *J. Am. Chem. Soc.* **1994**, *116*, 1880.

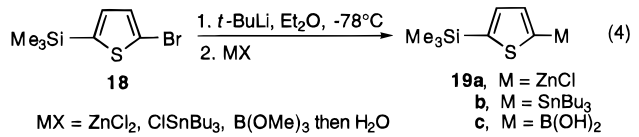
(14) For a discussion of polyphenylene, see: (a) Elsenbaumer, R. L.; Shacklette, L. W. in *Handbook of Conducting Polymers*, Skotheim, T. A., Ed.; Dekker: New York, 1986. (b) Tour, J. M. *Adv. Mater.* **1994**, *6*, 190.

(15) Heaney, H.; Millar, I. T. *Org. Synth.* **1960**, *40*, 105.

(16) Clarkson, R. G.; Gomberg, M. *J. Am. Chem. Soc.* **1930**, *52*, 2881.

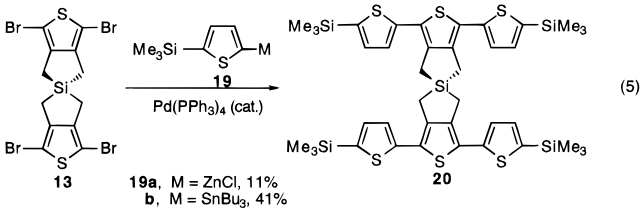
position since a 4-substituted moiety is essential to afford a semiconducting or conducting system.[14]

With the core units in hand, methods for selectively and equally extending the chains in all four directions were attempted. Coupling **13** with metalothiophenes using transition metal catalysis[17] could allow for the selective introduction of all four branching chains in a single operation. Accordingly, the organometallic reagents **19a**−**c** were prepared as described in eq 4.[18]



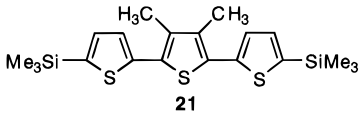
(4)

Treatment of **13** with the zinc reagent **19a** in the presence of $Pd(PPh_3)_4$ provided the desired product **20** in 11% yield along with much of the homocoupled bithiophene byproduct.[17a,b] However, treatment of **13** with the stannane **19b** in the presence of catalytic $Pd(PPh_3)_4$ afforded **20** in 41% yield (eq 5).[17c,d] When **13** was treated with the boronic acid **19c** under standard aque-



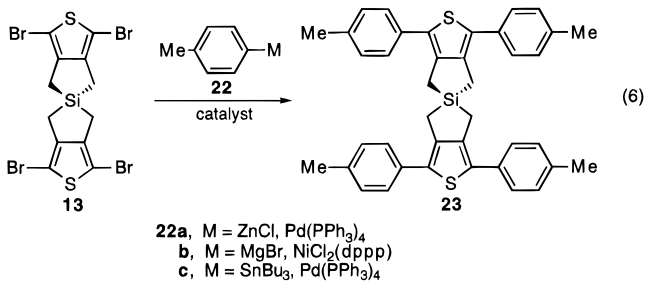
(5)

ous Suzuki coupling conditions,[19] the spiro core was destroyed; the dimethyl-substituted trimer **21** was afforded. Anhydrous conditions for the boron-containing coupling reactions,[20] such as $Pd(OAc)_2$, PPh_3, and NEt_3



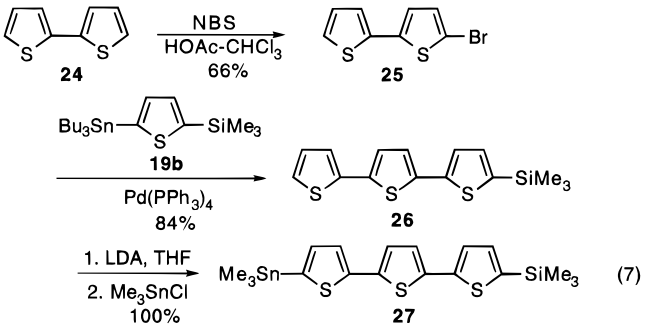
in DMF at 100 °C and $Pd(PPh_3)_4$ and NEt_3 in DME at 80 °C were screened; however, only starting material was recovered. Additionally, when toluyl organometallic reagents **22a**−**c** (prepared from the *p*-bromotoluene by lithium−halogen exchange followed by transmetalation) were used for the coupling reaction with **13** under the same conditions, the yields of **23** were generally less than 20% (eq 6).

In an effort to now extend the length of the branching units, bromination of the spiro trimer **20** with bromine in dichloromethane was attempted; however, insoluble material was obtained which retarded purification and analysis. Therefore, in order to make the spiro oligomers with longer branching arms, it was necessary to make the 2,5-oligothiophenes with stannanes at one end and



(6)

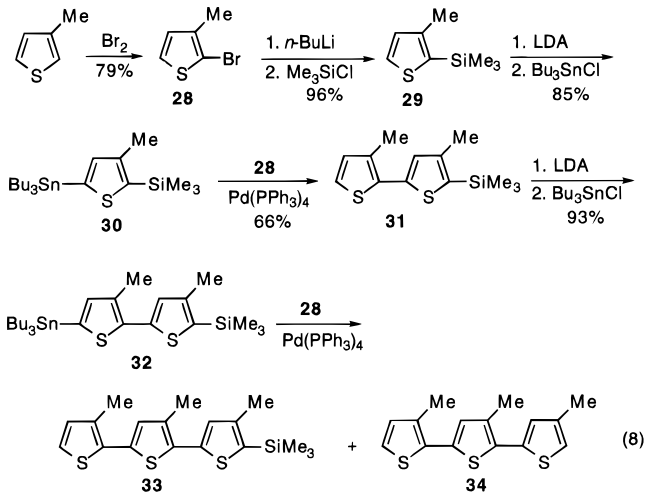
trimethylsilyl substituents, for solubility, at the other end. The synthesis of an appropriately functionalized terthiophene is shown in eq 7.[21] Though **27** could be formed in high yield, it underwent significant decomposi-



(7)

tion on chromatographic purification. Even more frustrating was the coupling between **27** and the core **13**; red precipitates, possibly containing the desired product, were afforded which were insoluble; therefore purification and analysis were not possible.

In light of the solubility problems, we turned our attention to the synthesis of oligo(3-alkylthiophene)s. Initially, we chose to have a 3-methyl group on every thiophene unit (eq 8).



(8)

Though we could cleanly prepare the dimer **31**, the trimer **33** underwent significant amounts of desilylation to afford **34**, and the two trimeric products were inseparable. It was found that the protodesilylation occurred during the purification by chromatography on silica gel.

(17) (a) Negishi, E.; Baba, S. *J. Chem. Soc., Chem. Commun.* **1976**, 596. (b) Negishi, E.; Takahashi, T.; Baba, S.; Van Horn, D. E.; Okukado, N. *J. Am. Chem. Soc.* **1987**, *109*, 2393. (c) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (d) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.

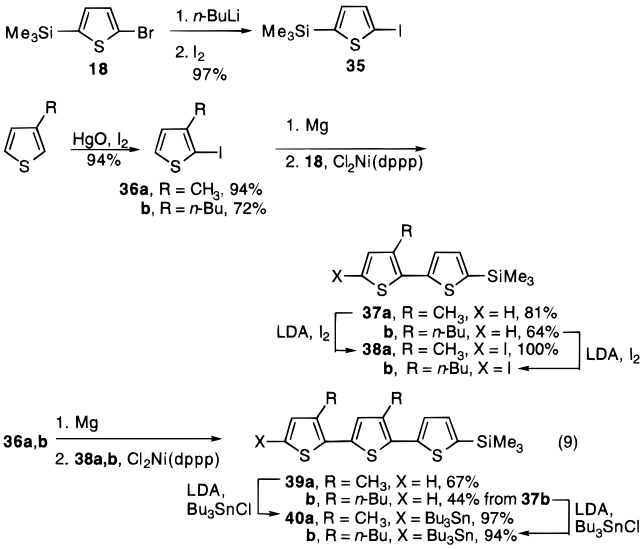
(18) Roncali, J. *Chem. Rev.* **1992**, *92*, 711.

(19) (a) Miyaura, N.; Yanagi, T.; Suzuki, A. *Synth. Commun.* **1981**, *11*, 513. (b) Siddiqui, M. A.; Snieckus, V. *Tetrahedron Lett.* **1988**, *29*, 5463. (c) Gronowitz, S.; Lawitz, K. *Chem. Scripta* **1984**, *24*, 5.

(20) (a) Moriya, T.; Miyaura, N.; Suzuki. A. *Synlett* **1994**, *149*, 304. (b) Brown, H. C.; Vara Prasad, J. V. N. *J. Am. Chem. Soc.* **1986**, *108*, 2049. (c) Miyaura, N.; Ishiyama, T.; Sasaki, H.; Ishikawa, M.; Satoh, M.; Suzuki, A. *J. Am. Chem. Soc.* **1989**, *111*, 314.

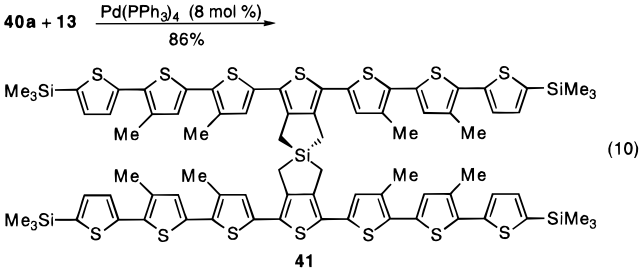
(21) For some routes to trimethylsilyl-terminated thiophene oligomers, see: Tour, J. M.; Wu, R. *Macromolecules* **1992**, *25*, 1901.

Even with triethylamine-washed silica gel, the protodesilylation could not be prevented. Using a triethylsilyl group instead of a trimethylsilyl moiety through the above sequence also resulted in protodesilylation of the trimer. The carbocationic character at the 3-position was sufficiently stabilized in the trimer (not the monomer or dimer) by both the β-silicon and α-methyl to allow for this rapid protodesilylation. *tert*-Butyldimethylsilyl chloride (TBDMSCl) was also used for the preparation of trimer; however, the yield for the formation of the TBDMS-protected monomer, in the lithium−halogen exchange step, was only 26%. As a result of these difficulties, we chose to keep the terminal thiophene unit nonalkylated which served to prevent the desilylation (eq 9).[22]



These trimers possess several desired features, namely (1) a terminal tributylstannyl substituent for attachment to the core units, (2) alkyl groups for maintaining the solubility, and (3) a terminal trimethylsilyl group for solubility enhancement and future chemoselective modification of the final orthogonal oligomers to permit adhesion to nanolithographic probes via attachment of molecular alligator clips (i.e. thiols for attachment to gold probes).[1bb,cc,3]

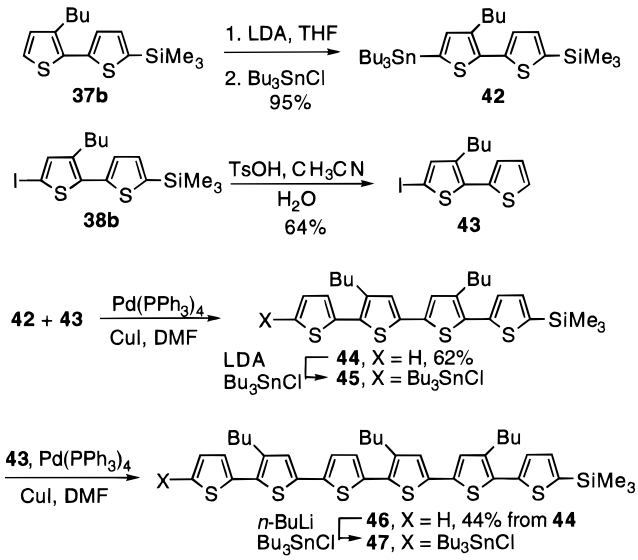
Treatment of the core **13** with excess trimer stannane **40a** in the presence of $Pd(PPh_3)_4$ afforded the target orthogonal thiophene system **41** (eq 10). **41** is approximately 34 Å long as determined by molecular



(10)

modeling using MM2 force field calculations.[23] **41** is quite soluble in THF, CH_2Cl_2, and $CHCl_3$. Interestingly, while most fast atom bombardment mass spectra (FAB/MS) resemble chemical ionization spectra in providing primarily even-electron cations or anions (i.e., M + H),[24] **41** readily showed M^+ data in 3-nitrobenzyl alcohol (NBA) and *o*-nitrophenyl octyl ether (ONPOE) matrices. This is an indication of the ease of oxidation of the oligomer which was confirmed in cyclic voltammetry studies on **41** that showed two redox processes with anodic peak potentials (E_{pa}) at 0.68 and 1.05 V.[7,25]

Scheme 2



In an effort to make the final orthogonally fused oligomers with the ≥50 Å lengths originally proposed by Aviram,[4] we sought several methods to make soluble hexameric oligothiophenes that were appropriately functionalized. After numerous unsuccessful routes had been attempted, we finally succeeded in preparing the target alkyl-substituted hexathiophene (Scheme 2). The coupling of **47** (prepared in situ from **46**) to spiro core **13** was attempted; however, the low overall efficiency of the synthesis of **47**, the low yields of the coupling to the spiro core, and the difficulties in final separation curtailed this approach to the desired macromolecular spiro-fused systems.

We then altered our approach to the branching chains by using an iterative divergent/convergent approach to make tetra(thiophene−ethynylene) oligomers.[1ff] The tetrameric arms were prepared as described in Scheme 3. Using this iterative strategy, the branching arms could be prepared far more efficiently than in our oligothiophene approaches. Unfortunately, in an effort to obtain the desired spiro target **58**, reaction of **57** with the spiro core **13** using Pd/Cu catalysis gave us a repeatedly low yields (<10%) of the desired product. Significant decomposition of the core seemed to occur under the basic conditions needed for the couplings. The low yields precluded proper analytical confirmation of the structure; therefore, we turned our attention to the preparation of the larger fused systems using the spirobifluorene **17**.

In preparing orthogonally fused systems based on **17**, we found that cross coupling reactions were useful for

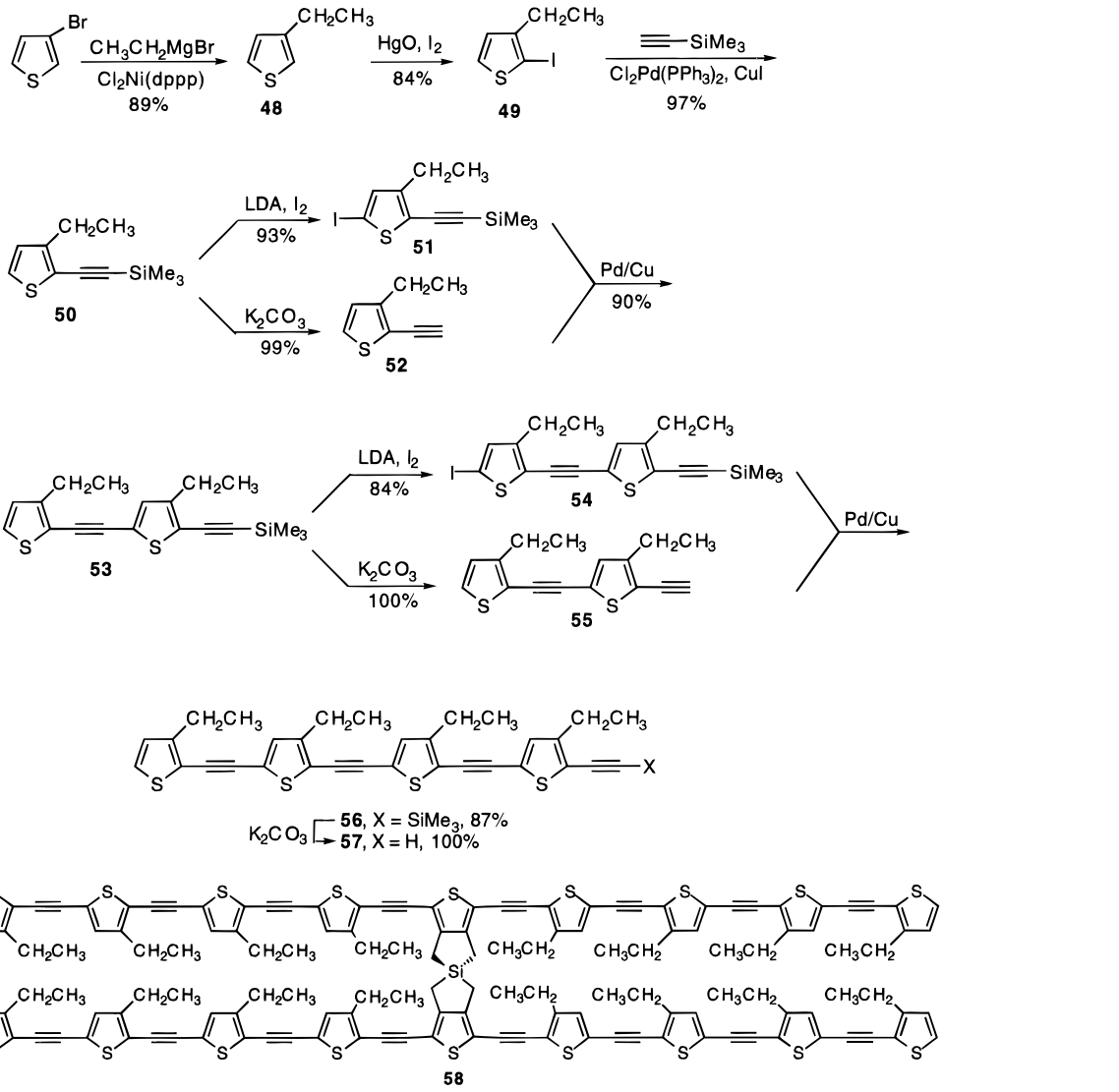
(22) Chan, T. H.; Fleming, I. *Synthesis* **1979**, 761.

(23) 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.

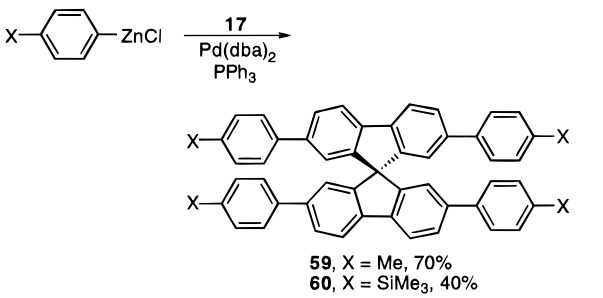
(24) Fenselau, C.; Cotter, R. J. *Chem. Rev.* **1987**, *87*, 501.

(25) Recorded with a 1 mm Pt disc working electrode and SCE double junction reference electrode at a scan rate of 50 mV/s at 10^{-4} M in dichloromethane using 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte.

Scheme 3

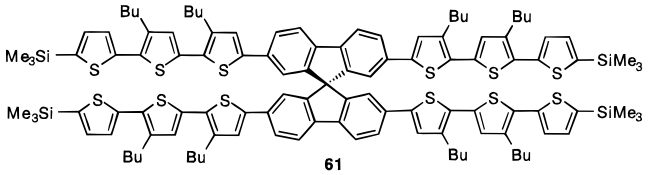


the attachment of *p*-toluyl (**22a**) and *p*-(trimethylsilyl)-phenyl units to afford **59** and **60** in 70% and 40% yields, respectively (eq 11).



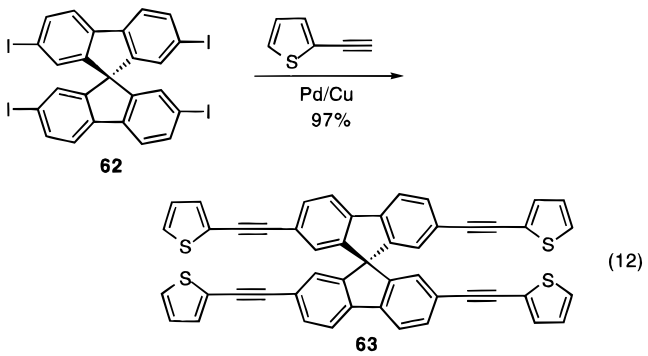
(11)

Since *p*-oligophenylenes are highly insoluble,[14] the synthesis of the larger oligomeric versions based on the spirobifluorene core would necessitate use of 3-alkylthiophenes as the branching chain units. Alkylated phenylenes would not be useful since they have inferior conductivities due to the severe out-of-plane distortions of the consecutive aryl units.[14b] Thus **40b** was coupled to the core **17** using $Pd(PPh_3)_4$ to afford **61** in 60% yield. **61** is approximately 38 Å long.[23] The butyl groups permit **61** to remain quite soluble in THF. Analogous to the observed FAB/MS behavior for **41** described previously,

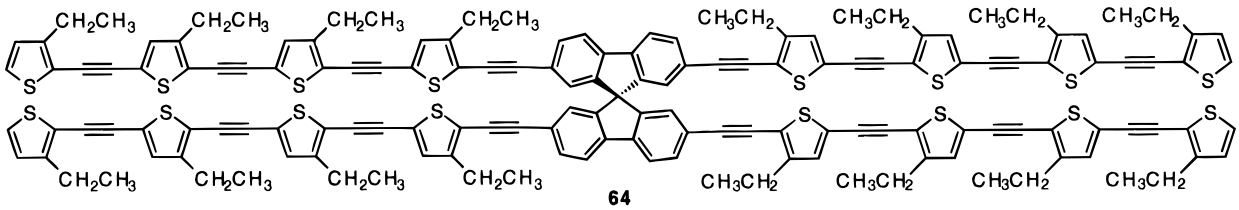


61 showed M^+ data in 3-nitrobenzyl alcohol (NBA) and *o*-nitrophenyl octyl ether (ONPOE) matrices.[24]

In order to enhance the coupling efficiency of the spirobifluorene core with terminal alkynes, the tetraiodospirobifluorene core **62** was prepared. **62** was then coupled with 2-ethynylthiophene to afford, in excellent



(12)



64

yield, **63** (eq 12). We then affixed the larger branching chains **57** to the core **62** to afford the final target **64** in 78% yield. **64** is 59 Å long.[23]

These synthetic approaches demonstrated the power of modern synthetic methods for the preparation of precisely defined orthogonally fused macromolecular systems that may be suitable for incorporation into future molecular scale devices. The convergent approach, where the core was first synthesized, then the branching arms were all affixed in a single operation, provided a facile method for the construction. In order to reach a macromolecule with >50 Å length, we had to use an iterative approach to oligo(thiophene−ethynylene)s which were used for the branching chains.

Experimental Section

General. Unless otherwise noted, all operations were carried out under a dry, oxygen-free nitrogen atmosphere. Capillary GC analyses were obtained using an Alltech Model 932525 (25 m × 0.25 mm, 0.2 μm film of AT-1 stationary phase) capillary GC column. 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. Gravity column chromatography, silica gel plugs, and flash chromatography were carried out using silica gel (230−400 mesh from EM Science). Thin layer chromatography was performed using glass plates precoated with silica gel 60 F_{254} with a layer thickness of 0.25 mm purchased from EM Science. The Pd/Cu couplings were carried out in a manner analogous to that described by Suffert.[26] The 2-halogenation of 3-alkylthiophenes was carried out according to the procedure of Uhlenbroek and Reinecke.[27] The terminal alkynes larger than the monomer stage were oxidatively unstable, and they were used immediately after their preparation. Unless otherwise noted, all compounds were >97% pure as judged by NMR, GC, or combustion analysis.

3-Bromo-1-(trimethylsilyl)propyne (9).[1hh] Method A: Diisopropylamine (6.1 g, 8.4 mL, 60 mmol) was added over 15 min to a solution of *n*-butyllithium (23 mL, 60 mmol, 2.6 M in hexanes) in ether (65 mL) at −78 °C. The obtained solution was cooled to −80 °C to −90 °C, and propargyl bromide (5.9 g, 3.8 mL, 50 mmol) was added dropwise over 5 min while keeping the temperature between −75 °C and −80 °C. After an additional 5 min at −80 °C, chlorotrimethylsilane was added between −80 and −90 °C. Subsequently, a mixture of dry HMPA (7.5 mL) and ether (7.5 mL) was added dropwise with vigorous stirring while carefully keeping the temperature within this range. After this addition, the cooling bath was occasionally removed and the temperature was allowed to rise gradually over 30 min to −40 °C and then to 10 °C. The white suspension was then poured into 3 N aqueous hydrochloric acid (500 mL), and the product was extracted with ether. The combined organic phase was washed with sodium bicarbonate and brine. After drying over anhydrous sodium sulfate, the solvent was removed by distillation through a Vigreux column. The residue was distilled at 72−74 °C/25 mmHg to afford 7.17 g (75%) of the title product.

Method B: To propargyl alcohol (28.0 g, 29.0 mL, 0.50 mol) in THF (1 L) was added *n*-butyllithium (584 mL, 1.05 mol, 1.8 M in hexanes) dropwise by a dropping funnel while maintaining the internal temperature below −60 °C, and stirring was continued at this temperature for 0.5 h. Trimethylchlorosilane (114 g, 133 mL, 1.05 mol) was added dropwise by dropping funnel, and the mixture was allowed to warm to room temperature and stirred for 0.5 h. Hydrochloric acid (3 N, 600 mL) was added, and the solution was stirred vigorously for 1 h to deprotect the alcohol. The mixture was then poured into water and extracted with ether (3 × 100 mL). The combined organic phase was washed with sodium bicarbonate and brine and then dried over sodium sulfate. The solvent was removed by distillation through a Vigreux column until the volume was about 700 mL. The flask was cooled to −78 °C, and *n*-butyllithium (306 mL, 550 mmol) was added dropwise by a dropping funnel. The mixture was stirred at this temperature for 0.5 h, and *p*-toluenesulfonyl chloride (104.8 g, 550 mmol) in THF (300 mL) was added dropwise by a dropping funnel. The mixture was allowed to warm to room temperature for 1 h and then poured into water and extracted with ether (3 × 100 mL). The combined organic phase was washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation. The residue was added to lithium bromide (87.0 g, 1 mol) in acetone (1 L) at room temperature and stirred overnight. The solution was poured into water and extracted with ether (3 × 100 mL), and the combined organic phase was washed with brine and dried over sodium sulfate. The solvent was distilled through a Vigreux column. The residue was distilled at 62.5−64.5 °C/15 mmHg to afford 55.88 g (59%) of the title product as a colorless liquid. FTIR (neat) 2960, 2908, 2185, 1412, 1250, 1205, 1040, 850, 760, 705, 640, 620 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 3.88 (s, 2 H), 0.15 (s, 9 H).

Tetrakis(3′-(trimethysilyl)-2′-propynyl)silane (10).[1hh] To magnesium turnings (0.26 g, 10.5 mmol) and ether (10 mL) in a 100 mL round bottom flask equipped with a reflux condenser and magnetic stirring bar was added 3-bromo-1-(trimethylsilyl)propyne (1.3 g, 7.0 mmol) in ether (6 mL). The mixture began to reflux within 1 or 2 min and an ice bath was used to maintain a mild reflux. When the initially vigorous reaction had subsided, the solution was left to stir at room temperature for 1 h. The Grignard reagent was then transferred via cannula to a 100 mL round bottom flask and was cooled to −78 °C. To this solution was slowly added silicon tetrachloride (0.17 g, 0.12 mL, 1.0 mmol). The mixture was allowed to warm to room temperature for 2 h. Water was carefully added to quench the reaction. The aqueous layer was extracted with ether, and the combined ether layers were washed with brine and then dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation. Distillation (200 °C/0.1 mmHg, Kugelrohr) afforded 0.87 g (90%) of the title compound as a light yellow waxy solid. FTIR (neat) 2987, 2187, 1251, 845 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 1.93 (s, 8 H), 0.12 (s, 36 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 102.16 (4 C, alkyne), 84.95 (4 C, alkyne), 2.81 (4 C, CH_2), 0.14 (12 C, $SiCH_3$). MS [$M^+ - CH_3$] 457, [$M^+ - TMS$] 399, [$M^+ - TMSCCCH_2$] 361. HRMS calcd for $C_{24}H_{44}Si_5$ 472.2289, found: 472.2271.

Compound 11.[12] To a solution of zirconocene dichloride (0.307 g, 1.05 mmol) in THF (3.5 mL) was added *n*-butyllithium in hexane (0.75 mL, 2.1 mmol, 2.8 M in hexanes) at −78 °C. The mixture was stirred for 1 h, and **10** (0.24 g, 0.5

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

(27) (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.

mmol) in THF (1.5 mL) was added. The reaction mixture was allowed to warm to room temperature and was stirred for 10 h. The mixture was quenched with 3 N hydrochloric acid and extracted with ether. The ether extracts were washed with aqueous sodium bicarbonate and brine and dried over sodium sulfate. The residue was purified by column chromatography (silicon gel, hexane) to provide 0.132 g (55%) of the title compound as a colorless liquid. ^{1}H NMR (300 MHz, $CDCl_3$) δ 5.90 (s, 4 H), 1.81 (d, 8 H, J = 1.8 Hz), 0.11 (s, 36 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 159.44, 122.83, 20.64, −0.29. HRMS calcd for $C_{24}H_{48}Si$ 476.2602, found 476.2612.

Spirotetrakis(trimethylsilyl)bithiophene 12.[1hh] To a solution of zirconocene dichloride (0.387 g, 1.15 mmol) in THF (4.5 mL) was slowly added at −78 °C *n*-butyllithium (0.89 mL, 2.3 mmol, 2.8 M in hexanes). The mixture was stirred for 1 h, and **10** (0.25 g, 0.52 mmol) in THF (2 mL) was added. The reaction mixture was allowed to warm to room temperature and was stirred at this temperature for 1 h. Sulfur monochloride (0.15 g, 0.088 mL, 1.15 mmol) in hexane (2 mL) was added dropwise from an addition funnel at 0 °C. The solution was stirred for 15 min at room temperature before the reaction was quenched with 3 N hydrochloric acid and extracted with ether. The combined ether extracts were washed with saturated sodium bicarbonate and dried over sodium sulfate. The solvent was removed by rotary evaporation. The residue was purified by column chromatography (silica gel, hexane) to provide 0.110 g (41%) of the title compound as colorless crystals (dec 198 °C). FTIR (KBr) 2984, 1395, 1252, 1131, 837 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.13 (s, 8 H), 0.32 (s, 36 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 152.62, 136.81, 15.59, −0.24. HRMS calcd for $C_{24}H_{44}S_2Si_5$ 536.1731, found 536.1739.

Spirotetrabromobithiophene 13.[1hh] To a solution of **12** (0.412 g, 0.767 mmol) in carbon tetrachloride (5.0 mL) was slowly added bromine (0.488 g, 0.156 mL, 3.07 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred for 40 min before quenching with water. The aqueous layer was extracted with dichloromethane (4 × 10 mL), and organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the product was recrystallized from dichloromethane to provide 0.382 g (88%) of the title compound as colorless crystals. FTIR (KBr) 1548, 1383, 1309, 1139, 965, 872 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.08 (s, 8 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 143.71, 106.06, 16.49. HRMS calcd for $C_{12}H_8Br_4S_2Si$ 561.6550, found 561.6567. Anal. Calcd for $C_{12}H_8Br_4S_2Si$: C, 25.55; H, 1.43, found: C, 25.43, 25.35; H, 1.41, 1.45.

Spirotetraiodobithiophene 14. To a solution of **12** (0.167 g, 0.31 mmol) in carbon tetrachloride (3.0 mL) was slowly added iodine monochloride (0.201 g, 0.062 mL, 1.24 mmol) by syringe at 0 °C. The mixture was stirred at this temperature for 0.5 h, poured into aqueous sodium thiosulfate solution, and extracted with dichloromethane. The combined organic extracts were dried over anhydrous sodium sulfate, and the solvent was removed at reduced pressure to provide 0.193 g (83%) of the title product. FTIR (KBr) 3394, 1654, 1384, 1144, 1016, 671, 540 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 2.01 (8 H). ^{13}C NMR was not attainable due to the limited solubility. LRMS calcd for $C_{12}H_8I_4S_2Si$ 752, found 752.

Spirobithiophene 15. To a solution of **12** (0.079 g, 0.147 mmol) in benzene (4.00 mL) was added hydriodic acid (0.038 g, 0.08 mL, 0.294 mmol, 48.8% in water) dropwise at room temperature, and the mixture was stirred at room temperature for 1.5 h. Saturated sodium bicarbonate was added, and the mixture was extracted with ether. The organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation. The residue was purified by preparative TLC to provide 0.030 g (82%) of the title product as colorless crystals. FTIR (KBr) 3105, 2885, 1397, 1348, 1165, 1127, 813 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.90 (s, 4 H), 2.10 (s, 8 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 143.45, 118.45, 14.14. Anal. Calcd for $C_{12}H_{12}S_2Si$: C, 58.00; H, 4.87. Found: C, 57.57; H, 4.92.

2-Iodobiphenyl.[15] To a solution of 2-aminobiphenyl (2.53 g, 15.0 mmol) in concentrated hydrochloric acid (3 mL) and water (15 mL) at 0 °C was added sodium nitrite (1.17 g, 17.0 mmol) in water (5 mL). The temperature was held at 0 °C throughout the addition. The resulting brown solution was stirred for 45 min at 0 °C and then poured into potassium iodide (4.9 g, 30 mmol) in water (50 mL). The solution was stirred overnight, and the solution was extracted with ether (4×). The combined organic layers were washed with 3 N hydrochloric acid (3 × 10 mL), aqueous sodium bicarbonate, and brine. After drying over magnesium sulfate, the solvent was removed *in vacuo* to afford 3.57 g (85%) of the title compound as a dark purple liquid. FTIR (neat) 3055.7, 1578.4, 1460.0, 1426.6, 1016.7, 1004.1, 746.9 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.95 (dd, J = 8.1, 1.2 Hz, 1 H), 7.34 (m, 7 H), 7.03 (tt, J = 7.3, 1.9 Hz, 1 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 146.3, 143.9, 139.3, 129.9, 129.1, 128.6, 128.0, 127.8, 127.5, 98.6. HRMS calcd for $C_{12}H_9I$ 279.9749, found 279.9739.

9-(2′-Biphenyl)-9-fluorenol (16).[16] To a solution of 2-iodobiphenyl (4.93 g, 17.6 mmol) in ether (20 mL) was added at −78 °C *tert*-butyllithium (22.8 mL, 38.7 mmol, 1.7 M in pentane) over 30 min. The resulting slurry was stirred at −78 °C for 1 h, and 9-fluorenone (3.17 g, 17.6 mmol) was added in ether (15 mL) over 10 min. The solution was warmed to room temperature for 30 min and poured into water. The aqueous layer was extracted with ether (3 × 15 mL), and the combined organic layers were washed with brine and dried over magnesium sulfate. The crude product was recrystallized from ethanol to afford 5.06 g (86%) of the title product as a white solid. FTIR (KBr) 3590, 3063, 3023, 1450, 1344, 1160 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 8.45 (d, J = 8.0 Hz, 1 H), 7.51 (td, J = 7.4, 1.5 Hz, 1 H), 7.2−7.1 (m, 1 H), 6.88 (dd, J = 7.5, 1.4 Hz, 1 H), 6.80 (td, J = 7.5, 1.3 Hz 1 H), 6.58 (br t, J = 7.9 Hz, 2 H), 5.98 (dd J = 8.1, 1.1 Hz, 2 H), 2.2 (s, 1 H).

9,9′-Spirobifluorene.[16] To a solution of 9-(2′-biphenyl)-9-fluorenol (11.8 g, 35.3 mmol) in refluxing acetic acid was added concentrated hydrochloric acid (0.1 mL) and the solution heated to reflux for 20 min. The solution was cooled to room temperature, and water (50 mL) was added. The resulting white solid was filtered and washed with water and dried *in vacuo*. No further purification was required to afford 10.9 g (98%) of the title compound as a white solid. FTIR (KBr) 3038.2, 3011.0, 1654.2, 1560.1, 1447.6, 749.3 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.82 (d, J = 7.7 Hz, 4 H), 7.34 (t, J = 7.5 Hz, 4 H), 7.08 (t, J = 7.5 Hz, 4 H), 6.71 (d, J = 7.6 Hz, 4 H).

2,2′,7,7′-Tetrabromo-9,9′-spirobifluorene (17).[1hh] To a solution of 9,9′-spirobifluorene (0.316 g, 1.0 mmol) in chloroform (1.5 mL) at 0 °C were added ferric chloride (8 mg, 0.05 mmol) and bromine (0.4 mL, 4.1 mmol). The solution was warmed to room temperature and stirred for 3 h. The resulting slurry was poured into water and washed with saturated sodium thiosulfate until the red color disappeared. The aqueous layer was extracted with dichloromethane (2×), and the combined organic layers were dried over magnesium sulfate to afford 0.63 g (100%) of the title product as a white solid. FTIR (KBr) 3051.6, 1594.7, 1570.8, 1450.1, 1396.2, 1249.3, 1059.7, 950.6 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.67 (d, J = 8.4 Hz, 4 H), 7.5 (dd, J = 8.2, 1.8 Hz, 4 H), 6.8 (d, J = 1.5 Hz, 4 H). ^{13}C NMR (75 MHz, CD_2Cl_2) δ 149.3, 140.2, 132.1, 127.7, 122.4, 122.3, 65.7. HRMS calcd for $C_{25}H_{12}Br_4$ 631.7632, found 631.7630. Anal. Calcd for $C_{25}H_{12}Br_4$: C, 47.51; H, 1.91, found: C, 47.01; H, 1.97. The position of the bromide was confirmed by a single crystal X-ray structure of the title compound. 2D-NMR with a 500 MHz probe was not sufficient to provide the connectivity of the system due to the unusually long relaxation time of the central carbon atom. The relaxation time could not be sufficiently increased even with chromium acetoacetonate. Cooling of the sample to shorten the relaxation time caused precipitation, hence, insufficient signal.

2-Bromo-5-(trimethylsilyl)thiophene (18).[21] To a solution of *n*-butyllithium (7.41 mL, 12 mmol, 1.62 M in hexanes) in THF (10.0 mL) was added dropwise at −78 °C diisopropyl-

amine (1.42 g, 1.96 mL, 14 mmol). The mixture was warmed to 0 °C for 5 min and then recooled to −78 °C. 2-Bromothiophene (1.63 g, 0.97 mL, 10 mmol) was added, and the solution was warmed to 0 °C for 5 min. After recooling to −78 °C, chlorotrimethylsilane (1.30 g, 1.52 mL, 12 mmol) was added in one portion, and the solution was allowed to warm to room temperature for 30 min. The mixture was poured into water with a few drops of 3 N hydrochloric acid to remove the emulsion, and the aqueous layer was extracted with ether. The organic extracts were washed with sodium bicarbonate and brine. After drying over sodium sulfate, the solvent was removed by rotary evaporation. Vacuum distillation (70 °C/2 mmHg) afforded 1.8 g (77%) of the title product as a colorless liquid. FTIR (neat) 2957, 1406, 1288, 1251, 1204, 1068, 1001, 956, 841, 796, 756, 697, 648 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.06 (d, J = 3.49 Hz, 1 H), 6.97 (d, J = 3.49 Hz, 1 H), 0.28 (s, 9 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 143.05, 134.31, 131.11, 116.72, −0.20.

2-(Tributylstannyl)-5-(trimethylsilyl)thiophene (19b).[21] To a solution of *tert*-butyllithium (20.0 mL, 33.6 mmol, 1.68 M in pentane) in ether (18.0 mL) was added slowly at −78 °C 2-bromo-5-(trimethylsilyl)thiophene (**18**) (3.95 g, 16.8 mmol), and the resulting mixture was stirred at −78 °C for 1 h. To this mixture was added slowly tributyltin chloride (5.47 g, 4.56 mL, 16.8 mmol), and the solution was allowed to warm to room temperature for 2 h before pouring into water with a few drops of 3 N hydrochloric acid to remove the emulsion. The aqueous layer was extracted with ether. The organic extracts were washed with sodium bicarbonate and brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the crude material was filtered through a silica plug (hexane) to provide 5.84 g (78%) of the title product as a colorless liquid which was used with no further purification. FTIR (neat) 2957, 2928, 1485, 1464, 1406, 1377, 1249, 1214, 1200, 1082, 992, 840, 800, 757, 704 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.46 (d, J = 3.1 Hz, 1 H), 7.32 (d, J = 3.1 Hz, 1 H), 1.60 (q, J = 8.0 Hz, 6 H), 1.47−1.17 (m, 12 H), 0.96 (t, J = 7.3 Hz, 9 H), 0.39 (s, 1 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 145.71, 142.07, 136.18, 134.77, 29.05, 27.33, 13.65, 10.93, 0.21.

2-(Trimethylsilyl)-5-thienylboronic acid (19c).[21] To a solution of *tert*-butyllithium (3.53 mL, 6.0 mmol, 1.7 M in pentane) in ether (3.0 mL) was added 2-bromo-5-(trimethylsilyl)thiophene (**18**) (0.706 g, 3.0 mmol) in ether (3.0 mL) at −78 °C. The mixture was stirred at −78 °C for 1 h and transferred via cannula to a solution of triisopropyl borate (1.128 g, 1.38 mL, 6.0 mmol) in THF (2.0 mL) at −78 °C. The mixture was allowed to warm to room temperature and stirred for 10 min. Hydrochloric acid (5%, 2.0 mL) was added, and the aqueous layer was extracted with ether. The organic extracts were washed with 1 N sodium hydroxide (4 × 10 mL). The sodium hydroxide solution was washed with ether, and the aqueous solution was then acidified with 3 N hydrochloric acid and then extracted with ether. The combined organic extracts were dried over magnesium sulfate. The solvent was removed under reduced pressure to provide 0.422 g (70%) of the title product as a off-white thick liquid which was used directly for the next reaction. FTIR (neat) 3354, 2957, 1506, 1344, 1250, 1119, 1072, 987, 841, 756, 715, 636 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 8.04 (d, J = 3.3 Hz, 2 H), 7.40 (d, J = 3.3 Hz, 2 H), 0.37 (s, 9 H).

Compound 20.[1hh] A flame-dried flask was sequentially charged with **13** (0.282 g, 0.5 mmol), 2-(tributylstannyl)-5-(trimethylsilyl)thiophene (**19b**) (1.78 g, 4.0 mmol), tetrakis(triphenylphosphine)palladium(0) (0.115 g, 0.10 mmol), and toluene (9.0 mL). The mixture was stirred at room temperature for 1 h and heated to 100 °C for 20 h. The resulting solution was poured into water with a few drops of 3 N hydrochloric acid to remove the emulsion, and the organic layer was separated. The aqueous layer was extracted with ether, and the combined organic extracts were washed with sodium bicarbonate and brine and dried over magnesium sulfate. The crude material was filtered through alumina to remove the palladium residue and then was purified by column chromatography (silica gel, hexane) to provide 0.177 g (41%) of the title product as yellow-green crystals. FTIR (KBr) 2955, 1431, 1249, 1208, 1130, 1076, 983, 841, 799, 757 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.29 (d, J = 3.51 Hz, 4 H), 7.18 (d, J = 3.51 Hz, 4 H), 2.33, (s, 8 H), 0.35 (s, 36 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 142.54, 140.87, 139.51, 134.40, 128.31, 125.10, 16.71, 0.00. Anal. Calcd for $C_{40}H_{52}S_6Si_5$: C, 55.50; H, 6.05. Found: C, 55.09, 54.99; H, 6.03, 6.04. HRMS calcd for $C_{40}H_{52}S_6Si_5$ 864.1219, found 864.1240.

Compound 23. To a solution of 4-bromotoluene (1.368 g, 0.984 mL, 8.0 mmol) in anhydrous ether (15 mL) was slowly added *tert*-butyllithium (9.41 mL, 16 mmol, 1.7 M in pentane) by syringe pump (0.20 mL/min) at −78 °C. The solution was stirred at −78 °C for 1 h and was added via cannula to a solution of anhydrous zinc chloride (1.53 g, 11.2 mmol) in THF (10 mL). The mixture was stirred at room temperature for 1 h. To a solution of **13** (0.282 g, 0.5 mmol) in THF (2.5 mL) was added a solution of tetrakis(triphenylphosphine)palladium(0), formed in situ by stirring $Pd_2dba_3CHCl_3$ (0.015 g, 0.014 mmol) and triphenylphosphine (0.026 g, 0.10 mmol) in THF (2.5 mL). To this solution was added the zinc reagent by cannula, and the mixture was stirred at room temperature for 1 h followed by warming at 60 °C (bath temperature) overnight. The solution was poured onto water and was extracted with dichloromethane. The combined organic extracts were washed with brine and dried over sodium sulfate, and the solvent was removed *in vacuo*. The residue was dissolved in dichloromethane and filtered through a silica gel plug, and the solvent was removed *in vacuo*. The residue was then dissolved in carbon tetrachloride and was purified by chromatography (silica gel, hexane, 1:20 dichloromethane: hexane, 1:10 dichloromethane:hexane, 1:5 dichloromethane: hexane) to provide 57 mg (18%) of the title compound as white crystals. FTIR (KBr) 2918, 1504, 1387, 1262, 1138, 1011, 813, 758, 579 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.50 (d, J = 8.2 Hz, 8 H), 7.17 (d, J = 8.0 Hz, 8 H), 2.35 (s, 12 H), 2.26 (s, 8 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 140.03, 136.69, 132.23, 129.31, 127.40, 21.16, 15.91.

2,2′-Bithiophene (24).[21] To magnesium turnings (0.912 g, 37.5 mmol) in ether (15.0 mL) was added about 0.5 mL of 2-bromothiophene (4.076 g, 2.42 mL, 25 mmol). An exothermic reaction occurred within a few minutes, and the remaining bromide was added dropwise with an ice bath used occasionally to maintain a mild reflux. After the addition, the resulting mixture was heated to reflux for 30 min and cooled to room temperature. To a solution of 2-bromothiophene (3.26 g, 1.94 mL, 20 mmol) and [1,3-bis(diphenylphosphino)propane]-nickel(II) chloride (15 mg) in ether (10.0 mL) was added dropwise via cannula the above Grignard reagent at 0 °C. The resulting mixture was heated to reflux for 4 h and poured into water with a few drops of 3 N hydrochloric acid to destroy the emulsion. The aqueous layer was extracted with ether, and the organic extracts were washed with sodium bicarbonate and brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, hexane) to afford 3.32 g (99.8%) of the title product as a colorless liquid. FTIR (neat) 3064, 1794, 1649, 1500, 1416, 1238, 1208, 1078, 1051, 856, 817, 704 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (dd, J = 5.1, 1.2 Hz, 2 H), 7.17 (dd, J = 3.6, 1.2 Hz, 2 H), 7.01 (dd, J = 5.1, 3.6 Hz, 2 H).

2-Bromo-5-(2′-thienyl)thiophene (25).[28] A flame-dried flask was charged with 2,2′-bithiophene (**24**) (1.66 g, 10.0 mmol), *N*-bromosuccinimide (1.78 g, 10.0 mmol), chloroform (20.0 mL), and acetic acid (20.0 mL). The mixture was stirred at room temperature under N_2 overnight and then washed several times with aqueous sodium bicarbonate and brine. The aqueous layer was extracted with ether, and the organic extracts were dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, hexane) to provide 1.62 g (66%) of the title product as a light-blue liquid along with 0.43 g (13%) of dibromide and 0.177 g of the starting material. FTIR (neat) 3084, 1737, 1504, 1443, 1418, 1241, 1200, 1051, 970, 882, 838, 789, 696 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.21 (dd, J = 5.1, 1.2 Hz, 1 H), 7.09 (dd, J = 3.6, 1.2 Hz, 1 H),

(28) Nakayama, J.; Konishi, T.; Murabayashi, S.; Hoshino, M. *Heterocycles* **1987**, *26*, 1793.

6.99 (dd, J = 5.1, 3.6 Hz, 1 H), 6.95 (d, J = 3.8 Hz, 1 H), 6.90 (d, J = 3.8 Hz, 1 H).

5-(Trimethylsilyl)-2,2′:5′,2″-terthiophene (26). A flame-dried flask was charged with 2-(tributylstannyl)-5-(trimethylsilyl)thiophene (**19b**) (4.41 g, 9.9 mmol), 2-bromo-5-(2′-thienyl)thiophene (**25**) (1.66 g, 6.6 mmol), tetrakis(triphenylphosphine)palladium(0) (0.38 g, 0.33 mmol), and toluene (30.0 mL). The mixture was heated to 100 °C (oil temp) overnight under N_2 and poured into water with a few drops of 3 N hydrochloric acid to destroy the emulsion. The aqueous layer was extracted with ether, and the organic extracts were washed with sodium bicarbonate and brine and then dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, hexane) to provide 1.78 g (84%) of the title product as bright-yellow crystals. FTIR (KBr) 1426, 1253, 1076, 994, 835, 794, 754, 684, 468 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.21 (d, J = 3.5 Hz, 1 H), 7.20 (dd, J = 5.1, 1.2 Hz, 1 H), 7.16 (dd, J = 3.6, 1.2 Hz, 1 H), 7.12 (d, J = 3.5 Hz, 1 H), 7.07 (d, J = 0.5 Hz, 2 H), 7.00 (dd, J = 5.1, 3.6 Hz, 1 H), 0.32 (s, 9 H).

5-(Trimethylsilyl)-5″-(trimethylstannyl)-2,2′:5′,2″-terthiophene (27). To a solution of diisopropylamine (0.304 g, 0.42 mL, 3.0 mmol) in THF (2.0 mL) was added *n*-butyllithium (1.34 mL, 3.0 mmol, 2.24 M in hexanes) dropwise at −78 °C. The mixture was allowed to warm to 0 °C for 10 min and recooled to −78 °C. To the above solution was added dropwise **26** (0.641 g, 2.0 mmol) in THF (2.0 mL) via cannula. The resulting mixture was stirred at this temperature for 2 h, and trimethyltin chloride (0.73 g, 3.66 mmol) in THF (2.0 mL) was added dropwise via cannula. The solution was allowed to warm to room temperature for 1 h and poured into brine. The aqueous layer was extracted with ether, and the organic extracts were dried over sodium sulfate. The solvent was removed by rotary evaporation to provide quantitatively the title product as deep-green crystals. NMR analysis of the crude product indicated that virtually pure product was formed. The compound darkened during workup and decomposed to starting material when it was purified by column chromatography (silica gel, hexane). FTIR (KBr) 1249, 1200, 985, 9432, 910, 841, 794, 538, 476 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.26 (d, J = 3.4 Hz, 1 H), 7.20 (d, J = 3.4 Hz, 1 H), 7.07 (d, J = 3.4 Hz, 1 H), 7.05 (d, J = 1.8 Hz, 2 H), 0.37 (s, 9 H), 0.31 (s, 9 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 142.63, 142.22, 139.82, 136.39, 135.95, 135.89 (2 C), 134.74, 124.85, 124.79, 124.37, 124.15, −0.14, −8.25.

2-Bromo-3-methylthiophene (28).[21] To a solution of 3-methylthiophene (7.20 g, 7.07 mL, 73.3 mmol) in dioxane (36.0 mL) was added dropwise with magnetic stirring bromine (11.72 g, 3.76 mL, 73.3 mmol) in dioxane (72.0 mL) at room temperature. The mixture was stirred at this temperature for 4 h and poured into water. The aqueous layer was extracted with ether, and the organic extracts were washed with 1 N sodium hydroxide and brine and dried over sodium sulfate. The solvent was removed by distillation, and the residue was distilled at 66−69 °C (17 mmHg) to provide 10.3 g (79%) of the title product as a colorless liquid. FTIR (neat) 2922, 1546, 1407, 1230, 991, 923, 827, 700 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.18 (d, J = 5.5 Hz, 1 H), 6.80 (d, J = 5.5 Hz, 1 H), 2.25 (s, 3 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 136.91, 129.02, 124.83, 109.13, 14.91.

2-(Trimethylsilyl)-3-methylthiophene (29).[21] To a solution of 2-bromo-3-methylthiophene (**28**) (3.54 g, 20 mmol) in ether (50.0 mL) was added dropwise *n*-butyllithium (9.4 mL, 20 mmol, 2.12 M in hexanes) at −78 °C. The mixture was stirred at this temperature for 20 min, chlorotrimethylsilane (3.26 g, 3.8 mL, 30 mmol) was added dropwise, and the resulting mixture was allowed to warm to room temperature and then poured into water. The aqueous layer was extracted with ether and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, hexane) to provide 3.29 g (96%) the title compound as a colorless liquid. FTIR (neat) 2957, 1392, 1251, 1099, 1028, 839, 756, 714 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.42 (d, J = 4.6 Hz, 1 H), 6.97 (d, J = 4.6 Hz, 1 H), 2.34 (s, 3 H), 0.32 (s, 9 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 144.60, 132.66, 131.83, 129.10, 16.43, −0.03.

2-(Trimethylsilyl)-3-methyl-5-(tributylstannyl)-thiophene (30).[21] To a solution of diisopropylamine (0.511 g, 0.71 mL, 5.05 mmol) in THF (5.0 mL) was added dropwise *n*-butyllithium (2.38 mL, 5.05 mmol, 2.12 M in hexanes) at −78 °C. The mixture was warmed to 0 °C for 10 min and recooled to −78 °C, and **29** (0.86 g, 5.05 mmol) in THF (5.0 mL) was added dropwise via cannula. The mixture was stirred at this temperature for 30 min, tributyltin chloride (1.64 g, 1.37 mL, 5.05 mmol) was added dropwise, and the mixture was allowed to warm to room temperature for 2 h and then poured into water. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel washed with 10% triethylamine in hexane, hexane eluent) to provide 1.97 g (85%) of the title product as a colorless liquid. FTIR (neat) 2957, 1464, 1376, 1316, 1250, 1053, 839, 754 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.04 (s, 1 H), 2.39 (s, 3 H), 1.58 (m, 6 H), 1.36 (m, 6 H), 1.10 (m, 6 H), 0.90 (t, 9 H), 0.35 (s, 9 H). ^{13}C NMR (20 MHz, $CDCl_3$) δ 145.45, 141.10, 140.23, 138.76, 28.99, 27.29, 16.12, 13.63, 10.86, 0.11.

3′,4-Dimethyl-5-(trimethylsilyl)-2,2′-bithiophene (31).[21] A flame-dried flask was charged with **30** (1.89 g, 4.11 mmol), **28** (0.728 g, 4.11 mmol), bis(triphenylphosphine)palladium(II) chloride (0.144 g, 0.20 mmol), triphenylphosphine (0.052 g, 0.20 mmol), and toluene (20.0 mL). The mixture was stirred at room temperature for 4 h, warmed to 100 °C for 4 h, and then poured into saturated ammonium chloride. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, hexane) to provide 0.727 g (66%) of the title product as a light-green liquid. FTIR (neat) 2955, 1401, 1250, 1057, 839, 755, 705 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.09 (d, J = 5.1 Hz, 1 H), 7.00 (s, 1 H), 6.85 (d, J = 5.1 Hz, 1 H), 2.38 (s, 3 H), 2.32 (s, 3 H), 0.34 (s, 9 H).

2-(Tributylstannyl)-3,4′-dimethyl-5′-(trimethylsilyl)-2,2′-bithiophene (32).[21] To a solution of diisopropylamine (0.536 g, 0.74 mL, 5.3 mmol) in THF (4.0 mL) was added dropwise *n*-butyllithium (2.5 mL, 5.3 mmol, 2.12 M in hexanes) at −78 °C. The mixture was warmed to 0 °C for 10 min and was recooled to −78 °C, **31** (1.42 g, 5.3 mmol) in THF (4.0 mL) was added dropwise via cannula, and the mixture was stirred at this temperature for 0.5 h. Tributyltin chloride (1.73 g, 1.44 mL, 5.3 mmol) was added dropwise, and the mixture was allowed to warm to room temperature for 2 h. The mixture was poured into water, and the aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was filtered through a silica plug washed with 10% triethylamine using hexane to provide 2.72 g (93%) of the title product as a light-green liquid. FTIR (neat) 2956, 1464, 1250, 1059, 839 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 6.99 (s, 1 H), 6.88 (s, 1 H), 2.39 (s, 3 H), 2.31 (s, 3 H), 1.53 (m, 6 H), 1.32 (m, 6 H), 1.07 (t, 6 H), 0.88 (t, 9 H), 0.33 (s, 9 H).

2-Iodo-5-(trimethylsilyl)thiophene (35).[21] To a solution of 2-bromo-5-(trimethylsilyl)thiophene (**18**) (17.96 g, 76.4 mmol) in ether (100 mL) at −78 °C was added dropwise *n*-butyllithium (30.81 mL, 76.4 mmol, 2.48 M in hexanes). The mixture was stirred at −78 °C for 1 h, iodine (19.39 g, 76.4 mmol) in ether (100 mL) was added dropwise, and the mixture was allowed to warm to room temperature. The solution was poured into water and extracted with ether. The organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation to provide 20.91 g (97%) of the title product as a pale-red liquid that was virtually pure by spectroscopic analysis and used without purification. FTIR (neat) 2956, 1397, 1250, 1202, 1067, 991, 841, 796, 756 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.24 (d, J = 3.40 Hz, 1 H), 6.90 (d, J = 3.44 Hz, 1 H) 0.28 (s, 9 H).

3-Butylthiophene.[1gg] To magnesium turnings (1.82 g, 75 mmol) in ether (20.0 mL) was added dropwise 1-bromobutane (10.3 g, 75 mmol) in ether (20.0 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 [1,3-bis(diphenylphosphino)propane]nickel(II) chloride (30 mg, 0.055 mmol) in ether (20.0 mL) at 0 °C. The mixture was then allowed to warm to room temperature and stirred 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 column chromatography (silica gel, hexane) to provide 5.93 g (85%) of the title product as a colorless liquid. FTIR (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 (p, J = 7.58 Hz, 2 H), 1.32 (sext, J = 7.38 Hz, 2 H), 0.92 (t, J = 7.32 Hz, 3 H).

2-Iodo-3-methylthiophene (36a).[21] To a solution of 3-methylthiophene (9.8 g, 100 mmol) in benzene (20.0 mL) were added (alternately, in small portion) mercuric oxide (20 g, 92.5 mmol, yellow) and iodine (26 g, 102.5 mmol) at 0 °C. The mixture was stirred at room temperature for 0.5 h, and the precipitate was filtered and washed with ether. The filtrate and washings were washed with aqueous sodium thiosulfate and dried over sodium sulfate. The solvent was removed by rotary evaporation to provide 21.15 g (94%) of the title product as a pale-red liquid which that virtually pure without further purification. FTIR (neat) 2918, 1396, 1227, 967, 916, 825, 703 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.33 (d, J = 5.4 Hz, 1 H), 6.74 (d, J = 5.4 Hz, 1 H), 2.21 (s, 3 H).

3-Butyl-2-iodothiophene (36b).[1gg] To a solution of 3-butylthiophene (5.89 g, 42 mmol) in benzene (10.0 mL) was alternately added mercuric oxide (8.41 g, 38.9 mmol, yellow) 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 column chromatography (silica gel, hexane) to provide 8.06 g (72%) of the title product as a colorless liquid. FTIR (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-Methyl-2-(5′-(trimethylsilyl)thienyl)thiophene (37a).[21] To magnesium turnings (0.93 g, 38.3 mmol) in ether (15.0 mL) was added dropwise 2-iodo-3-methylthiophene (**36a**) (5.71 g, 25.5 mmol) at 0 °C. The mixture was stirred for 2 h at room temperature and was transferred to a solution of 2-bromo-5-(trimethylsilyl)thiophene (**18**) (3.95 g, 17.0 mmol), and (1,3-bis(diphenylphosphino)propane)nickel(II) chloride (0.461 g, 0.85 mmol) in ether (10.0 mL) at 0 °C and then heated to reflux overnight. The mixture was poured into water and filtered through Celite. The aqueous layer was extracted with ether, and the organic extracts were washed brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by column chromatography (silica gel, hexane) to provide 3.46 g (81%) of the title product as a yellow liquid. FTIR (neat) 2955, 1443, 1250, 1071, 990, 840, 756, 707 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (AB_q, J = 3.4 Hz, $\Delta\nu$ = 5.4 Hz, 2 H), 7.11 (d, J = 5.1 Hz, 1 H), 6.86 (d, J = 5.1 Hz, 1 H), 2.39 (s, 3 H), 0.33 (s, 9 H).

2-(5′-(Trimethylsilyl)thienyl)-3-butylthiophene (37b).[1gg] To magnesium turnings (0.547 g, 22.5 mmol) in ether (15.0 mL) was added dropwise 3-butyl-2-iodothiophene (**36b**) (4.03 g, 15 mmol) at room temperature while an ice bath was used occasionally to maintain a mild reflux. The mixture was stirred at room temperature for 2 h and transferred via cannula to a solution of 2-bromo-5-(trimethylsilyl)thiophene (**18**) (2.35 g, 10.0 mmol) and [1,3-bis(diphenylphosphino)-propane]nickel(II) chloride (0.271 g, 0.5 mmol) at 0 °C. The mixture was allowed to warm to room temperature and stirred 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 column chromatography (silica gel, hexane) to provide 1.89 g (64%) of the title product as a colorless liquid which was estimated to be ca. 80% pure. FTIR (neat) 2956, 1444, 1250, 1069, 991, 840, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.15 (m, 3 H), 6.91 (d, J = 5.17 Hz, 1 H), 2.75 (t, J = 7.79 Hz, 2 H), 1.61 (p, J = 7.40 Hz, 2 H), 1.37 (sext, J = 7.43 Hz, 2 H), 0.91 (t, J = 7.30 Hz, 3 H).

5-Iodo-3-methyl-2-(5′-(trimethylsilyl)thienyl)thiophene (38a).[21] To a solution of diisopropylamine (0.401 g, 0.56 mL, 3.96 mmol) in THF (5.0 mL) was added dropwise *n*-butyllithium (1.60 mL, 3.96 mmol, 2.48 M in hexanes) at −78 °C. The mixture was warmed to 0 °C for 5 min and then recooled to −78 °C. 3-Methyl-2-(5′-(trimethylsilyl)thienyl)-thiophene (**37a**) (1.00 g, 3.96 mmol) in THF (50 mL) was added dropwise, and the solution stirred at −78 °C for 1 h. Iodine (1.01 g, 3.96 mmol) in THF (5.0 mL) was added dropwise, and the solution was allowed to warm to room temperature for 30 min. The mixture was poured into water, and the aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was virtually pure by spectroscopic analysis and used without purification. ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, J = 3.47 Hz, 1 H), 7.11 (d, J = 3.42 Hz, 1 H), 7.01 (s, 1 H), 2.34 (s, 3 H), 0.32 (s, 9 H).

2-(5′-(Trimethylsilyl)thienyl)-3-methyl-5-(trimethylstannyl)thiophene. To a solution of diisopropylamine (0.494 g, 0.68 mL, 4.88 mmol) in THF (5.0 mL) was added dropwise *n*-butyllithium (4.03 mL, 4.88 mmol, 1.21 M in hexanes) at −78 °C. The mixture was warmed to 0 °C for 10 min and then recooled to −78 °C. 2-(5′-(Trimethylsilyl)thienyl)-3-methylthiophene (**37a**) (0.822 g, 3.26 mmol) in THF (3.0 mL) was added dropwise via cannula. The mixture was stirred at this temperature for 2 h, and trimethyltin chloride (0.97 g, 4.88 mmol) in THF (3.0 mL) was added via cannula. The mixture was warmed to room temperature for 0.5 h and poured into water. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation to provide 1.35 g (100%) of the title product as a thick yellow oil. FTIR (neat) 2956, 1440, 1250, 1192, 1072, 991, 907, 840, 771 cm^{-1}. ^1H NMR (300 Hz, $CDCl_3$) δ 7.16 (s, 2 H), 6.94 (s, 1 H), 2.40 (s, 3 H), 0.35 (s, 9 H), 0.32 (s, 9 H).

3′,3″-Dimethyl-5-(trimethylsilyl)-2,2′:5′,2″-terthiophene (39a).[21] Method A: A flame-dried flask was charged with 2-(5′-(trimethylsilyl)thienyl)-3-methyl-5-(trimethylstannyl)thiophene (2.13 g, 5.13 mmol), 2-iodo-3-methylthiophene (**36a**) (1.72 g, 7.68 mmol), bis(triphenylphosphine)palladium(II) chloride (0.072 g, 0.103 mmol), and DMF (10.0 mL), and the mixture was stirred at room temperature for 40 h and then 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 column chromatography (silica gel, hexane) to provide 0.631 g (35%) of the title product as a thick light-green liquid.

Method B: To a solution of diisopropylamine (1.11 g, 1.54 mL, 11.0 mmol) in THF (10.0 mL) was added dropwise *n*-butyllithium (9.09 mL, 11.0 mmol, 1.21 M in hexanes) at −78 °C. The mixture was warmed to 0 °C for 10 min and then recooled to −78 °C. To this solution was added dropwise 2-(5′-(trimethylsilyl)thienyl)-3-methylthiophene (**37a**) (2.78 g, 11.0 mmol) in THF (10.0 mL), and the mixture was stirred at this temperature for 2 h. Iodine (2.79 g, 11.0 mmol) in THF (20.0 mL) was added dropwise, and the mixture was stirred at this temperature for 30 min and poured into water. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue, crude **38a**, was used directly for next reaction. To a solution of **38a**,

[1,3-bis(diphenylphosphino)propane]nickel(II) chloride (0.271 g, 0.5 mmol) in ether (10.0 mL) was added dropwise by syringe at 0 °C one-half of a solution of 2-(3-methylthienyl)magnesium iodide, made from 2-iodo-3-methylthiophene (**36a**) (3.36 g, 15.0 mmol) and magnesium (0.547 g, 22.5 mmol) in ether (10.0 mL). The mixture was stirred at room temperature overnight and then 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 column chromatography on silica gel (hexane) to provide 1.35 g (75%) of the title product as a thick light-green liquid along with 1.48 g of recovered starting material. FTIR (neat) 2954, 1448, 1250, 1075, 991, 840, 756, 707 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.18 (AB_q, J = 3.46 Hz, $\Delta\nu$ = 7.30 Hz, 2 H), 7.11 (d, J = 5.13 Hz, 1 H), 6.91 (s, 1 H), 6.86 (d, J = 5.13 Hz, 1 H), 2.40 (s, 3 H), 2.39 (s, 3 H), 0.33 (s, 9 H).

3′,3″-Dibutyl-5-(trimethylsilyl)-2,2′:5′,2″-terthiophene (39b).[1gg] To a solution of diisopropylamine (0.65 g, 0.90 mL, 6.42 mmol) in THF (6.0 mL) was added dropwise *n*-butyllithium (3.9 mL, 6.42 mmol, 2.5 M in hexanes) at −78 °C. The mixture was warmed to 0 °C for 10 min and recooled to −78 °C. To this solution was added dropwise 2-(5′-(trimethylsilyl)thienyl-3-butylthiophene (**37b**) (1.89 g, 6.42 mmol) in THF (6.0 mL), and the mixture was stirred at −78 °C for 2 h before slowly adding iodine (1.63 g, 6.42 mmol) in THF (10.0 mL). The mixture was allowed to warm to room temperature and stirred for 30 min before being 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 **38b** was used directly for the next reaction. 3-Butyl-2-thienylmagnesium iodide [made from 3-butyl-2-iodothiophene (**36b**) (2.56 g, 9.63 mmol) and magnesium (0.35 g, 14.4 mmol) in ether (10.0 mL)] was transferred into the solution of **38b** and (1,3-bis(diphenylphosphino)-propane)nickel(II) chloride (4 mg, 0.007 mmol) in ether (5.0 mL) at 0 °C. The mixture was allowed to warm to room temperature and was stirred overnight. The mixture was poured into water and filtered through Celite, and the aqueous layer was extracted with ether. The organic extracts were washed with brine and dried over magnesium sulfate, and the solvent was removed by rotary evaporation. The residue was purified by column chromatography on silica gel (hexane) to provide 1.22 g (44%) of the title product as a light-green thick liquid in ca. 90% purity. FTIR (neat) 2956, 1458, 1250, 991, 840, 756 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.17 (s, 2 H), 7.13 (d, J = 5.2 Hz, 1 H), 6.93 (s, 1 H), 6.90 (d, J = 5.2 Hz, 1 H), 2.74 (two overlapping t, J = 7.5 Hz, 4 H), 1.62 (two overlapping p, J = 8.5 Hz, 4 H), 1.39 (two overlapping sext, appearing as br sept, J = 7.5 Hz, 6 H), 0.93 (t, J = 7.35 Hz, 3 H), 0.92 (t, J = 7.29 Hz, 3 H), 0.33 (s, 9 H).

3,4′-Dimethyl-5-(tributylstannyl)-5″-(trimethylsilyl)-2,2′:5′,2″-terthiophene (40a).[21] To a solution of diisopropylamine (0.65 g, 0.90 mL, 6.43 mmol) in THF (10.0 mL) was added dropwise at −78 °C *n*-butyllithium (3.92 mL, 6.43 mmol, 1.64 M in hexanes). The mixture was warmed to 0 °C for 10 min and then recooled to −78 °C. 3′,3″-Dimethyl-5-(trimethylsilyl)-2,2′:5′,2″-terthiophene (**39a**) (2.24 g, 6.43 mmol) in THF (6.0 mL) was added dropwise via cannula. The mixture was stirred at −78 °C for 2 h, and tributyltin chloride (2.09 g, 1.74 mL, 6.65 mmol) was added dropwise. The mixture was warmed to room temperature for 0.5 h and poured into water. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed by reduced pressure to provide 3.98 g (97%) of the title product as a thick dark-yellow oil which is >95% pure by spectroscopic analysis. FTIR (neat) 2956, 1459, 1250, 1073, 992, 840, 756 cm^{-1}. ^1H NMR (300 Hz, $CDCl_3$) δ 7.17 (AB_q, J = 3.0 Hz, $\Delta\nu$ = 6.0 Hz, 2 H), 6.91 (s, 1 H), 6.89 (s, 1 H), 2.41 (s, 3 H), 2.39 (s, 3 H), 1.55 (m, 6 H), 1.34 (sext, J = 7.28 Hz, 6 H), 1.09 (m, 6 H), 0.89 (t, J = 7.28 Hz, 9 H), 0.32 (s, 9 H).

2-(Tributylstannyl)-4,4′-dibutyl-5″-(trimethylsilyl)-5,2′:5′,2″-terthiophene (40b).[1gg] To a solution of diisopropylamine (1.22 g, 2.8 mmol) in THF (3.0 mL) was added dropwise *n*-butyllithium (1.71 mL, 2.8 mmol, 1.64 M in hexanes) at −78 °C. The solution was warmed to 0 °C for 5 min and recooled to −78 °C. 3′,3″-Dibutyl-5-(trimethylsilyl)-2,2′:5′,2″-terthiophene (**39b**) in THF (2.0 mL) was added dropwise to the above solution via cannula, and the mixture was stirred at −78 °C for 1 h before the addition of tributyltin chloride (0.911 g, 2.8 mmol). The mixture was allowed to warm to room temperature for 20 min and poured into water. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure to afford 1.90 g (94%) of the title product as a thick light-yellow liquid which was used without further purification. FTIR (neat) 2956, 1464, 1250, 991, 840 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.16 (s, 2 H), 6.93 (s, 2 H), 2.77−2.72 (m, 4 H), 1.63−1.51 (m, 10 H), 1.41−1.22 (m, 10 H), 1.19−1.06 (m, 6 H), 0.95−0.87 (m, 15 H), 0.32 (s, 9 H).

2-(Trimethylstannyl)-4,4′-dimethyl-5″-(trimethylsilyl)-5,2′:5′,2″-terthiophene. To a solution of diisopropylamine (0.653 g, 0.90 mL, 6.65 mmol) in THF (10.0 mL) was added dropwise *n*-butyllithium (5.5 mL, 6.65 mmol, 1.21 M in hexanes) at −78 °C. The mixture was warmed to 0 °C for 10 min and then recooled to −78 °C. 3′,3″-Dimethyl-5-(trimethylsilyl)-2,2′:5′,2″-terthiophene (**39a**) (2.25 g, 6.65 mmol) in THF (6.0 mL) was added dropwise via cannula. The mixture was stirred at this temperature for 2 h, and trimethyltin chloride (1.33 g, 6.65 mmol) in THF (6.0 mL) was added via cannula. The mixture was warmed to room temperature for 0.5 h and poured into water. The aqueous layer was extracted with ether, and the organic extracts were washed with brine and dried over sodium sulfate. The solvent was removed under reduced pressure to provide 3.09 g (96%) of the title product as a thick dark-yellow oil. FTIR (neat) 2955, 1429, 1250, 1074, 991, 840, 757 cm^{-1}. ^1H NMR (300 Hz, $CDCl_3$) δ 7.17 (AB_q, J = 3.6 Hz, $\Delta\nu$ = 6.9 Hz, 2 H), 6.93 (s, 1 H), 6.90 (s, 1 H), 2.40 (s, 3 H), 2.39 (s, 3 H), 0.36 (s, 9 H), 0.32 (s, 9 H).

Spiroheptamer Compound 41.[1gg] A flame-dried flask was charged with **13** (0.054 g, 0.1 mmol), 3,4′-dimethyl-5-(tributylstannyl)-5″-(trimethylsilyl)-2,2′:5′,2″-terthiophene (**40a**)-(0.57 g, 0.90 mmol), tetrakis(triphenylphosphine)palladium(0) (0.0093g, 0.008 mmol), and toluene (1.00 mL). The mixture was heated at 40 °C for 2 h, then 60 °C for 2 h, and then at 100 °C (bath temp) overnight. The solvent was removed by rotary evaporation and the residue was washed with ethanol and then hexane to provide 140 mg (86%) of the title product as dark red crystals. Mp: 260 °C dec UV ($CHCl_3$) λ_{max} 456 nm, ϵ_{max} 2.94 × 10^4, tailing edge 545 nm. FTIR (KBr) 2950, 1132, 991, 839 cm^{-1}. ^1H NMR (500 MHz, $CDCl_3$) δ 7.19 ($^1/_2$ ABq, J = 2.5 Hz, 4 H), 7.15 ($^1/_2$ ABq, J = 2.5 Hz, 4 H), 6.99 (s, 4 H), 6.93 (s, 4 H), 2.40 (s, 12 H), 2.37 (s, 12 H), 2.33 (s, 8 H), 0.31 (s, 36 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 141.94, 141.22, 140.61, 134.82, 134.80, 134.60, 134.58, 134.25, 131.34, 130.78, 129.60, 128.64, 128.44, 126.77, 17.08, 16.12, 16.00, 0.31. FAB/MS (NBA) calcd relative isotopic intensities for $C_{80}H_{84}S_{14}Si_5$ (M^+): 1632 (64%), 1633 (80%), 1634 (100%), 1635 (83%), 1636 (83%), 1637 (40%), 1638 (23%). Found: 1632 (77%), 1633 (96%), 1634 (100%), 1635 (94%), 1636 (79%), 1637 (56%), 1638 (45%).

2-(5′-(Trimethylsilyl)thienyl)-3-butyl-5-(tributylstannyl)thiophene (42). To a solution of diisopropylamine (0.697 g, 0.965 mL, 6.89 mmol) in THF (5.0 mL) was added *n*-butyllithium (4.10 mL, 5.74 mmol, 1.4 M in hexanes) dropwise at −78 °C. The mixture was warmed to 0 °C for 5 min and recooled to −78 °C. **37b** (1.69 g, 5.74 mmol) in THF (5.0 mL) was added dropwise via cannula, and the mixture was stirred at −78 °C for 1 h. Tributyltin chloride (1.87 g, 1.56 mL, 5.74 mmol) was added, and the mixture was allowed to warm to room temperature for 30 min and then poured into water. The aqueous solution was extracted with ether, and the combined organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure to provide 3.18 g (95%) of the title product as a thick light-yellow liquid which was virtually pure and was used without further purification. FTIR (neat) 2956, 1464, 1414, 1377, 1250, 1206, 1072, 991, 840, 800, 756 cm^{-1}. ^1H NMR ($CDCl_3$, 300 MHz) δ 7.14 (ABq, J = 3.45 Hz, $\Delta\nu$ = 4.96 Hz, 2

H), 6.93 (s, 1 H), 2.77 (t, J = 7.84 Hz, 2 H), 1.70−1.50 (m, 2 H), 1.32 (sext, J = 7.28 Hz, 2 H), 1.09 (t, J = 8.08 Hz, 2 H), 0.89 (t, J = 7.27 Hz, 3 H), 0.31 (s, 9 H).

3-Ethyl-2-iodo-5,2′-bithiophene (43). To **38b** (4.97 g, 11.85 mmol) was added acetonitrile (35 mL), water (1 mL), and *p*-tolunenesulfonic acid (0.370 g, 2.37 mmol). The solution was heated to reflux for 4 h and poured into water, and the aqueous phase was extracted with ether. The combined organic phase was washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and gravity column chromatography (silica gel, hexane) afforded 2.63 g (64%) of the title compound which was ca. 85% pure as judged by ^{1}H NMR analysis. However, the material was used for the next step at that level of purity. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.29 (dd, J = 2.77 Hz, 1 H), 7.0 (m, 3 H), 2.68 (t, J = 7.70 Hz, 2 H), 1.55 (pent, J = 7.44 Hz, 2 H), 1.37 (sext, J = 7.30 Hz, 2 H), 0.89 (t, J = 7.29 Hz, 3 H).

3′,4″-Di-*n*-butyl-5-(trimethylsilyl)-2,2′:5′,2″:5″:2‴-quaterthiophene (44). A round bottom flask was charged with **42** (3.18 g, 5.45 mmol), **43** (2.11 g, 6.06 mmol), copper(I) iodide (0.023 g, 0.123 mmol), and tetrakis(triphenylphosphine)-palladium(0) (0.094 g, 0.082 mmol). The mixture was then degassed *in vacuo* followed by introducing nitrogen and DMF (5.0 mL). The mixture was stirred at room temperature overnight and then heated to 75−80 °C (oil temp) overnight. The solution was poured into saturated ammonium chloride. The aqueous solution was extracted with ether, and the combined organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by gravity chromatography (silica gel, hexane) to provide 1.74 g (62%) of the title product as a light-yellow liquid. FTIR (neat) 3068, 2955, 2858, 1507, 1458, 1378, 1250, 1207, 1076, 991, 840, 756, 692 cm^{-1}. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 7.28 (d, J = 5.10 Hz, 1 H), 7.16 (s, 2 H), 7.11 (d, J = 3.41 Hz, 1 H), 7.05 (dd, J = 5.14, 3.57 Hz, 1 H), 6.98 (d, J = 1.05 Hz, 2 H), 2.73 (overlapping t, J = 7.70 Hz, 4 H), 1.65 (m, 4 H), 1.40 (m, 4 H), 0.96−0.87 (overlapping t, J = 7.30 Hz, 6 H), 0.33 (s, 9 H).

3′,4″,4‴-Tri-*n*-butyl-2-(trimethylsilyl)-2,2′:5′,2″:5″,2‴:5‴,2⁗:5⁗,2′′′′-sexithiophene (46). To a solution of diisopropylamine (0.410 g, 0.60 mL, 4.06 mmol) in THF (5.0 mL) was added dropwise *n*-butyllithium (1.35 mL, 3.38 mmol, 2.5 M in hexanes) at −78 °C. The mixture was warmed to 0 °C for 5 min and recooled to −78 °C. Tetramer **44** (1.74 g, 3.38 mmol) in THF (10.0 mL) was added dropwise via cannula. The mixture was warmed to 0 °C for 5 min and recooled to −78 °C, and tributyltin chloride (1.10 g, 0.92 mL, 3.38 mmol) was added in one portion. The mixture was allowed to warm to room temperature for 10 min and poured into water. The aqueous solution was extracted with ether, and the combined organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed under reduced pressure, and the crude product **45** was used directly for the next reaction. The crude **45** (assumed to be 3.38 mmol), **43** (1.30 g, ca. 3.72 mmol), tetrakis(triphenylphosphine)palladium(0) (0.059 g, 0.051 mmol), and copper(I) iodide (0.015 g, 0.077 mmol) were mixed in DMF (3.0 mL, sparged with N_2) under N_2 at room temperature. The mixture was stirred at room temperature overnight and then heated to 75−80 °C (oil temp) overnight and poured into water. The mixture was filtered through Celite, and the aqueous solution was extracted with ether. The combined organic extracts were washed with brine and dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by gravity chromatography (silica gel, hexane) to provide 1.09 g (44% from **44**) of the title product as a thick light-red liquid. FTIR (neat) 3066, 2955, 2858, 1503, 1456, 1378, 1250, 1214, 1077, 990, 838, 794, 756, 692 cm^{-1}. ^{1}H NMR (300 MHz, C_6D_6) δ 7.27 (d, J = 3.45 Hz, 1 H), 7.07 (d, J = 3.45 Hz, 1 H), 7.06 (s, 1 H), 7.05 (dd, J = 3.58, 1.16 Hz, 1 H), 7.03 (s, 1 H), 6.98 (s, 1 H), 6.96 (ABq, J = 3.79 Hz, $\Delta\nu$ = 6.56 Hz, 2 H), 6.83 (dd, J = 5.18, 1.18 Hz, 1 H), 6.72 (dd, J = 5.18, 3.56 Hz, 1 H), 2.72 (t, J = 7.81 Hz, 2 H), 2.67 (t, J = 7.81 Hz, 2 H), 2.62 (t, J = 7.81 Hz, 2 H), 1.60−1.40 (m, 6 H), 1.29 (overlap pent, J = 7.40 Hz, 6 H), 0.85 (t, J = 7.46 Hz, 3 H), 0.84 (t, J = 7.28 Hz, 3 H), 0.82 (t, J = 7.47 Hz, 3 H), 0.25 (s, 9 H). ^{13}C NMR (75 MHz, C_6D_6) δ 141.75, 140.65, 140.56, 140.53, 140.41, 137.19, 136.27, 135.46, 135.34, 135.27, 134.98, 128.33, 128.01, 127.68, 127.52, 127.42, 126.94, 128.84, 126.79, 126.66, 126.14, 126.09, 125.50, 124.34, 32.95, 32.92, 32.84, 29.71, 29.58, 29.42, 23.09, 23.05, 23.01, 14.24, 14.18 (2 C), −0.04.

3-Ethylthiophene (48).[1ff] To magnesium turnings (10.96 g, 450 mmol) in ether (150 mL) was added dropwise 1-bromoethane (59.42 g, 40 mL, 545 mmol) at room temperature, and an ice bath was used occassionaly 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 (49.60 g, 304 mmol) and (1,3-bis(diphenylphosphino)propane)-nickel(II) chloride (0.18 g, 0.34 mmol) in ether (150 mL) at −78 °C. The mixture was then slowly allowed to warm to room temperature. This solution was then stirred 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, and the residue was purified by flash chromatography (silica gel, hexane) to afford 30.39 g (89%) of the title compound as a light brown liquid. FTIR (neat) 2965, 2931, 1461, 1410, 1317, 857, 769 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.23 (m, 1 H), 6.93 (m, 2 H), 2.65 (q, J = 7.55 Hz, 2 H), 1.24 (t, J = 7.56 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 144.68, 128.02, 125.18, 119.21, 23.45, 14.74.

3-Ethyl-2-iodothiophene (49).[1ff] To a solution of 3-ethylthiophene (**48**) (20.19 g, 180 mmol) in benzene (100 mL) at 0 °C was added mercuric oxide (38.98 g, 180 mmol). Iodine (50.27 g, 198 mmol) in benzene (300 mL) and dichloromethane (50 mL) was added dropwise to the solution at 0 °C. The mixture was stirred at room temperature overnight before filtration through Celite. The filtered solution 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. The residue was purified by flash chromatography (silica gel, hexane) to afford 36.01 g (84%) of the title product as a faint yellow liquid. FTIR (neat) 3102, 2966, 2930, 2873, 1459, 1399, 963, 893, 826, 717, 632 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.37 (d, J = 5.44 Hz, 1 H), 6.76 (d, J = 5.47 Hz, 1 H), 2.56 (q, J = 7.58 Hz, 2 H), 1.17 (t, J = 7.58 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 148.38, 130.54, 127.57, 73.63, 25.69, 14.61. HRMS calcd for C_6H_7IS 237.9313, found 237.9306.

3-Ethyl-2-((trimethylsilyl)ethynyl)thiophene (50).[1ff] To a solution of **49** (14.79 g, 63 mmol) in THF (50 mL) were added diisopropylamine (9.56 g, 13.2 mL, 94.5 mmol), (trimethylsilyl)-acetylene (6.81 g, 9.8 mL, 69.3 mmol), bis(triphenylphosphine)-palladium(II) chloride (2.23 g, 3.15 mmol), and copper(I) iodide (0.30 g, 1.57 mmol) (the two catalysts were degassed *in vacuo* for 30 min immediately before use). The reaction was stirred overnight before being poured into water. The aqueous layer was extracted with dichloromethane, and the organic extracts were washed with brine. The dichloromethane layers were dried over magnesium sulfate. The solvent was removed by rotary evaportation, and the residue was purified by gravity chromatography (silica gel, hexane) to provide 12.71 g (97%) of the title product as an orange-brown liquid. UV (dichloromethane) λ_{max} 278 nm. FTIR (neat) 2965, 2144, 1526, 1461, 1420, 1321, 1250, 1184, 1084, 1056, 903, 843, 759, 724, 670, 650 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.11 (d, J = 5.15 Hz, 1 H), 6.83 (d, J = 5.15 Hz,1 H), 2.70 (q, J = 7.60 Hz, 2 H), 1.21 (t, J = 7.60 Hz, 3 H), 0.23 (s, 9 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.31, 127.94, 126.44, 118.33, 101.16, 97.87, 23.25, 14.87, 0.44. HRMS calcd for $C_{11}H_{16}SSi$ 208.0742, found 208.0743.

3-Ethyl-5-iodo-2-((trimethylsilyl)ethynyl)thiophene (51).[1ff] To a solution of diisopropylamine (12.14 g, 17 mL, 120 mmol) in ether (100 mL) at −78 °C was added dropwise *n*-butyllithium (74 mL, 110 mmol, 1.49 M in hexanes). The mixture was warmed to 0 °C for 30 min and then recooled to −78 °C. **50** (11.49 g, 55 mmol) in ether (50 mL) at room temperature was then added dropwise, and the solution was warmed from −78 °C to 0 °C for 10 min. Next, the solution was recooled to −78 °C. While at −78 °C, iodine (30.52 g, 120 mmol) in ether (150 mL) was added via cannula, and the

solution was allowed to warm up to room temperature overnight. The mixture was quenched with water, and the aqueous layer was extracted with ether. The organic extracts were washed with brine and aqueous sodium thiosulfate. The ether layers were dried over magnesium sulfate. The solvent was removed by rotary evaportation, and the residue was purified by flash chromatography (silica gel, hexane) to provide 17.20 g (93%) of the title product as a yellow liquid that darkened upon standing. FTIR (neat) 2965, 2141, 1526, 1460, 1411, 1250, 1191, 1056, 950, 843, 759, 685 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 6.98 (s, 1 H), 2.65 (q, J = 7.56 Hz, 2 H), 1.17 (t, J = 7.60 Hz, 3 H), 0.22 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.40, 137.48, 124.07, 102.82, 95.92, 73.96, 22.59, 14.37, −0.06. HRMS calcd for $C_{11}H_{15}ISSi$ 333.9708, found 333.9697.

3-Ethyl-2-ethynylthiophene (52).[1ff] To a solution of **50** (12.50 g, 60 mmol) in methanol (60 mL) was added potassium carbonate (24.89 g, 180 mmol). The solution was allowed to stir for 4.5 h before being poured into water. The aqueous layer was extracted with dichloromethane, 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 8.17 g (99%) of the title compound as a light brown liquid. FTIR (neat) 3299, 3105, 2968, 2934, 2100, 1528, 1460, 1418, 1157, 1056, 903, 837, 728, 659 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.14 (d, J = 5.16 Hz, 1 H), 6.86 (d, J = 5.17 Hz, 1 H), 3.42 (s, 1 H), 2.72 (q, J = 7.60 Hz, 2 H), 1.21 (t, J = 7.61 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.33, 127.59, 126.32, 116.65, 83.26, 76.64, 22.74, 14.60. LRMS calcd for C_8H_8S 136, found 136.

Dimer 53.[1ff] To a solution of **51** (3.35 g, 10 mmol) in THF (15 mL) were added diisopropylamine (1.51 g, 2.1 mL, 15 mmol), **52** (1.28 g, 9.54 mmol), bis(triphenylphosphine)palladium(II) chloride (0.35 g, 0.50 mmol), and copper iodide (0.05 g, 0.28 mmol) (the two catalysts were degassed *in vacuo* for 30 min immediately before use). The reaction was allowed to stir for 2 d before being poured into water. The aqueous layer was extracted with dichloromethane, and the organic extracts were washed with brine. The dichloromethane layers were dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by gravity chromatography (silica gel, hexane) to provide 2.95 g (90%) of the title compound as a medium yellow liquid. UV (dichloromethane) λ_{max} 348 nm. FTIR (neat) 3103, 2967, 2193, 2141, 1519, 1461, 1412, 1322, 1249, 1195, 1061, 903, 857, 760, 735, 633 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.19 (d, J = 5.16 Hz, 1 H), 6.98 (s, 1 H), 6.89 (d, J = 5.17 Hz, 1 H), 2.74 (q, J = 7.60 Hz, 2 H), 2.65 (q, J = 7.59 Hz, 2 H), 1.23 (t, J = 7.62 Hz, 3 H), 1.21 (t, J = 7.67 Hz, 3 H), 0.24 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.86, 149.78, 132.03, 127.87, 126.92, 123.07, 119.55, 117.30, 102.33, 96.75, 88.32, 86.49, 23.01, 22.88, 14.72, 14.35, −0.03. HRMS calcd for $C_{19}H_{22}S_2Si$ 342.0932, found 342.0929.

Iodinated Dimer 54.[1ff] To a solution of diisopropylamine (0.16 g, 0.22 mL, 1.6 mmol) in THF (2.5 mL) at −78 °C was added dropwise *n*-butyllithium (0.94 mL, 1.5 mmol, 1.6 M in hexanes). The solution was warmed to 0 °C for 10 min and then recooled to −78 °C. **53** (0.34 g, 1.0 mmol) in THF (5 mL) was then added dropwise, and the solution was stirred at −78 °C for 10 min. While still at −78 °C, iodine (0.41 g, 1.6 mmol) in THF (2.5 mL) was added via cannula and the solution was allowed to stir at −78 °C for 2 h. The mixture was quenched with water at −78 °C, and the aqueous layer was extracted with ether. The organic extracts were washed with brine and aqueous sodium thiosulfate. The ether layers were dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by gravity column chromatography (silica gel, hexane) to provide 0.39 g (84%) of the title product as a yellow liquid which darkened upon exposure to air. FTIR (neat) 2966, 2141, 1518, 1460, 1408, 1383, 1321, 1249, 1196, 1058, 987, 950, 843, 759, 696 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.03 (s, 1 H), 6.98 (s, 1 H), 2.69 (q, J = 7.59 Hz, 2 H), 2.65 (q, J = 7.59 Hz, 2 H), 1.20 (t, J = 7.60 Hz, 6 H), 0.24 (s, 9 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 151.17, 149.83, 137.76, 132.30, 123.42, 122.52, 119.99, 102.61, 96.63, 90.01, 85.05, 74.88, 22.84, 22.74, 14.60, 14.30, −0.05. HRMS calcd for $C_{19}H_{21}IS_2Si$ 467.9899, found 467.9895.

Protodesilylated Dimer 55.[1ff] To a solution of **53** (7.41 g, 21.6 mmol) in methanol (20 mL) was added potassium carbonate (9.17 g, 66.3 mmol). The solution was allowed to stir for 5 h before being poured into water. The aqueous layer was extracted with dichloromethane, 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 5.84 g (100%) of the title compound as a brown liquid. FTIR (neat) 3298, 3103, 2968, 2933, 2874, 2193, 2097, 1459, 1061, 902, 836 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, J = 5.17 Hz, 1 H), 7.01 (s, 1 H), 6.90 (d, J = 5.17 Hz, 1 H), 3.48 (s, 1 H), 2.75 (q, J = 7.60 Hz, 2 H), 2.69 (q, J = 7.59 Hz, 2 H), 1.25 (t, J = 7.62 Hz, 3 H), 1.22 (t, J = 7.64 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.24, 149.86, 131.97, 127.86, 126.97, 123.51, 118.24, 117.20, 88.09, 86.53, 84.31, 76.14, 22.99, 22.79, 14.67, 14.48.

Tetramer 56.[1ff] To a solution of **54** (0.90 g, 1.92 mmol) in THF (5 mL) was added **55** (0.69 g, 2.55 mmol), diisopropylamine (0.30 g, 0.42 mL, 3.0 mmol), bis(triphenylphosphine)-palladium(II) chloride (0.05 g, 0.07 mmol), and copper iodide (0.01 g, 0.04 mmol) (the two catalysts were degassed *in vacuo* for 30 min immediately before use). The reaction was allowed to stir for 1 d. The reaction was quenched with water, and the aqueous layer was extracted with dichloromethane. The organic extracts were washed with brine. The organic layers were dried over magnesium sulfate. The solvent was removed by rotary evaportaion, and the residue was purified by gravity chromatography (silica gel, hexane) to provide 1.02 g (87%) of the title product as a fluorescent yellow liquid which darkened upon exposure to the air. UV (dichloromethane) λ_{max} 404 nm. FTIR (neat) 2967, 2873, 2185, 2140, 1459, 1250, 1190, 1062, 902, 845, 760 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 5.17 Hz, 1 H), 7.05 (s, 1 H), 7.04 (s, 1 H), 7.01 (s, 1 H), 6.90 (d, J = 5.16 Hz, 1 H), 2.69 (10 line m, 8 H), 1.24 (t, J = 7.64 Hz, 6 H), 1.21 (t , J = 7.71 Hz, 6 H), 0.25 (s, 9 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 149.92, 149.85, 149.63, 149.61, 132.56, 132.40, 132.25, 127.89, 127.02, 124.00, 123.44, 122.58, 120.06, 119.39, 118.91, 117.28, 102.68, 96.66, 89.72, 89.44, 88.29, 87.19, 86.71, 86.03, 23.04, 22.88, 22.74, 14.73, 14.58, 14.34, 14.21, −0.04. HRMS calcd for $C_{35}H_{34}S_4Si$ 610.1313, found 610.1303.

Protodesilylated Tetramer 57.[1ff] To a solution of **56** (4.47 g, 7.3 mmol) in methanol (5 mL) and dichloromethane (5 mL) was added potassium carbonate (3.05 g, 21.9 mmol). The solution was allowed to stir for 6 h before being poured into water. The aqueous layer was extracted with dichloromethane, 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 3.92 g (100%) of the title compound as a yellow-brown liquid which had to be used immediately due to its instability in air. FTIR (neat) 3298, 2967, 2932, 2182, 2097, 1459, 1189, 1061, 902, 843 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.20 (d, J = 5.17 Hz, 1 H), 7.05 (s, 1 H), 7.03 (s, 1 H), 7.02 (s, 1 H), 6.89 (d, J = 5.16 Hz, 1 H), 3.48 (s, 1 H), 2.71 (9 line m, 8H), 1.24 (t, J = 7.61 Hz, 3 H), 1.24 (t, J = 7.57 Hz, 6 H), 1.21 (t, J = 7.62 Hz, 3 H). ^{13}C NMR (100 MHz, $CDCl_3$) δ 150.30, 149.85, 149.68, 149.63, 132.53, 132.33, 127.86, 126.97, 123.96, 123.49, 123.00, 119.21, 118.83, 118.69, 117.22, 89.38, 89.32, 88.22, 87.12, 86.68, 86.00, 84.51, 76.02, 22.97, 22.75, 14.65, 14.49, 14.48, 14.44.

1-Bromo-4-(trimethylsilyl)benzene.[29] To a solution of 1,4-dibromobenzene (12.7 g, 50.0 mmol) in ether (100 mL) was added at −78 °C *n*-butyllithium (20.04 mL, 50.1 mmol, 2.5 M in hexanes) over 20 min. The solution was stirred for 1 h at −78 °C, and chlorotrimethylsilane (6.98 mL, 55.0 mmol) was added over 10 min. The solution was warmed to room temperature for 30 min and poured into water. The aqueous layer was extracted with ether (3 × 10 mL), and the combined organic layers were washed with brine and dried over magnesium sulfate. No further purification was needed to afford 9.8 g (86%) of the the title compound as a clear colorless oil. FTIR (neat) 2956, 1574, 1479, 1376, 1251, 1106, 1067, 1012,

(29) Stephens, E. B.; Kinsey, K. E.; Davis, J. F.; Tour, J. M. *Macromolecules* **1993**, *26*, 3519.

841 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.47 (d, J = 8.3 Hz, 2 H), 7.36 (d, J = 8.3 Hz, 2 H), 0.24 (s, 9 H).

2,2′,7,7′-Tetrakis(4″-methylphenyl)-9,9′-spirobifluorene (59). To a solution of 4-bromotoluene (1.97 mL, 16 mmol) in ether (30 mL) was added at −78 °C *tert*-butyllithium (19.8 mL, 33.6 mmol, 1.7 M in pentane). The solution was stirred at −78 °C for 1 h and transferred by use of a cannula into annhydrous zinc chloride (3.05 g, 22.4 mmol) in THF (20 mL) at room temperature. The resulting slurry was stirred for 1 h at room temperature and then transferred via cannula into tetrakis(triphenylphosphine)palladium(0) (made from tris(dibenzylideneacetone)bispalladium(0) chloroform complex (0.03 g, 0.03 mmol) and triphenylphosphine (0.052 g, 0.2 mmol) in THF) and 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene (**17**) (0.632 g, 1.0 mmol) in THF (10 mL). The solution was heated to 55 °C for 16 h and cooled to room temperature. The solution was poured into water, and the aqueous layer was extracted with chloroform (3 × 5 mL). The combined organic layers were washed with 3 N hydrochloric acid and water and dried over magnesium sulfate. The solvent was removed, the resulting black solid was dissolved in dichloromethane (10 mL) and filtered through a plug of silica gel, and the solvent was removed once again. The resulting solid was rinsed with hexane (3 × 5 mL) and the hexane decanted. The solid was purified by flash chromatography (silica gel, 2:1 chloroform:hexane) to yield 0.47 g (70%) of the title compound as a white solid. FTIR (KBr) 3020, 2917, 1517, 1464, 1246, 1018, 806 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.89 (d, J = 7.9 Hz, 4 H), 7.60 (d, J = 7.9 Hz, 4 H), 7.32 (d, J = 8.1 Hz, 8 H), 7.09 (d, J = 8.0 Hz, 8 H), 6.97 (s, 4 H), 2.28 (s, 12 H). HRMS calcd for $C_{53}H_{40}$ 676.3130, found 676.3134.

2,2′,7,7′-Tetrakis(4″-(trimethylsilyl)phenyl)-9,9′-spirobifluorene (60).[1hh] To a solution of 1-bromo-4-(trimethylsilyl)benzene (1.88 g, 8.2 mmol) in ether (15 mL) was added at −78 °C *tert*-butyllithium (10.1 mL, 17.2 mmol, 1.7 M in pentane). The solution was stirred at −78 °C for 1 h and transfered via cannula into anhydrous zinc chloride (1.56 g, 11.5 mmol) in THF (10 mL) at room temperature. The resulting slurry was stirred for 1 h at room temperature and then transfered via cannula into tetrakis(triphenylphosphine)-palladium(0) (made from tris(dibenzylideneacetone)bispalladium(0) chloroform complex (15 mg, 0.014 mmol) and triphenylphosphine (26 mg, 0.1 mmol) in THF) and 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene (**17**) (0.312 g, 0.5 mmol) in THF (5 mL). The solution was heated to 55 °C for 16 h and cooled to room temperature. The solution was poured into water, and the aqueous layer was extracted with chloroform (3 × 5 mL). The combined organic layers rinsed with 3 N hydrochloric acid, aqueous sodium bicarbonate, and brine and dried over magnesium sulfate. The solvent was removed, and the resulting black solid was dissolved in dichloromethane (10 mL) and filtered through a plug of silica gel, and the solvent was removed once again. The resulting solid was rinsed with hexane (3 × 5 mL) and the hexane decanted off to afford 0.18 g (40%) of the title compound as a white solid. FTIR (KBr) 2954, 1598, 1464, 1385, 1248, 1112, 850, 808 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.91 (d, J = 8.0 Hz, 4 H), 7.61 (d, J = 7.9 Hz, 4 H), 7.45 ($^1/_2$ABq, J = 8.3 Hz, 8 H), 7.40 ($^1/_2$ABq, J = 8.8 Hz, 8 H), 6.98 (s, 4 H), 0.20 (s, 36 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.2, 141.8, 141.5, 141.2, 139.6, 134.1, 127.4, 126.9, 123.5, 120.8, 66.6, −0.7. HRMS calcd for $C_{61}H_{64}Si_4$ 908.4085, found 908.4102.

2,2′,7,7′-Tetrakis(4,4′-dibutyl-5″-(trimethylsilyl)-5,2′:5′,2″-terthiophene)-9,9′-spirobifluorene (61).[1hh] To a solution of 2,2′,7,7′-tetrabromo-9,9′-spirobifluorene (**17**) (0.063 g, 0.1 mmol) and 2-(tri-*n*-butylstannyl)-4,4′-di-*n*-butyl-5″-(trimethylsilyl)-5,2′:5′,2″-terthiophene (**40b**) (0.65 g, 0.9 mmol) in toluene (1 mL) under a nitrogen atmosphere was added tetrakis(triphenylphosphine)palladium(0) (9.3 mg, 0.008 mmol). The reaction was heated to 100 °C for 2.5 days and then cooled to room temperature. The reaction was poured into water, and the aqueous layer was extracted with dichloromethane (3 × 10 mL). The organic layer was dried over magnesium sulfate, and the product was purified by flash chromatography (silica gel, 9:1 hexane:dichloromethane) and dried *in vacuo* to afford 0.123 g (60%) of the title compound as a bright orange solid. UV ($CHCl_3$) λ_{max} 418 nm, tailing edge 495 nm. FTIR (thin film) 2955, 2927, 1458, 1250, 990 cm^{-1}. ^{1}H NMR (500 MHz, $CDCl_3$) δ 7.86 (d, J = 7.9 Hz, 4 H), 7.65 (dd, J = 8.1, 1.6 Hz, 4 H), 7.14 ($^1/_2$ ABq, J = 3.4 Hz, 4 H), 7.13 ($^1/_2$ ABq, J = 3.4 Hz, 4 H), 6.98 (s, 4 H), 6.95 (d, J = 1.4 Hz, 4 H), 6.89 (s, 4 H), 2.71 (t, J = 7.7 Hz, 8 H), 2.67 (t, J = 8.1 Hz, 8 H), 1.65−1.52 (m, 16 H), 1.36 (sext, J = 7.7 Hz, 16 H), 0.91 (t, J = 7.5 Hz, 12 H), 0.87 (t, J = 7.4 Hz, 12 H), 0.31 (s, 36 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 149.9, 141.8, 141.6, 141.2, 140.8, 140.0, 134.8, 134.47, 134.45, 131.0, 130.7, 128.8, 127.3, 126.9, 126.2, 121.4, 121.1, 66.4, 33.2, 33.1, 29.8, 29.5, 23.2, 23.1, 14.39, 14.38, 0.4. FAB/MS in (ONPOE) calcd relative isotopic intensities for $C_{117}H_{136}S_{12}Si_4$ (M^+): 2037 (51%), 2038 (83%), 2039 (100%), 2040 (89%), 2041 (67%), 2042 (43%), 2043 (25%), 2044 (13%), 2045 (6%). Found: 2037 (61%), 2038 (88%), 2039 (100%), 2040 (93%), 2041 (72%), 2042 (50%), 2043 (34%), 2044 (21%), 2045 (11%). Anal. Calcd for $C_{117}H_{136}S_{12}Si_4$: C, 68.96; H, 6.68. Found: C, 68.14; H, 6.86.

2,2′,7,7′-Tetraiodo-9,9′-spirobifluorene (62). To a solution of 9,9′-spirobifluorene (0.32 g, 1.0 mmol) in acetic acid (5 mL) and water (0.2 mL) at 80 °C were added concentrated sulfuric acid (0.06 mL), iodic acid (0.28 g, 1.6 mmol), and iodine (0.81 g, 3.2 mmol). The solution was stirred at 80 °C for 3 h, and the resulting solid was filtered and washed with ethanol:benzene (3:1) to afford 0.69 g (84%) of the title compound as a white solid. FTIR (KBr) 3448, 1448, 1391, 1122, 1004, 809 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.71 (dd, J = 8.1, 1.6 Hz, 4 H), 7.53 (d, J = 8.1 Hz, 4 H), 6.98 (d, J = 1.4 Hz, 4 H).

1-(Trimethylsilyl)-2-(2′-thienyl)acetylene. To a solution of 2-bromothiophene (1.63 g, 0.97 mL, 10 mmol) in THF (10 mL) were added diisopropylamine (1.14 g, 1.58 mL, 11.2 mmol), (trimethylsilyl)acetylene (1.17 g, 1.69 mL, 12 mmol), bis(triphenylphosphino)palladium(II) chloride (0.250 g, 0.36 mmol), and copper iodide (0.028 g, 0.15 mmol). The reaction was stirred overnight before being poured into water. The aqueous layer was extracted with dichloromethane, and the organic extracts were washed with brine. The dichloromethane layers were dried over sodium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by plug filtration through silica gel (hexane) to provide 1.71 g (95%) of the title product as a medium brown liquid. FTIR (neat) 2959, 2147, 1514, 1421, 1250, 1164, 1140, 1076, 845, 760, 700, 642 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.21 (d, J = 4.37 Hz, 2 H), 6.93 (app t, J = 4.41 Hz, 1 H), 0.23 (s, 9 H).

2-Ethynylthiophene. To 1-(trimethylsilyl)-2-(2′-thienyl)-acetylene (36.0 g, 200 mmol) in methanol (100 mL) was added potassium carbonate (55.3 g, 400 mmol). The reaction was stirred at room temperature for 30 min. The reaction was poured into water, and the aqueous layer was extracted with ether. The organic layer was dried over magnesium sulfate, and the solvent was removed by distillation. The product was distilled with a short path condensor to afford 21.4 g (98%) of the title compound as a clear colorless oil. FTIR (neat) 3294, 3108, 2957, 2106, 1419, 1228, 1040, 853 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.27−7.26 (m, 2 H), 6.96 (ABq, J = 5.2, 5.2 Hz, 1 H), 3.32 (s, 1 H), 0.05 (s, 9 H).

2,2′,7,7′-Tetrakis(1″-(2‴-thienyl)ethynyl)-9,9′-spirobifluorene (63). To an oven-dried flask containing bis(dibenzylideneacetone)bispalladium(0) (11.4 mg, 0.02 mmol), triphenylphosphine (26.2 mg, 0.1 mmol), copper(I) iodide (7.6 mg, 0.04 mmol), **62** (82 mg, 0.1 mmol), and 2-ethynylthiophene (0.43 g, 4.0 mmol) in THF (1 mL) was added diisopropylamine (1 mL). The reaction was heated to 60 °C for 48 h and poured into water. The organic layer was extracted with dichloromethane (3 × 10 mL), and the organic layer was dried over magnesium sulfate. The crude sample was purified by flash chromatography (silica gel, 3:1 hexane:dichloromethane) to yield 72.1 mg (97%) of the title compound as a brown solid. FTIR (KBr) 2925, 2198, 1465, 1414, 1218 cm^{-1}. ^{1}H NMR (300 MHz, $CDCl_3$) δ 7.81 (d, J = 8.0 Hz, 4 H), 7.55 (dd, J = 7.9, 1.4 Hz, 4 H), 7.21 (dd, J = 5.1, 1.1 Hz, 4 H), 7.15 (dd, J = 3.6, 1.1 Hz, 4 H), 6.93 (dd, J = 5.1, 3.7 Hz, 4 H). ^{13}C NMR (75 MHz, $CDCl_3$) δ 148.2, 141.2, 131.9, 131.7, 127.4, 127.1, 123.1, 122.8, 120.5, 96.1, 93.1, 83.6, 65.2. HRMS calcd for $C_{49}H_{24}S_4$ 740.0761, found 740.0766.

Compound 64. 62 (0.12 g, 0.15 mmol) was added to a solution of **57** (0.38 g, 4.0 mmol) in THF (1 mL). Diisopropylamine (0.10 g, 1 mL, 7.14 mmol), bis(triphenylphosphino)-palladium(II) chloride (0.03 g, 0.04 mmol), and copper iodide (0.01 g, 0.05 mmol) (both metal catalysts were degassed in a vacuum chamber for 2 h immediately before the addition) were then added. The reaction was allowed to stir at room temperature for 2 d. The reaction was then quenched with water, and the organic layer was extracted with dichloromethane (3×). The combined organic extracts were washed with brine. The organic phase was dried over magnesium sulfate. The solvent was removed by rotary evaporation, and the residue was purified by flash chromatography on silica gel. The eluent was initially hexane and then increased to 9:1 hexane−dichloromethane and finally to 7:3 hexane−dichloromethane to provide the title product (0.29 g, 78%) as a red-orange solid. UV (dichloromethane) λ_{max} 422 nm. FTIR (neat) 2969, 2934, 2875, 2248, 2188, 1461, 907, 734 cm^{-1}. ^1H NMR (300 MHz, $CDCl_3$) δ 7.82 (d, J = 7.92 Hz, 4 H), 7.54 (d, J = 7.85 Hz, 4 H), 7.20 (d, J = 5.12 Hz, 4 H), 7.04 (s, 4 H), 7.03 (s, 4 H), 7.01 (s, 4 H), 6.90 (d, J = 5.17 Hz, 4 H), 6.89 (s, 4 H), 2.70 (overlapping q, J = 7.6 Hz, 32 H), 1.22 (overlapping t, J = 7.6 Hz, 48 H). ^{13}C NMR (125 MHz, $CDCl_3$) δ 150.24, 150.00, 149.94, 149.46, 148.51, 141.63, 132.93, 132.63, 132.32, 128.27, 127.37, 127.17, 124.34, 123.78, 123.24, 123.14, 120.98, 120.29, 119.80, 119.31, 117.66, 97.17, 90.15, 89.83, 88.67, 87.54, 87.07, 86.74, 83.39, 65.62, 23.39, 23.28, 15.06, 14.91, 14.88. Anal. Calcd for $C_{153}H_{112}S_{16}$: C, 74.59; H, 4.58. Found: C, 74.46; H, 4.69.

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Supporting Information Available: ^1H NMR spectra for compounds **10**−**12**, **14**, **23**, **26**, **27**, **39a**, **39b**, **40a**, **40b**, **41**−**46**, **49**−**57**, **59**, **60**, **62**, and **63** (30 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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