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Synthesis of Orthogonally Fused Conducting Oligomers for Molecular Electronic Devices

by

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Described is an approach to orthogonally fused conjugated organic compounds that may act as molecular switching devices. Four thiophene trimers are added in a single operation to spiro-fused cores to afford the target molecules. A spiro-fused thiophene-based monomer system is converted to a spiro-fused heptamer that is 25 Å long. The synthesis of a mixed phenylene-thiophene system is described that provides a spiro-fused octamer that is 30 Å long. In each case, alkyl substituents on the thiophenes afford soluble materials. Trimethylsilyl end groups flank each orthogonally fused system. Organopalladium- and organonickel-catalyzed procedures are used extensively for the synthesis of the orthogonally fused compounds.

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Synthesis of Orthogonally Fused Conducting Oligomers for Molecular Electronic Devices[1]

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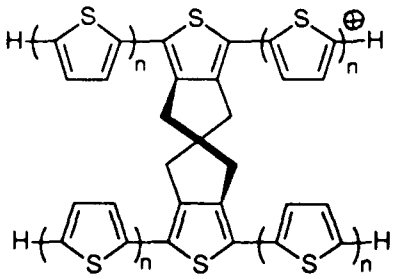
Since the time of the first room-filling computers, there has been a tremendous drive to compress the size of computing instruments. In order to bring this desire to its extreme, it was conceived that one may be able to construct single molecules that could each function as a self-contained electronic device.[2,3] Here we outline the convergent and flexible synthesis of two different macromolecules that approach the size necessary for molecular switch testing. Hence, the feasibility of molecular electronic devices, whether the architectures be of single molecule or ensemble arrangements, may soon be experimentally addressed.

Recently, Aviram of the IBM Corporation suggested that molecules ~50 Å long that contain a pro-conducting (non-doped or non-oxidized system, hence insulating) chain that is fixed at a 90° angle via a non-conjugated sigma bonded network to a conducting (doped or oxidized system) chain should exhibit properties that would make them suitable for interconnectic into future molecular electronic devices. These devices may be useful for the memory, logic, and amplification computing systems.[4] **1**, in doped form, is an



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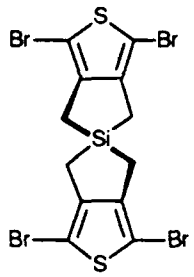
example of a pro-conducting/σ/conducting molecule. Until recently, all experimental studies on orthogonal systems had dealt only with the spiro core of related molecules and no synthetic approach demonstrated incorporation of the oligomeric chains.[5,6]

We described a facile approach to the core of two molecules which fit the general class of systems necessary for this electronic model.[7] The thiophene-based core (**2**) was synthesized in two steps from the tetra-alkyne (**3**) by treatment with $Cp_2Zr(n\text{-}Bu)_2$ and S_2Cl_2 followed by bromodesilylation with Br_2. The phenylene-based core (**4**) was prepared in a four step sequence from 2-aminobiphenyl.[7,8] In



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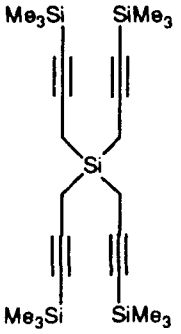

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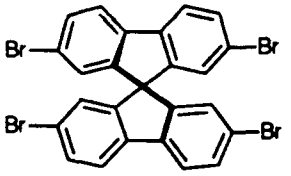

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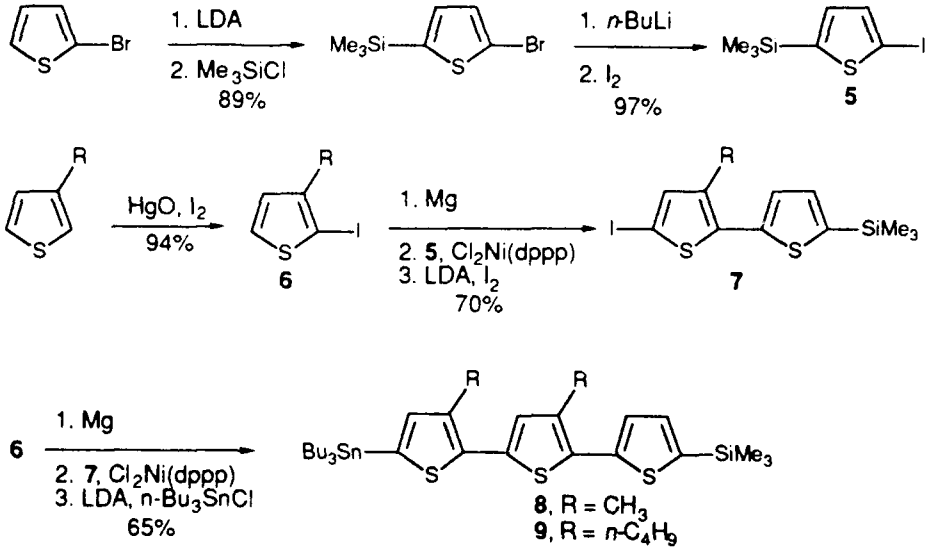
a single operation, we hoped to introduce the four branches onto the core units. In order to keep the final products soluble, it was necessary to use 3-alkylthiophenes as the branching units. Alkylated phenylenes have inferior conductivities due to the severe out of plane distortions of the consecutive aryl units.[9-11]

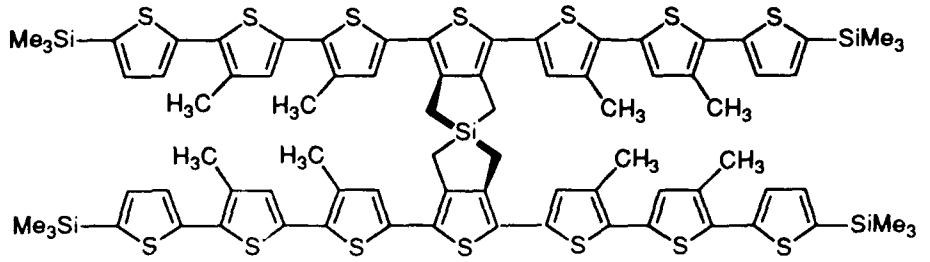
Scheme I



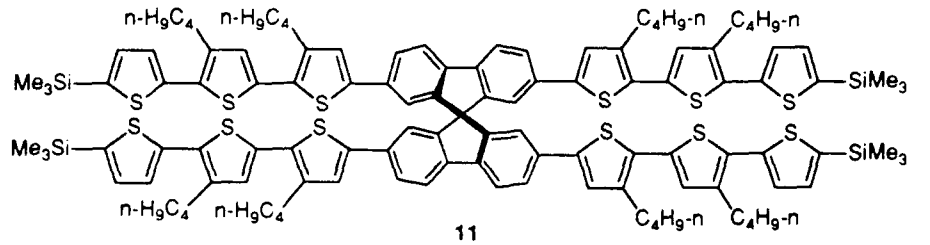
Functionalized and alkylated thiophene trimers were synthesized as shown in scheme I (yields listed for R = CH_3).[12-14] When the silylated thiophene unit in **8** had a 3-methyl substituent, desilylation was rapid upon silica gel chromatography (even with amine-washed silica gel). Carbocationic character 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. Thus we chose to keep the terminal thiophene unit free of an alkyl substituent. These trimers possesses several of the desired properties, namely (1) a terminal tributylstannyl substituent for attachment to the cores (2) alkyl groups for maintaining the solubility, and (3) a terminal trimethylsilyl group for

future chemoselective modification of the final orthogonal oligomers to permit adhesion to nanolithographic probes.[15]

Treatment of the core **2** with excess **8** in the presence of 8 mol % of $Pd(PPh_3)_4$ afforded the target orthogonal thiophene system **10** in 86 % yield.[16,17] Similarly, the core **4** was treated with **9** and 8 mol % of $Pd(PPh_3)_4$ to give the mixed phenylene-thiophene spiro fused octamer **11** in 60 % yield.[18] Compounds



10



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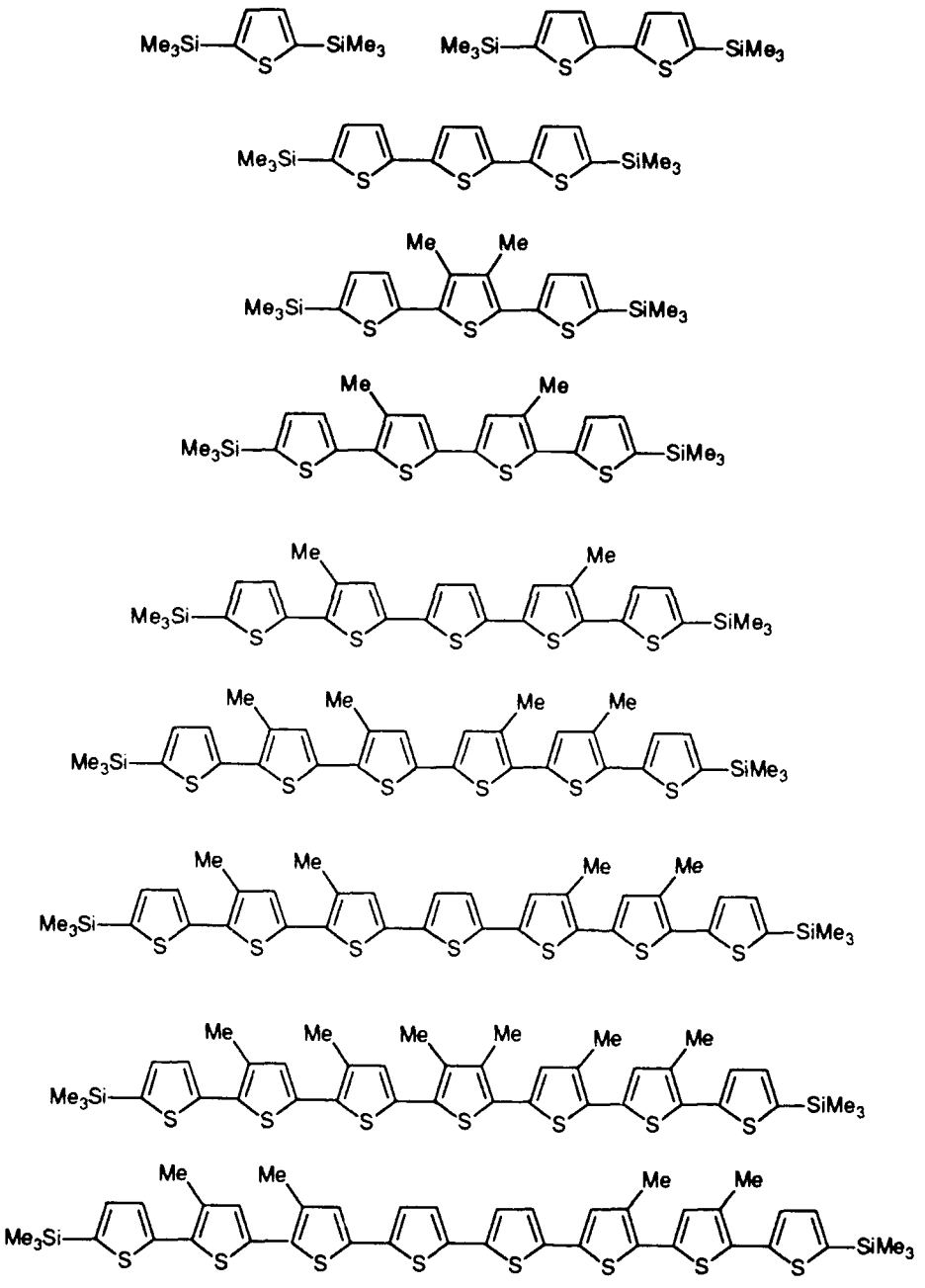
10 and **11** are approximately 25 Å and 30 Å in length (excluding the trimethylsilyl substituents), respectively, as determined by MMX with extended π Hückel parameters.[19] Both **10** and **11** are soluble in many organic solvents which will allow simple processing; however, without the alkyl substituents, these materials are intractable. 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),[20] both **10** and **11** readily showed M+ data in 3-nitrobenzyl alcohol (NBA) and *o*-nitrophenyloctylether (ONPOE) matrices, respectively.[17,18] This is an indication of the ease of oxidation of these oligomers which was confirmed in cyclic voltammetry studies on **10** that showed two reversible waves with anodic peak potentials (E_{pa}) at 0.68 and 1.05 V.[21,22]

In order to understand the orthogonally fused systems more fully, several oligothiophenes (shown below) were prepared and their electrochemical properties were investigated.[23]



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References and Notes

(1) A preliminary communication on a portion of this work was recently presented. Tour, J. M.; Wu, R.; Schumm. J. S. *J. Am. Chem. Soc.* **1991**, *113*, 7065.

(2) Hammeroff, S. R. *Ultimate Computing. Biomolecular Consciousness and Nano Technology;* North Holland: Amsterdam, 1987.

(3) (a) Bowden, M. J. in *Electronic and Photonic Applications of Polymers*; Bowden, M. J.; Turner, S. R., Eds; (Advances in Chemistry, 218) American Chemical Society: Washington DC, 1988. (b) *Molecular Electronic Devices*; Carter, F. L., Ed.; Marcel Dekker: New York, 1982. (c) *Molecular Electronic Devices II*; Carter, F. L., Ed.; Marcel Dekker: New York, 1984. (d) Franks, A. *J. Phys. E: Sci Instum.* **1987**, *20*, 1442. (e) For a recent presentation of the potential and obstacles for molecular electronic device fabrication, see: Miller, J. S. *Adv. Mater.* **1990**, *2*, 378, 495, 601.

(4) (a) Aviram, A. *J. Am. Chem. Soc.* **1988**, *110*, 5687. (b) Hush, N. S.; Wong, A. T.; Bacskay, G. B.; Reimers, J. R. *J. Am. Chem. Soc.* **1990**, *112*, 4192. (c) Farazdel, A.; Dupuis, M.; Clementi, E.; Aviram. A. *J. Am. Chem. Soc.* **1990**, *112*, 4206.

(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) Tour, J. M.; Wu, R.; Schumm, J. S. *J. Am. Chem. Soc.* **1990**, *112*, 5662. (b) Tour, J. M.; Wu, R.; Schumm, J. S. *Polym. Preprints* **1990**, *31*, 408.

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

(9) For a discussion of polythiophene and its derivatives, see: (a) Tourillon, G. In *Handbook of Conducting Polymers*; Skotheim, T. A., Ed.; Dekker: New York, 1986. (b) Tourillon, G.; Garnier, F. *J. Electroanal. Chem.* **1984**, *161*, 51.

(10) For a discussion of polyphenylene and its derivatives, see: (a) Elsenbaumer, R. L.; Shacklette, L. W. in ref 9a. (b) Kovacic, P.; Jones, M. B. *Chem. Rev.* **1987**, *87*, 357. (c) Noren, G. K.; Stille, J. K. *Macromolec. Rev.* **1971**, *5*, 385. (d) Baughman, R. H.; Bredas, J. L.; Chance, R. R.; Elsenbaumer, R. L.; Shacklette, L. W. *Chem. Rev.* **1982**, *82*, 209.

(11) For an example of mixed thiophene/phenylene semiconductors, see: Pelter, A.; Maud, J. M.; Jenkins, I.; Sadeka, C.; Coles, G. *Tetrahedron Lett.* **1989**, *30*, 3461.

(12) All new compounds were characterized spectroscopically. All reported yields pertain to isolated homogeneous materials.

(13) Uhlenbroek, J. H.; Bijloo, J. D. *Rec. Trav. Chim.* **1960**, *79*, 1181.

(14) Tamao, K.; Kodama, S.; Nakajima, I.; Kumada, M.; Minato, A.; Suzuki, K. *Tetrahedron* **1982**, *38*, 3347.

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

(16) (a) Stille, J. K. *Angew. Chem., Int. Ed. Engl.* **1986**, *25*, 508. (b) Stille, J. K. *Pure Appl. Chem.* **1985**, *57*, 1771.

(17) Spectral data for **10**. UV ($CHCl_3$) λ_{max} 456 nm, ε_{max} 2.94 x 10^4, tailing edge 545 nm. IR (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). FAB/MS (NBA) calc'd 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%).

(18) Spectral data for **11**. UV ($CHCl_3$) λ_{max} 418 nm, ε_{max} 2.91 x 10^5, tailing edge 495 nm. IR (thin film) 2955, 2927, 1458, 1250, 990 cm^{-1}. ^1H 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). FAB/MS in (ONPOE) calc'd 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. calc'd for $C_{117}H_{136}S_{12}Si_4$: C, 68.96; H, 6.68. Found: C, 68.14; H, 6.86.

(19) P.C. Model version 4.1 from Serena Software (Box 3076, Bloomington, IN 47402-3076) using MMX mode with extended π-Hückel calculations.

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

(21) 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 CH_2Cl_2 using 0.1 M tetrabutylammonium tetrafluoroborate as the electrolyte.

(22) An orthogonally fused thiophene trimer (see ref 7) exhibited only one reversible wave with E_{pa} = 1.07 V. Thus the heptamer is considerably easier to oxidize.

(23) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Materials* in the reviewing process.