Synthesis and Electronic Structure Investigations of α,ω-Bis(arylthio)oligothiophenes: Toward Understanding Wire-Linker Interactions in Molecular-Scale Electronic Materials

Robin G. Hicks* and Matthew B. Nodwell

Contribution from the Department of Chemistry, University of Victoria, P.O. Box 3065, Victoria, British Columbia V8W 3V6, Canada

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Abstract: Several oligothiophenes with 2-mesitylthio (MesS) substituents have been prepared and studied by UV−visible spectroscopy and cyclic voltammetry. These compounds can be considered as models for thiol-terminated conjugated oligomers, which have attracted intense interest as materials for molecular-scale electronics. Three types of oligomers were prepared: α,ω-bis(mesitylthio)oligothiophenes **4−7**, α,ω-bis(mesitylthio)oligo(3,4-ethylelendioxythiophene)s **12−14**, and α,ω-bis(mesitylthio)oligomers **15−19** containing both thiophene and 3,4-ethylenedioxythiophene rings. The mesitylthio groups were introduced via nucleophilic attack of lithiated thiophenes on mesitylenesulfenyl chloride. The oligomers were assembled by oxidative coupling or palladium-catalyzed Stille coupling of 2-stannylthiophenes with 2-bromothiophenes. The solution electronic spectra of all oligomers display a red-shift in the lowest-energy transition maximum (λ_{max}) relative to oligothiophenes lacking the MesS- group. The red-shift arises from conjugative overlap of a mesitylthio sulfur lone pair with the oligothiophene π system. Cyclic voltammetry studies indicate that the MesS group significantly lowers the first and second oxidation potentials of the oligomers and improves the stability of the incipient radical cations and dications relative to alkyl-capped oligothiophenes. Additionally, the difference between first and second oxidation potentials in the MesS-substituted oligomers is much lower than known alkyl-substituted oligomers. This effect is due to the terminal MesS groups which cause charge density in the radical cations to concentrate at the chain ends, thereby lowering the Coulombic barrier to introduction of a second charge. The electronic structure perturbations caused by the MesS- group are discussed in the context of single-molecule conduction in thiol-terminated conjugated oligomers bound to gold electrodes.

Introduction

Research into the chemical and physical properties of oligothiophenes has developed largely along two interdependent themes: The "model compound" approach, and the "bulk properties" approach. With respect to the former, the spectroscopic and electrochemical properties of well-defined, monodisperse oligothiophenes have been heavily investigated as model systems for the technologically relevant (but less easily studied) polythiophenes. These efforts have produced a variety of new insights into the electronic, optical, and charge transport behavior of conjugated polymers, thereby demonstrating the effectiveness of the model compound approach.[1−15] In the context of bulk properties, many oligothiophenes exhibit an array of novel electrical or optical properties in their own right.[16] This has led to intense interest in the fabrication of thiophene-based electronic devices such as transistors,[17−21] electroluminescent devices,[22−24] and photovoltaic cells.[25] The collective successes in both fundamental and applied endeavors have made oligothiophenes arguably the single most important family of compounds in molecular/organic materials chemistry.[26]

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

(2) Guay, J.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 254.

(3) Guay, J.; Kasai, P.; Diaz, A.; Wu, R.; Tour, J. M.; Dao, L. H. *Chem. Mater.* **1992**, *4*, 1097.

(4) Hill, M. G.; Mann, K. R.; Miller, L. L.; Penneau, J. F. *J. Am. Chem. Soc.* **1992**, *114*, 2728.

(5) Graf, D. D.; Campbell, J. P.; Miller, L. L.; Mann, K. R. *J. Am. Chem. Soc.* **1996**, *118*, 5480.

(6) Bäuerle, P.; Segelbacher, U.; Gaudl, K. U.; Huttenlocher, D.; Mehring, M. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 76.

(7) Bäuerle, P.; Segelbacher, U.; Maier, A.; Mehring, M. *J. Am. Chem. Soc.* **1993**, *115*, 10217.

(8) Caspar, J. V.; Ramamurthy, V.; Corbin, D. R. *J. Am. Chem. Soc.* **1991**, *113*, 600.

(9) Bidan, G.; Nicola, A. D.; Enée, V.; Guillerez, S. *Chem. Mater.* **1998**, *10*, 1052.

(10) Zotti, G.; Schiavon, G.; Berlin, A.; Pagani, G. *Chem. Mater.* **1993**, *5*, 620.

(11) Alemán, C.; Brillas, E.; Davies, A. G.; Fajarí, L.; Giró, D.; Juliá, L.; Peréz, J. J.; Ruis, J. *J. Org. Chem.* **1993**, *58*, 3091.

(12) Hapiot, P.; Audebert, P.; Monnier, K.; Pernaut, J. M.; Garcia, P. *Chem. Mater.* **1994**, *6*, 1549.

(13) Nessakh, B.; Horowitz, G.; Garnier, F.; Deloffre, F.; Srivastava, P.; Yassar, A. *J. Electroanal. Chem.* **1995**, *399*, 97.

(14) Haare, J. A. E. H. v.; Havinga, E. E.; Dongen, J. L. J. v.; Jannsen, R. A. J.; Cornil, J.; Brédas, J. L. *Chem. Eur. J.* **1998**, *4*, 1509.

(15) Levillain, E.; Roncali, J. *J. Am. Chem. Soc.* **1999**, *121*, 8760.

(16) Fichou, D. *J. Mater. Chem.* **2000**, *10*, 571.

(17) Horowitz, G. *Adv. Mater.* **1998**, *10*, 365.

(18) Garnier, F.; Horowitz, G.; Peng, X.; Fichou, D. *Adv. Mater.* **1990**, *2*, 592.

(19) Horowitz, G.; Garnier, F.; Yassar, A.; Hajloaui, R.; Kouki, F. *Adv. Mater.* **1996**, *8*, 52.

(20) Dodabalapur, A.; Torsi, L.; Katz, H. E. *Science* **1995**, *268*, 270.

(21) Dodabalapur, A.; Katz, H. E.; Torsi, L.; Haddon, R. C. *Science* **1995**, *269*, 1560.

(22) Horowitz, G.; Delannoy, P.; Bouchriha, H.; Deloffre, F.; Fave, J. L.; Garnier, F.; Hajlaoui, R.; Heyman, M.; Kouki, F.; Valat, P.; Wintgens, V.; Yassar, A. *Adv. Mater.* **1994**, *6*, 752.

(23) Noda, T.; Shirota, Y. *J. Am. Chem. Soc.* **1998**, *120*, 9714.

(24) Noda, T.; Ogawa, H.; Shirota, Y. *Adv. Mater.* **1999**, *11*, 283.

(25) Noma, N.; Tsuzuki, T.; Shirota, Y. *Adv. Mater.* **1995**, *7*, 647.

10.1021/ja000752t CCC: $19.00

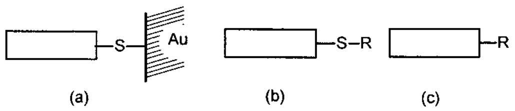
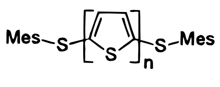


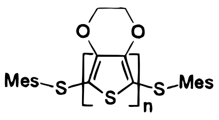
Figure 1. Schematic diagrams of (a) a thiol-terminated conjugated oligomer bound to a gold surface, (b) a thioether-capped oligomer, and (c) the corresponding oligomer without a sulfur end group.

In recent years there have also been parallel developments in molecular *scale* electronic devices.[27−29] Most of these efforts have been carried out by attaching conjugated oligomers to electrodes to probe charge transport phenomena on a molecular level. This has been accomplished principally by taking advantage of the well-known propensity of thiols to “self-assemble” onto gold surfaces.[30] Many experimental and theoretical studies have been devoted to understanding the assembly and electrical behavior of surface-bound, thiol-terminated conjugated oligomers based on thiophene,[31,32] 2-thienylacetylene,[32] benzene[33−36] and *p*-phenylacetylene.[37−41] Much attention has been devoted to the synthesis of sulfur-derivitized oligomers,[42−44] the ordering properties of the surface-bound monolayers[32] and the nature of S−Au interactions.[45] However, there have been remarkably few studies dealing with the interactions between the sulfur “linker” and the organic substrate itself. The surface-bound molecules can be viewed as conjugated oligomers bearing a thioether (-SR) substituent, where the “substituent” R is in fact the metal surface (Figure 1). In this context, the question of how the electronic properties of conjugated oligomers are altered by sulfur-containing end groups relative to the parent (unsubstituted or alkyl-substituted) oligomers has barely been addressed.[35,46] Such effects would be expected to have important consequences for the nature of charge transport in single molecules and, by extension, for the possibility of making molecular-scale electronic devices.

We opted to focus on oligothiophenes as probe systems for a variety of reasons. Although they have not been the most common species to be assembled onto gold surfaces, the redox and spectroscopic properties of oligothiophenes have been studied more than any other conjugated oligomer family.[26] We reasoned that the availability of electrochemical and UV−vis data for a broad range of compounds would facilitate comparisons with the species presented herein. In addition, the electrochemical behavior of oligothiophenes is generally better (i.e., their oxidation processes are more commonly reversible) compared to that of other oligomers. With respect to the end groups, oligomers with -SH substituents must be avoided because thiols are unstable with respect to oxidation, particularly when they are directly attached to conjugated π systems. Fortunately, this oxidative instability can be remedied by replacing the thiol proton with a redox-inactive organic group. We selected the mesityl functionality because of this group’s solubilizing ability and for synthetic practical reasons (vide infra). Thus, our target systems are a range of α,*ω*-bis(mesitylthio)oligothiophenes in which the oligomeric chain consists of parent thiophenes **(A)**, the more electron-rich 3,4-ethylenedioxythiophene (“EDOT”) (**B**), as well as oligomers containing both thiophene and EDOT rings. Herein we describe the synthesis of these systems and present experimental investigations into their electronic structure, with the specific goals of understanding the influence of -SR groups on the conjugated oligomers as a function of the oligomer chain length and degree of “electron richness”.



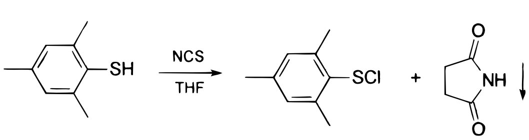
A



B

Synthesis

Schemes 1−4 outline the synthetic routes to the mesitylthio-capped oligothiophenes. There are several examples of oligothiophenes with S-alkyl groups, most of which are prepared by attack of a lithiated thiophene species on a dialkyl disulfude.[47−52] However, the corresponding dimesityl disulfide (MesSSMes) proved to be surprisingly inert toward a range of thienyllithum reagents. We therefore turned to a more reactive source of electrophilic “MesS$^+$”, namely mesitylenesulfenyl chloride (MesSCl). This could be conveniently and quantitatively generated by treatment of mesitylenethiol with NCS in THF (eq 1).



(1)

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(26) *Handbook of Oligo- and Polythiophenes*; Fichou, D., Ed.; Wiley-VCH: Weinheim, 1998.

(27) *Molecular Electronics: Science and Technology*; Aviram, A., Ratner, M., Eds.; New York Academy of Science: New York, 1998; Vol. 852.

(28) Ward, M. D. *Chem. Ind.* **1996**, 568.

(29) Waldeck, D. H.; Beratan, D. N. *Science* **1993**, *261*, 576.

(30) DuBois, L. H.; Nuzzo, R. G. *Annu. Rev. Phys. Chem.* **1992**, *43*, 437.

(31) Purcell, S. T.; Garcia, N.; Binh, V. T.; II, L. J.; Tour, J. M. *J. Am. Chem. Soc.* **1994**, *116*, 11985.

(32) Tour, J. M.; Jones, L.; Pearson, D. L.; Lamba, J. J. S.; Burgin, T. P.; Whitesides, G. M.; Allara, D. L.; Parikh, A. N.; Atre, S. V. *J. Am. Chem. Soc.* **1995**, *117*, 9529.

(33) Reed, M. A.; Zhou, C.; Muller, C. J.; Burgin, T. P.; Tour, J. M. *Science* **1997**, *278*, 252.

(34) Datta, S.; Tam, W.; Hong, S.; Riefenberger, R.; Henderson, J. I.; Kubiak, C. P. *Phys. Rev. Lett.* **1997**, *B79*, 2530.

(35) Yaliraki, S. N.; Kemp, M.; Ratner, M. A. *J. Am. Chem. Soc.* **1999**, *121*, 3428.

(36) Samanta, M. P.; Tian, W.; Datta, S.; Henderson, J. I.; Kubiak, C. P. *Phys. Rev. B* **1996**, *53*, R7626.

(37) Creager, S.; Yu, C. J.; Bamdad, C.; O’Connor, S.; MacLean, T.; Lam, E.; Chong, Y.; Olsen, G. T.; Luo, J.; Gozin, M.; Kayyem, J. F. *J. Am. Chem. Soc.* **1999**, *121*, 1059.

(38) Cygan, M. T.; Dunbar, T. D.; Arnold, J. J.; Bumm, L. A.; Shedlock, N. F.; Burgin, T. P.; II, L. J.; Allara, D. L.; Tour, J. M.; Weiss, P. S. *J. Am. Chem. Soc.* **1998**, *120*, 2721.

(39) Seminario, J. M.; Zacaias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1998**, *120*, 3970.

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

(41) Dhirani, A. A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. *J. Am. Chem. Soc.* **1996**, *118*, 3319.

(42) Wu, R.; Schumm, J. S.; Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1996**, *61*, 6906.

(43) L. Jones, I.; Schumm, J. S.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1388.

(44) Pearson, D. L.; Tour, J. M. *J. Org. Chem.* **1997**, *62*, 1376.

(45) Seminario, J. M.; Zacarias, A. G.; Tour, J. M. *J. Am. Chem. Soc.* **1999**, *121*, 411.

(46) Emberly, E. G.; Kirczenow, G. In *Molecular Electronics: Science and Technology*; Aviram, A., Ratner, M., Eds.; New York Academy of Science: New York, 1998; Vol. 852, p 54.

(47) Bäuerle, P.; Gotz, G.; Synowczyk, A.; Heinze, J. *Liebeigs Ann.* **1996**, 279.

(48) Antolini, L.; Goldini, F.; Iarossi, D.; Mucci, A.; Schenetti, L. *J. Chem. Soc., Perkin Trans 2* **1997**, 1957.

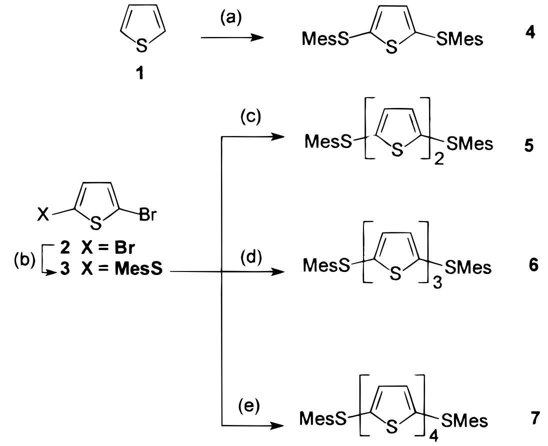
(49) Folli, U.; Iarossi, D.; Montorsi, M.; Mucci, A.; Schenetti, L. *J. Chem. Soc., Perkin Trans 1* **1995**, 537.

(50) Hill, M. G.; Penneau, J. F.; Zinger, B.; Mann, K. R.; Miller, L. L. *Chem. Mater.* **1992**, *4*, 1106.

The succinimide byproduct was easily removed by precipitation from hexanes. This sulfenyl chloride could be isolated and stored under inert atmosphere (unlike the far more reactive benzenesulfenyl chloride, PhSCl), but we found it more convenient to simply generate the desired quantity in situ for introduction onto thiophene substrates.

Scheme 1 outlines the syntheses of the α,*ω*-bis(mesitylthio) oligothiophenes **4**−**7** from the "monothiophene" to quaterthiophene. 2,5-Bis(mesitylthio)thiophene **4** was made directly from thiophene via treatment with butyllithium followed by MesSCl. The syntheses of the corresponding bi-, ter-, and quaterthiophenes **5**−**7** were all carried out with 2-bromo-(5-mesitylthio)thiophene **3**, which was readily made from 2,5-dibromothiophene via a similar BuLi/MesSCl sequence. Lithium/halogen exchange of **3** produced the 2-lithio species, which could then be oxidatively coupled ($CuCl_2$) to give the capped bithiophene **5**. Stille coupling methodology was employed in converting **3** into terthiophene **6** and quaterthiophene **7**. Thus, treatment of **3** with 2,5-bis(tributylstannylthiophene) and $Pd(PPh_3)_4$ (5 mol %) afforded **6**, while the analogous reaction of **3** with 5,5′-bis(tributylstannyl)-2,2′-bithiophene gave **7** in good yields.

Scheme 1[a]

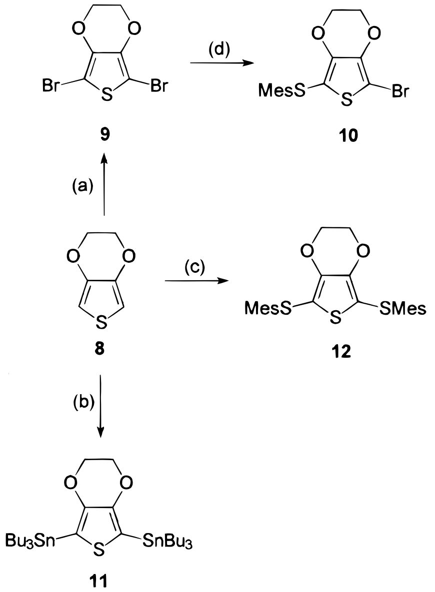


[a] Reagents: (a) 2 BuLi then 2 MesSCl. (b) BuLi then MesSCl. (c) BuLi then $CuCl_2$. (d) 2,5-Bis(tributylstannyl)thiophene, cat. $Pd(PPh_3)_4$. (e) 5,5′-Bis(tributylstannyl)-2,2′-bithiophene, cat. $Pd(PPh_3)_4$.

The synthesis of capped oligomers of 3,4-ethylenedioxythiophene **8** required the preparation of several derivatives which could be employed as "building blocks" (Scheme 2). The 2,5-dibromo derivative **9** was prepared in quantitative yield by a modified version of the literature procedure.[53] This compound was then converted to (2-bromo-3,4-ethylenedioxy-5-mesitylthio)thiophene **10** via the BuLi/MesSCl sequence. 2,5-Bis(tributylstannyl)-3,4-ethylenedioxythiophene **11** was prepared by double deprotonation of **8** followed by quenching with Bu_3SnCl. This procedure produces crude **11** in ∼80% yield with the major contaminant being the partially substituted 2-tributylstannylthipohene. Attempts to purify **11** by chromatography or distillation were frustrated by extensive decomposition. Thus, the in situ generated **11** was used in subsequent reactions.

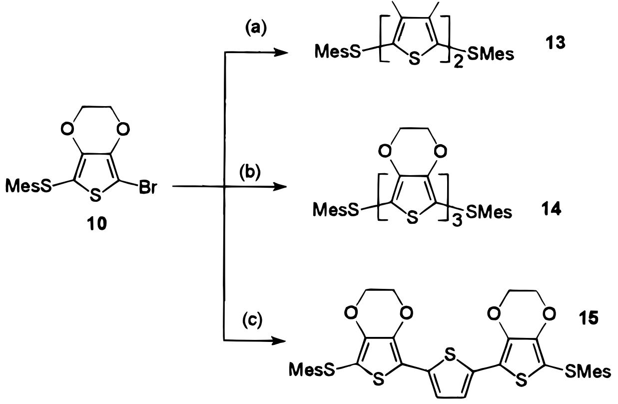
The introduction of two MesS substituents onto EDOT **8** was accomplished by double deprotonation of **8** followed by 2 equiv of MesSCl, giving **12** in good yield. Scheme 3 outlines the synthesis of the higher homologues of capped EDOT derivatives. By analogy with the parent oligothiophenes, lithiation of bromo derivative **10** followed by oxidative coupling gave mesitylthio-capped biEDOT **13**, while Stille coupling of **10** with **11** gave the analogous terEDOT **14**. We were unable to prepare the EDOT-based quaterthiophene analogue of **7** because all attempts to prepare any biEDOT derivative with reactive end groups (H, Br, SnR_3)—the necessary precursors for quaterthiophene synthesis—failed.

Scheme 2[a]



[a] Reagents: (a) NBS. (b) BuLi (2 equiv), then Bu_3SnCl (2 equiv). (c) BuLi (2 equiv) then MesSCl (2 equiv). (d) BuLi (1 equiv) then MesSCl (1 equiv).

Scheme 3[a]



[a] Reagents: (a) BuLi then $CuCl_2$. (b) 0.5 equiv **11**, $Pd(PPh_3)_4$ cat. (c) 0.5 equiv 2,5-bis(tributylstannyl)thiophene, cat. $Pd(PPh_3)_4$.

We then prepared a series of "mixed" thiophene/EDOT-containing oligomers. Stille coupling of **10** with 2,5-bis(tributylstannyl)thiophene afforded the "mixed" terthiophene **15** in which two EDOT moieties flank a central thiophene ring (Scheme 3). The remainder of the mixed oligomers were prepared as shown in Scheme 4. Stille coupling of **3** with **11** gave the mixed terthiophene **16** with one EDOT group in the center of the molecule. Finally, two mixed quaterthiophenes were prepared. Stille coupling of **3** with 2-tributylstannylth-

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(51) Tabakovic, I.; Maki, T.; Miller, L. L.; Yu, Y. *Chem. Commun.* **1996**, 1911.

(52) Tabakovic, I.; Maki, T.; Miller, L. L. *J. Electroanal. Chem.* **1997**, *424*, 35.

(53) Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Chem. Mater.* **1996**, *8*, 882.

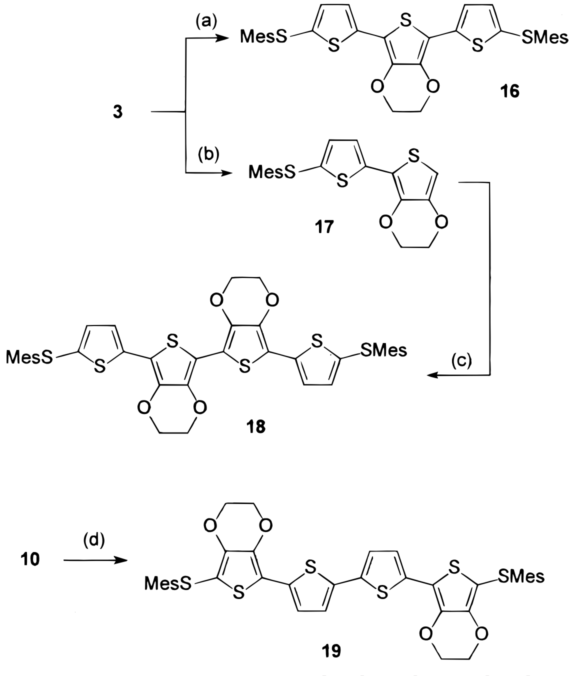
Table 1. Lowest-Energy Electronic Transitions (λ_{max}, nm) for Selected Oligothiophenes[a]

compound	no. of thiophene rings	λ_{max} (nm)
thiophene	1	243
4	1	302
12	1	305
bithiophene	2	302
5	2	358
13	2	362
terthiophene	3	354
6	3	386
14	3	401
15	3	401
16	3	406
quaterthiophene	4	390
7	4	420
18	4	431
19	4	458

[a] Values for the parent oligothiophenes are taken from the literature.[67]

iophene gave mono-capped bithiophene **17** which was deprotonated (BuLi) and oxidatively coupled (Fe(acac)$_3$) to give the mixed quaterthiophene **18** with two EDOTs located on the “inside” positions of the quaterthiophene chain. The other symmetrical isomer, so-called “outside” analogue **19**, was made by Stille coupling of **10** with 5,5′-bis(tributylstannyl)-2,2′-bithiophene.

Scheme 4[a]



[a] Reagents: (a) 0.5 equiv **11**, cat. Pd(PPh$_3$)$_4$. (b) 2-Tributylstannyl-3,4-ethylenedioxythiophene, cat. Pd(PPh$_3$)$_4$. (c) BuLi then Fe(acac)$_3$. (d) 5,5′-Bis(tributylstannyl)-2,2′-bithiophene, cat. Pd(PPh$_3$)$_4$.

Electronic Spectra

Table 1 presents the lowest-energy electronic transitions (λ_{max}) for the α,ω-bis(mesitylthio)oligothiophenes, along with literature data for the parent oligothiophenes. For each homologous series of compounds (i.e., **4**−**7** or **12**−**14**), λ_{max} increases with thiophene chain length, a trend that is consistent with virtually all other oligothiophenes. However, the values of λ_{max} for the mesitylthio-substituted compounds are red-shifted relative to their unsubstituted analogues of identical chain length, and the magnitude of this red-shift diminishes with increasing chain length. This red-shift is due to conjugative overlap of the mesitylthio sulfur lone pairs with the oligothiophene π-chromophore. Interestingly, the effects of the β-oxygen groups on λ_{max} appear to be less important. For example, there is virtually no difference in λ_{max} between, for example, **4** vs **12** or **5** vs **13**. In each of these pairs of compounds the only difference in molecular structure is the presence of the ethylenedioxy group. Although the oxygen lone pairs can overlap with the thiophene π system at the β carbon atoms, the thiophene π-HOMO has its largest atomic orbital coefficients at the 2 and 5 (α) carbons and moderately smaller contributions from the 3 and 4 (β) carbons. Thus the overlap effects of substituents are expected (and found) to be more important at the α than the β positions. Similar effects have been observed, for example, in α,ω-disubstituted oligothiophenes with electron-withdrawing substituents, [54,55] and β-methoxy-substituted oligothiophenes.[56] The former have λ_{max} significantly red-shifted relative to the unsubstituted oligomers, while the latter have λ_{max} which are not very different from oligomers lacking the methoxy substituents.

Table 2. Oxidation Potentials of α,ω-Bis(mesitylthio)Oligothiophenes[a]

compound	E_1°	E_2°	$E_2^\circ - E_1^\circ$
4	1.05		
5	0.87	1.25	0.37
6	0.86	1.02	0.16
7	0.83	0.91	0.08
12	0.87		
13	0.57	0.94	0.37
14	0.42	0.65	0.23
15	0.57	0.76	0.19
16	0.67	0.93	0.26
18	0.49	0.73	0.24
19	0.61	0.66	0.05

[a] All values are in V vs SCE.

Thus, the oligothiophene chain length and the presence of -SR substituents are the primary determinants of the position of λ_{max}. The mesityl group itself seems to be unimportant, as evidenced by the fact that λ_{max} of terthiophene **6** (386 nm) is virtually identical to that of the analogous α,ω-bis(methylthio)-terthiophene (390 nm).[50] This suggests that conjugation of the mesityl group with the rest of the π framework is either ineffective or may be unfavorable because of steric factors. The latter reason is favored on the basis of molecular mechanics calculations on **4** and **12**. The optimized structures of these two compounds are similar: the bond between the mesityl *ipso* carbon and the neighboring sulfur atom is essentially coplanar with the plane of thiophene ring, but the orientation of the mesityl group is twisted by about 54° with respect to this plane. Thus, the conjugative overlap between the two cyclic π systems is far from optimal.

Cyclic Voltammetry Studies

Within the context of molecular electronics, electrochemical studies into oxidative processes in oligothiophenes are directly relevant to hole transport through single molecules. The redox properties of the α,ω-bis(mesitylthio) oligothiophenes **4**−**7**, **12**−**16**, **18**, and **19** were examined by cyclic voltammetry; the results of these studies are presented in Table 2. The most striking electrochemical feature common to all of the compounds is the stability of the radical cations and dications generated. All of the compounds exhibit at least one fully reversible one-electron

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(54) Barclay, T. M.; Cordes, A. W.; MacKinnon, C. D.; Oakley, R. T.; Reed, R. W. *Chem. Mater.* **1997**, *9*, 981.

(55) Wei, Y.; Yang, Y.; Yeh, J. M. *Chem. Mater.* **1996**, *8*, 2659.

(56) Miller, L. L.; Yu, Y. *J. Org. Chem.* **1995**, *60*, 6813.

oxidation, and a second reversible oxidation is also found for all derivatives with at least two thiophene rings (i.e., all but **4** and **12**). Reversibility was observed at scan rates as low as 10 mV/s and was established by the equivalence of anodic (i_{pa}) and cathodic (i_{pc}) peak currents, separation of 60−70 mV between anodic (E_{pa}) and cathodic (E_{pc}) peak potentials, and scan rate-independence of E_{pa} and E_{pc}. Blocking the end-carbons with alkyl or aryl groups is known to inhibit irreversible decomposition pathways (in particular oxidative polymerization) open to the α,ω-unsubstituted compounds. However, most of the known oligothiophene radical cations and dications with terminal alkyl groups remain very reactive species. Oxidative chemical and electrochemical reversibility is very unusual for short oligothiophenes with three or fewer thiophene rings. In fact, the only other thiophene and bithiophene derivatives with comparable electrochemical stability have a similar array of substituents. Reversible radical cation and dication formation has been reported for short thiophene oligomers bearing β-methoxy groups and alkylthio substituents on the α and ω carbons,[51,52] as well as α,ω-bis(methylthio) terthiophene.[50]

We attribute the radical cation/dication stability in the present compounds primarily to the presence of the mesitylthio groups. In general, the radical cations of end-substituted oligothiophenes are expected to be less reactive than the unsubstituted oligothiophene radical cations, regardless of the nature of the substituents at the β carbon atoms. For example, even uncapped oligomers of EDOT, which possess very strongly electron-donating -OR groups ($\sigma_p^+ = -0.78$ for -OCH$_3$), form poly(EDOT) when oxidized to radical cations. [53,57] In addition to the generic (α,ω) substituent-based radical cation stabilization, however, we believe that the electron-donating capabilities of the -SR group ($\sigma_p+ = -0.60$ for -SCH$_3$) serves to further stabilize the positive charge. This is manifested in both the apparent stability and also in the lowering of the first oxidation potentials (vide infra). The steric bulk of the mesityl group may also play a role in lowering the reactivity, although the aforementioned stability of cationic states of α,ω-bis(methylthio)terthiophene suggests that steric protection is not necessary for stability. The ethylenedioxy groups present in **12**−**16**, **18**, and **19** may also contribute to the radical cation stability, although their contribution is probably secondary compared to the -SR groups at the α positions.

The first oxidation potentials ($E_1°$) of the bis(mesitylthio)-capped oligothiophene series **4**−**7** drop as the chain length increases, a trend that is consistent with most other thiophene oligomer series. However, the values of $E_1°$ for **4**−**7** are markedly lower than most other derivatives. For example, thiophene itself is oxidized irreversibly at roughly +1.8V vs SCE and alkyl-substituted "monothiophenes" are irreversibly oxidized at +1.3 to 1.5 V.[7] In contrast, monothiophene **4** is oxidized *reversibly* to a radical cation at only +1.05V. Similar differences are found in comparing alkyl-[7] or silyl-substituted[3] bithiophenes (which are irreversibly oxidized at +1.0 to +1.5 V) to **5** (+0.87 V, reversible). As the oligothiophene chain length increases, the effects of the MesS- group on $E_1°$ clearly decrease in magnitude: The $E_1°$ values of the -SR substituted oligomers and the alkyl-substituted homologues begin to converge (and in fact the alkyl-capped quaterthiophene has an $E_1°$ value (+0.75 V, reversible)[7] that is slightly lower than that of mesitylthio compound **7** (+0.83 V)). However, the addition of ethylenedioxy groups to the oligothiophene skeleton further lowers the first oxidation potentials. The EDOT-based oligomers **12**−**14** are all significantly more easily oxidized than the congeners **4**−**6**, and the difference in $E_1°$ between analogous thiophene and EDOT-based species *increases* with chain length. This is likely to be simply an additive effect; as the chain length increases, there is an increasing difference between oligothiophene and oligo(EDOT) derivatives in the *number* of electron-donating groups. Indeed, the homopolymer based on EDOT is by far the most easily oxidized polythiophene known.[58]

There is a crude correlation between the number of strong electron-donating groups and $E_1°$. This is evidenced by the trends in the electrochemical properties of the series of terthiophenes **6**→**16**→**15**→**14**. Each terthiophene in this series has two more oxygen donors than the one prior to it, and there is a concomitant lowering of $E_1°$ (0.76→0.67→0.57→0.42V) with the increase in number of oxygen donors. Thus, there is ample opportunity to "tune" the occupied energy levels of these oligomers by controlling the number of electron-donating groups. However, it is important to note that the correlation between electron-releasing substituents is not simply additive. For example, the $E_1°$ values for **18** and **19,** which have the same set of substituents (they are in fact isomers), differ by 0.12 V. The position of the substituents must also be taken into account.

Further comparisons between the isomeric quaterthiophenes **18** and **19** are revealing. As mentioned above, isomer **19** with two EDOT rings on the "outside" is 0.12 V more difficult to oxidize than the "inside" isomer **18**. However, this trend is *reversed* for the second oxidation potential: **19** is 0.08 V more easily oxidized to the dication than **18**. This suggests significant differences in the electronic structures of these two compounds, which we attribute to the differences in distribution of oxygen and sulfur donors on the oligomeric chain. The spin and charge distribution in most oligothiophene radical cations is largest at the center of the molecule and decreases toward the chain ends. As the thiophene chain length increases, the barrier to introduction of a second positive charge to the radical cation decreases and this is expressed as a decrease in the difference between $E_2°$ and $E_1°$. Extrapolation of this trend eventually leads to a single two-electron oxidation process, which in alkyl-substituted oligomers requires a minimum oligomer chain length of about nine thiophenes.[14,59] However, each of the terminal thiophene rings of **19** contain three strongly electron-releasing groups. From the electrochemical data we infer that oxidation of **19** produces a radical cation in which the charge is much more confined to the ends of the molecule, which are the most electron-rich regions. This significantly lowers the Coulombic repulsion to introduction of a second positive charge, which produces a dication in which each end of **19**$^{2+}$ carries the bulk of the positive charge. The manifestation of this effect is an extremely small value of $E_2° - E_1°$ ($\Delta = 0.05$ V) compared to alkyl-substituted quaterthiophenes in which $E_2° - E_1°$ is typically at least 0.30 V.[3,7]

Examination of $E_1°$ and $E_2°$ for the triad **13**, **15**, and **19** reveals how this picture of the electronic structure evolves. These three compounds contain two mesitylthio-capped EDOT rings bridged by a "spacer" which is nothing (**13**), thiophene (**15**), or bithiophene (**19**). Figure 2 displays the CVs for these three compounds. In contrast to the trend for nearly all other oligothiophenes, $E_1°$ *increases* with increasing chain length (0.57→0.57→0.61 V). The mesitylthio-substituted EDOT with a MesS cap is sufficiently electron-rich that addition of a thiophene (for **15**) or bithiophene (**19**) ring in conjugation does

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[57] Sotzing, G. A.; Reynolds, J. R.; Steel, P. J. *Adv. Mater.* **1997**, *9*, 795.

[58] Q. Pei; Zuccarello, G.; Ahlskog, M.; Inganas, O. *Polymer* **1994**, *35*, 1347.

[59] Sato, M.; Hiroi, M. *Polymer* **1996**, *37*, 1685.

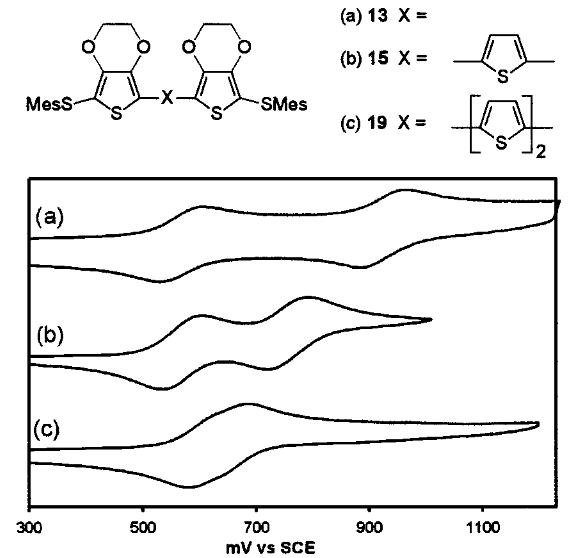

Figure 2. CVs (scan rates 100 mV/s) of (a) **13**, (b) **15**, and (c) **19**.

not further decrease the first oxidation potential. However, the trends in E_2° are quite different. As the chain length increases, E_2° decreases steadily along the series **13**→**15**→**19** (0.94→0.76→0.66 V), consequently so does $E_2^\circ - E_1^\circ$ (0.37→0.19→0.05 V). The quaterthiophene **19** may be best described as two electrophores (the mesitylthio-capped EDOT moiety) weakly coupled by a bithiophene spacer. Examination of the electrochemical data of **4**−**7** in this light suggests that the mesitylthio groups (more generally, the α substituents) are the most important contributors to this evolution in redox behavior. The values of $E_2^\circ - E_1^\circ$ of **5** and **13** are identical (0.37 V), and the corresponding values of terthiophenes **6** (0.16 V) and **15** (0.19 V) are nearly so, as are the values for quaterthiophenes **7** (0.08 V) and **19** (0.05 V). This overhaul of electronic structure has been seen in mixed thiophene−pyrrole oligomers, in which "outside" pyrrole rings are coupled weakly through an oligothiophene bridge.[60] Our results demonstrate that similar effects can be achieved in oligomers based on a single heterocyclic system through substituent effects. The electrochemical trends found in the series **13**→**15**→**19** are also seen in the electrochemical data for the series **5**→**6**→**7**, and in fact the observation (noted earlier) that **7** has a higher E_1° than an alkyl-capped quaterthiophene can also be attributed to the -SR group's perturbation of the electronic structure of the thiophene chain.

Summary

The bis(mesitylthio) oligothiophenes described here can be considered as models for thiol-terminated conjugated oligomers, the latter of which have been established as important building blocks for molecular scale electronics. Introduction of -SR groups, which are strong electron-donating substituents, has been shown to strongly perturb the electronic structure of oligothiophenes. The electron richness of these compounds produces a number of significant effects. First, electron-donating substituents clearly play an important role in determining the redox properties of oligothiophenes—and by extrapolation those of other conjugated oligomers as well. This is not a new revelation, but in the context of electron conduction through single molecules, it is highly significant. One of the critical features for both bulk[61−63] and molecular-scale[35,36,46] electronics is the match between the Fermi energy of the electrode material and the frontier orbitals of the molecule at the molecule−electrode interface. We have demonstrated that the introduction of sulfur-based end groups raises the oligothiophene HOMO, and that additional electron-donating groups further lower the oxidation potential. These effects are manifested in the solution electrochemical data as well as the electronic spectra of the oligomers. Thus, the degree of electron richness, and by extension the molecular orbital energy levels, can be fine-tuned by molecular design. Second, the necessary positioning of -SR groups at the thiophene chain ends causes a major reorganization of the electronic structure of these compounds, and the results of these changes have implications for single-molecule conduction. The radical cations of these molecules are static models for hole transport in devices—and the positive charge in the oxidized bis(arylthio)oligothiophenes is confined to the chain ends containing the arylthio groups, and importantly this effect does *not* diminish with increasing chain length. This raises an intriguing issue: The electron-rich ends of these oligomers may behave as hole traps when incorporated into single molecule devices, the consequences of which may be detrimental to charge flow based on a band-type conduction model. On the other hand, localized electron-rich moieties may actually contribute to a hole-hopping conduction mechanism, as is believed to be the case in DNA structures.[64]

Finally, the stability of the bis(arylthio)oligothiophene radical cations appears to be significantly improved compared to that of most other derivatives. Thus, the necessity of employing thiol groups to attach molecules to a gold surface has the (serendipitous) advantage of improving radical cation stability, which has implications for the durability of these molecules in current-carrying mode. In a more general context, the stability exhibited by these oligothiophene radical cations and dications will facilitate further investigations into their solution- and solid-state properties and structures. Work to this end is underway and will be reported in due course.

Experimental Section

General. Unless otherwise indicated, all reactions were carried out under an argon atmosphere using standard Schlenk techniques. Glassware was oven dried at 125 °C for 24 h prior to use. THF was distilled from Na/benzophenone, and dichloromethane, toluene, and hexanes were distilled from CaH_2. All reagents were used as received. The following compounds were prepared according to literature procedures: 2-mesitylenethiol,[65] 2-tributylstannyl-3,4-ethylenedioxythiophene,[66] 2,5-bis(tributylstannyl)thiophene,[56] and 5,5′-bis(tributylstannyl)-2,2′-bithiophene.[56]

All NMR spectra were recorded on 300 MHz or 360 MHz instruments. UV−vis−NIR spectra were recorded on a Varian Cary 5 instrument in distilled dichloromethane. Mass spectra were recorded on a Kratos Concept IH mass spectrometer system. Elemental analyses were performed by Canadian Microanalytical Services, New Westminster, B.C. Melting points were taken on a Reichert hotstage microscope and are uncorrected. Cyclic voltammetry studies were performed using a BAS CV-50W instrument in three-electrode electrochemical cells. The working electrode was a glassy carbon disk,

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(60) Haare, J. A. E. H. v.; Groenendaal, L.; Peerlings, H. W. I.; Havinga, E. E.; Vekemans, J. A. J. M.; Janssen, R. A. J.; Meijer, E. W. *Chem. Mater.* **1995**, *7*, 1984.

(61) Dodabalapur, A.; Katz, H. E.; Torsi, L. *Adv. Mater.* **1996**, *8*, 853.

(62) Haddon, R. C.; Siegrist, T.; Fleming, R. M.; Bridenbaugh, P. M.; Laudise, R. A. *J. Mater. Chem.* **1995**, *5*, 1719.

(63) Ishii, H.; Sugiyama, K.; Ito, E.; Seki, K. *Adv. Mater.* **1999**, *11*, 972.

(64) Meggers, E.; Michel-Beyerle, M. E.; Giese, B. *J. Am. Chem. Soc.* **1998**, *120*, 12950.

(65) Chisholm, M. H.; Corning, J. F.; Huffman, J. C. *Inorg. Chem.* **1984**, *23*, 754.

(66) Zhu, S. S.; Swager, T. M. *J. Am. Chem. Soc.* **1997**, *119*, 12568.

(67) Pham, C. V.; Burkhardt, A.; Shabana, R.; Cunningham, D. D.; Mark, H. B.; Zimmer, H. *Phosphorus, Sulfur Silicon* **1989**, *46*, 153.

the counter electrode was a Pt wire, and the reference electrode was an acetonitrile-based Ag wire/$AgNO_3$ solution. All cell solutions contained approximately 1 mmol of analyte and 0.1 M Bu_4NBF_4 electrolyte in dry, deoxygenated dichloromethane. Peak potentials are reported referenced to standard calomel electrode (SCE), using ferrocene as an added (∼0.5 mmol) internal standard. The redox couple of ferrocene was taken to be 0.470 V vs SCE in dichloromethane.[14]

Generation of 2-Mesitylenesulfenyl Chloride, MesSCl. In a typical preparation, mesitylenethiol (2.52 g, 16.6 mmol) in 5 mL of dry THF was added dropwise to a slurry of *N*-chlorosuccinimide (2.22 g, 16.6 mmol) in 10 mL of THF. The resulting bright yellow solution was stirred for 1 h, upon which the solution turned bright orange. The THF was removed under vacuum, and the resulting orange solid was redissolved in 20 mL of dry hexanes. The resulting succinimide precipitate was filtered off to afford solutions of 2-mesitylenesulfenyl chloride in quantitative yield by NMR. ^{1}H NMR ($CDCl_3$) δ 6.98 (s, 2H), 2.61 (s, 6H), 2.29 ppm (s, 3H). ^{13}C NMR ($CDCl_3$) δ 145.5, 143.3, 129.4, 128.9, 21.5, 21.4 ppm.

2-Bromo-5-(mesitylthio)-thiophene (3). A solution of 2,5-dibromothiophene (5.0 g, 20.7 mmol) in THF (20 mL) cooled to −78 °C was treated dropwise with *n*-BuLi (13.5 mL, 21.7 mmol). The resulting cloudy colorless solution was stirred for 1.5 h at −78 °C. A solution of MesSCl (20.7 mmol) in hexanes (15 mL) was added, and the reaction was stirred for 30 min at −78 °C and then allowed to warm to room temperature. The solvent was evaporated, and the residue was redissolved in dichloromethane (50 mL). This solution was washed with water (3 × 30 mL), and the organic phase was dried over $MgSO_4$ and concentrated to yield a brownish oil which crystallized upon standing. Recrystallization from EtOH produced **3** (3.6 g, 11.8 mmol, 57%) as very pale purple needles, mp 47−48 °C. ^{1}H NMR ($CDCl_3$) δ 6.94 (s, 2H), 6.81 (d, $J = 4$ Hz, 1H), 6.69 (d, $J = 4$ Hz, 1H), 2.49 (s, 6H), 2.26 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 142.72, 139.59, 138.61, 129.91, 129.43, 128.67, 110.99, 21.75, 21.06. MS (FAB, *m*/*z*) 312 (M^+, ^{79}Br, 90%) 314 (M^+, ^{81}Br, 100%). Anal. Calcd for $C_{13}H_{13}BrS_2$: C, 49.84; H, 4.18; S, 20.47%. Found: C, 49.99; H, 4.20; S, 20.51%.

2,5-Bis(mesitylthio)thiophene (4). A 20 mL THF solution containing thiophene (1.0 mL, 12.5 mmol) and TMEDA (3.02 g, 26.0 mmol) was treated with ^{n}BuLi (16.3 mL, 26.0 mmol) and then refluxed for 30 min. The solution was then cooled to 0 °C, and a freshly prepared solution of MesSCl (26.0 mmol) in hexanes (40 mL) was added dropwise. The resulting solution was stirred overnight and then washed with H_2O (3 × 75 mL), followed by saturated aqueous $CuSO_4$ solution (3 × 75 mL). The organic phase was dried over $MgSO_4$ and evaporated to yield a blood-red oil. This was chromatographed (silica, 5:1 hexanes: EtOAc) to give crude **2** which was recrystallized from hexanes/EtOH as slightly brown crystals (2.16 g, 5.61 mmol, 45%) mp 93−94 °C. UV−vis (CH_2Cl_2) λ_{max} 302 nm ($\epsilon = 13.0 \times 10^3$). ^{1}H NMR ($CDCl_3$) δ 6.90 (s, 4H) 6.65 (s, 2H) 2.45 (s, 12H) 2.25 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 142.66, 139.18, 137.45, 129.31, 128.85, 21.83, 21.05. MS (FAB, *m*/*z*) 384.1 (M^+, 100%). Anal. Calcd for $C_{22}H_{24}S_3$: C, 68.7; H, 6.29; S, 25.01%. Found: C, 68.13; H, 6.26; S, 25.41%.

5,5′-Bis(mesitylthio)-2,2′-bithiophene (5). A solution of **3** (0.61 g, 1.95 mmol) in dry THF (20 mL) was cooled to −78 °C and treated slowly with ^{n}BuLi (1.28 mL, 2.05 mmol). Upon addition of the ^{n}BuLi, the slightly purple solution immediately turned dull yellow. The solution was stirred for 1.5 h, and solid $CuCl_2$ (0.262 g, 1.95 mmol) was added. The brown solution was then allowed to warm to room temperature, stirred for 10 min, and then heated to 50 °C for 2 h. The black solution was cooled to room temperature and was passed quickly through a silica frit, eluting with $CHCl_3$ to yield a deep purple solution. The $CHCl_3$ was removed and the solid purple residue was recrystallized from benzene/MeOH to yield **5** (0.30 g, 0.642 mmol, 66%) as purple crystals, mp = 145−147 °C. UV−vis (CH_2Cl_2) λ_{max} 358 nm ($\epsilon = 24.5 \times 10^3$). ^{1}H NMR ($CDCl_3$) δ 6.93 (s, 4H), 6.76 (d, $J = 4$ Hz 2H), 6.73 (d, $J = 4$ Hz, 2H), 2.48 (s, 12H), 2.26 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 142.76, 139.42, 137.45, 136.59, 129.40, 128.67, 123.19, 21.78, 21.08. MS (FAB, *m*/*z*) 466 (M^+, 100%). Anal. Calcd for $C_{26}H_{26}S_4$: C, 66.91; H, 5.62; S, 27.48%. Found: C, 66.49; H, 5.62; S 27.26%.

2,5′′-Bis(mesitylthio)- 2,2′:5′,2′′-terthiophene (6). A 20 mL toluene solution containing **3** (0.67 g, 2.14 mmol), 2,5-bis(tributylstannyl)-thiophene (0.638 g, 0.963 mmol), and $Pd(PPh_3)_4$ (0.125 g, 5.1 mol %) was refluxed for 24 h. The solvent was removed and the residue recrystallized from acetone/MeOH to yield **6** (0.36 g, 0.66 mmol, 69%) as bright yellow crystals, mp 164 °C. UV−vis (CH_2Cl_2) λ_{max} 386 nm ($\epsilon = 30.9 \times 10^3$). ^{1}H NMR ($CDCl_3$) δ 6.95 (s, 4H), 6.82 (m, 6H), 2.50 (s, 12H), 2.27 (s, 6H). ^{13}C NMR ($CDCl_3$) δ 142.81, 139.51, 137.28, 137.04, 135.65, 129.43, 128.64, 123.83, 123.41, 21.79, 21.09 ppm. MS (FAB, *m*/*z*) 548 (M^+, 100%). Anal. Calcd for $C_{30}H_{28}S_5$: C, 65.65; H, 5.14; S, 29.21%. Found: C, 65.69; H, 5.21; S, 29.08%.

5,5′′′-Bis(mesitylthio)-2,2′:5′,2′′:5′′,2′′′-quaterthiophene (7). A 20 mL toluene solution containing **3** (0.551 g, 1.76 mmol), 5,5′-bis-(tributylstannyl)-2,2′-bithiophene (0.625 g, 0.840 mmol), and $Pd(PPh_3)_4$ (0.121 g, 5.95 mol %) was refluxed for 24 h. The solvent volume was reduced to 5 mL, and 100 mL of hexanes was added, causing an orange precipitate to form. This solid was recrystallized from toluene to yield **7** (0.23 g, 0.365 mmol, 43.4%) as a bright orange microcrystalline solid, mp 219−220 °C. UV−vis (CH_2Cl_2) λ_{max} 420 nm ($\epsilon = 16.2 \times 10^3$). ^{1}H NMR ($CDCl_3$) δ 6.94−6.77 (m, 12H), 2.50 (s, 12H), 2.27 (s, 6H). ^{13}C NMR (360 MHz, $CDCl_3$) δ 142.82, 139.55, 137.23, 137.19, 135.99, 135.54, 129.45, 128.63, 124.08, 123.98, 123.55, 21.80, 21.10. MS (EI, *m*/*z*) 630 (M^+, 33%). Anal. Calcd for $C_{34}H_{30}S_6$: C, 64.72; H, 4.79; S, 30.49%. Found: C, 64.48; H, 4.79; S, 29.77%.

2,5-Dibromo-3,4-ethylenedioxythiophene (9). This compound was prepared by modification of the literature procedure.[53] EDOT **8** (5.0 g, 35.2 mmol) was dissolved in a mixture of THF (20 mL) and glacial acetic acid (20 mL). To this was added solid NBS in small portions. After stirring at room temperature for 2 h, the deep red solution was poured onto 100 mL of water, effecting precipitation of **9** quantitatively as a light yellow solid. ^{1}H NMR (DMSO-d_6) δ 4.07 (s). This compound was used without further purification.

2-Bromo-5-mesitylthio-3,4-ethylenedioxythiophene (10). A solution of **9** (4.99 g, 16.6 mmol) in THF (20 mL) was cooled to −78 °C, and BuLi (10.88 mL, 17.4 mmol) was added dropwise. Upon the addition, the dark brown solution turned deep purple. This mixture was stirred at −78 °C for 1.5 h. A solution of MesSCl (16.6 mmol) in 20 mL of hexanes was then added slowly, giving a clear red solution. The solution was stirred at −78 °C for 30 min, then warmed to room temperature, and stirred for an additional 30 min. The mixture was washed with distilled water (3 × 50 mL), and the organic layer was dried with $MgSO_4$ and concentrated, causing **12** to crystallize as a red solid (4.5 g, 12.1 mmol, 73%), mp 95−96 °C. ^{1}H NMR ($CDCl_3$) δ 6.91 (s, 2H), 4.23 (s, 4H), 2.52 (s, 6H), 2.24 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 142.74, 141.22, 139.43, 139.28, 139.20, 129.35, 109.42, 87.29, 64.84, 64.80, 22.05, 21.06. MS, (CI *m*/*z*) 370 (M^+, ^{79}Br, 63%), 371 (M + 1, ^{79}Br, 86%), 372 (M^+, ^{81}Br, 74%), 373 (M + 1, ^{81}Br, 81%). Anal. Calcd for $C_{15}H_{15}O_2S_2Br$: C, 48.52; H, 4.07; S, 17.27%. Found; C, 48.27; H, 4.14; S, 17.53%.

2,5-Bis(tributylstannyl)-3,4-ethylenedioxythiophene (11). A solution of EDOT **8** (1.0 g, 7.03 mmol) in dry THF (20 mL) was treated with ^{n}BuLi (9.0 mL, 14.4 mmol). Immediately a white precipitate formed, and the reaction mixture was refluxed gently for 45 min. The solution was then cooled to room temperature, and tributyltin chloride (3.91 mL, 14.4 mmol) was added to the solution purely via syringe. The solution turned from white to dark red, and a precipitate formed. The solution was then refluxed for 18 h. The THF was removed under vacuum, and the remaining red residue was dissolved in hexanes. The resulting solution was filtered, washed with hexanes, and concentrated to yield a mixture of **8** and 2-tributylstannyl-3,4-ethylenedioxythiophene in a 5:1 ratio by ^{1}H NMR. Attempts to separate the mixture by column chromatography or distillation led to decomposition of the product. ^{1}H NMR ($CDCl_3$) δ *6.56 (s), 4.14 (s),* 4.11 (s), 1.58 (m), 1.33 (m), 1.10 (m), 0.896 (m). The listed ^{1}H peaks in italics are assigned to the monostannylated product.

2,5-Bis(mesitylthio)-3,4-ethylenedioxythiophene (12). ^{n}BuLi (4.40 mL, 7.1 mmol) was added dropwise to a solution of EDOT **8** (0.5 g, 3.5 mmol) in THF (20 mL) at room temperature, and the solution was then stirred for 1.5 h. To this was added a solution of freshly prepared MesSCl (7.7 mmol) in hexanes (20 mL). The resulting dark red solution was stirred at 0 °C for 1.5 h. The solution was washed with 3 × 50 mL of water, and the organic phase was dried over $MgSO_4$ and then concentrated to give a red oil. This was filtered through a silica frit, eluting with hexanes, and the filtrate was chromatographed (5:1 hexanes:

ethyl acetate) to give **12** which crystallized from the filtrate on evaporation of the solution under vacuum. (0.706 g, 1.59 mmol, 45%). Mp 156−7 °C. UV−vis (CH_2Cl_2) λ_{max} 285 nm ($\epsilon = 12.6 \times 10^3$). ^1H NMR ($CDCl_3$) δ 6.87 (s, 4H), 4.21 (s, 4H), 2.47 (s, 6H), 2.23 (s, 3H). ^{13}C NMR ($CDCl_3$) δ 142.52, 141.04, 138.73, 129.42, 129.16, 110.08, 64.55, 21.96, 20.93. MS (FAB, *m/z*) 442.1 (M^+, 100%). Anal. Calcd for $C_{24}H_{26}O_2S_3$: C, 65.12; H, 5.92; S, 21.73%. Found: C, 65.01; H, 5.94; S, 21.75%.

5,5′-Bis(mesitylthio)-2,2′-bis(3,4-ethylenedioxythiophene) (13). To a cold (−78 °C) solution of **10** (1.00 g, 2.69 mmol) in THF (15 mL) was added dropwise ^{n}BuLi (1.7 mL, 2.72 mmol). The resulting dark red solution was stirred at −78 °C for 1 h. A solution of $MgBr_2{\cdot}Et_2O$ (0.770 g, 2.70 mmol) in THF (20 mL) was then added slowly. This mixture was stirred at −78 °C for 30 min, and then solid $CuCl_2$ (0.362 g, 2.69 mmol) was added. The solution was then stirred for 45 min at −78 °C, warmed to room temperature, and stirred for 12 h. The solution was then poured into 100 mL of distilled water, causing a pale yellow precipitate to form. This was filtered off and recrystallized from benzene to yield 0.430 g (0.736 mmol, 55%) **13** as yellow crystals, mp 274−276 °C. UV−vis (CH_2Cl_2) λ_{max} 364 nm ($\epsilon = 31.4 \times 10^3$). ^1H NMR ($CDCl_3$) δ 6.87 (s, 4H), 4.22 (s br, 8H), 2.51 (s, 12H), 2.22 (s, 6H). ^{13}C NMR (360 MHz, C_6D_6) δ 142.91, 141.96, 138.59, 136.88, 130.58, 111.63, 107.63, 64.37, 64.26, 22.39, 20.94 ppm. FAB-HRMS calcd for $C_{30}H_{30}O_4S_4$: 582.8300. Found: 582.1041. Anal. Calcd for $C_{30}H_{30}O_4S_4$: C, 61.83; H, 5.19; S, 22.01%. Found: C, 61.53; H, 5.22; S, 22.57%.

5,5″-Bis(mesitylthio)-2,2′:5′,2″-ter(3,4-ethylenedioxythiophene) (14). A solution of **10** (2.00 g, 5.38 mmol), **11** (0.77 g, 2.5 mmol) and Pd-$(PPh_3)_4$ (75 mg, 2.8 mol %) in toluene (40 mL) was refluxed for 18 h. The solution was then cooled to room temperature, the solvent volume was reduced and hexanes (150 mL) was added to the mixture resulting in a shiny gold precipitate which was filtered. This material was purified by chromatography (5:1 hexanes: EtOAc) to yield **14**, yield 28%. ^1H NMR (CD_2Cl_2) δ 6.95 (s, 4H) 4.31 (m, 12H) 2.55 (s, 12H) 2.30 (s, 6H) ppm. MS (FAB, *m/z*) 722 (M+, 30%). The tendency of this material to oxidize has precluded satisfactory elemental analysis.

3,4,3″,4″-Bis(ethylenedioxy)-2,5″-bis(mesitylthio)-2,2′:5′2″-terthiophene (15). A solution of **10** (0.80 g, 2.15 mmol) 2,5-bis-(tributylstannyl)thiophene (0.641 g, 0.97 mmol), and $Pd(PPh_3)_4$ (42 mg) in 20 mL toluene was refluxed for 24 h. After cooling to room temperature, the solution was subjected to column chromatography (silica, 5:1 hexanes:EtOAc). The product so obtained was recrystallized from $CHCl_3$/MeOH to yield **12** (0.31 g, 48%) as a bright yellow solid, mp 213−214 °C. UV−vis (CH_2Cl_2) λ_{max} 401 nm ($\epsilon = 40.6 \times 10^3$). ^1H NMR (CD_2Cl_2) δ 6.95 and 6.94 (overlapping s, 6H), 4.30 (s, 8H), 2.54 (s, 12H), 2.26 (s, 6H). ^{13}C NMR (DMSO) δ 142.09, 138.92, 136.96, 131.82, 129.28, 128.79, 122.97, 111.55, 105.50, 64.93, 64.66, 21.60, 20.55. MS (FAB, *m/z*) 664.1 (M^+, 20%). Anal. Calcd for $C_{34}H_{32}O_4S_5$: C, 61.42; H, 4.70; O, 9.77%. Found: C, 60.85; H, 4.85; O, 9.62%.

3′,4′-Ethylenedioxy-2,5″-bis(mesitylthio)-2,2′:5′2″-terthiophene (16). A 20 mL toluene solution containing **3** (1.17 g, 3.74 mmol), (**11**) (0.77 g, 1.78 mmol), and $Pd(PPh_3)_4$ (110 mg,) was refluxed for 24 h. After the solution cooled, the volume was reduced to 10 mL which was then poured into hexanes. The resulting green precipitate was filtered and recrystallized from $CHCl_3$/MeOH to yield (**16**) (0.4 g, 0.66 mmol, 18.6%) as slightly green microcrystals. UV−vis (CH_2Cl_2) λ_{max} 406 nm ($\epsilon = 46.4 \times 10^3$). ^1H NMR (CD_2Cl_2) δ 6.96−6.84 (m, 8H), 4.29 (s, 4H), 2.51 (s, 12H), 2.28 (s, 6H). ^{13}C NMR (360 MHz, CD_2Cl_2) δ 143.07, 139.88, 137.90, 136.23, 135.54, 130.16, 129.75, 129.46, 122.91, 109.46, 65.43, 21.99, 21.20. MS (FAB, *m/z*) 606 (M^+, 100%). Anal. Calcd for $C_{32}H_{30}O_2S_5$: C, 63.33; H, 4.98; O, 5.27%. Found: C, 62.93; H, 4.93; O, 5.48%.

3,4-Ethylenedioxy-5′-mesitylthio-2,2′-bithiophene (17). A 20 mL toluene solution containing **3** (1.95 g, 6.23 mmol), 2-tributylstannyl-3,4-ethylenedioxythiophene (2.69 g, 6.23 mmol), and $Pd(PPh_3)_4$ (125 mg) was refluxed in the dark for 21 h. Upon cooling, the solution was poured into hexanes (150 mL) and filtered. The supernatant was then concentrated and chromatographed (5:1 hexanes:ethyl acetate), and the product so obtained was recrystallized from benzene/MeOH to yield bright yellow crystals of (**17**) (1.67 g, 4.45 mmol, 71.6%) mp 101−102 °C. ^1H NMR (CD_2Cl_2) δ 7.0−6.86 (m, 4H), 6.18 (s, 1H), 4.29−4.18 (m, 4H), 2.52 (s, 6H), 2.28 (s, 3H). ^{13}C NMR (360 MHz, CD_2Cl_2) δ 142.99, 142.27, 139.76, 137.90, 136.17, 135.69, 130.22, 129.69, 129.49, 122.76, 112.06, 97.06, 65.42, 64.98, 21.97, 21.15 MS (FAB, *m/z*) 374 (M^+, 100%) Anal. Calcd for $C_{19}H_{18}O_2S_3$: C, 60.93; S, 25.68%. Found: C, 61.08; S, 25.44%.

3′,4′,3″,4″-Bis(ethylenedioxy)-5,5‴-bis(mesitylthio)-2,2′:5′,2″:5″,2‴-quaterthiophene (18). A solution of **17** (0.297 g, 0.793 mmol) in THF (10 mL) was cooled to 0 °C and treated with ^{n}BuLi (0.5 mL, 0.8 mmol). The dirty green solution was stirred for 45 min at 0 °C and was then transferred via cannula to a refluxing solution of $Fe(acac)_3$ (0.28 g, 0.793 mmol) in THF (20 mL). The solution was then refluxed for 44 h. The solvent was then removed, and the bright red residue was chromatographed (silica, 1:1 $CHCl_3$:hexanes) to yield a red solid. Recrystallization from THF produced **18** (0.35 g, 0.134 mmol, 59%) as a bright orange/red solid, mp 296−298 °C. UV−vis (CH_2Cl_2) λ_{max} 467 nm ($\epsilon = 50.5 \times 10^3$), 441 nm ($\epsilon = 57.0 \times 10^3$). ^1H NMR (CD_2Cl_2) δ 7.00−6.86 (m, 8H), 4.33 (s, 8H), 2.52 (s, 12H), 2.28 (s, 6H). MS (FAB, *m/z*) 746 (M^+, 100%). Anal. Calcd for $C_{38}H_{34}O_4S_6$: C, 61.10; H, 4.59; S, 25.75%. Found: C, 61.25; H, 4.51; S, 26.21%.

3,4,3‴,4‴-Bis(ethylenedioxy)-5,5‴-bis(mesitylthio)-2,2′:5′,2″:5″,2‴-quaterthiophene (19). A 20 mL toluene solution of **10** (0.56 g, 1.51 mmol), 5,5′-bis(tributylstannyl)-2,2′-bithiophene (0.51 g, 0.680 mmol), and $Pd(PPh_3)_4$ (0.140 g, 8.0 mol %) refluxed for 22 h. The solution was cooled and poured into hexanes (100 mL), resulting in a brick-red precipitate which was recrystallized from benzene to yield **19** (0.37 g, 0.495 mmol, 72.7%) as a brick-red solid, mp 245−247 °C. UV−vis (CH_2Cl_2) λ_{max} 435 nm ($\epsilon = 54.4 \times 10^3$). ^1H NMR (CD_2Cl_2) δ 7.01−6.95 (m, 8H), 4.32 (s, 8H), 2.54 (s, 12H), 2.26 (s, 6H). ^{13}C NMR (360 MHz, CD_2Cl_2) δ 143.05, 142.18, 139.59, 137.43, 135.69, 133.48, 129.77, 129.63, 123.60, 112.91, 107.71, 65.34, 65.30, 22.12, 21.11. MS (FAB, *m/z*) 746 (M^+, 50%). Anal. Calcd for $C_{38}H_{34}O_4S_6$: C, 61.10; S, 25.75%. Found: C, 61.00; S, 25.74%.

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