Synthesis and Electropolymerization Behavior of Bis (Oligothienyl) Sulfides. Generation of Heteroaromatic Poly(*p*-phenylene sulfide) Analogs

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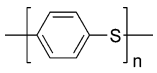
The synthesis and electrochemical properties of a series of bis(thiophene) sulfides is presented. The molecules were synthesized via either thiophenethiol substitution reactions with thienyl bromides or treatment of lithiated thiophenes with bis(phenylsulfonyl) sulfide. Bis(oligothienyl) sulfides based on thiophene, 3-hexylthiophene, and 3,4-ethylenedioxythiophene were similarly prepared. Investigation of the electrochemical properties reveal that, despite the presence of α,ω-CH positions on the two thiophene termini, not all derivatives formed polymers upon electro-oxidation. In some cases the inherent stability of the radical cation precluded coupling reactions; in others, radical cation solubility prevented electrodeposition of the putative polymer. Five of the monomers could be electropolymerized to afford poly(oligothienyl sulfides) which were characterized by electronic spectroscopy and electrochemical studies. Good correlations were found between the polymer redox properties and corresponding bis(arylthio) oligothiophene molecules previously reported.

Introduction

The introduction of inorganic components into the backbone of conjugated organic polymers offers great potential for the modification and diversification of the properties of the resulting hybrid polymeric systems. Transition-metal-based approaches have been extremely popular in this regard,[1,2] and there are also several organic/inorganic polymer variants based on main group elements. Polyaniline, i.e., "poly-*p*-phenyleneamine", is a well-known example of such systems; the electrochemical, optical, and charge transport properties of polyaniline and its derivatives are well described. Other conjugated polymers incorporating other elements such as boron,[3] silicon,[4] and the heavier group 15 elements[5] have been established as well. Among group 16 elements, it has long been known that the conductivity of poly(*p*-phenylene)sulfide (PPS) **1** can be greatly enhanced by oxidative doping.[6] However, the doped/conducting form of this polymer exhibits poor environmental stability and undergoes irreversible cross-linking. Similar problems plague the related poly(vinylene sulfide).[7]



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The poor stability of doped **1** and related materials is puzzling in some respects, even though PPS is not a formally fully conjugated polymer; given that divalent sulfur (−SR) substituents are excellent pi donors and as such might be expected to provide better stability to oxidatively doped polyaromatics. We have demonstrated that divalent sulfur *as a terminal substituent* imparts excellent stability characteristics to oligothiophenes,[8] and we recently reported that a PPS-like polymer based on bis(ethylenedioxythiophene) units *linked* by sulfides (see below) exhibits outstanding electrochemical stability.[9] The excellent redox stability in the oligomeric and polymeric systems is assisted in part by the sulfur substituent/linker, but is also to the more electron-rich nature of oligo- and polythiophenes,[10,11] and in particular derivatives based on 3,4-ethylenedioxythiophene benefit from

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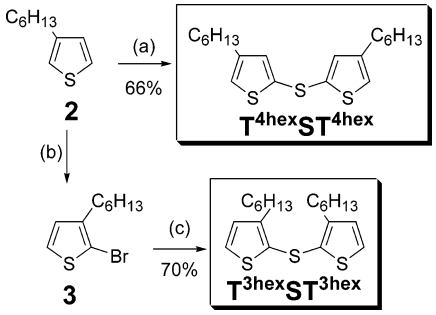
Scheme 1[a]



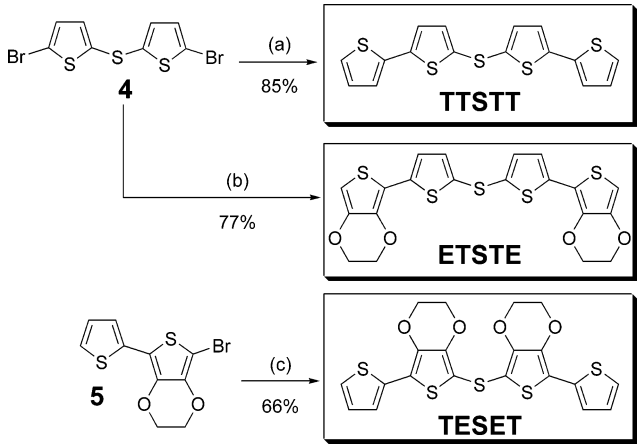
[a] Reagents: (a) LDA then $(PhSO_2)_2S$ (0.5 equiv); (b) NBS; (c) *n*-BuLi then $(PhSO_2)_2S$ (0.5 equiv).

the strong donating effect of the ethylenedioxy group.[12] Given the growing importance of thiol-terminated or sulfide-linked conjugated organics as molecular wires,[13] we were interested to examine more deeply the interplay between monomer structure, polymer stability in the doped state, and charge transport characteristics in sulfur-linked and terminated conjugated oligomers and polymers as models for thiol terminated oligomers and polymers. To address some of these issues, we have prepared a series of monomers based on the basic template of (oligo)thiophene units linked via sulfide moieties and with terminal α carbon positions unsubstituted so that electropolymerization reactions can (in principle) occur. Herein we present the synthesis and electropolymerization characteristics of several bis(oligothienyl)sulfide derivatives.

Synthesis

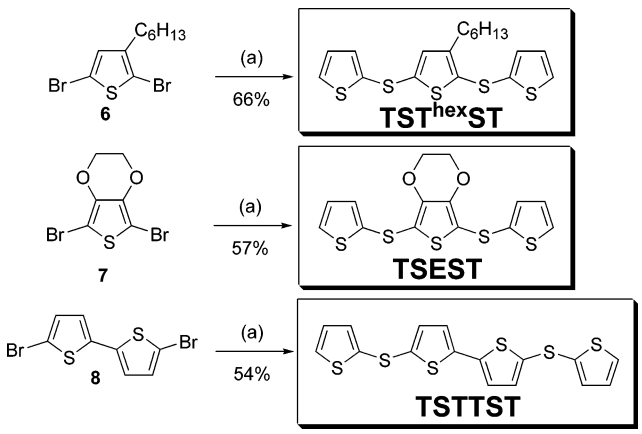
Schemes 1−3 outline the synthetic routes to the sulfur-bridged thiophene oligomers. Two pathways were utilized. The first involves carbon−sulfur bond formation by treatment of a suitable arylthiol with an aryl bromide in basic conditions with a copper(I) salt. Nakayama et al. have successfully used this route to prepare a series of oligo(thio-2,5-thienylenes), although no physical properties were reported.[14] They were able to prepare bis(2-thienyl) sulfide **TST**[15] in good yield by reacting 2-bromothiophene with the cuprous salt of 2-thiophenethiol in DMF.

Scheme 2[a]

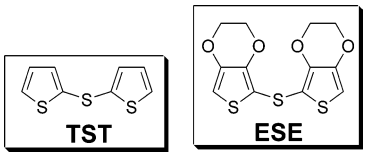


[a] Reagents: (a) 2 equiv. 2-(tributylstannyl)thiophene, cat. $Pd(PPh_3)_4$; (b) 2 equiv. 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene, cat. $Pd(PPh_3)_4$; (c) *n*-BuLi then $(PhSO_2)_2S$ (0.5 equiv).

Scheme 3[a]



[a] Reagents: (a) 2-thiophenethiol, KOH, and Cu_2O.



The second method involves reacting two equivalents of an aryl Grignard or analogous lithiated species with bis(phenylsulfonyl) sulfide $PhSO_2)_2S$. We have previously shown that bis(3,4-ethylenedioxy-2-thienyl)sulfide **ESE** could be obtained in this way by treating the anion of 3,4-ethylenedioxythiophene (EDOT) with bis(phenylsulfonyl) sulfide.[9] This methodology was also employed in the synthesis of two regiospecific hexyl-substituted monomers **T**^{4hex}**ST**^{4hex} and **T**^{3hex}**ST**^{3hex} by strategic lithiation, followed by quenching the anion with $(PhSO_2)_2S$ (Scheme 1). For instance, when lithium diisopropylamide (LDA) is used as

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(15) Because of the large number of related target compounds the following shorthand notation is used to identify compounds: **T** = thiophene; **E** = 3,4-ethylenedioxy; **T**$^{n-hex}$ = (*n*-hexyl)thiophene; **S** = sulfur atom; **Mes** = 2,4,6-trimethylphenyl.

Table 1. Lowest Energy Electronic Transitions for Oligothiophene Target Compounds

compound	λ_{max} (nm)
TST	268
ESE	270
$\mathbf{T^{4hex}ST^{4hex}}$	270
$\mathbf{T^{3hex}ST^{3hex}}$	250
TTSTT	335
ETSTE	345
TESET	345
$\mathbf{TST^{3hex}ST}$	280
TSEST	280
TSTTST	350

base at −78 °C, 3-hexylthiophene **2** is selectively metalated at the 5-position. Subsequent treatment with $(PhSO_2)_2S$ afforded $\mathbf{T^{4hex}ST^{4hex}}$ in 66% yield. Alternatively, lithium−halogen exchange of 2-bromo-3-hexylthiophene **3** produced the 2-lithio species, which could then be treated in situ with $(PhSO_2)_2S$ to give $\mathbf{T^{3hex}ST^{3hex}}$. The two isomers can be readily distinguished from one another on the basis of the coupling constant between the two thienyl protons ($J = 1.1$ Hz in $\mathbf{T^{4hex}ST^{4hex}}$ and 5.1 Hz in $\mathbf{T^{3hex}ST^{3hex}}$).

A series of bis(bithienyl)sulfides was also prepared as outlined in Scheme 2. Bis(thienyl)sulfide **TST** was brominated to give compound **4**, which was subsequently converted via Stille coupling with 2-tributylstannylthiophene to give **TTSTT**. The corresponding Stille reaction with 2,-tributylstannyl-3,4-ethylenedioxythiophene yielded bis(bithienyl)sulfide **ETSTE** in which the ethylenedioxy-substituted thiophenes are situated at the ends of the molecule. The isomer of this compound with the EDOT rings on the "inside", i.e., **TESET**, was prepared by lithium−halogen exchange on monobrominated compound **5** followed by reaction with bis(phenylsulfonyl)sulfide.

Finally, three thiophene oligomers were prepared containing three (oligo)thiophene segments connected by two internal sulfide bridges (Scheme 3). The cuprous salt of 2-thiophenethiol (generated by treating the potassium thiolate with copper(I) oxide) reacted with 2,5-dibromo-3-hexylthiophene **6** in DMF to furnish $\mathbf{TST^{hex}ST}$ in 66% yield. Under the same reaction conditions, both **TSEST** and **TSTTST** were prepared, in 57% and 54% yields, respectively, by treating either 2,5-dibromo-3,4-ethylenedioxythiophene **7** or 5,5′-dibromo-2,2′-bithiophene **8** with 2-thiophenethiol in the presence of potassium hydroxide and copper(I) oxide.

The solution spectra of the target monomers herein, together with the bis(mesitylthio) oligothiophenes previously reported,[8] provide some insight into how terminal and internal sulfur atoms perturb the π-chromophores of oligothiophenes. Solution absorption spectra are presented in Table 1. The four derivatives containing two monothiophenes linked by a single sulfur atom—**TST**, **ESE**, $\mathbf{T^{4hex}ST^{4hex}}$, and $\mathbf{T^{3hex}ST^{3hex}}$—all have λ_{max} values intermediate between thiophene with no −SR substituents (λ_{max} 243 nm) and the bis(mesitylthio)thiophenes **MesSTSMes** (λ_{max} 302 nm) and **MesSESMes** (λ_{max} 305 nm) bearing two −SR groups. This indicates that (i) the effects of −SR substituents on the HOMO−LUMO gap are approximately additive, and (ii) the placement of two thiophenes about a single sulfur atom does not lead to significant extension of the conjugation. Thus **TST**, **ESE**, and the hexyl-substituted analogues should be considered as consisting of two thiophene chromophores rather than being bithiophene-type molecules. Similar conclusions can be drawn in comparing the λ_{max} value for **TTSTT** (335 nm) (as well as the EDOT-containing chromophores **ETSTE** or **TESET**) to that of bithiophene (302 nm) and **MesS-TT-SMes** (358 nm), i.e., the former appears to be two weakly coupled bithiophenes rather than a single quaterthiophene chromophore.

Table 2. Oxidation Potential of Bis(oligothienyl) Sulfides

monomer	$E^1{}_a{}^a$ (V)
TST	1.55
ESE	1.18
$\mathbf{T^{4hex}ST^{4hex}}$	1.41
$\mathbf{T^{3hex}ST^{3hex}}$	1.39
TTSTT	1.37
ETSTE	1.01
TESET	0.96
$\mathbf{TST^{hex}ST}$	1.29 (1.25)[b]
TSEST	1.20 (1.16)[b]
TSTTST	1.25 (1.21)[b]

[a] Anodic peak potential vs Ag/AgCl at 0.1 V/s. [b] Reversible; first number is anodic peak potential and number in parenthesis is $E_1°$.

Electrochemical Properties

Electrochemical investigations were undertaken on the target compounds described in the previous section. Each of these "monomers" contains thiophene moieties with unsubstituted α carbon atoms at both termini of the molecules. Upon electrochemical oxidation, coupling of the incipient radical cations could in principle occur to yield poly(thienyl)sulfides by analogy to the conventional method of electropolymerization of simple thiophene derivatives.[10]

Electrochemical data for the thiophene monomers of interest are summarized in Table 2. The anodic peak potentials of the monomers displaying irreversible oxidations can be generally correlated with molecular structure features. For example, **ESE** is oxidized at considerably lower potential relative to its unsubstituted thiophene congener **TST** owing to the presence of the highly electron rich EDOT rings in the former. Increased conjugation length within the thienyl units (e.g., **TTSTT** vs. **TST**) also has the expected effect of lowering the oxidation potential. Within the series of three bis(bithienyl) sulfides—**TTSTT**, **ETSTE**, and **TESET**—the presence and position of the EDOT moieties influences the monomer (and polymer, vide infra) oxidation potential. Thus, **TTSTT** lacks any EDOT rings and has a higher oxidation potential than either **ETSTE** or **TESET**, the latter two of which are isomers of bithiophenes containing one EDOT group. In comparing these two molecules with each other, the former has the EDOTs at the terminal positions with unsubstituted thiophenes flanking the central sulfur atom, while the latter has the EDOTs directly attached to the sulfur. As such, **ETSTE** can be thought of as a derivative of **TST** (i.e., with additional EDOT groups at the ends) while **TESET** is a derivative of the more electron rich **ESE** (i.e., with additional thiophene groups). The increase in conjugation length rationalizes the decrease in oxidation potential on going from **TST** to **TTSTT** and from **ESE** to **TESET**, and the more electron rich "interior" of the latter renders it more easily oxidized than its isomer **ESTSE**. Thus, the monomer

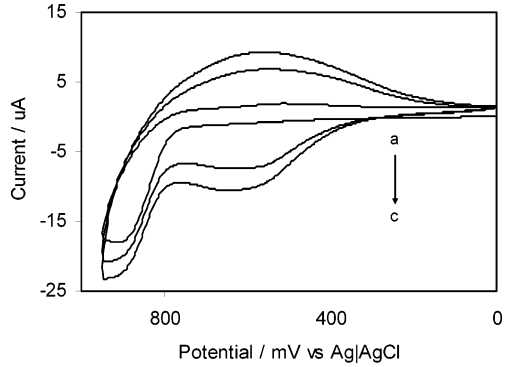
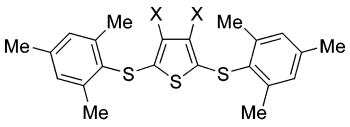


Figure 1. Electropolymerization of **ETSTE** in CH_2Cl_2 at 0.1 V/s: (a) 1st scan, (b) 5th scan, (c) 10th scan.

oxidation potential in this series can be tuned by subtle but rational changes in molecular design.

Three of the compounds—**TST^{hex}ST**, **TSEST**, and **TSTTST**—can be *reversibly* oxidized to radical cations and even dications, despite the presence of two unsubstituted α carbon atoms at the ends of the molecule. These compounds all consist of central thiophene moieties (3-hexylthiophene for **TST^{hex}ST**, 3,4-ethylenedioxythiophene for **TSEST**, and 2,2′bithiophene for **TSTTST**) flanked by two 2-thiophenethio (ArS−) substituents. These central units benefit from two electron donating ArS− groups and, as such, closely resemble the 2,5-bis(mesitylthio)thiophenes **MesSTSMes** and **MesSESMes** which were previously demonstrated to possess stable radical cationic states on the electrochemical time scale.[8] We ascribe the reversibility of the oxidation processes in **TST^{hex}ST**, **TSEST**, and **TSTTST** to the fact that the spin and charge of the radical cations of these species are confined largely to the central (bi)thiophene moiety, with little spin or charge distribution on the outer thiophene rings. Thus, although these three molecules possess the α-unsubstituted carbon atoms on the terminal thiophene rings normally required for electropolymerization, the electropolymerization process is thwarted by the concentration of spin and charge on the inner thiophene portion of these molecules.



MesSTSMes X,X = H,H
MesSESMes X,X = OCH_2CH_2O

The other monomers displayed irreversible oxidation waves and, to varying degrees of success, CV behavior indicative of electropolymerization (increasing peak current with increasing number of scans, and the formation of a colored polymer film on the electrode surface). As a representative example, Figure 1 displays the CV of ETSTE after 1 scan (the irreversible process with the anodic peak potential at approximately 960 mV), 5 scans, and 10 scans (the reversible process with the anodic and cathodic processes at ∼640 mV).

After electropolymerization, the polymer-coated electrodes were washed and placed in monomer-free electrolyte solution. Cyclic voltammetry studies of a film of **(ETSTE)$_n$** showed a broad, reversible oxidation wave (Figure 2). The

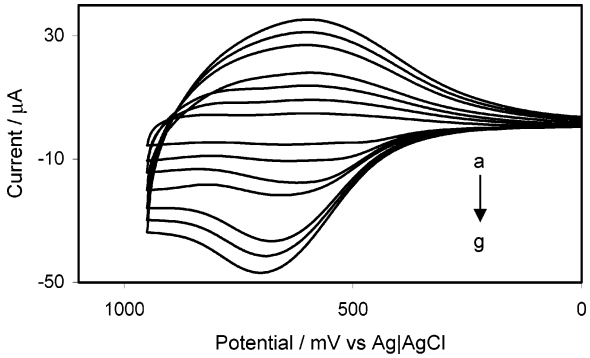


Figure 2. CV of the film of **(ETSTE)$_n$** at different scan rates: (a) 0.025, (b) 0.05, (c) 0.075, (d) 0.1, (e) 0.15, (f) 0.175, and (g) 0.2 V/s.

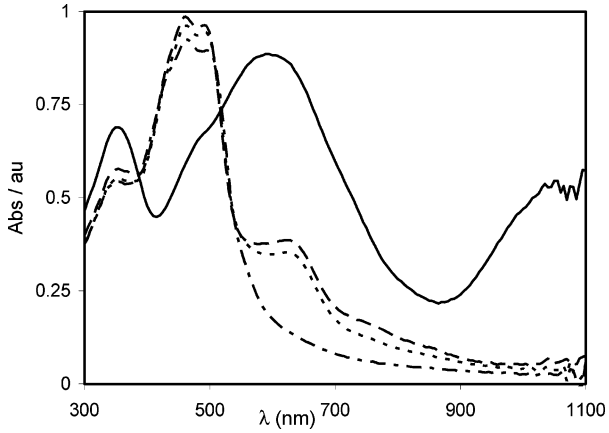


Figure 3. Electronic spectra of **(ETSTE)$_n$** at (—) 1.0, (− −) 0.0, (- - -) −0.2, and (− - − -) −1.0 V vs Ag/AgCl.

variation of peak current of the modified electrode was found to be linearly dependent on scan rate, indicative of an electroactive surface-bound species. No change was observed in the electrochemical properties of the polymer after repeated cycling one hundred times or after exposure to air. The stability of the polymer is unusual given that this is not formally a fully conjugated polymer but rather one consisting of oligothiophenes linked by sulfur atoms. We have previously demonstrated that small molecule analogues of these polymers are highly stable in their radical cation and dication forms due to the EDOT moiety (which is well known to both lower oxidation potentials and provide chemical stability to the resulting radical cations) and the presence of the divalent sulfur which provides further stability to the oxidized (doped) species.[8]

The electronic spectra as a function of applied potential on ITO-deposited films of the polymers were examined. Figure 3 displays the spectra of **(ETSTE)$_n$** as a function of potential. At +1.0 V, **(ETSTE)$_n$** is deep blue and shows two absorption maxima at 595 and 1050 nm. As the potential is lowered, these maxima disappear gradually and are replaced by new peaks at 460, 490, and 630 nm. The doping/dedoping processes are fully reversible; repeated electrochemical cycling does not produce significant changes in the electronic spectrum.

Monomers **ESE**, **TTSTT**, and **TESET** could all be electropolymerized in a manner similar to that described for **ESTSE** above. The two hexyl-substituted monomers **T^{4hex}ST^{4hex}** and **T^{3hex}ST^{3hex}** also displayed irreversible oxidations; however, repeated electrochemical cycling did not lead

Table 3. Electrochemical and Optical Properties of Bis(oligothienyl) Sulfide Polymers

polymer	$\lambda_{monomer}$ (nm)	λ_{doped} (nm)	$\lambda_{de-doped}$ (nm)	$E_{1/2}$ (V)
$(ESE)_n$	270	600, 1020	435, 450, 480	0.600
$(TTSTT)_n$	335	620	345, 410	1.310
$(ETSTE)_n$	345	345, 595, 1050	350, 460, 490	0.630
$(TESET)_n$	345	345, 690	345, 430	0.870

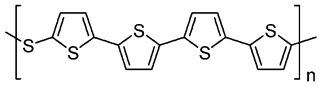
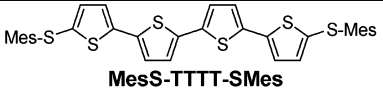
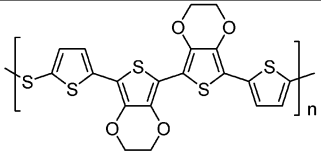
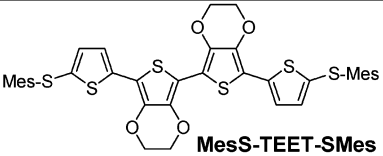
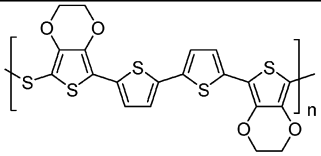
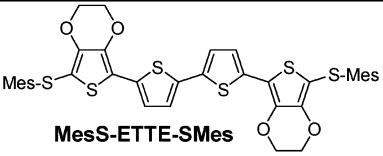
to deposition of any material on the electrode, and the electrode eventually was rendered inactive. This may be due to the presence of the hexyl groups, which could render the incipient radical cations too soluble for deposition as well as provide additional chemical reaction pathways for the radical cation; the observed electrode passivation after a few electrochemical cycles suggests the latter is a major contributor. Finally, the "parent" monomer in this series—compound **TST**—could be electropolymerized but the resulting polymer films were extremely unstable. Repeated electrochemical cycling led to rapid film decomposition. The polymer resulting from **TTSTT** is somewhat more stable than that derived from **TST** but the former does degrade upon application of multiple electrochemical oxidation/reduction processes. These findings are broadly consistent with the known high reactivity of poly(*p*-phenylene sulfide)—evidently either longer thiophene chains or incorporation of the rich EDOT are required for stable electroactive polymers of this type.

Table 3 presents the optical and electrochemical data for the poly(thienyl sulfide) polymers prepared in this study. It is instructive to compare the redox properties of the polymer to those of model compounds bearing similar oligothiophene repeat units (Table 4). Monomers **TTSTT**, **ETSTE**, and **TESET** all produce polymer structures with quaterthiophene-based chromophores connected by sulfur atoms, and for each of these polymers we have previously described a "capped monomer" molecule consisting of the respective quaterthiophenes with two mesitylthio groups at each end of the chromophore (Table 4).[8] The oxidation of **(TTSTT)*n*** occurs at a significantly higher potential than either of the two EDOT-containing polymers **(ETSTE)*n*** and **(TESET)*n***. The same trend is found in comparing the first (reversible) oxidation potential of the model for **(TTSTT)*n***, i.e., **MesS-TTTT-SMes** ($E_1° = +0.83$ V vs SCE) compared to **MesS-TEET-SMes** ($E_1° = +0.49$ V) and **MesS-ETTE-SMes** ($E_1° = +0.61$ V). This is perhaps not surprising given the more electron-rich nature of the EDOT moiety relative to unsubstituted thiophene: **(ETSTE)*n*** and **(TESET)*n*** are simply more electron rich than **(TTSTT)*n***, and in a similar vein **MesS-TEET-SMes** and **MesS-ETTE-SMes** are also more electron rich than **MesS-TTTT-SMes**. However, closer comparison between **ETSTE**, **TESET**, their corresponding polymers, and model monomers also reveals some self-consistency in the relationship between molecular structure and electrochemical properties. As discussed previously,[8] **MesS-TEET-SMes** is easier to oxidize than **MesS-ETTE-SMes** because of the disposition of the EDOT and thiophene groups. The same trend is prevalent in **(ETSTE)*n*** compared to **(TESET)*n***, which contain the basic EDOT/thiophene chromophores present in **MesS-TEET-SMes** and **MesS-ETTE-SMes**, respectively, as repeat units. This is despite the fact that *monomer* **ETSTE** is a little more difficult to oxidize than monomer **TESET**.

Conclusion

In summary we have described the synthesis and characterization of a new series of sulfide bridged thiophene derivatives. The ease of oxidation of the monomers can be understood on the basis of conjugation length and substitution patterns. Several of the monomers were successfully electropolymerized to afford novel poly(thienyl sulfides), some of which are very stable to repeated electrochemical oxidation/reduction processes. In particular the EDOT-containing materials showed outstanding electrochemical stability. The coloration/de-coloration are fully reversible, which is a promising feature for applications in electrochromic devices. The relative redox characteristics of the polymers can be understood by invoking comparisons to bis(mesitylthio) oligothiophene model compounds. However, it is worth noting that there are quantitative dissimilarities in the model

Table 4. Selected Monomer/Polymer Structures and Related Oligomer Model Compounds

Monomer	Polymer structure	Model compound
TTSTT		 **MesS-TTTT-SMes**
ETSTE		 **MesS-TEET-SMes**
TESET		 **MesS-ETTE-SMes**

compound comparisons relative to the polymer comparisons, which may arise due to a combination of effects in the polymer (electronic communication between thiophene chromophores, pi stacking) which are not operative in the model capped oligomers. One way to address the issue of electronic communication between thiophene moieties via a bridging sulfur would be to make molecules analogous to e.g., **TTSTT**, **ETSTE**, and **TESET** but with their terminal positions "capped" by groups designed to prevent polymerization. This should render the oxidation of the monomers reversible and permit thorough investigation of the issue of inter-chromophore electronic communication in these systems. These studies are well underway and will be the subject of a future publication.

Experimental Section

General. Unless stated otherwise, all reactions and manipulations were carried out under an argon atmosphere using standard Schlenk line or glovebox techniques. Glassware was oven-dried at 125 °C for 24 h prior to use. Solvents were dried and distilled under argon prior to use (dichloromethane, acetonitrile, and hexanes, from CaH_2; toluene, diethyl ether, and tetrahydrofuran, from sodium/benzophenone). All reagents were purchased from commercial sources and used as received except as stated otherwise. The following compounds were prepared according to literature procedures: bis(2-thienyl)sulfide (**TST**),[14] 2-bromo-3-hexylthiophene (**3**),[16] 5,5′-dibromo-bis(2-thienyl)sulfide (**4**),[14] 2-(tributylstannyl)thiophene,[17] 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene,[1] 2-bromo-5-thienyl-3,4-ethylenedioxythiophene (**5**),[18] 2,5-dibromo-3-hexylthiophene (**6**),[16] 2,5-dibromo-3,4-ethylenedioxythiophene (**7**),[8] 5,5′-dibromo-2,2′-bithiophene (**8**),[19] 2-thiophenethiol,[20] and bis(phenylsulfonyl) sulfide.[21]

^{1}H NMR spectra were recorded at 300 MHz and ^{13}C NMR spectra were recorded at 75 MHz. Melting points are uncorrected. All UV−Vis−NIR studies were performed in freshly distilled dichloromethane. Voltammetric measurements were performed at room temperature (22 ± 2 °C) in CH_2Cl_2 containing 0.1 M substrate and 1 M of *n*-Bu_4NBF_4 as electrolyte. Platinum button (diameter 1.6 mm) or ITO was used as the working electrode. Platinum wire and Ag wire were used as counter and reference electrodes, respectively. The working electrode was polished on alumina before use. *iR* compensations were applied for all experiments for potential measurements.

Bis(4-hexyl-2-thienyl) Sulfide ($T^{4hex}ST^{4hex}$). A 1.6 M hexanes solution of *n*-butyllithium (10.0 mL, 16.0 mmol) was added dropwise to a solution of diisopropylamine (2.24 mL, 16.0 mmol) in THF at 0 °C. After the solution was stirred for 30 min it was cooled to −78 °C, and a solution of **2** (2.64 g, 15.7 mmol) in THF (60 mL) was added dropwise. The suspension was stirred at −78 °C for 1 h and then a solution of bis(phenylsulfonyl) sulfide (2.48 g, 7.90 mmol) in THF (20 mL) was added dropwise via cannula. After stirring at −78 °C for 3 h, the reaction mixture was allowed to warm to room temperature and stirred for an additional 30 min. The mixture was poured onto water (100 mL), and the aqueous layer was extracted with ether. The combined organic extracts were washed with water and dried (Na_2SO_4). The residue was subjected to column chromatography (silica, pentane) to give $\mathbf{T^{4hex}ST^{4hex}}$ as colorless oil, yield 1.90 g (66%). ^{1}H NMR (CD_2Cl_2): δ 7.05 (d, J = 1.1 Hz, 2H), 6.91 (d, J = 1.1 Hz, 2H), 2.55 (t, J = 7.7 Hz, 4H), 1.58 (m, 4H), 1.32 (m, 12H), 0.91 (t, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (CD_2Cl_2): δ 146.9, 129.8, 129.1, 128.0, 32.1, 30.9, 29.5, 29.4, 23.0, 14.2 ppm. UV−vis (CH_2Cl_2) λ_{max}(ϵ*10^{-4}) 270 (0.9). MS (LSIMS): *m*/*z* 366 (M^+, 100%). HRMS (LSIMS) for $C_{20}H_{30}S_3$ [M^+] calcd, 366.1510; found, 366.1503.

Bis(3-hexyl-2-thienyl) Sulfide ($T^{3hex}ST^{3hex}$). A 1.6 M hexanes solution of *n*-butyllithium (4.0 mL, 6.4 mmol) was added slowly to a stirred solution of **3** (1.51 g, 6.12 mmol) in THF (40 mL) at −78 °C. The solution was stirred at −78 °C for 1 h and then a solution of bis(phenylsulfonyl) sulfide (0.980 g, 3.13 mmol) in THF (5 mL) was added dropwise over 10 min. After stirring at −78 °C for 3 h, the reaction mixture was allowed to warm to room temperature and stirred for an additional 30 min. The mixture was poured onto water (100 mL), and the aqueous layer was extracted with ether. The combined organics were dried ($MgSO_4$) and filtered, and the solvent was evaporated under reduced pressure. The residue was subjected to column chromatography (silica, pentane) to give $\mathbf{T^{3hex}ST^{3hex}}$ as a colorless oil, yield 785 mg (70%). ^{1}H NMR (CD_2Cl_2): δ 7.27 (d, J = 5.1 Hz, 2H), 6.90 (d, J = 5.1 Hz, 2H), 2.75 (t, J = 7.7 Hz, 4H), 1.58 (m, 4H), 1.32 (m, 12H), 0.90 (t, J = 6.6 Hz, 6H) ppm. ^{13}C NMR (CD_2Cl_2): δ 144.4, 135.0, 134.4, 124.7, 32.0, 30.8, 30.7, 29.3, 23.0, 14.2 ppm. UV−vis (CH_2Cl_2) λ_{max}(ϵ*10^{-4}) 250 (1.2). MS (LSIMS): *m*/*z* 366 (M^+, 100%). HRMS (LSIMS) for $C_{20}H_{30}S_3$ [M^+] calcd, 366.1510; found, 366.1503.

Bis(5:2′-bithien-2-yl)sulfide (TTSTT). A 10-mL toluene solution containing 2-(tributylstannyl)thiophene (1.85 g, 2.25 mmol), **4** (800 mg, 2.25 mmol), and $Pd(PPh_3)_4$ (130 mg) was refluxed in the dark for 20 h. After the black mixture was cooled to room temperature, it was diluted with ether (100 mL) and poured into saturated potassium fluoride (100 mL). The resulting tributyltin fluoride was filtered off and washed with cold ether (3 × 15 mL). The organic phase was collected, washed with brine, and dried (Na_2SO_4). The solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica, 1:1 hexane/diethyl ether) to provide a bright yellow solid. This was recrystallized from hexanes/dichloromethane to give **TTSTT** as yellow plates, yield 692 mg (85%). Mp: 96 °C. ^{1}H NMR ($CDCl_3$): δ 6.96−7.20 (m, 5H) ppm. ^{13}C NMR ($CDCl_3$): δ 141.6, 136.7, 133.9, 133.7, 127.9, 124.9, 124.2, 123.8. UV−vis (CH_2Cl_2) λ_{max}(ϵ*10^{-4}) 335 (1.1). MS (LSIMS): *m*/*z* 362 (M^+, 100%). Anal. Calcd for $C_{16}H_{10}S_5$: C, 53.00; H, 2.78; S, 44.22%. Found: C, 52.80; H, 2.81; S, 44.43%.

Bis(5-(3,4-ethylenedioxythien-2-yl)-thien-2-yl)sulfide (ETSTE). A solution of 2-(tributylstannyl)-3,4-(ethylenedioxy)thiophene (2.50 g, 5.80 mmol), **4** (860 mg, 2.41 mmol), and $Pd(PPh_3)_4$ (140 mg) in toluene (15 mL) was refluxed for 20 h. The toluene was removed under vacuum, and the remaining dark yellow residue was dissolved in a minimal amount of dichloromethane. The crude product was precipitated by the addition of hexanes. This material was further purified by column chromatography (silica, 1:1 hexanes/chloroform) to give **ETSTE** as a bright yellow solid, yield 890 mg (77%). Mp: 130 °C. ^{1}H NMR ($CDCl_3$): δ 7.10 (d, J = 3.7 Hz, 2H), 7.01 (d, J = 3.7 Hz, 2H), 6.20 (s, 2H), 4.30−4.28 (m, 4H), 4.27−4.18 (m, 4H) ppm. ^{13}C NMR ($CDCl_3$): δ 142.0, 139.3, 138.1, 133.5, 133.2, 122.8, 109.7, 97.7, 65.2, 64.8 ppm. UV−vis (CH_2Cl_2) λ_{max}(ϵ*10^{-4}) 345 (2.6). MS (LSIMS): *m*/*z* 478 (M^+, 100%). Anal. Calcd for $C_{20}H_{14}O_4S_5$: C, 50.19; H, 2.95; S, 33.50%. Found: C, 50.01; H, 2.99; S, 33.68%.

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Bis(5-thienyl-3,4-ethylenedioxy-2-thienyll)sulfide (TESET). A solution of **5** (2.00 g, 6.60 mmol) in THF (30 mL) cooled to −78 °C was treated dropwise with a 1.6 M hexanes solution of *n*-butyllithium (4.12 mL, 6.60 mmol). The resulting bright red solution was stirred for 1.5 h at −78 °C. A solution of bis-(phenylsulfonyl) sulfide (1.04 g, 3.30 mmol) in THF (10 mL) was added dropwise via cannula and the resulting yellow solution was stirred at −78 °C for an additional 30 min. The mixture was poured onto water (100 mL), extracted with diethyl ether, and dried (Na_2SO_4). The solvent was removed by rotary evaporation and the residue was purified by column chromatography (silica, 1:1 hexanes/chloroform) to afford a yellow solid. This was recrystallized from methanol/chloroform to give **TESET** as yellow needles, yield 1.04 g (66%). Mp: 176 °C. ^{1}H NMR ($CDCl_3$): δ 7.25 (dd, $J = 5.1$, 1.5 Hz, 2H), 7.22 (dd, $J = 3.7$, 1.5 Hz, 2H), 7.01 (dd, $J = 5.1$, 3.7 Hz, 2H), 4.33 (m, 8H) ppm. ^{13}C NMR ($CDCl_3$): δ 143.9, 136.9, 134.3, 127.3, 124.7, 123.7, 115.7, 104.6, 65.2, 64.9 ppm. UV−vis (CH_2Cl_2) λ_{max} (ϵ*10^{-4}) 345 (2.7). HRMS (EI) for $C_{20}H_{14}O_4S_5$ [M$^+$] calcd, 477.9496; found, 477.9495. Anal. Calcd for $C_{20}H_{14}O_4S_5$: C, 50.19; H, 2.95%. Found: C, 49.94; H, 2.80%.

2,5-Bis(2-thiophenethio)-3-hexylthiophene (TST^{hex}ST). A solution of 2-thiophenethiol (720 mg, 6.20 mmol) in DMF (5 mL) was added dropwise to a stirred slurry of **6** (0.980 g, 3.00 mmol), KOH (368 mg, 6.57 mmol), and copper (I) oxide (230 mg, 1.60 mmol) in DMF (20 mL) at room temperature. The reaction mixture was then stirred at 120 °C for 20 h. The resulting dark brown mixture was cooled to room temperature and poured into 6 M HCl (20 mL). Dichloromethane (100 mL) was added to this and the mixture was filtered through a small pad of Celite. The organic layer was separated, washed with water, and dried ($MgSO_4$). Chromatography (silica, hexanes) gave 820 mg (66%) of **TST^{3hex}ST** as a colorless oil. ^{1}H NMR (CD_2Cl_2): δ 7.35−7.25 (m, 2H), 7.15−7.05 (m, 2H), 6.92−6.85 (m, 2H), 6.80 (s, 1H), 2.60 (t, $J = 7.7$ Hz, 2H), 1.50 (m, 2H), 1.25 (m, 6H), 0.80 (t, $J = 7.0$ Hz, 3H) ppm. ^{13}C NMR (CD_2Cl_2): δ 147.8, 138.7, 135.6, 134.0, 133.9, 132.8, 132.5, 132.0, 130.6, 129.5, 127.8, 127.6, 31.9, 30.6, 29.3 (2 CH_2) 22.8, 14.3 ppm. MS (EI): *m*/*z* 396 (M$^+$, 100%). UV−vis (CH_2Cl_2) λ_{max}(ϵ*10^{-4}) 280 (1.3). HRMS for $C_{18}H_{20}S_5$ [M$^+$] calcd, 396.0169; found, 396.0159.

2,5-Bis(2-thiophenethio)-3,4-ethylenedioxythiophene (TSEST). A solution of 2-thiophenethiol (1.32 g, 11.3 mmol) in DMF (5 mL) was added dropwise to a stirred slurry of **7** (1.69 g, 5.63 mmol), KOH (624 mg, 11.1 mmol), and copper (I) oxide (936 mg, 3.14 mmol) in DMF (20 mL) at room temperature. The reaction mixture was then stirred at 140 °C for 20 h. The resulting dark brown mixture was cooled to room temperature and poured into 6 M HCl (25 mL). Dichloromethane (100 mL) was added to this and the mixture was filtered through a small pad of Celite. The organic layer was separated, washed with water, and dried ($MgSO_4$). Chromatography (silica, 7:3 dichloromethane/pentane) gave colorless oil. The oil was dissolved in a minimal amount of dichloromethane and a white solid was precipitated by the addition of pentane, yield 1.20 g (57%). Mp: 50 °C. ^{1}H NMR (CD_2Cl_2): δ 7.35 (m, 2H), 7.20 (m, 2H), 6.95 (m, 2H), 4.30 (s, 4H) ppm. ^{13}C NMR (CD_2Cl_2): δ 143.7, 134.7, 133.6, 130.3, 128.1, 111.3, 65.4 ppm. UV−vis (CH_2Cl_2) λ_{max}(ϵ*10^{-4}) 280 (1.7). MS (LSIMS): *m*/*z* 370 (M$^+$, 55%). Anal. Calcd for $C_{14}H_{10}O_2S_5$: C, 45.38; H, 2.72%. Found: C, 45.62; H; 2.62%.

5,5′-Bis(2-thiophenethio)-2,2′-bithiophene (TSTTST). A solution of 2-thiophenethiol (806 mg, 6.95 mmol) in DMF (5 mL) was added dropwise to a stirred slurry of **8** (1.10 g, 3.42 mmol), KOH (406 mg, 7.25 mmol), and copper (I) oxide (450 mg, 3.14 mmol) in DMF (50 mL) at room temperature. The reaction mixture was then stirred at 120 °C for 20 h. The resulting dark brown mixture was cooled to room temperature and poured into 6 M HCl (60 mL). Dichloromethane (100 mL) was added to this and the mixture was filtered through a small pad of Celite. The organic layer was separated, washed with water, and dried ($MgSO_4$). Chromatography (silica, pentane) gave 720 mg (54%) of **TSTTST** as a pale yellow solid. Mp: 92 °C. ^{1}H NMR ($CDCl_3$) δ 7.40 (m, 2H), 7.25 (m, 2H), 7.08 (d, $J = 3.7$ Hz, 2H), 7.00 (m, 2H), 6.96 (d, $J = 3.7$ Hz, 2H) ppm. ^{13}C NMR ($CDCl_3$): δ 140.9, 136.0, 135.1, 134.1, 133.8, 130.9, 128.3, 124.7 ppm. UV−vis (CH_2Cl_2) λ_{max}(ϵ*10^{-4}) 350 (2.7). MS (EI): *m*/*z* 394 (M$^+$, 100%). Anal. Calcd for $C_{16}H_{10}S_6$: C, 48.69; H, 2.55%. Found: C, 48.06; H, 2.63%.

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Supporting Information Available: Electronic spectra and electrochemical data for remaining monomers and polymers (pdf). This material is available free of charge via the Internet at http://pubs.acs.org.

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