Synthesis and properties of end-capped bis(oligothienyl) sulfides

Daniel J. T. Myles, M'hamed Chahma, and Robin G. Hicks

Abstract: The synthesis, and the optical and electrochemical properties, of a series of mesitylthio (MesS-) end-capped bis(oligothienyl) sulfides are presented. The target compounds were synthesized principally by convergent protocols, whereby a series of short thiophene oligomers bearing one terminal mesitylthio (MesS-) substituent were first assembled by metal-catalyzed cross-coupling reactions and then coupled via divalent sulfur through reactions with bis(phenylsulfonyl) sulfide. The spectroscopic and electrochemical features of the bis(oligothienyl) sulfides are qualitatively similar to those of the related mesitylthio-capped fully conjugated oligothiophenes, suggesting that the degree of electronic communication between the two oligothiophene chromophores in the bis(oligothienyl) sulfides is low. Cyclic voltammetry studies on the bis(oligothienyl) sulfides reveal that these species can be reversibly oxidized to radical cations, but the reversibility of subsequent oxidations depends on oligothienyl chain length and the presence and position of more electron-rich ethylenedioxythiophene (EDOT) groups. In general, the bis(oligothienyl) sulfides possess fewer than the expected number of reversible oxidations based on comparisons with their corresponding mesitylthio-capped fully conjugated oligothiophenes; excessive charge accumulation at or near the central linking sulfur atom is believed to be responsible for the irreversible behavior. Analysis of the irreversible voltammetric response of one of the bis(oligothienyl) sulfides leads to the suggestion of a decomposition mechanism for the cationic species involving carbon-sulfur bond cleavage and subsequent coupling of thiophene fragments — a finding with potential implications for the poor environmental stability of doped poly(*p*-phenylene sulfide), one of the prototypical conducting polymers.

Key words: conjugated materials, conducting polymers, oligothiophenes, electronic communication.

Résumé : On a effectué la synthèse d'une série de bis(oligothiényl)sulfures fermés aux extrémités par des groupes mésitylthio (MesS-) et on en a déterminé les propriétés optiques et électrochimiques rapportées ici. Les produits recherchés ont été synthétisés par des protocoles convergents dans lesquels une série d'oligomères courts du thiophène portant un substituant terminal mésitylthio sont d'abord assemblés par des réactions de couplage croisées catalysées par un métal avant d'être couplés avec du soufre bivalent par le biais de réactions avec du sulfure de bis(phénylsulfonyle). Les caractéristiques spectroscopiques et électrochimiques des sulfures de bis(oligothiényle) sont qualitativement semblables à celles des oligothiophènes apparentés complètement conjugués et fermés aux extrémités par des groupes mésitylthio; ceci suggère que le degré de communication électronique est faible entre les deux chroromophores oligothiophènes des sulfures d'oligothiényle. Les études de voltampérométrie cyclique sur les sulfures de bis(oligothiényle) révèlent que ces espèces peuvent être oxydées d'une façon réversible en cations radicaux, mais que la réversibilité des oxydations subséquentes dépend de la longueur de la chaîne oligothiényle et de la présence et de la position de groupes éthylènedioxythiophène (EDOT) plus riches en électrons. En général, les sulfures de bis(oligothiényle) possèdent des nombres d'oxydation réversibles inférieurs à ceux qui pourraient être attendus sur la base de comparaison avec les oligothiophènes apparentés complètement conjugués et fermés aux extrémités par des groupes mésitylthio; l'accumulation excessive de charge au ou près de l'atome de soufre central pourrait être responsable de ce comportement irréversible. Une analyse de la réponse voltampérométrique irréversible d'un des sulfures de bis(oligothiényle) conduit à suggérer un mécanisme de décomposition pour l'espèce cationique impliquant une rupture de la liaison carbone-soufre et un couplage subséquent des fragments thiophènes, une observation qui présente des implications potentielles pour la mauvaise stabilité environnementale du poly(sulfure de p-phénylène) dopé, un des prototypes de polymères conducteurs.

Mots-clés : matériaux conjugués, polymères conducteurs, oligothiophènes, communication électronique.

[Traduit par la Rédaction]

D.J.T. Myles, M. Chahma,¹ and R.G. Hicks.² Department of Chemistry, University of Victoria, Victoria, BC, V8W 3V6, Canada.

¹Present address: Department of Chemistry and Biochemistry, Laurentian University, Sudbury, ON P3E 2C6, Canada. ²Corresponding author (e-mail: rhicks@uvic.ca).

Received 11 June 2008. Accepted 26 July 2008. Published on the NRC Research Pres Web site at canjchem.nrc.ca on 13 September 2008.

Introduction

The development of structure-property (electrochemical, spectroscopic, conducting, emissive) relationships for π -conjugated oligomers is a well-entrenched field of study (1). Many of these studies have produced important insights for the less well-defined — but technologically important — conjugated polymers. For example, the notion of π stacking as a mechanism for charge transport in conducting polymers was largely facilitated by electrochemical and spectroscopic studies on oligothiophenes (2). In addition, many conjugated oligomers are emerging as viable components of new electronic materials in their own right (3).

The diversity of functional polymers has increased greatly through the incorporation of inorganic segments into otherwise conventional organic systems. Many of these hybrid polymers are based on transition metals, (4), but there is a growing body of "organomain group" polymers containing p-block elements in the main chain (5). Polyaniline can be considered as a prototypical example (6), but polymers containing group 13 (7), 14 (8), or 15 (9) elements have been developed as well. Polymers containing group 16 elements in the main chain have a more sporadic history. Poly(thiazyl) $(SN)_x$ is noteworthy for its conducting and superconducting properties and as the forerunner to the field of organic conducting polymers (10). Poly(p-phenylene sulfide) (PPS) was one of the first conducting doped polymers and the first based on a commodity polymer (11). This material suffers from serious environmental stability problems in its oxidized (doped) forms. Related sulfur-bridged polymers are similarly unstable when doped (12). Nakayama and co-workers (13) have reported the synthesis of oligomeric analogues of PPS in which the *p*-phenylene is replaced by 2,5-thiophenediyl; no physical properties were presented. Finally, Manners and co-workers (14) have prepared poly(thiaferrocenes) via the ring-opening polymerization of [1]thiaferrocenophanes; the electronic properties of short, well-defined oligomers were also investigated as models for the polymer — a rare example of the application of the "oligomers approach" in conjugated main group polymer chemistry.

We have been investigating small molecule and polymeric conjugated oligothiophene-sulfur materials. We have demonstrated that mesitylthio- (MesS-) capped oligothiophenes ^{MesS}T_n^{SMes} (n = 1-4) can be reversibly oxidized to radical cations and dications, some of which exhibit exceptional stability (15). The stability of the oxidized forms arises from both the blocking of the terminal (α and ω) carbon atoms of the oligothiophene segment as well as the strong π -donating nature of the thioether (-SR) group. We separately described several bis(oligothienyl) sulfides that could be electropolymerized to give poly(oligothienyl sulfide)s in which conjugated oligothiophene segments are linked together by divalent sulfur (16, 17); related poly(aryl sulfide)s and disulfides have been subsequently reported by other groups (18). The electrochemical properties of our poly(oligothienyl sulfide)s varied based on the structure of the monomer; generally, the polymers based on the electron-rich ethylenedioxythiophene (EDOT) building block showed reversible redox behavior, but those based on unsubstituted thiophenes showed significant irreversibility in their oxidative electrochemistry. The apparent differences between the oligomers Scheme 1.



capped by SR groups and the polymers in which thiophene chromophores are *linked* by sulfur prompted us to prepare a series of model systems based on $^{\text{MesS}}T_nST_n^{\text{SMes}}$ where T_nST_n is a bis(oligothienyl) sulfide segment — essentially a segment of the polymers — in which both terminal positions are also capped by SR groups to prevent electropolymerization (as opposed to the uncapped T_nST_n compounds, which upon electro-oxidation, polymerize to $(T_nST_n)_m$.

Results and discussion

Synthesis

Scheme 1 outlines the general synthetic route to the mesitylthio end-capped bis(oligothienyl) sulfides. The target compounds were assembled by a convergent protocol, whereby two equivalents of an unsymmetrically substituted oligothiophene were metallated and then reacted with bis(phenylsulfonyl) sulfide; this sulfur transfer reagent has proven to be better than sulfur dichloride (SCl₂), for which these reactions typically proceed in low yield (14, 19, 20). (2-Mesitylthio)thiophene 1 was prepared by the reaction of 2-thienylmagnesium bromide with 2-mesitylenesulfenyl chloride (MesSCl). Subsequent lithiation of 1 with 1 equiv. of BuLi, followed by treatment with 0.5 equiv. of (PhSO₂)₂S provided the desired sulfide $^{\text{MesS}}TST^{\text{SMes}}$ in 80% yield. The bis(bithienyl) sulfide $^{\text{MesS}}T_2ST_2^{\text{SMes}}$ was prepared by lithiation of bithiophene 2 (synthesized from 2,2'-bithiophene by deprotonation and reaction with MesSCl) and subsequent quenching with (PhSO₂)₂S. The bis(terthienyl) sulfide $^{MesS}T_3ST_3^{SMes}$ required a slightly more elaborate route. Compound 2 was selectively brominated at the other terminal position with NBS in DMF (21) and then subsequently coupled with 2-tributylstannylthiophene using $Pd(PPh_3)_4$ as a catalyst to give **3** in 88% yield. Terthiophene 3 was converted to the targeted sulfide MesST₃ST₃SMes by

lithiation and quenching with $(PhSO_2)_2S$. Variants of ^{MesS}TST^{SMes} were also targetted in which the parent thiophene unit is replaced with the well-known (22) electron-rich 3,4-ethylenedioxythiophene moiety. However, the preparation of ^{MesS}ESE^{SMes} by a convergent strategy was abandoned owing to difficulties in preparing the necessary precursor, namely, 2-mesitylthio-3,4-ethylenedioxythiophene **4**. The reaction of α -lithiated EDOT with 1 equiv. of

	Neutral	Radical cation	Dication	
Compound	λ_{max} (nm)	λ_{max} (nm)	λ_{max} (nm)	Reference
TST	268	_		17
MesSTST ^{SMes}	310	555, 896	_	This work
MesSTSMes	302	412, 638	—	15
T_2ST_2	335	_	—	15
MesST2ST2SMes	360	563, 865	_	This work
MesST2 SMes	358	572, 905	520	15
MesST4 SMes	420	756, 1420	893	15
MesST3ST3SMes	395	_	680 ^a	This work
MesST ₃ SMes	386	676, 1170	696	15
ESE	270	_	_	17
MesSESE ^{SMes}	309	520, 860	_	This work
MesSESMes	305	405, 551	_	15
MesSE2SMes	362	509, 900	—	15
ETSTE	345	_	—	17
MesSETSTE ^{SMes}	375	_	788, 892	This work
MesSETTE ^{SMes}	458	_	860	15
TESET	345	_	—	17
MesSTESET ^{SMes}	375	725, 1241	—	This work
MesSTEET ^{SMes}	431	721, 1240	900	15

Table 1. Lowest energy electronic transitions for bis(oligothienyl) sulfides and related compounds in various charge states.

Scheme 3.



MesSCl preferentially gives the disubstituted compound 5

over the monosubstituted compound 4 (Scheme 2) (15). The preparation of $^{MesS}ESE^{SMes}$ was accomplished by dilithiating bis(3,4-ethylenedioxythienyl) sulfide (6) ESE followed by treatment with 2 equiv. of MesSCl (Scheme 3). Two isomeric EDOT containing bis(bithienyl) sulfide derivatives were also prepared using convergent protocols as shown in Scheme 3. Lithiation of 6 (15) with n-BuLi followed by quenching with (PhSO₂)₂S gave MesSTESET^{SMes-} with two EDOTs connected to the central sulfide, in 68% yield. The isomeric species required building block 8, which was made by lithium-halogen exchange (BuLi) of 7 (25), followed by reaction with MesSCl to give the

monosubstituted 8 in 66% yield. Finally, lithiation of 8, followed by introduction of sulfur with (PhSO₂)₂S, afforded MesSETSTE^{SMes}, in which the EDOT groups occupy the outer positions of the conjugated moieties, in 72% yield.

Electronic spectra

The solution spectra of the bis(oligothienyl) sulfides, towith the fully conjugated bis(mesitylthio) gether oligothiophenes previously reported (15), provide some insights into how the terminal and internal sulfur atoms perturb the π chromophores of oligothiophenes. The solution absorption spectral data are summarized in Table 1.

We have previously shown that mesitylthio (MesS-) substituents at the terminal (α, ω) positions cause moderate (~30 nm) red shifts in the lowest energy electronic transitions of oligothiophenes. This effect is apparent in the current series of bis(thienyl) sulfides. For example, the low energy transitions for the uncapped bis(thienyl) sulfides TST and T_2ST_2 are at 268 and 335 nm, respectively; the maxima for the mesitylthio-capped analogues MessTSTSMes and MessT₂ST₂^{SMes} are 310 and 360 respectively. The incorporation of ethylenedioxy groups on the β -carbons also produces predictably moderate red shifts. On the other hand, the internal bridging sulfur units have little effect on extending the overall conjugation length. For example, λ_{max} for $^{\text{MesS}}T_2ST_2^{\text{SMes}}$, with two single bithiophenes flanking a central sulfur, is only red-shifted by 2 nm relative to $^{\text{MesS}}T_2^{\text{SMes}}$. which has a single bithiophene chromophore. In contrast, which has a single bitmophene chromophore. In contrast, λ_{max} for $^{MesS}T_4^{SMes}$, a fully conjugated tetrathiophene, is red-shifted by 50 nm relative to $^{MesS}T_2ST_2^{SMes}$. Comparisons be-tween other analogous pairs of oligomers (e.g., $^{MesS}TST^{SMes}$ vs. $^{MesS}T^{SMes}$; $^{MesS}ESE^{SMes}$ vs. $^{MesS}E^{SMes}$) reveal similar trends; overall the lowest energy absorption maxima is dominated by the nature of the individual thienyl segment: there is little additional delocalization between the two oligomeric units

through the central sulfur bridge. This is further corroborated by the fact that the extinction coefficients of the capped bis(thienyl) sulfides $^{\text{MesS}}T_nST_n^{\text{SMes}}$ (see Experimental section) are *roughly* twice as large as the corresponding coefficients of the straight conjugated capped oligomers $^{\text{MesS}}T_n^{\text{SMes}}$ (15). Thus, although the linking sulfur atom has two lone pairs of electrons, one of which in principle could engage in π overlap with the oligothienyl π system, the spectroscopic data suggests that the orientation of the thienyl units with respect to the S lone pair orbitals is not optimal for overlap and (or) π donation by S into what is already an electron-rich π system is ineffective.

Electronic spectra of the oxidized forms of several mesitylthio-capped oligothiophenes and bis (oligothienyl) sulfides were obtained either by electrochemical oxidation of the neutral species in solution or by chemical oxidation with NOBF₄. The cationic states of the "uncapped" oligomers are too reactive to observe, as they undergo the expected rapid coupling to yield polymers (16). Spectra of the cationic α, ω -bis-(mesitylthio) oligothiophenes MesST_n SMes (n = 1-4) and ^{MesS}E^{SMes} were obtained by chemical oxidation with NOBF₄ in CH₂Cl₂. Stable radical cations could be generated for all of these compounds, in accord with closely related bis(mesitylthio)oligothiophenes reported by us (15). Radical cation spectra could not be obtained for $^{MesS}ETSTE^{SMes}$ or $^{MesS}T_3ST_3^{SMes}$ owing to the small difference between first and second oxidation potentials for these compounds (see below); for the former, this problem is compounded by the instability of the dicationic state.

The electronic absorption spectrum for the radical cation of ^{MesS}T^{SMes} has two absorption maxima at 412 and 638 nm. The corresponding EDOT-based compound ^{MesS}E^{SMes} also has peaks at 405 and 551 nm. Within the thiophene series ^{MesS}T_n^{SMes} (n = 1-4), as the thiophene chain length increases there is a shift to lower energies for the radical cation series and the (more limited) dication spectral series. The spectral features of these radical cations do not show any dependence on temperature (between -5 and +20 °C) or concentration (between 10^{-5} and 10^{-4} mol/L), suggesting that radical cation π dimerization does not occur. Dimer formation is most likely suppressed because of the steric hindrance of the capping mesityl groups.

Spectra of several of the capped bis(oligothienyl) sulfides in cationic states were also obtained. The radical cation of bis(thienyl) sulfide ^{MesS}TST^{SMes} has two major bands at 555 and 896 nm. These are significantly red-shifted in comparison to the radical cation spectrum of MesSTSMes (412 and 638 nm). This sharply contrasts comparisons between the two neutral compounds, which are nearly identical to one another. This suggests that there may be a strong interaction between the two thiophene units via the sulfur bridge for MesSTST^{SMes} in its radical cation state. This may arise from the fact that removal of an electron from the oligothiophene renders it a more electron-deficient π system, thereby facilitating stabilization (and hence delocalization) from a sulfur lone pair orbital. π -Dimer bands can be ruled out, based on the fact that the intensities of the 555 and 896 nm peaks show neither a concentration nor temperature dependence. Similar comparisons can be made for the EDOT analogues of these species: the radical cation of MesSESMes has peaks at 405 and 551 nm, whereas bis(3,4-ethyelenedioxythienyl)

Table 2. Oxidation potentials of bis(oligothienyl) sulfides and related compounds as determined by cyclic voltammetry experiments (see Experimental section for details).

Compound	Oxidation potentials (V)	Reference
MesSTSTSMes	+1.14, +1.43*	This work
MesSTSMes	1.05	(15)
^{MesS} T ₂ ST ₂ ^{SMes}	+0.99, +1.15, +1.50	This work
MesST ₂ SMes	+0.87, +1.25	(15)
MesST ₄ SMes	+0.83, +0.91	(15)
MesST3ST3SMes	+0.91, +1.02, +1.13. +1.49*	This work
MesST ₃ SMes	+0.86, +1.02	(15)
MesSESESMes	+0.90, +1.14*	This work
MesSESMes	0.87	(15)
MesSE2 SMes	+0.57, +0.94	(15)
MesSETSTE ^{SMes}	+0.78, +0.93, +1.31, +1.70*	This work
MesSETTE ^{SMes}	+0.61, +0.66	(15)
MesSTESET ^{SMes}	+0.78, +0.97*	This work
MesSTEET ^{SMes}	+0.49, +0.73	(15)

Note: All potentials are given as formal potentials $(E_{1/2})$ vs. SCE except for numbers denoted with an asterisk (*), which correspond to anodic peak potentials for irreversible oxidations.

sulfide ^{MesS}ESE^{SMes} radical cation absorbs at 520 and 860 nm.

Comparisons between the various compounds containing conjugated bithiophene chromophores are more complex. The radical cations of $^{\text{MesS}}\text{T}_2\text{ST}_2^{\text{SMes}}$ (563 and 865 nm) and $^{MesS}T_2^{SMes}$ (572 and 905 nm) have similar spectroscopic features, and in fact the absorption maxima of the former are actually slightly blue-shifted with respect to the latter. This indicates that little to no electronic coupling occurs between adjacent bithiophenes via the sulfur bridge, presumably be-cause the radical cation in $^{MesS}T_2ST_2^{SMes}$ is strongly localized in the bithiophene cores. However, this picture is complicated upon consideration of the spectrum of the radical cation of ^{MesS}TESET^{SMes}; the absorption maxima (725 and 1241 nm) are dramatically red-shifted compared with the all-thiophene analogue $^{MesS}T_2ST_2^{SMes}$. This may suggest that the placement of the more electron-rich EDOT groups on the "internal" positions serves to concentrate spin and (or) charge closer to the central sulfur linker, thereby facilitating more effective delocalization.

The properties of the mesitylthio- capped model compounds can also be compared with the previously reported poly(oligothienyl sulfide)s. As a representative example, $^{MesS}E_2^{SMes}$ has a S-EE-S unit that is also present in the polymer poly(ESE). Neutral poly(ESE) has its absorption maxima at 455 and 484 nm, whereas $^{MesS}E_2^{SMes}$ absorbs at 362 nm. The fact that poly(ESE) has its absorptions redshifted with respect to $^{MesS}E_2^{SMes}$ provides evidence that the biEDOT units are electronically coupled in the neutral polymer; in this regard the "capped" molecules are analogous to the "uncapped" monomers (i.e., ESE) that were actually employed to synthesize the polymers. Furthermore, the doped polymer has absorptions at 605 and 1020 nm whereas the radical cation of $^{MesS}E_2^{SMes}$ has two absorption bands at 509 and 900 nm. The red-shift is most likely due to strong intrachain electronic coupling of the biEDOT groups in the polymer, although interchain effects cannot be ruled out.

Electrochemical studies

The redox properties of the bis(thienyl) sulfides were studied using cyclic voltammetry. The results of these studies are summarized in Table 2, which also contains electrochemical data for the previously reported bis(mesitylthio)capped oligothiophenes (15). Our previous work on the latter compounds established that the mesitylthio substituents provide stability to the oxidized forms of the oligothiophenes. This stability arises in part by "blocking" the α and ω positions, thereby preventing polymerization (via oxidative coupling) of the thiophene radical cation; the π -donating effect of the sulfur substituent also contributes to the stability of the cationic forms of the oligomers. These effects are also manifested in the bis(thienyl) sulfide compounds presented here. All of the new compounds exhibit at least one chemically reversible oxidation process (equivalence of anodic and cathodic peak currents, peak potentials that are scan-rateindependent); the anodic and cathodic peak separations for each compound lie in the range of 60-90 mV, which is comparable to that of the ferrocene/ferrocenium redox couple under the same experimental conditions and suggestive of quasi-reversible electrochemical behavior. Many of the bis(thienyl) sulfides can be reversibly oxidized to dications or even trications in a few cases.

In general, the oxidation potentials of oligothiophene are influenced by their chain length; longer oligomers are oxidized at lower potentials. Among the homologous series of bis(thienyl) sulfides $^{\text{MesS}}T_nST_n^{\text{SMes}}$ (n = 1-3), this trend holds; however, the change in first oxidation potential as a function of chain length for this series is comparable to the corresponding changes in the fully conjugated thiophenes. The first oxidation potential of $^{MesS}T^{SMes}$ is +1.05 V. Extending the conjugated segment from one to two thiophenes (i.e., $^{MesS}T_2^{SMes}$, $E_1^{\circ} = +0.87$ V) leads to a drop in first oxidation potential of 0.18 V. Analogous comparisons between $^{\text{MesS}}\text{TST}^{\text{SMes}}$ ($E_1^{\circ} = +1.14$ V) and $^{\text{MesS}}\text{T}_2\text{ST}_2^{\text{SMes}}$ ($E_1^{\circ} = -1.14$ V) +0.99 V) produce qualitatively similar results: the first oxidation potential for the longer oligomers is +0.15 V lower. Thus, although $^{\text{MesS}}T_2ST_2^{\text{SMes}}$ is *two* thiophene units longer than MesSTST^{SMes}, the comparative electrochemical properties (in conjunction with the electronic spectra, see above) suggest that the connection of two thiophene segments by a divalent sulfur linker does not lead to an extension of effective conjugation length.

Given that the bis(thienyl) sulfides contain two thiophene chromophores sharing a common linker, the electrochemical responses of these might naïvely be expected to consist of the sum of the individual processes associated with each thiophene segment, i.e., $^{\text{MesS}}T_nST_n^{SMes}$ should possess twice as many oxidations as $^{\text{MesS}}T_nST_n^{SMes}$. This is not the case. Figure 1 shows the cyclic voltammograms of $^{\text{MesS}}T_nST_n^{SMes}$ (n = 1-3). For example, $^{\text{MesS}}T^{SMes}$ and $^{\text{MesS}}E^{SMes}$ both possess one reversible oxidation process. Given that the bis(thienyl) sulfide analogues $^{\text{MesS}}TST^{SMes}$ and $^{\text{MesS}}ESE^{SMes}$ contain two "monothiophenes", these compounds might be expected to have two oxidation waves corresponding to one-electron removal from each of the two thiophene units. However, both of these can only be reversibly oxidized to radical cations; the second oxidation process in both compounds is irreversible. In a similar vein, all of the other "parent" oligomers $^{\text{MesS}}T_n^{SMes}(n > 1)$ can be reversibly oxidized

Fig. 1. Cyclic voltammograms of (*a*) $^{\text{MesS}}\text{TST}^{\text{SMes}}$ (first oxidation only), (*b*) $^{\text{MesS}}\text{TST}^{\text{SMes}}$ (full scan), (*c*) $^{\text{MesS}}\text{T}_2\text{ST}_2^{\text{SMes}}$; and (*d*) $^{\text{MesS}}\text{T}_3\text{ST}_3^{\text{SMes}}$. The redox process labelled with an asterisk in (*c*) corresponds to the ferrocene/ferrocenium redox couple (added as a reference). See Experimental section for details.



to radical cations and dications, but the corresponding bis(thienyl) sulfides $^{\text{MesS}}T_nST_n^{SMes}$ (n = 2, 3) have fewer than the expected four reversible oxidation waves: the bis(bithienyl) sulfide $^{\text{MesS}}T_2ST_2^{SMes}$ has two reversible and one quasi-reversible wave, and the bis(terthienyl) sulfide $^{\text{MesS}}T_3ST_3^{SMes}$ has three very closely spaced reversible oxidations and a fourth irreversible one at higher potentials. Overall, the charge storage capacity of these compounds is relatively limited compared with the parent, fully conjugated counterparts.

The two mixed thiophene–EDOT compounds MesSTESET^{SMes} and MesSETSTE^{SMes} contain the same fundamental chromophore — a bis(thioether) substituted unsymmetric bithiophene ^{RS}ET^{SR}. Given the analyses of the electrochemical properties of the other bis(thienyl) sulfides, it is not surprising that the first oxidation of MesSTESET^{SMes} and MesSETSTESMes occur at the same potential. However, the electrochemical behavior of these two isomers beyond the first oxidations differs markedly. The former compound can only be reversibly oxidized to a radical cation, whereas the latter has two fully reversible oxidations and a third that is quasi-reversible (tending towards reversibility at high scan rates); it is not until the fourth oxidation that decomposition occurs. The differences in electrochemical responses between these compounds can be understood by consideration of the location of the more electron-rich EDOT moieties. MesSTESET^{SMes} has the EDOTs directly flanking the central sulfur atom. The first two oxidations correspond to electron removal from each of the "ET" moieties, but with the spin and charge on both components more localized on the EDOT moieties. Thus the dication of this compound appears to have sufficient spin and charge concentration to render it unstable (a proposal of how this compound may degrade is provided below). In contrast, the isomeric MesSETSTESMes





has the EDOTs located near the ends of the molecule. The dication of this compound should therefore have its spin and (or) charge driven towards each end, meaning that the two cationic chromophores do not perturb one another to the same extent, and thereby providing stability to the dication. We have previously rationalized the differences between the electrochemical properties of fully conjugated mixed EDOT-thiophene compounds ^{MesS}TEET^{SMes} and ^{MesS}ETTEE^{SMes} based on similar topological arguments (15).

Electrochemical cycling through the second (irreversible) oxidation of ^{MesS}TESET^{SMes} leads to the appearance of a growth of a new reversible redox couple on the second anodic scan at a potential of +0.5 V, substantially lower than the first oxidation potential of this compound (Fig. 2). The potential for this new process matches the first oxidation potential of ^{MesS}TEET^{SMes} (Table 2). We suggest that this species is in fact being formed during the course of the oxidative decomposition of ^{MesS}TESET^{SMes}. Although the precise mechanistic details are unclear, one possible process involves decomposition of the dication via carbon–sulfur bond scission involving the central sulfur atom. The resulting "ET^{SMes}" fragments could then couple via CC bond formation between two EDOTs to give ^{MesS}TEET^{SMes}.

Conclusions

Several bis(oligothienyl) sulfides have been prepared and their redox and spectroscopic properties investigated. The terminal mesitylthio substituents prevent oxidative polymerization of these species and facilitate the detailed examination of structure–property relationships. Overall, the "electronic communication", i.e., delocalization, between two oligothiophene segments via a sulfur atom connector is relatively weak. Nonetheless, there are clear sequential oneelectron oxidation processes corresponding to electron loss from each of the two segments in the cyclic voltammograms of most of the oligomers. Electrostatic effects are the most likely reason behind this behavior, (i.e., the proximity of the first positive charge can make it harder to create a second positive charge) and can produce the same effect.

The capped bis(oligothienyl) sulfides can all be reversibly oxidized, but after that, deleterious effects of excessive charge begin to appear. We have previously established that MesS-capped oligothiophenes can be oxidized twice, in some cases affording very stable cationic species. The bis(oligothienyl) sulfides have two such moieties and also can be oxidized, though the charge storage capability does not scale with the doubling of thiophene chromophores. This may explain why the poly(oligothienyl sulfide)s were not as well-behaved electrochemically (17) — overoxidation leads to decomposition (a common fate of fully conjugated polymer redox processes). In fact PPS was one of the first polymers to be doped to conducting form, though the doped forms are highly reactive. Our electrochemical studies are consistent with the relatively poor charge storage capacity of these systems; the suggestion that carbon-sulfur bond cleavage as a major decomposition route, which is supported by the recent description of synthetically useful version of this reaction (23), may be a possible model for doped PPS (and relatives) itself.

Experimental³

General

Unless stated otherwise, all reactions and manipulations were carried out under an argon atmosphere using standard Schlenk line or glovebox techniques. Glassware was dried in an oven at 125 °C for 24 h prior to use. Solvents were dried and distilled under argon prior to use (acetonitrile, dichloromethane, and hexanes from CaH₂; diethyl ether, tetrahydrofuran, and toluene from sodium benzophenone ketyl). All reagents were purchased from commercial sources and used as received except as otherwise stated. The following compounds were prepared according to literature procedures: 2-mesitylenesulfenyl chloride (15), bis(phenylsulfonyl) sulfide (19), 2,2'-bithiophene (24), bis(3,4-ethylenedioxy-2-thienyl) sulfide (ESE) (16), 3,4-ethylenedioxy-5'-mesityl-thio-2,2'-bithiophene (7, 25).

¹H NMR spectra were recorded at 300 MHz and ¹³C NMR spectra were recorded at 75 MHz, unless otherwise noted. Melting points are uncorrected. Electronic spectra were recorded on a Varian Cary 5 spectrometer using 10 mm quartz cuvettes. All UV–vis and NIR studies were performed in freshly distilled dichloromethane. Voltammetric measurements were performed at RT (22 ± 2 °C) (except for variable temperature studies) in dichloromethane containing 1 mmol/L substrate (except for the variable concentration studies) and 1 mol/L of *n*-Bu₄NBF₄ as electrolyte. Platinum

³Supplementary data for this article are available on the journal Web site (canjchem.nrc.ca) or may be purchased from the Depository of Unpublished Data, Document Delivery, CISTI, National Research Council Canada, Ottawa, ON K1A 0R6, Canada. DUD 3816. For more information on obtaining material refer to cisti-icist.nrc-cnrc.gc.ca/cms/unpub_e.shtml.

button (diameter 1.6 mm) was used as the working electrode. Platinum wire and silver wire were used as the counter and quasi-reference electrodes, respectively. The working electrode was polished on alumina before use. iR compensations were applied for all experiments for potential measurements. All redox potentials were calibrated by comparing to ferrocene, which was added as an internal reference and then reported vs. SCE (Fc/Fc₊ E_0 = +0.46 V vs SCE in CH₂Cl₂). The number of electrons associated with the redox processes were determined by comparison of the peak current magnitudes with those of equimolar quantities of the internal reference. Solutions of cationic species were generated either electrochemically (by constant potential bulk electrolysis in a two-compartment cell using two 3 cm \times 3 cm platinum plates as cathode and anode) or chemically (by additions of aliquots of substoichiometric quantities, typically 0.2 equiv. at a time, of $NOBF_4$ solutions as oxidant).

2-(Mesitylthio)thiophene (1)

2-Bromothiophene (4.00 g, 24.5 mmol) was added to a slurry of magnesium powder (0.90 g, 37.0 mmol) in diethyl ether (20 mL). The reaction was initiated with a small amount of the bromo reagent and a crystal of iodine. Once the exothermic reaction had started, the remaining bromo reagent was added dropwise to the ice-cooled magnesium slurry over the course of 20 min. The solution was allowed to warm to RT and then refluxed for 1 h, after which the brown Grignard solution was recooled to 0 °C, and a solution of 2-mesitylenesulfenyl chloride (4.57 g, 24.5 mmol) in hexanes (25 mL) was added dropwise via cannula. The resulting pale brown solution was stirred at 0 °C for an additional 30 min. The mixture was then warmed to RT and poured into brine (100 mL). The aqueous layer was extracted with ether $(3 \times 50 \text{ mL})$, and the combined organic extracts were further washed with water $(3 \times 50 \text{ mL})$ and dried over anhydrous sodium sulfate. After filtration, removal of the solvent gave a dark brown oil, which was purified by flash chromatography (silica gel, hexanes) to provide a pale yellow liquid of 1, yield 4.41 g (77%). ¹H NMR $(CD_2Cl_2) \delta$: 7.16 (dd, J = 5.1, 1.5 Hz, 1H), 6.95 (s, 2H), 6.92 (dd, J = 3.7, 1.5 Hz, 1H), 6.88 (dd, J = 5.1, 3.7 Hz)1H), 2.49 (s, 6H), 2.25 (s, 3H). ¹³C NMR (CDCl₃) δ: 142.82, 139.27, 137.42, 130.03, 129.36, 128.24, 127.09, 126.07, 21.82, 21.09. HRMS (EI) for C13H14S2 [M⁺]: calcd. 234.0537; found 234.0541.

Bis(5-mesitylthio-2-thienyl) sulfide ($^{MesS}TST^{SMes}$)

This compound has been prepared previously by a different route (26). A solution of **1** (5.00 g, 21.3 mmol) in THF (100 mL) cooled to -70 °C was treated dropwise with *n*butyllithium (13.3 mL, 21.3 mmol, 1.6 mol/L in hexanes). The resulting yellow solution was stirred at -70 °C for 1 h, after which a solution of bis(phenylsulfonyl) sulfide (3.34 g, 10.6 mmol) in THF (20 mL) was added dropwise via cannula, and the resulting golden yellow solution was stirred at -70 °C for an additional 1 h. The mixture was warmed to RT and poured into water (100 mL). The aqueous layer was extracted with ether (3 × 50 mL), and the combined organic extracts were further washed with water (3 × 50 mL), and dried over anhydrous sodium sulfate. After filtration, removal of the solvent gave a yellow oil, which was purified by column chromatography (silica gel, hexanes/ethyl acetate (9:1 v/v)) to provide a slightly yellow solid. Recrystallization from methanol/chloroform produced white crystalline flakes of ^{MesS}TST^{SMes}, yield 4.26 g (80%), mp 92 °C. UV–vis (CH₂Cl₂) λ_{max} (nm): 310 (ϵ 1.9 × 10⁴). Remaining spectroscopic data are identical to those found in ref. 26.

5-Mesitylthio-2,2'-bithiophene (2)

To a solution of 2,2'-bithiophene (3.00 g, 18.0 mmol) in THF (60 mL) was added dropwise *n*-butyllithium (11.3 mL, 18.1 mmol, 1.6 mol/L in hexanes) at 0 °C. The mixture was warmed to RT and stirred for 1.5 h. The mixture was cooled to -70 °C, and a solution 2-mesitylenesulfenyl chloride (3.38 g, 18.1 mmol) in hexanes (25 mL) was then added dropwise via cannula. Stirring was continued at -70 °C for 0.5 h, then the mixture was allowed to warm to RT, and water (50 mL) was added. The aqueous layer was washed with ether (50 mL), and the organic extracts were washed with brine $(3 \times 50 \text{ mL})$, and dried over anhydrous magnesium sulfate. The solvent was removed by rotary evaporation, and the green oily residue was purified by column chromatography (silica gel, hexanes) to provide a slightly yellow solid. Subsequent recrystallization from methanol produced white crystalline flakes of 2, yield 3.60 g (63%), mp 46 °C. ¹H NMR (500 MHz, CDCl₃) δ : 7.13 (dd, J = 5.1, 1.1 Hz, 1H), 7.01 (dd, J = 3.6, 1.1 Hz, 1H), 6.96 (s, 2H), 6.94–6.92 (m, 2H), 6.81 (d, J = 3.7 Hz, 1H), 2.53 (s, 6H), 2.28 (s, 3H). ¹³C NMR (CDCl₃) δ: 142.82, 139.46, 137.77, 137.17, 136.74, 129.55, 129.44, 128.82, 127.71, 124.15, 123.56, 123.44, 21.84, 21.11. MS (LSI) m/z: 316 (M⁺, 100%). Anal. calcd. C₁₇H₁₆S₃: C 64.51, H 5.10, S 30.39; found: C 64.58, H 5.29, S 30.07.

Bis(5'-mesitylthio-5,2'-bithien-2-yl) sulfide (^{MesS}T₂ST₂^{SMes})

A solution of 2 (6.00 g, 18.9 mmol) in THF (150 mL) cooled to -70 °C was treated dropwise with *n*-butyllithium (11.9 mL, 19.0 mmol, 1.6 mol/L in hexanes). The resulting bright yellow solution was stirred at -70 °C for 1 h. After which, a solution of bis(phenylsulfonyl) sulfide (2.98 g, 9.48 mmol) in THF (20 mL) was added dropwise via cannula, and the resulting orange solution was stirred at -70 °C for an additional 1 h. The mixture was warmed to RT and poured into water (100 mL). The fine yellow precipitate was filtered off and washed with cold methanol (3×50 mL). This solid was recrystallized from a mixture of chloroform and methanol (120 mL, 1:1 v/v) to afford $^{MesS}T_2ST_2^{SMes}$ as pale yellow needles, yield 4.90 g (78%), mp 154 °C. UV-vis $(CH_2Cl_2) \lambda_{max}$ (nm): 360 ($\epsilon 3.9 \times 10^4$). ¹H NMR (CDCl₃) δ : 7.00 (d, J = 3.7 Hz, 2H), 6.94 (s, 4H), 6.86 (d, J = 4.4 Hz, 2H), 6.80 (d, J = 3.7 Hz, 2H), 6.74 (d, J = 4.4 Hz, 2H), 2.48 (s, 12H), 2.27 (s, 6H). ¹³C NMR (CDCl₃) δ: 142.82, 141.33, 139.57, 137.89, 136.72, 133.58, 133.48, 129.46, 129.27, 128.38, 124.02, 123.28, 21.78, 21.10. MS (EI) m/z: 662 (M⁺, 100%). Anal. calcd. for C₃₄H₃₀S₇: C 61.59, H 4.56, S 33.85; found: C 61.40, H 4.49, S 33.85.

5-Bromo-5'-mesitylthio-2,2'-bithiophene

5-Mesitylthio-2,2'-bithiophene 2 (6.32 g, 20.0 mmol) was dissolved in DMF (100 mL). In the absence of light, NBS

(3.91 g, 22.0 mmol) was added portionwise to the solution at RT. After addition, the solution was stirred at RT overnight in the dark. The resulting pale yellow solution was diluted with dichloromethane (100 mL) and poured into brine (100 mL). The aqueous phase was collected and washed with a second portion of dichloromethane (100 mL). All organics were collected and extracted with water (5 \times 100 mL) to remove any remaining DMF. The dichloromethane layer was dried over anhydrous sodium sulfate, filtered, and evaporated. The obtained pale orange liquid was purified by column chromatography (silica gel, hexanes/ dichloromethane (4:1 v/v) to provide 5-bromo-5'-mesityl-2,2'-bithiophene as a yellow liquid, yield 7.10 g (90%). This compound was used in the next step without further purification. ¹H NMR (CDCl₃) δ : 6.94 (s, 2H), 6.87 (d, J = 4.4 Hz, 1H), 6.84 (d, J = 3.7 Hz, 1H), 6.75 (d, J = 3.7 Hz, 1H), 6.72 (d, J = 3.7 Hz, 1H), 2.49 (s, 6H), 2.26 (s, 3H). MS (LSI) m/z: 394 (M⁺, ⁷⁹Br, 90%), 395 (M + 1, ⁷⁹Br, 28%), 396 (M⁺, ⁸¹Br, 100%), 397 (M + 1, ⁸¹Br, 27%).

5-Mesitylthio-2,2':5',2"-terthiophene (3)

A flask was charged with 2-(tributylstannyl)thiophene (3.05 mL, 9.59 mmol), 5-bromo-5'-mesitylthio-2,2'bithiophene (3.79 g, 9.59 mmol), $Pd(PPh_3)_4$ (554 mg), and toluene (20 mL). The mixture was heated to reflux for 20 h. After cooling to RT, the black mixture 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 $(3 \times 15 \text{ mL})$. The organic phase was collected, washed with brine $(3 \times 100 \text{ mL})$, and dried over anhydrous sodium sulfate. The solvent was removed by rotary evaporation, and the dark yellow residue was purified by column chromatography (silica gel, hexane/EtOAc (9:1 v/v)) to provide a bright yellow solid. Recrystallization from ethanol produced yellow crystalline plates of 3, yield 3.36 g (88%), mp 80 °C. ¹H NMR (500 MHz, CDCl₃) δ: 7.18 (dd, J = 5.1, 1.1 Hz, 1H), 7.11 (dd, J = 3.6, 1.1 Hz, 1H), 6.99 (d, J = 3.8 Hz, 1H), 6.98 (dd, J = 5.1, 3.6 Hz, 1H), 6.96 (s, 2H), 6.92 (d, J = 3.7 Hz, 1H), 6.90 (d, J = 3.8 Hz, 1H), 6.80 (d, J = 3.8J = 3.8 Hz, 1H), 2.52 (s, 6H), 2.28 (s, 3H). MS (LSI) m/z: 398 (M⁺, 100%). Anal. calcd. C₂₁H₁₈S₄: C 63.27, H 4.55, S 32.18; found: C 63.47, H 4.51, S 31.92.

Bis(5''-mesitylthio-5,2':5',2''-terthien-2-yl) sulfide $(^{MesS}T_3ST_3^{SMes})$

A solution of **3** (765 mg, 1.92 mmol) in THF (25 mL), cooled to -70 °C, was treated dropwise with *n*-butyllithium (1.20 mL, 1.92 mmol, 1.6 mol/L in hexanes). The resulting bright orange solution was stirred at -70 °C for 1 h. After which, a solution of bis(phenylsulfonyl) sulfide (302 mg, 0.96 mmol) in THF (10 mL) was added dropwise via cannula, and the resulting orange solution was stirred at -70 °C for an additional 1 h. The mixture was then warmed to RT and poured into a cold mixture of diethyl ether and water (120 mL, 1:5 v/v). The fine yellow precipitate was filtered off and washed with cold methanol $(3 \times 15 \text{ mL})$. This solid was recrystallized from a mixture of tetrahydrofuran and methanol (40 mL, 1:1 v/v) to afford ^{MesS}T₃ST₃^{SMes} as dark golden yellow crystals, yield 400 mg (50%), mp 156 °C. UV-vis (CH₂Cl₂) λ_{max} (nm) 395 (ϵ 6.5 × 10⁴). ¹H NMR $(500 \text{ MHz}, \text{CDCl}_3) \delta$: 7.08 d, J = 3.7 Hz, 2H), 6.93–6.95 (m, 8H), 6.90 (d, J = 3.7 Hz, 2H), 6.86 (d, J = 3.8 Hz, 2H), 6.78 (d, J = 3.7 Hz, 2H), 2.50 (s, 12H), 2.27 (s, 6H). ¹³C NMR (125 MHz, CDCl₃) δ : 143.06, 141.51, 139.78, 137.74, 137.22, 136.82, 135.30, 134.07, 133.89, 129.68, 129.54, 128.77, 124.91, 124.14, 123.94, 123.77, 22.01, 21.32. MS (LSI) *m/z*: 826 (M⁺, 10%). Anal. calcd. C₄₂H₃₄S₉: C 60.97, H 4.14, S 34.88; found: C 60.67, H 4.17, S 34.27.

Bis(5-mesitylthio-3,4-ethylenedioxy-2-thienyl) sulfide (^{MesS}ESE^{SMes})

A solution of bis(3.4-ethylenedioxy-2-thienyl) sulfide ESE (2.06 g, 6.55 mmol) was cooled to -40 °C and treated slowly with n-butyllithium (8.19 mL, 13.1 mmol, 1.6 mol/L in hexanes). The bright red solution was stirred for 1.5 h at -40 °C. After which, the solution was cooled to -70 °C, and a freshly prepared solution of 2-mesitylenesulfenyl chloride (2.45 g, 13.1 mmol) in hexanes (15 mL) was added dropwise via cannula. The resulting pale brown solution was stirred at -70 °C for an additional 30 min. The mixture was then warmed to RT and poured into water (100 mL). The fine white precipitate of MesSESESMes was filtered off, washed with cold methanol (3×20 mL), and dried in vacuo. Yield 2.10 g (52%), mp 206 °C. UV–vis (CH₂Cl₂) λ_{max} (nm) 309 $(\epsilon 2.3 \times 10^4)$. ¹H NMR (CDCl₃) δ : 6.90 (s, 4H), 4.19 (m, 8H), 2.48 (s, 12H), 2.25 (s, 6H). ¹³C NMR (CDCl₃) δ : 143.13, 142.92, 140.55, 139.40, 129.53, 128.99, 113.53, 107.17, 64.95, 64.77, 22.19, 21.27. MS (LSI) m/z: 614 (M⁺, 18%), 463 ((M – $C_9H_{11}S)^+$, 100%). Anal. calcd. C30H30O4S5: C 58.60, H 4.92, S 26.07; found: C 58.21, H 4.72, S 26.07.

Bis(5'-mesitylthio-3,4-ethylenedioxy-5,2'-bithien-2yl)sulfide (^{MesS}TESET^{SMes})

A solution of 3,4-ethylenedioxy-5'-mesitylthio-2,2'bithiophene 6 (0.85 g, 2.27 mmol) in THF (15 mL) cooled to -40 °C was treated dropwise with n-butyllithium (1.42 mL, 2.27 mmol, 1.6 mol/L in hexanes). The bright orange solution was stirred at -40 °C for 1.5 h. After which, the solution was cooled to -70 °C, and a solution of bis(phenylsulfonyl) sulfide (0.36 g, 1.15 mmol) in THF (10 mL) was added dropwise via cannula. The resulting yellow solution was stirred at -70 °C for an additional 30 min. The mixture was then warmed to RT and poured into a cold mixture of diethyl ether and water (120 mL, 1:5 v/v). The fine yellow precipitate was filtered off and washed with cold water $(3 \times 15 \text{ mL})$. This solid was recrystallized from a mixture of chloroform and methanol (80 mL, 3:5 v/v) to afford MesSTESET^{SMes} as yellow flakes, yield 0.60 g (68%), mp 198 °C. UV–vis (CH₂Cl₂) λ_{max} (nm) 375 (ϵ 4.2 × 10⁴). ¹H NMR (CDCl₃) δ : 6.93 d, J = 3.7 Hz, 2H), 6.92 (s, 4H), 6.76 (d, J = 3.7 Hz, 2H), 4.26 (m, 8H), 2.48 (s, 12H), 2.25 (s,)6H). ¹³C NMR (CDCl₃) δ: 143.70, 142.94, 139.45, 136.82, 136.70, 134.90, 129.85, 129.60, 128.86, 123.55, 115.51, 104.47, 65.14, 64.85, 22.07, 21.29. HRMS (LSI) for C₃₈H₃₄O₄S₇ [M⁺]: calcd. 778.0502; found 778.0502. Anal. calcd. for C38H34O4S7: C 58.58, H 4.40, S 28.81; found: C 58.47, H 4.39, S 28.38.

3,4-Ethylenedioxy-5-mesitylthio-2,2'-bithiophene (8)

A solution of 3,4-ethylenedioxy-5-bromo-2,2'-bithiophene 7 (3.90 g, 12.9 mmol) in THF (40 mL) cooled to -78 °C was

treated dropwise with *n*-butyllithium (8.04 mL, 12.9 mmol, 1.6 mol/L in hexanes). The resulting bright red solution was stirred for 1.5 h at -78 °C. A solution of 2-mesitylenesulfenyl chloride (2.41 g, 12.9 mmol) in hexanes (20 mL) was added dropwise via cannula, and the resulting rusty red solution was stirred at -78 °C for an additional 30 min. The mixture was warmed to RT and poured into water (100 mL). The aqueous layer was extracted with ether (3 \times 50 mL), and the combined organic extracts were further washed with water $(3 \times 50 \text{ mL})$ and dried over anhydrous sodium sulfate. After filtration, removal of the solvent gave a dark yellow solid, which was purified by column chromatography (silica gel, hexanes/dichloromethane (1:1 v/v)) to provide a bright yellow solid. Recrystallization from methanol/chloroform produced bright yellow needles of 8, yield 3.20 g (66%), mp 120 °C. ¹H NMR (500 MHz, CDCl₃) δ: 7.15 dd, J = 5.1, 1.1 Hz, 1H), 7.08 (dd, J = 3.7, 1.1 Hz, 1H), 6.94 (dd, J = 5.1, 3.7 Hz, 1 H), 6.92 (s, 2H), 4.29 (m, 4H),2.56 (s, 6H), 2.25 (s, 3H). ¹³C NMR (125 MHz, CDCl₃) δ: 142.68, 141.51, 138.91, 136.52, 134.25, 129.44, 129.23, 126.93, 123.74, 122.74, 113.00, 107.07, 64.76, 64.69, 21.97, 20.95. MS (EI) m/z: 374 (M⁺, 100%). Anal. calcd. C₁₉H₁₈O₂S₃: C 60.93, H 4.84, S 25.68; found: C 60.75, H 4.92, S 25.67.

$Bis(5'-mesitylthio-3',4'-ethylenedioxy-5-2'-bithien-2-yl) sulfide \ ({}^{MesS}ETSTE^{SMes})$

A solution of 8 (1.00 g, 2.67 mmol) in THF (30 mL), cooled to -40 °C, was treated dropwise with *n*-butyllithium (1.67 mL, 2.67 mmol, 1.6 mol/L in hexanes). The dark red solution was stirred at -40 °C for 1 h. After which, the solution was cooled to -70 °C, and a solution of bis(phenylsulfonyl) sulfide (0.42 g, 1.34 mmol) in THF (10 mL) was added dropwise via cannula. The resulting pale red solution was stirred at -70 °C for an additional 30 min. The mixture was then warmed to RT and poured into water (75 mL). The fine yellow precipitate was filtered off and washed with cold methanol (3 \times 20 mL). This solid was recrystallized from a mixture of chloroform and methanol (80 mL, 3:5 v/v) to afford MesSETSTE^{SMes} as yellow needles, yield 0.75 g, (72%), mp 213 °C. UV–vis (CH₂Cl₂) λ_{max} (nm) 375 ($\epsilon 4.4 \times 10^4$). ¹H NMR (500 MHz, THF- d_8) δ : 7.05 d, J = 3.9 Hz, 2H), 6.92 (s, 4H), 6.91 (d, J = 3.9 Hz, 2H), 4.27 (m, 8H), 2.51 (s, 12H), 2.22 (s, 6H). ¹³C NMR (125 MHz, THF- d_8) δ : 143.48, 142.99, 139.84, 139.78, 138.69, 134.03, 133.77, 130.35, 130.10, 123.03, 112.90, 108.54, 65.96, 65.78, 22.26, 21.11. HRMS (LSI) for C₃₈H₃₄O₄S₇ [M⁺]: calcd. 778.0502, found 778.0490. Anal. calcd. for $C_{38}H_{34}O_4S_7\!\!:$ C 58.58, H 4.40, S 28.81; found: C 58.67, H 4.42, S 28.55.

Acknowledgements

We thank the University of Victoria, the Natural Sciences and Engineering Research Council of Canada, and Defence R&D Canada-Atlantic for support of this work.

References

1. Electronic materials: The oligomer approach. *Edited by* K. Mullen and G. Wegner. Wiley, Chichester, NY. 1998.

- (a) J. Guay, A. Diaz, R.L. Wu, J.M. Tour, and L.H. Dao. Chem. Mater. 4, 254 (1992); (b) J. Guay, P. Kasai, A. Diaz, R.L. Wu, J.M. Tour, and L.H. Dao. Chem. Mater. 4, 1097 (1992); (c) M.G. Hill, K.R. Mann, L.L. Miller, and J.F. Penneau. J. Am. Chem. Soc. 114, 2728 (1992); (d) M.G. Hill, J.F. Penneau, B. Zinger, K.R. Mann, and L.L. Miller. Chem. Mater. 4, 1106 (1992).
- (a) D. Fichou. J. Mater. Chem. 10, 571 (2000); (b) A.R. Murphy and J.M J. Frechet. Chem. Rev. 107, 1066 (2007).
- 4. (a) R.P. Kingsborough and T.M. Swager. Prog. Inorg. Chem.
 48, 123 (1999); (b) P.G. Pickup. J. Mater. Chem. 9, 1641 (1999); (c) M.O. Wolf. Adv. Mater. 13, 545 (2001).
- 5. I. Manners. Angew. Chem. Int. Ed. 35, 1603 (1996).
- (a) F. Wudl, R.O. Angus, F.L. Lu, P.M. Allemand, D.J. Vachon, M. Nowak, Z.X. Liu, and A.J. Heeger. J. Am. Chem. Soc. 109, 3677 (1987); (b) A.G. Macdiarmid and A.J. Epstein. Faraday Disc. 317 (1989); (c) X.L. Wei, Y.Z. Wang, S.M. Long, C. Bobeczko, and A.J. Epstein. J. Am. Chem. Soc. 118, 2545 (1996); (d) E. Shoji and M.S. Freund. J. Am. Chem. Soc. 124, 12486 (2002).
- (a) R.J.P. Corriu, T. Deforth, W.E. Douglas, G. Guerrero, and W.S. Siebert. Chem. Commun. 963 (1998); (b) N. Matsumi, K. Naka, and Y. Chujo. Macromolecules, **31**, 8047 (1998); (c) N. Matsumi, K. Naka, and Y. Chujo. J. Am. Chem. Soc. **120**, 10776 (1998); (d) N. Matsumi, K. Naka, and Y. Chujo. J. Am. Chem. Soc. **120**, 5112 (1998); (e) K. Naka, T. Umeyama, and Y. Chujo. Macromolecules, **33**, 7467 (2000); (f) A. Sundararaman, M. Victor, R. Varughese, and F. Jakle. J. Am. Chem. Soc. **127**, 13748 (2005); (g) J.B. Heilmann, Y. Qin, F. Jakle, H.W. Lerner, and M. Wagner. Inorg. Chim. Acta, **359**, 4802 (2006); (h) J.B. Heilmann, M. Scheibitz, Y. Qin, A. Sundararaman, F. Jakle, T. Kretz, M. Bolte, H.W. Lerner, M.C. Holthausen, and M. Wagner. Angew. Chem. Int. Ed. **45**, 920 (2006); (i) F. Jakle. Coord. Chem. Rev. **250**, 1107 (2006).
- (a) R.J.P. Corriu, C. Guerin, B. Henner, T. Kuhlmann, A. Jean, F. Garnier, and A. Yassar. Chem. Mater. 2, 351 (1990); (b) P. Chicart, R.J.P. Corriu, J.J.E. Moreau, F. Garnier, and A. Yassar. Chem. Mater. 3, 8 (1991); (c) K. Tamao, S. Yamaguchi, and M. Shiro. J. Am. Chem. Soc. 116, 11715 (1994); (d) S. Yamaguchi, T. Goto, and K. Tamao. Angew. Chem. Int. Ed. 39, 1695 (2000); (e) Y. Lee, S. Sadki, B. Tsuie, and J.R. Reynolds. Chem. Mater. 13, 2234 (2001).
- (a) Z. Jin and B.L. Lucht. J. Organometal. Chem. 653, 167 (2002); (b) K. Naka, T. Umeyama, and Y. Chujo. J. Am. Chem. Soc. 124, 6600 (2002); (c) V.A. Wright and D.P. Gates. Angew. Chem. Int. Ed. 41, 2389 (2002); (d) R.C. Smith and J.D. Protasiewicz. Eur. J. Inorg. Chem. 998 (2004); (e) R.C. Smith and J.D. Protasiewicz. J. Am. Chem. Soc. 126, 2268 (2004); (f) T. Baumgartner and R. Reau. Chem. Rev. 106, 4681 (2006); (g) V.A. Wright, B.O. Patrick, C. Schneider, and D.P. Gates. J. Am. Chem. Soc. 128, 8836 (2006).
- 10. M.M. Labes, P. Love, and L.F. Nichols. Chem. Rev. 79, 1 (1979).
- (a) R.R. Chance, L.W. Shacklette, G.G. Miller, D.M. Ivory, J.M. Sowa, R.L. Elsenbaumer, and R.H. Baughman. J. Chem. Soc. Chem. Commun. 348 (1980); (b) J.F. Rabolt, T.C. Clarke, K.K. Kanazawa, J.R. Reynolds, and G.B. Street. J. Chem. Soc. Chem. Commun. 347 (1980); (c) R.H. Friend and J.R.M. Giles. J. Chem. Soc. Chem. Commun. 1101 (1984); (d) K.F. Schoch, J.F. Chance, and K.E. Pfeiffer. Macromolecules, 18, 2389 (1985); (e) E. Tsuchida, K. Yamamoto, M. Jikei, and H. Nishide. Macromolecules, 23, 930 (1990); (f) J. Leuninger, C.S. Wang, T. Soczka-Guth, V. Enkelmann, T. Pakula, and K. Mullen. Macromolecules, 31, 1720 (1998).

- (a) Y. Ikeda, M. Ozaki, and T. Arakawa. J. Chem. Soc. Chem. Commun. 1518 (1983); (b) K.Y. Jen, N. Benfaremo, M.P. Cava, W.S. Huang, and A.G. Macdiarmid. J. Chem. Soc. Chem. Commun. 633 (1983); (c) A. Berlin, G.A. Pagani, and F. Sannicolo. J. Chem. Soc. Chem. Commun. 1663 (1986).
- (*a*) J. Nakayama, N. Katano, Y. Shimura, Y. Sugihara, and A. Ishii. J. Org. Chem. **61**, 7608 (1996); (*b*) J. Nakayama, N. Katano, Y. Sugihara, and A. Ishii. Chem. Lett. 897 (1997); (*c*) N. Katano, Y. Sugihara, A. Ishii, and J. Nakayama. Bull. Chem. Soc. Jpn. **71**, 2695 (1998).
- R. Rulkens, D.P. Gates, D. Balaishis, J.K. Pudelski, D.F. McIntosh, A.J. Lough, and I. Manners. J. Am. Chem. Soc. 119, 10976 (1997).
- R.G. Hicks and M.B. Nodwell. J. Am. Chem. Soc. 122, 6746 (2000).
- M. Chahma, R.G. Hicks, and D.J.T. Myles. Macromolecules, 37, 2010 (2004).
- 17. M. Chahma, D.J.T. Myles, and R.G. Hicks. Chem. Mater. 17, 2672 (2005).
- (a) Y. Kiya, G.R. Hutchison, J.C. Henderson, T. Sarukawa, O. Hatozaki, N. Oyama, and H.D. Abruna. Langmuir, 22, 10554

(2006); (*b*) S.P. Mishra, K. Krishnamoorthy, R. Sahoo, and A. Kumar. J. Mater. Chem. **16**, 3297 (2006).

- 19. F.D. Jong and M.J. Janssen. J. Org. Chem. 36, 1645 (1971).
- X.C. Li, H. Sirringhaus, F. Garnier, A.B. Holmes, S.C. Moratti, N. Feeder, W. Clegg, S.J. Teat, and R.H. Friend. J. Am. Chem. Soc. **120**, 2206 (1998).
- R.H. Mitchell, Y.H. Lai, and R.V. Williams. J. Org. Chem. 44, 4733 (1979).
- (a) B.L. Groenendaal, F. Jonas, D. Freitag, H. Pielartzik, and J.R. Reynolds. Adv. Mater. **12**, 481 (2000); (b) B.L. Groenendaal, G. Zotti, P.H. Aubert, S.M. Waybright, and J.R. Reynolds. Adv. Mater. **15**, 855 (2003).
- T. Nokami, A. Shibuya, H. Tsuyama, S. Suga, A.A. Bowers, D. Crich, and J.I. Yoshida. J. Am. Chem. Soc. **129**, 10922 (2007).
- 24. (a) R.L. Wu, J.S. Schumm, D.L. Pearson, and J.M. Tour. J. Org. Chem. 61, 6906 (1996).
- 25. M. Turbiez, P. Frere, P. Blanchard, and J. Roncali. Tetrahedron Lett. **41**, 5521 (2000).
- 26. M. Chahma. Synth. Met. 155, 474 (2005).