

# Synthesis and Characterization of Soluble Low-Bandgap Oligothiophene-[all]-*S,S*-dioxides-Based Conjugated Oligomers and Polymers

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**ABSTRACT:** The synthesis and characterization of a new family of soluble oligothiophene-*S,S*-dioxides and their use as building blocks to form polythiophene-*S,S*-dioxides via microwave-assisted Stille coupling polymerization are described. Incorporation of the sulfone group into the polythiophene backbone leads to narrowing of the polymer bandgap, and while the energies of both Frontier orbitals in polythiophene-*S,S*-dioxide are lower with respect to polythiophenes, this tendency is

considerably stronger for the lowest unoccupied molecular orbital than for the highest occupied molecular orbital, resulting in greater electron-accepting ability. © 2011 Wiley Periodicals, Inc. *J Polym Sci Part A: Polym Chem* 49: 1933–1941, 2011

**KEYWORDS:** conjugated polymers; crystal structures; oligomers; synthesis; UV–vis spectroscopy

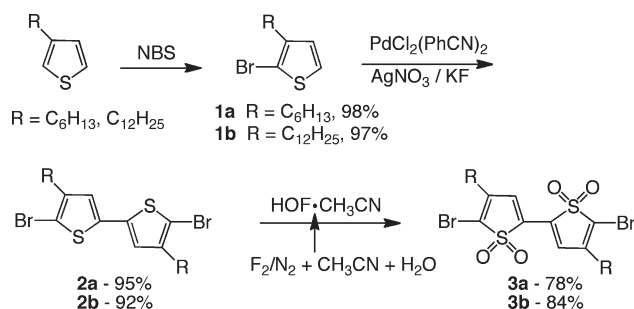
**INTRODUCTION** The development of solution-processable small molecules and polymeric materials with good electron-transporting properties is highly desired for various applications in organic-based electronics. The vast majority of materials known today exhibit p-channel (hole-transporting) behavior.<sup>1</sup> In direct contrast, air-stable n-channel (electron-transporting) semiconductors and polymeric materials that show solid-state transport of both hole and electron carriers are significantly less developed. Consequently, a major research challenge in this field is to synthesize electron-poor building blocks having the energy of the lowest unoccupied molecular orbital (LUMO) decreased to such an extent that the compound is easily reduced and capable of acting as an n-channel device.<sup>2</sup> It was shown that incorporation of electron-withdrawing groups such as fluorine<sup>3</sup> and/or carbonyl<sup>4,5</sup> into oligo and polythiophene skeletons can increase the n-type character of the corresponding device. Building on this strategy, thiophene-*S,S*-dioxides<sup>6,7</sup> have been examined as electron-poor units<sup>8</sup> with Barbarella and coworkers reporting the preparation of partially oxygenated oligothiophenes where transformation of one or several aromatic thiophene rings into the corresponding *S,S*-dioxides inserts a strong electron-withdrawing group into the  $\pi$ -conjugated main chain.<sup>9</sup> This leads to an increase in electron-affinity, electron delocalization, and a reduction in the optical bandgap of the oligothiophene, allowing the transport prop-

erties of oligo and polythiophenes to be tuned from p-type to n-type. These findings triggered investigations into the synthesis of various chemical architectures containing partially oxygenated oligothiophene-*S,S*-dioxides, their characterization, and applications in electronic devices,<sup>10</sup> with one noticeable example being the synthesis of oligothiophene-[all]-*S,S*-dioxides.<sup>11</sup> In comparison with their partially oxygenated counterparts, complete dearomatization of the oligothiophenes resulted in a significant redshift of the absorption maxima, indicating a considerable narrowing of the energy gap. Theoretical calculations in combination with electrochemical measurements indicated that the energies of the Frontier orbitals of oligothiophene-[all]-*S,S*-dioxides were reduced, with the values of the LUMO dropping almost twice as much as the highest occupied molecular orbital (HOMO). Despite their promising characteristics, the use of oligothiophene-[all]-*S,S*-dioxides in applications was limited due to their poor solubility in common organic solvents.

In this study, we describe the synthesis of bi-, *ter*-, and quater-thiophenes incorporating solubilizing alkyl groups in the oligomer skeleton and the subsequent use of these systems as modular building blocks for the preparation of conjugated systems based on thiophene-*S,S*-dioxides. Oxygenation of these oligothiophenes using the acetonitrile complex of hypofluorous acid,  $\text{HOF}\bullet\text{CH}_3\text{CN}$ , resulted in the formation of a new family of oligothiophene-[all]-*S,S*-dioxides that are

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**SCHEME 1** Synthetic route to soluble bithiophene-[all]-S,S-dioxides (**3a** and **3b**).

completely soluble in a variety of organic solvents and can be easily processed into thin films. Oxygenated oligothiophenes were characterized utilizing UV-vis spectroscopy, thermal gravimetric analysis (TGA), and X-ray diffraction. In addition, bi- and *ter*-thiophene-[all]-S,S-dioxides were used as building blocks to prepare soluble conjugated polythiophenes with narrow optical bandgaps.

## RESULTS AND DISCUSSION

2-Bromo-3-hexylthiophene (**1a**) and 2-bromo-3-dodecylthiophene (**1b**) were obtained in near quantitative yield from reaction of the corresponding 3-alkylthiophenes with *N*-bromosuccinimide (NBS). Palladium-catalyzed C–H homocoupling of **1a** and **1b** afforded the aromatic bithiophenes **2a** and **2b**, bearing alkyl groups in the 4 and 4' positions.<sup>12</sup> Oxidation of **2a** and **2b** was then carried out by adding freshly prepared HOF•CH<sub>3</sub>CN solution, prepared by bubbling commercial 15% F<sub>2</sub> in nitrogen into a mixture of water and acetonitrile at –15 °C, to the dichloromethane solution of the aromatic bithiophene at room temperature.<sup>13</sup> The reaction reached completion after 15 min, affording previously unknown bithiophene-[all]-S,S-dioxides (**3a**, **3b**) in high yield (Scheme 1).

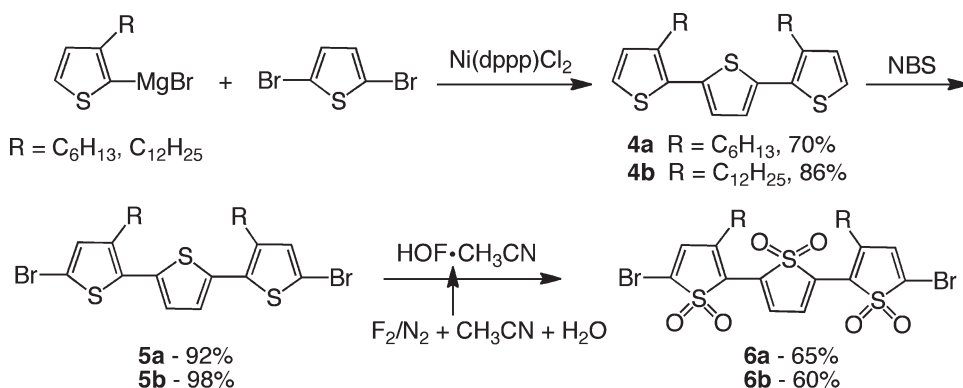
Using a similar methodology, the soluble terthiophene-based oligomers **4a** and **4b** were obtained in good yield from 2,5-dibromothiophene and Grignard reagents derived from 2-bromo-3-hexylthiophene **1a** and 2-bromo-3-dodecylthiophene **1b**, using Kumada coupling conditions.<sup>14</sup> Bromination of **4a** and **4b** with NBS gave the corresponding dibromoter-

thiophene derivatives **5a** and **5b**, which could be fully oxidized to form terthiophene-[all]-S,S-dioxides **6a** and **6b** in 65 and 60% yield, respectively (Scheme 2). It should be noted that HOF•CH<sub>3</sub>CN, while an extremely strong oxidizing reagent, is selective and allows oligomers **3a**, **3b**, **6a**, and **6b** to be prepared with terminal C–Br groups. A consequence of this is that these systems are now available for subsequent transition metal-catalyzed coupling reactions and can be used as building blocks, leading to more complex conjugated systems.

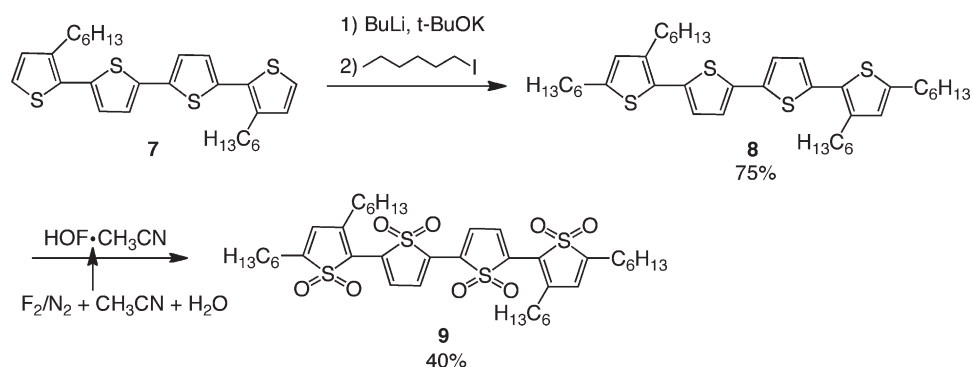
To construct a derivative with four thienyl rings, commercially available 3,3'-dihexylquaterthiophene (**7**) was alkylated with 1-iodohexane to form the tetra-substituted aromatic oligomer (**8**). Significantly, oxygenation with HOF•CH<sub>3</sub>CN could be carried out at room temperature using a twofold excess of the reagent, yielding compound **9** after introduction of eight oxygen atoms and dearomatization of all four thiophene rings in 40% (Scheme 3). Because of the presence of the long alkyl side chains, all oligothiophene-S,S-dioxides mentioned above were found to be completely soluble in common organic solvents such as dichloromethane, chloroform, and chlorobenzene. This is in contrast to previous study,<sup>11</sup> where oxygenated oligothiophenes, bearing bromines, methyl, or *t*-butyl groups only at the terminal carbons adjacent to the sulfur atoms, were only partially or slightly soluble in chlorinated solvents.

UV-vis measurements were performed on all the oxygenated oligothiophenes and their aromatic precursors. We report here the results for the hexyl-substituted derivatives **2a**, **3a**, **5a**, **6a**, **8**, and **9**. On comparison with the starting aromatic oligothiophenes that show a broad absorption band, the corresponding oligothiophene-[all]-S,S-dioxides exhibit well-defined vibronic fine structures typical of rigid conjugated systems.<sup>15</sup> Furthermore, the absorption maximum for the oxygenated bithiophene-S,S-dioxide (**3a**) was redshifted by ~63 nm with respect to the aromatic bithiophene (**2a**). This trend is maintained for all oligomers with even larger shifts of 103 and 106 nm for the terthiophene-[all]-S,S-dioxide (**6a**) and quaterthiophene-[all]-S,S-dioxide (**9**), respectively (Fig. 1).

The bathochromic shift is fully consistent with the transformation of the starting oligothiophenes into the



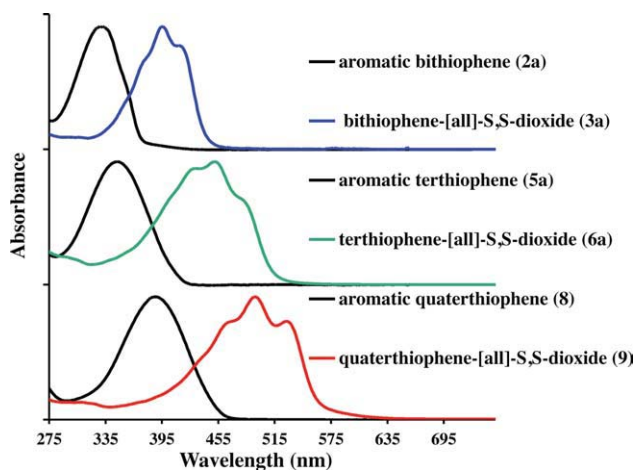
**SCHEME 2** Synthesis of terthiophene-[all]-S,S-dioxides (**6a** and **6b**).



**SCHEME 3** Synthesis of quaterthiophene-[all]-*S,S*-dioxide (**9**).

corresponding oligothiophene-[all]-*S,S*-dioxides, leading to narrowing of the optical bandgap. Optical bandgaps were estimated by the onset point of the absorption band and are summarized in Table 1. For all studied oligomers, on dearomatization of all thiophenes rings, a reduction of more than 0.5 eV in the energy gap was observed.

Thermal properties of the oxygenated oligomers were analyzed by TGA, revealing a two-step degradation process in all cases. The initial weight loss of  $\sim 30\%$  can be attributed to the elimination of  $\text{SO}_2$  from all sulfone groups along the oligothiophene backbone. This assumption is supported by a previous report showing that in sulfone-containing polymers, due to the relatively weak C—S bonds, thermally induced chemical disintegration leads to initial loss of  $\text{SO}_2$  groups.<sup>8b</sup> Furthermore, on increasing the length of the oligomer, thermally induced degradation was observed at lower temperatures, with an onset temperature of 164 °C for bithiophene-[all]-*S,S*-dioxide **3a**, 158 °C for terthiophene-[all]-*S,S*-dioxide **6a**, and 144 °C for quaterthiophene **9** (Fig. 2). A rationale for this trend is the increasing number of the electron-withdrawing sulfone groups, weakening the neighboring C—S bonds, resulting in lower decomposition temperatures with increasing oligomer length.



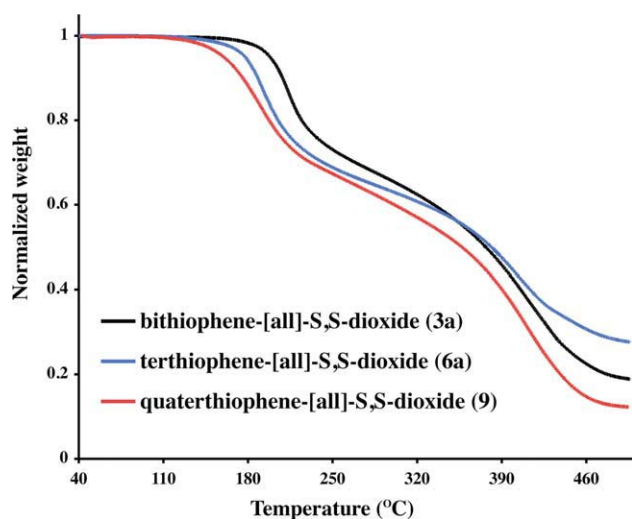
**FIGURE 1** UV-vis spectra, measured in chloroform, for the bithiophene (**2a**), bithiophene-[all]-*S,S*-dioxide (**3a**), terthiophene (**5a**), terthiophene-[all]-*S,S*-dioxide (**6a**), quaterthiophene (**8**), and quaterthiophene-[all]-*S,S*-dioxide (**9**).

The limited structural data on oligothiophene-[all]-*S,S*-dioxides with an exception of terthiophene,<sup>11</sup> prompted a thorough evaluation of molecular structures and cell packing motifs for the oxygenated oligomers **3a** and **9**. Bithiophene-*S,S*-dioxide (**3a**) crystallizes in a triclinic system with a P-1 space group. Thiophene rings exhibit an *anti*, nearly planar conformation with the torsion angle between the mean planes of the rings of 2° [Fig. 3(A)]. This torsion angle is smaller than the values reported for the fully oxygenated oligomer consisted of three thiophene rings.<sup>11</sup> Furthermore, cell packing reveals that oligomer **3a** adopts a  $\pi$ - $\pi$  stacking arrangement of the molecular chains with an angle of 0° between the main planes of the adjacent molecules [Fig. 3(B)]. The sulfone groups of adjacent oligomers are in *syn* conformation relative to each other, and to avoid unfavorable electronic interactions, the molecules adopt an alignment where a slight displacement along the long molecular axis takes place. In this packing motif, the shortest intermolecular distance measured between the oxygen atom of one molecule and the thiophene carbon atom of another molecule is 3.3 Å.

In comparison, the quaterthiophene-*S,S*-dioxide (**9**) crystallizes in a monoclinic system with a C2/*c* space group. The conformation of the thiophene-*S,S*-dioxide rings is again almost planar with torsion angles of 2.7 and 5.2° [Fig. 4(A)]. Analysis of the unit cell configuration reveals an interesting alignment, which is different from the one observed for the oxygenated bithiophene **3a**. Molecular chains are oriented in an alternating motif with each molecule being parallel to another molecule and perpendicular to a third one [Fig. 4(B)]. In addition, the parallel chains undergo long-axis

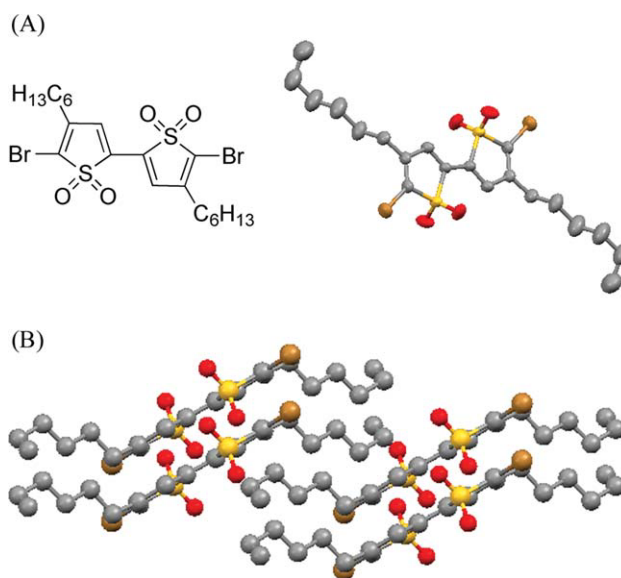
**TABLE 1** Absorption Maxima and Optical Bandgaps for the Starting Oligothiophenes (**2a**, **5a**, and **8**) and the Corresponding Oligothiophene-[all]-*S,S*-dioxides (**3a**, **6a**, **9**)

Compound	$\lambda_{\text{max}}$ (nm)	$E_g$ (eV)	$\Delta E_g$ (eV)
<b>2a</b>	332	3.31	0.55
<b>3a</b>	395	2.76	
<b>5a</b>	348	2.95	0.59
<b>6a</b>	451	2.36	
<b>8</b>	388	2.70	0.56
<b>9</b>	494	2.14	



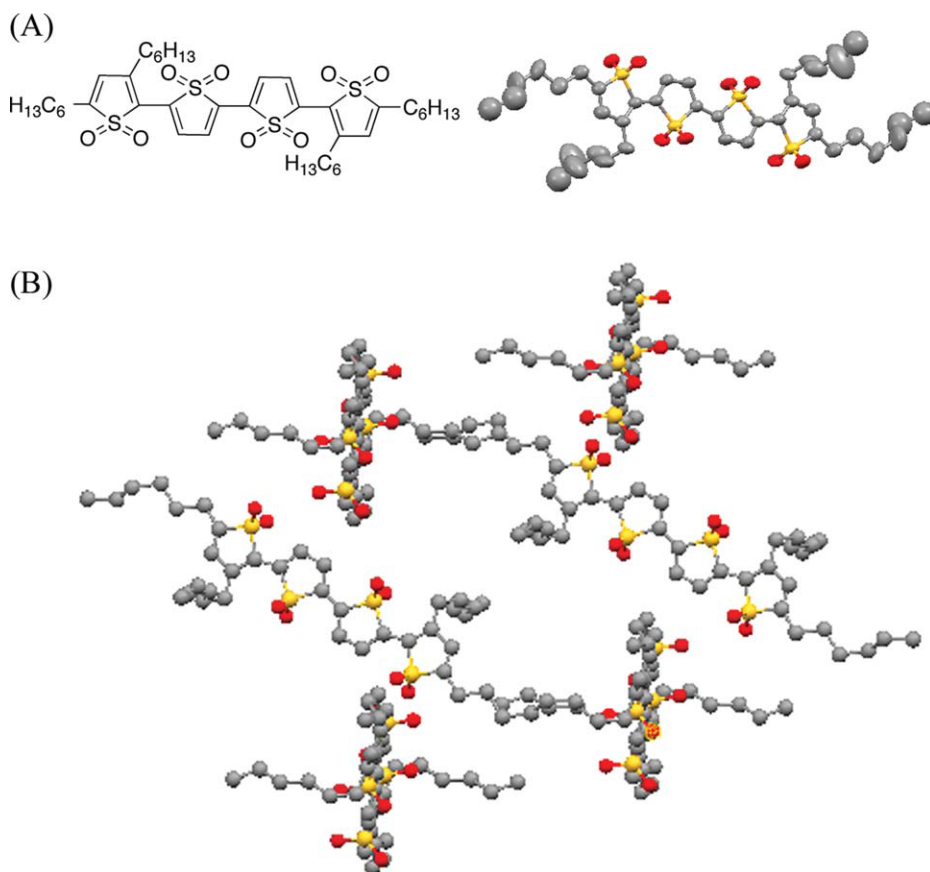
**FIGURE 2** TGA analysis for the oligothiophene-[all]-S,S-dioxides, **3a**, **6a**, and **9**.

sliding most likely to afford better cofacial stacking and to minimize steric hindrance from the alkyl chains, allowing greater interdigitation. A similar perpendicular alignment trend was previously reported when electron-withdrawing fluorine atoms were incorporated into a pentacene skeleton.<sup>16</sup>

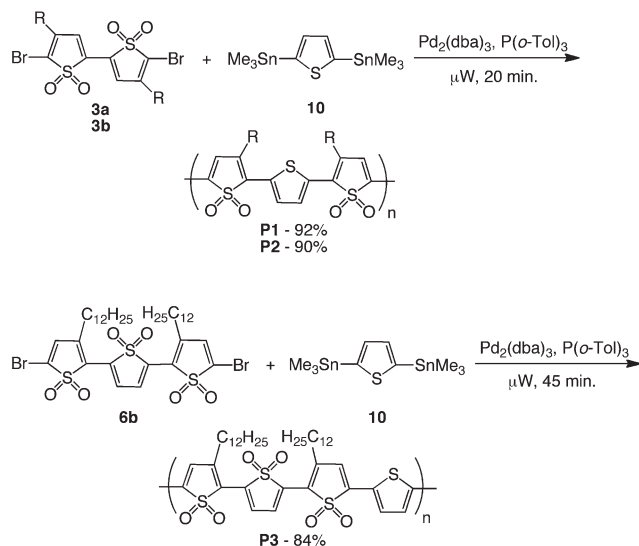


**FIGURE 3** (A) Molecular structure and (B) cell packing diagram for the 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiophene-[all]-S,S-dioxide (**3a**).

The availability of well-defined, strongly electron-deficient oligomers now permits their use as building blocks for the construction of conjugated polymeric materials to be examined. Bromine atoms at the terminal carbons of the



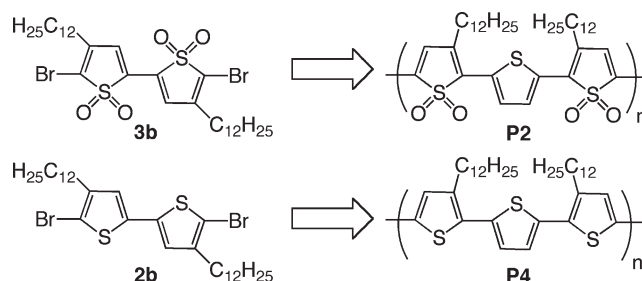
**FIGURE 4** (A) Molecular structure and (B) cell packing diagram for the quaterthiophene-[all]-S,S-dioxide (**9**).



**SCHEME 4** Synthetic route to polymers **P1**–**P3**.

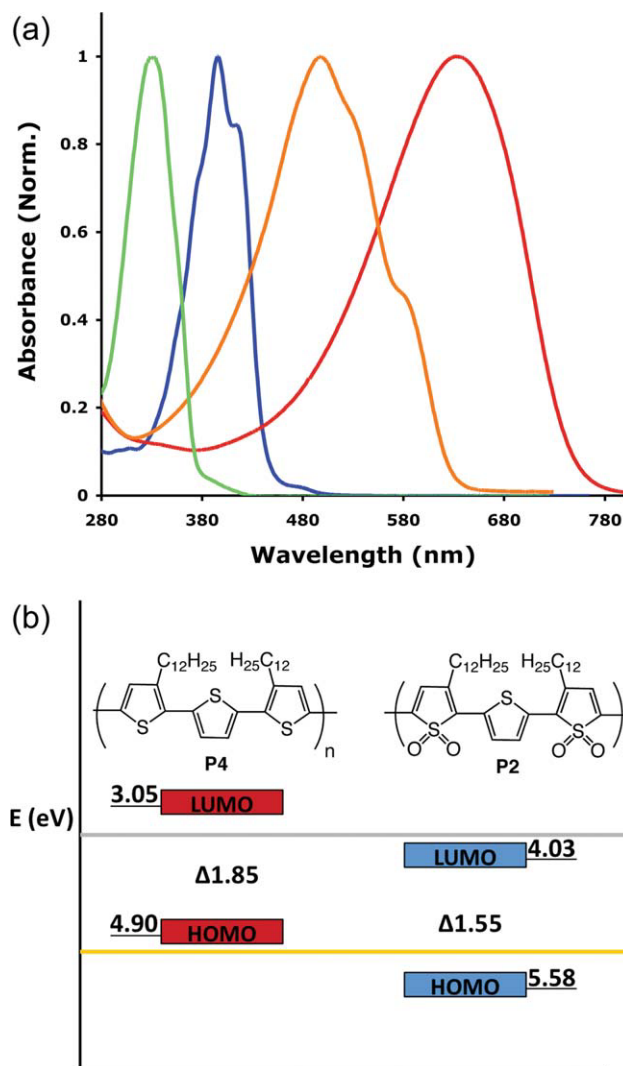
oligomers **3a**, **3b**, **6a**, and **6b** make them suitable candidates for various transition metal-catalyzed coupling reactions. Initial attempts to polymerize 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiophene-[all]-*S,S*-dioxide (**3a**) using  $\text{Pd}(\text{PPh}_3)_4$  with 2,5-bis(trimethylstannyl)thiophene (**10**),<sup>17</sup> resulted in low-molecular weight material ( $M_n = 3.1$  K) that was isolated in 30% yield after 4 days of reflux in *N,N*-dimethylformamide. In contrast to the reactions carried out under conventional heating, microwave irradiation allows reaction times to be reduced significantly, yielding products in high yield with less side products.<sup>18</sup> Consequently, by using microwave-assisted Stille coupling conditions using  $\text{Pd}_2(\text{dba})_3/\text{P}(o\text{-tol})_3$  as a catalyst system and chlorobenzene as a solvent, we were successful in increasing molecular weight and product yield considerably. Polymerization of **3a** and **10** now gave polythiophene-*S,S*-dioxide, **P1**, after only 20 min in 92% yield with  $M_n = 8.5$  K, PDI = 2.7 (Scheme 4). Following the same reaction conditions, polymer **P2** with 4,4'-didodecyl-2,2'-bithiophene-[all]-*S,S*-dioxide incorporated in the backbone was formed in 90% yield with higher molecular weight and lower polydispersity index ( $M_n = 10.8$  K, PDI = 1.9). In the case of polymerization of terthiophene-*S,S*-dioxide (**6b**), the reaction time was extended to 45 min with the product polymer, **P3**, having a relatively high polydispersity index (PDI = 4.1) and moderate molecular weight  $M_n = 5.7$  kDa. This is most likely due to the fact that in the precursor monomer, **6b**, carbon atoms that undergo the coupling reaction are more deactivated due to the presence of an additional electron withdrawing sulfone unit in comparison with bithiophene-*S,S*-dioxides. We should emphasize that all the sulfone-containing polymers are soluble in chloroform or chlorobenzene, air-stable, and can be stored at room temperature without degradation.

Finally, we examined the influence of incorporation of electron-withdrawing bithiophene-*S,S*-dioxide unit in polythiophene on the optical bandgap and energy levels of the Frontier molecular orbitals. Because the structural similarity



**SCHEME 5** Chemical structures for the polymers, **P2** and **P4**.

between the polymers **P1** and **P2**, we focused on the dodecyl derivative **P2** in this work. For direct comparison, polymer, **P4**, with all aromatic thiophene rings was synthesized using similar polymerization conditions. **P4** was obtained with comparable molecular weight ( $M_n = 11.0$  kDa, PDI = 1.4) in



**FIGURE 5** (a) UV-vis spectra, measured in chloroform, for bithiophene, **2b** (green), bithiophene-[all]-*S,S*-dioxide, **3b** (blue), **P4** (orange), **P2** (red). (b) HOMO and LUMO energy levels for the as cast **P2** and **P4**.

high yield (see Experimental Section). Chemical structures of the **P2** and **P4**, as well as the precursor monomers are shown in Scheme 5.

UV-vis absorption spectra in chloroform of the polymers **P2** and **P4**, and their respective monomers, **3b** and **2b** are shown in Figure 5(A). In analogy with the prior oligomer studies, the results show a strong bathochromic shift of  $\sim 60$  nm for the bithiophene-[all]-*S,S*-dioxide building block, **3b**, relatively to its aromatic counterpart, **2b**. The extended conjugation length of the polymers leads to a further redshift as reflected by the absorption maximum at 631 nm for polythiophene-*S,S*-dioxide **P2** compared with 496 nm for aromatic polythiophene **P4** ( $\Delta\lambda_{\text{max}} = 135$  nm). The optical bandgap was estimated by the onset point of the absorption band and corresponded to 1.55 eV for **P2**. This value is lower than the optical bandgap of the aromatic polymer **P4** (1.85 eV), owing to the incorporation of the bithiophene-[all]-*S,S*-dioxide as an electron-withdrawing subunit along the polymer backbone.

Ultraviolet photoelectron spectroscopy (UPS) was then used to obtain the energy of the HOMO of the polymers.<sup>19,20</sup> UPS measurements revealed that the HOMO energy levels for the as cast polymers **P2** and **P4** are 5.58 and 4.90 eV, respectively, [Fig. 5(B)]. In addition, annealing at 110 °C for 5 min led to a change in the HOMO energies in both polymers to a value of 5.77 eV (**P2**) and 4.97 eV (**P4**). This result is expected, because on annealing, conducting polymers typically show slight changes to the HOMO, associated with an increase in crystallinity.<sup>20</sup> LUMO values were estimated by using the optical gap and HOMO energies (Formula 1).<sup>19</sup>

$$E_{\text{LUMO}} = E_{\text{g}} - E_{\text{HOMO}} \quad (1)$$

The LUMO energy of the aromatic polythiophene **P4** is 3.05 eV, while the LUMO of the polythiophene-*S,S*-dioxide derivative **P2** is lower by about 1 eV (4.03 eV).

Significantly, these results indicate that the energies of the Frontier orbitals in polythiophenes can be fine-tuned by the incorporation of sulfones in the repeating unit. Furthermore, the presence of the electron-withdrawing *S,S*-dioxide group has a stronger effect on the lowering of the LUMO than the HOMO level, leading to potentially better electron-accepting properties for the thiophene-*S,S*-dioxide containing polymers with respect to the aromatic polythiophenes. These materials show promise when compared with traditional fullerene structures<sup>21</sup> in terms of modularity and tuning of electronic and physical properties.

## EXPERIMENTAL

### Materials

Chemicals were purchased from Sigma-Aldrich (St. Louis, MO, USA) and used without further purification. Deuterated solvents were obtained from Cambridge Isotope Laboratories, and 2-bromo-3-hexylthiophene (**1a**) and 2-bromo-3-dodecylthiophene (**1b**) were synthesized following the literature procedure.<sup>22</sup> 5,5'-Dibromo-4,4'-dihexyl-2,2'-bithiophene (**2a**)

and 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene (**2b**) were made according to the coupling procedure,<sup>12</sup> with reaction times being extended to 12 h. Preparation of 3,3''-dihexyl-2,2':5',2''-terthiophene (**4a**)<sup>23</sup> and 3,3''-didodecyl-2,2':5',2''-terthiophene (**4b**)<sup>24</sup> was carried out following Kumada coupling conditions.<sup>14</sup> Crystal structures for the compounds **3a** and **9** were deposited at the Cambridge Crystallographic Data Center and allocated the deposition numbers CCDC 810108 and CCDC 810107, respectively. Flash chromatography was performed with EM science 37–75  $\mu\text{m}$  silica gel. Analytical thin layer chromatography was performed on EM science silica plates with F-254 indicator, and the visualization was accomplished by UV lamp or using the molybdic acid stain mixture.

### Instrumentation

All materials were characterized by nuclear magnetic resonance (NMR) spectroscopy using Varian 200-, Varian 400-, and Varian 500-MHz spectrometers as indicated. Chemical shifts are reported in ppm and referenced to the solvent (proton and carbon). Microwave-assisted reactions were conducted on a Biotage Microwave reactor at a frequency of 2.5 GHz. VG70 Magnetic Sector and Waters GCT Premier TOF instruments were used for low and high resolution mass analysis by electron ionization (EI). Micromass QTOF2 Quadrupole/Time-of-Flight Tandem mass spectrometer was used for high-resolution mass analysis using electrospray ionization (ESI). Gel permeation chromatography (GPC) was performed in THF on a Waters system (Millford, MA, USA) equipped with four 5-mm Waters columns ( $300 \times 7.7 \text{ mm}^2$ ) connected in series with increasing pore size ( $10^2$ ,  $10^3$ ,  $10^4$ , and  $10^6$  Å). Waters 410 differential refractometer index and Waters 996 photodiode array detectors were used. The molecular weights of the polymers were calculated relative to linear PS standards. UV-vis spectra were recorded on Agilent 8453 spectrophotometer using chloroform solutions.

### General Procedure for Producing HOF•CH<sub>3</sub>CN Complex

Mixture of 20% F<sub>2</sub> with nitrogen was used in this work. It was passed at a rate of about 400 mL per minute through a cold (−15 °C) mixture of CH<sub>3</sub>CN (60 mL) and H<sub>2</sub>O (6 mL). The development of the oxidizing power was monitored by reacting aliquots with an acidic aqueous solution of KI. The liberated iodine was then titrated with thiosulfate. Typical concentrations of the oxidizing reagent were around 0.4–0.6 M.

### General Procedure for Oxidations

The oligothiophene (usually 2–4 mmol) was dissolved in CH<sub>2</sub>Cl<sub>2</sub> at room temperature. The HOF•CH<sub>3</sub>CN solution was slowly added to the reaction mixture, and the reaction was stopped after 15–30 min by adding a saturated solution of NaHCO<sub>3</sub>. The organic material was extracted with CH<sub>2</sub>Cl<sub>2</sub>, washed with water, and dried over MgSO<sub>4</sub>. The crude product was usually purified either by vacuum flash chromatography, using silica-gel 60-H (Merck), or recrystallization.

### General Procedure for Polymerizations

A 5-mL glass vial was charged with a stirrer bar, 5,5'-dibromo-oligothiophene (usually 0.2–0.4 mmol), equimolar

amount of 2,5-bis(trimethylstannyl)thiophene,<sup>17</sup> Pd<sub>2</sub>(dba)<sub>3</sub> (4 mol % Pd), P(*o*-tol)<sub>3</sub> (8 mol %), and chlorobenzene (2 mL). The glass vial was purged with nitrogen and securely sealed. The glass vial was placed into a microwave reactor and heated at 200 °C for 20–45 min with stirring. After cooling to room temperature, the reaction mixture was precipitated into a mixture of methanol (50 mL) and 37% HCl (5 mL) and stirred for 2 h. The polymer was filtered off and washed with methanol, following by further purification by sequential Soxhlet extraction with methanol, hexanes, and dichloromethane.

5,5'-Dibromo-4,4'-dihexyl-2,2'-bithiophene-[all]-*S,S*-dioxide (**3a**) was prepared from **2a** as described above in 78% yield. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, ppm): δ 7.12 (1H, s), 2.46 (2 H, t, *J* = 8 Hz), 1.62–1.55 (2H, m), 1.40–1.33 (6H, m), 0.90 (3H, t, *J* = 7 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, ppm): δ 142.9, 131.0, 128.4, 118.3, 32.0, 30.7, 29.5, 27.0, 23.1, 14.7. HRMS (EI) (*m/z*): (*M*)<sup>+</sup> calcd for C<sub>20</sub>H<sub>28</sub>Br<sub>2</sub>O<sub>4</sub>S<sub>2</sub> 553.9796; found, 553.9803.

5,5'-Dibromo-4,4'-didodecyl-2,2'-bithiophene-[all]-*S,S*-dioxide (**3b**) was prepared from **2b** as described above in 84% yield. <sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, ppm): δ 7.12 (1H, s), 2.46 (2H, t, *J* = 8 Hz), 1.62–1.57 (2H, m), 1.31–1.26 (18H, m), 0.88 (3H, t, *J* = 7 Hz). <sup>13</sup>C NMR (50 MHz, CDCl<sub>3</sub>, ppm): δ 142.9, 131.0, 128.4, 118.2, 32.6, 30.7, 30.3, 30.2, 30.1, 30.0, 29.9, 27.1, 23.4, 14.8. HRMS (ESI) (*m/z*): (*M*+Na)<sup>+</sup> calcd for C<sub>32</sub>H<sub>52</sub>Br<sub>2</sub>NaO<sub>4</sub>S<sub>2</sub> 745.1571; found, 745.1552.

5,5''-Dibromo-3,3''-dihexyl-2,2':5',2''-terthiophene (**5a**)<sup>25</sup> and 5,5''-dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene (**5b**) were prepared in 92 and 98% yield, respectively. The synthesis of **5b** is described below. NBS (0.29 g, 3.2 mmol) was added in portions to a solution of the **4b** (0.96 g, 1.6 mmol) in DMF (12 mL) in dark and stirred for 12 h at room temperature. After the reaction completion, the reaction mixture was partitioned between water and diethyl ether. The organic layer was extracted, dried over MgSO<sub>4</sub>, and evaporated under reduced pressure to obtain the crude product, which was purified by silica gel column chromatography using hexanes.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 6.98 (2H, s), 6.90 (2H, s), 2.70 (4H, t, *J* = 8 Hz), 1.60 (4H, q, *J* = 8 Hz), 1.40–1.20 (36H, m), 0.88 (6H, t, *J* = 7 Hz). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 140.4, 135.1, 132.6, 131.6, 126.3, 110.6, 31.9, 30.5, 29.7, 29.6, 29.5, 29.4, 29.4, 29.3, 29.2, 22.7, 14.1. HRMS (EI) (*m/z*): (*M*)<sup>+</sup> calcd for C<sub>36</sub>H<sub>54</sub>Br<sub>2</sub>S<sub>3</sub> 740.1754; found, 740.1751.

5,5''-Dibromo-3,3''-dihexyl-2,2':5',2''-terthiophene-[all]-*S,S*-dioxide (**6a**) was made by oxidation of **5a** using a freshly prepared solution of HOF•CH<sub>3</sub>CN complex in 65% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.42 (1H, s), 6.96 (1H, s), 2.84 (2H, t, *J* = 8 Hz), 1.65–1.58 (2H, m), 1.45–1.38 (2H, m), 1.32–1.29 (4H, m), 0.90–0.87 (3H, m). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 144.4, 132.4, 131.3, 127.2, 125.1, 123.3, 32.1, 31.5, 29.2, 28.4, 22.6, 14.1. HRMS (ESI) (*m/z*): (*M*+Na)<sup>+</sup> calcd for C<sub>24</sub>H<sub>30</sub>Br<sub>2</sub>NaO<sub>6</sub>S<sub>3</sub> 690.9469; found, 690.9446.

5,5''-Dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene-[all]-*S,S*-dioxide (**6b**) was made by oxidation of **5b** using a freshly prepared solution of HOF•CH<sub>3</sub>CN complex in 60% yield.

<sup>1</sup>H NMR (400 MHz, CDCl<sub>3</sub>, ppm): δ 7.43 (1H, s), 6.96 (1H, s), 2.84 (2H, t, *J* = 8 Hz), 1.66–1.58 (2H, m), 1.43–1.38 (2H, m), 1.32–1.26 (16H, m), 0.88 (3H, t, *J* = 7 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 144.3, 132.4, 131.3, 127.2, 125.1, 123.3, 32.09, 32.07, 29.81, 29.79, 29.75, 29.6, 29.5, 29.4, 28.5, 22.8, 14.3. HRMS (ESI) (*m/z*): (*M*+Na)<sup>+</sup> calcd for C<sub>36</sub>H<sub>54</sub>Br<sub>2</sub>NaO<sub>6</sub>S<sub>3</sub> 859.1347; found, 859.1334.

3,3''',5,5'''-Tetrahexyl-2,2':5',2''':5''''-quaterthiophene (**8**) was obtained from quaterthiophene **7** in 75% yield. A solution of quaterthiophene **7** (3 g, 6 mmol) in 10 mL of dry THF was cooled to –78 °C, and a solution of *n*-BuLi (1.6 M in hexanes, 20 mmol) was added dropwise. The reaction mixture was stirred for 10 min at –78 °C, following by the addition of *t*-BuOK (24 mmol) in THF. The stirring was continued for 15 min at –78 °C, and then 1-iodohexane (13.2 mmol) was added. The reaction mixture was allowed to reach room temperature and stirred overnight, quenched by slow addition of water, and extracted with hexanes. The organic phase was dried with MgSO<sub>4</sub>, following by solvent removal under reduced pressure. The crude solid was purified by column chromatography.

<sup>1</sup>H NMR (500 MHz, CDCl<sub>3</sub>, ppm): δ 7.08 (1H, d, *J* = 4 Hz), 6.96 (1H, d, *J* = 4 Hz), 6.62 (1H, s), 2.77–2.69 (4H, m), 1.69–1.60 (4H, m), 1.39–1.30 (12H, m), 0.91–0.86 (6H, m). <sup>13</sup>C NMR (125 MHz, CDCl<sub>3</sub>, ppm): δ 144.6, 139.7, 136.5, 135.9, 127.8, 127.5, 126.0, 123.8, 34.9, 31.9, 31.8, 31.7, 30.8, 30.3, 29.5, 29.1, 25.5, 22.8, 14.32, 14.31. HRMS (EI) (*m/z*): (*M*)<sup>+</sup> calcd for C<sub>40</sub>H<sub>58</sub>S<sub>4</sub> 666.3421; found, 666.3419.

3,3''',5,5'''-Tetrahexyl-2,2':5',2''':5''''-quaterthiophene-[all]-*S,S*-dioxide (**9**) was made by the oxidation of **5b** using a freshly prepared solution of HOF•CH<sub>3</sub>CN complex in 40% yield.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, ppm): δ 7.43 (1H, d, *J* = 4 Hz), 7.30 (1H, d, *J* = 4 Hz), 6.47 (1H, s), 2.84 (2H, t, *J* = 8 Hz), 2.59 (2H, t, *J* = 7 Hz), 1.72–1.25 (16H, m), 0.90 (6H, t, *J* = 6 Hz). <sup>13</sup>C NMR (100 MHz, CDCl<sub>3</sub>, ppm): δ 148.0, 144.2, 133.5, 129.3, 127.1, 126.0, 125.1, 124.2, 32.0, 31.6, 31.5, 29.3, 28.9, 28.5, 26.7, 24.7, 22.6, 22.0, 14.2, 14.1. HRMS (ESI) (*m/z*): (*M*+Na)<sup>+</sup> calcd for C<sub>40</sub>H<sub>58</sub>Br<sub>2</sub>NaO<sub>8</sub>S<sub>4</sub> 817.2912; found, 817.2885.

**P1** was synthesized from 5,5'-dibromo-4,4'-dihexyl-2,2'-bithiophene-[all]-*S,S*-dioxide (**3a**) and 2,5-bistrimethylstannylthiophene (**10**) in 92% yield.

<sup>1</sup>H NMR (200 MHz, CDCl<sub>3</sub>, ppm): δ 7.81–7.71 (1H, m), 7.39–7.19 (1H, m), 2.76 (2H, broad s), 1.70–1.36 (8H, m), 0.91 (3H, broad s). GPC *M*<sub>n</sub> = 8.5K, *M*<sub>w</sub>/*M*<sub>n</sub> = 2.72.

**P2** was synthesized from 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene-[all]-*S,S*-dioxide (**3b**) and 2,5-bistrimethylstannylthiophene (**10**) in 90% yield.

<sup>1</sup>H NMR (400 MHz, CD<sub>2</sub>Cl<sub>2</sub>, ppm): δ 7.79–7.65 (1H, m), 7.40–7.30 (1H, m), 2.78 (2H, broad s), 1.73 (2H, broad s), 1.49–1.28 (18H, m), 0.88 (3H, broad s). GPC *M*<sub>n</sub> = 10.8K, *M*<sub>w</sub>/*M*<sub>n</sub> = 1.96.

**P3** was synthesized from 5,5''-dibromo-3,3''-didodecyl-2,2':5',2''-terthiophene-[all]-*S,S*-dioxide (**6b**) and 2,5-bistrimethylstannylthiophene (**10**) in 84% yield.

$^1\text{H}$  NMR (400 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.71–7.64 (1H, m), 7.48–7.42 (1H, m), 6.89–6.77 (1H, m), 2.92 (2H, broad s), 1.69–1.25 (17H, m), 0.90 (6H, broad s). GPC  $M_n = 5.7\text{K}$ ,  $M_w/M_n = 4.1$ .

**P4** was synthesized from 5,5'-dibromo-4,4'-didodecyl-2,2'-bithiophene (**2b**) and 2,5-bistrimethylstannylthiophene (**10**) in 95% yield.

$^1\text{H}$  NMR (200 MHz,  $\text{CDCl}_3$ , ppm):  $\delta$  7.09 (1H, broad s), 7.02 (1H, broad s), 2.82–2.75 (2H, m), 1.73–1.66 (2H, m), 1.45–1.27 (18H, m), 0.87 (3H, t,  $J = 6$  Hz). GPC  $M_n = 11.0\text{K}$ ,  $M_w/M_n = 1.38$ .

## CONCLUSIONS

We have introduced a new synthetic route for the preparation of soluble oligothiophenes-[all]-*S,S*-dioxides. Incorporation of hexyl and dodecyl groups into bi-, *tert*-, and quaterthiophene backbones leads to enhanced solubility, while the oligothiophene-[all]-*S,S*-dioxides also display a reduced energy gap with respect to the aromatic oligothiophene precursors. The solubility of these materials allows for their facile processability, thus, making them useful for various applications in organic-based electronic devices. The high solubility also allows them to be used as building blocks for the preparation of thiophene-based conjugated polymers containing bithiophene-*S,S*-dioxide units in the backbone. Incorporation of electron-withdrawing sulfones along the polymer backbone leads to the narrowing of the energy gap with the energies of both frontier orbitals in bithiophene-[all]-*S,S*-dioxide containing polymers being lower with respect to the aromatic polythiophene. This tendency is considerably stronger for the LUMO than for the HOMO, leading to materials with greater electron-accepting ability. The modularity of our approach can potentially allow the energy levels of polythiophenes to be controlled based on the number and position of the thiophene-*S,S*-dioxide units. Small molecule- and polymer-based devices, such as thin film transistors, based on oligothiophene-[all]-*S,S*-dioxides are currently under investigation.

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