

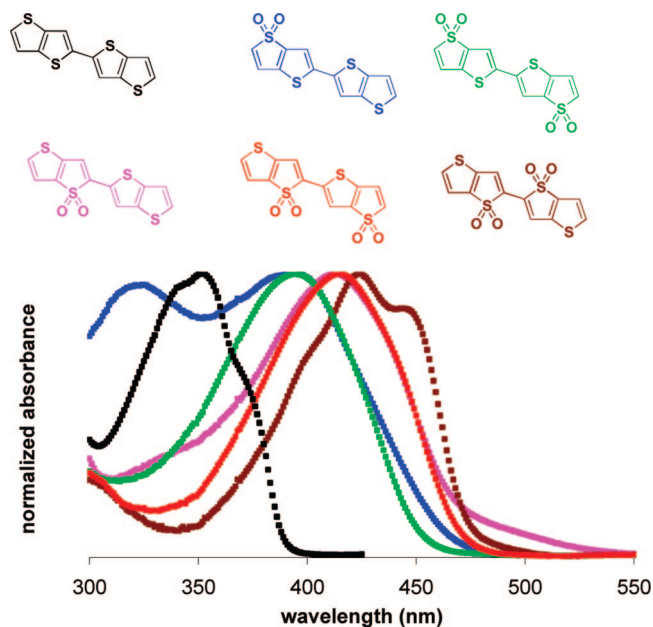
## Regiochemical Effects of Sulfur Oxidation on the Electronic and Solid-State Properties of Planarized Oligothiophenes Containing Thieno[3,2-*b*]thiophene Units

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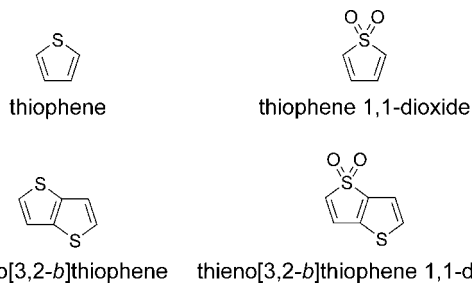
The effect of position and degree of sulfur oxidation on the fundamental properties of a series of planarized thieno[3,2-*b*]thiophene *S,S*-dioxides derivatives was studied. The optical data reveal a red shift in the longest wavelength of absorption relative to the nonoxidized analogues that is indicative of a reduced HOMO–LUMO gap. The position of oxidation rather than the extent of oxidation is the most critical factor in controlling electronic properties. Single-crystal analysis reveals that some of the oligothiophene *S,S*-dioxides studied present  $\pi$ – $\pi$  interactions which are completely absent in the nonoxidized analogue.

### Introduction

Organic semiconductors have generated considerable interest in both academia and industry due to their application in electronic devices such as organic thin film transistors (OTFT),<sup>1–4</sup> organic light emitting diodes (OLED),<sup>5,6</sup> and photovoltaic cells.<sup>7,8</sup> The majority of research on oligothiophene-based electronic devices has focused on p-type materials;<sup>3</sup> however,

n-type semiconductors are needed for the development of photovoltaic cells and the design of complementary circuits.<sup>9</sup> Different approaches have been explored to functionalize p-type oligothiophenes into n-type semiconductors. For example, the addition of electron-withdrawing groups, such as perfluoroalkyl and cyano groups, to the molecular backbone of oligothiophenes results in materials showing n-type semiconducting properties.<sup>10–13</sup> Another route toward the functionalization of oligothiophenes to materials that could potentially act as n-type transporters is the chemical transformation of the thienyl sulfur into the corresponding *S,S*-dioxide.<sup>14–21</sup> Selective oxidation of

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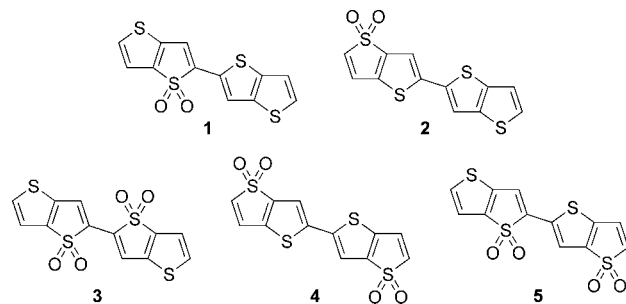


**FIGURE 1.** Chemical structures of thiophene, thiophene 1,1-dioxide, thieno[3,2-*b*]thiophene, and thieno[3,2-*b*]thiophene 1,1-dioxide.

one or more sulfur atoms in an oligothiophene dramatically affects the electronic properties; in particular, the electron delocalization decreases within the ring while it increases along the molecular backbone and the electron affinity of the molecule also increases. Because of these properties, this new class of oligothiophene *S,S*-dioxides has the potential to function as *n*-type semiconductors.

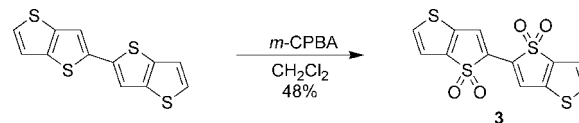
Nonfused ring oligothiophene *S,S*-dioxides have been previously studied with a primary focus on the exploration of optical and electrochemical properties as a function of the position and degree of sulfur oxidation. For example, a series of oligomers based on thiophene and thiophene 1,1-dioxide (Figure 1), where the position and degree of the oxidized moiety is varied as well as the molecular length, has been synthesized and characterized.<sup>14–17</sup> The regioselective insertion of thiophene 1,1-dioxide into the backbone of oligothiophenes allows the continuous modulation of the electronic and redox properties of these materials. This new class of oligothiophene *S,S*-dioxides shows increased electron delocalization and electron affinity with respect to the parent oligomers as evidenced by a red shift in the longest wavelength ( $\lambda_{\max}$ ) of absorption and a less negative reduction potential. This drastic change in the electronic properties can be attributed to breaking of the aromaticity of the thiophene ring, which is a result of the sulfur lone pair electrons being employed in the formation of the sulfur–oxygen bonds.<sup>16</sup>

The incorporation of fused-ring thieno[3,2-*b*]thiophene units into oligothiophenes imparts planarity to the system resulting



**FIGURE 2.** Chemical structures of a series of oligothiophene *S,S*-dioxides based on thieno[3,2-*b*]thiophene fused ring units.

### SCHEME 1. Synthesis of Compound 3



in better ordering in the solid-state relative to the nonfused oligomers.<sup>22–24</sup> However, oxidation of fused-ring oligothiophenes based on thieno[3,2-*b*]thiophene has yet to be explored, and combining the ring-fusion and sulfur oxidation methods represents an approach to understand the fundamental properties of a new class of materials that should show both increased electron delocalization and favorable solid-state ordering while also having the potential to act as *n*-type semiconductors. Moreover, partial oxidation of fused-ring thieno[3,2-*b*]thiophene results in a nonsymmetrical unit, thieno[3,2-*b*]thiophene *S,S*-dioxide, (Figure 1) which, in oligomers, gives rise to new regiochemical issues. Therefore, to investigate the regiochemical effect of sulfur oxidation on the optical and solid-state properties of partially planarized  $\alpha$ -linked oligomers, a series of 4-ring oligothiophenes based on thieno[3,2-*b*]thiophene was synthesized where the degree and position of the fused-ring oxidized moiety was varied (Figure 2).

### Results and Discussion

**Synthesis.** Capitalizing on the fact that thiophene rings with  $\alpha$ -substituents are generally more readily oxidized than those that are unsubstituted,<sup>17</sup> the synthesis of compound 1 can be envisioned by the direct and selective oxidation of the parent oligomer, the dimer of thieno[3,2-*b*]thiophene. This route presents the possibility of oxidation of more than one thienyl sulfur and the oxidized product may not be regiochemically pure. In fact, the direct oxidation of the dimer of thieno[3,2-*b*]thiophene produces compound 3 where the two sulfurs in the internal region of the molecule are oxidized (Scheme 1).

With this synthetic approach, the selective oxidation of just one thienyl sulfur is not readily achieved but the oxidized oligomer is regiochemically pure. However, building up the oxidized oligomer starting from the appropriate building blocks offers the advantage of obtaining the desired regioisomer. The oxidation of 2-bromothieno[3,2-*b*]thiophene with *m*-chloroperoxybenzoic acid (*m*-CPBA) results in the formation of 2-bromothieno[3,2-*b*]thiophene 1,1-dioxide (6), which is the appropriate building block for the synthesis of compound 1 (Scheme

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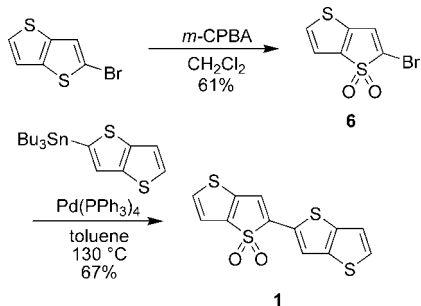
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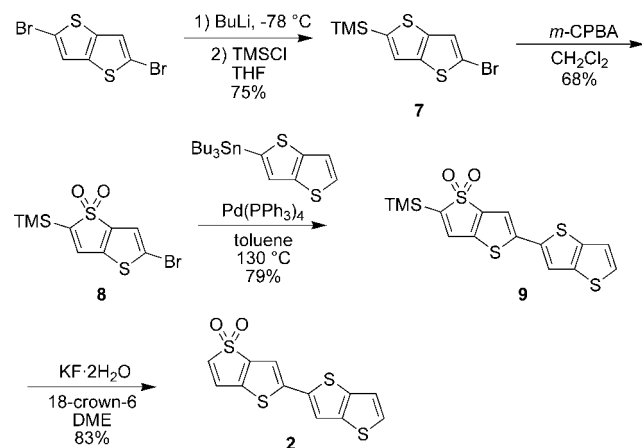
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## SCHEME 2. Synthesis of Compound 1



## SCHEME 3. Synthesis of Compound 2



2). The cross-coupling reaction of compound **6** and 2-(tributylstannyl)thieno[3,2-*b*]thiophene under Stille conditions affords oligomer **1** (Scheme 2).

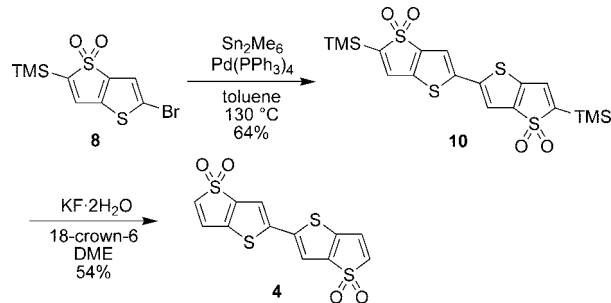
The regioisomer of **1**, compound **2**, was also obtained from a Stille cross-coupling reaction (Scheme 3). The challenge in this synthesis is to obtain a suitable thieno[3,2-*b*]thiophene precursor that upon oxidation produces the appropriate building block. The incorporation of a trimethylsilyl (TMS) group on the brominated thieno[3,2-*b*]thiophene unit changes the selectivity of the oxidation to the sulfur atom next to the TMS group as opposed to the sulfur atom adjacent to the bromine. This allows access to oligomers in which the oxidized sulfur atom is in the outer position of the molecule. Compound **8** was formed by the oxidation with *m*-CPBA of 5-bromo-2-(trimethylsilyl)thieno[3,2-*b*]thiophene (**7**), prepared by the lithium–halogen exchange of 2,5-dibromothieno[3,2-*b*]thiophene followed by the addition of trimethylsilyl chloride (TMSCl) (Scheme 3).

Attempts to remove the TMS group with acidic conditions (TFA in THF) were unsuccessful. In addition, protodesilylation of compound **9** with TBAF was found to cause decomposition of the oxidized oligomer. However, the TMS group in compound **9** was readily removed using KF·2H<sub>2</sub>O and 18-crown-6 in DME. Compound **4** was available through Stille-type homocoupling of compound **8**, followed by the desilylation of compound **10** (Scheme 4).

Compound **5**, the regioisomer of compounds **3** and **4**, was synthesized by direct oxidation of compound **2** with *m*-CPBA as shown in Scheme 5. This indicates that further oxidation of an oligomer carrying one oxidized sulfur occurs in the nonoxidized ring and selectively oxidizes the internal sulfur atom.

**Optical Properties.** The electronic properties of oligomers **1–5** were studied by UV–vis and fluorescence spectroscopies

## SCHEME 4. Synthesis of Compound 4



## SCHEME 5. Synthesis of Compound 5

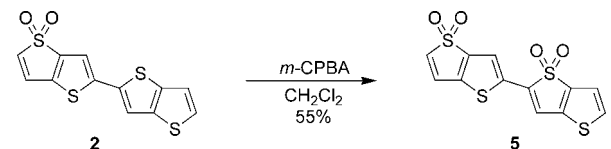


TABLE 1. Longest Wavelength of Absorption and Emission Maxima for a Series of Oligothiophene *S,S*-Dioxides and the Dimer of Thieno[3,2-*b*]thiophene (**11**)

compd	$\lambda_{\max}$ (nm)	
	absorption	emission
<b>11</b>	350	412
<b>2</b>	393	529
<b>4</b>	394	498
<b>1</b>	413	507
<b>5</b>	414	515
<b>3</b>	443	507

and compared to the dimer of thieno[3,2-*b*]thiophene (**11**); these data are listed in Table 1.

Inspection of Table 1 reveals that the oxidation of one or more thienyl sulfur atoms of the dimer of thieno[3,2-*b*]thiophene brings about a 43–93 nm red shift of the maximum wavelength of absorption depending on the number and position of sulfonyl moieties introduced (Figure 3).

For example, compound **1** in which the oxidized sulfur is in the internal region of the molecule has a bathochromic shift of 63 nm relative to the nonoxidized oligomer. Oxidation of two thienyl sulfur atoms in the internal region of the oligomer results in a 93 nm red shift of the  $\lambda_{\max}$  of absorption with respect to the nonoxidized counterpart. Thus, sulfur oxidation leads to a dramatic enhancement of the electron delocalization and to a decrease of the optical HOMO–LUMO gap. Comparing the addition of one and two sulfonyl units in compounds **1** and **3**, the first oxidation causes a red shift of the  $\lambda_{\max}$  of absorption of 63 nm, but the oxidation of an

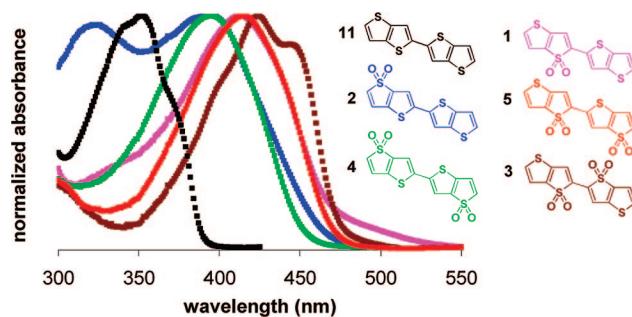
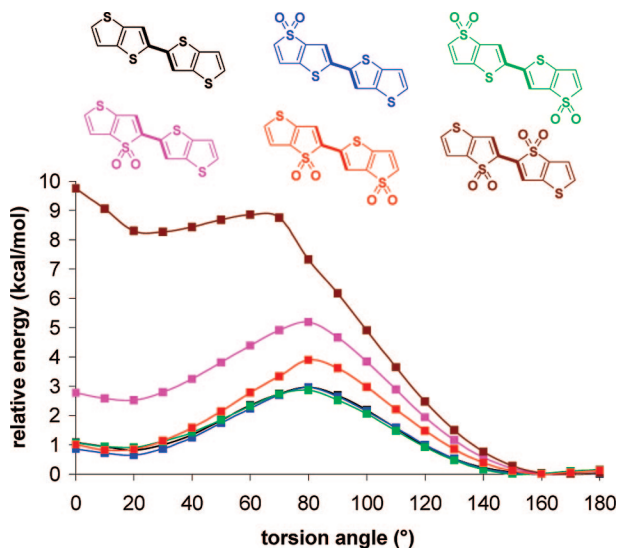


FIGURE 3. UV–vis absorption data for compounds **1–5** and reference compound **11**.

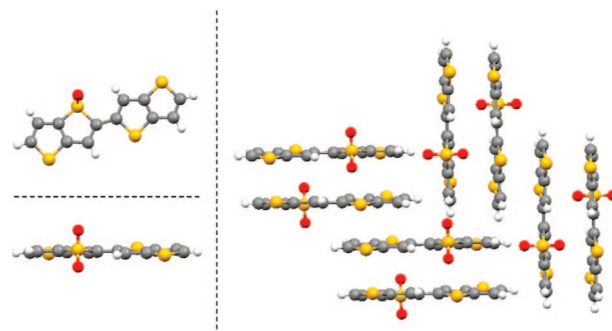


**FIGURE 4.** Calculated energy profile for compounds **1–5** and reference compound **11** at different torsion angles (C–C–C–C, shown in bold) going from a syn to an anti conformation.

additional sulfur leads to a smaller red shift of the  $\lambda_{\max}$  of absorption of 30 nm. From these data, it is clear that the oxidation of the second thienyl sulfur has a less dramatic effect on the optical properties and that the position of the oxidized sulfur also influences the electronic behavior. The position of the oxidized unit, rather than just the number of oxidized sulfurs, plays a major role in determining the optical properties. For example, regioisomers **1** and **2** display different  $\lambda_{\max}$  of absorption (413 and 393 nm, respectively) and emission (507 and 529 nm, respectively). Compound **1** where the oxidized moiety is in the internal region of the molecule has a longer  $\lambda_{\max}$  of absorption than compound **2** in which the oxidized sulfur atom is in the external region of the oligomer. A similar trend is observed for regioisomers **3** and **4**, demonstrating that the oxidation of the internal sulfur results in a more conjugated system with a reduced HOMO–LUMO gap. However, compound **5**, a regioisomer of **3** and **4**, has a  $\lambda_{\max}$  of absorption that lies between **3** and **4**. These data indicate that moving the sulfonyl moiety from the external regions to an internal position results in an increase in delocalization. In general, the position of the oxidized sulfur strongly influences the optical properties and the oxidation of the internal thienyl sulfurs has the more dramatic effect in the electronic properties. Similar trends have been observed for nonfused oligothiophene *S,S*-dioxides based on quaterthiophene and quinquethiophene.<sup>15,17</sup>

To further elucidate the effect of the degree and position of the oxidized sulfur on molecular conformation and thus the optical properties of these materials, computational studies were performed. DFT calculations (B3LYP/6-31G\*) of twenty different torsion angles rotating 180° around the single bond linkage between rings going from a syn to an anti conformation for compounds **1–5** and reference compound **11** were examined to determine their minimum energy geometry and the energy barrier for adopting a planar conformation (Figure 4).

Computations predict a nearly planar anti conformation for all studied compounds. However, a higher rotation barrier going from an anti to a syn conformation is observed for compounds in which the oxidized sulfurs are located in the internal region of the molecule. For example, compound **3** in which the two



**FIGURE 5.** Crystal structure diagram of compound **1** illustrating molecular conformation and packing motif.

internal thienyl sulfur are oxidized possess the highest rotation barrier. This can be attributed to steric interactions caused by the close proximity of the sulfonyl groups upon rotation from an anti to syn conformation. In general, the inclusion of the oxidized moieties onto different positions of the backbone of the molecule does not affect molecular planarity. Based on the optical and computational data, having the oxidized sulfur in the internal region of the oxidized oligomer has a larger effect on increasing the electron delocalization of the system and thus reducing the HOMO–LUMO gap. This can be attributed to the fact that oxidizing the internal sulfur atom breaks the aromaticity of the inner ring imparting a greater diene character to that region of the molecule which increases the electron communication between rings.

**Solid-State Packing.** To investigate the solid-state properties of this series of oligothiophene *S,S*-dioxides, specifically the role of intermolecular interactions on packing motif, single-crystal structures for **1–3** were determined. The structure of **1** reveals a nearly planar molecular conformation with a packing arrangement in which the two fused ring units adopt an anti conformation with a dihedral angle of 168°. The molecules exist as face-to-face  $\pi$ -stacked dimers that are arranged in slipped  $\pi$ -stacked columns with displacement along the long molecular axis (Figure 5). Face-to-face  $\pi$ -stacked dimers are separated by 3.58 Å, and these dimers are packed such that the interplanar spacing between thieno[3,2-*b*]thiophene moieties is 3.40 Å creating slipped  $\pi$  dimer pairs. Furthermore, short C–H···O contacts are present between adjacent slipped  $\pi$ -stacked columns ranging from 2.39 to 2.62 Å.<sup>25</sup> A close intermolecular C–H···S distance of 2.72 Å, a value considerably shorter than the sum of the van der Waals radii of sulfur and hydrogen (3.00 Å), is also observed.

A comparison of the crystal structure of **1** with its nonoxidized analogue, the dimer of thieno[3,2-*b*]thiophene, reveals a marked difference in solid-state packing; the former presents columns of slipped  $\pi$ -stacked dimers whereas the nonoxidized analog shows herringbone packing.<sup>23</sup> Differing from the packing motif of **1**, the crystal structure of **2** reveals a sandwich-herringbone packing motif consisting of edge-to-face  $\pi$ -stacked dimers separated by 3.47 Å (Figure 6). In addition, the two fused-ring units adopt a nearly planar anti conformation with a dihedral angle of 172°. Short intermolecular C–H···O distances ranging from 2.35 to 2.69 Å and an intermolecular C–H···S contact of 2.90 Å are also observed.

On the other hand, the oxidation of two internal thienyl sulfurs yields compound **3** and induces a significant change

(25) For determination of inter- and intramolecular distances, all carbon–hydrogen bond lengths were normalized to 1.083 Å.

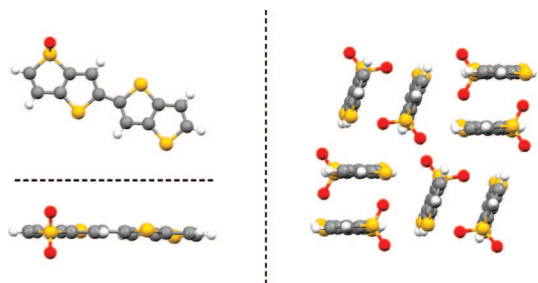


FIGURE 6. Crystal structure diagram of compound **2** illustrating molecular conformation and packing motif.

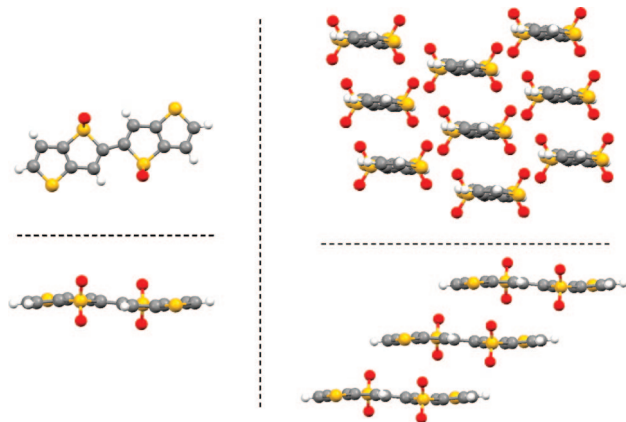


FIGURE 7. Crystal structure diagram of compound **3** illustrating molecular conformation and packing motif.

in both conformation and packing motif. Compound **3** adopts a curved conformation in the crystal and the molecules arrange in a similar fashion to  $\pi$ -stacked columns slipped along the long molecular axis. However, the distances between the mean planes of the molecule's rings range from 3.90 to 4.31 Å (Figure 7), indicating that no close  $\pi$ -interactions exist. Instead, the close contacts are between the sulfonyl oxygen in one molecule to the thienyl sulfurs on a neighboring molecule in an adjacent column (3.07 Å) and between the sulfonyl oxygen of one molecule to the  $\pi$ -system of an adjacent molecule along the column (3.03 Å) (Figure 7). The packing arrangement of compound **3** lacks of  $\pi$ - $\pi$  interactions which are observed for compounds **1** and **2** and this can be attributed to the fact that compound **3** has an additional sulfonyl group which precludes  $\pi$ -stacking, but allows for a dense structure with a variety of other close contacts.

## Conclusion

In summary, a series of 4-ring oligothiophene *S,S*-dioxides based on thieno[3,2-*b*]thiophene was synthesized. The optical data reveal a red shift in the longest wavelength of absorption relative to the nonoxidized analogs which is indicative of a reduced HOMO–LUMO gap and the tunability is more dependent on the position of oxidation rather than the extent of oxidation. In the solid-state, compounds **1** and **2** present  $\pi$ - $\pi$  interactions which are absent in the nonoxidized analogue. Therefore, combining sulfur oxidation and fused-ring approaches allows the tuning of the optical and solid-state properties, which is a powerful method for obtaining semiconducting materials with a variety of desirable attributes.

## Experimental Section

**General Methods.** THF, toluene, ether, and  $\text{CH}_2\text{Cl}_2$  were dried by passage through a column packed with activated alumina. UV–vis absorption spectra were recorded in  $\text{CH}_2\text{Cl}_2$  solution ( $<10^{-5}$  M). Emission spectra were recorded in  $\text{CH}_2\text{Cl}_2$  solution ( $<10^{-8}$  M). The excitation wavelength employed for each oligomer corresponds to the longest wavelength absorption peak (Table 1). Crystals of compounds **1–3** suitable for single-crystal X-ray diffraction were obtained upon slow evaporation from  $\text{CH}_2\text{Cl}_2$  solutions.

**General Thienyl Sulfur Oxidation Procedure A.** A solution of *m*-chloroperoxybenzoic acid (5.2 equiv) in  $\text{CH}_2\text{Cl}_2$  (0.07 M) was added dropwise to a solution of the thiophene-based compound (1 equiv) in  $\text{CH}_2\text{Cl}_2$  (0.1 M). After the solution was stirred overnight, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$  and washed with 1 M NaOH (3 $\times$ ), water, and brine. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$ , and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with  $\text{CH}_2\text{Cl}_2$ .

**General Coupling Procedure B.**  $\text{Pd}(\text{PPh}_3)_4$  (0.025 equiv per coupling) was added to a mixture of the stannylated thiophene-based compound (1.1 equiv) and the brominated thiophene-based compound (1 equiv) in toluene (0.1 M) under a  $\text{N}_2$  atmosphere. The solution was stirred overnight at 130 °C in a glass pressure vessel. The reaction mixture was cooled to rt and diluted with  $\text{CH}_2\text{Cl}_2$ , and the organic layer was washed with water (2 $\times$ ) and brine. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with  $\text{CH}_2\text{Cl}_2$ .

**General Desilylation Procedure C.** A solution of silylated thiophene-based compound (1 equiv) in DME (0.01 M) under a  $\text{N}_2$  atmosphere was added to a reaction flask containing  $\text{KF}\cdot 2\text{H}_2\text{O}$  (81 equiv) and 18-crown-6 ether (1.2 equiv). After being stirred for 1 h, the reaction mixture was diluted with  $\text{CH}_2\text{Cl}_2$ , filtered, and washed with water and brine. The organic layer was dried over anhydrous  $\text{Na}_2\text{SO}_4$  and the solvent removed under reduced pressure. The residue was purified by column chromatography on silica gel eluting with  $\text{CH}_2\text{Cl}_2$ .

**2-Bromothieno[3,2-*b*]thiophene 1,1-dioxide (6): Procedure A.** *m*-Chloroperoxybenzoic acid (5.46 g, 23.7 mmol) and 2-bromothieno[3,2-*b*]thiophene (1.00 g, 4.56 mmol): yield 0.699 g (61%); mp 151–152 °C;  $^1\text{H}$  NMR (500 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ ) 7.96 (d,  $J$  = 5.1 Hz, 1H), 7.89 (s, 1H), 7.59 (d,  $J$  = 5.1 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ ) 140.8, 135.8, 133.9, 125.9, 121.4, 120.5; IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ): 3118 (w), 3097 (w), 3064 (m), 1481 (w), 1432 (w), 1403 (w), 1351 (w), 1303 (vs), 1205 (s), 1168 (m), 1139 (vs), 1122 (s), 1108 (m), 883 (m), 875 (m), 811 (m), 742 (m), 640 (m), 621 (m), 609 (s), 553 (s), 536 (s), 482 (m); MS (EI, 70 eV)  $m/z$  (relative intensity) 251.9 (100,  $\text{M}^+$ ), 250.0 (55.3), 171.0 (38.6), 145.0 (18.2), 143.8 (15.9), 115.1 (33.4), 107.0 (15.0), 96.9 (15.9), 85.0 (15.3), 71.1 (40.9), 69.0 (29.0), 62.8 (58.0), 61.8 (32.5). Anal. Calcd for  $\text{C}_6\text{H}_3\text{BrO}_2\text{S}_2$ : C, 28.70, H, 1.20. Found: C, 28.60, H, 1.15.

**2,2'-Bi(thieno[3,2-*b*]thiophenyl) 1,1-Dioxide (1): Procedure B.**  $\text{Pd}(\text{PPh}_3)_4$  (29.0 mg, 0.0251 mmol), 2-(tributylstannyl)thieno[3,2-*b*]thiophene<sup>22</sup> (0.474 g, 1.10 mmol), and compound **6** (0.252 g, 1.00 mmol): yield 0.208 g (67%); mp 222–224 °C; UV–vis ( $\text{CH}_2\text{Cl}_2$ )  $\lambda_{\text{max}}$  (log  $\epsilon$ ) 413 (4.36) nm;  $^1\text{H}$  NMR (400 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ ) 7.89 (d,  $J$  = 5.0 Hz, 1H), 7.88 (s, 1H), 7.86 (d,  $J$  = 5.3 Hz, 1H), 7.74 (s, 1H), 7.59 (d,  $J$  = 5.0 Hz, 1H), 7.52 (d,  $J$  = 5.3 Hz, 1H);  $^{13}\text{C}$  NMR (100 MHz,  $\text{DMSO}-d_6$ ,  $\delta$ ) 141.6, 139.8, 139.7, 139.2, 136.9, 133.9, 132.0, 130.4, 120.3, 120.1, 120.0, 116.2; IR (KBr)  $\nu_{\text{max}}$  ( $\text{cm}^{-1}$ ) 3104 (w), 3076 (w), 1570 (m), 1489 (w), 1415 (m), 1354 (w), 1294 (vs), 1205 (m), 1196 (m), 1145 (s), 1124 (s), 936 (m), 800 (m), 696 (s), 615 (m), 571 (m), 514 (m), 493 (m); MS (EI, 70 eV)  $m/z$  (relative intensity) 312.0 (25.2), 311.0 (22.7), 310.0 (100,  $\text{M}^+$ ), 278.0 (12.0), 267.0 (10.9), 265.0 (28.2), 264.0 (11.1), 263.0 (11.9), 262.0 (57.3), 248.0 (13.2), 247.0 (11.7), 246.0 (33.7),

245.0 (14.1), 234.0 (23.3), 233.0 (12.8), 214.0 (20.8), 202.0 (18.1), 201.0 (40.4), 170.0 (12.2), 169.0 (13.5), 167.0 (37.8), 143.0 (17.7), 93.0 (14.2), 69.0 (31.0). Anal. Calcd for  $C_{12}H_6O_2S_4$ : C, 46.43, H, 1.95. Found: C, 46.13, H, 2.11.

**5-Bromo-2-(trimethylsilyl)thieno[3,2-*b*]thiophene (7).** BuLi (2.1 mL, 1.6 M in hexanes, 3.36 mmol) was added dropwise to a stirred solution of 2,5-dibromothieno[3,2-*b*]thiophene<sup>26</sup> (1.00 g, 3.36 mmol) in THF (150 mL) at  $-78\text{ }^\circ\text{C}$ , and the resulting mixture was stirred for a further 10 min. The anion was quenched by the addition of TMSCl (0.47 mL, 0.400 g, 3.36 mmol) at  $-78\text{ }^\circ\text{C}$ . The reaction mixture was then allowed to warm slowly to rt, diluted with hexanes (100 mL), and washed with water (200 mL) and brine (200 mL). The organic layer was dried over anhydrous  $Na_2SO_4$  and concentrated under reduced pressure. The resulting crude product was purified by column chromatography eluting with hexanes: yield 0.734 g (75%);  $^1H$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ ) 7.64 (s, 1H), 7.51 (s, 1H), 0.31 (s, 9H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ,  $\delta$ ) 142.4, 141.9, 140.6, 126.0, 122.6, 113.7,  $-0.38$ ; IR (neat)  $\nu_{max}$  ( $cm^{-1}$ ) 2954 (w), 1488 (w), 1442 (w), 1407 (w), 1326 (w), 1297 (w), 1280 (w), 1249 (m), 1170 (w), 1149 (w), 1008 (m), 958 (m), 838 (m), 756 (m), 698 (w), 640 (w); MS (EI, 70 eV)  $m/z$  (relative intensity) 292.9 (10.6), 291.8 (100,  $M^+$ ), 290.9 (15.2), 289.9 (79.6), 277.9 (11.8), 276.9 (64.6), 275.9 (11.4), 274.9 (71.2), 232.9 (10.9), 196.0 (61.3), 153.0 (12.4), 121.0 (12.5), 75.0 (29.4). Anal. Calcd for  $C_9H_{11}BrS_2Si$ : C, 37.11, H, 3.81. Found: C, 36.94, H, 3.51.

**5-Bromo-2-(trimethylsilyl)thieno[3,2-*b*]thiophene 1,1-Dioxide (8): Procedure A.** *m*-Chloroperoxybenzoic acid (2.05 g, 8.93 mmol) and compound **7** (0.500 g, 1.72 mmol): yield 0.379 g (68%); mp 126–127  $^\circ\text{C}$ ;  $^1H$  NMR (300 MHz, DMSO- $d_6$ ,  $\delta$ ) 7.78 (s, 1H), 7.60 (s, 1H), 0.31 (s, 9H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ,  $\delta$ ): 146.8, 141.5, 140.9, 132.9, 122.7, 120.3,  $-1.80$ ; IR (KBr)  $\nu_{max}$  ( $cm^{-1}$ ) 3089 (s), 2954 (m), 2896 (w), 1766 (w), 1689 (w), 1548 (m), 1537 (m), 1492 (m), 1411 (s), 1342 (vs), 1294 (vs), 1272 (vs), 1249 (s), 1182 (s), 1162 (s), 1135 (vs), 1105 (s), 991 (s), 960 (vs), 842 (vs), 761 (s), 700 (m), 630 (s), 609 (vs), 563 (vs), 553 (vs), 482 (vs); MS (EI, 70 eV)  $m/z$  (relative intensity) 323.8 (100,  $M^+$ ), 322.8 (19.4), 321.8 (60.7), 306.8 (11.4), 278.9 (81.6), 277.0 (12.9), 264.9 (12.1), 263.9 (18.2), 261.9 (20.2), 250.9 (16.8), 250.0 (50.6), 247.9 (17.7), 233.9 (16.9), 221.0 (21.4), 219.8 (11.9), 208.9 (10.3), 206.9 (39.2), 163.9 (12.2), 139.9 (20.3), 138.9 (51.4), 126.0 (36.3), 122.0 (12.5), 121.1 (23.8), 106.0 (18.5), 101.0 (20.5), 97.1 (10.3), 93.0 (27.3), 89.0 (13.2), 77.0 (23.6), 75.0 (72.8), 73.1 (45.8), 69.0 (40.5). Anal. Calcd for  $C_9H_{11}BrO_2S_2Si$ : C, 33.44, H, 3.43. Found: C, 33.23, H, 3.41.

**5-(Trimethylsilyl)-2,2'-bi(thieno[3,2-*b*]thiophenyl) 4,4-Dioxide (9): Procedure B.** Pd(PPh<sub>3</sub>)<sub>4</sub> (89.4 mg, 0.0773 mmol), 2-(tributylstannyl)thieno[3,2-*b*]thiophene (1.92 g, 4.48 mmol), and compound **8** (1.00 g, 3.09 mmol): yield 0.942 g (79%); mp 234–236  $^\circ\text{C}$ ; UV–vis ( $CH_2Cl_2$ )  $\lambda_{max}$  (log  $\epsilon$ ) 403 (3.94) nm;  $^1H$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ ) 7.89 (s, 1H), 7.81 (s, 1H), 7.76 (d,  $J = 5.2$ , 1H), 7.68 (s, 1H), 7.48 (d,  $J = 5.2$ , 1H), 0.33 (s, 9H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ,  $\delta$ ) 147.4, 145.4, 142.5, 139.5, 139.1, 138.8, 136.1, 133.4, 129.9, 120.1, 118.3, 115.9,  $-1.70$ ; IR (KBr)  $\nu_{max}$  ( $cm^{-1}$ ) 3103 (w), 3089 (w), 3079 (w), 2956 (w), 1538 (m), 1456 (w), 1371 (m), 1292 (vs), 1249 (s), 1191 (m), 1133 (vs), 979 (s), 894 (m), 844 (s), 819 (m), 759 (m), 717 (m), 632 (m), 611 (m), 549 (m), 482 (m); MS (EI, 70 eV)  $m/z$  (relative intensity) 384.0 (29.5), 383.0 (29.5), 382.0 (100,  $M^+$ ), 339.0 (13.8), 303.0 (20.7), 293.0 (31.1), 183.0 (8.8), 86.0 (9.0), 75.0 (10.1), 73.1 (25.5), 69.0 (13.4). Anal. Calcd for  $C_{15}H_{14}O_2S_4Si$ : C, 47.09, H, 3.69. Found: C, 47.13, H, 3.76.

**2,2'-Bi(thieno[3,2-*b*]thiophenyl) 4,4-Dioxide (2): Procedure C.** Compound **9** (0.902 g, 2.36 mmol), KF $\cdot$ 2H<sub>2</sub>O (18.1 g, 191 mmol), and 18-crown-6 (0.779 g, 2.95 mmol): yield 0.608 g (83%); mp 240–242  $^\circ\text{C}$ ; UV–vis ( $CH_2Cl_2$ ):  $\lambda_{max}$  (log  $\epsilon$ ) 3.93 (4.16) nm;  $^1H$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ ): 7.88 (s, 1H), 7.81 (s, 1H), 7.77 (d,  $J = 5.1$  Hz, 1H), 7.63 (d,  $J = 6.8$  Hz, 1H), 7.49 (d,  $J = 5.1$  Hz, 1H), 7.22 (d,  $J = 6.8$  Hz, 1H); IR (KBr)  $\nu_{max}$  ( $cm^{-1}$ ) 3120 (w), 3095 (m), 3076 (w), 3068 (w), 1525 (w), 1454 (w), 1411 (w), 1369

(m), 1303 (vs), 1182 (m), 1145 (s), 1135 (vs), 1052 (w), 871 (m), 810 (m), 792 (m), 705 (s), 605 (m), 520 (s); MS (EI, 70 eV)  $m/z$  (relative intensity) 312.1 (24.8), 311.1 (22.2), 310.1 (100,  $M^+$ ), 293.1 (15.9), 281.0 (16.2), 261.0 (13.9), 183.0 (4.4), 83.9 (11.6), 75.9 (11.8), 57.0 (13.4), 44.0 (17.4), 43.0 (10.6). Anal. Calcd for  $C_{12}H_6O_2S_4$ : C, 46.43, H, 1.95. Found: C, 46.09, H, 2.07.

**2,2'-Bi(thieno[3,2-*b*]thiophenyl) 1,1,1',1'-Tetraoxide (3): Procedure A.** *m*-Chloroperoxybenzoic acid (2.58 g, 11.2 mmol) and  $\alpha$ -bis(thieno[3,2-*b*]thiophene)<sup>22</sup> (0.200 g, 0.721 mmol): yield 0.118 g (48%); mp  $>350\text{ }^\circ\text{C}$ ; UV–vis ( $CH_2Cl_2$ )  $\lambda_{max}$  (log  $\epsilon$ ) 443 (4.21), 423 (4.27) nm;  $^1H$  NMR (400 MHz, DMSO- $d_6$ ,  $\delta$ ) 8.04 (d,  $J = 5.0$  Hz, 2H), 7.97 (s, 2H), 7.65 (d,  $J = 5.0$  Hz, 2H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ,  $\delta$ ) 141.5, 137.9, 137.1, 131.9, 121.2, 120.1; IR (KBr)  $\nu_{max}$  ( $cm^{-1}$ ) 3108 (m), 3077 (m), 1481 (w), 1409 (m), 1357 (m), 1307 (vs), 1272 (s), 1211 (m), 1176 (m), 1137 (vs), 1079 (w), 923 (m), 877 (w), 858 (w), 806 (m), 721 (s), 611 (m), 563 (m), 540 (s), 451 (m); MS (EI, 70 eV)  $m/z$  (relative intensity) 344.0 (11.0), 343.0 (8.8), 342.0 (100,  $M^+$ ), 170.1 (12.3), 169.1 (19.2), 145.0 (10.0), 143.0 (37.0), 85.9 (47.4), 83.9 (72.4), 69.0 (10.6). Anal. Calcd for  $C_{12}H_6O_4S_4$ : C, 42.09, H, 1.77. Found: C, 42.13, H, 1.90.

**5,5'-Bis-(trimethylsilyl)-2,2'-bi(thieno[3,2-*b*]thiophenyl) 4,4,4',4'-Tetraoxide (10): Procedure B.** Pd(PPh<sub>3</sub>)<sub>4</sub> (71.5 mg, 0.0619 mmol), hexamethylditin ( $Sn_2Me_6$ , 0.203 g, 0.619 mmol), and compound **8** (0.400 g, 1.24 mmol): yield 0.193 g (64%); mp 311–313  $^\circ\text{C}$ ; UV–vis ( $CH_2Cl_2$ )  $\lambda_{max}$  (log  $\epsilon$ ) 411 (4.03) nm;  $^1H$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ ) 7.95 (s, 2H), 7.71 (s, 2H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ,  $\delta$ ) 148.1, 143.2, 142.4, 140.7, 133.4, 117.4,  $-1.72$ ; IR (KBr)  $\nu_{max}$  ( $cm^{-1}$ ): 3081 (w), 2958 (w), 1538 (m), 1479 (w), 1429 (w), 1348 (w), 1297 (vs), 1251 (s), 1133 (vs), 977 (s), 937 (w), 918 (w), 844 (s), 761 (m), 702 (w), 638 (w), 613 (m), 565 (m), 547 (m), 480 (m); MS (EI, 70 eV)  $m/z$  (relative intensity) 489.0 (11.9), 488.0 (35.2), 487.0 (39.7), 486.0 (100,  $M^+$ ), 413.9 (22.5), 407.0 (12.7), 215.0 (24.2), 143.0 (14.4), 75.0 (20.7), 73.0 (63.5), 45.0 (20.0), 43.0 (11.5). Anal. Calcd for  $C_{18}H_{22}O_4S_4Si_2$ : C, 44.41, H, 4.56. Found: C, 44.15, H, 4.54.

**2,2'-Bi(thieno[3,2-*b*]thiophenyl) 4,4,4',4'-Tetraoxide (4): Procedure C.** Compound **10** (0.189 g, 0.388 mmol), KF $\cdot$ 2H<sub>2</sub>O (2.98 g, 31.4 mmol), and 18-crown-6 ether (0.128 g, 0.485 mmol): yield 71.1 mg (54%); mp  $>350\text{ }^\circ\text{C}$ ; UV–vis ( $CH_2Cl_2$ )  $\lambda_{max}$  (log  $\epsilon$ ) 394 (4.17) nm;  $^1H$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ ) 7.95 (s, 2H), 7.65 (d,  $J = 6.8$  Hz, 2H), 7.26 (d,  $J = 6.8$  Hz, 2H);  $^{13}C$  NMR (100 MHz, DMSO- $d_6$ ,  $\delta$ ) 142.5, 139.7, 139.1, 133.3, 126.8, 117.5; IR (KBr)  $\nu_{max}$  ( $cm^{-1}$ ) 3118 (w), 3083 (w), 3049 (w), 2956 (w), 2919 (w), 2850 (w), 1317 (s), 1299 (vs), 1184 (m), 1143 (w), 1056 (w), 921 (w), 879 (m), 810 (m), 717 (m), 709 (m), 615 (s), 520 (s), 441 (m); MS (EI, 70 eV)  $m/z$  (relative intensity) 343.0 (12.9), 342.0 (100,  $M^+$ ), 216.1 (8.16), 149.1 (7.18), 86.0 (28.3), 84.0 (40.8), 72.1 (10.1), 64.0 (10.0), 57.1 (14.0). Anal. Calcd for  $C_{12}H_6O_4S_4$ : C, 42.09, H, 1.77. Found: C, 42.33, H, 1.95.

**2,2'-Bi(thieno[3,2-*b*]thiophenyl) 1,1,4',4'-tetraoxide (5): Procedure A.** *m*-Chloroperoxybenzoic acid (0.417 g, 1.811 mmol) and compound **2** (0.108 g, 0.348 mmol): yield 65.5 mg (55%); mp  $>350\text{ }^\circ\text{C}$ ; UV–vis ( $CH_2Cl_2$ )  $\lambda_{max}$  (log  $\epsilon$ ) 414 nm;  $^1H$  NMR (500 MHz, DMSO- $d_6$ ,  $\delta$ ) 7.98 (d,  $J = 5.2$  Hz, 1H), 7.97 (s, 1H), 7.82 (s, 1H), 7.68 (d,  $J = 6.7$  Hz, 1H), 7.64 (d,  $J = 5.2$  Hz, 1H), 7.34 (d,  $J = 6.7$  Hz, 1H); IR (KBr)  $\nu_{max}$  ( $cm^{-1}$ ) 3109 (w), 3085 (w), 1365 (w), 1309 (vs), 1191 (m), 1149 (vs), 840 (w), 802 (w), 713 (w), 642 (w), 617 (m), 524 (m), 497 (w); MS (EI, 70 eV)  $m/z$  (relative intensity) 343.6 (17.9), 341.9 (100,  $M^+$ ), 276.9 (13.6), 274.9 (11.6), 149.0 (22.1), 143.0 (19.3), 139.0 (27.3), 127.1 (10.1), 125.1 (11.1), 123.1 (10.5), 113.1 (11.5), 111.1 (16.4), 109.1 (14.3), 105.1 (12.8), 100.0 (13.8), 97.1 (21.3), 95.1 (18.2), 91.1 (11.6), 85.9 (39.1), 85.1 (29.7), 84.1 (17.5), 83.1 (25.2), 82.0 (13.9), 81.1 (17.9), 77.0 (11.4), 73.0 (14.0), 71.1 (39.2), 70.1 (13.1), 69.1 (36.0), 69.0 (18.3), 67.1 (16.5), 66.0 (14.7). Anal. Calcd for  $C_{12}H_6O_4S_4$ : C, 42.09, H, 1.77. Found: C, 42.40, H, 1.76.

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**Supporting Information Available:** NMR spectra for compounds **1–10**, normalized emission spectra and computational

data for compounds **1–5** and **11**, and crystallographic data for compounds **1–3**. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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