

Oligothiophene-*S,S*-dioxides: a New Class of Thiophene-based Materials

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Currently, thiophene-based oligomers and polymers are a matter of intense research activity in view of their technological applications in electrical and optical devices.^{1–4} The efficiency of such devices is strictly related to the HOMO–LUMO energy gap of these materials, and a great amount of work has been done to functionalize oligo- and polythiophenes with a variety of α - and β -substituents as well as to incorporate nonaromatic moieties, with the aim of reducing the energy gap.^{1–5}

No attention, however, has been paid so far to the possibility of tuning the HOMO–LUMO energy gap of oligo- and polythiophenes by taking advantage of the hypervalent nature of the sulfur atom, which allows the functionalization of the thienyl sulfurs to be carried out. Nevertheless, stable thiophene 1,1-dioxides were described long ago^{6a} while more recent work has confirmed that stable thiophene 1,1-dioxides are easily obtained from α - and β -substituted thiophenes.^{6b–f} In addition, theoretical calculations have predicted a marked decrease

of the HOMO–LUMO energy gap in poly(thiophene 1,1-dioxide), due to modifications in the frontier orbital pattern.⁷

We report here that bissilylated oligothiophenes may be selectively oxidized at the thienyl sulfurs by *m*-chloroperbenzoic acid (*m*-CPBA) to afford stable *S,S*-dioxides having alternate aromatic and nonaromatic moieties. These compounds are characterized by enhanced electron delocalization, smaller optical gap, and greater electron affinity than the “fully aromatic” precursors.

The structure, reaction conditions, and λ_{\max} values of α,ω -bissilylated oligothiophenes *S,S*-dioxides and of their precursors (compounds **1–12**) are given in Table 1.

The synthesis of the precursor oligothiophenes was carried out according to standard methods.^{8–10} In this respect, it is only worth mentioning that the synthesis of bissilylated quaterthiophene through the coupling of the appropriate lithiated bithiophene with Fe(acac)₃ afforded a highly pure compound useful for the preparation of thin film field effect transistors.¹¹

The oxidation of thienyl sulfurs was accomplished in moderate to good yield by reacting the oligothiophene with variable amounts of *m*-CPBA in methylene chloride at room temperature, while the time required for oxidation to occur increased drastically upon increasing the length of the oligomer.

The oxidation of 2,5-bissilylthiophene was almost quantitative (95%) and relatively high oxidation yields were also obtained with the longer oligomers. Starting from 2,5'-bissilyl-2,2'-bithiophene, the oxidation afforded mixtures of mono- and bis-*S,S*-dioxides, which, however, were easily separated by silica gel chromatography or by crystallization from methanol (see the Experimental Section). In the case of quaterthiophene, regioisomers of both the mono- and the bis-*S,S*-dioxides were also obtained. The mono-sulfones **10** and **11** were separated by silica gel chromatography. However, from the mixture of bis-sulfones it was possible to separate, in the pure form, only bis-sulfone **12**, which was the main regioisomer formed (nearly 80%). Experimental evidence from ¹H NMR and mass spectroscopy indicates that both the other two possible regioisomeric bis-*S,S*-dioxides of **9** are formed, although in much smaller amounts.

The results relative to the oxidation of terthiophene **6** and quaterthiophene **9** show that the terminal thienyl rings are more easily oxidized than the inner ones. In the case of terthiophene, no oxidation of the inner ring occurs. In the case of quaterthiophene the mono-dioxide having one terminal SO₂ group (**10**, 25% yield) was formed in an amount 3 times greater than its regioisomeric counterpart with an internal SO₂ (**11**, 10% yield), while the symmetric bis-sulfone **12** with two terminal

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

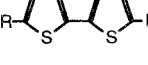
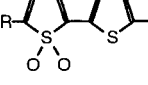
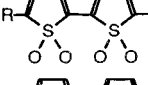
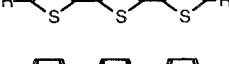
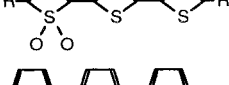
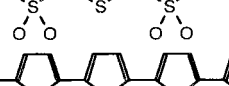

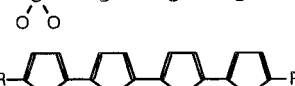
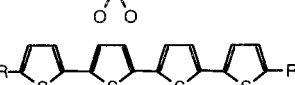
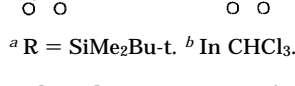
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Table 1. Structure, Yields, and λ_{\max} Values of α,ω -Bissilylated Oligothiophene *S,S*-Dioxides and of Their Precursors

Product ^a	$\lambda_{\max}(\text{nm})^b$	Yield (%)	Item
	248	41	1
	314	95	2
	326	34	3
	390	31	4
	406	47	5
	368	29	6
	480	17	7
	460	54	8
	412	76	9
	470	25	10
	480	8	11
	494	10	12

^a R = SiMe₂Bu-t. ^b In CHCl₃.

S,S-dioxide groups was formed in an amount 4 times greater than the mixture of the other two possible isomers. Application of different oxidation methodologies with longer oligothiophenes is under way and will be reported in due course.

Inspection of Table 1 reveals that the formation of the *S,S*-dioxide moiety brings about a 60–110 nm red shift of the maximum wavelength absorption with respect to that of the starting oligothiophenes. Thus, dearomatization of one or more thienyl rings leads to a marked enhancement of the electron delocalization and to the decrease of the optical HOMO–LUMO energy gap.

Cyclic voltammetry shows that the LUMO of oligothiophene *S,S*-dioxides lies at lower energies than those of the precursor oligothiophenes, indicating a much greater electron affinity of the former with respect to the latter substrates. As an example, the oxidation and reduction potentials (vs Ag/AgCl) of silyl-capped bithiophene **3** and of the corresponding mono- and bis-

Table 2. Reduction ($E_{\text{ip,c}}$) and Oxidation ($E_{\text{ip,a}}$) Potentials^a of 5,5'-Bis(dimethyl-*tert*-butylsilyl)-2,2'-bithiophene (3**) and of the Corresponding Mono- (**4**) and Bis- (**5**) *S,S*-Dioxides and Calculated^b HOMO and LUMO Energies (E_{HOMO} , E_{LUMO}) for 2,2'-Bithiophene and the Corresponding Mono- and Bis-*S,S*-dioxides**

compd	$E_{\text{ip,c}}$	$E_{\text{ip,a}}$	E_{LUMO}	E_{HOMO}
3	< -2.1	1.29		
4	-1.34	1.6		
5	-0.85	1.84		
B ^c			2.27	-7.89
BO ^c			0.94	-8.61
BOO ^c			0.16	-9.43

^a V vs Ag/AgCl, by cyclic voltammetry at 200 mV/s in CH₃CN/ Et₄NBF₄ (0.1 M). ^b HF/3-21G* ab initio calculations,¹⁵ eV. ^c B = 2,2'-bithiophene. BO = 2,2'-bithiophene 1,1-dioxide. BOO = 2,2'-bithiophene 1,1',1'-bis-dioxide.

dioxides **4** and **5** are given in Table 2. It can be seen that the oxidation potential of the bis-dioxide is increased by 0.6 V while the reduction potential is shifted toward less negative values by at least 1.2 V with respect to the precursor bithiophene. Both **4** and **5** are more easily reduced than oxidized with respect to **3** and to what is generally observed for oligo- and polythiophenes.³ Electrochemical results of compounds **1–12** have been obtained and will be published elsewhere in detail.¹²

The HF/3-21G* ab initio calculated HOMO and LUMO energies of 2,2'-bithiophene and of the corresponding mono- and bis-*S,S*-dioxides are also given in Table 2. The results of the calculations indicate a trend of variation of the HOMO and LUMO energies which parallels the variation of the oxidation and reduction potentials of the bissilylated counterparts **3–5**. Indeed, according to the calculations, the oxidation of bithiophene to the corresponding dioxides progressively decreases the energy of both the HOMO and the LUMO, but that of the latter more than that of the former. This also leads to a decrease of the HOMO–LUMO energy gap, in agreement with the red shift of the maximum wavelength absorption measured for **4** and **5** with respect to **3**. Contrary to what has been reported for poly(thiophene 1,1-dioxide),⁷ we found that the frontier orbitals of bithiophene *S,S*-dioxides remain of the π, π^* type. The results of calculations will also be reported in a paper to follow and discussed in detail.

In conclusion, we have synthesized, for the first time, oligothiophene *S,S*-dioxides, a new class of thiophene-based materials with high electron affinity, increased electron delocalization, and decreased HOMO–LUMO energy gap. The transformation of one or more thienyl sulfurs into the corresponding sulfones allows for the tuning of the redox properties of oligothiophenes and enhances their potential for use in sensors¹³ and in electrooptical devices.¹⁴ In addition, it is worth noting

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that oligothiophene *S,S*-dioxides are also precursors for a large number of organic substrates.^{6b-e}

Experimental Section

General Procedures. BuLi (2.5 M in hexane) and *t*-BuMe₂-SnCl were purchased from Aldrich. 2,2'-Bithiophene was purchased from Lancaster. 2,2':5,2''-Terthiophene was obtained by Grignard coupling as described in ref 8b. All solvents used in reactions and chromatographies were dried by standard procedures. Flash chromatographies were carried out using silica gel (230–400 mesh ASTM) and analytical thin layer chromatography (TLCs) using 0.2 mm silica gel plates (Merk). The visualization in TLC was accomplished by UV light.

5,5'-Bis(dimethyl-*tert*-butylsilyl)-2,2'-bithiophene (3). To a solution of 2.43 g (0.015 mol) of 2,2'-bithiophene in 20 mL of dry THF was added dropwise 12 mL (0.03 mol) of 2.5 N *n*-butyllithium in hexane at room temperature. After 1 h, a solution of 4.42 g (0.03 mol) of dimethyl-*tert*-butylsilyl chloride in 20 mL of THF was added dropwise. The reaction mixture was allowed to stir at rt overnight. Then water was added, the aqueous layer was extracted twice with ether, and the combined organic phases were dried over MgSO₄ and evaporated. After vacuum distillation, 0.84 g of 5-(dimethyl-*tert*-butylsilyl)-2,2'-bithiophene was recovered as a green solid, mp 45–46 °C (20% yield). The undistilled residue was crystallized from methanol and 2.01 g of 5,5'-bis(dimethyl-*tert*-butylsilyl)-2,2'-bithiophene (**3**) was obtained as a green solid, mp 118 °C (34% yield). MS: *m/e* 394 (M⁺). λ_{max} (CHCl₃): 326 nm. ¹H NMR (200 MHz, CDCl₃, ppm): 7.25 (d, *J* = 3.4 Hz, 2 H), 7.13 (d, *J* = 3.4 Hz, 2 H), 0.95 (s, 18 H), 0.30 (s, 12 H). ¹³C NMR (50 MHz, CDCl₃, ppm): 142.7, 136.9, 135.9, 124.9, 26.4, 17.2. Anal. Calcd For C₂₀H₃₄S₂Si₂: C, 61.16; H, 8.72. Found: C, 60.95; H, 8.89.

5-(Dimethyl-*tert*-butylsilyl)-2,2'-bithiophene. MS: *m/e* 280 (M⁺). λ_{max} (CHCl₃): 310 nm. ¹H NMR (200 MHz, CDCl₃, ppm): 7.29 (d, *J* = 3.4 Hz, 1 H), 7.23 (m, 2 H), 7.19 (d, *J* = 3.4 Hz, 1 H), 7.04 (m, 1 H), 0.98 (s, 9 H), 0.31 (s, 6 H). ¹³C NMR (50 MHz, CDCl₃, ppm): 142.6, 137.4, 136.7, 135.8, 124.8, 124.3, 123.7, 26.3, 16.9. Anal. Calcd for C₁₄H₂₀S₂Si: C, 59.94; H, 7.19. Found: C, 60.07; H, 7.42.

Oxidation of 5,5'-Bis(dimethyl-*tert*-butylsilyl)-2,2'-bithiophene (3). To a solution of 0.3 g (0.76 mmol) of **3** in 20 mL of methylene chloride was added stepwise 0.875 g (3 mmol) of *m*-chloroperbenzoic acid (*m*-CPBA, 60%) at room temperature. The solution was stirred for about 12 h at rt. Then the mixture was quenched with a saturated solution of NaHCO₃ and extracted with CH₂Cl₂, and the organic phase was separated, dried over MgSO₂, and evaporated. The residue was treated with 5 mL of methanol and the insoluble precipitate separated. After recrystallization from pentane, 0.162 g of bis-sulfone **5** was recovered (47% yield) as a yellow solid, mp 226 °C. The residue obtained after removal of methanol was recrystallized from pentane to afford 0.1 g (31% yield) of mono-sulfone **4** as a yellow solid, mp 137 °C.

4. MS: *m/e* 426 (M⁺). λ_{max} (CHCl₃): 390 nm. ¹H NMR (200 MHz, CDCl₃, ppm): 7.68 (d, *J* = 3.6 Hz, 1 H), 7.25 (d, *J* = 3.6 Hz, 1 H), 6.96 (d, *J* = 4.5 Hz, 1 H), 6.62 (d, *J* = 4.5 Hz, 1 H), 1.00 (s, 9 H), 0.92 (s, 9H), 0.34 (s, 6 H), 0.30 (s, 6 H). ¹³C NMR (50 MHz, CDCl₃, ppm): 142.8, 142.6, 140.9, 138.8, 136.5, 134.6, 129.8, 117.3, 26.34, 26.31, 16.7, 16.8. Anal. Calcd for C₂₀H₃₄O₂S₂Si₂: C, 59.94; H, 7.19. Found: C, 60.07; H, 7.42.

5. MS: *m/e* 458 (M⁺). λ_{max} (CHCl₃): 406 nm. ¹H NMR (200 MHz, CDCl₃, ppm): 7.12 (d, *J* = 4.3 Hz, 2 H), 7.06 (d, *J* = 4.3 Hz, 2 H), 0.99 (s, 18 H), 0.34 (s, 12H). ¹³C NMR (50 MHz, CDCl₃, ppm): 146.8, 138.5, 133.6, 124.4, 26.3, 17.4. Anal. Calcd for C₂₀H₃₄O₄S₂Si₂: C, 52.58; H, 7.50. Found: C, 52.16; H, 7.38.

5,5''-Bis(dimethyl-*tert*-butylsilyl)-2,2':5,2''-terthiophene (6). To a solution of 1.2 g (4.8 mmol) of 2,2':5,2''-terthiophene in 10 mL of dry THF was added dropwise 3.85 mL (9.6 mmol) of *n*-BuLi in hexane. After 1 h, a solution of 1.45 g (9.6 mmol) of dimethyl-*tert*-butylsilyl chloride in 10 mL of THF

was added. The reaction mixture was allowed to stir at rt overnight. Then water was added, the aqueous layer was extracted twice with ether, and the combined organic phases were dried over MgSO₄ and evaporated. The residue was treated with methanol at refluxing temperature for about 5 min. After filtration the fraction soluble in methanol afforded 0.46 g of 5-(dimethyl-*tert*-butylsilyl)-2,2':5,2''-terthiophene (26% yield) as a green solid, mp 82 °C. The fraction insoluble in methanol afforded 0.68 g of 5,5''-bis(dimethyl-*tert*-butylsilyl)-2,2':5,2''-terthiophene (**6**) (29% yield) as a yellow solid, mp 115–116 °C. MS: *m/e* 476 (M⁺). λ_{max} (CHCl₃): 368 nm. ¹H NMR (200 MHz, CDCl₃, ppm): 7.23 (d, *J* = 3.5 Hz, 2 H), 7.14 (d, *J* = 3.5 Hz, 2 H), 7.09 (s, 2 H), 0.94 (s, 18 H), 0.30 (s, 12 H). ¹³C NMR (50 MHz, CDCl₃, ppm): 142.4, 137.1, 136.4, 136.0, 124.8, 124.4, 26.4, 17.0. Anal. Calcd For C₂₄H₃₆S₃Si₂: C, 60.44; H, 7.61. Found: C, 60.29; H, 7.54.

Oxidation of 5,5''-Bis(dimethyl-*tert*-butylsilyl)-2,2':5,2''-terthiophene (6). To a solution of 0.42 g (0.88 mmol) of **6** in 30 mL of methylene chloride was added stepwise 1.52 g (5.3 mmol) of *m*-CPBA (60%) at room temperature. The solution was stirred for about 48 h at rt. Then the mixture was quenched with a saturated solution of NaHCO₃ and extracted with CH₂-Cl₂, and the organic phase was separated, dried over MgSO₂, and evaporated. The residue was chromatographed on silica gel using cyclohexane:ethyl acetate (6:1) as the eluent. Mono-sulfone **7** (0.078 g, 17% yield) was recovered as an orange solid, mp 158 °C. Bis-sulfone **8** (0.255 g, 54% yield) was recovered as an orange solid, mp 206–207 °C.

7. MS: *m/e* 508 (M⁺). λ_{max} (CHCl₃): 480 nm. ¹H NMR (200 MHz, CDCl₃, ppm): 7.55 (d, *J* = 4.0 Hz, 1 H), 7.30 (d, *J* = 3.5 Hz, 1 H), 7.21 (d, *J* = 4.0 Hz, 1 H), 7.16 (d, *J* = 3.5 Hz, 1 H), 6.98 (d, *J* = 4.6 Hz, 1 H), 6.56 (d, *J* = 4.6 Hz, 1 H), 1.02 (s, 9 H), 0.95 (s, 9H), 0.35 (s, 6 H), 0.31 (s, 6 H). ¹³C NMR (50 MHz, CDCl₃, ppm): 146.5, 145.0, 138.9, 138.7, 136.7, 134.0, 133.9, 130.1, 129.2, 126.4, 122.0, 118.4, 26.3, 17.4, 17.0. Anal. Calcd for C₂₄H₃₆O₂S₃Si₂: C, 56.64; H, 7.13. Found: C, 56.32; H, 7.12.

8. MS: *m/e* 540 (M⁺). λ_{max} (CHCl₃): 460 nm. ¹H NMR (200 MHz, CDCl₃, ppm): 7.61 (d, *J* = 4.6 Hz, 2 H), 6.98 (d, *J* = 4.6 Hz, 2 H), 1.00 (s, 18 H), 0.34 (s, 12H). ¹³C NMR (50 MHz, CDCl₃, ppm): 144.5, 140.2, 138.3, 132.4, 130.1, 119.3, 26.3, 17.3. Anal. Calcd for C₂₄H₃₆O₄S₃Si₂: C, 53.29; H, 6.71. Found: C, 53.17; H, 6.56.

5,5'''-Bis(dimethyl-*tert*-butylsilyl)-2,2':5,2''':5,2''-quaterthiophene (9). To a solution of 1.26 g (4.5 mmol) of 5-(dimethyl-*tert*-butylsilyl)-2,2'-bithiophene in 20 mL of dry THF were added dropwise 1.8 mL (4.5 mmol) of *n*-BuLi in hexane. After 1 h, the reaction mixture was cooled to –60 °C and 1.6 g (4.5 mmol) of Fe(acac)₃ were added stepwise. Then the solution was allowed to warm to rt, 35 mL of 3M HCl were added, the mixture was extracted with CH₂Cl₂, the organic layer washed with brine, dried over MgSO₄ and evaporated. After evaporation the residue was washed with ethyl ether and 0.95 g (76% yield) of **9** as a green solid, mp 163–164 °C were recovered. MS: *m/e* 558 (M⁺). λ_{max} (CHCl₃): 412 nm. ¹H NMR (200 MHz, CDCl₃, ppm): 7.23 (d, *J* = 3.4 Hz, 2 H), 7.14 (d, *J* = 3.4 Hz, 2 H), 7.09 (d, *J* = 3.6 Hz, 2 H), 7.07 (d, *J* = 3.6 Hz, 2H), 0.95 (s, 18 H), 0.31 (s, 12 H). ¹³C NMR (50 MHz, CDCl₃, ppm): 142.3, 137.3, 136.5, 136.1, 136.0, 124.9, 124.5, 124.3, 25.4, 16.9. Anal. Calcd For C₂₈H₃₈S₄Si₂: C, 60.16; H, 6.85. Found: C, 59.70; H, 6.99.

Oxidation of 5,5'''-bis(dimethyl-*tert*-butylsilyl)-2,2':5,2''':5,2''-quaterthiophene (9). To a solution of 0.19 g (0.34 mmol) of **9** in 20 mL of methylene chloride were added stepwise 0.29 g (1.02 mmol) of *m*-CPBA (60%) at room temperature. The solution was stirred one week at rt. Then the mixture was quenched with a saturated solution of NaHCO₃, extracted with CH₂Cl₂, the organic phase separated, dried over MgSO₂ and evaporated. The residue was chromatographed on silicagel using first a cyclohexane:ethyl acetate 6:1 mixture and then a cyclohexane:ethyl acetate 4:1 as the eluent. The first fraction recovered (0.072 g, 36% yield) contained mono sulfones **10** and **11** in the ratio 3:1. The latter fraction (0.032 g, 15% yield) contained 80% (by ¹H NMR) of bis-sulfone **12**. Pure **12** (0.021 g, 10% yield) was obtained as a red solid, mp 249–250 °C following crystallization from acetone. The regioisomeric mono-sulfones **10** (0.051 g, 25% yield, red solid, mp 182–183 °C) and **11** (0.016 g, 8% yield, red solid, mp 179–180 °C) were separated by silicagel chromatography using hexane:methylene chloride

3:1 as the eluent. **10.** MS: m/e 590 (M^+). λ_{\max} (CHCl_3): 470 nm. ^1H NMR (200 MHz, CDCl_3 , ppm): 7.55 (d, $J = 3.9$ Hz, 1 H), 7.26 (d, $J = 3.4$ Hz, 1 H), 7.17 (d, $J = 4.0$ Hz, 1 H), 7.14 (d, $J = 3.8$ Hz, 1 H), 7.13 (d, $J = 3.7$ Hz, 1 H), 7.12 (d, $J = 3.6$ Hz, 1 H), 6.98 (d, $J = 4.5$ Hz, 1 H), 6.56 (d, $J = 4.5$ Hz, 1 H), 1.01 (s, 9 H), 0.94 (s, 9H), 0.34 (s, 6 H), 0.31 (s, 6 H). ^{13}C NMR (50 MHz, CDCl_3 , ppm): 142.6, 141.7, 140.4, 138.9, 138.0, 137.9, 136.0, 134.8, 130.3, 128.5, 128.1, 125.8, 125.3, 124.8, 124.6, 116.5, 26.3, 26.2, 17.3, 17.0. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_2\text{S}_4\text{Si}_2$: C, 56.9; H, 6.48. Found: C, 56.71; H, 6.51.

11. MS: m/e 590 (M^+). λ_{\max} (CHCl_3): 480 nm. ^1H NMR (200 MHz, CDCl_3 , ppm): 7.68 (d, $J = 3.0$ Hz, 1 H), 7.54 (d, $J = 4.0$ Hz, 1 H), 7.30 (d, $J = 3.6$ Hz, 1 H), 7.21 (d, $J = 4.0$ Hz, 1 H), 7.16 (d, $J = 3.0$ Hz, 1 H), 7.13 (d, $J = 3.7$ Hz, 1 H), 6.80 (d, $J = 5.0$ Hz, 1 H), 6.71 (d, $J = 5.0$ Hz, 1 H), 1.01 (s, 9 H), 0.94 (s, 9H), 0.34 (s, 6 H), 0.31 (s, 6 H). ^{13}C NMR (50 MHz, CDCl_3 , ppm): 142.2, 141.4, 140.3, 139.1, 136.5, 136.1, 135.6, 135.5, 134.5, 130.4, 129.0, 128.5, 126.1, 125.1, 118.8, 117.8, 26.3, 17.0. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_2\text{S}_4\text{Si}_2$: C, 56.9; H, 6.48. Found: C, 56.9; H, 6.46.

12. MS: m/e 622 (M^+). λ_{\max} (CHCl_3): 494 nm. ^1H NMR (200 MHz, CDCl_3 , ppm): 7.56 (d, $J = 4.0$ Hz, 2 H), 7.24 (d, $J = 4.0$

Hz, 2 H), 6.98 (d, $J = 4.0$ Hz, 2 H), 6.60 (d, $J = 4.5$ Hz, 2H), 1.01 (s, 18 H), 0.32 (s, 12H). ^{13}C NMR (50 MHz, CDCl_3 , ppm): 143.3, 140.1, 138.7, 130.2, 130.0, 127.8, 126.3, 117.5, 26.0, 17.0. Anal. Calcd for $\text{C}_{28}\text{H}_{38}\text{O}_4\text{S}_4\text{Si}_2$: C, 53.98; H, 6.15. Found: C, 53.81; H, 6.16.

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Supporting Information Available: Fully optimized geometries and energies of 2,2'-bithiophene and of the corresponding mono- and bis-*S,S*-dioxides (3 pages). This material is contained in libraries on microfiche, immediately follows this article in the microfilm version of the journal, and can be ordered from the ACS; see and current masthead page for ordering information.

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