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all-S,S-Dioxygenated Star Oligothiophenes

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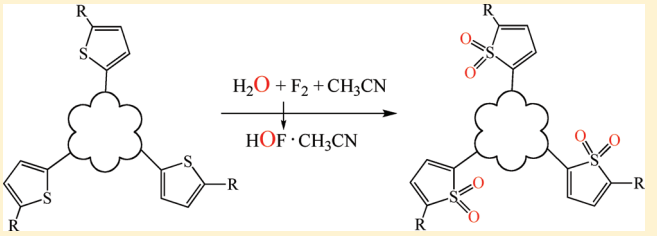
Supporting Information

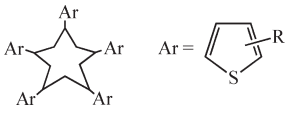
ABSTRACT: Star-shaped oligothiophenes are promising materials for applications in the organic electronics field. For the first time, a range of star-oligothiophenes was oxidized to the corresponding *all-S,S*-dioxides by using the HOF·CH_3CN complex. These materials exhibit considerable thermal stability and red-shift absorptions in the UV/vis relative to the parent compounds.



Oligothiophenes are widely utilized as building blocks in the preparation of materials for use as organic semiconductors.[1] This is due to their excellent electronic properties and other features such as chemical resistance and relative ease of synthesis. As a result, there are many classes of oligothiophenes that serve in applications such as organic field-effect transistors (OFET),[2] organic light emitting diodes (OLEDs),[3] and much more.[4]

A theoretical study predicted that by replacing all sulfur atoms of polythiophenes with sulfone groups, the HOMO−LUMO gap would be significantly reduced[5]—a very desirable feature. None of the orthodox oxidizing agents, however, was able to convert all sulfur atoms in various types of oligothiophenes to the corresponding sulfones.[6] We began to change the situation by employing the HOF·CH_3CN complex, and indeed, the HOMO−LUMO gap of the conjugated *all-S,S*-dioxides narrowed considerably.[7]

Recently, star-shaped oligothiophenes (SOTs) have received considerable attention, not only because of their aesthetic appeal. This family constitutes branched oligothiophenes, which are promising materials for applications such as active layers in multifunctional organic devices.[8] These multi-dimensional cross-conjugated materials have come to the forefront, both as monomers in cross-linked semiconducting polymers[9] and as components of conjugated dendrimers.[10]



Despite the understandable desire to check the properties of the potential *all-S,S*-dioxide star-shaped oligothiophenes, it has never been accomplished simply because none of the relevant material was known. A few experiments we have conducted with per-acids and dimethyl dioxirane revealed the reason. None of the SOTs could be transformed into the *all-S,S*-dioxo derivative by *m*-CPBA or by DMDO even after prolonged reaction times.

The acetonitrile complex of the hypofluorous acid, easily prepared from diluted fluorine and aqueous acetonitrile,[11] derives its oxygen transfer ability from the highly electrophilic oxygen atom. It was instrumental in quite a few successful difficult transformations, including oxygenation of aromatic rings,[12] fast Bayer−Villiger rearrangements validating Bayer's original proposed mechanism,[13] converting azides, amines, and vicinal diamines into the corresponding nitro[14] and dinitro[15] derivatives, epoxidation of electron-deficient olefins,[16] and formation of various *N*-oxides,[17] including the synthesis of the then elusive 1,10-phenanthroline *N,N′*-dioxide.[18] This oxygen transfer agent was also used for the oxidation of electron-deficient sulfides to hard-to-get sulfones[19] including glycosyl sulfones,[20] episulfones[21], and many other first or difficult transformations.[22]

The above, and the fact that SOTs could not be oxygenated with traditional oxygen-transfer agents, prompted us to explore the possibilities of reacting this family of oligothiophenes with the HOF·CH_3CN complex.

Both the synthetic challenge and HOMO−LUMO gap reduction met with success. We report here a general method for the preparation of *all-S,S*-dioxide star-shaped oligothiophenes using the HOF·CH_3CN complex.

Tris(5-bromo-2-thienyl)methane (**1**),[23] with its three thiophene rings attached to a central methane unit, was reacted at 0 °C with 8 molar equiv of HOF·CH_3CN. Within 5 min, the novel tris(5-bromo-2-thienyl 1,1-dioxide)methane (**2**) was formed in 82% yield (Scheme 1). No partly oxidized or other byproduct, usually associated with long reaction times and high temperatures, condition characteristic to common oxidant, was observed. It should be mentioned that reactions with HOF·CH_3CN and sulfides always produce sulfones rather than sulfoxides, unless special conditions are employed (see ref 19).

Similarly, the star-shaped oligothiophene **3a**,[24] in which three thiophene units are placed around a central benzene ring, was reacted with 8 molar equiv of HOF·CH_3CN for 2 min, affording the previously unknown 1,3,5-tris(5-methyl-2-thienyl 1,1-dioxide)benzene (**4a**) in 85% yield. In order to determine whether the

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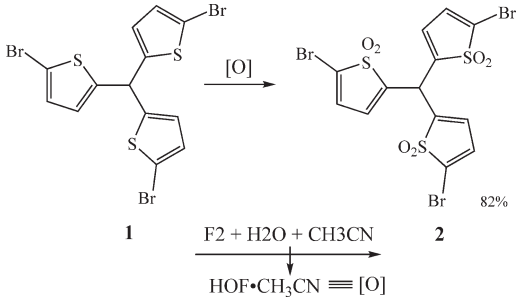
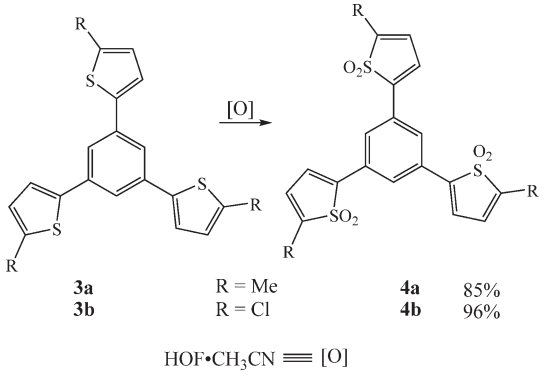
Scheme 1. Star Oligothiophene with a Central Methane Unit



Scheme 2. Star Oligothiophene with a Central Benzene Unit

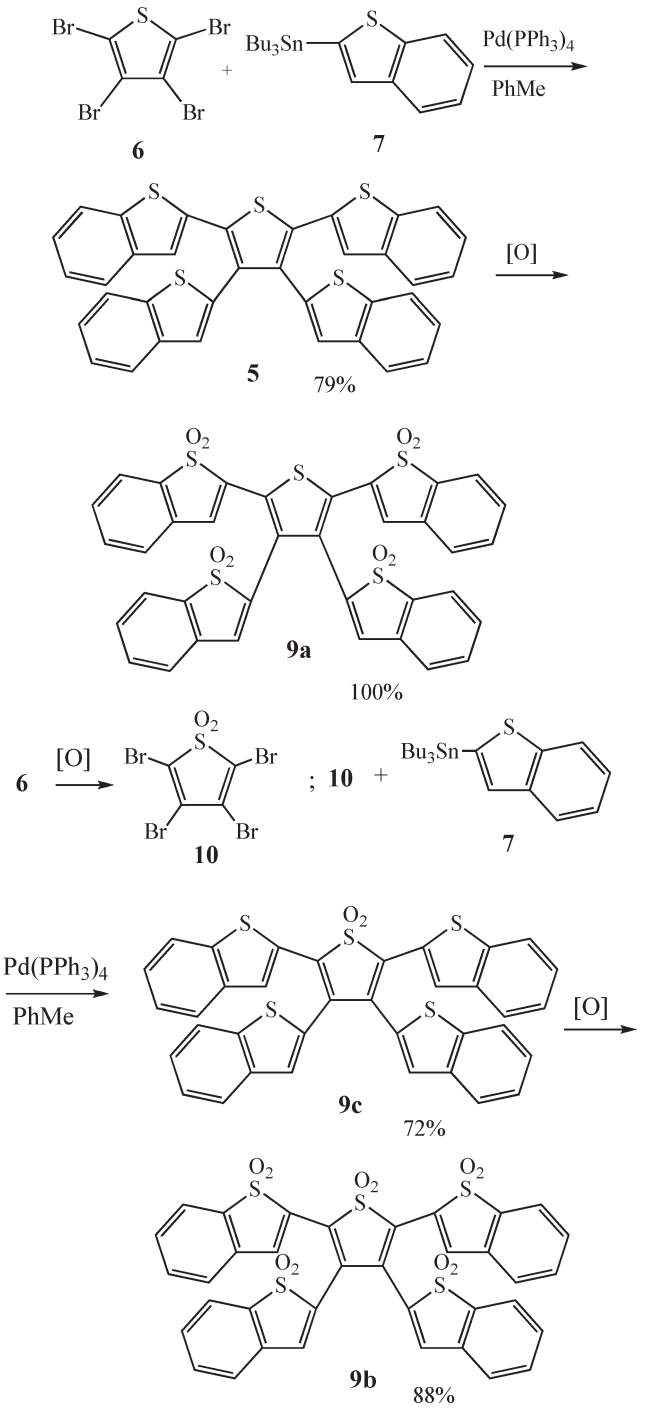


electron-donating methyl groups have something to do with the ease of the electrophilic oxygenation through increasing basicity at the sulfur atoms, we replaced all three methyls at the 5,5′,5″ positions with three electron-withdrawing chlorine atoms and reacted 1,3,5-tris(5-chloro-2-thienyl)benzene[24] (**3b**) with HOF·CH_3CN. This change did not have any negative effect on the reaction, and 1,3,5-tris(5-chloro-2-thienyl-1,1-dioxide)benzene **4b** was obtained after 5 min in 96% yield (Scheme 2).

A more complicated star-thiophene system constituted of five thiophene rings with four of them surrounding a central thiophene unit. We synthesized the previously unknown 2,3,4,5-tetakis(2-benzothienyl)thiophene (**5**) by reacting tetrabromothiophene (**6**)[25] with 2-tributylstannylbenzo[*b*]thiophene (**7**)[26] under the Stille cross-coupling reaction conditions. Reacting this crowded molecule with 12 equiv of HOF·CH_3CN gave the symmetrical octaoxide **9a** as a sole product in practically quantitative yield. Any attempt to fully oxidize **5** to its decaoxide derivative **9b** by adding an excess of HOF·CH_3CN was unsuccessful. Two factors contributed to the inertness of **9a**. The first is due to the formation of four benzothiophene−sulfone groups reducing the nucleophilic character of the central sulfur atom to the extent of preventing an additional electrophilic oxygen being transferred to it. The second factor is a considerable sterical hindrance which the four peripheral benzo-*S*,*S*-dioxothiophene units impose on the central ring. An indirect approach had to be adopted starting with the central ring.

In the past, we have prepared tetrabromothiophene 1,1-dioxide (**10**) from the tetrabromo parent compound **6**.[27] This derivative which contains the sulfonyl moiety was then reacted with 2-tributylstannylbenzo[*b*]thiophene **7**, under the Stille cross-coupling conditions, to form in 72% yield the star-thiophene with

Scheme 3. Star Oligothiophene with a Central Thiophene Unit



already oxidized central ring **9c**. Next, the monodioxo **9c** was submitted to oxygenation with 12 equiv of HOF·CH_3CN, forming at last the desired decaoxide **9b** in 88% yield and which is the single molecule (not part of a polymer) with the most thiophene *S*,*S*-dioxide units (Scheme 3).

Two physical properties are characteristic to the oxygenated star-thiophenes. The first is their thermal stability as evident from their melting points which, in most cases, are above 300 °C.[7b] The second is their electronic properties as deduced from their

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Table 1. Absorption λ_{max} (in nm) and HOMO−LUMO Energy Gap (ΔE_g,[a] in eV) in Solution[b]

compd	λ_{max} (ΔE_g)	$\Delta\Delta E_g$[c]
1	215 (5.77)	
2	325 (3.81)	1.95
3a	302 (4.11)	
4a	337 (3.68)	0.43
3b	303 (4.09)	
4b	347 (3.57)	0.52
5	374 (3.32)	
9a	369 (3.36)	−0.04[d]
9b	415 (2.98)	0.33[d]
9b	415 (2.98)	−0.33[e]
9c	467 (2.65)	0.66[d]

[a] $\Delta E_g = hc/\lambda$. [b] CH_2Cl_2 solution. [c] $\Delta\Delta E_g = \Delta E_g$(nonoxygenated compd) − ΔE_g(oxygenated compd). [d] Compared to **5**. [e] Compared to **9c**.

UV−vis spectra. Table 1 lists the maximum wavelength absorption (λ_{max}), the HOMO−LUMO energy gap (ΔE_g), and the difference of the HOMO−LUMO energy gap between the *S,S*-dioxo and the oxygen-free compounds ($\Delta\Delta E_g$). Table 1 reveals that the per-oxygenation of these cross-conjugated compounds resulted in considerable red-shift of the maximum wavelength absorption (λ_{max}). This indicates that very desirable lowering of the HOMO−LUMO energy gap ($\Delta\Delta E_g$) has taken place.

The red-shifted absorbances, however, are different for each class of materials. Oxygenation of the least conjugated **1** has the most dramatic effect, a red shift of 110 nm (1.95 eV). Transferring the cross-conjugated compounds **3** to **4** caused a red-shift of only 35−45 nm (0.43−0.52 eV). With compounds sprung from star-thiophene **5** the trend is more complicated. The oxygenation of the central ring to its corresponding SO_2 derivative **9c** causes the strongest reduction of the HOMO−LUMO energy gap (93 nm, 0.66 eV), while oxygenation of the peripheral sulfur atoms alone (**5** to **9a**) resulted in a slight hypsochromic shift. Similarly, the last step toward full oxygenation (**9c** to the all-SO_2 **9b**) resulted in somewhat blue-shifted absorbances, probably due to the molecule's deviation from planarity, which decreases the π-orbital overlap.

In conclusion, it was shown that a variety of nonlinear, cross-conjugated SOTs, could be effectively oxygenated using the HOF·CH_3CN complex with high yields and under mild conditions. It seems that no other oxygen transfer agent can achieve this goal. The oxygenation turns the compounds thermally more stable and reduces the HOMO−LUMO energy gap. While the reaction requires working with fluorine, it is much less complicated than many may think. One can dilute the commercial fluorine on the spot[17] or purchase premixed fluorine/nitrogen mixtures. The reactions were carried out in regular glass vessels. We have never had any problems working with this element.

EXPERIMENTAL SECTION

General Experimental Procedures. MS spectra were measured under MALDI conditions. UV spectra were recorded in CH_2Cl_2. ^1H NMR and ^{13}C NMR were obtained at 400 and 100 MHz, respectively, with $CDCl_3$ (for compounds **4a**, **5**, **9a**, and **9c**), acetone-d_6 (for compounds **2** and **4b**), and DMSO-d_6 (for compound **9b**) as solvents and Me_4Si as an internal standard. In the ^{1}HNMR spectra of **2**, **4b**, and **9b**, signals at 2.96 and 3.33 ppm originate from water in acetone-d_6 and DMSO-d_6 solvents, respectively. These peaks disappear upon addition of D_2O.

General Procedure for Working with Fluorine. Fluorine is a strong oxidant and a corrosive material. It should be used only with an appropriate vacuum line.[17] For the occasional user, however, various premixed mixtures of F_2 in inert gases are commercially available, thereby simplifying the process. Unreacted fluorine should be captured by a simple trap containing a base such as soda lime located at the outlet of the glass reactor. If elementary precautions are taken, the work with fluorine is simple, and we have never experienced difficulties working with it.

General Procedure for Producing HOF·CH_3CN. A mixture of 20% F_2 in nitrogen was used throughout this work. The gas mixture was prepared in a secondary container prior to the reaction and passed at a rate of about 400 mL per minute through a cold (−15 °C) mixture of 30 mL of CH_3CN and 3 mL of H_2O in a regular glass reactor. 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 0.5−0.6 mol/L.

General Procedure A. *Working with HOF·CH_3CN.* An SOT derivative was dissolved in CH_2Cl_2, and the mixture was cooled to 0 °C. The solution with the oxidizing agent was then added in one portion to the reaction vessel. The reaction was stopped after a few minutes, and the excess of HOF·CH_3CN was quenched with saturated sodium bicarbonate. The mixture was then poured into water and extracted with CH_2Cl_2, the organic layer dried over $MgSO_4$, and the solvent evaporated. The crude product was usually purified by recrystallization.

General Procedure B. *Stille-Type Cross-Coupling.* Tetrabromothiophene or tetrabromothiophene 1,1-dioxide, 2-tributylstannylbenzo[*b*]thiophene, and $Pd(PPh_3)_4$ were dissolved in dry toluene. The mixture was degassed for 20 min and refluxed under nitrogen. The solvent was washed with water, dried over $MgSO_4$, and removed by rotary evaporation. The crude product was purified by vacuum flash chromatography followed by recrystallization.

Tris(5-bromo-2-thienyl 1,1-dioxide)methane (2). Compound **2** was prepared from **1**[23] (580 mg, 1.16 mmol) as described in general procedure A, using 8 equiv of the oxidizing agent for 5 min. The product was recrystallized from acetone/hexane. A greenish solid (570 mg, 82%) was obtained: mp > 300 °C; λ_{max} 325 nm; ^1H NMR (acetone-d_6) 5.22 (1H, d, J = 1.4 Hz), 7.30 (3H, dd, J_1 = 5.1 Hz, J_2 = 1.4 Hz), 7.39 (3H, d, J = 5.1 Hz); ^{13}C NMR 31.0, 122.0, 128.9, 132.0, 136.3. Anal. Calcd for $C_{13}H_7O_6S_3Br_3$: C, 26.24; H, 1.19; S, 16.16; Br, 40.28. Found: C, 26.19; H, 1.16; S, 15.70; Br, 40.67.

1,3,5-Tris(5-methyl-2-thienyl 1,1-dioxide)benzene (4a). Compound **4a** was prepared from **3a**[24] (190 mg, 0.52 mmol) as described in general procedure A using 8 equiv of the oxidizing agent for 2 min. The product was recrystallized from acetone/hexane. An off-white solid (205 mg, 85%) was obtained: mp > 300 °C; λ_{max} 337 nm; ^1H NMR ($CDCl_3$) 2.23 (9H, s), 6.54 (3H, m), 7.08 (3H, d, J = 4.4 Hz), 8.03 (3H, s); ^{13}C NMR 10.3, 123.4, 124.1, 125.1, 130.1, 139.9, 142.2. Anal. Calcd for $C_{21}H_{18}O_6S_3$: C, 54.53; H, 3.92; S, 20.80. Found: C, 53.98; H, 3.80; S, 20.24.

1,3,5-Tris(5-chloro-2-thienyl 1,1-dioxide)benzene (4b). Compound **4b** was prepared from **3b**[24] (404 mg, 0.94 mmol) as described in general procedure A using 8 equiv of the oxidizing agent for 5 min. The product was recrystallized from acetone/hexane. An off-white solid (472 mg, 96%) was obtained: mp > 300 °C; λ_{max} 347 nm; ^1H NMR (acetone-d_6) 7.31 (3H, d, J = 5.3 Hz), 7.66 (3H, d, J = 5.3 Hz) 8.22 (3H, s); ^{13}C NMR (acetone-d_6) 125.5, 125.7, 125.8, 130.4, 133.5, 138.8; HRMS m/z calcd for $C_{18}H_9O_6S_3Cl_3Na$ 544.8525 (M + Na), found 544.8528. Anal. Calcd for $C_{18}H_9O_6S_3Cl_3$: C, 41.27; H, 1.73; S, 18.36. Found: C, 40.90; H, 1.65; S, 18.00.

2,3,4,5-Tetakis(2-benzothienyl)thiophene (5). Compound **5** was prepared from the reaction of **6**[25] (1.175 gr, 2.94 mmol) and **7**[26] (8.09 gr, 19.11 mmol) in 45 mL of dry toluene in the presence of $Pd(PPh_3)_4$ (220 mg, 6.5%) as described in general procedure B. The mixture was refluxed over nitrogen overnight. The product was chromatographed and

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recrystallized from benzene/methanol. A yellow solid (1.425 gr, 79%) was obtained: mp = 286 °C; λ_{max} 268, 302, 374 nm; ^{1}H NMR ($CDCl_3$) 7.66−7.55 (6H, m), 7.44 (2H, s), 7.25−7.35 (12H, m); ^{13}C NMR 122.8, 123.0, 124.0, 124.5, 124.7, 124.8, 125.1, 125.3, 125.6, 127.5, 135.7, 136.3, 140.0, 142.0; HRMS *m*/*z* calcd for $C_{36}H_{20}S_5$ 612.0169 (M), found 612.0161. Anal. Calcd for $C_{36}H_{20}S_5$: C, 70.55; H, 3.29; S, 26.16. Found: C, 70.81; H, 3.30; S, 26.19.

2,3,4,5-Tetakis(2-benzothienyl 1,1-dioxide)thiophene (9a). Compound **9a** was prepared from **5** (182 mg, 0.297 mmol) as described in general procedure A, using 12 equiv of the oxidizing agent for 10 min. The product was recrystallized from chloroform/hexane. A yellow solid (220 mg, 100%) was obtained: mp blackens at 259 °C; λ_{max} 321, 369 nm; ^{1}H NMR ($CDCl_3$) 7.33−7.79 (20H, m); ^{13}C NMR 122.3, 122.6, 126.9, 127.1, 131.1, 131.2, 131.4, 131.6, 132.0, 133.5, 135.5, 134.5, 134.6, 135.5, 135.6, 135.7, 137.1; HRMS *m*/*z* calcd for $C_{36}H_{20}O_8S_5Na$ 762.9659 (M + Na), found 762.9628. Anal. Calcd for $C_{36}H_{20}O_8S_5$: C, 58.36; H, 2.72. Found: C, 57.81; H, 2.53.

2,3,4,5-Tetakis(2-benzothienyl)thiophene 1,1-Dioxide (9c). Compound **9c** was prepared from the reaction of **10**[27] (1.42 gr, 3.3 mmol) and **7**[27] (9.08 gr, 21.45 mmol) in 50 mL of dry toluene in the presence of $Pd(PPh_3)_4$ (240 mg, 6.5%) as described in general procedure B. The mixture was refluxed over nitrogen for 5 h. The product was chromatographed and recrystallized from toluene/methanol, but we were not able to get an analytical sample. A red solid (1.524 gr, 72%) was obtained: mp > 300 °C; λ_{max} 467 nm; ^{1}H NMR ($CDCl_3$) 7.31−7.38 (8H, m), 7.47 (2H, s), 7.58 (2H, d, *J* = 7.8 Hz), 7.75−7.80 (4H, m), 7.87 (2H, d, *J* = 7.8 Hz), 8.19 (2H, s). ^{13}C NMR 122.7, 123.3, 125.4, 125.7, 125.8, 126.1, 127.4, 129.0, 129.2, 129.5, 131.0, 131.8, 134.9, 139.4, 139.7, 141.7, 142.7; HRMS *m*/*z* calcd for $C_{36}H_{20}O_2S_5$ 644.0067 (M), found 644.0046.

2,3,4,5-Tetakis(2-benzothienyl 1,1-dioxide)thiophene 1,1-Dioxide (9b). Compound **9b** was prepared from **9c** (120 mg, 0.186 mmol) as described in general procedure A using 12 equiv of the oxidizing agent for 10 min. The product was recrystallized from chloroform/hexane. An orange solid (127 mg, 88%) was obtained: mp > 300 °C; λ_{max} 309, 415 nm; ^{1}H NMR (DMSO-d_6) 7.56−7.94 (18H, m), 8.395 (2H, s). Solubility was too low to measure the ^{13}C NMR spectrum. Anal. Calcd for $C_{36}H_{20}O_{10}S_5$: C, 55.95; H, 2.61. Found: C, 56.32; H, 2.44.

■ ASSOCIATED CONTENT

Supporting Information. ^{1}H NMR and ^{13}C NMR spectra for all new compounds. This material is available free of charge via the Internet at http://pubs.acs.org.

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