

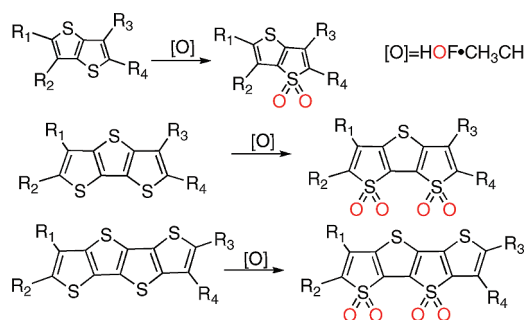
Synthesis of Oxygenated Fused Oligothiophenes with $\text{HO}\cdot\text{F}\cdot\text{CH}_3\text{CN}$

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For the first time a range of fused oligothiophenes was oxidized with use of the $\text{HO}\cdot\text{F}\cdot\text{CH}_3\text{CN}$ complex by transferring one or more sulfur atoms to sulfonyl groups under very mild conditions. These materials exhibit considerable red-shift absorptions in the UV/visible relative to the parent compounds. Their highly interesting photoluminescence properties and molecular packing in the solid state are also reported.

Introduction

Over the past decade, conjugated and fused oligothiophenes have received great attention due to their electrical and optical properties, frequently expressed in such applications as field effect transistors (FET),¹ light emitting diodes (LED),² and solar cells.³ About 20 years ago a theoretical study predicted that by attaching two oxygen atoms to each sulfur atom of these oligothiophenes, namely replacing the sulfur atoms with sulfone groups, the HOMO–LUMO gap would be significantly reduced⁴—a very desirable feature. None of the orthodox oxidizing agents, however, were able to convert all sulfur atoms in oligothiophenes to the corresponding sulfones.⁵ The only exception was the $\text{HO}\cdot\text{F}\cdot\text{CH}_3\text{CN}$ complex and indeed the

HOMO–LUMO gap of the conjugated [all]-*S,S*-dioxo-polythiophene narrowed considerably.⁶

The acetonitrile complex of the hypofluorous acid, easily prepared from diluted fluorine⁷ and aqueous acetonitrile, was developed by us some years ago.⁸ It derives its oxygen transfer ability from the highly electrophilic oxygen atom and this remarkable reactivity is instrumental in the success of a series of difficult transformations, including oxygenating aromatic rings,⁹ converting azides, amines, and vicinal diamines into the corresponding nitro¹⁰ and dinitro¹¹ derivatives, the epoxidation of electron-deficient olefins,¹² and the formation of various *N*-oxides from pyridine rings.¹³ The synthesis of 1,10-phenanthroline *N,N'*-dioxide is especially noteworthy since this compound eluded chemists for many decades.¹⁴

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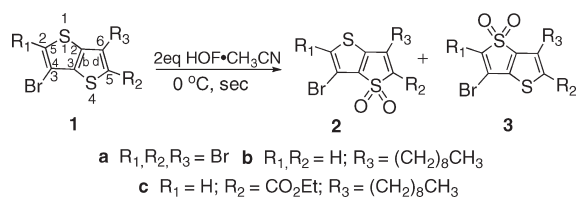
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SCHEME 1. Oxygenation of Thienothiophene



This oxygen transfer agent was also used for the oxidation of sulfides to hard-to-get sulfones including glycosyl sulfones¹⁵ and episulfones¹⁶ and many other initial or difficult transformations.¹⁷ These and especially the reaction of oxidizing polythiophenes into the corresponding [all]-SO₂ derivatives prompted us to explore the possibilities of making some fused oligothiophene *S,S*-dioxides (OTDOs) which, as mentioned above, are promising candidates for electronic applications. This report concentrates on a novel synthetic route and certain spectroscopic characteristics of some of these fused OTDOs prepared with the help of HOF·CH₃CN.

Results and Discussion

2,3,5,6-Tetrabromothieno[3,2-*b*]thiophene¹⁸ (**1a**), which contains two sulfur atoms, was reacted at 0 °C with 2 mol equiv of HOF·CH₃CN. Within a few seconds, 2,3,5,6-tetrabromothieno[3,2-*b*]thiophene 1,1-dioxide (**2a**) was formed in 90% yield (Scheme 1). Any attempt to fully oxidize **1a** to its tetraoxide derivative by adding an excess of HOF·CH₃CN was unsuccessful. At this point, we would like to emphasize that no two adjacent thiophene units in any fused oligothiophene could be converted to the tetraoxide. It appears that the first formed SO₂ group reduces the nucleophilic character of the nearby sulfur atom to the extent of preventing an additional electrophilic oxygen being transferred to any adjacent sulfur atom.

To obtain support for this assumption, we carried out DFT calculations (B3LYP/6-311G(d,p)) on the parent skeletons. The focus of this computational study is the Mulliken charge distribution each sulfur atom bears before and after oxidation. Table 1 reveals that the partly oxidized fused oligothiophenes considerably reduce the negative charges on the remaining sulfur, compared to the starting materials. This is in line with the experimental outcome mentioned above that no two sulfur atoms in any adjacent fused oligothiophene rings could be oxidized by an electrophilic oxygen. Transferring oxygen atoms to two alternate sulfurs, however, is possible as is evident from both the calculation and experimental results.

3-Bromo-6-nonanylethylthieno[3,2-*b*]thiophene¹⁹ (**1b**), in which the two thiophene rings are quite different, was reacted at 0 °C with 2 mol equiv of HOF·CH₃CN and two products were isolated and identified as 3-bromo-6-nonanylethylthieno[3,2-*b*]thiophene 4,4-dioxide (**2b**) and 3-bromo-6-nonanylethylthieno[3,2-*b*]thiophene 1,1-dioxide (**3b**) in 85% and 15% yields,

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TABLE 1. Mulliken Charge on the Sulfur Atom

compound	S ₁ , S ₃ ^a	S ₂ ^a
	0.260504	0.260504
	0.993372	0.322179
	R=H 0.277402 ^b R=Me 0.264409 ^b R=COOEt 0.346555 ^b	R=H 0.26251 R=Me 0.254572 R=COOEt 0.280820
	0.324951 ^b	1.037217
	S ₁ =0.995773 S ₃ =0.315796	0.329872
	1.012443 ^b	0.365767

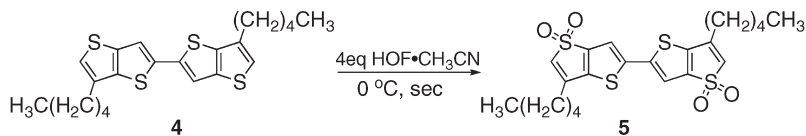
^aAtomic units. ^bS₁ = S₃.

respectively. Adding an excess of HOF·CH₃CN (e.g., 5 mol equiv) did not considerably change the ratio between the two isomers. In the case of two fused thiophene rings, with similar aromaticity, the nature of the substituent seems to be responsible for the regioselectivity of the oxygenation.

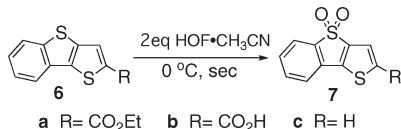
The incorporation of an electron-withdrawing group at the 5-position changed the selectivity of the oxidation only marginally. When 3-bromo-6-nonanylethylthieno[3,2-*b*]thiophene 5-carboxylate¹⁹ (**1c**) was reacted with 2 mol equiv of HOF·CH₃CN 3-bromo-6-nonanylethylthieno[3,2-*b*]thiophene-5-carboxylate 4,4-dioxide (**2c**) was formed in 70% yield along with 3-bromo-6-nonanylethylthieno[3,2-*b*]thiophene-5-carboxylate 1,1-dioxide (**3c**)—30% yield. We believe that this regioselectivity is the result of the hydrogen bond formation between the HOF·CH₃CN and the ester carbonyl in **1c**. This intermolecular interaction can direct the electrophilic oxygen of the reagent toward the neighboring sulfur atom. We proposed that this neighboring group effect overwrites the electron withdrawing power of the ester group and leads to the observed selectivity. Parallel examples of such hydrogen bonding effect were previously observed^{16,20} (Scheme 1).

The regiochemistry revealed in **2b**, **2c**, **3b**, and **3c** was evident from the ¹H NMR spectrum. The oxidation of the sulfur ring of **2b** and **3b** produces distinctive and characteristic upfield shift (around −0.65 ppm) of the hydrogen next to the oxidized sulfur, while the hydrogen α to the nonoxidized one

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SCHEME 2. Oxygenation of 2,2'-Bithieno[3,2-*b*]thiophene

SCHEME 3. Oxygenation of Thienobenzothiophene



exhibited only a slight downfield shift (around +0.15 ppm). This assignment was also supported by the use of the lanthanide shift reagent Pr(FOD)₃, which induced a larger upfield chemical shift of the hydrogen next to the SO₂ group (−0.15 ppm) than on the sole aromatic one (−0.05 ppm). The two different hydrogens could also be readily distinguished by the different multiplicity they exhibit. The no longer aromatic H-5 of **2b** appears as a quartet ($J_6 = J_4 = 1.6$ Hz) while the aromatic hydrogen appears as a doublet ($J_6 = 1.6$ Hz). A similar situation was observed for **3b** as well as for the rest of the products described in this work. These results are consistent with the spectral behavior of thiophenes and their dioxides.²⁰

Selective oxidation can also be performed on 2,2'-bithieno[3,2-*b*]thiophenes as in **4**. A sample of 4 mol equiv or more of HOF·CH₃CN, when reacted with **4**, produced one regioisomer, which proved to be 6,6'-bis(pentyl)-2,2'-bithieno[3,2-*b*]thiophene 4,4,4',4'-tetraoxide (**5**) in 85% yield (Scheme 2). It should be noted that Matzger had prepared similar compounds by various coupling reactions between two fused thieno[3,2-*b*]thiophene molecules.²¹

Thieno[3,2-*b*][1]benzothiophenes such as ethylthieno[3,2-*b*][1]benzothiophene 2-carboxylate (**6a**) and thieno[3,2-*b*][1]benzothiophene 2-carboxylic acid (**6b**) with two sulfur atoms were also treated successfully with HOF·CH₃CN. The corresponding ethylthieno[3,2-*b*][1]benzothiophene-2-carboxylate 4,4-dioxide (**7a**) and thieno[3,2-*b*][1]benzothiophene-2-carboxylic acid 4,4-dioxide (**7b**) were obtained within a few seconds in 97% and 90% yields, respectively. The electronic properties of the substituents did not change the outcome and thieno[3,2-*b*][1]benzothiophene²² (**6c**) was also oxidized to form the thieno[3,2-*b*][1]benzothiophene 4,4-dioxide (**7c**)²³ in 95% yield (Scheme 3).

It should be noted that despite the two sulfur atoms found in **6**, the oxygen atoms were only transferred to the sulfur attached to the phenylene moiety. This could be rationalized by both factors favoring the attack on the less aromatic thiophene ring and to the attraction of the electrophilic oxygen of the reagent by the electronic cloud of the benzene ring. This selectivity is hardly dependent on the electronic properties of the substituents.

Somewhat different results were recorded when three fused thiophene units were reacted with the HOF·CH₃CN complex. When 2,6-dimethyldithieno[3,2-*b*;2',3'-*d*]thiophene²⁴ (**8a**) was reacted with 2 mol equiv of the reagent at 0 °C, 2,6-dimethyldithieno[3,2-*b*;2',3'-*d*]thiophene 4,4-dioxide (**9a**) was formed in 90% yield within a few seconds. The latter, however, could not be further oxidized. The reason for the attack on the central sulfur atom is understandable since compounds **8** resemble polycyclic aromatic hydrocarbons where the degree of the aromaticity is higher on the outer rings compared to the inner one.²⁵ Additionally, as is evident from the DFT calculation above (Table 1), the central sulfur atom has a larger negative charge and therefore is a stronger nucleophile.

However, using an excess of HOF·CH₃CN (7 mol equiv) resulted in equal amounts of **9a** and 2,6-dimethyldithieno[3,2-*b*;2',3'-*d*]thiophene 1,1,7,7-tetraoxide (**11a**) (45% yield each). It is clear that the latter was obtained from the 2,6-dimethyldithieno[3,2-*b*;2',3'-*d*]thiophene 1,1-dioxide (**10a**), which we were able to detect and further oxidize quantitatively to **11a**. To the best of our knowledge, such direct oxidation leading to dithienothiophenes *S,S,S',S'*-tetraoxide has never been reported.

Excess of HOF·CH₃CN causes the reaction to be more vigorous, leading to an immediate oxygenation of any nearby sulfur atoms. Therefore the reverse selectivity can be explained by the fact that there are two side thiophene units for every central one. It could also be understandable based on the electronic influence from alkyl substitutions of the outer rings, which increase the negative charges on their sulfur atoms and consequently moderate the differences between all the heteroatoms as shown by the DFT calculation (Table 1).

Replacing the methyl groups with the bulky *tert*-butyl ones, as in **8b**,²⁴ did not change the outcome. When 2 mol equiv of the HOF·CH₃CN complex were used, 2,6-di-*tert*-butyldithieno[3,2-*b*;2',3'-*d*]thiophene 4,4-dioxide (**9b**) was obtained in 95% yield. Again, with an excess of HOF·CH₃CN (7 mol equiv) a mixture was obtained from which we isolated **9b** in 45% and 2,6-di-*tert*-butyldithieno[3,2-*b*;2',3'-*d*]thiophene 1,1,7,7-tetraoxide (**11b**) in 25% yield. The intermediate, 2,6-di-*tert*-butyldithieno[3,2-*b*;2',3'-*d*]thiophene 1,1-dioxide (**10b**), was also formed and could be further oxidized by HOF·CH₃CN, raising the overall yield of the tetraoxide **11b** to 50%.

Fused oligothiophenes with strong electron withdrawing groups are entirely beyond the oxidizing power of common oxidizers. Applying 2 mol equiv of HOF·CH₃CN complex to diethyl 2,6-dithieno[3,2-*b*;2',3'-*d*]thiophene dicarboxylate²⁶

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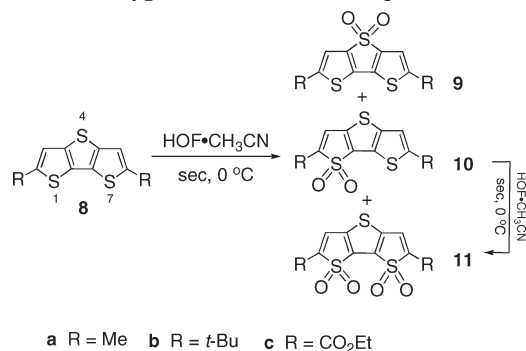
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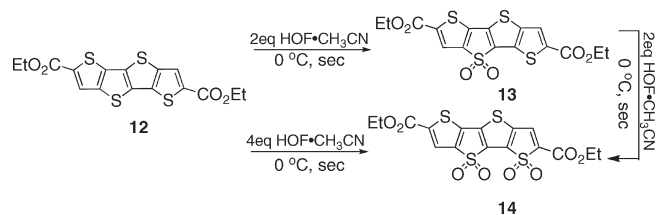
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SCHEME 4. Oxygenation of Dithienothiophene



SCHEME 5. Oxygenation of Tetrathienoacene



(8c), however, efficiently converted this compound to **9c** within a few seconds and in 95% yield (Scheme 4). It is not surprising that, in this case, no oxidation took place on either of the outer rings despite the large excess of the reagent. The electron withdrawing nature of the COOEt groups of the outer rings reduces significantly the charges on the outer sulfur atoms making it impossible to oxidize them, as is evident from the DFT calculation summarized in Table 1.

A similar pattern was observed with derivatives containing four sequentially fused thiophene rings. When the tetrathienoacene (**12**)¹⁹ was reacted with 2 mol equiv of HOF·CH₃CN at 0 °C 2,6-dicarboethoxythieno[3,2-*b*]thieno[2',3':4,5]-thieno[2,3-*d*]thiophene 4,4-dioxide (**13**) was formed in 95% yield. Further oxidation of **13** with additional 2 mol equiv of HOF·CH₃CN at 0 °C formed 2,6-dicarboethoxythieno[3,2-*b*]thieno[2',3':4,5]thieno[2,3-*d*]thiophene 4,4,5,5-tetraoxide (**14**) in excellent yield (Scheme 5). Needless to say the oxidation of **12** with 4 mol equiv or more of HOF·CH₃CN at 0 °C also formed **14** in a very good yield.

Compounds **7a**, **9c**, and **11a** were characterized by X-ray crystallography²⁷ with toluene, acetonitrile–toluene, and acetonitrile, respectively, as the solvent for crystallization. The first two compounds revealed a monoclinic system with a *P2(1)/m* and *C2/c* space group having two and four molecules in the unit cell, respectively. The C and S backbone atoms of **7a** are fully coplanar with no deviations from planarity while those of **9c** are slightly less coplanar with a maximum atomic deviation of 0.092 Å (views a–c in Figure 1). It is important to note that the molecular packing of both **7a** and **9c** consists of planar molecules parallel to each other in a face-to-face π -stacking fashion. The interfacial distance is about 3.400 (**7a**) to 3.362 (**9c**) Å

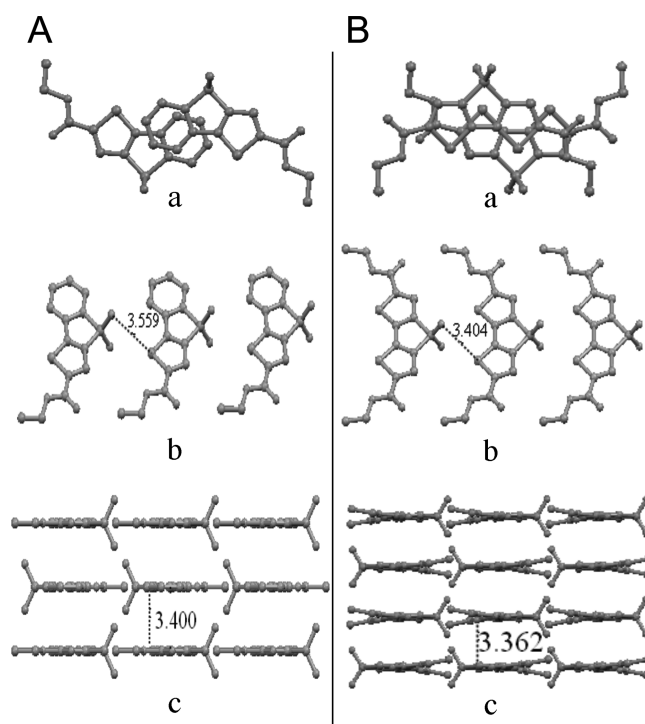


FIGURE 1. Three views of the molecular packing of (A) **7a** (no H) and (B) **9c** (no H).

(views a and c in Figure 1). The nearest intermolecular S–O distance is 3.559 (**7a**) to 3.404 (**9c**) Å (views b in Figure 1). This arrangement is essential for electronic devices based on organic molecules, since such packing constitutes a more favorable morphology for electron transport.¹⁹

Compound **11a** crystallizes in an orthorhombic system with a *Pnma* space group, having four molecules in the unit cell with the C and S backbone atoms fully coplanar without any deviations from planarity. The molecules form face-to-face π -stacking columns along the direction of the *b*-axis and are antiparallel with respect to one another. The interlayer distance is about 3.609 Å and the nearest S–O distance is 3.320 Å (view a, Figure 2). On the other hand in the *ac* plane (view b, Figure 2), there is no remarkable π -overlap of the rings and a herringbone structure with a dihedral angle of 74.4° could be seen.

The electronic properties of the compounds discussed in this paper were studied by UV–vis as well as by fluorescence spectroscopy. Table 2 lists the maximum wavelength absorption (λ_{max}), emission (λ_{PL}), HOMO–LUMO energy gap (ΔE_{g}), the lowering of the HOMO–LUMO energy gap following the oxygen-transfer reaction ($\Delta\Delta E_{\text{g}}$), and the absolute photoluminescence (PL) quantum yields (Φ_{F}) in solution for the starting, *S,S*-dioxide, and *S,S,S',S'*-tetraoxide oligomers. The photoluminescence quantum yield for solid state **9c** is also reported.

Inspection of Table 2 reveals that the oxidation of one or more thienyl sulfur atoms brings about a 17–74 nm red shift of the maximum wavelength of absorption (λ_{max}). This indicates that very desirable lowering of the HOMO–LUMO energy gap ($\Delta\Delta E_{\text{g}}$) has taken place. Also, the oxidation of one thiophene ring tends to enhance the fluorescence intensity (Φ_{F}), in particular, the quantum yields of **9a–c** were found to be 76%, 72%, and 91%, respectively. In

(27) CCDC 730672 (**7a**), 689953 (**9c**) and 689954 (**11a**) contain the supplementary crystallographic data for this paper. Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (Fax: + 44-1223/336- 033; E-mail: deposit@ccdc.cam.ac.uk; data_request/data_request/cif).

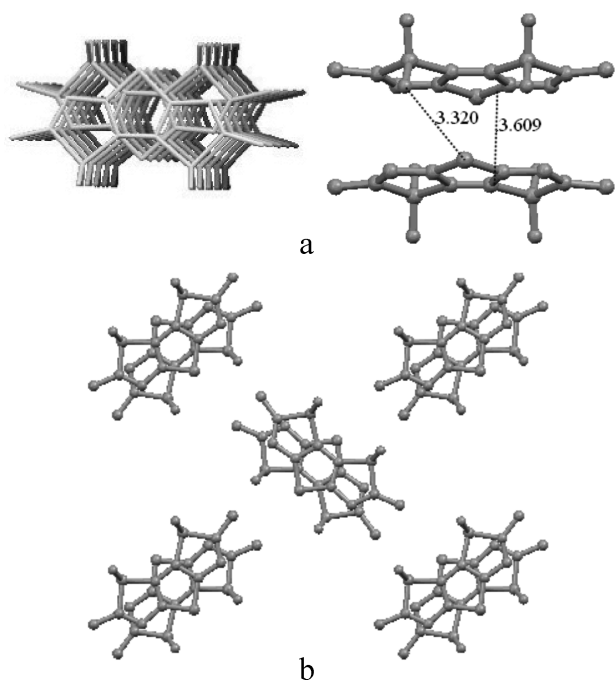


FIGURE 2. Molecular packing of **11a** (no H).

TABLE 2. Absorption (λ_{\max} , nm), HOMO-LUMO Energy Gap (ΔE_g ,^a eV), PL (λ_{PL} , nm) Wavelengths, HOMO-LUMO Energy Gap Change ($\Delta\Delta E_g$,^b eV), and PL Quantum Yields (Φ_F , %)^c in Solution^{d,f}

compd	λ_{\max} (ΔE_g)	$\Delta\Delta E_g$	λ_{PL}	Φ_F
1a	279 (4.44)			
2a	365 (3.40)	1.04	433 (2.86) ^e	< 1
1b	261 (4.75)			
2b	358 (3.46)	1.29	464 (2.67)	< 1
3b	335 (3.70)	1.05	466 (2.66)	< 1
1c	292 (4.25)			
2c	358 (3.46)	0.79	455 (2.73)	< 1
3c	335 (3.70)	0.55	459 (2.70)	< 1
4	355 (3.49)			
5	392 (3.16)	0.33	503(2.46)	< 5
6a	309 (4.01)			
7a	326 (3.80)	0.21	405 (3.06)	< 5
6b	307 (4.04)			
7b	324 (3.83)	0.21	412 (2.99)	< 5
6c	262 (4.73)			
7c	326 (3.80)	0.86	416 (2.98)	< 5
8a	300 (4.13)			
9a	370 (3.35)	0.78	470 (2.64)	76
11a	361 (3.43)	0.7	467 (2.65)	< 1
8b	292 (4.25)			
9b	374 (3.35)	0.9	466 (2.66)	72
11b	363 (3.42)	0.83	464 (2.67)	< 1
8c	338 (3.67)			
9c	370 (3.35)	0.32	453 (2.76)	91
12	362 (3.43)			
13	398 (3.12)	0.31	466 (2.66)	41
14	375 (3.31)	0.12	456 (2.72)	28

^a $\Delta E_g = hc/\lambda$. ^b $\Delta\Delta E_g = \Delta E_g(\text{starting material}) - \Delta E_g(\text{product})$. ^cThe PLQEs were estimated by comparison with standards of known quantum yield. ^d CH_2Cl_2 solution. ^eValues in parentheses are in eV units. ^f3,5-Dimethyldithieno[3,2-*b*:2',3'-*d*]thiophene 4,4-dioxide²⁸ was used as reference compound for the PLQE calculation under UV irradiation ($\lambda_{\text{exc}} = 363$ nm).

contrast, the doubly oxidized products **11a,b** show only moderate fluorescence. In solution, large stoke shifts (up to 1 eV) from UV absorption to emission in the visible blue range ($\lambda_{\max}(\Delta E_g) - \lambda_{\text{PL}}(\Delta E_g)$) were observed for all fused OTDOs.

By comparing molecules having one and two sulfonyl units, it is clear that the position of the single oxidized sulfur has a substantial influence on the optical and electronic behavior, while the oxidation of a second thienyl unit exerts a less dramatic effect on the physical properties. For instance, the oxidation of the mid sulfur, as in compounds **9a–c**, has a larger effect on increasing the electron delocalization of the system relative to compounds **11a** and **11b**, which is reflected in the further reduction of the HOMO–LUMO gap. This can be attributed to the fact that the middle sulfur atom breaks the aromaticity of the oligomer, imparting a greater diene character to the molecule and increasing the electron communication between rings. The optical properties of these compounds also depends on the functionalization type and the size of the oligomers. An increase in the number of double bonds results in a higher conjugated system directing the absorption and emission maxima to a longer wavelength and increasing fluorescent quantum yield.

Selective oxidation decreases the electron delocalization within the ring, while increasing it along the molecular backbone. The electron affinity of the molecule also increases with respect to the parent oligomers as is evident by the red shift in the longest wavelength (λ_{\max}) of the absorption. In addition, these features make these compounds excellent candidates as building blocks for the preparation of molecular materials for electroluminescent devices, such as flat panel display technology, biolabeling,²⁹ LED,² lasers,³⁰ and more. The oxygen addition to compounds **8** and especially to **8c**, leading to **9c**, results in the strong increase of the emission efficiency as indicated by its high photoluminescence quantum yield (PLQE) in solution. To the best of our knowledge, the Φ_F value measured for **9c** is the highest PL efficiency value ever reported for any fused oligothiophenes in solution. As tight packing and strong intermolecular interactions often lead to high PL efficiencies in polythiophenes derivatives,³¹ the self-assembly of **9c** into a face-to-face arrangement, as demonstrated by its X-ray crystallography (Figure 1B), contributes to the remarkable solid state PL efficiencies as well.

We have measured these Φ_F values by using the time-correlated single-photon counting (TCSPC) technique to measure the time-resolved emission, as demonstrated for **9c**, in solution and in the solid state.³² The time-resolved fluorescence signal is reported in Figure 3. The fluorescence mono-exponential time decay is about 5.33 ns in solvent (CH_2Cl_2) measured from the slope of the decay curve. A lifetime reduction to 3.28 ns is observed in the solid state. Since the fluorescence quantum efficiency is strongly dependent on the decay rate,³³ the knowledge of the Φ_F in solvent and the fluorescence decay rate (κ), both in solvent and in the solid state, allows us to determine the Φ_F of **9c** in the solid state ($\Phi_F(\text{solid}) = \Phi_F(\text{solution})\kappa(\text{solid})/\kappa(\text{solution})$). Thus the PLQE of

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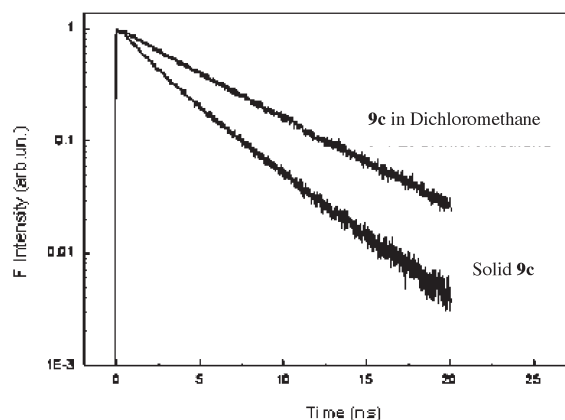


FIGURE 3. Time-resolved PL single of **9c** in CH_2Cl_2 and in the solid phase.

solid **9c** was found to be 56%, which is the highest $\Phi_{\text{F}}(\text{solid})$ measured for any solid fused oligothiophene *S,S*-dioxide thus far.

Conclusion

In conclusion, it is clear that $\text{HOF} \cdot \text{CH}_3\text{CN}$ complex can oxidize a wide range of fused thiophenes to the corresponding OTDOs in unparalleled good yields and under mild conditions. The presented data confirm that these oxygenated materials have many desirable optical properties, high electron affinity, increased electron delocalization, and decreased HOMO–LUMO energy gap. In addition, considering the commercial availability of premixed fluorine/nitrogen mixtures and the technical ease of the reaction (no special equipment is needed), it is indicative that this oxygen transfer reaction may become the method of choice for many cases where the alternatives are not sufficiently suitable.

Experimental Section

General Procedure for Working with $\text{HOF} \cdot \text{CH}_3\text{CN}$. A fused thiophene derivative was dissolved in CH_2Cl_2 , and the mixture was cooled to 0°C . One portion of the oxidizing agent was then added to the reaction vessel. The reaction was stopped after a few seconds and the excess of $\text{HOF} \cdot \text{CH}_3\text{CN}$ was quenched with saturated sodium bicarbonate. The mixture was then poured into water and extracted with CH_2Cl_2 , the organic layer was dried over MgSO_4 , and the solvent was evaporated. The crude product was usually purified, either by vacuum flash chromatography with silica gel 60-H (Merck) with an increasing portion of EtOAc in PE as an eluent, or by recrystallization.

2,6-Dimethyldithieno[3,2-*b*;2',3'-*d'*]thiophene 4,4-Dioxide (9a**).** **9a** was prepared from **8a**²⁴ (0.4 g, 1.8 mmol) as described above, using 2 equiv of the oxidizing agent, and chromatographed on silica gel with PE:EtOAc 80:20 as eluent. A crystalline yellow solid (0.41 g, 90% yield) was obtained: mp 226°C (from hexane); λ_{max} 370 nm; IR 1293, 1138 cm^{-1} ; ^1H NMR 6.869 (q, $^4J = 1.2$ Hz, 2H), 2.519 ppm (d, $^4J = 1.2$ Hz, 6H); ^{13}C NMR 16.1, 118.0, 134.0, 141.6, 144.9 ppm; HRMS (CI) (m/z) calcd for $\text{C}_{10}\text{H}_8\text{O}_2\text{S}_3$ 256.976470 (MH^+), found 256.975966. Anal. Calcd for $\text{C}_{10}\text{H}_8\text{O}_2\text{S}_3$: C, 46.85; H, 3.15; S, 37.52. Found: C, 46.63; H, 3.07; S, 37.01.

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Supporting Information Available: General experimental methods, ^1H and ^{13}C NMR data of all new compounds, crystallographic data for **7a**, **9c**, and **11a**, and theoretical calculation details (including *z*-matrix). This material is available free of charge via the Internet at <http://pubs.acs.org>.