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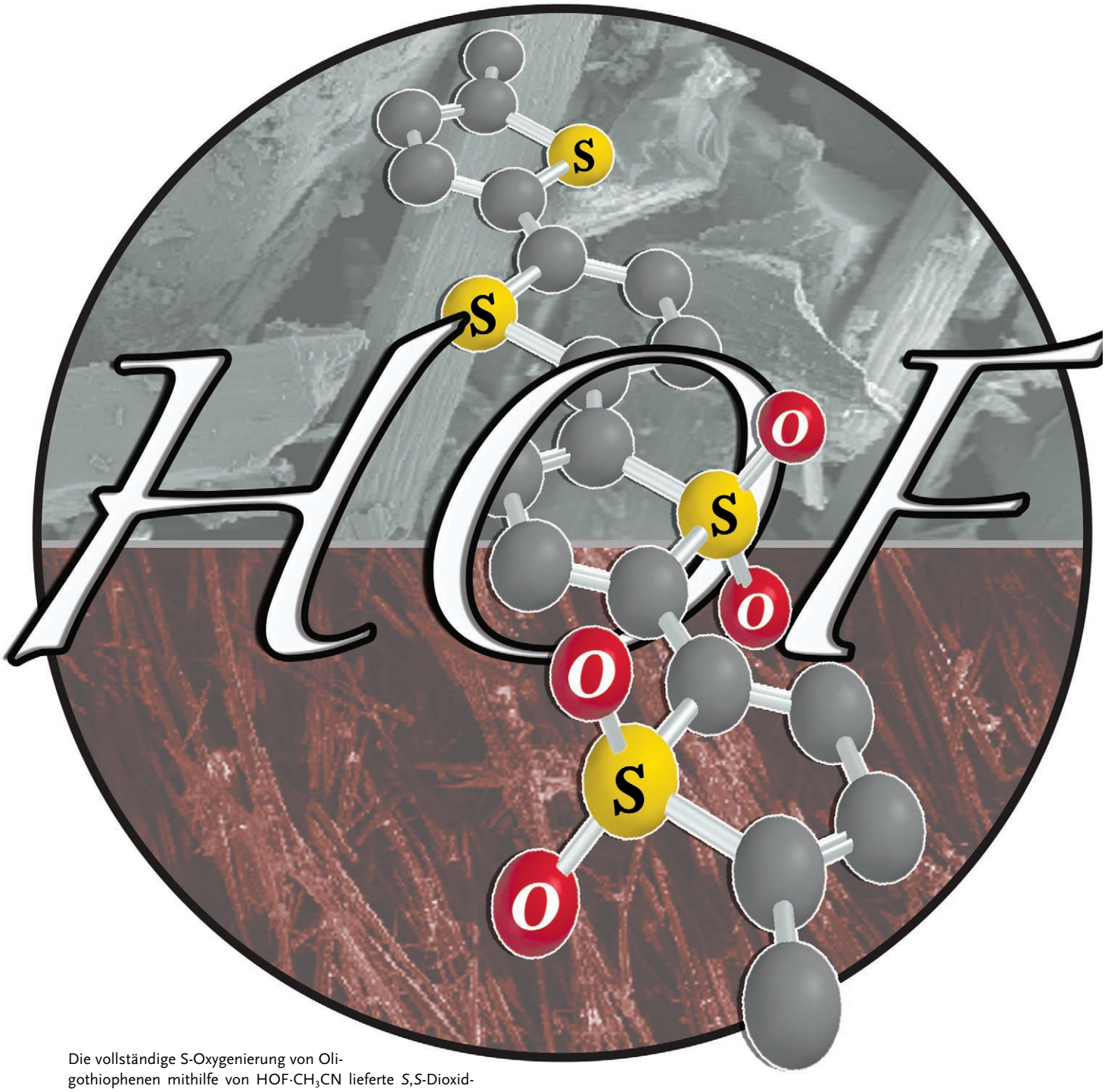

Die vollständige S-Oxygenierung von Oligothiophenen mithilfe von HOF·CH_3CN lieferte *S*,*S*-Dioxidoligothiophen-Derivate. Als Hintergrund sind rasterelektronenmikroskopische Aufnahmen der Oligothiophen-Reaktanten (oben) und der besser organisierten Cluster der Produkte (unten) zu sehen. Mehr über diese Synthesen finden Sie in der Zuschrift von E. Amir und S. Rozen auf den folgenden Seiten.

Oligomers

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Synthesis of [all]-*S*,*S*-Dioxide Oligothiophenes Using HOF·CH_3CN**

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The last decade witnessed an exponential growth in the number of reports devoted to the development of electronic devices based on organic materials. The main synthetic effort is centered on oligothiophenes (OTs) and their many derivatives, such as thienylenvinylenes,[1] alkyl fluoride oligothiophenes,[2] ethylenedioxidethiophenes,[3] or thiazolothiazol thiophenes,[4] to mention just a few. A short search in the *Chemical Abstracts* resulted in thousands of reports concerning this subject from the last five years alone.

The channeling of such huge research efforts started in the late 1980s when Garnier and co-workers had shown for the first time that short conjugated thiophene oligomers could serve as efficient active layers in field-effect transistors (FETs).[5] Since then, the will to develop such organic semiconductors for light-emitting diodes (LEDs), molecular wires, and many other optoelectronic devices[6] has become an irresistible driving force for many chemists to continue the exploration of the possibilities offered by various types of oligothiophenes.

The major goals of the numerous OT modifications are to lower the highest-occupied molecular orbital (HOMO)–lowest-unoccupied molecular orbital (LUMO) gap and obtain highly ordered semiconducting films, as both features are responsible for the efficiency of n-type semiconductors. One of most obvious and promising modifications had already been suggested in 1989: A theoretical prediction had been made that the corresponding *S*,*S*-dioxides of OT would be better materials than OTs themselves, as the HOMO–LUMO gap should be significantly smaller.[7] Chemists tried to test this hypothesis, but the use of orthodox oxygen-transfer agents was the main reason for a complete synthetic failure of making [all]-*S*,*S*-dioxide OTs longer than bithiophene. Each time such an attempt was undertaken, only a low yield of partially oxygenated thiophene rings was achieved, even after prolonged reaction times.[8] Another approach toward the synthesis of partially oxygenated *S*,*S*-dioxide OTs was taken by Barbarella et al. who coupled 2-(dimethyl-*tert*-butylsilyl)-5-bromothiophene-*S*,*S*-dioxide with the corresponding oxygen-free derivatives, thus obtaining alternately oxygenated OTs.[9]

Some years ago, we developed a new type of oxygen-transfer agent, HOF·CH_3CN, which was unique in the sense of that it possessed a truly electrophilic oxygen center.[10] After some time, this complex was dubbed the best oxygen-transfer agent offered in organic chemistry and was instrumental in the first synthesis of 1,10-*N*,*N*-phenanthroline dioxides,[11] the first oxidation of geminal diamines[12] and azides,[13] the epoxidation of electron-depleted olefins,[14] and many other firsts or difficult transformations.[15] Among these reactions was also the mild oxidation of various thiophenes to their corresponding *S*,*S*-dioxides[16]—not an easy task considering the harsh conditions usually required to overcome the aromatic stabilization—thus possibly leading to Diels–Alder reactions and/or SO_2 eliminations. The successful preparation of these monothiophene *S*,*S*-dioxides with HOF·CH_3CN prompted us to explore the possibilities of making the long sought after oligothiophene *S*,*S*-dioxides (OTDOs). This reagent, prepared from diluted elemental fluorine and aqueous acetonitrile, was indeed able to transfer as many oxygen atoms as needed to construct the oligothiophene [all]-*S*,*S*-dioxides investigated. We report herein the synthesis and certain characteristics of some of these OTDO compounds. It is worth mentioning that previous attempts to fully oxidize 5,5′-dihexyl-2,2-bithiophene (**1e**) with *m*-chloroperoxybenzoic acid (MCPBA) were unsuccessful and only 5,5′-bis(dimethyl-*tert*-butylsilyl)-[2,2′]bithiophene (**1f**) could be oxidized to the tetraoxide **2f** in 47% yield after 12 h.[8,9] So far, this reaction was the only example of a preparation of a fully oxygenated *S*,*S*-dioxide OT; however, HOF·CH_3CN has changed this situation.

5,5′-Dimethyl-[2,2′]bithiophene (**1a**)[17] was cooled to −10 °C and treated with a slight excess of the acetonitrile complex of hypofluorous acid.[18] The corresponding, previously unknown, bis(*S*,*S*-dioxide) **2a** was obtained in about 10 s and in 85% yield. No partly oxidized regioisomers or other by-products, usually associated with long reaction times and high temperatures, were observed. Replacing the methyl groups with the bulky *tert*-butyl groups, as in **1b**,[17] did not change the outcome, and the as-yet unknown bis(*S*,*S*-dioxide) **2b** was obtained in a short reaction time at 0 °C in 83% yield. Replacing one or even both of the electron-donating alkyl groups at the 5,5′ positions with the electron-withdrawing bromine atom(s), as in 5-bromo-5′-hexyl-[2,2′]bithiophene (**1c**)[19] or 5,5′-dibromo-[2,2′]bithiophene (**1d**),[20] did not have a negative effect on the reaction and **2c** and **2d** were obtained after 5 min in 87 and 66% yield, respectively (Scheme 1).

Longer OTs were also treated successfully. It took only one minute for HOF·CH_3CN to transfer six oxygen atoms to all three sulfur atoms of the 5,5″-di-*tert*-butyl-[2,2′,5′,2″]terthiophene (**3b**),[21] thus affording the tris(*S*,*S*-dioxide) **4b** in 82% yield. This reaction is the first example of a fully oxygenated terthiophene compound. For comparison, treatment of terthiophene with MCPBA for 48 h resulted in the transfer of oxygen atoms to only the terminal rings.[8] Again, leaving two electron-withdrawing groups for future synthetic manipulation, as in 5,5″-dibromo-[2,2′,5′,2″]terthiophene

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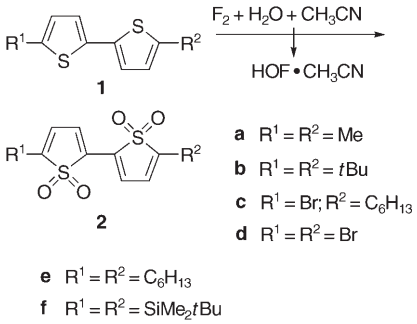
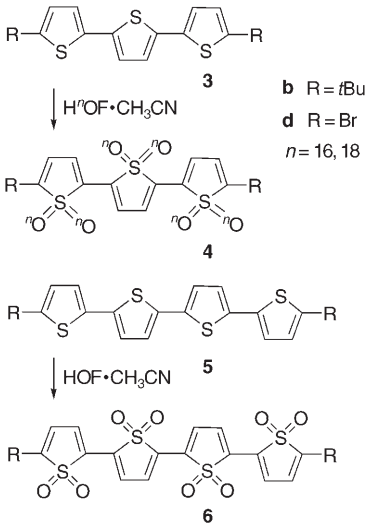


Scheme 1. Oxygenation of dithiophenes.

(**3d**),[20] did not prevent the oxygen-transfer process that forms tris(*S*,*S*-dioxide) **4d** in 60% yield. One of the advantages of HOF·CH_3CN is the origin of its electrophilic oxygen atom from water, which is the most convenient source for all oxygen isotopes; therefore, an opportunity to prepare **4b** with all six oxygen atoms being the expected ^{18}O isotope (EI MS: *m*/*z* 468.1 [M^+]) was presented.

The derivative with four thienyl rings, 5,5‴-di-*tert*-butyl-[2,2′,5′,2″,5″,2‴]quaterthiophene (**5b**),[21] was also subjected to oxygenation with the HOF·CH_3CN complex. In this case, a twofold excess (16 molar equivalent) of the oxidant and reaction times of up to 40 minutes at room temperature were required, but the main product was the tetra-*S*,*S*-dioxide **6b** in 52% yield (Scheme 2). It seems that the somewhat smaller



Scheme 2. Oxygenation of oligothiophenes.

yield in this case is caused by solubility problems, and we are working now on the preparation of some more soluble derivatives.

These results enabled us to test some of the theoretical predictions about the OTDOs prepared so far. Table 1 lists the UV/Vis data for both starting materials and the *S*,*S*-dioxo oligomers. There are two well-defined differences between the spectra of the two groups. Whereas in the starting materials, as well as in the partially oxygenated *S*,*S*-dioxides,

Table 1: UV/Vis spectroscopic data and the derived HOMO–LUMO energy gaps[a].

Compound	$\lambda_{1-3,max}$ [nm][b]	Energy gaps [eV]			
		ΔE_g[c]	ΔE_g[d]	$\Delta\Delta E_g$[e]	$\Delta\Delta E_g$[f]
1a	317	3.91			
2a	351, 369, 387	3.20		0.71	
1b	317	3.91	4.22		
2b	359, 374, 392	3.16	3.34	0.75	0.88
1c	320	3.87			
2c	365, 383, 401	3.09		0.78	
1d	320	3.87	3.96		
2d	370, 388, 412	3.01	3.13	0.86	0.83
3b	365	3.40	3.41		
4b	410, 434, 461	2.69	2.66	0.71	0.75
3d	364	3.41	3.34		
4d	414, 441, 468	2.65	2.56	0.76	0.78
5b	398	3.12	3.13		
6b	448, 480, 512	2.42	2.26	0.70	0.87

[a] HOMO–LUMO energy gap was derived from the UV/Vis spectroscopic data and DFT calculations. [b] These spectra consist of an underlined maximum and corresponding vibronic splitting. [c] HOMO–LUMO gap from the low-energy band of the UV/Vis spectrum. [d] These calculations obtained from DFT computations are in very good agreement with the UV measurements (for comparison purpose, see reference [9]). [e,f] Lowering the HOMO–LUMO gap following the oxygen-transfer reaction ([e] from spectral data, [f] from DFT calculations).

the reported spectrum presents a single absorption maximum, the corresponding [all]-*S*,*S*-dioxides display three major peaks because of the rigidification of the OTDO backbone.[9] A constant interval in the order of 18–32 nm between the high-energy band ($\lambda_{1,max}$), main absorption ($\lambda_{2,max}$), and low-energy transition ($\lambda_{3,max}$) was observed in all products. This energy spacing can be attributed to the stretching mode of the conjugated double bonds of the oxidized OT core. As reported previously,[22] the bathochromic shift between an OT and the same compound with one oxygenated thiophene ring is about 60 nm, whereas a second *S*,*S*-dioxide unit adds an additional shift of about 20 nm. This trend of additivity is fully expressed in the completely *S*,*S*-oxygenated derivatives. As a result, dearomatized oligothiophenes show a maximal bathochromic shift that indicates a considerable narrowing of the HOMO–LUMO gap (ΔEg), as reflected by the low-energy transition ($\lambda_{3,max}$) absorptions of the products[22] (Table 1).

To obtain a good estimation of the frontier molecular orbitals, we performed ab initio DFT/B3PW91 computations using 6-311G** and 6-31G* bases sets for the bromo and *t*Bu derivatives, respectively. The results indicated that the energies of both the HOMO and LUMO were indeed considerably lower for the oxygenated compounds, with the LUMO values dropping almost twice as much as those of the HOMO. Consequently, this lowering leads to derivatives with a significantly higher electron affinities. Table 1 reveals quite a good agreement between the computed energy-gap values and those obtained from the UV/Vis measurements concerning the narrowing of the HOMO–LUMO gap between the starting materials and the products.

Cyclic-voltammetric measurements for the pairs **1b** and **2b** and **3b** and **4b** (starting materials and products, respec-

tively) were carried out on Pt electrodes (1.44 cm^2) in CH_3CN/Et_4NBF_4 (0.1M) and with 1×10^{-3}M substrate at 20 $mV\,s^{-1}$. The voltage was measured versus a Ag/AgCl electrode. The obtained oxidation ($E_{Ip,a}$) and reduction ($E_{Ip,c}$) peak potentials are presented in Table 2 and Figure 1.

Table 2: Oxidation ($E_{Ip,a}$) and reduction ($E_{Ip,c}$) peak potentials.

Compound	$E_{Ip,a}$ [V]	$E_{Ip,c}$ [V]
1b	1.21	−1.22
2b	2.24	−0.93
3b	1.06	−1.40
4b	2.14	−0.44

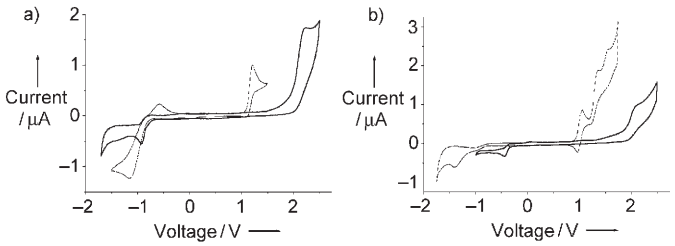


Figure 1. Cyclic voltammograms: a) dashed line: **1b**, solid line: **2b**; b) dashed line: **3b**, solid line: **4b**.

These results indicate that the reduction potential of **2b** is shifted toward the more positive value relative to its fully aromatic precursor **1b**, and the shift for the tris(*S*,*S*-dioxide) (transformation of **3b** into **4b**) is even more conspicuous. It should be emphasized, however, that although the trend is clear, it is difficult to address quantitatively the actual oxidation–reduction potentials from the above peak potentials as no reversible redox couple is observed and the addition of one electron to the oligomer alters its dimensions. What is more, caution should be exercised in the comparison of the electrochemical results of OTs that possess different chemical and regiochemical substitution because rules for such permutations have not yet been formalized.[2] The above observations, however, clearly indicate that full *S*,*S*-oxygenation of OTs leads to materials that are better electron acceptors, a trend that is strongly enhanced when the length of the oligomer is increased. As the reduction potentials are related to the LUMO energies, the conclusion is that the longer the fully *S*,*S*-oxygenated OTs are, the lower their LUMO values. This feature is of course desirable when the issue is the acceptance of electrons from an outside source. The very high oxidation peak potentials, relative to other partially oxygenated OTs,[23] points to yet another advantage, namely, a greater stability of the fully oxygenated OTs toward air and damaging oxidation processes. In addition, indirect indication of the stability of these compounds can be deduced from their melting points. All OTDOs tested were thermally stable up to 250–300 °C and beyond; they tend to blacken at these temperatures, but in some cases do not melt even at 350 °C (see the Supporting Information).

X-ray structural analysis was performed on **4d**,[24] which showed that it crystallizes in a monoclinic system with a *C*2/*c* space group and has four molecules in the unit cell. The thienyl rings of each molecule exhibit an all-*anti,* nearly planar conformation, and the torsion angles between the mean planes of the rings are 3–9° (Figure 2a), which are in a

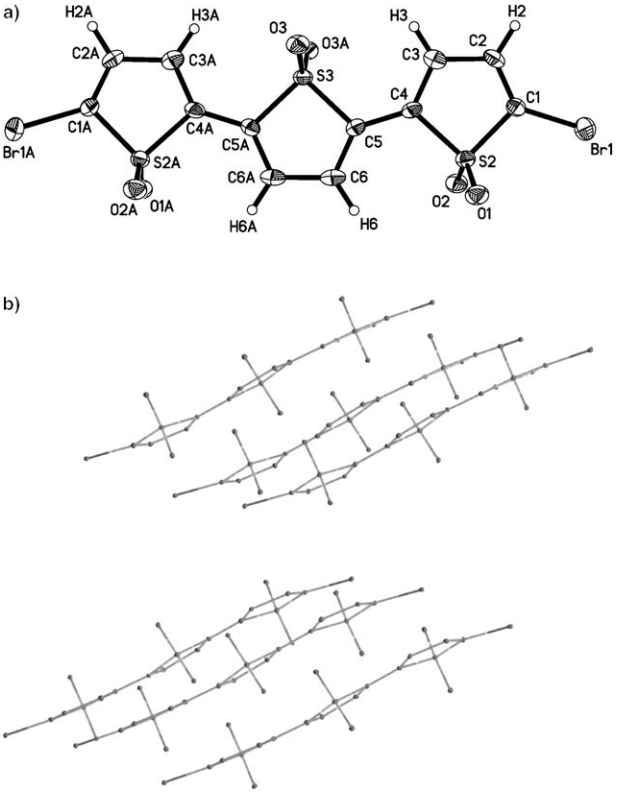


Figure 2. a) X-ray structure of **4d** and b) molecular structure and crystal packing of the unit cell of **4d**.

good agreement with the values reported for the unsubstituted α-3T.[25] The most promising feature of **4d**, however, is found in the molecular packing. It has been shown previously that, with a few exceptions,[3,26] most OTs studied so far have a typical "herringbone" (HB) arrangement with angles of 40–70° between the mean planes of the adjacent molecules. This packing is probably the best way for those molecules to decrease the intermolecular repulsion between the π orbitals, but it may also be responsible for their decreased transport properties in the direction of the long molecular axis.[27] In contrast, **4d** overcomes such repulsion and adopts an important π–π stacking arrangement of the molecular chains with an angle of 0° between the mean planes of the adjacent molecules (Figure 2b).

This favorable solid-state organization of the molecular chains may have an influence on the molecular nanoscale packing of the oligothiophene *S*,*S*-dioxides relative to the starting materials. Although not much can be said in this stage on the images obtained by scanning electron microscopy (SEM) for the OT **3b** and the product OTDO **4b**, there are some obvious differences in size and spatial distribution of the corresponding clusters. Under identical conditions, **3b** is rougher and has obvious discontinuities at grain boundaries. The *S*,*S*-dioxide **4b** displays many more clusters per a given

area that are about ten times smaller in width, thus hinting at a greater cohesion between its crystals (Figure 3).

In conclusion, contrary to a long-held belief, working with dilute fluorine is not problematic. HOF·CH_3CN generated

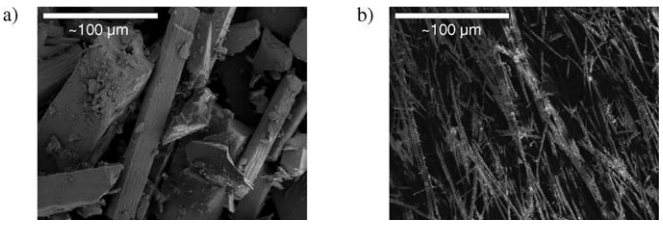


Figure 3. SEM images of a) OT **3b** and b) OTDO **4b**. Enlargement: 500× (≈100 μm).

in situ easily from F_2 and H_2O seems indeed to be the best oxygen-transfer agent offered in chemistry. Its strongly electrophilic oxygen atom opens up the only route so far that leads to the synthesis of the long sought after oligothiophene [all]-*S*,*S*-dioxides, whose initial characteristics are promising for use as field-effect transistors and other optoelectronic devices.

Experimental Section

A detailed procedure of how to work with F_2 and prepare HOF·CH_3CN can be found in reference [18]. We present a typical experiment for making the hexaoxide of the terthiophene **4b**. For full characterization of all the oxygenated compounds, see the Supporting Information.

4b: Terthiophene **3b**[21] was dissolved in CH_2Cl_2 at 0°C. A solution of HOF·CH_3CN, kept at a similar or lower temperature, was added in one portion to the reaction mixture and the reaction was stopped after 1 min by addition of $NaHCO_3$. The organic material was extracted with CH_2Cl_2, washed with water, and dried over $MgSO_4$. The product was purified by vacuum flash chromatography on silica gel 60-H (Merck) and recrystallized from $CHCl_3$. Yield: 82%. M.p. 290–292°C (turning black; from $CHCl_3$); ^{1}H NMR (200 MHz, $CDCl_3$): 7.28 (2H, s), 7.13 (2H, d, $J = 5$ Hz), 6.61 (2H, d, $J = 5$ Hz), 1.42 ppm (18H, s); ^{13}C NMR(50.2 MHz, $CDCl_3$): 155.3, 130.6, 129.3, 124.2, 123.9, 121.9, 35.0, 29.0 ppm; EI MS *m*/*z* (%): 456.1 ([M^+]); elemental analysis (%) calcd for $C_{20}H_{24}O_6S_3$: C 52.61, H 5.30, S 21.07; found: C 52.82, H 5.45, S 20.92.

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