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Chemo- and enantioselective sulfoxidation of bis(ethylenedithio)-tetrathiafulvalene (BEDT-TTF) into chiral BEDT-TTF-sulfoxide†

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Selective sulfoxidation of BEDT-TTF (bis(ethylenedithio)-tetrathiafulvalene) with enantiopure (camphoryl-sulfonyl)oxaziridine derivatives provided the *inner* monosulfoxide, as demonstrated using single crystal X-ray analysis, with an enantiomeric excess of 44% (up to 74% after recrystallization).

The introduction of chirality into radical cation salts or mixed valence compounds based on tetrathiafulvalenes (TTF),[1] a well known class of sulfur-rich precursors for organic conductors and superconductors,[2] has recently received a growing interest within the frame of multifunctional molecular materials, generally defined as compounds in which at least two different physical properties coexist or interplay.[3] Moreover, the first experimental evidence by Rikken *et al.* of an electrical magneto–chiral anisotropy effect in the magneto-transport properties of chiral carbon nanotubes emphasized the synergy between chirality and conductivity.[4] Besides this *intrinsic* effect on the conductivity, the chirality may also influence indirectly the transport properties by modulating the structural disorder in crystalline TTF-based radical cation salts, such as was recently highlighted within the first complete series of (±), (*R*) and (*S*) molecular conductors based on chiral EDT-TTF-oxazolines.[5] However, it should be pointed out that the possible influence of the chirality on the conducting properties of this family of materials has been previously addressed by Dunitz, Wallis *et al.* through the synthesis of the first chiral BEDT-TTF (bis(ethylenedithio)-tetrathiafulvalene), *S*,*S*,*S*,*S*-tetramethyl-BEDT-TTF (Chart 1).[6]

In this respect, straightforward access to chiral TTF precursors is of paramount importance, and thus several synthetic strategies have been devised for this purpose.[7] Note that the complementary strategy consisting of the use of chiral anions in radical cation salts based on achiral TTFs might also be envisaged, yet, in this case, the chiral information is not intimately related to the conducting lattice.[8] In most of the chiral TTF donors known to date, the source of chirality is punctual, being provided by asymmetric carbon atoms from the backbone of the TTF unit, such as the family of ethylene bridge substituted BEDT-TTFs and related compounds,[7] or the series of TTF-oxazolines.[9] Several compounds containing binaphthyl blocks as sources of axial chirality have been also described.[10] Nevertheless, in all these chiral donors, it is obvious that the chiral information is rather remote from the TTF redox active cores, which contain the potentially mobile electrons, responsible for the conducting properties in extended solid state structures, often observed in crystalline TTF radical cation salts. Intuitively, one might anticipate that closer proximity between the chiral centers and electron conduction pathways would provide a better chance to induce a synergy between chirality and conductivity. We have therefore decided to investigate the possibility of introducing chiral information directly on the TTF core.

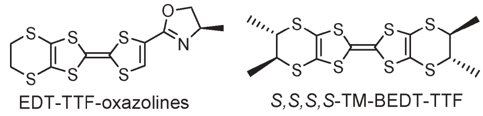

Chart 1

In this respect, a highly appealing strategy consists of the selective transformation of one out of the four sulfur atoms to a sulfoxide, of RR'SO type, thus leading to a chiral sulfur atom. Moreover, we could find two early reports in the literature, back in 1978–1979, dealing with the preparation of TTF-sulfoxides in racemic form, using a sulfoxidation reaction with *m*-chloroperbenzoic acid in both cases.[11] Interestingly, the report of Cava, Garito *et al.* mentioned the *reversible electrochemical oxidation* of their TTF-sulfoxides,[11a] albeit at quite higher potentials than the starting TTFs. Since the BEDT-TTF donor provided by far most of the known organic conductors and superconductors,[2] we have focused our efforts on its sulfoxidation. However, in this case, beside the enantioselectivity issue which has not been previously addressed,[11] one has to cope also with chemo- and regioselectivity problems, as eight sulfur atoms of two different types, *i.e. inner* and *outer*, are present in the BEDT-TTF molecule. Yet, on the basis of theoretical calculations on BEDT-TTF, showing that the *inner* S atoms largely contribute to the HOMO orbital,[12] we anticipated that an oxygen transfer reagent would preferentially attack one of the *inner* S atoms rather than an *outer* one, because of kinetic reasons. In recent years, many different strategies for the enantioselective transformation of sulfides into sulfoxides have been developed,[13] and certainly one of the most convenient methods, described by Davis *et al.*,[14] takes advantage of the reactivity of chiral oxaziridines towards prochiral sulfides. Since the commercially available derivative (8,8-dichlorocamphoryl-sulfonyl)oxaziridine **1** proved to be one of the most effective in terms of activity and chiral induction,[14a] we reacted it with BEDT-TTF in stoichiometric conditions to afford the BEDT-TTF

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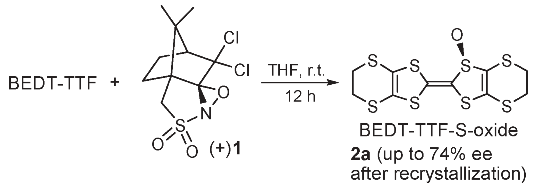
† Electronic supplementary information (ESI) available: Experimental, HPLC details, single crystal and powder X-ray data, and theoretical calculations. See DOI: 10.1039/b714245e



Scheme 1 Synthesis of BEDT-TTF-sulfoxide.

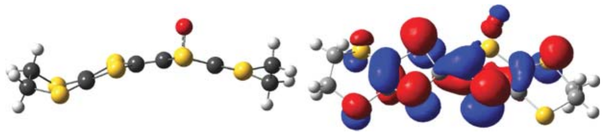


Fig. 2 Optimized geometry (left) and HOMO (right) ($E_{\mathrm{HOMO}} = -5.556$ eV) for **2**. DFT/B3LYP/6-31+G*.

sulfoxide **2a** as a single reaction product, which represents a remarkable chemoselectivity (Scheme 1). Chiral HPLC analyses show a fair selectivity for this reaction, since the enantiomeric excess (ee) amounts to about 44% for the yellow solid purified by column chromatography. Interestingly, two successive recrystallizations in toluene allowed an improvement to 74% ee for the mother liquors, whereas in the solid material the ee is around 35%. It is worth noting that we could find chiral HPLC conditions to achieve an excellent separation of the two enantiomers.†

It is known that enantiomeric enrichment often occurs upon recrystallization when starting from non-racemic mixtures, and, depending on the phase behavior and initial ee, the enrichment is observed either in (crystalline) solid or in solution.[15] The main enantiomer in **2a** is very likely the (*S*) one, as usually observed for sulfoxidation reactions with (+)-oxaziridines.[13,14] As expected, oxidation of BEDT-TTF with (−)-**1** in the same conditions affords the BEDT-TTF-sulfoxide **2b**, which is the same as **2a** but enriched in the opposite enantiomer, while the use of a racemic mixture of **1** provides the racemic **2c**. It is well established that partially resolved enantiomeric mixtures can produce crystals as racemates, conglomerates or, more rarely, solid solutions.[16] In our case, suitable single crystals for an X-ray analysis have been separated from the solid obtained from a CH_2Cl_2 solution of **2a** upon slow evaporation. These crystals, for which the powder X-ray pattern is different from that of the polycrystalline solid recrystallized from toluene,† proved to be a racemate of **2**, and, moreover, they could be obtained in much larger amounts starting from the racemic mixture **2c**. The compound crystallizes in the monoclinic system, centrosymmetric space group $P2_1/c$, with one independent molecule in the asymmetric unit.‡ As anticipated, the sulfoxidation took place at one of the *inner* sulfur atoms, affording a monosulfoxide, which, in the crystals we analyzed, presents an occupational site disorder for the oxygen atom (Fig. 1).

A side view of the molecule allows the observation of the folded conformation (25°) along the S2···S7 hinge, induced by the tri-coordination of the sulfur atom, which is certainly much less flexible than the non-substituted S3···S6 counterpart. The S7–O1 and central C3=C4 distances amount to 1.492(4) Å and 1.353(5) Å, respectively, and the S–C and C=C distances are in the normal range for a TTF derivative, yet with longer S–C bonds for the oxygen substituted sulfur atom.

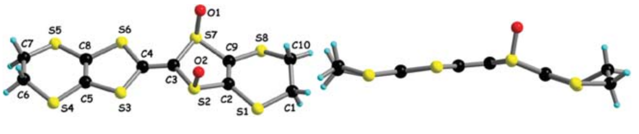


Fig. 1 Molecular structure of **2** along with the numbering scheme (left). The site occupational factors (s.o.f.) have been refined to 0.8 for O1 and 0.2 for O2. The C6–C7 bridge is disordered. Side view of the molecule (right).

In order to understand the origin of this high chemoselectivity, since no double or multiple oxidation products were observed, and also to estimate the orbital and electronic influence provided by the presence of the sulfoxide group, we performed theoretical calculations at the DFT level on the BEDT-TTF-sulfoxide **2**.† The optimized geometry (Fig. 2) corresponds to an equilibrium configuration (only positive frequencies) in agreement with the experimental one, reproducing well the folding along the S(O)···S hinge, while the S–O (1.51 Å) and central C=C (1.35 Å) distances closely match the experimental values.

Interestingly, the sulfoxide group participates in the HOMO (and SOMO)† of the molecule, which is strongly perturbed with respect to the parent BEDT-TTF, especially on the side containing the SO group. This feature demonstrates that in the eventual radical cation salts based on **2**, the chiral information would be in close proximity to the mobile electrons that are able to engage in extended delocalization upon close packing in the solid state. However, the energy of the HOMO, amounting to −5.556 eV, is much lower when compared to that of the HOMO of BEDT-TTF (−4.827 eV),† indicating that the electron donating properties of **2** are massively weakened, and also that the monosulfoxide is much less reactive towards oxygen capture than the starting BEDT-TTF, and hence the observed chemoselectivity. Unexpectedly, and in sharp contrast with the results claimed by Garito, Cava *et al.*,[11a,17] cyclic voltammetry measurements show only partially reversible oxidation for **2** in its radical cation $\mathbf{2}^{+\bullet}$, at +0.95 V *vs.* SCE, with cumulative formation of BEDT-TTF upon repetitive cycling. This proves that in MeCN solution, in the presence of the supporting electrolyte, the radical cation $\mathbf{2}^{+\bullet}$ is only moderately stable. However, when we tested the chemical oxidation of BEDT-TTF-sulfoxide **2** with the strong chemical oxidant $TCNQF_4$ (tetrafluoro-tetracyano-quinodimethane) in CH_2Cl_2 as solvent, the resulting solution immediately became dark green.† Upon slow evaporation of the solvent, small black needle-like crystals were obtained. The single crystal X-ray analysis‡ confirms that compound **3**, which crystallizes in the monoclinic space group *Cc*, is a charge transfer (CT) complex, formulated, surprisingly, as [BEDT-TTF-bis(sulfoxide)][$TCNQF_4$]. Indeed, the oxygen s.o.f. refinement indicates that an oxygen atom, equally disordered over two positions, is present on S3 (O2A and O2B) and S5 (O1A and O1B) (Fig. 3), respectively, a likely consequence of a second oxidation process due either to an intermolecular oxygen transfer or to aerial oxidation. The molecular entities organize in mixed donor–acceptor layers along *a*, in which alternated chair-like homotype chains are established along *b*. Intermolecular S···O distances, as short as 2.97 Å (O2A···S4), can be disclosed within the TTF-bis(sulfoxide) chains. The CT degree can be estimated through comparison between the bond lengths in the $TCNQF_4$ moieties with those in the neutral and radical anion $TCNQF_4$,

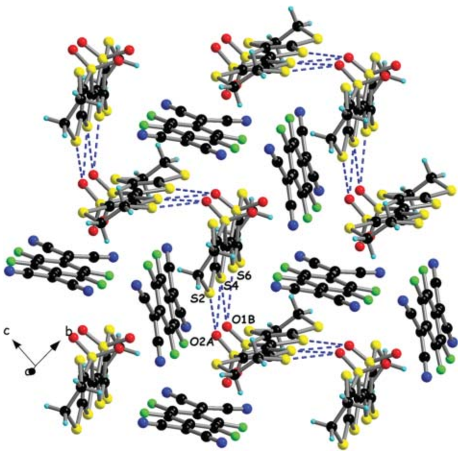


Fig. 3 Packing diagram for [BEDT-TTF-bis(sulfoxide)][TCNQF$_4$], with an emphasis on the short intermolecular S···O distances.

since upon reduction there is a change from quinoid to aromatic geometry. Accordingly,[18] we deduce for our compound a CT degree $\rho = -0.5$ e, which also correlates with the shift of the IR absorption bands for the C≡N bonds to lower frequencies (2192 and 2165 cm^{-1}) when compared with the neutral TCNQF$_4$ (2227 cm^{-1}).

Thus, the preparation of this crystalline CT complex clearly demonstrates that, in spite of the moderate kinetic stability in solution of the radical cation **2**$^{+\bullet}$, the isolation in certain conditions of stable solid CT compounds or radical cation salts derived from **2** should be possible. Another interesting aspect to investigate concerns the recently demonstrated potential of TTF derivatives as organic field effect transistors,[19] in which the charge transfer is promoted in the solid state.

In summary, we have synthesized and structurally characterized the first chiral BEDT-TTF-sulfoxide through a chemo and enantioselective sulfoxidation method. Chiral HPLC analyses revealed up to 74% ee selectivity and a very good separation of the enantiomers, which is promising for an application at preparative scale. Theoretical calculations demonstrate that the *inner* chiral sulfoxide directly participates in the electron delocalization in the corresponding radical cation salt. These results, together with the isolation of a crystalline charge transfer complex with TCNQF$_4$, demonstrate that the strategy of introducing chiral information at the sulfur atoms of BEDT-TTF is very promising and opens up new perspectives in the field of molecular electronics. Also, the introduction of an oxygen atom on the *outer* sulfur atoms, in order to lower the oxidation potential of the TTF-sulfoxide and to gain in kinetic stability, is under investigation.

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Notes and references

‡ Crystal data for **2c**: $C_{10}H_8O_1S_8$, $M = 400.64$, monoclinic, space group $P2_1/c$, $a = 6.581$, $b = 28.674$, $c = 8.284$ Å, $\alpha = 90$, $\beta = 106.91$, $\gamma = 90°$, $V = 1495.5$ Å^3, $Z = 4$, $T = 293(2)$ K, $\mu = 1.179$ mm^{-1}, $D_c = 1.779$ g cm^{-3}, 22 487 refl. measured, 1979 refl. with $I > 2\sigma(I)$, $R1 = 0.057$, w$R2 = 0.120$.

For **3**: $C_{22}H_8F_4N_4O_2S_8$, $M = 692.80$, monoclinic, space group Cc, $a = 26.776$, $b = 9.890$, $c = 10.644$ Å, $\alpha = 90$, $\beta = 110.44$, $\gamma = 90°$, $V = 2641.2$ Å^3, $Z = 4$, $T = 293(2)$ K, $\mu = 0.737$ mm^{-1}, $D_c = 1.742$ g cm^{-3}, 16 031 refl. measured, 3398 refl. with $I > 2\sigma(I)$, $R1 = 0.045$, w$R2 = 0.099$. CCDC 661107 (**2c**) and CCDC 661108 (**3**). For crystallographic data in CIF or other electronic format, see DOI: 10.1039/b714245e

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