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To cite this version:

HAL Id: hal-00502141
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Submitted on 15 Jul 2013

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Combining halogen bonding and chirality in a two-dimensional organic metal (EDT-TTF-I\(_2\))\(_2\)(D-camphorsulfonate)\(\cdot\)H\(_2\)O

Mariya Brezgunova,\(^a\) Kyung-Soon Shin,\(^a\) Pascale Auban-Senzier,\(^b\) Olivier Jeannin\(^a\) and Marc Fourmigué\(^{a,a}\)

Received 1st March 2010, Accepted 30th March 2010
First published as an Advance Article on the web 27th April 2010
DOI: 10.1039/c0cc00175a

A chiral organic conductor with metallic conductivity has been obtained by electrocrystallisation of a diiodotetrathiafulvalene derivative and enantiopure D-camphorsulfonate anion, associated in the solid state by halogen bonding interactions.

Within the field of molecular conductors, the search for a new phenomenon, the electrical magneto-chiral anisotropy effect,\(^1\) has led recently to an increasing effort toward the introduction of chirality in these materials.\(^2,3\) Up to now however, the formation of helical stacks still remains a challenge which has been met only once in the crystalline state from the spontaneous resolution of a TTF salt with mellitic acid.\(^4\) Besides, one can mention (i) chiral conducting polymers, based on pendant chiral substituents in polythiophenes,\(^5,6\) or on doping of polyaniline with chiral D-camphor sulfonic acid,\(^7\) and (ii) chiral conducting gels.\(^8\)

For tetrathiafulvalene-based (TTF) crystalline materials, essentially three routes have been investigated, (i) chiral TTFs donor molecules, (ii) chiral counter ions for electrocrystallisation experiments with achiral TTF derivatives, (iii) ternary phases with inclusion of a chiral solvent molecule.

While the first approach has offered several chiral conductors\(^9\) as well as complete series (\(R, S\) and \(R/S\)) of TTF-oxazoline-based metals,\(^10\) the two other approaches, obviously less costly synthetically, have met with more limited success. One can mention BEDT-TTF salts with either antimony tartrate dianion, [Sb\(_2\)(L-tart)]\(^{2-}\),\(^11\) or with iron tris(oxalate) \([\text{NH}_2\text{Fe(C}_2\text{O}_4)_3]\)^\(-\) complex in the presence of chiral \((S)/\text{c}-\text{sec}-\)phenethyl alcohol as guest molecule.\(^12\) In both salts, the chirality of the anion/solvent counterpart does not appear to strongly influence the organisation of the conducting slabs which adopt typical packing motifs known in BEDT-TTF salts\(^13\) such as \(\alpha\)-type in the former,\(^11\) \(\alpha\) and \(\beta''\)-type in the latter.\(^12\)

We postulated that the introduction, in crystalline organic conductors, of specific \(\text{intermolecular}\) interactions between the anionic and cationic moieties, could favour a more efficient chiral induction, for example between a chiral anion and the conducting slabs. In that respect, tetrathiafulvalene derivatives bearing halogeno substituents have been successfully used in the elaboration of conducting solids, exhibiting halogen bonding interactions with the counter-ions.\(^14\) This halogen bonding describes a non-covalent interaction involving halogens as electrophiles.\(^15\) Based on its high strength and directionality, it appears now as a very efficient tool in crystal engineering,\(^16\) also used for example for the resolution of racemic organic halides.\(^17\) Note also that the oxidation of such halogeno TTF derivatives into radical \(cations\) actually enhances their halogen bond donor ability.\(^18\)

We describe here a very first example along these lines, where a partially oxidised iodinated tetrathiafulvalene, EDT-TTF-I\(_2\),\(^19\) is anchored to a chiral anion, D-camphor sulfonate, through strong halogen bonding interactions, to afford a highly conductive metallic salt.

Electrocrystallisation of EDT-TTF-I\(_2\) in the presence of tetrabutylammonium D-camphorsulfonate\(^19\) (noted D-Camph) in 1,1,2-trichloroethane (TCE) afforded black parallelepipedic crystals formulated as (EDT-TTF-I\(_2\))(D-Camphorsulfonate)\(\cdot\)H\(_2\)O (I), together with a second less crystalline phase (brown thin plates) incorporating solvent. Salt I crystallises in the triclinic system,\(^4\) in the chiral space group \(P1\), with two crystallographically independent EDT-TTF-I\(_2\) molecules (noted A and B in the following) in the unit cell, with one chiral D-camphor sulfonate and one water molecule (Fig. 1).

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\(^a\) Sciences Chimiques de Rennes, Université Rennes 1 & CNRS UMR 6226, Campus de Beaulieu, 35042 Rennes, France. E-mail: marc.fourmigue@univ-rennes1.fr
\(^b\) Laboratoire de Physique des Solides, Université Paris-Sud, UMR CNRS 8502, Bât. 510, 91405 Orsay, France

\(^\dagger\) Electronic supplementary information (ESI) available: Crystallographic data for I and Fig. S1–S2. CCDC 768025. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/c0cc00175a

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Fig. 1 Projection view along \(a\) of the unit cell of I.
The SO$_3$ moiety is disordered on two positions with refined occupation ratio of 58:42. The compound adopts a layered structure with segregation of the partially oxidised donor molecules, and the water molecule embedded in the anionic layer. Of particular note is the halogen bonding interaction network which develops at the conducting/anionic interface.

As shown in Fig. 2, donor molecule A takes part in two I–O contacts (Table 1), the shortest of the two with the anionic SO$_3^-$ moiety, the longer with the carbonyl oxygen atom. On the other hand, molecule B interacts only through one iodine atom with the water molecule. The water molecule is found at close distance of oxygen atoms of two SO$_3^-$ groups (2.82–2.98 Å), indicative of HO–H⋯O–S hydrogen bonds.

Most importantly, these halogen interactions with the enantiopure chiral anion are also correlated with the A and B molecules geometry and charge. Indeed, we observe (Fig. 2) that in molecule A, the inner C=C bond length is notably longer and the C=S notably shorter (av. value 1.729 Å) than in molecule B (av. C=S value: 1.750 Å). These bond length evolutions are known to be correlated with the actual charge of the TTF donor molecules and clearly indicate that some charge disproportionation has taken place, with the most oxidized molecule (A) more strongly halogen bonded to the chiral anion, an illustration of the electrostatic nature of this interaction. A comparison with literature data on EDT-TTFI salts (Fig. S1, ESI) gives an approximate $\Delta Q$ charge distribution. Despite this charge alternation, the salt exhibits a metallic behaviour (Fig. 3) above 200 K. A weak localization takes place below 200 K with an activation energy of 0.016 eV (Fig. S2, ESI).

This salt stands out among other halogen bonded TTF-based salts by two distinct features, (i) a sizeable charge disproportionation between molecules A and B with the most oxidized one favoured for halogen bonding interaction with the chiral anion, (ii) a metallic behaviour despite this charge disproportionation, as an insulating charge-ordered state would have been anticipated. In order to understand this peculiar behaviour, tight-binding band structure calculations\textsuperscript{21} of the extended wavefunction were conducted.\textsuperscript{23} Calculations of the six different $\beta_{\text{HOMO-HOMO}}$ interaction energies between molecules within the conducting slab (Fig. 4) show strong and comparable interactions within the stacks running along $b$ ($\beta_{AB1} = 0.34$ eV, $\beta_{AB2} = 0.31$ eV) while weaker interactions characterise the inter-stack contacts ($\beta_{aa} = 0.045$ eV, $\beta_{bb} = 0.043$ eV, $\beta_{ab1} \approx 0.0$ eV, $\beta_{ab2} \approx 0.016$ eV).

This solid state organisation and interaction network within the slabs shown in Fig. 4 is reminiscent of the so-called $\beta$ phases observed in BEDT-TTF salts,\textsuperscript{13} but with a regular bond-over-ring interaction all along the stacks (Fig. 5). Indeed, the weak dimerisation ($\beta_{ab1} \approx \beta_{ab2}$) found here is not typical of $\beta$ phases, usually characterised by a sizeable alternation within the stacks.

The other difference with the $\beta$ phases arises here from the loss of inversion centre and the inequivalence of the two TTF molecules taking part in the head-to-tail association within the stacks, since one is strongly halogen bonded to the chiral anion, while the other is not.

The band structure (Fig. 6a) shows that the Fermi level cuts the upper band no only along the $\Gamma \rightarrow Y$ stacking direction but also along the $\Gamma \rightarrow X$ direction, indicating here a remarkable two-dimensional character for the electronic structure of the salt, also confirmed by the calculated closed Fermi surface (Fig. 6b). Even if this result may appear as surprising, the larger number of interchain interactions and the weakened intrachain interaction associated with the large energy difference between the HOMOs of the two different TTFs lead quite naturally to this result.

**Table 1** Geometrical features of the halogen bond interactions in I

<table>
<thead>
<tr>
<th>Interaction</th>
<th>$I \cdots O$ (Å)</th>
<th>$C \cdots O$ (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$I_1 \cdots O_1$</td>
<td>2.999(8)</td>
<td>149.6(3)</td>
</tr>
<tr>
<td>$I_2 \cdots O_{1A}$</td>
<td>2.703(15)</td>
<td>174.8(4)</td>
</tr>
<tr>
<td>$I_2 \cdots O_{1B}$</td>
<td>2.796(17)</td>
<td>171.8(4)</td>
</tr>
<tr>
<td>$I_3 \cdots O_2$</td>
<td>2.811(9)</td>
<td>179.2(3)</td>
</tr>
</tbody>
</table>

**Fig. 2** Detail of the halogen bonding interactions in I.

**Fig. 3** Temperature dependence of the resistivity of I.

**Fig. 4** Lateral view of the conducting slab in I, showing the intermolecular interactions (noted in red).
This salt represents the very first example of an organic conductor with metallic character, where a strong intermolecular interaction links together the conducting slabs and a chiral anionic counterpart. The loss of inversion centre imposed by the presence of the enantiopure D-camphor sulfonate anion leads to two crystallographically independent donor molecules, which are strongly differentiated here through the setting of specific halogen bonding interactions with the most oxidized one.

This result opens wide perspectives toward the elaboration of chiral conductors and developments are now considered with other functionalised TTF molecules, and the same D-camphor sulfonate anion. Furthermore, considering the very large number of potential chiral organic anions easily available which can act as hydrogen or halogen bond acceptors toward properly substituted TTF derivatives (amides, halides, etc), this route appears as extremely promising, as already demonstrated here.

Financial support was from the ANR (France) through contract n° ANR-08-BLAN-0091-02. We also thank CDFIX (Rennes) for access to X-ray diffraction facilities and E. Canadell (ICMAB, Barcelona) for insightful comments about the electronic structure calculations.

Notes and references

† Crystal data for I: C_{6}H_{12}I_{2}O_{5}S_{13}, M = 1339.82 g mol^{-1}, crystal dimensions 0.20 × 0.16 × 0.05 mm, triclinic, space group P1, a = 7.6737(2), b = 8.1634(2), c = 17.7545(6) Å, α = 79.5930(19), β = 87.517(2), γ = 65.233(2), V = 992.64(5) Å^3, Z = 1, \rho_{calcd} = 2.241 g cm^{-3}, F(000) = 669, \mu_{calcd} = 3.98 mm^{-1}. \rho = 293 K, \omega_{min} = 54.98°. Final results (for 447 parameters) were \R = 0.0265, w/R^2 = 0.0628 and S = 1.022 for 7679 reflections [6453 with I > 2\sigma(I)]. § Electrical resistivity was measured on single crystals in a four points configuration with annular contacts made by gold evaporation and gold wires attached with silver paste. A low-frequency lock-in detection was used with a current intensity I = 1 μA and low temperature (in the range 20–300 K) was provided by a cryocooler set up.

19 This salt was prepared from D-camphor sulfonic acid and nBu4NOH in water, filtration of the precipitate, extraction with CH2Cl2, drying on MgSO4 and evaporation. See (a) R. Echarri, M. I. Mathieu, C. Claver, S. Castillon, A. Alvarez-Larena and J. F. Piniella, Tetrahedron Lett., 1997, 38, 6457; (b) N. Mofaddel, H. Krajian, D. Villemín and P. L. Desbene, J. Chromatogr., A, 2008, A1211, 142.