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Combining halogen bonding and chirality in a two-dimensional organic metal (EDT-TTF-I$_2$)$_2$(*D*-camphorsulfonate)·H$_2$O†

Mariya Brezgunova,[a] Kyung-Soon Shin,[a] Pascale Auban-Senzier,[b] Olivier Jeannin[a] and Marc Fourmigué*[a]

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)$_2$]$^{2-}$,[11] or with iron tris(oxalate) [(NH$_4$)Fe(C$_2$O$_4$)$_3$]$^{2-}$ complex in the presence of chiral (*S*)-*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 α-type in the former,[11] α and β''-type in the latter.[12]

We postulated that the introduction, in crystalline organic conductors, of specific *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$_2$,[18] is anchored to a chiral anion, *D*-camphor sulfonate, through strong halogen bonding interactions, to afford a highly conducting metallic salt.
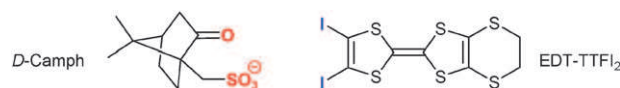
Electrocrystallisation of EDT–TTF-I$_2$ in the presence of tetrabutylammonium *D*-camphorsulfonate[19] (noted *D*-Camph) in 1,1,2-trichloroethane (TCE) afforded black parallelepipedic crystals formulated as (EDT-TTF-I$_2$)$_2$(*D*-Camphorsulfonate)·H$_2$O (**I**), together with a second less crystalline phase (brown thin plates) incorporating solvent. Salt **I** crystallises in the triclinic system,‡ 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).
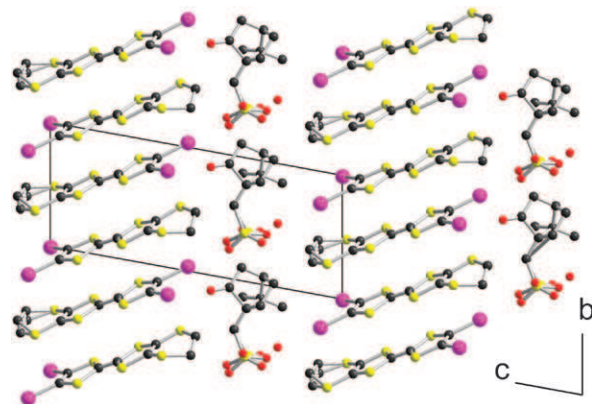

Fig. 1 Projection view along *a* of the unit cell of **I**.

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† 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

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 $C_i\!=\!C_i$ bond length is notably longer and the C_i–S notably shorter (av. value 1.729 Å) than in molecule B (av. C_i–S value: 1.750 Å). These bond length evolutions are known to be correlated with the actual charge of the TTF donor molecules[20] 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$_2$ salts (Fig. S1, ESI)† gives an approximate $[A^{+0.75}B^{+0.25}]$ charge distribution. Despite this charge alternation, the salt exhibits elevated room temperature conductivity ($\sigma_{RT} \approx 3$–5 S cm^{-1}) and 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[21] of the extended
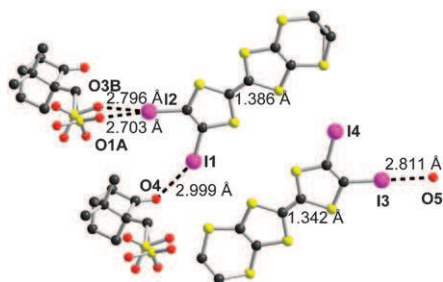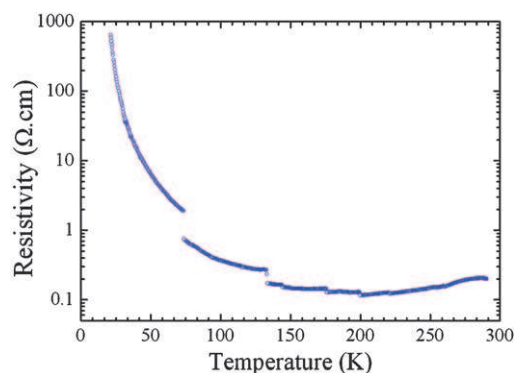

Fig. 3 Temperature dependence of the resistivity of **I**.

Hückel type[22] were conducted.[23] Calculations of the six different $\beta_{HOMO\cdots HOMO}$ 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, $\beta_{ab2} = 0.016$ eV).

This solid state organisation and interaction network within the slabs shown in Fig. 4 is reminiscent of the so-called β phases observed in BEDT-TTF salts,[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 β phases, usually characterised by a sizeable alternation within the stacks.

The other difference with the β 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.
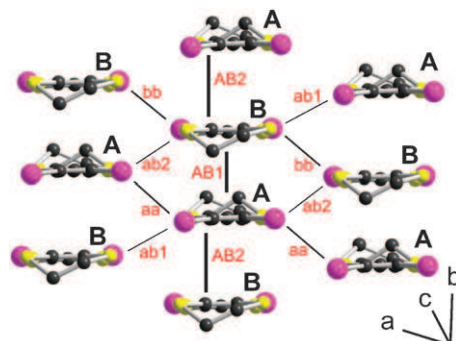

Fig. 2 Detail of the halogen bonding interactions in **I**.

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

Interaction	I···O (Å)	C–I···O (°)
$I_1\cdots O_4$	2.999(8)	149.6(3)
$I_2\cdots O_{1A}$	2.703(15)	174.8(4)
$I_2\cdots O_{3B}$	2.796(17)	171.8(4)
$I_3\cdots O_5$	2.811(9)	179.2(3)

Fig. 4 Lateral view of the conducting slab in **I**, showing the inter-molecular interactions (noted in red).
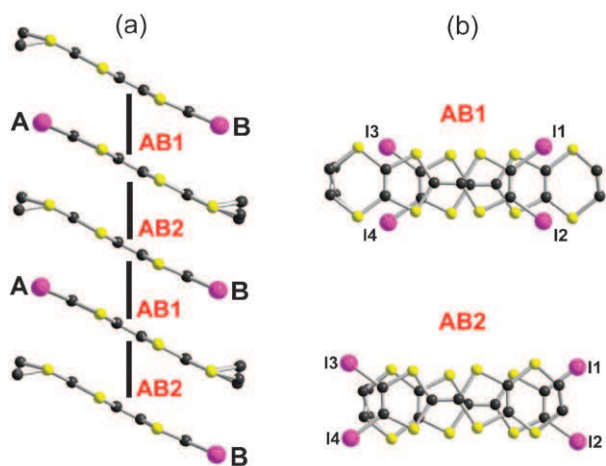
Fig. 5 (a) View of one stack running along *b* and (b) detail of the overlap interactions AB1 and AB2 within the stack.

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.
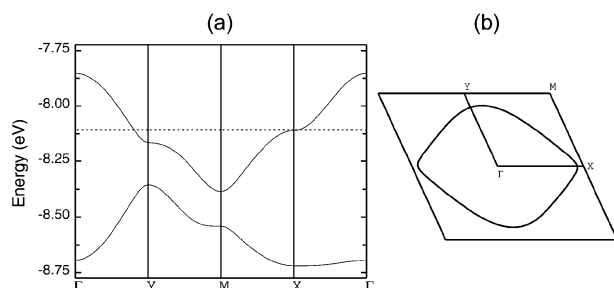
Fig. 6 (a) Calculated band structure of **I**. The dotted line indicates the Fermi level. (b) Calculated Fermi surface for **I**. $\Gamma = (0,0)$, $X = (a^*/2, 0)$, $Y = (0, b^*/2)$, $M = (a^*/2, b^*/2)$.

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