Anion size control of the packing in the metallic versus semiconducting chiral radical cation salts (DM-EDT-TTF)$_2$XF$_6$ (X = P, As, Sb)†

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Control of the structural type in metallic enantiopure and racemic radical cation salts is achieved through hydrogen bonding interactions between the chiral donor DM-EDT-TTF and the XF$_6$ anions (X = P, As, Sb), determined by the anion size and the chiral information.

Chiral tetrathiafulvalenes (TTF) have attracted much attention especially in the last decade, as they can provide chiral crystalline molecular conductors which, among other interesting features, should in principle show electrical magneto-chiral anisotropy (eMChA), recently observed for the first time in TTF based materials. The corresponding enantiomeric conductors (DM-EDT-TTF)$_2$ClO$_4$ have been obtained by electrocrystallization of either (S,S) and (R,R) dimethyl-ethylenedithio-tetrathiafulvalene (DM-EDT-TTF) (Scheme 1). Here the chirality conferred by the two stereogenic carbon atoms has been transferred at the microscopic scale providing enantiomorphous crystals.

While chirality in TTF precursors has been introduced through various functions such as stereogenic carbon atoms, sulfoxides, allenes, binapthyls, helicenes, para-cyclophanes, and even expressed at supramolecular level in helical aggregates, examples of conducting chiral radical cation salts are still rare comparatively. Besides the ones derived from DM-EDT-TTF, they include those prepared out of dimethylated (DM-BEDT-TTF) and taramethylated bis(ethylenedithio)-tetrathiafulvalene (TM-BEDT-TTF), the last donor representing the first reported enantiopure TTF derivative.

Besides the manifestation of eMChA, which is a synergistic effect of the chirality on the resistivity of chiral conductors measured in a magnetic field collinear with the current, the conductivity of enantiopure conductors can be higher than that of the racemic counterparts when structural disorder is present in the latter despite identical cell parameters and donor anion ratio. Such differences have been observed in enantiomeric and racemic radical cation salts based either on TTF-oxazolines or TM-BEDT-TTF. However, in the absence of crystalline disorder the conducting properties of the enantiopure and racemic forms were found to be similar. Less often is the case where enantiopure and racemic salts prepared from the same donor in the same conditions show completely different packings. In this respect we have recently described the complete series of radical cation salts (DM-EDT-TTF)$_2$PF$_6$ for which the enantiopure compounds crystallized in the monoclinic space group P2$_1$ with four independent donor molecules and two anions in the unit cell, while the racemic salt crystallized in the triclinic centrosymmetric space group P1 with one independent donor in the asymmetric unit and the anion located on an inversion centre, An interesting feature of these salts concerns the templating role of the PF$_6$ anion through the establishment of C–H···F hydrogen bonding, leading to packings where donor layers are interconnected via the anions, all the fluorine atoms being involved in hydrogen bonding with either vinyl C=CH$_2$ methyne CH$_3$ or methyl protons. The final architectures very likely result from a delicate balance between these anion–donor hydrogen bonding and van der Waals S···S and orbital overlap interactions typical for oxidized TTF donors. We hypothesize that the massive difference in packing, and subsequently in transport properties, between the racemic and enantiopure salts finds its origin in this competition of intermolecular interactions. Thus, the use of the bigger congeners AsF$_6$ and SbF$_6$ could possibly influence on the stability of one or the

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other phase, i.e. monoclinic or triclinic, or maybe lead to completely new packings. Although generally for a given TTF type donor isoradical structural radical cation salts are observed within the series PF$_6$, AsF$_6$, SbF$_6$, there are only few cases$^{22,23}$ to the best of our knowledge, where structural differences occur, including the (EDT-TTF)$_2$X$_n$ (X = P, As) salts, where the one with PF$_6$ crystallized in an orthorhombic phase, while for the AsF$_6$ salt a second triclinic phase was observed.$^{22}$ We describe herein complete series of chiral radical cation salts of DM-EDT-TTF with AsF$_6$ and SbF$_6$ anions and compare their structural features and conducting properties with the previously reported PF$_6$ counterparts.

Enantiopure and racemic donor 1, prepared as previously described,$^{20}$ have been electrocrystallized in chloroform in the presence of [(n-Bu)$_2$N]X$_n$ (X = As, Sb), the experimental conditions being identical in all the experiments with those employed for the PF$_6$ series.$^{20}$ Unexpectedly, while for the SbF$_6$ anion only one crystalline phase has been obtained either for the enantiopure or the racemic donor, in the electrolycrystallization cells with the AsF$_6$ anion three types of crystals have been collected for enantiopure 1 and only one type when racemic 1 was used. The racemic AsF$_6$ and SbF$_6$ crystalline compounds are formulated as $(rac)1$X$_n$ (X = As, Sb) and are isostructural with the previous described PF$_6$ metallic salt.$^{20}$ They crystallize in the triclinic centrosymmetric space group $\overline{P}$1 with one independent donor molecule and half of anion, located on an inversion centre, in the asymmetric unit (see ESI† for details on single crystal X-ray measurements and Table S1 for crystal parameters). The central C–C bond lengths (1.371(6) Å and 1.369(5) Å for As and Sb, respectively) together with the internal C–S bond lengths, with an average value of 1.738 Å for both compounds, are in agreement with a +0.5 oxidation state of the donor and are comparable with the values measured for the PF$_6$ salt (Table S2, ESI†). The paramount role of the anion in the solid state architecture is evidenced through the complex set of hydrogen bonding interactions established between the fluorine atoms and CH$_3$, CH$_2$, and CH$_{Me}$ hydrogen atoms$^{24}$ leading to a packing where the anions are surrounded by donors, all the F atoms being involved in such short C–H···F contacts (Fig. 1 for SbF$_6$ Fig. S1 and S2 for PF$_6$ and AsF$_6$ and Table S3, ESI† for C–H···F distances and angles).

When comparing the three racemic structures there is a clear increase of the average C–H···F distances by changing the anion from PF$_6$ to AsF$_6$, and then to SbF$_6$ (Table S3, ESI†), while the intrastack intermolecular S···S distances remain essentially the same, in the range of 3.63–3.69 Å (vide infra), thus ensuring an optimum overlap between open shell species. As the average X–F bond length varies from 1.57 Å for P to 1.69 Å for As, and then to 1.85 Å for Sb, clearly the average C–H···F distance has to vary in the opposite way in order to keep the same arrangement of the donors, providing a fine control of the solid state architecture at the nanoscale level. However, this type of packing allows the involvement of the six fluorine atoms in short C–H···F contacts for the three anions in spite of their difference in size.

The situation is more complex for the enantiopure donors, since, as mentioned above, three different crystalline phases were obtained with the AsF$_6$ anion, while only one phase was isolated with SbF$_6$ and PF$_6$. As the enantiomeric pairs (S,S) and (R,R) were isostructural according to crystal cell determination, only the former will be detailed for the new phases. The enantiopure radical cation salt with the SbF$_6$ anion formulated as [(S,S)-1]SbF$_6$, is, interestingly, isostructural with the racemic phase, excepting the space group which is the non-centrosymmetric $P$ in this case. The asymmetric unit contains one anion and two independent donor molecules A and B alternating in the stack (Fig. 2). This is in sharp contrast with the previous results in the PF$_6$ system where the monoclinic P2$_1$ structure was formed by 4 independent donor molecules and 2 anions.$^{20}$ Interestingly, the link between the two situations is provided by the AsF$_6$ anion for which both crystalline phases are formed, i.e. triclinic $P$ [[(S,S)-1]AsF$_6$ and monoclinic P2$_1$ [(S,S)-1]AsF$_6$, together with a third one, monoclinic P2$_1$ [(S,S)-1]AsF$_6$]. The second is thus isostructural with the poorly conducting [(S,S)-1]PF$_6$ phase$^{20}$ and will not be further detailed. As for the racemic counterparts, in the enantiopure triclinic phases [(S,S)-1]X$_n$: (X = As, Sb) the bond distances indicate donor molecules in mixed valence state (Table S4, ESI†). While the packings of $[(rac)1]$SbF$_6$ (Fig. 1), [(S,S)-1]SbF$_6$ (Fig. 2) and [(S,S)-1]AsF$_6$ (Fig. S3, ESI†) present the same general features, some very fine differences in the C–H···F contacts can be disclosed, as the disposition of the stereo- genic centres is different. Accordingly, the differences concern especially the interactions involving CH$_{Me}$ and CH$_2$ groups. In order to satisfy at maximum the hydrogen bonding demand of the fluorine atoms, the donors slightly shift within the stack in order to optimize the C–H···F contacts (Table S5, ESI†).

The C–H···F distances are clearly larger in average for the AsF$_6$ salt (3.50 and 3.46 Å for H$_2$C–···F and MeH–···F distances, respectively) than for the SbF$_6$ one (3.45 and 3.40 Å for H$_2$C–···F and MeH–···F distances, respectively) (Table S5, ESI†). Consequently, the fluorine atoms will be less involved in stabilizing hydrogen bonding contacts when going from SbF$_6$ to AsF$_6$ in the triclinic
phase, therefore the donors will tend to adopt a different packing with the AsF$_6$ anion in the monoclinic 4:2 phase in order to maximize the hydrogen bonding interactions. This tendency is even higher for the PF$_6$ anion, smallest of the series, exclusively providing the monoclinic phase in which all the fluorine atoms are involved in short C–H⋯F contacts (Fig. S4–S6, ESI†). Clearly, throughout this series, the chiral centres play the determining role in the fine tuning of the intermolecular interactions in the donors–anion aggregates, favouring either the triclinic (SbF$_6$), monoclinic (PF$_6$) or both (AsF$_6$) phases. Worth mentioning is that in the structures discussed thus far the methyl groups adopt equatorial (eq, eq) positions. However, in the third crystalline phase obtained with the AsF$_6$ anion the methyl groups show axial (ax, ax) disposition (Fig. S7 and S8, ESI†). This compound, formulated as [(S,S)-1]$_2$(AsF$_6$)$_2$ (its enantiomeric (R,R) counterpart is isostructural), crystallizes in the monoclinic non-centrosymmetric space group $P2_1/a$ with two independent donors and two anions in the asymmetric unit. The anions engage in hydrogen bonding interactions with the donors (Fig. S7, ESI†) which form strong dimers according to the very short intradimer S⋯S distances (Fig. S8, ESI†). The dimers further arrange in step-chains along the $a$ direction. This type of arrangement is reminiscent with the one observed in the isorotational insulating radical cation salt [(rac-1)ClO$_4$]$_2$.

Single crystal temperature dependent resistivity measurements on triclinic [1]$_2$XF$_6$ (X = As, Sb) show metallic behaviour in the high temperature range both for racemic (Fig. S9, ESI†) and enantiopure salts (Fig. 3).

Room temperature conductivity values are of the same order of magnitude for the enantiopure salts, i.e. 90 S cm$^{-1}$ for SbF$_6$ and 70 S cm$^{-1}$ for AsF$_6$, being slightly lower than those for the racemic salts, amounting to 250 S cm$^{-1}$ for PF$_6$ and 125 S cm$^{-1}$ for AsF$_6$. Most importantly, the enantiopure phases are metallic with a broad minimum of resistivity around 200 K then a metal to insulator (MI) transition takes place around 130–135 K. This temperature dependence of the resistivity is similar to that of racemic salts with only one symmetry non-equivalent donor (Fig. 3), amounting to 250 S cm$^{-1}$ for PF$_6$ and 125 S cm$^{-1}$ for AsF$_6$. Most importantly, the enantiopure phases are metallic with a broad minimum of resistivity around 200 K then a metal to insulator (MI) transition takes place around 130–135 K. This temperature dependence of the resistivity is similar to that of racemic salts with only one symmetry non-equivalent donor. This analysis is confirmed by the calculated Fermi surface (Fig. 5a) for [(S,S)-1]$_2$SbF$_6$ and Tables S7–S10 (ESI†) for the other salts. Thus, from the viewpoint of the HOMO–HOMO interactions, these stacks are quite uniform chains of interacting HOMOs. Since the stacks run along the $(a-b)$ direction, the two bands of the system (there are two donors per repeat unit of the donor layer) should exhibit strong dispersion along this direction (not far from $\Gamma \rightarrow S$ in reciprocal space) and considerably smaller along the perpendicular direction (not far from $\Gamma \rightarrow M$ in reciprocal space).

This is in fact what the calculated band structure (Fig. 5a for [(S,S)-1]$_2$SbF$_6$, see ESI†) shows. The interstack interactions (III to V/VI) are one order of magnitude smaller but their contributions add to give a quite sizeable dispersion to the upper band along the interstack direction (i.e. approximately along $\Gamma \rightarrow M$) so that the system should be seen as a series of substantially coupled and quite uniform stacks along the $(a-b)$ direction. Because of the stoichiometry, the two HOMO bands (Fig. 5a) should contain one hole so that the upper band is half-filled. Since this band is quite dispersive, these salts are predicted to be metallic, in agreement with our conductivity measurements.

This analysis is confirmed by the calculated Fermi surface (Fig. 5b) which is built from a series of warped open lines perpendicular to the stacks direction. Thus, the present salts should be pseudo-one-dimensional metals at room temperature.

Can this analysis provide any guideline in trying to correlate the structural and transport properties of this family of salts? This is admittedly not an easy task because of the similarity in electronic structures and conductivity measurements (considering a larger number of crystals for every compound may be also important) along the series. Looking at the different interaction energies for all compounds of this series (Tables S6–S10, ESI†) we note that the two types of interstack interactions (III/IV and V/VI) are not only one order of magnitude smaller than the intrastack ones but their

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**Fig. 3** Temperature dependence of the electrical resistivity $\rho$ for a single crystal of [(S,S)-1]$_2$AsF$_6$ (red line) and a single crystal of [(S,S)-1]$_2$SbF$_6$ (blue line).
variation along the series is also considerably smaller. Thus, the intrastack HOMO⋯HOMO interactions are those dominating the shape of the upper partially filled band, i.e. the transport properties of the salts. For chains like those along (a-b) in Fig. 4, with two different but strong interactions along the chain, the slope of the upper band around the Fermi level should be dominated by the strength of the weaker of the two interactions. Thus the $|\langle \text{HOMO-HOMO} \rangle|$ value for interaction II should be an adequate electron structure parameter allowing classifying the different salts according to their conductivity: larger values of this parameter should be associated with higher conductivities. Using this simple guideline and the calculated $|\langle \text{HOMO-HOMO} \rangle|$ values it follows that: (i) the conductivity should decrease along a given type of salt when the size of the anion increases, (ii) for the same anion the (rac)-salts should be more conductive when there is no disorder. When examining the structural origin of the variation in the $|\langle \text{HOMO-HOMO} \rangle|$ values it is clear that the main factor lies in the evolution of the intermolecular $S\cdots S$ contacts and to a lesser extent the slight sliding motions induced by the different anions. Thus, the chiral information is transmitted to the conductivity carriers through the F$_{\text{anion}}$⋯H$_{\text{donor}}$ interactions which, in turn, together with the anion size, influence the intrastack interactions, and, more specially, the weaker of the two intrastack interactions. This simple approach represents a step further with respect to similar anion size based ideas since suggests differences between the enantiopure and racemic salts. The presently known conductivity results are grossly in agreement with these ideas although more extensive work is in order. In particular the values for the SbF$_6$ salts may require further attention.

Further work in this series will be devoted to the investigation of the conducting properties of the enantiopure salts under magnetic field and the use of variable composition alloys of XF$_6$ anions in order to have a complete picture of these intriguing systems.

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### Notes and references