Chiral EDT-TTF precursors with one stereogenic centre: substituent size modulation of the conducting properties in the (R-EDT-TTF)₂PF₆ (R = Me or Et) series

Nabil Mroweh,^a Pascale Auban-Senzier,^b Nicolas Vanthuyne,^c Enric Canadell^d and Narcis Avarvari^{*a}

^a MOLTECH-Anjou, UMR 6200, CNRS, UNIV Angers, 2 bd Lavoisier, 49045 ANGERS Cedex, France. E-mail: narcis.avarvari@univ-angers.fr

^b Laboratoire de Physique des Solides, UMR 8502, Bât. 510, Université Paris-Sud, 91405 Orsay, France

^c Aix Marseille Université, CNRS, Centrale Marseille, iSm2, Marseille, France

^d Institut de Ciència de Materials de Barcelona (CSIC), Campus de la UAB, E-08193 Bellaterra, Spain

Abstract

Modulation of the packing of the donors in the solid state and of the conducting behaviour is achieved in chiral radical cation salts based on the mono-alkylated donors methyl-ethylenedithio-tetrathiafulvalene (Me-EDT-TTF **1**) and ethyl-ethylenedithio-tetrathiafulvalene (Et-EDT-TTF **2**), underlying the paramount role of the number of stereogenic centres and substituent steric hindrance. Both donors have been prepared as racemates and then separated as pure enantiomers by chiral HPLC. Electrocrystallization experiments provided two complete series of crystalline radical cations salts formulated as [(R)-**1**]₂PF₆, [(S)-**1**]₂PF₆, [(rac)-**1**]₂PF₆ and [(R)-**2**]₂PF₆, [(S)-**2**]₂PF₆ and [(rac)-**2**]₂PF₆•(THF), respectively. The mixed valence salts of **1** show metal-like conductivity in the high temperature regime, while the radical cation salts of **2** are semiconductors, with a much higher conductivity for the enantiopure compounds than the racemic one. Tight-binding band structure calculations of the extended Hückel type performed for all the materials explain the observed conducting behaviour and put forward the differences in the intermolecular interactions triggered by the change of substituent between **1** and **2**.

1. Introduction

The influence of chirality on the conducting properties is a fascinating topic within the frame of the multifunctional materials,¹ as it can give rise to new phenomena such as the electrical magnetochiral anisotropy (eMChA) effect when an external magnetic field is applied parallel to the direction of the current.² This synergistic effect has been experimentally observed so far only in few chiral systems including helical bismuth wires,² single-walled carbon nanotubes,³ superconducting WS₂ nanotubes,⁴ or elemental tellurium.⁵ However, the only observation of eMChA in a bulk molecular system was recently reported for enantiomorphous crystalline radical cation salts (DM-EDT-TTF)₂ClO₄ (DM-EDT-TTF = dimethyl-ethylenedithio-tetrathiafulvalene, Scheme 1) showing metal-like conductivity.⁶ Beside the eMChA effect observed in the latter, other chirality induced influence on conductivity was observed in radical cation salts series such as (TM-BEDT-TTF)I₃ (TM-BEDT-TTF = tetramethyl-bis(ethylenedithio)-tetrathiafulvalene, Scheme 1) where the enantiopure forms shown higher conductivity than the racemic counterpart because of the structural disorder in the latter,⁷ or (DM-EDT-TTF)₂PF₆ for which the enantiopure compounds were semiconductors, while the racemic material shown metallic conductivity,⁸ as a consequence of the different packing and charge localization. Since tetrathiafulvalenes (TTF) undoubtedly represent the most important molecular scaffold to introduce chirality in order to access electroactive precursors for chiral conductors,⁹ much endeavour has been devoted to the preparation of various families of chiral TTFs such as TTF-oxazolines,^{10,11,12,13} substituted BEDT-TTFs (BEDT-TTF = bis(ethylenedithio)-tetrathiafulvalene),^{14, 15} TTF-sulfoxides,¹⁶ bis(pyrrolo)-TTF,^{17, 18} TTF-*para*-cyclophanes,^{19,20} TTF-helicenes,²¹ TTF-binaphthyls,^{22,23} and others. Nevertheless, conducting radical cation salts have been especially obtained with DM-EDT-TTF (Scheme 1),^{6,8,24,25} dimethyl-BEDT-TTF (DM-BEDT-TTF, Scheme 1)^{26,27} and TM-BEDT-TTF (Scheme 1)^{28, 29, 30} methylated precursors, thus containing at least two stereogenic centres. Since the introduction of two methyl groups on the ethylene bridge of EDT-TTF drastically influence the crystallization of the radical cation salts, the packing of the donors and, consequently, the electron transport properties, we have decided in the present investigation to reduce to one only the number of stereogenic centres in EDT-TTF and also to modulate the steric hindrance of the substituents. Besides, the interest of the EDT-TTF moiety relies as well on the propensity of the oxidized form to engage in intermolecular hydrogen bonding with the counter ions, thus highlighting the templating role of the anion allowing the

modulation of the crystalline packing, as observed in the series (DM-EDT-TTF)₂XF₆ (X = P, As, Sb).^{8,24}

Scheme 1 Enantiopure BEDT-TTF and EDT-TTF based donors; Me-EDT-TTF (**1**) and Et-EDT-TTF (**2**) are described in this work.

We describe herein the synthesis and characterization of the unprecedented enantiopure TTF donors Me-EDT-TTF **1** and Et-EDT-TTF **2** (Scheme 1) containing only one stereogenic centre together with complete series of radical cation salts of **1** and **2** with the PF₆[−] anion. The conducting properties of the new chiral conductors were investigated and correlated with tight-binding band structure calculations.

2. Results and discussion

2.1 Synthesis and characterization of the neutral donors **1** and **2**

The key step in the synthesis of donors **1** and **2** is the double nucleophilic substitution reaction between the 2-thioxo-1,3-dithiole-4,5-dithiolato (dmit^{2−}), generated *in situ* from the protected dithiolate **3**, and 1,2-dibromo-propane or 1,2-dibromo-butane, respectively, to provide the thiones **4** and **5** as racemic mixtures (Scheme 2 and ESI). Then, phosphite mediated heterocoupling between **4** or **5** and the dithiolone diester **6**, followed by a double decarboxylation of the resultant TTF-diester **7** and **8**, afforded racemic **1** and **2**.

Scheme 2 Synthesis of racemic Me-EDT-TTF (**1**) and Et-EDT-TTF (**2**).

Note that while the preparation of (*rac*)-Me-EDT-TTF **1** has been previously briefly mentioned, though without any mention to chirality,^{31,32} the donor **2** has not been reported to date. Cyclic voltammetry measurements show the characteristic pair of reversible oxidation processes occurring at +0.45 (**1**) and +0.45 (**2**) (V vs. SCE) for the formation of the radical cation, and then at +0.75 (**1**) and +0.76 (**2**) (V vs. SCE) for the formation of the dication (Fig. S1, ESI), suggesting the new donors are valuable precursors for the preparation of chiral radical cation salts by electrocrystallization. Both racemic donors have been successfully separated as pure enantiomers by semi-preparative chiral HPLC on Lux-Cellulose-3 column (Fig. S2-S4 for **1** and Fig. S5-S7 for **2**, ESI). The optical rotations and circular dichroism (CD) spectra were measured for the two pairs of enantiomers and are indicative for their optical purity (ESI). The absolute configurations for (*R*)-**1**/*S*)-**1** and (*R*)-**2**/*S*)-**2**, respectively, have been attributed by comparison of the CD spectra with those of TM-BEDT-TTF⁷ and DM-EDT-TTF³³ previously described, and, ultimately, by single crystal X-ray diffraction analysis (*vide infra*). As chiroptical characteristics of these monoalkylated EDT-TTF derivatives one can mention that the (*R*)-**1** and (*R*)-**2** enantiomers are dextrorotatory, with specific optical rotation values of +70 and +88 deg·mL·g⁻¹·dm⁻¹ ([α]_D²⁵ in CH₂Cl₂), respectively, while in the CD spectra sequences of two weak negative and one intense positive bands peaking at 364 nm, 299 nm and 262 nm for (*R*)-**1** and 368 nm, 213 nm and 270 nm for (*R*)-**2** are observed. Mirror-image CD spectra were obtained for the (*S*) enantiomers which are levorotatory (Fig. S8-S9, ESI). An additional proof for the correct assignment of the absolute configuration was provided by the single crystal X-ray analysis (Tables S1-S3, ESI) performed on both enantiomers (*R*)-**2** and (*S*)-**2** for which suitable crystals were obtained by slow evaporation of dichloromethane solutions. The compounds crystallized in the orthorhombic non-centrosymmetric space group *P*2₁2₁2₁, with one independent molecule in the asymmetric unit (Fig. S10-S11, ESI). The bond lengths values are in agreement with the neutral state of the donor and the ethyl substituent occupies an

equatorial position, although in solution an equilibrium between the equatorial and axial conformers takes place.^{7,33} The solid state structure of (*rac*)-**2**, which crystallized in the centrosymmetric orthorhombic space group *Pbca*, has been determined as well. Similar bond lengths values (Tables S4-S6, ESI) and equatorial position of the ethyl substituent, as for the enantiopure forms, are observed (Fig. S12, ESI).

2.2 Radical cation salts

Both racemic and enantiopure donors **1** and **2** were engaged in electrocrystallization experiments in THF in the presence of (*n*-Bu₄N)PF₆ as supporting electrolyte. For the former, black crystalline plates of mixed valence radical cation salts formulated as [(*R*)-**1**]₂PF₆, [(*S*)-**1**]₂PF₆ and [(*rac*)-**1**]₂PF₆ were collected after one week on the platinum electrode. The three isostructural salts crystallized in the triclinic system, space group *P1* for the enantiopure forms and *P*-1 for the racemic one, with two independent donor molecules and one anion in the asymmetric unit for the former and one independent donor and half of anion located on the inversion centre for the latter, four of the fluorine atoms of the anion being disordered (Fig. S13-S15, ESI). The central C=C and internal C-S bond lengths have typical values for mixed valence oxidation state donors (Tables S7-S9, ESI). In the organic layers the donors organize in parallel columns reminiscent of the β -type packing, with short intra- and interstack S $\cdots$ S contacts and the methyl substituent in equatorial position, while the anions play a template role through the establishment of a complex set of intermolecular C-H $\cdots$ F hydrogen bonding interactions (Fig. 1).

Fig. 1 Packing of the donors in the structure of $[(R)\text{-}1]_2\text{PF}_6$ with an emphasis on the $\text{S}\cdots\text{S}$ short contacts: red (3.57 Å), blue (3.54 Å), green (3.63–3.65 Å) and violet (3.61 Å) (top); $\text{C}\cdots\text{H}\cdots\text{F}$ short contacts: blue for CH_{vinyl} (2.52–2.57 Å), violet for CH_2 (2.46–2.63 Å), orange for Me (2.46–2.93 Å) and green for CH_{Me} (2.61 Å) (bottom).

Similar kind of $\text{C}\cdots\text{H}\cdots\text{F}$ interactions, and thus template role of the anion, packing pattern of the donors and crystal cell parameters (Table S2, ESI) have been observed throughout the series $(\text{DM-EDT-TTF})_2\text{XF}_6$ ($\text{X} = \text{P}, \text{As}, \text{Sb}$) endowed with metal-like conducting behaviour,^{8,24} yet excepting the semiconducting enantiopure salts $(\text{DM-EDT-TTF})_4(\text{PF}_6)_2$ which crystallized in the monoclinic space group $P2_1$, with four independent donors showing charge localization at room temperature.⁸ The reduction of the number of stereogenic centres from two in DM-EDT-TTF to one in Me-EDT-TTF **1** has thus a tremendous effect on their enantiopure radical cation salts with the PF_6^- anion, massively impacting the conducting properties (*vide infra*).

Donor **2** provided as well the complete series of radical cation salts which crystallized as black needles for the enantiopure forms and black prismatic blocks for the racemic salt, further analysed by single crystal X-ray diffraction. While the enantiopure compounds are formulated as $[(R)\text{-}2]_2\text{PF}_6$ and $[(S)\text{-}2]_2\text{PF}_6$, with the donors in a mixed valence state, the racemic crystalline salt $[(rac)\text{-}2]\text{PF}_6\cdot(\text{C}_4\text{H}_8\text{O})$ shows 1:1 stoichiometry, with one independent donor and two anion halves located on inversion centres, and the presence of a THF molecule in the unit cell (Fig. S16, Table S10, ESI). The fully oxidized donors form strong head-to-tail dimers which interact with the anions through a set of $\text{C}\cdots\text{H}\cdots\text{F}$ interactions.

In the structure of the enantiopure salts the donors organize in dimers, laterally shifted along the stack. The dimers are of A-B type (A and B are the two independent donors, Fig. 2 for $[(R)\text{-}2]_2\text{PF}_6$) and interact laterally along the a direction through $\text{S}\cdots\text{S}$ contacts, an architecture reminiscent of the β' structural type in the BEDT-TTF series.³⁴ Moreover, there is no organic-inorganic segregation in the packing as the PF_6^- anions strongly interact with

surrounding donor molecules through various C–H···F short contacts (Fig. 2 and S17 for [(*R*)-**2**]₂PF₆ and Fig. S18 for [(*S*)-**2**]₂PF₆, Tables S11-S12, ESI).

Fig. 2 Molecular structure of [(*R*)-**2**]₂PF₆ with the two independent donors together with the atom numbering scheme (top), packing diagram highlighting short S···S contacts (middle) and focus on the C–H···F short contacts: red dotted lines for CH_{vinyl} (2.62 - 2.73), blue dotted lines for CH₂ (2.58 - 2.84), green dotted lines for Me (2.65 - 2.78 Å) and black dotted line for CH_{Me} (2.71 - 2.78 Å).

2.3 Single crystal conductivity measurements and band structure calculations

The structural analysis of the two series of radical cations salts clearly emphasizes major differences in the type of packing upon variation of the substituent size which should also alter the electron transport properties. In spite of the fragility of the samples, temperature dependent

resistivity measurements could be performed in most cases on single crystals with the two point contact method which underestimates however the actual value of conductivity because of the contribution of the resistance of the contacts. Only one crystal of $[(rac)\text{-}\mathbf{1}]_2\text{PF}_6$ could be measured in four contacts, the room temperature conductivity ($\sigma_{\text{RT}} \approx 50 \text{ S cm}^{-1}$) being slightly higher than the values ($\sigma_{\text{RT}} \approx 1\text{-}10 \text{ S cm}^{-1}$) obtained for two points measurements performed on crystals of the whole series $[\mathbf{1}]_2\text{PF}_6$ (Fig. 2 and S19). However, the difference in σ_{RT} between the three phases remains in the uncertainty related to the geometrical factor. Resistivity data in four points show metal like behaviour in the high temperature regime followed by a smooth localization below 150 K. This metallic regime cannot be detected by two point measurements but the activated behaviour is recovered below 150 K with a slightly lower activation energy (Fig. 3 and S19). This behaviour is comparable with the conductivity of the (DM-EDT-TTF) $_2\text{XF}_6$ (X = P, As, Sb) series.²⁴

Fig. 3 Temperature dependence of the electrical resistivity ρ for two single crystals of $[(rac)\text{-}\mathbf{1}]_2\text{PF}_6$ (green curve) measured using four contacts and two contacts and for a single crystal of $[(S)\text{-}\mathbf{1}]_2\text{PF}_6$ (red curve) and a single crystal of $[(R)\text{-}\mathbf{1}]_2\text{PF}_6$ (blue curve) both measured using two contacts.

Note that the racemic salt $[(rac)\text{-}\mathbf{1}]_2\text{PF}_6$, for which the resistivity could be measured using four point contacts, exhibits a slightly larger value of room temperature conductivity. A much higher difference in conductivity is observed between the racemic and enantiopure forms of the radical cation salts of donor **2**, which is not unexpected when considering the donor/anion stoichiometry and the packing of the donors. The racemic salt $[(rac)\text{-}\mathbf{2}]\text{PF}_6\bullet(\text{C}_4\text{H}_8\text{O})$ is a poor semiconductor with $\sigma_{\text{RT}} \approx 10^{-7} \text{ S cm}^{-1}$ and an activation energy of around 2500 K, in the temperature range 250-300 K, which is decreasing at lower temperature down to 1000 K around 100 K (Fig. S20). The enantiopure materials are semiconducting as well with comparable activation energy (around 1500 K) but a much higher conductivity $\sigma_{\text{RT}} \approx 2\text{-}5 \cdot 10^{-3} \text{ S cm}^{-1}$ (Fig. 4

and S21), in line with the semiconducting behaviour shown by the BEDT-TTF salts with a β -type packing.³⁴

Fig. 4 Temperature dependence of the electrical resistivity ρ for a single crystal of $[(S)-2]_2PF_6$ (red data points) and a single crystal of $[(R)-2]_2PF_6$ (blue data points) measured using two contacts. The black lines are the fit to the activation law $\rho = \rho_0 \exp(E_a/T)$ in the 100-220 K temperature range.

Let us now analyse the correlation between solid state structures and electron transport properties from a band structure perspective. In the isostructural series $[1]_2PF_6$ the band diagrams and Fermi surfaces are essentially identical for the three salts. The donor layers of $[(R)-1]_2PF_6$ contain two symmetry non-equivalent donors and six different donor···donor interactions labelled I to VI (Fig. 5).

Fig. 5 Donor layer of the $[(R)-1]_2PF_6$ salt where the different donors and intermolecular interactions are labelled.

These layers are made of a series of parallel chains along the (*a-b*)-direction. The two donors are practically identical from the electronic viewpoint since the HOMO energies differ by less than 0.01 eV. The racemic salt contains essentially the same type of layer although the A and B donors as well as interactions V and VI are now equivalent through inversion symmetry. The strength of the different HOMO···HOMO intermolecular interactions can be assessed from the so-called $|\beta_{\text{HOMO-HOMO}}|$ interaction energies,³⁵ reported in Table 1 for the (*R*) and (*rac*) salts.

Interaction	S···S (<3.9 Å)	$ \beta_{\text{HOMO-HOMO}} $ (eV)
I	3.581, 3.613, 3.618, 3.636 (3.600 (x2), 3.613 (x2))	0.7613 (0.7620)
II	3.555, 3.595, 3.855, 3.872 (3.576 (x2), 3.874 (x2))	0.5978 (0.5973)
III	3.584, 3.729, 3.825 (3.637 (x2), 3.820 (x2))	0.0556 (0.0553)
IV	3.455, 3.653, 3.702, 3.808 (3.550 (x2), 3.762 (x2))	0.0785 (0.0825)
V	3.680, 3.683, 3.840 (3.650, 3.691)	0.0221 (0.0205)
VI	3.633, 3.688 (3.650, 3.691)	0.0282 (0.0205)

Table 1 S···S distances shorter than 3.9 Å and absolute values of the $|\beta_{\text{HOMO-HOMO}}|$ interaction energies (eV) for the different donor···donor interactions in the [(*R*)-**1**]₂PF₆ salt. The values in parenthesis are those for [(*rac*)-**1**]₂PF₆ salt

Both in terms of the different S···S contacts and the $|\beta_{\text{HOMO-HOMO}}|$ interaction energies it is clear that the two donor layers are practically identical. The interactions along the chain direction (I and II) are one order of magnitude larger than those coupling the chains. Within the chain, the ratio between the two interactions is only ~1.3 so that the system is only slightly dimerized. The different chains are coupled through four different interactions (III to VI) which are weaker but by all means not negligible. Consequently, from the viewpoint of the HOMO···HOMO interactions, which are those determining the transport properties of the system, this salt should be considered as a moderately coupled slightly dimerized system, i.e. a pseudo one-dimensional (1D) conductor. The previous analysis is consistent with the calculated electronic structure of the donor layers (Fig. 6). The two bands in Fig. 4a are based on the HOMO of the donor. The band structure along the direction of the chain, which is intermediate between the Γ -Y and Γ -S lines, is made of two strongly dispersive bands (strong

HOMO···HOMO interactions) exhibiting a small gap (dimerization gap) at the border of the Brillouin zone. In addition, the upper band along the direction perpendicular to the chains, which almost coincides with the Γ -M line in Fig. 4a, exhibits dispersion although neatly smaller (i.e. around one-half that along the chain direction). This is exactly what is expected for chains along the $(a-b)$ -direction somewhat interacting along the inter-chain $(a+b)$ -direction.

Fig. 6 Calculated band structure (a) and Fermi surface (b) for the donor layers of $[(R)\text{-}1]_2\text{PF}_6$ where $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $Y = (0, b^*/2)$, $M = (a^*/2, b^*/2)$ and $S = (-a^*/2, b^*/2)$. The dashed line refers to the Fermi level.

It is worth noting that the electronic structure of the present salts is extremely similar to those of the large family of $[\text{DM-EDT-TTF}]_2\text{XF}_6$ ($X = \text{P, As, Sb}$) salts (except for the structurally different enantiopure PF_6 salts).^{8,24} This is not surprising because the structural organization of the layers and the HOMO···HOMO interactions are very similar. All of these salts exhibited a room temperature metallic conductivity although the conductivity becomes activated at lower temperatures. As noted before,⁸ the very broad nature of the transition, which is suppressed by a pressure of 11.5 kbar, is strongly suggestive of a non-structural origin of the transition.

The analysis of the donor layers of (R) - and $[(S)\text{-}2]_2\text{PF}_6$ shows they are very similar; indeed they both contain two symmetry non-equivalent donors A and B and six different donor···donor interactions labelled I to VI in Fig. 7a.

Fig. 7 (a) Donor layer of the [(R)-2]₂PF₆ salt where the different donors and intermolecular interactions are labelled, (b) top view on interaction I, and (c) lateral view of interaction V where the S...S contacts shorter than 3.9 Å are shown in red.

These layers are made of a series of donor double ribbons along the *a*-direction and every ribbon is built from one single type of donors, A or B. The strength of the different HOMO...HOMO intermolecular interactions can be assessed from the so-called $|\beta_{\text{HOMO-HOMO}}|$ interaction energies. Those calculated for the (*R*)- enantiomeric salt are reported in Table 2.

Table 2 S...S distances shorter than 3.9 Å and absolute values of the $|\beta_{\text{HOMO-HOMO}}|$ interaction energies (eV) for the different donor...donor interactions in the [(R)-2]₂PF₆ salt at room temperature.

Interaction	S...S (<3.9 Å)	$ \beta_{\text{HOMO-HOMO}} $ (eV)
I (A-B)	3.550, 3.607, 3.619, 3.637, 3.806, 3.824	0.5483
II (A-A)	3.379, 3.561, 3.758	0.0556
III (B-B)	3.377, 3.512, 3.879	0.0968
IV (A-B)	3.794	0.0805
V (A-B)	3.631, 3.773, 3.800	0.2079
VI (A-B)	3.780	0.0186

Interaction I is by far the strongest. Because of the bulky Et-substituent, the two donors arrange on-top of each other but displaced along the long molecular axis (see Fig. 7b). In that way a series of quite short S $\cdots$ S contacts are generated. In addition, a series of short S $\cdots$ C contacts very well oriented to make strong S 3p $_z$ $\cdots$ C 2p $_z$ σ -type interactions also occur. Both factors contribute to the strong interaction. The lateral interactions II and III leading to the ribbons of A and B donors respectively are associated with the shorter S $\cdots$ S contacts of the layer. However, because of the π -type nature of the S 3p $_z$ $\cdots$ S 3p $_z$ interactions they are considerably weaker, around ten and six times smaller, respectively. There is only another type of interaction within the double ribbon, interaction IV, which is associated with only one S $\cdots$ S contact relatively long so that this interaction is also considerably weaker than interaction I. Consequently, as far as the HOMO $\cdots$ HOMO interactions are concerned, the double ribbons along the *a*-direction should be considered as a series of weakly coupled A-B dimers.

The double ribbons repeat along the *b*-direction in such a way that the Et- substituents face the empty space between donors of the next double ribbon. In this way two very different interactions are established, V and VI. In V (see Fig. 7c) the two donors only overlap through the outer S atoms which make very good S 3p $_z$ $\cdots$ S 3p $_z$ σ -type interactions leading to a considerably strong interaction, only slightly less than half that of the strong interaction I. In contrast, there is only one S $\cdots$ S contact in interaction VI which is neither very short nor well oriented to make a good S 3p $_z$ $\cdots$ S 3p $_z$ overlap and leads to the weakest interaction in the layer. Consequently it is clear that the donor layers of these salts should be considered as built from weakly interacting step-chains of A-B dimers along the *b*-direction.

Fig. 8 Calculated band structure for the donor layers of [(R)-2]₂PF₆ where $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $Y = (0, b^*/2)$, $M = (a^*/2, b^*/2)$ and $S = (-a^*/2, b^*/2)$.

The calculated band structure for the donor lattice of $[(R)\text{-}\mathbf{2}]\text{PF}_6$ is shown in Fig. 8. Because of the stoichiometry the average charge of the donors is $+1/2$ so that there must be one hole in the HOMO bands. Consequently, the upper band of Fig. 8 should be half-filled. The band structure along the Γ -Y direction is typical of a dimerized system with strong interactions along b , i.e. two dispersive bands with a gap at the border of the Brillouin zone (the dimerization gap). Here the gap is substantial because interaction I is strong. This means that the upper band of Fig. 8 is built from the antibonding combination of the two HOMOs associated with the A-B dimer of interaction I (Ψ_{HO}^+). This band exhibits dispersion along b^* but is practically dispersionless along the a^* direction in agreement with the previous analysis. However, the dispersion along the step-chains direction (Γ -Y) is only moderate (~ 0.25 eV). This fact, together with the quite strong dimerization which will make the intra-site electron repulsion weak, favours the electronic localization in the individual Ψ_{HO}^+ orbitals of every dimer with respect to the electron delocalization through the step-chains. Thus, we can conclude that the holes in the donor slab will remain localized in the different A-B dimers (interaction I) making chains of interacting $[\text{AB}]^{\bullet+}$ radicals along the direction of the step-chains, b , and the conductivity will be activated. Note that the two HOMOs are different, that of donor B being somewhat lower in energy ($\Delta E \sim 0.06$ eV). This means that the antibonding combination of the two HOMOs of the A-B dimer leading to the upper band is more strongly localized on donor A which thus holds a larger hole density. The HOMO $\cdots$ HOMO interactions in the donor layers of the salts of the (*R*) and (*S*) enantiomers are practically identical so that the calculated band structure for $[(S)\text{-}\mathbf{2}]\text{PF}_6$ (Fig. S22) is practically identical to that of Fig. 8. Let us note that the calculated Fermi surface for the hypothetical metallic state of these salts (Fig. S23) exhibits slightly warped lines which can be superposed by a $b^*/2$ nesting vector. Consequently, even if the electron localization could be suppressed, for instance applying pressure, these salts would easily recover an activated conductivity through the opening of a band gap as a result of a structural dimerization along the step chains direction, b , although in that case the gap and the activation energy would be of different origin.

The salt $[(rac)\text{-}\mathbf{2}]\text{PF}_6$ exhibits a structure built from donor layers repeating along the c -direction (Fig. 9a).

Fig. 9 (a) Donor layers of the $[(rac)\text{-}2]\text{PF}_6$ salt where the different intermolecular interactions are labelled. (b) Calculated band structure for the donor layers of $[(rac)\text{-}2]\text{PF}_6$ where $\Gamma = (0, 0)$, $X = (a^*/2, 0)$, $Y = (0, b^*/2)$, $M = (a^*/2, b^*/2)$ and $S = (-a^*/2, b^*/2)$.

These layers have three different donor $\cdots$ donor interactions. The short $\text{S}\cdots\text{S}$ contacts and absolute values of the $|\beta_{\text{HOMO-HOMO}}|$ interaction energies are those in Table 3.

Table 3 $\text{S}\cdots\text{S}$ distances shorter than 3.9 Å and absolute values of the $|\beta_{\text{HOMO-HOMO}}|$ interaction energies (eV) for the different donor $\cdots$ donor interactions in the $[(rac)\text{-}2]\text{PF}_6$ salt at room temperature.

Interaction	$\text{S}\cdots\text{S}$ (<3.9 Å)	$ \beta_{\text{HOMO-HOMO}} $ (eV)
I	3.438 ($\times 2$), 3.555 ($\times 2$)	1.0257
II	3.645 ($\times 2$), 3.875	0.0889
III	3.377 ($\times 2$), 3.854 ($\times 2$)	0.2735

Interaction I is associated with a very strong dimerization. However it is interesting to remark that the two different types of inter-dimer interactions (II and III) are considerably different, with that along the a -direction (III) being as strong as the inter-dimer interactions along the step-chains in the two salts of the pure enantiomers. Consequently, this salt should also be considered as a series of step-chains of dimers but now along a . The calculated band structure (Fig. 9b) is identical in every detail with that of Fig. 8 once the a^* - and b^* -directions are interchanged clearly showing that we have exactly the same type of band structure except for the larger dimerization gap which is approximately twice larger now. Since the stoichiometry is now 1:1 the upper band is completely empty. Consequently, the conductivity will also be activated as for the two pure enantiomeric salts but for a different reason, the existence of a band gap. Since this gap is large the conductivity should be quite small. However it is interesting to note that even if the pure enantiomeric and racemic salts are structurally very

different, the building block of the electronic structure is the same: step-chains of dimeric units, each dimer being associated with an unpaired electron in the pure enantiomers or with a large energy gap in the racemic salt.

3. Conclusions

Chiral methyl and ethyl substituted EDT-TTF donors **1** and **2** have been synthesized as racemic mixtures and then separated in pure enantiomers by chiral HPLC. The absolute configuration has been determined by a combination of CD spectroscopy, optical rotation measurements and single crystal X-ray diffraction analysis and comparison with the dimethylated donor DM-EDT-TTF.^{8,33} Electrocrystallization experiments provided complete series of crystalline radical cations salts for both donors with the PF_6^- monoanion. The presence of only one methyl substituent in the six-membered ring of EDT-TTF promotes the crystallization of the enantiopure PF_6 metallic triclinic phase, in sharp contrast to DM-EDT-TTF.⁸ As a consequence, both enantiopure and racemic salts (**1**) PF_6 show metal-like conductivity in the high temperature regime, with a smooth localization taking place below 150 K. Band structure calculations are in agreement with a pseudo one-dimensional conducting behaviour. In contrast, the presence of a slightly more extended group, as the ethyl substituent in the radical cation salts of **2**, completely reconstructs the layer and thus, changes the nature of the HOMO...HOMO interactions and shifts the transport regime towards an activated conductivity in the series (**2**) PF_6 . Further work in these families of materials will be devoted to conductivity measurements under pressure and under magnetic field. Moreover, the use of larger anions, such as AsF_6^- and SbF_6^- ,²⁴ or tetrahedral monoanions such as ClO_4^- and ReO_4^- , in electrocrystallization with **1** and **2** is also a direction worth of investigation. Clearly, the modulation of the number of stereogenic centres and the steric hindrance represents a valuable strategy to access new chiral conductors.

4. Experimental

4.1 Materials and methods

Reactions were carried out under nitrogen, dry solvents were obtained from distillation machines. Nuclear magnetic resonance spectra were recorded on a Bruker Avance DRX 300 spectrometer operating at 300 MHz for ^1H and 75 MHz for ^{13}C . Chemical shifts are expressed in parts per million (ppm) downfield from external TMS. The following abbreviations are used:

s, singlet; d, doublet; dq, doublet of quadruplets; m, massif. MALDI- TOF MS spectra were recorded on Bruker Biflex-IIITM apparatus, equipped with a 337nm N₂ laser. Elemental analysis were recorded using Flash 2000 Fisher Scientific Thermo Electron analyzer. The synthesis of compound **3** is described in the ESI.

4.2 Synthesis

(rac)-5-methyl-5,6-dihydro-[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione ((rac)-4): compound **3** (6.1 g, 20 mmol) was added into a 250 mL Schlenk round bottomed flask under argon, then dry THF (400 mL) was poured into the flask. After 10 min a solution of caesium hydroxide (10 g, 60 mmol) in dry methanol (20 mL) was added dropwise and the colour started to turn violet. Then the resulting solution was left under stirring for 1 hour at room temperature, followed by the addition of 1,2-dibromopropane (4.5 g, 22 mmol) and reflux for 1 night. After cooling to room temperature, the solvent was removed under vacuum, and the solid residue was extracted twice with DCM and water (250/500 mL). The combined organic phase was concentrated and the residue was purified by column chromatography (petroleum ether/DCM 8:2) to give the compound **4** (2.7 g, 51%). ¹H NMR (300 MHz, CDCl₃) δ ppm: 3.86-3.66 (m, 1H, S-CH), 3.31 (dd, *J* = 13.2, 2.8 Hz, 1H, CH₂), 3.12 (dd, *J* = 13.2, 7.6 Hz, 1H, CH₂), 1.53 (d, *J* = 6.8 Hz, 3H, CH₃). ¹³C NMR (76 MHz, CDCl₃) δ ppm: 208.2 (C=S), 123.7, 121.5 (C=C), 38.6 (-S-CH), 36.3 (CH₂), 20.9 (CH₃); MS (EI, *m/z*) = 238.91 (*M*_{th} = 237.91). Elemental Analysis calcd. (%) for C₆H₆S₅: C 30.23, H 2.54, S 67.24; found: C 30.54, H 2.59, S 67.13.

(rac)-Me-EDT-TTF-(COOMe)₂ ((rac)-7): compound **3** (0.5 g, 2.1 mmol) and dimethyl 2-oxo-1,3-dithiole-4,5-dicarboxylate **6** (0.85 g, 3.6 mmol, 1.7 eq) were mixed under argon in freshly distilled trimethyl phosphite (15 mL), and the mixture was heated at 110 °C for 5 h. After this period the solvent was evaporated in a rotary evaporator, and then toluene (40 mL) were added and evaporated. The last procedure was repeated twice. The product was solubilized in dichloromethane and passed down a silica column to remove the remaining phosphite and then purified by chromatography using petroleum spirit/dichloromethane 1/1 to afford a red-brown solid (0.45 g, 51%). ¹H NMR (300 MHz, CDCl₃) δ ppm: 3.84 (s, 6H, O-CH₃), 3.75-3.60 (m, 1H, S-CH), 3.21 (dd, *J* = 13.0, 3.1 Hz, 1H, CH₂), 3.02 (dd, *J* = 13.0, 7.5 Hz, 1H, CH₂), 1.48 (d, *J* = 6.8 Hz, 3H, CH₃); ¹³C NMR (76 MHz, CDCl₃) δ ppm: 159.9 (C=O), 132.0, 114.7, 112.8, 111.0, 110.7 (C=C), 53.4 (O-CH₃), 39.1 (S-CH), 37.0 (CH₂), 20.9 (CH₃); MS (MALDI-TOF) *m/z*: 437.4 (*M*_{th} = 437.92). Elemental Analysis calcd. (%) for C₁₃H₁₂O₄S₆: C 36.77; H 2.85, O 15.07, S 45.30; found: C 36.58, H 2.92, O 15.26, S 45.24.

(rac)-Me-EDT-TTF ((rac)-1): compound **7** (0.45 g, 1.05 mmol) and LiBr (1.3 g, 15 mmol, 14 eq) were mixed in dimethylformamide (45 mL). The solution was stirred at 150 °C for 30 min, the formation of the product being monitored by TLC. The product was extracted with dichloromethane, and the organic phase was washed with brine and water and then dried over MgSO₄. The solvent was removed under vacuum, and the product was purified by chromatography on a silica gel column with petroleum spirit/dichloromethane 6/4 to afford a red solid (0.12 g, 37%). ¹H NMR (300 MHz, CDCl₃) δ ppm: 6.25 (s, 2H, CH=CH), 3.73-3.60 (m, 1H, S-CH), 3.20 (dd, *J* = 13.0, 2.3 Hz, 1H, CH₂), 3.02 (dd, *J* = 13.0, 7.5 Hz, 1H, CH₂), 1.47 (d, *J* = 6.7 Hz, 3H, CH₃); ¹³C NMR (76 MHz, CDCl₃) δ ppm: 119.0, 118.4, 114.7, 112.7, 104.5 (C=C), 39.1 (CH), 37.1 (CH₂), 21.0 (CH₃); MS (MALDI-TOF) *m/z*: 307.89 (*M*_{th} = 307.91); Elemental Analysis calcd. (%) for C₉H₈S₆: C 35.04, H 2.61, S 62.35; found: C 35.36, H 2.65, S 62.12.

(rac)-5-ethyl-5,6-dihydro-[1,3]dithiolo[4,5-b][1,4]dithiine-2-thione ((rac)-5) : compound **3** (5 g, 16 mmol) was added into a 250 ml Schlenk round bottomed flask under argon, and dry THF (400 mL) was then poured into the flask. After 10 min a solution of caesium hydroxide (7.5 g, 44.6 mmol) in dry methanol (20 mL) was added dropwise and the colour started to turn violet. Then the resulting solution was left under stirring for 1 hour at room temperature, followed by the addition of 1,2 dibromobutane (4 mL, 33.2 mmol) and reflux for 1 night. After cooling to room temperature, the solvent was removed under vacuum, and the solid residue extracted twice with DCM and water (250/500 mL). The combined organic phase was concentrated and the residue was purified by column chromatography (petroleum ether/DCM 8:2) to give compound **5** (2.2 g, 54%). ¹H NMR (300 MHz, CDCl₃) δ ppm: 3.54 (qd, 1H, *J* = 7.4, 2.8 Hz, CH₂-CH-S), 3.34 (dd, 1H, *J* = 13.1, 2.8 Hz, CH₂-S), 3.16 (dd, *J* = 13.3, 7.6 Hz, 1H, CH₂-S), 1.93-1.77 (m, 2H, CH₃-CH₂), 1.11 (t, 3H, *J* = 7.4 Hz, CH₃) ppm. ¹³C NMR (75 MHz, CDCl₃) δ ppm: 208.27 (C=S), 123.64, 121.88 (C=C), 45.66 (CH₂-CH-S), 34.53 (CH₂-S), 28.17 (CH₃-CH₂), 11.38 (CH₃). MS (EI, *m/z*) = 251.92 (*M*_{th}=251.92). Elemental Analysis calcd. (%) for C₇H₈S₅: C 33.31, H 3.19, S 63.50, found: C 33.43, H 3.27, S 63.74.

(rac)-Et-EDT-TTF-(COOMe)₂ ((rac)-8) : compound **5** (0.8 g, 3.1 mmol) and dimethyl-2-oxo-1,3-dithiole-4,5-dicarboxylate **6** (1.45 g, 6.2 mmol, 2 eq) were mixed under argon in freshly distilled trimethyl phosphite (15 mL), and the mixture was heated at 110 °C for 5 h. The solvent was evaporated in a rotary evaporator, and then toluene (40 mL) was added and

evaporated. The last procedure was repeated twice. The product was solubilized in dichloromethane and passed down a silica column to remove the remaining phosphite and then purified by chromatography using petroleum spirit/dichloromethane 1/1 to afford a red-brown solid (0.65 g, 47%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 3.77 (s, 6H, O- CH_3), 3.39 (qd, $J = 7.3$, 3.2 Hz, 1H, $\text{CH}_2\text{-CH-S}$), 3.20 (dd, $J = 13.1$, 3.1 Hz, 1H, $\text{CH}_2\text{-S}$), 2.99 (dd, $J = 13.1$, 7.5 Hz, 1H, $\text{CH}_2\text{-S}$), 1.88-1.73 (m, 2H, $\text{CH}_2\text{-CH}_3$), 1.00 (t, 1H, $J = 7.4$ Hz, CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ ppm: 159.8 (C=O), 131.9, 112.2, 110.7, 110.4 (C=C), 53.3 (O- CH_3), 45.6 ($\text{CH}_2\text{-CH-S}$), 34.5 ($\text{CH}_2\text{-S}$), 28.2 ($\text{CH}_2\text{-CH}_3$), 11.4 (CH_3) ppm; MS (MALDI-TOF) m/z : 437.4 ($M_{\text{th}}=437.92$). Elemental Analysis calcd. (%) for $\text{C}_{14}\text{H}_{14}\text{O}_4\text{S}_6$: C 38.34, H 3.22; O 14.59, S 43.86; found: C 38.49, H 3.34, O 14.63, S 43.82.

(rac)-Et-EDT-TTF ((rac)-2): compound **8** (0.65 g, 1.5 mmol) and LiBr (2.34 g, 27 mmol, 18 eq) were mixed in dimethylformamide (60 mL). The solution was stirred at 150 °C for 30 min, the formation of the product being monitored by TLC. The product was extracted with dichloromethane, and the organic phase was washed with brine and water and then dried over MgSO_4 . The solvent was removed under vacuum, and the product was purified by chromatography on a silica column with petroleum spirit/dichloromethane 6/4 to afford a red solid (0.21 g, 41%). ^1H NMR (300 MHz, CDCl_3) δ ppm: 6.32 (s, 2H), 3.45 (qd, $J = 7.2$, 3.1 Hz, 1H, ($\text{CH}_2\text{-CH-CH}_2$), 3.26 (dd, $J = 13.1$, 3.1 Hz, 1H, $\text{CH}_2\text{-S}$), 3.05 (dd, $J = 13.1$, 7.5 Hz, 1H, $\text{CH}_2\text{-S}$), 1.91 – 1.77 (m, 2H, $\text{CH}_3\text{-CH}_2$), 1.06 (t, $J = 7.4$ Hz, 3H, CH_3). ^{13}C NMR (75 MHz, CDCl_3) δ ppm: 118.97, 118.40, 114.57, 113.01, 104.49 (C=C), 46.26 ($\text{CH}_2\text{-CH-CH}_2$), 35.27 ($\text{CH}_2\text{-S}$), 28.20 ($\text{CH}_3\text{-CH}_2$), 11.59 (CH_3); MS (MALDI-TOF) m/z : 322.2 ($M_{\text{th}} = 321.91$); Elemental analysis calcd. (%) for $\text{C}_{10}\text{H}_{10}\text{S}_6$: C 37.23, H 3.13, S 59.64; found: C 36.98, H 3.11, S 59.97.

4.3 Electrocrystallization

[(R)-1] $_2$ PF $_6$: 20 mg of $[\text{NBu}_4]\text{PF}_6$ was dissolved in THF (6 mL), and then the solution was poured into the cathodic compartment of an electrocrystallization cell. The anodic chamber was filled with 5 mg of (R)-**1** dissolved in THF (6 mL). Crystalline black plates of the salt $[(R)\text{-1}]_2\text{PF}_6$ were grown at 3 °C over a period of one week on the platinum wire electrode, by applying a constant current of 1 μA .

[(S)-1] $_2$ PF $_6$ was prepared as previously by using (S)-**1** as donor.

$[(rac)\text{-}1]_2\text{PF}_6$ was prepared as previously by using $(rac)\text{-}1$ as donor.

$[(R)\text{-}2]_2\text{PF}_6$: 20 mg of $[\text{NBu}_4]\text{PF}_6$ was dissolved in THF (6 mL), and then the solution was poured into the cathodic compartment of an electrocrystallization cell. The anodic chamber was filled with 5 mg of $[(R)\text{-}2]$ dissolved in THF (6 mL). Crystalline black needles of the salt $[(R)\text{-}2]_2\text{PF}_6$ were grown at 3 °C over a period of one week on a platinum wire electrode and on the bottom of the cell, by applying a constant current of 1 μA .

$[(S)\text{-}2]_2\text{PF}_6$ was prepared as previously by using $(S)\text{-}2$ as donor.

$[(rac)\text{-}2]\text{PF}_6\cdot(\text{THF})$ was prepared as previously by using $(rac)\text{-}2$ as donor. The collected crystals are black prismatic blocks.

4.4 X-Ray structure determinations

Details about data collection and solution refinement are given in Tables S1, S2 and S3. Single crystals of the compounds were mounted on glass fibre loops using a viscous hydrocarbon oil to coat the crystal and then transferred directly to cold nitrogen stream for data collection. Data collection were mostly performed at 150 K on an Agilent Supernova with $\text{CuK}\alpha$ ($\lambda = 1.54184$ Å). The structures were solved by direct methods with the SIR92 program and refined against all F_2 values with the SHELXL-97 program using the WinGX graphical user interface.

All non-H atoms were refined anisotropically. Hydrogen atoms were introduced at calculated positions (riding model), included in structure factor calculations but not refined.

Crystallographic data for the nine structures have been deposited with the Cambridge Crystallographic Data Centre, deposition numbers CCDC 1937687 ($(rac)\text{-}2$), 1938735 ($(R)\text{-}2$), 1937689 ($(S)\text{-}2$), 1938736 ($[(rac)\text{-}1]_2\text{PF}_6$), 1937685 ($[(R)\text{-}1]_2\text{PF}_6$), 1937688 ($[(S)\text{-}1]_2\text{PF}_6$), 1938737 ($[(rac)\text{-}2]\text{PF}_6$), 1937686 ($[(R)\text{-}2]_2\text{PF}_6$), 1937690 ($[(S)\text{-}2]_2\text{PF}_6$). These data can be obtained free of charge from CCDC, 12 Union road, Cambridge CB2 1EZ, UK (e-mail: deposit@ccdc.cam.ac.uk or <http://www.ccdc.cam.ac.uk>).

4.5 Conductivity measurements

Electrical resistivity was measured on needle-shaped single crystals 0.3-0.5 mm long. Gold wires were glued with silver paste directly on both ends of the crystals. Only one crystal of $[(rac)\text{-}1]_2\text{PF}_6$ could be measured in four contacts using an AC current of 10 μA and low-frequency (< 100 Hz) lock-in detection. Different techniques were used to measure

resistivity in two points, either applying a DC current (1 - 0.1 μ A) and measuring the voltage with a Keithley 2401 microvoltmeter (data in Figures 2-S19) or, for higher resistance values, applying a constant voltage of 0.1 - 0.2 V (data in Figures S21-S22) or 10 V (data in Figure S20) and measuring the current using a Keithley 6487 Picoammeter/Voltage Source. We have checked for each crystal that both techniques give the same resistance value at room temperature. Low temperature was provided by a homemade cryostat equipped with a 4 K pulse-tube.

4.6 Band structure calculations

The tight-binding band structure calculations were of the extended Hückel type.³⁶ A modified Wolfsberg-Helmholtz formula was used to calculate the non-diagonal $H_{\mu\nu}$ values.³⁷ All valence electrons were taken into account in the calculations and the basis set consisted of Slater-type orbitals of double- ζ quality for C 2s and 2p, S 3s and 3p and of single- ζ quality for H. The ionization potentials, contraction coefficients and exponents were taken from previous work.³⁸

Conflicts of interest

There are no conflicts to declare.

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