



Journal Name

ARTICLE

Semiconducting radical-cation salts of chiral bis(2-hydroxypropylthio)ethylenedithioTTF with bromide, chloride, perchlorate or hexafluorophosphate anions.

Received 00th January 20xx,
Accepted 00th January 20xx

DOI: 10.1039/x0xx00000x

www.rsc.org/

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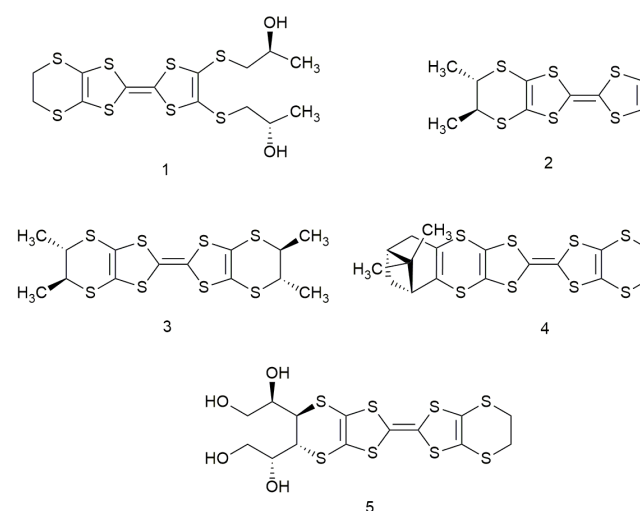
Electrocrystallisations of the chiral donor molecule *S,S*-bis(2-hydroxypropylthio)ethylenedithiotetrathiafulvalene have produced a series of 1:1 semiconducting radical-cation salts with anions bromide, chloride, perchlorate and hexafluorophosphate. The flexibility and hydrogen bonding ability of the donor's chiral side chains lead to three quite different packing arrangements of donor cation pairs. Conductivity is maintained despite significant separations of donor cation pairs in some cases.

Introduction

The effect of chirality upon electron transport has not previously been deeply investigated owing to a limited number of suitable materials. Recently, the first observation of the effect of chirality upon superconductivity was reported in an individual nanotube of tungsten disulphide.¹ Asymmetric electron transport is observed when a magnetic field is applied parallel to the WS₂ nanotube axis. Electrical magneto-chiral anisotropy in conducting systems has been studied in bismuth helices,² and in carbon nanotubes³ where the resistivity along nanotubes of opposing chirality differs in a coaxial magnetic field.

The synthesis of radical-cation salts from enantiopure donors, anions and/or solvents provides an opportunity to study semiconducting, metallic or superconducting behaviours and magnetic properties in a chiral lattice. Radical-cation salts have been synthesized from a variety of chiral or racemic anions including [Cr(2,2'-bipy)(oxalate)₂]^{4a}, [Sb₂(L-tartrate)₂]²,^{4b} [Fe(croconate)₃]³,^{4c} [Fe(chloranilate)₃]³,^{4d} TRISPHAT,^{4e} D-camphorsulfonate,^{4f} Co^{III} complexes of optically pure pyridinecarboxamide anions,^{4g} and B(malate)₂.^{4h} A large number of radical-cation salts of BEDT-TTF have also been obtained when using racemic tris(oxalato)metallate anions (Metal = Fe,^{5a} Cr,^{5b} Al,^{5c} Co,^{5c} Ga,^{5d} Ru^{5e} Mn,^{5f} Rh^{5g}, Ge^{5h}). The distribution of the Δ and Λ enantiomers of tris(oxalato)metallate in the anion layers determines the

packing motif of the BEDT-TTF donors and thus the conducting properties. The anion layers in these salts have hexagonal cavities which makes it possible to introduce a chiral guest into the lattice. Crystals formed by inclusion of either (*S*) or racemic *sec*-phenethyl alcohol show a difference in their electrical transport behaviours owing to the disorder between guest enantiomers in the latter case.⁶ (*R*)-Carvone is too large to fit into the anion layer's cavities but the presence of (*R*)-carvone during electrochemical growth with racemic tris(oxalato)chromate leads to a BEDT-TTF salt containing only a single enantiomer of the tris(oxalato)chromate.⁷ Chirality can also be introduced into the donor molecule, and a range of enantiopure donors based on EDT-TTF or BEDT-TTF such as **1-5** have been prepared and studied (Scheme 1).⁸⁻¹³



Scheme 1. Structures of chiral organosulfur donor molecules **1-5**.

Enantiopure radical-cation salts of (*S,S*)- and (*R,R*)-(DM-EDT-TTF)₂ClO₄ **2** crystallise in the enantiomorphic space group pair

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$P6_22$ and $P6_422$, respectively.⁹ These salts show metallic behaviour down to 40K and electrical magneto-chiral anisotropy in these salts confirms the chiral nature of charge transport along the chiral crystal axis. Hexafluorophosphate salts from this donor show metal-like conductivity for the racemate, whilst showing semiconducting behaviour and room temperature charge ordering for the enantiopure salts owing to a completely different packing arrangement.¹⁰

We have previously reported the synthesis of the novel chiral donor molecule bis(2-hydroxypropylthio) ethylenedithio-tetrathiafulvalene (BHPT-EDT-TTF **1**) in the enantiopure *R,R* or *S,S* form, and also the *meso/rac* form which contains a mixture of *R,R*, *S,S* and *R,S-1*.⁸ This donor has proven to be fruitful at forming radical-cation salts with a variety of anions owing, in part, to the flexibility and the hydrogen-bonding ability of the 2-hydroxypropylthio side-chains.^{14,15} In the first examples of radical-cation salts from this donor we have observed a multitude of donor packing motifs with the anions I_3^- , I_8^- , $Fe_2(oxalate)_5^{4-}$, BF_4^- or $TCNQ-F_4$.^{8,14,15} We report here a series of new 1:1 radical-cation salts prepared by electrocrystallisation of the enantiopure donor *S,S*-BHPT-EDT-TTF (**(S,S)-1**) with bromide, chloride, perchlorate and hexafluorophosphate anions, along with their *R,R* and *meso/rac* analogues for the latter two anions.

Experimental

Enantiopure donor *S,S*-BHPT-EDT-TTF (**1**) was synthesized by the method previously described.⁸ The *R,R* and *meso/rac* forms of BHPT-EDT-TTF were obtained by the same method but starting from *R*- or *rac*-methyloxirane, respectively. Single crystals of all radical-cation salts were grown *via* electrocrystallisation.

Crystal structures were determined by X-ray diffraction.[‡]

Synthesis of (S,S)-1.ClO₄

100 mg of tetrabutylammonium perchlorate was dissolved in 20 ml of chlorobenzene and added to the cathode side of a H-shaped cell. 10mg of donor **(S,S)-1** was placed in the anode side of the H-shaped cell with 20 ml of chlorobenzene. A current of 0.1 μ A was passed through the platinum electrodes and black needle crystals grew on the anode over 3 weeks. *R,R* and *meso/rac* salts were grown *via* the same method but using **(R,R)-1** or **(meso/rac)-1**, respectively. For the *meso/rac* form it proved much more difficult to produce single crystals of high enough quality for full physical characterisation. The crystals were extremely thin.

Synthesis of (S,S)-1.PF₆

100 mg of tetrabutylammonium hexafluorophosphate was dissolved in 20 ml of chlorobenzene and added to the cathode side of a H-shaped cell. 10mg of donor **(S,S)-1** was placed in the anode side of the H-shaped cell with 20 ml of chlorobenzene. A current of 0.1 μ A was passed through the platinum electrodes and black needle crystals grew on the anode over 3 weeks. *R,R* and *meso/rac* salts were grown *via* the same method but using **(R,R)-1** or **(meso/rac)-1**, respectively. The *meso/rac* crystals were

thin and fragile.

Synthesis of (S,S)-1.Cl.H₂O

100 mg of tetrabutylammonium chloride was dissolved in 20 ml of nitromethane and added to the cathode side of a H-shaped cell. 10mg of donor **(S,S)-1** was placed in the anode side of the H-shaped cell with 20 ml of nitromethane. A current of 0.2 μ A was passed through the platinum electrodes and black rectangular crystals grew on the anode over 2 weeks.

Synthesis of (S,S)-1.Br

100 mg of tetrabutylammonium tribromide was dissolved in 20 ml of 1:1 acetonitrile:dichloromethane and added to the cathode side of a H-shaped cell. 10mg of donor **(S,S)-1** was placed in the anode side of the H-shaped cell with 20 ml of acetonitrile:dichloromethane. A current of 0.1 μ A was passed through the platinum electrodes and black rectangular crystals grew on the anode over 3 weeks.

Resistivity measurements

Four-probe DC transport measurements were made on crystals of **(S,S)-1.ClO₄**, **(R,R)-1.ClO₄**, **(S,S)-1.PF₆**, **(R,R)-1.PF₆**, **(S,S)-1.Cl.H₂O** and **(S,S)-1.Br** using a HUSO HECS 994C multi-channel conductometer. Gold wires (15 μ m diameter) were attached to the crystal, and the attached wires were connected to a four-pin integrated circuit plug with gold conductive cement.

Measurements were made by cooling the samples down from room temperature to the temperature at which the resistance value exceeds the limit of the multimeter. Measurements were then also made as the samples were warmed back up to room temperature. Measurements were made on two single crystals of each salt except for the extremely thin crystals of **(meso/rac)-1.ClO₄** and **(meso/rac)-1.PF₆** which made them too fragile to mount for study, and **(R,R)-1.PF₆** for which there was only one suitable single crystal.

In one sample of **(R,R)-1.ClO₄** there is a small difference in resistivity observed between cooling and heating runs. However, the changes in E_a and ρRT are negligible and it can be concluded that no change in electronic structure has occurred and the hysteresis is due to defects in the structural integrity of the thin needle crystals.

Results and Discussion

Structures and resistivities of perchlorate and hexafluorophosphate salts

Both enantiomers and the *rac/meso* form of donor **1** produce 1:1 salts with perchlorate or hexafluorophosphate which have very similar crystal structures, and which are very closely related to those of the tetrafluoroborate salts.¹⁴ The structures of the *(R,R)* and *rac/meso* salts were measured at 100 K and the *(S,S)* salts at 296 K. The *R,R* perchlorate salt was measured using synchrotron radiation. Salts **(S,S)-1.ClO₄** (Table 1, Fig. 1) and **(S,S)-1.PF₆** (Table 2, Fig. 2) both crystallise in the orthorhombic crystal system in chiral space group $C222_1$ and are isostructural

with their *R,R* analogues. Crystals grown from the *meso/rac*-1 donor had similar unit cell dimensions but are in the monoclinic space group *C2/c* with unit cell angles β of 91.78 (ClO_4) and 93.57° (PF_6). The asymmetric units of all salts consist of one donor cation molecule and two crystallographically independent anions. The latter lie on 2-fold axes for the enantiomeric salts while for the *meso/rac* salt one lies on an inversion centre and the other on a 2 fold axis. In the enantiopure perchlorate salts the ClO_4 anions are disordered. Due to the low quality of crystals and resulting X-ray data for the two *meso/rac* salts, full structure determinations could not be achieved and they will not be discussed in detail, though the relative positions of the donor and anion moieties are clear and are very similar to those of the enantiopure salts.

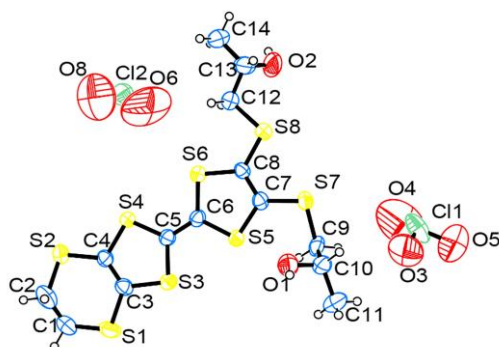


Fig. 1 ORTEP image of **(*S,S*)-1.ClO₄**. Both **(*R,R*)-1.ClO₄**, and ***meso/rac*-1.ClO₄** follow a similar numbering scheme. Perchlorate anions are disordered.

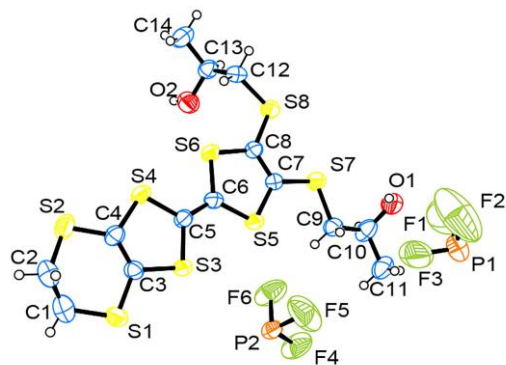


Fig. 2 ORTEP image of **(*S,S*)-1.PF₆**. Both **(*R,R*)-1.PF₆**, and ***meso/rac*-1.PF₆** follow a similar numbering scheme.

In all four enantiopure salts the donor cations are stacked in the *a* direction with adjacent stacks segregated in the *b* direction by the anions as well as the donor side chains (Fig. 3-5). A pair of donor cations related by a 2-fold axis form a head-to-tail, face-to-face dimer with short S---S contacts between the four central TTF sulfur atoms as shown in Fig. 6. The best planes of the donor cations lie at an angle of *ca.* 62-65° to the donor stacking axis, and the slip distance between the donor cations in the dimer is *ca.* 0.9 Å. The dimers form stacks, and the separation between the donor planes between pairs is larger than within the pair.

For the PF_6 series, the values are 3.78 and 3.48 Å respectively for the *S,S* salt at 298 K, and these values are about 0.1 Å smaller, 3.67 and 3.40 Å, for the *R,R* salt at 100 K. The S---S contacts between TTF units within a dimer are in the range 3.47-3.62 Å for all enantiopure salts showing little variation with temperature of measurement (Tables 3 and 4). The dimers are strongly slipped relative to each other by *ca.* 2.3 Å, and the shortest six S---S contacts between them are in the range 3.57-3.81 Å for the structures measured at 100 K, and 3.76-3.93 Å for the salts measured at room temperature consistent with the thermal expansion of the unit cells.

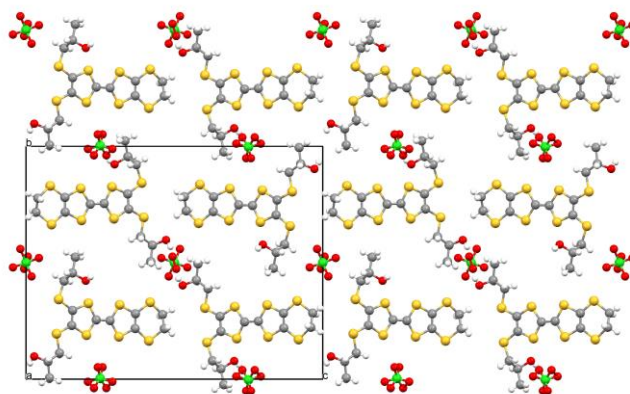


Fig. 3 Crystal structure of **(*S,S*)-1.ClO₄** viewed down the *a* axis, the perchlorate ions are disordered.

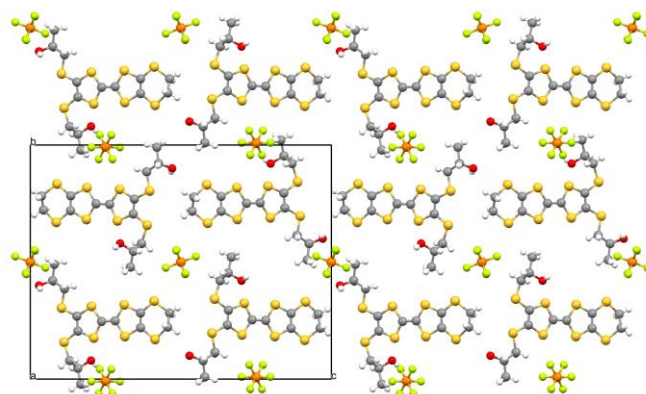


Fig. 4 Crystal structure of **(*S,S*)-1.PF₆** viewed down the *a* axis.

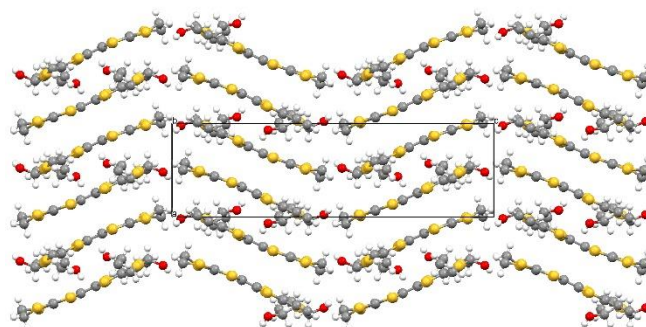


Fig. 5 Donor layers of **(*S,S*)-1.ClO₄** viewed down the *b* axis. A very similar arrangement occurs in **(*S,S*)-1.PF₆**.

One donor side chain is extended out in the plane of the donor in a zigzag conformation, while the other one is twisted about the S-CH₂ bond by *ca.* 94° so that the hydroxyl oxygen atom makes a rather short 1,6 contact with a TTF S atom in the range 2.924-2.999 Å. Interestingly this O atom makes two longer contacts to two TTF sulfurs belonging to the next donor in the stack (3.183-3.363 Å). This corresponds to a bridging between two donor cation pairs and thus across the longer gap in the stack of donor cations. Furthermore, this O atom is close to a symmetry related O atom from another donor side chain (O...O: 2.75-2.86 Å) which also bridges between the same two donor cations (Fig. 6). For each enantiopure salt there are two crystallographically unique anions which lie in somewhat different environments. For each anions there are two short contacts to symmetry related hydroxyl O atoms (P...O: 3.97-4.27 Å and Cl...O: 3.93-4.08 Å) which may involve hydrogen bonds to the outer atoms of these spherical complex anions.

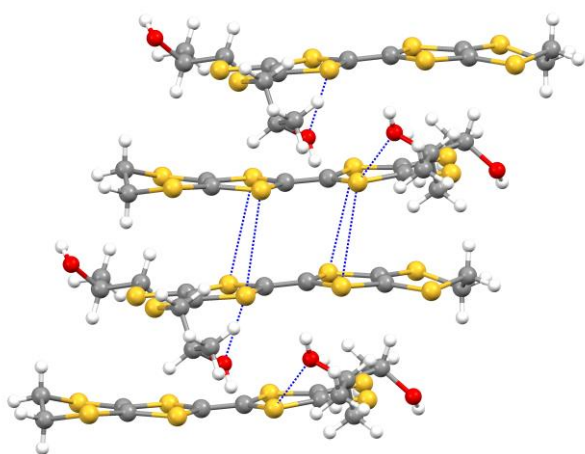


Fig. 6 Stacking of donors showing close S-S contacts for **(S,S)-1.ClO₄**, and also short intramolecular S...O contacts. A very similar arrangement occurs in **(S,S)-1.PF₆**.

The central TTF C=C bond length in all four enantiopure salts is close to the expected value for a TTF donor charge of 1⁺: **(S,S)-1.ClO₄** 1.402(7) Å, **(R,R)-1.ClO₄** 1.36(3) Å, **(S,S)-1.PF₆** 1.379(6) Å and **(R,R)-1.PF₆** 1.381(12) Å.

Four-probe transport measurements were performed parallel to the longest axis of the needle-shaped crystals. Semiconducting behaviour was observed for all of the enantiopure perchlorate and hexafluorophosphate salts but the extremely thin crystals of *meso/rac*-**1.ClO₄** and *meso/rac*-**1.PF₆** made them too fragile to mount for study. Room temperature resistivities were in the range 3 × 10² to 8 × 10³ Ohm cm, with similar activation energies (0.16-0.18 eV) for all four enantiopure salts (Tables 5 and 6), which are comparable to the results from the corresponding tetrafluoroborate salts.¹⁴

The resistivities for these three series of isostructural salts are quite low, given there are significantly wide gaps in the stack between donor pairs and no interstack S...S contacts. The

bridging of these gaps by two hydroxyl groups may play a role, but requires further study.

Structure and resistivity of **(S,S)-1.Cl.H₂O**

X-ray diffraction studies at room temperature show that salt **(S,S)-1.Cl.H₂O** crystallises in the triclinic crystal system in space group *P*1 (Table 7, Fig. 7). The unit cell contains two donor cations, two chloride anions and two water molecules. The donor cations form head-to-tail, face-to-face, dimers which are stacked in the *a* direction (Fig. 8). Within a pair the donors lie parallel and slipped along their long axis by *ca.* 1.2 Å with respect to each other. The S₂TTF₂S₂ portions of the donor cations are planar and lie *ca.* 3.53 Å apart with short S...S contacts between their central TTF units in the range 3.509-3.758 Å (Table 8). Adjacent donor pairs in the stack lie *ca.* 3.87 Å apart, with shortest S...S contacts of 3.863 and 3.958 Å. These separations are slightly longer than those observed in the room temperature measurement of the **(S,S)-1.PF₆** salt. The lengths of the central C=C bonds of both donor cations 1.387(11) and 1.369(11) Å are close to the expected value for a TTF donor charge of 1⁺.

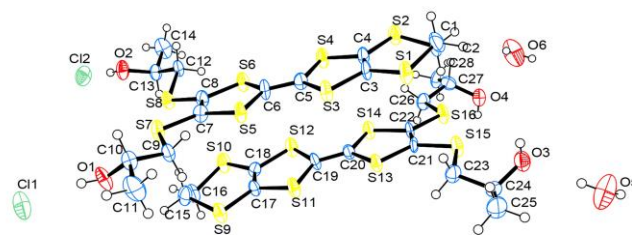


Fig. 7 ORTEP image of **(S,S)-1.Cl.H₂O**.

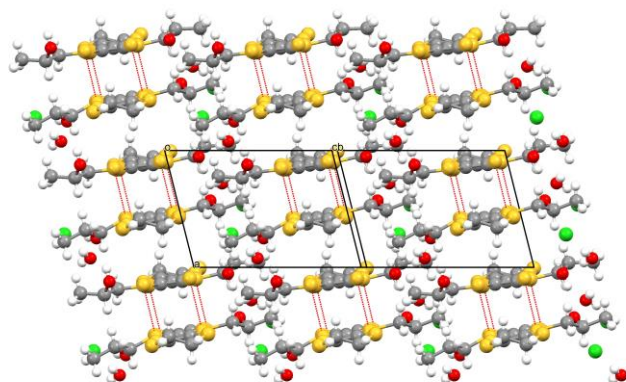


Fig. 8 Crystal structure of **(S,S)-1.Cl.H₂O** showing the donor cation stacks surrounded on either side by the chloride/hydroxyl/water hydrogen bonding networks and S...S contacts within a donor cation pair (3.509-3.758 Å).

The 2-hydroxypropylthio side chains adopt zigzag conformations which are directed out to either side of the donor pair and lie close to the plane of their donor cation (Fig. 9). The four side chain OH groups, the two chlorides and two

waters are involved in a hydrogen bonding network lying in between the stacks. Chloride ions are linked with bridges comprising two donor OH groups and a water molecule, with Cl---O and O---O distances of 2.994–3.009 Å and 2.784–3.207 Å respectively (Fig. 10). Each chloride ion makes a pair of short contacts to two sulfur atoms of one donor cation (one TTF sulfur and one dithiin sulfur) and one contact to a TTF sulfur of the next donor in the stack. Thus Cl1 bridges the two molecules of a donor pair with contacts to sulfur of 3.684 and 3.775 Å to one donor cation and 3.592 Å to the other one. In contrast, Cl2 bridges *between* donor pairs, with contacts to sulfur of 3.549 and 3.737 Å to one donor cation and 3.819 Å to a sulfur of the other cation.

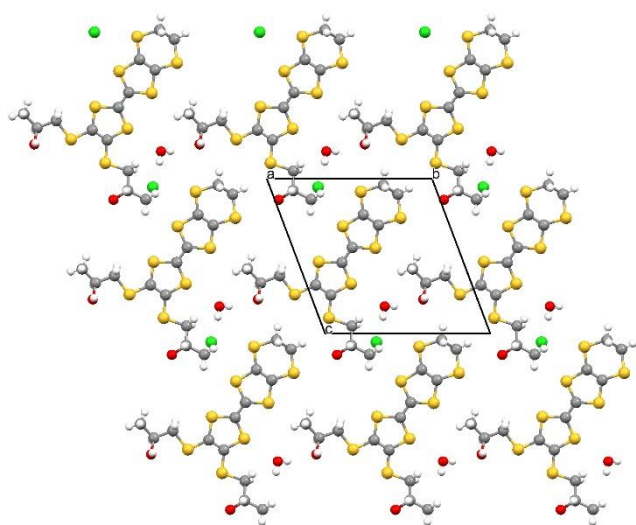
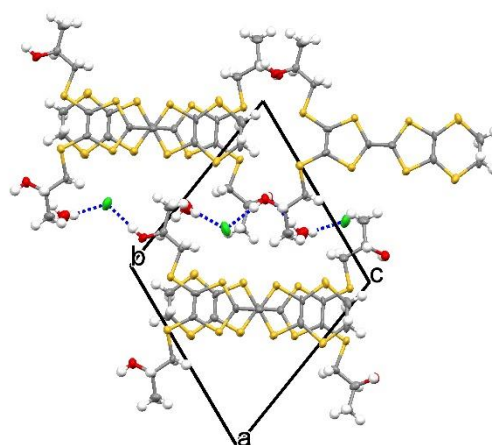


Fig. 9 Crystal structure of (S,S) -1.Cl.H₂O viewed down the *a* axis.

Four-probe transport measurements were performed upon two crystals of (S,S) -1.Cl.H₂O and results are shown in Table 9. Semiconducting behaviour is observed with room temperature resistivities of 4.9×10^2 and 7.2×10^2 Ohm cm and activation energies and 0.177 and 0.207 eV, respectively, for the two crystals. These resistivities are quite low, given the significant gap between the adjacent donor cation pairs in the stack of 3.87 Å and the location of the hydrogen bonding networks in between stacks preventing any side to side inter-stack contacts. Indeed the shortest S---S contact between adjacent donor cation pairs is 3.863 Å, and most lie in the range 3.96–4.35 Å. It is notable that a chloride ion bridges this gap as did hydroxyl groups in the structures of the perchlorate and hexafluorophosphate salts.

(a)



(b)

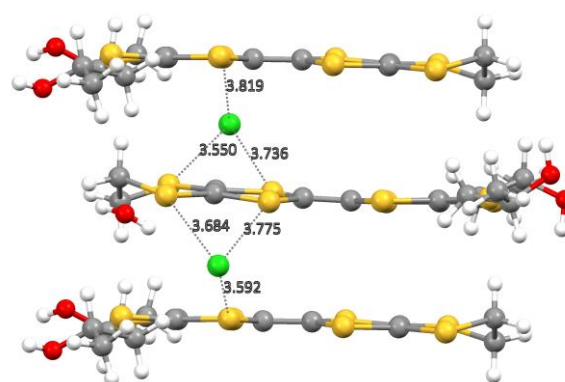


Fig. 10 Crystal structure of (S,S) -1.Cl.H₂O (a) showing hydrogen bonding interactions between side chains, chloride ions and water molecules, and (b) showing the bridging of donor cations by chloride ions.

Structure and resistivity of (S,S) -1.Br

Salt (S,S) -1.Br crystallises in the monoclinic crystal system in space group $P2_1$ (Table 7). The asymmetric unit consists of two donor cations and two bromide anions (Fig. 11). Unlike the chloride salt there is no water included in the structure and the donors are not organised in stacks. The two crystallographically unique donor cations form a head-to-tail, face-to-face, dimer pair (Fig. 12 and 13) whose main axis lies at *ca.* 43° to the monoclinic *b* axis. The bromide ions lie to either side of the pair's TTF units and are hydrogen bonded to hydroxyl groups belonging to other donor cation pairs. Each bromide makes two contacts to TTF sulfur atoms in the same donor, one significantly shorter than the other: 3.459 and 3.809 Å for Br1 and 3.613 and 3.862 Å for Br2. The O---Br distances in the O-H---Br hydrogen bonds lie in the range 3.208–3.340 Å.

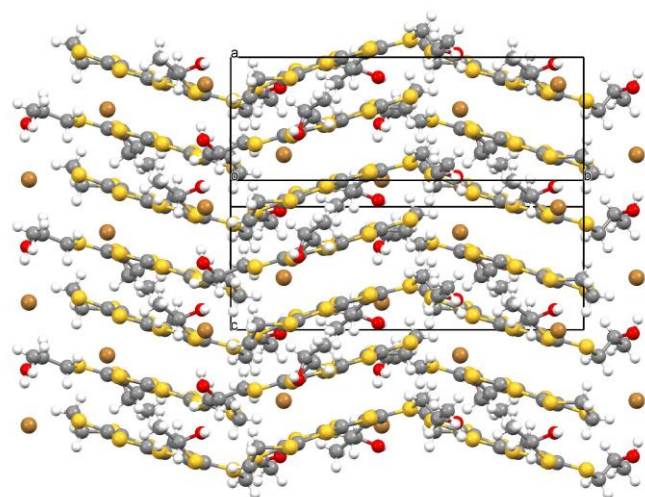
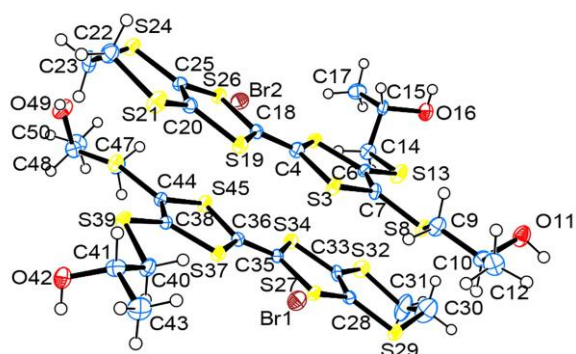


Fig. 12 Crystal structure of **(S,S)-1.Br** showing the effect of the 2_1 screw axis along b .

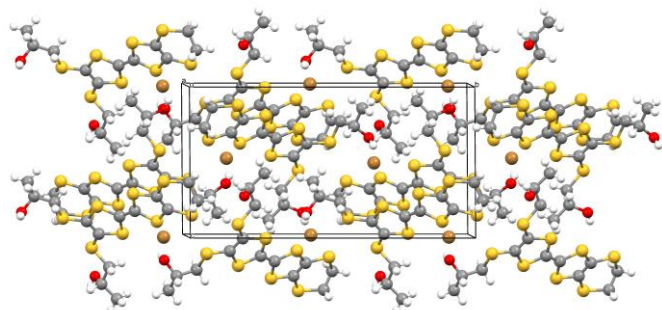


Fig. 13 Crystal structure of **(S,S)-1.Br** viewed down the c axis.

Parallel donor pairs in the a direction make three edge to edge S---S contacts (3.730–3.803 Å) with one another. The two fold screw axis results in the donor pairs forming a herringbone-like arrangement along the b axis. There is just one short S---S contact between donors related by the screw axis which involves a side chain sulfur and dithiin sulfur (3.554 Å). Within a dimer the TTF units are slipped with respect to each other by *ca.* 1.35 Å so that there is a short C---C contact (3.28 Å) between the two central double bonds. There are also four short face-to-face S---S contacts between TTF sulfur atoms (3.475–3.582 Å) (Fig. 14, Table 10). The central TTF C=C bond lengths of both donors are close to the expected value for a TTF donor charge of 1^+ : 1.375(7) and 1.383(7) Å. Each of the 2-hydroxypropylthio chains is directed out from its donor cation, with a zigzag conformation along the chain; three of these lie close to the donor plane, while the fourth one is twisted about the S-CH₂ bond so that the C7-S7-C9-C10 torsion angle is 104° (Fig. 15). Four-probe transport measurements were performed upon two crystals of **(S,S)-1.Br** (Table 9). Semiconducting behaviour is observed with room temperature resistivities of 3.2 and 4.4 × 10⁴ Ohm cm, considerably higher than for the chloride salt, and estimates of activation energies of 0.198 eV and 0.297 eV, respectively, for the two crystals.

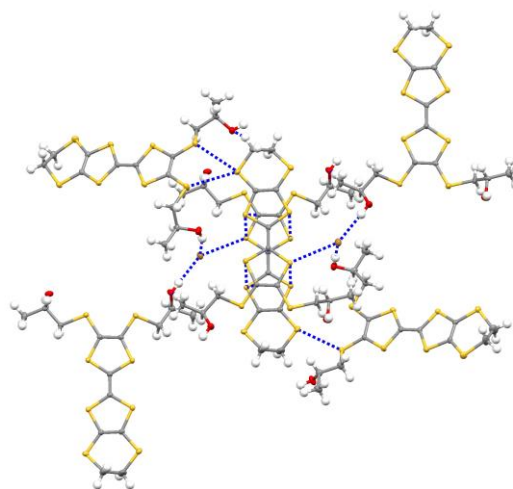


Fig. 14 Sulphur...sulphur and hydrogen bonding contacts for **(S,S)-1.Br**.

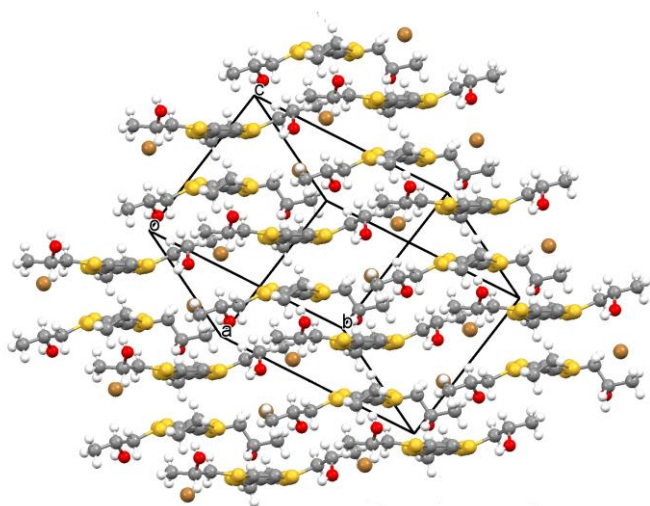


Fig. 15 Packing of donor molecules in **(S,S)-1.Br** in a layer perpendicular to the *b* axis.

Conclusions

We report the crystal structures and resistivities of a series of new 1:1 salts of the enantiopure donor bis(2-hydroxypropylthio)ethylenedithiotetrathiafulvalene with bromide, chloride, perchlorate or hexafluorophosphate anions. The crystal structures, room temperature resistivities and activation energies are similar for all four enantiopure salts from perchlorate and hexafluorophosphate salts, and are comparable to those from the isostructural tetrafluoroborate salts which was reported previously. The crystal structures of the hydrated chloride salt and the bromide salt are quite different. The flexibility and hydrogen-bonding ability of the side-chains of the donor molecule are responsible for producing the variety in packing motifs, and the hydroxyl groups are involved in interactions with the anions in the cases reported here. In contrast for the salts with polyiodide ions, the hydrogen bonding almost exclusively involves interactions between side chains. The resistivities and E_a values are in the range expected for TTF-based salts.²⁴ The resistivities of some of the chiral radical-cation salts reported here are lower than might have been expected for TTF or EDT-TTF (donor)₂²⁺ dimers having inter-dimer S...S contacts >3.7 Å to the nearest neighbouring dimer. This donor has now produced a family of semiconductors and a single metallic radical-cation salt with triiodide. We are continuing to explore the production of further salts using the pool of chiral and achiral anions available to produce radical-cation salts in which the individual chirality of the donor molecule is expressed throughout the crystal structure. The synthesis of these chiral conductors will allow the investigation of the electrical magnetochiral anisotropy effect.

Table 1. Crystallographic data for ClO₄ salts of **1**.^a

	(<i>S,S</i>)- 1 .ClO ₄	(<i>R,R</i>)- 1 .ClO ₄
Formula	C ₁₄ H ₁₈ ClO ₆ S ₈	C ₁₄ H ₁₈ ClO ₆ S ₈
<i>M_r</i> / g mol ⁻¹	574.22	574.22
T / K	296(2)	100(2)
λ / Å	0.71075	0.68890
μ / mm ⁻¹	0.934	0.906
Crystal System	Orthorhombic	Orthorhombic
Space Group	C222 ₁	C222 ₁
<i>a</i> /Å	7.8561(6)	7.707(16)
<i>b</i> /Å	21.2753(16)	21.04(4)
<i>c</i> /Å	27.155(2)	26.59(5)
α/°	90	90
β/°	90	90
γ/°	90	90
<i>V</i> / Å ³	4538.6(6)	4312(15)
<i>Z</i>	8	8
ρ / g cm ⁻³	1.681	1.769
Flack parameter	-0.09(15)	-0.2(5)
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0589	0.1393
<i>wR</i> [all data]	0.1424	0.3991
CCDC No.	1548672	1548676

^a*meso/rac-1*.ClO₄ unit cell at 100(2)K, monoclinic, *C2/c*, 7.6787(3), 21.1403(8), 26.7794(10) Å, 91.782(4)°, *V* = 4345.0(3) Å³, *Z* = 8.

Table 2. Crystallographic data for PF₆ salts of **1**.^b

	(<i>S,S</i>)- 1 .PF ₆	(<i>R,R</i>)- 1 .PF ₆
Formula	C ₁₄ H ₁₈ F ₆ O ₂ PS ₈	C ₁₄ H ₁₈ F ₆ O ₂ PS ₈
<i>M_r</i> / g mol ⁻¹	619.74	619.74
T / K	298(2)	100(2)
λ / Å	0.71075	0.71075
μ / mm ⁻¹	0.884	0.918
Crystal System	Orthorhombic	Orthorhombic
Space Group	C222 ₁	C222 ₁
<i>a</i> /Å	7.9370(7)	7.8564(18)
<i>b</i> /Å	21.4936(16)	21.389(5)
<i>c</i> /Å	27.622(3)	27.036(6)
α/°	90	90
β/°	90	90
γ/°	90	90
<i>V</i> / Å ³	4712.3(7)	4543.1(18)
<i>Z</i>	8	8
ρ / g cm ⁻³	1.747	1.812
Flack parameter	0.07(12)	0.08(7)
<i>R</i> 1 [<i>I</i> > 2σ(<i>I</i>)]	0.0517	0.0678
<i>wR</i> [all data]	0.1618	0.1568
CCDC No.	1548679	1548675

^b*meso/rac-1*.PF₆ unit cell at 100(2)K, monoclinic, *C2/c*, 7.958(14), 21.56(4), 26.95(5) Å, 93.67(2)°, *V* = 4614(15) Å³, *Z* = 8.

Table 3. Short S---S contacts between TTF units of a dimer pair for the ClO₄ salts of **1**: **(S,S)**-**1**.ClO₄ at 296 K, **(R,R)**-**1**.ClO₄ at 100 K (/ \AA).

	(S,S) - 1 .ClO ₄	(R,R) - 1 .ClO ₄
S3...S5	3.475(2)	3.497(13)
S4...S6	3.565(2)	3.569(13)

Table 4. Short S---S contacts between TTF units of a dimer pair for the PF₆ salts of **1**: **(S,S)**-**1**.PF₆ at 298 K, **(R,R)**-**1**.PF₆ at 100 K (/ \AA).

	(S,S) - 1 .PF ₆	(R,R) - 1 .PF ₆
S3...S5	3.6129(15)	3.591(3)
S4...S6	3.5237(17)	3.474(3)

Table 5. Activation energy, E_a , and room temperature resistivity values for measurements on two single crystals of **(S,S)**-**1**.ClO₄ and two single crystals of **(R,R)**-**1**.ClO₄. †

(S,S) - 1 .ClO ₄	(R,R) - 1 .ClO ₄
0.157 eV	0.176 eV
3.4×10^3 Ohm cm	3.9×10^3 Ohm cm
0.168 eV	0.166 eV
9.1×10^2 Ohm cm	8.0×10^3 Ohm cm

Table 6. Activation energy, E_a , and room temperature resistivity values for measurements on two single crystals of **(S,S)**-**1**.PF₆ and one single crystal of **(R,R)**-**1**.PF₆.^{a†}

(S,S) - 1 .PF ₆	(R,R) - 1 .PF ₆
0.166 eV	0.165 eV
4.7×10^2 Ohm cm	9.2×10^2 Ohm cm
0.163 eV	
3.3×10^2 Ohm cm	

^aThere were insufficient suitable crystals of **(R,R)**-**1**.PF₆ for further study.

Table 7. Crystallographic data for Cl and Br salts of **1**.[†]

	(S,S) - 1 .Cl.H ₂ O	(S,S) - 1 .Br
Formula	C ₁₄ H ₂₀ ClO ₃ S ₈	C ₁₄ H ₁₈ BrO ₂ S ₈
M_r / g mol ⁻¹	528.24	554.66
T / K	296(2)	150(2)
λ / \AA	0.71075	0.71073
μ / mm ⁻¹	0.981	2.815
Crystal System	Triclinic	Monoclinic
Space Group	<i>P</i> 1	<i>P</i> 2 ₁
a / \AA	7.4332(12)	9.8310(2)
b / \AA	12.5638(19)	19.9437(4)
c / \AA	12.657(2)	10.6022(2)
α / °	67.799(10)	90
β / °	78.034(13)	97.857(2)
γ / °	78.704(13)	90
V / \AA^3	1061.6(3)	2029.21(5)
Z	2	4
ρ / g cm ⁻³	1.653	1.789
Flack parameter	0.00(7)	0.002(6)
$R1$ [$I > 2\sigma(I)$]	0.0497	0.0342
wR [all data]	0.1401	0.0759
CCDC No.	1548677	1548680

Table 8. Face-to face S---S contacts for the four central sulphur of the TTF core for **(S,S)**-**1**.Cl.H₂O (/ \AA).

	(S,S) - 1 .Cl.H ₂ O
S3...S13	3.565(3)
S4...S14	3.728(3)
S5...S11	3.758(3)
S6...S12	3.509(3)

Table 9. Activation energy, E_a , and room temperature resistivity values for measurements on two single crystals of **(S,S)**-**1**.Cl.H₂O and two single crystals of **(S,S)**-**1**.Br. †

(S,S) - 1 .Cl.H ₂ O	(S,S) - 1 .Br
0.207 eV	0.198 eV
7.2×10^2 Ohm cm	3.2×10^4 Ohm cm
0.177 eV	0.297 eV
4.9×10^2 Ohm cm	4.4×10^4 Ohm cm

Table 10. Face-to face S---S contacts for the four central sulphur of the TTF core for **(S,S)**-**1**.Br (/ \AA).

	(S,S) - 1 .Br
S19...S37	3.4744(16)
S26...S45	3.5828(16)
S5...S34	3.5135(16)
S3...S27	3.5805(16)

Acknowledgements

This work has been supported by the Royal Society [Research Grants (RG100853 and RG081209), International Exchange Scheme (IE130367 and IE150152), and International Joint Project (JP0869972)]. JRL and LM would like to thank Nottingham Trent University for PhD funding.

Notes and references

*Electronic supplementary information (ESI) available. CCDC 1548672-1548680. For ESI and crystallographic data in CIF or other electronic format see DOI: 10.1039/????????????

† X-ray single crystal diffraction measurements for (*S,S*)-1.CIO₄, (*S,S*)-1.PF₆ and (*S,S*)-1.Cl.H₂O were performed using a Rigaku Mercury 2 CCD configured with Rigaku MicroMax-007HF generator and VariMax confocal mirror at room temperature using MoK α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods and refined by full-matrix least squared techniques based on F^2 (SHELXL97¹⁶).

X-Ray single crystal diffraction measurements for (*R,R*)-1.PF₆ and (*meso/rac*)-1.CIO₄ were performed using a Rigaku AFC12 diffractometer at 100K using MoK α radiation ($\lambda = 0.71073$ Å). Structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 (SHELXL17).

X-ray single crystal diffraction measurements for (*meso/rac*)-1.PF₆ and (*R,R*)-1.CIO₄ were performed at the Diamond Light Source, UK using Beamline I19 synchrotron X-ray radiation ($\lambda = 0.6889$ Å) situated on an undulator insertion device with a combination of double crystal monochromator, vertical and horizontal focussing mirrors and a series of beam slits (primary white beam and either side of the focussing mirrors). The experimental hutch (EH1) is equipped with a Crystal Logic 4-circle kappa geometry goniometer with a Rigaku Saturn 724 CCD detector and an Oxford Cryosystems Cryostream Plus cryostat (80–500 K). Data reduction, cell refinement and absorption correction were performed using CrystalClear. The structure was solved with SUPERFLIP¹⁸ and refined with SHELXL2013¹⁹ within OLEX2²⁰.

X-Ray single crystal diffraction measurements for (*S,S*)-1.Br were performed using a Rigaku Oxford Diffraction Xcalibur System equipped with a Sapphire detector at room temperature using MoK α radiation ($\lambda = 0.71073$ Å) with the Crystalis software²¹. The structures were solved by direct methods and refined by full-matrix least squares techniques based on F^2 using CRYSTALS.²² All molecular illustrations were prepared with Mercury.²³

- 1 F. Qin, W. Shi, T. Ideue, M. Yoshida, A. Zak, R. Tenne, T. Kikitsu, D. Inoue, D. Hashizume and Y. Iwasa, *Nature Commun.*, 2017, **8**, 14465 doi: 10.1038/ncomms14465 (2017).
- 2 G. L. J. A. Rikken, and E. Raupach, *Nature*, 1997, **390**, 493-494; G. L. J. A. Rikken, J. Folling and P. Wyder, *Phys. Rev. Lett.*, 2001, **87**, 236602/1-4.
- 3 V. Krstic, S. Roth, M. Burghard, K. Kern and G. L. J. A. Rikken, *J. Chem. Phys.*, 2002, **117**, 11315-11319; V. Krstic and G. L. J. A. Rikken, *Chem. Phys. Lett.*, 2002, **364**, 51-56; G. L. J. A. Rikken, *Science*, 2011, **331**, 864-865.
- 4 (a) A. M. Madalan, E. Canadell, P. Auban-Senzier, D. Brânzea, N. Avarvari and M. Andruh, *New J. Chem.*, 2008, **32**, 333-339; (b) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, A. Murcia-Martinez and E. Canadell, *Inorg. Chem.*, 2004, **43**, 8072-8077; (c) C. J. Gómez-García, E. Coronado, S. Curreli, Carlos Giménez-Saiz, P. Deplano, M. L. Mercuri, L. Pilia, A. Serpe, C. Faulmann and E. Canadell, *Chem. Commun.*, 2006, 4931-4933; (d) M. Atzori, F. Pop, P. Auban-Senzier, C. J. Gómez-García, E. Canadell, F. Artizzu, A. Serpe, P. Deplano, N. Avarvari and M. L. Mercuri, *Inorg. Chem.*, 2014, **53**, 7028-7039; M. Atzori, F. Pop, P. Auban-Senzier, R. Clérac, E. Canadell, M. L. Mercuri, and N. Avarvari, *Inorg. Chem.* 2015, **54**, 3643-3653; (e) M. Clemente-León, E. Coronado, C. J. Gómez-García, A. Soriano-Portillo, S. Constant, R. Frantz and J. Lacour, *Inorg. Chim. Acta*, 2007, **360**, 955-960; (f) M. Brezgunova, K.-S. Shin, P. Auban-Senzier, O. Jeannin and M. Fourmigué, *Chem. Commun.*, 2010, **46**, 3926-3928; (g) N. P. Chmel, L. E. N. Allana, J. M. Becker, G. J. Clarkson, S. S. Turner and P. Scott, *Dalton Trans.*, 2011, **40**, 1722-1731; (h) J. R. Lopez, L. Martin, J. D. Wallis, H. Akutsu, Y. Nakazawa, J.-i. Yamada, T. Kadoya, S. J. Coles and C. Wilson, *Dalton Trans.*, 2016, **45**, 9285-9293.
- 5 (a) M. Kurmoo, A. W. Graham, P. Day, S. J. Coles, M.B. Hursthouse, J. L. Caulfield, J. Singleton, F. L. Pratt, W. Hayes, L. Ducasse and P. Guionneau, *J. Am. Chem. Soc.*, 1995, **117**, 12209-12217; (b) L. Martin, S. S. Turner, P. Day, K. M. A. Malik, S. J. Coles and M. B. Hursthouse, *Chem. Commun.*, 1999, 513-514; (c) L. Martin, S. S. Turner, P. Day, P. Guionneau, J. A. K. Howard, D. E. Hibbs, M. E. Light, M. B. Hursthouse, M. Uruichi and K. Yakushi, *Inorg. Chem.*, 2001, **40**, 1363-1371; (d) H. Akutsu, A. Akutsu-Sato, S. S. Turner, D. Le Pevelen, P. Day, V. Laukhin, A. Klehe, J. Singleton, D. A. Tocher, M. R. Probert and J. A. K. Howard, *J. Am. Chem. Soc.*, 2002, **124**, 12430-12431; (e) T. G. Prokhorova, L. V. Zorina, S. V. Simonov, V. N. Zverev, E. Canadell, R. P. Shibaeva and E. B. Yagubskii, *CrystEngComm*, 2013, **15**, 7048-7055; (f) S. Benmansour, Y. Sánchez-Mañez and C. J. Gómez-García, *Magnetochemistry*, 2017, **3**, 7; (g) L. Martin, A. L. Morritt, J. R. Lopez, H. Akutsu, Y. Nakazawa, S. Imajo and Y. Ihara, *Inorg. Chem.*, 2017, **56**, 717-720; (h) J. Lopez, H. Akutsu and L. Martin, *Synth. Met.*, 2015, **209**, 188-191.
- 6 L. Martin, P. Day, H. Akutsu, J.-i. Yamada, S.-i. Nakatsuji, W. Clegg, R. W. Harrington, P.N. Horton, M. B. Hursthouse, P. McMillan, and S. Firth, *CrystEngComm*, 2007, **9**, 865-867.
- 7 L. Martin, P. Day, S.-i. Nakatsuji, J.-i. Yamada, H. Akutsu and P. N. Horton, *CrystEngComm*, 2010, **12**, 1369-1372; L. Martin, H. Akutsu, P. N. Horton and M. B. Hursthouse, *CrystEngComm*, 2015, **17**, 2783-2790; L. Martin, P. Day, P. N. Horton, S.-i. Nakatsuji, J.-i. Yamada and H. Akutsu, *J. Mater.Chem.*, 2010, **20**, 2738-2742.
- 8 I. Awgheda, S. Krivickas, S. Yang, L. Martin, M. A. Guziak, A. C. Brooks, F. Pelletier, M. Le Kerneau, P. Day, P. Horton, H. Akutsu and J. D. Wallis, *Tetrahedron*, 2013, **69**, 8738-8750.
- 9 F. Pop, P. Auban-Senzier, E. Canadell, G. L. J. A. Rikken and N. Avarvari, *Nat. Commun.* 5:3757 doi: 10.1038/ncomms4757 (2014).
- 10 F. Pop, P. Auban-Senzier, A. Frackowiak, K. Ptaszyński, I. Olejniczak, J. D. Wallis, E. Canadell and N. Avarvari, *J. Am. Chem. Soc.*, 2013, **135**, 17176-17186.
- 11 J. D. Wallis, A. Karrer and J. D. Dunitz, *Helv. Chim. Acta*, 1986, **69**, 69-70; F. Pop, S. Laroussi, T. Cauchy, C. J. Gomez-Garcia, J. D. Wallis and N. Avarvari, *Chirality*, 2013, **25**, 466-474; S. Yang, F. Pop, C. Melan, A. C. Brooks, L. Martin, P. Horton, P. Auban-Senzier, G. L. J. A.

- Rikken, N. Avarvari and J. D. Wallis, *CrystEngComm.*, 2014, **16**, 3906-3916.
- 12 S. Yang, A. C. Brooks, L. Martin, P. Day, M. Pilkington, W. Clegg, R. W. Harrington, L. Russo and J. D. Wallis, *Tetrahedron*, 2010, **66**, 6977-6989.
- 13 R. J. Brown, A. C. Brooks, J.-P. Griffiths, B. Vital, P. Day and J. D. Wallis. *Org. Biomol. Chem.*, 2007, 3172-3182.
- 14 L. Martin, J. D. Wallis, M. A. Guziak, J. Oxspring, J. R. Lopez, S-i. Nakatsuji, J-i. Yamada and H. Akutsu, *CrystEngComm*, 2014, **16**, 5424-5429.
- 15 L. Martin, J. D. Wallis, M. Guziak, P. Maksymiwi, F. Konalian-Kempf, A. Christian, S-i. Nakatsuji, J-i. Yamada and H. Akutsu, *Dalton Trans.*, 2017, **46**, 4225-4234.
- 16 G. M. Sheldrick, *Acta. Crystallogr., Sect. A*, 2008, **64**, 112-122.
- 17 G. M. Sheldrick, *Acta. Crystallogr., Sect. C*, 2015, **71**, 3-8.
- 18 L. Palatinus and G. Chapuis, SUPERFLIP, *J. Appl. Cryst.*, 2007, **40**, 786-790.
- 19 G. M. Sheldrick, SHELX2013, University of Göttingen, Germany, 2012.
- 20 O. V. Dolomanov, L. J. Bourhis, R. J. Gildea, J. A. K. Howard and H. Puschmann, *OLEX2, J. Appl. Crystallogr.*, 2009, **42**, 339-341.
- 21 CrysAlisPro, Agilent Technologies, Version 1.171.35.15 (release 03-08-2011 CrysAlis171 .NET).
- 22 P. W. Betteridge, J. R. Carruthers, R. I. Cooper, K. Prout and D. J. Watkin, *J. Appl. Crystallogr.*, 2003, **36**, 1487.
- 23 C. F. Macrae, P. R. Edgington, P. McCabe, E. Pidcock, G. P. Shields, R. Taylor, M. Towler and J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453-457.
- 24 J.-i. Yamada and T. Sugimoto, TTF Chemistry. Fundamentals and Applications of Tetrathiafulvalene, Kodansha Tokyo and Springer Verlag, Berlin, Heidelberg, New York, 2004; C. Rovira, *Chem. Rev.*, 2004, **104**(11), 5289-5318; P. Frère and P. J. Skabara, *Chem. Soc. Rev.*, 2005, **34**, 69-98.