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# Enantiopure and racemic radical-cation salts of bis(2'-hydroxypropylthio)(ethylenedithio)TTF with polyiodide anions

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The chiral TTF-based donor molecule bis(2'-hydroxypropylthio)(ethylenedithio)tetrathiafulvalene (BHPT-EDT-TTF) has produced enantiopure *R,R* and *S,S* radical-cation salts with polyiodide anions  $I_3^-$  and  $I_8^{2-}$ . Enantiomeric 6:6 donor: $I_3$  phases grown from either the *R,R* or *S,S* donor are  
10 semiconducting with similar activation energies of 0.24-0.30 eV and 0.22-0.23 eV respectively, and contains three unique face-to-face donor pairs whose relative orientation is determined by side chain conformations and hydrogen bonding. Racemic material under the same conditions gave an insulating centrosymmetric phase with *R,R* and *S,S* donor cations in a face-to-face pair partnered with an octa-iodide dianion, and with a *ca* 3:1 disorder between the enantiomers. Enantiopure BHPT-EDT-TTF yielded two  
15 further insulating crystalline phases of composition 2:2 with triiodide and 2:1 with octa-iodide.

## Introduction

A great deal of research has been performed in the area of  
20 molecular organic conductors towards the combination of two different properties that may not be found together in the same crystal lattice in nature.<sup>1</sup> Recently there has been increased interest in the search for the combination of conductivity and chirality to understand the observation of magnetochiral anisotropy as seen in carbon nanotubes.<sup>2</sup> In the tetrathiafulvalene-based radical cation  
25 salts chirality can be introduced *via* a chiral counter anion, an included chiral solvent molecule, electrocrystallisation from a chiral solvent, or a chiral donor molecule.<sup>3</sup> Differences in the resistivities between the racemic and enantiopure form have been attributed to structural disorder in the racemate.

30 Radical-cation salts have been synthesized from a variety of chiral anions including  $[\text{Cr}(2,2'\text{-bipy})(\text{oxalate})_2]^-$ ,<sup>4a</sup>  $[\text{Sb}_2(\text{L-tartrate})_2]^{2-}$ ,<sup>4b</sup>  $[\text{Fe}(\text{croconate})_3]^{3-}$ ,<sup>4c</sup>  $[\text{Fe}(\text{chloranilate})_3]^{3-}$ ,<sup>4d</sup> TRISPHAT,<sup>4e</sup> D-camphorsulfonate,<sup>4f</sup>  $\text{Co}^{\text{III}}$  complexes of optically pure pyridinecarboxamide anions,<sup>4g</sup> and  $\text{B}(\text{malate})_2$ .<sup>4h</sup> The family  
35 of salts of the formula  $\text{BEDT-TTF}_4[(\text{NH}_4/\text{H}_3\text{O})\text{M}(\text{oxalate})_3]\cdot\text{guest}$  show superconducting or semiconducting behaviour depending on the distribution of  $\Delta$  and  $\Lambda$  enantiomers of  $\text{M}(\text{oxalate})_3^{3-}$  ( $\text{M} = \text{Fe}, \text{Cr}, \text{Co}, \text{Al}, \text{Ga}, \text{Ru}$ ) within the insulating layers. The guest solvent molecules included  
40 in the insulating layers can lead to different donor packing arrangements and thus a variety of conducting properties.<sup>5</sup> When an enantiopure guest molecule such as (*S*)-*sec*-phenethyl alcohol is included a more pronounced metal-insulator transition is observed than for the isostructural racemic analogue owing to disorder in the  
45 *R/S* salt.<sup>6</sup> Crystallisation from chiral solvents can also lead to salts containing only a single enantiomer of the  $\text{Cr}(\text{oxalate})_3$  anion through chiral induction.<sup>7</sup>

Since the first enantiopure donor molecule was synthesised, (*S,S,S,S*)-tetramethyl-BEDT-TTF,<sup>8</sup> there are now many examples  
50 of enantiopure donor molecules based on TTF. Salts of TTF-oxazolines have shown effects of structural disorder upon the conducting properties.<sup>9</sup> Enantiopure radical-cation salts of (*S,S*)- and (*R,R*)-(DM-EDT-TTF)<sub>2</sub>ClO<sub>4</sub> crystallise in space groups *P*6<sub>2</sub>22 and *P*6<sub>4</sub>22 and show metallic behavior down to 40K. The  
55 observation of electrical magneto-chiral anisotropy in these salts confirms the chiral nature of charge transport. The DM-EDT-TTF donor has also produced racemic salts from PF<sub>6</sub> which show metal-like conductivity, whilst the enantiopure salts have a completely different packing arrangement and room temperature charge  
60 ordering and semiconducting behaviour are observed.<sup>10</sup>

We have recently reported the synthesis of a novel enantiopure donor molecule which has the potential to form hydrogen bonds  
65 *via* its 2-hydroxypropylthio side chains.<sup>11</sup> Through electrocrystallisation with the anion BF<sub>4</sub><sup>-</sup> the enantiopure *R,R* or *S,S* salts were obtained which were both 1:1 semiconducting salts with activation energies of 0.19-0.24 eV, whilst the racemate has a smaller activation energy of 0.15-0.17 eV.<sup>12</sup> This is in contrast to previous observations in TTF-oxazoline-PF<sub>6</sub> and BEDT-TTF<sub>4</sub>[(NH<sub>4</sub>)Fe(oxalate)<sub>3</sub>].*sec*-phenethyl alcohol where the  
70 structural disorder had the effect of reducing the conductivity in the racemate.<sup>6,9</sup>

We report here the synthesis of a series of radical-cation salts of enantiopure or racemic bis(2'-hydroxypropylthio)(ethylenedithio)TTF (BHPT-EDT-TTF, Scheme 1) with  
75 polyiodide anions prepared by diffusion and electrocrystallisation methods

## Experimental

**Donor synthesis:** Enantiopure (*S,S*)-BHPT-EDT-TTF and (*R,R*)-BHPT-EDT-TTF were synthesized using the method described previously.<sup>11</sup> *rac*-BHPT-EDT-TTF was prepared by making a 50:50 mixture of (*S,S*)-BHPT-EDT-TTF and (*R,R*)-BHPT-EDT-TTF.

Single crystals of radical-cation salts were grown by slow diffusion or *via* electrocrystallisation in H-shaped cells as follows:

**Synthesis of (*S,S*)-1:** 5 mg of (*S,S*)-BHPT-EDT-TTF was dissolved in 3 ml of dichloromethane in a test tube. On top of this were added successive layers of 2 ml dichloromethane, 2 ml hexane, and 3 ml hexane containing 10 mg iodine. After several weeks, brown crystals were obtained as thin plates.

**Synthesis of (*R,R*)-1:** Same as for (*S,S*)-1 but starting from (*R,R*)-BHPT-EDT-TTF to give brown plates.

**Synthesis of (*S,S*)-2:** 120 mg of tetrabutylammonium triiodide dissolved in 20 ml tetrahydrofuran was added to the cathode side of a H-cell, and 10 mg of donor (*S,S*)-BHPT-EDT-TTF in tetrahydrofuran was added to the anode side. 0.1  $\mu$ A were passed through platinum electrodes on which thick black plate crystals of enantiopure (*S,S*)-2 grew over 3 weeks. Crystals of this phase were also grown by diffusion of iodine into 5 mg of (*S,S*)-BHPT-EDT-TTF dissolved in 3 ml of dichloromethane in a test tube. On top of this were added successive layers of 2 ml dichloromethane, 2 ml tetrahydrofuran, and 3 ml tetrahydrofuran containing 10 mg iodine. After two weeks crystals were obtained as black thick plates.

**Synthesis of (*R,R*)-2:** Same as for (*S,S*)-2 but starting from (*R,R*)-BHPT-EDT-TTF.

**Synthesis of (*S,S*)-3:** A few crystals of this phase were obtained in the batches following the method for (*S,S*)-1. Crystals were obtained as black needles.

**Synthesis of (*R,R*)-3:** Same as for (*S,S*)-3 but starting from (*R,R*)-BHPT-EDT-TTF.

**Synthesis of (*rac*)-4:** Same method as for either (*S,S*)-1 or (*S,S*)-2 but starting from a 50:50 mixture of (*S,S*)-BHPT-EDT-TTF and (*R,R*)-BHPT-EDT-TTF. Crystals were obtained as dark blue-green blocks.

All chemicals were purchased from Sigma Aldrich and used as received. The H-shaped cells had two platinum electrodes separated by a porous glass frit to prevent contamination. The electrodes were cleaned by applying a voltage across the electrodes in 1 M H<sub>2</sub>SO<sub>4</sub> in each direction resulting in the evolution of H<sub>2</sub> and O<sub>2</sub> at the electrodes. Finally the electrodes were washed in distilled water and thoroughly dried. The cells were fixed inside sand-filled compartments on a vibration-free table and kept at a constant temperature of 293 K.

Four-probe DC transport measurements were made on several crystals using a HUSO HECS 994C multi-channel conductometer. Gold wires (15  $\mu$ m diameter) were attached to the crystal, and the attached wires were connected to an four-pin integrated circuit plug with gold conductive cement.

X-Ray single crystal diffraction measurements were performed on (*S,S*) salts using a Rigaku Mercury 2 CCD configured with Rigaku MicroMax-007HF generator and VariMax confocal mirror using MoK $\alpha$  radiation ( $\lambda = 0.71073$  Å) at room temperature using the CrystalClear program suite.<sup>13</sup> Structures were solved by direct methods and refined by full-matrix least squares techniques based

on  $F^2$  solved and refined with programs from the SHELX family of computer programs.<sup>14</sup>

X-ray single crystal diffraction measurements were performed on (*R,R*) and racemic salts using a Rigaku Oxford Diffraction Excalibur System equipped with a Sapphire detector at 150-155 K using the CrysAlis software.<sup>15</sup> Structures were solved by direct methods (SHELXS-86<sup>16</sup>) and refined by full-matrix least squares techniques based on  $F^2$  using SHELXL-2014<sup>14</sup> and the XSEED<sup>17</sup> interface. Molecular illustrations were prepared with Mercury.<sup>18</sup>

Sample decomposition at the lowest laser power and exposure time precluded a Raman study of the charges on donor and iodide molecules.<sup>19</sup>

## Discussion

Diffusion of a hexane solution of iodine into a dichloromethane solution of (*R,R*)-BHPT-EDT-TTF over several days gave brown plates of a semiconducting salt with triiodide with a formula *R,R*-BHPT-EDT-TTF<sub>6</sub>(I<sub>3</sub>)<sub>6</sub>, (***R,R*-1**), as well as some black needles of an insulating phase (*R,R*-BHPT-EDT-TTF)<sub>2</sub>I<sub>8</sub> with octa-iodide, (***R,R*-3**). Use of the (*S,S*)-BHPT-EDT-TTF under the same conditions gave the corresponding salts of the *S,S* enantiomer, (***S,S*-1**) and (***S,S*-3**). When a THF solution of iodine was used for the diffusion into a dichloromethane solution of (*S,S*)-BHPT-EDT-TTF a different type of 1:1 salt with triiodide, (*S,S*-BHPT-EDT-TTF)I<sub>3</sub> (***S,S*-2**), was obtained which was insulating. This phase was also produced by electrocrystallisation with tetrabutylammonium triiodide in THF. When a 1:1 mixture of the two enantiomers of the donor was used under any of these conditions, the racemic salt, (BHPT-EDT-TTF)<sub>2</sub>I<sub>8</sub> (***rac*-4**), was always obtained which was composed of the two enantiomeric donor cations with the octa-iodide dianion. This material was insulating, and the crystal structure has some resemblance to that of ***S,S*-3**, but is not very closely related. The crystal structures of (***R,R*-1**), (***S,S*-1**), (***S,S*-2**), (***S,S*-3**) and (***rac*-4**) were measured by X-ray crystallography (Table 1).

### Salt 1

The salts (***S,S*-1**) and (***R,R*-1**) contain a 1:1 ratio of donor cation to triiodide which crystallise in the triclinic crystal system, in space group *P*1, but with six crystallographically independent BHPT-EDT-TTF radical cations and six crystallographically independent triiodide anions (Fig. 1). The crystal of the *R,R* enantiomeric salt was measured at 155 K and the crystal of the *S,S* enantiomeric salt was measured at 294 K; the former shows a slightly smaller unit cell (by *ca.* 3%). The structure of the *R,R* case will be discussed in detail (Fig. 2).

The six donor cations are organised into three pairs in which the two organosulfur systems pack face-to-face with the donor cations oriented head-to-tail. The two organosulfur systems are offset from each other (*cf.* structures ***S,S*-2** and ***S,S*-3** and ***rac*-4**) with four short S...S contacts between the central four S atoms in the range 3.309-3.567 Å (Fig. 3). The donor cations pairs will be referred to as donors 1 and 2, donors 3 and 4 and donors 5 and 6. The three pairs lie side by side with their long molecular axes oriented in the same general direction, but the three pairs are not exactly parallel to each other. Throughout the crystal these donor cation pairs form layers approximately perpendicular to the long axis of the organosulfur

system, with the donor cations in each pair projecting their hydroxylated side chains to opposite faces of the layer. Thus hydrogen bonding is important in the interlayer interactions.

**Table 1** Crystallographic data for **1-4** (Fig. S3)<sup>†</sup>

	( <i>S,S</i> )- <b>1</b>	( <i>R,R</i> )- <b>1</b>	( <i>S,S</i> )- <b>2</b>	( <i>S,S</i> )- <b>3</b>	( <i>rac</i> )- <b>4</b>
Formula	C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> S <sub>8</sub> I <sub>3</sub>	C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> S <sub>8</sub> I <sub>3</sub>	C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> S <sub>8</sub> I <sub>3</sub>	C <sub>28</sub> H <sub>36</sub> O <sub>4</sub> S <sub>16</sub> I <sub>8</sub>	C <sub>14</sub> H <sub>18</sub> O <sub>2</sub> S <sub>8</sub> I <sub>4</sub>
<i>M<sub>r</sub></i> / g mol <sup>-1</sup>	855.49	855.46	855.46	1964.73	982.36
Temp / K	293	155	294	294	150
Crystal System	triclinic	Triclinic	triclinic	triclinic	Triclinic
Space Group	<i>PI</i>	<i>PI</i>	<i>PI</i>	<i>PI</i>	<i>P-1</i>
<i>a</i> /Å	10.015(3)	9.9238(5)	9.7612(10)	9.591(4)	9.3381(3)
<i>b</i> /Å	16.004(4)	15.8805(7)	10.9021(19)	11.061(5)	10.5549(3)
<i>c</i> /Å	24.666(7)	24.2594(10)	13.4544(15)	14.298(6)	14.4495(5)
$\alpha^\circ$	91.869(6)	91.300(4)	80.710(14)	101.685(4)	86.528(3)
$\beta^\circ$	100.996(7)	101.304(4)	69.632(11)	104.936(6)	78.566(3)
$\gamma^\circ$	95.386(8)	95.309(4)	75.476(13)	101.288(7)	74.437(3)
<i>V</i> / Å <sup>3</sup>	3858.6(18)	3729.6(3)	1295.0(3)	1385.1(10)	1344.70(8)
<i>Z</i>	6	6	2	1	2
$\rho$ / g cm <sup>-3</sup>	2.209	2.285	2.194	2.356	2.426
Flack parameter	-0.03(2)	-0.01(2)	0.07(3)	0.02(4)	n/a
<i>R</i> 1 [ <i>I</i> > 2 $\sigma$ ( <i>I</i> )]	0.0645	0.0636	0.0471	0.0618	0.0510
<i>wR</i> [all data]	0.2059	0.122	0.1122	0.209	0.116
CCDC No.	1520875	1520876	1520877	1520878	1520879

<sup>†</sup>Unit cells were also obtained for the insulators (*R,R*)-**2** and (*R,R*)-**3** at 293 K. (*R,R*)-**2** *PI*, 9.7466(18), 10.8914(19), 13.434(2) Å, 80.662(11), 69.596(9), 75.522(12)°. (*R,R*)-**3** *PI*, 9.566(18), 10.996(15), 14.23(2) Å, 101.51(13), 105.23(16), 101.27(14)°.

The triiodides are oriented in the same general direction as the long axes of the donor cations and lie side by side with them. Structures have been observed previously where linear anions (I<sub>3</sub><sup>-</sup> AuBr<sub>2</sub><sup>-</sup>, IBr<sub>2</sub><sup>-</sup>, AuI<sub>2</sub><sup>-</sup>) are inserted in the organic layer with unsymmetrical donor molecules packing in the tau phase.<sup>20</sup> The triiodides' I-I bond lengths lie in the close range of 2.8575(18)-2.9799(19) Å. There are two "end-on" pairs of triiodides, which have I<sub>3</sub>---I<sub>3</sub> separations of 3.4708(2) and 3.6320(2) Å, which are each isolated from the corresponding anions in adjacent unit cells by much longer I<sub>3</sub>---I<sub>3</sub> separations of 5.1731(18) and 4.8927(21) Å, respectively. The (I<sub>3</sub>)<sub>2</sub> units are near to linear with angles at iodine in the range 164.54(5)-178.25(6)°, but offset from their neighbours with the angles at the terminal iodine atoms in the range 144.10(4)-146.71(4)°. However, the other set of two triiodides forms a roughly linear arrangement of anions running throughout the crystal. The two I<sub>3</sub>---I<sub>3</sub> contacts along the rows are similar 3.9186(2) and 4.0176(2) Å and all angles at iodine atoms lie in the range 164.54(5)-178.25(6)°. The shortest I<sub>3</sub>---I<sub>3</sub> contacts known are *ca.* 3.42 Å.<sup>11</sup>

The donor cations are linked together by hydrogen bonds between hydroxyl groups attached to the stereogenic centres, and eleven out of twelve of the hydroxyl groups are involved. The conformational freedom of the side chains allows considerable variation in their conformations, and it is not surprising that a rather irregular arrangement of cations and anions is possible. The conformations of the two 2*R*-2-hydroxypropylthio side chains in each donor cation can be characterised by three torsion angles (Table S1) and there is considerable variety among the twelve side chain conformations. For donor cations 1 and 2 the pairs of side chains have broadly similar conformations with both lying well out of the

donor plane, one with an extended three carbon chain, while the other one is twisted about the central C-C bond so that the oxygen atom completes the extended chain. For both donor cations 3 and 4 one chain lies so that the methylene group lies close to the organosulfur plane and the chain is

directed away from the plane and twisted so that the oxygen atom completes the extended conformation. The second chain lies out of organosulfur plane with different conformations about the central C-C bond for the two donor cations. There is thus no symmetry between these conformations within a donor cation pair. Similarly for donors 5 and 6 only one of the four side chains lies close to the organosulfur plane. For donor cations 1 and 2 only, the ethylene bridges of the donor cation, could be modelled as a *ca.* 1:1 mixture of two half chair conformations. Eleven of the hydroxyl groups are involved in hydrogen bonding to other hydroxyl groups at the interface between the layers of donor cations. The hydrogen bonding links are assigned from the O...O separations and the suitability of the angular dispositions of bonds and hydrogen bonds at the oxygens. Thus, there are three hydrogen bonding networks (ESI: Table 5, Figs. S1a-d), two involving four hydroxyl groups and one involving three hydroxyl groups, which each leaves one OH group without an acceptor. There are hydrogen bonds both between donor cations in the same layer and between donor cations in adjacent layers. The only OH group not involved is O(1)-H(1) on donor 1, for which O(1) lies 3.522 Å from the terminal iodine of a triiodide ion and a hydrogen bond (2.73 Å) is feasible. Together with the flexibility of the side chains, these hydrogen bonds act to determine the overall packing which is somewhat less orderly than in many related radical cation salts where there is not attractive bonding between side chains. There are seven short S...I contacts between donor cations and triiodide anions in the range 3.623-3.730 Å, and seven H...I

contacts in the range 3.03-3.17 Å.

The crystal structure of the *S,S* salt is related to the *R,R* salt by inversion symmetry but differs in that one of the side-chains of donor 2 is disordered 44:56 between two conformations in the room temperature structure of the *S,S* salt.

Resistivity measurements were performed on four crystals of (*S,S*)-**1** and two crystals of (*R,R*)-**1** (Table 2). Both show semiconducting behaviour with (*S,S*)-**1** having activation energies in the range 0.24-0.30 eV, and (*R,R*)-**1** slightly lower, in the range 0.22-0.23 eV. The room temperature resistivities for both are similar with values in the range  $0.5\text{--}6.3 \times 10^4 \text{ } \Omega\cdot\text{cm}$  for (*S,S*)-**1** and  $1.3\text{--}3.5 \times 10^4 \text{ } \Omega\cdot\text{cm}$  for (*R,R*)-**1** (Fig. 4).

**Table 2.**  $E_a$  and room temperature resistivity values for crystals of (*S,S*)-**1** and (*R,R*)-**1**.

( <i>S,S</i> )- <b>1</b>	( <i>R,R</i> )- <b>1</b>
$E_a = 0.28 \text{ eV}$ $\rho_{RT} = 4.3 \times 10^4 \text{ } \Omega\cdot\text{cm}$	$E_a = 0.22 \text{ eV}$ $\rho_{RT} = 1.3 \times 10^4 \text{ } \Omega\cdot\text{cm}$
$E_a = 0.30 \text{ eV}$ $\rho_{RT} = 2.2 \times 10^4 \text{ } \Omega\cdot\text{cm}$	$E_a = 0.23 \text{ eV}$ $\rho_{RT} = 3.5 \times 10^4 \text{ } \Omega\cdot\text{cm}$
$E_a = 0.24 \text{ eV}$ $\rho_{RT} = 6.3 \times 10^4 \text{ } \Omega\cdot\text{cm}$	
$E_a = 0.24 \text{ eV}$ $\rho_{RT} = 4.9 \times 10^3 \text{ } \Omega\cdot\text{cm}$	

### Salt (*S,S*)-**2**

Salt (*S,S*)-**2** is a 1:1 salt having the formula (*S,S*-BHPT-EDT-TTF)<sub>3</sub> and crystallising in the triclinic crystal system in the space group *P1*. The unit cell contains two crystallographically independent BHPT-EDT-TTF molecules and two triiodide anions (Fig. 4). The donor cations form face-to-face dimers, oriented head-to-tail, with the central four TTF sulfur atoms lying opposite each other with four short S...S contacts between them (3.32(1)-3.39(1) Å) (Fig. 5). Neighbouring donor cation pairs stack face-to-face in the *b* direction and side-to-side in the *a* direction, but in both cases they are separated by a triiodide anion and so have no short S...S contacts between them (Fig. 6). These two triiodides lie almost perpendicular to each other and parallel to the organosulfur plane of the donor cations (Fig. 7). The two triiodide anions are asymmetric and have a range of I-I bond lengths (2.865(1)-2.985(1) Å), but the two shorter ones involve terminal iodine atoms with notably larger and more ellipsoidal anisotropic displacement parameters indicative of some positional disorder. Each of the four terminal iodine atoms has a short contact with a hydrogen on a donor molecule side chain (H...I: 3.05-3.17 Å).

The side chains show a range of conformations but are all directed away from the donor cation pair (Table S2). The side chains of one donor cation form an intramolecular hydrogen bond between hydroxyl groups, while molecules of the other donor cation are linked by intermolecular hydrogen bonding along the *a* axis. There is an additional hydrogen bond between hydroxyl groups linking the two independent donors together along the *c* axis.

Resistivity of single crystals at room temperature showed insulating behaviour too high for measurement.

### Salt (*S,S*)-**3**

Salt (*S,S*)-**3** has the formula (*S,S*-BHPT-EDT-TTF)<sub>2</sub>I<sub>8</sub> and crystallises in the triclinic crystal system in the space group *P1*. The unit cell consists of two crystallographically independent BHPT-EDT-TTF molecules and one I<sub>8</sub><sup>2-</sup> anion (Fig. 8). The two donor cations form a face to face donor pair and are oriented head-to-tail (Fig. 9). The planar Z-shaped anions lie between the donor cation pairs with the central two iodine atoms lying between the chiral side chains (Figs. 10 and 11). The best planes of the anion and donor cations lie at *ca.* 23° to each other. The geometry of the polyiodide anion (Table 3) resembles two triiodide ions linked to the ends of an iodine molecule with I<sub>3</sub>...I<sub>2</sub> contacts of 3.262(5) and 3.317(5) Å with angles of 127.55(12) and 128.52(11)° at the third and sixth iodines in the I<sub>8</sub><sup>2-</sup> species, and almost linear at the four and fifth. These anions lie end to end with I...I contacts of 3.720(2) Å to form polyiodide ribbons running through the crystal (Figs. 12 and 13). There is one example of the inclusion of the polyiodide dianion I<sub>8</sub><sup>2-</sup> with BEDT-TTF: (BEDT-TTF)<sub>2</sub>(I<sub>3</sub>)(I<sub>8</sub>)<sub>0.5</sub>.<sup>21</sup> Octaiodide dianions have previously been found as a counter-anion to bulky cations such as M(II) tetrabenzob[bfj,n][1,5,9,13] tetraazacyclohexadecene,<sup>22a</sup> *N,N'*-dibenzyl-1,4,10,13-tetraoxo-7,16-diazacyclooctadecane,<sup>22b</sup> (crypt-2.2.2)H<sub>2</sub>,<sup>22c</sup> *N*-alkylurotropinium,<sup>21c</sup> Ni(phen)<sub>3</sub>,<sup>21c</sup> methyl-tri-*o*-tolylphosphonium,<sup>22d</sup> and Ni(2,5,8-trithia[9](2,9)-1,10-phenanthroline)(MeCN).<sup>22e</sup> The formation and shape of the polyiodides show sensitivity to the size and shape of the counter cation, with larger polyiodides preferring larger counter cations.<sup>23</sup> Typically the octaiodide dianion is planar, linear at most iodines but with angles of *ca* 90° at the third and sixth iodine atoms. In the case of *S,S*-**3** these two angles are larger but this is not unknown.

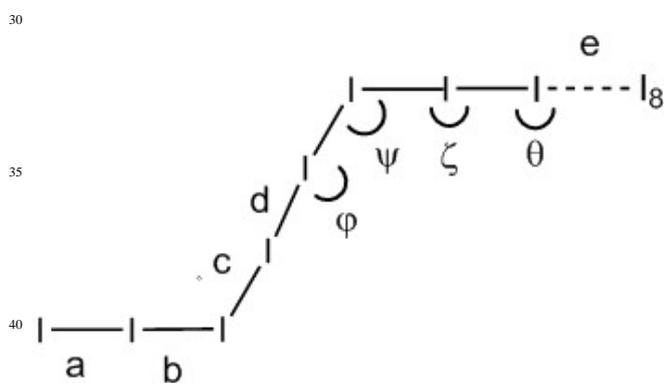
The two donor cations pack together in a face-to-face pair, oriented head-to-tail, and the organosulfur cores lie directly opposite of each other, with short S...S contacts between them for the central four S atoms (3.317(13)-3.512(13) Å) and one further short contact (3.592(15) Å) between two peripheral sulfur atoms. For both donor cations one side chain lies in the organosulfur plane with an extended carbon chain conformation, while the second side chain, while retaining the extended conformation, is rotated far out of the molecular plane, and by quite differing amounts for the two donor cations (torsions: S5-C7-S7-C9: 57.8°; S13-C21-S15-C23: 96.9°) (Table S3). There are just two short S...S contacts between donor cation pairs; these are between dithiin sulfur atoms at the unsubstituted ends of non-equivalent molecules (3.615(11) and 3.651(11) Å), with other sulfurs lying close to side chains or the polyiodide anion (Fig. 10). A O-H...O hydrogen bond links a side chain of one donor to the symmetry related donor in the *b* direction, and a further hydrogen bond links this side chain to the second donor cation lying in the *c* direction. There are four I...S contacts between donor cations and the polyiodide anion (I...S: 3.648-3.771 Å).

Resistivity of single crystals at room temperature showed insulating behaviour too high for measurement.

### rac-4

The crystal structure of the racemate salt is triclinic in space group *P*-1 and the unit cell contains the two enantiomers of the cation of (BHPT-EDT-TTF) along with the octaiodide dianion, though the relative orientation of cation and anion are different to that observed in *S,S*-3. The enantiomerically related cations lie face-to-face, organised head-to-tail, with the TTF units directly opposite each other with four short S...S contacts (3.302(3) and 3.491(3) Å). *R,R* and *S,S* enantiomers belonging to different radical cation pairs are linked by a hydrogen bond through the hydroxyl groups (ESI: Fig. S2). There is a *ca* 3:1 disorder between the enantiomers of the donor cation, though most atoms coincide with only the stereogenic centre and the hydroxyl group being modelled with two positions. The side chains take quite different conformations, the methylene group of one lies close to the donor plane, but for the other one it is strongly displaced from it (Table S4). The octaiodide dianion sits on a centre of symmetry so that only half the species in crystallographically unique. Its geometry differs from that observed in *S,S*-3 in that the angle at the fourth and fifth iodines is much smaller (84.23(2) *cf.* 127.55(12) and 128.51(11)°) (Table 3). There are three short I...S contacts between cation and anion in the range 3.587-3.739 Å. Resistivity of single crystals at room temperature showed insulating behaviour too high for measurement.

**Table 3** Bond lengths (Å) and angles (°) in the octa-iodides of *S,S*-3 and *rac*-4.



	a	b	c	d	e
<i>S,S</i> -3	3.2880(3), 2.872(3)	2.947(4), 2.980(4)	3.262(5), 3.317(5)	2.802(3)	3.720(2)

*rac*-4: 2.8419(6) 3.0027(7) 3.4089(9) 2.7654(15) 3.6079(10)

	φ	ψ	ζ	θ
<i>S,S</i> -3	175.54(10), 173.52(10)	127.55(12) 128.51(11)	175.85(10), 174.88(9)	154.12(8), 153.78(7)
<i>rac</i> -4	174.54(4)	84.23(2)	175.80(2)	150.50(3)

## Conclusions

- We report the first salts of each enantiomer of BHPT-EDT-TTF with triiodide and octaiodide. Both the *R,R* and *S,S* enantiomers of this donor give semiconducting 6:6 salts with triiodide, as well as an insulating 1:1 phase and a rare organosulfur donor salt with the  $I_8^{2-}$  dianion. Isostructural salts are not obtained when using the racemic donor which instead produces a 2:1 salt with the  $I_8^{2-}$  dianion whose crystal structure, although of the same composition, is not very closely related to the enantiopure octa-iodide salt. The semiconducting salts have complex crystal structures due to the conformational flexibility of the side chains and hydrogen bonding between them, in contrast to earlier examples of enantiopure/racemate salts where the side chain could not make such strong attractions. The semiconducting salt has short S...S contacts between dimers whilst the insulating salts have none owing to their segregation by iodide anions. In contrast to salts with BEDT-TTF, this series of salts have all involved radical cations of the donor, and no mixed valence salts. We are exploring the range of salts which can be made from this chiral donor with anions of other shapes, where hydrogen bonding to the anion may be as important as to other donors, in contrast to these polyiodide salts where the hydrogen bonding mainly involves just the donors.

## Acknowledgements

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## Notes and references

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<sup>‡</sup>CCDC 1520875-1520879 contains supplementary X-ray crystallographic data. This data can be obtained free of charge via <http://www.ccdc.cam.ac.uk/conts/retrieving.html>, or from the Cambridge Crystallographic Data Centre, Union Road, Cambridge, CB2 1EZ; fax:(+44) 1223-336-033 or email: [deposit@ccdc.cam.ac.uk](mailto:deposit@ccdc.cam.ac.uk).

## References

- E. Coronado, J. R. Galan-Mascaros, C. J. Gomez-Garcia and V. Laukhin, *Nature*, 2000, **408**, 447; A. Alberola, E. Coronado, J. R. Galan-Mascaros, C. Gimenez-Saiz and C. Gomez-Garcia, *J. Am. Chem. Soc.* 2003, **125**, 40, 10774; A. Akutsu-Sato, H. Akutsu, S. S. Turner, P. Day, M. R. Probert, J. A. K. Howard, T. Akutagawa, S. Takeda, T. Nakamura and T. Mori, *Angew. Chem., Int. Ed.*, 2005, **44**, 292.
- F. Pop, P. Auban-Senzier, E. Canadell, G.L.J.A. Rikken and N. Avarvari, *Nature Commun.*, 5:3757 DOI:10.1038/ncomms4757

- (2014); V. Krstić, S. Roth, M. Burghard, K. Kern and G. L. J. A. Rikken, *J. Phys. Chem.*, 2002, **117**, 11315.
- 3 N. Avarvari and J. D. Wallis, *J. Mater. Chem.*, 2009, **19**, 4061.
- 4 (a) A. M. Madalan, E. Canadell, P. Auban-Senzier, D. Brânzea, N. Avarvari and M. Andruh, *New J. Chem.*, 2008, **32**, 333; (b) E. Coronado, J. R. Galán-Mascarós, C. J. Gómez-García, A. Murcia-Martinez and E. Canadell, *Inorg. Chem.*, 2004, **43**, 8072; (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; (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; (e) M. Atzori, F. Pop, P. Auban-Senzier, R. Clérac, E. Canadell, M. L. Mercuri, and N. Avarvari, *Inorg. Chem.* 2015, **54**, 3643; (f) 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; (g) M. Brezgunova, K.-S. Shin, P. Auban-Senzier, O. Jeannin and M. Fourmigué, *Chem. Commun.*, 2010, **46**, 3926; (h) N. P. Chmel, L. E. N. Allana, J. M. Becker, G. J. Clarkon, S. S. Turner and P. Scott, *Dalton Trans.*, 2011, **40**, 1722; (i) 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.
- 5 L. Martin, S.S. Turner, P. Day, F.E. Mabbs and E.J.L. McInnes, *J. Chem. Soc., Chem. Commun.*, 1997, 1367; L. Martin, S.S. Turner, P. Day, P. Guionneau, J.K. Howard, D.E. Hibbs, M.E. Light, M.B. Hursthouse, M. Uruichi and K. Yakushi, *Inorg. Chem.*, 2001, **40**, 1368; A. Akutsu-Sato, H. Akutsu, S. S. Turner, P. Day, M. R. Probert, J. A. K. Howard, T. Akutagawa, S. Takeda, T. Nakamura and T. Mori, *Angew. Chem., Int. Ed.*, 2005, **44**, 292; L. V. Zorina, S. S. Khasanov, S. V. Simonov, R. P. Shibaeva, P. O. Bulanchuk, V. N. Zverev, E. Canadell, T. G. Prokhorova and E. B. Yagubskii, *CrystEngComm*, 2012, **14**, 460; E. Coronado, S. Curreli, C. Giménez-Saiz and C. J. Gómez-García, *Inorg. Chem.*, 2012, **51**, 1111.
- 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, **10**, 865.
- 7 L. Martin, S.-i. Nakatsuji, J.-i. Yamada, H. Akutsu and P. Day, *J. Mater. Chem.*, 2010, **20**, 2738; L. Martin, P. Day, S.-i. Nakatsuji, J.-i. Yamada, H. Akutsu and P. Horton, *CrystEngComm*, 2010, **12**, 1369; L. Martin, H. Akutsu, P. N. Horton, M. B. Hursthouse, R. W. Harrington and W. Clegg, *Eur.J.Inorg.Chem.*, 2015, **11**, 1865-1870; L. Martin, H. Akutsu, P. N. Horton and M. B. Hursthouse, *CrystEngComm*, 2015, **17**, 2783.
- 8 J. D. Dunitz, A. Karrer and J. D. Wallis, *Helv. Chim. Acta*, 1986, **69**, 69; A. Karrer, J. D. Wallis, J. D. Dunitz, B. Hilti, C. W. Mayer, M. Burkle and J. Pfeiffer, *Helv. Chim. Acta*, 1987, **70**, 942.
- 9 N. Avarvari, *Rev. Roum. Chim.*, 2009, **54**(6), 411.
- 10 F. Pop, P. Auban-Senzier, A. Frackowiak, K. Ptaszyński, I. Olejniczak, J. D. Wallis, E. Canadell, N. Avarvari, *J. Am. Chem. Soc.*, 2013, **135**, 17176.
- 11 I. Awgheda, S. Yang, L. Martin, S. Krivickas, A. C. Brooks, F. Pelletier, P. Day, M. Pilkington, P. Horton and J. D. Wallis, *Tetrahedron*, 2013, **69**, 8738.
- 12 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.
- 13 Crystal Clear-SM Expert 2.0 r11 (Rigaku, 2011).
- 14 G. M. Sheldrick, *Acta Crystallogr. Sect. A*, 2008, **64**, 112-122; 2015, **C71**, 3-8.
- 15 CrysAlisPro, Agilent Technologies, Version 1.171.35.15 (release 03-08-2011 CrysAlis171 .NET).
- 16 SHELXS86 - Sheldrick, G. M., In "Crystallographic Computing 3", Ed. G. M. Sheldrick, C. Kruger and R. Goddard, Oxford University Press, 1985, pp. 175.
- 17 L. J. Barbour, "X-Seed - A software tool for supramolecular crystallography" *J. Supramol. Chem.*, 2001, **1**, 189.
- 18 C.F. Macrae, P.R. Edgington, P. McCabe, E. Pidcock, G.P. Shields, R. Taylor, M. Towler, J. van de Streek, *J. Appl. Crystallogr.*, 2006, **39**, 453.
- 19 P. Deplano, J. R. Ferraro, M. L. Mercuri, E. F. Trogu, *Coord. Chem. Rev.*, 71, **188**, 1999.
- 20 J. S. Zambounis, J. Pfeiffer, G. C. Papavassiliou and D. J. Lagouvardos, *Solid State Commun.*, 1995, **95**, 211; P. Cauliez, C. Mézière, P. Auban-Senzier, R. Clérac and M. Fourmigué, *New J. Chem.*, 2008, **32**, 1561 and T. Devic, J. N. Bertran, B. Domercq, E. Canadell, N. Avarvari, P. Auban-Senzier and M. Fourmigué, *New J. Chem.*, 2001, **25**, 1418, and references therein.
- 21 R.P. Shibaeva, R.M. Lobkovskaya, E.B. Yagubskii, E.Z. Kostyuchenko, *Z. Kristallografiya*, 1986, **31**, 455.
- 22 (a) A.J. Jircitano, M. C. Colton and K.B. Mertes, *Inorg. Chem.* 1981, **20**, 890; (b) A. S. Gaballa, S. M. Teleb, E. Rusanov, and D. Steinborn, *Inorg. Chim. Acta*, 2004, **357**, 4144; (c) A. Kavoosian, *Z. Naturforsch. B*, 1998, **53**, 641; (d) F. Haghjoo, N. Barnes and R. Pritchard, *Acta Cryst. C*, 2011, **67**, o291; (e) M.C. Aragoni, M. Arca, F. Demartin, F. A. Devillanova, A. Garau, F. Isaia, V. Lippolis, S. Rizato and G. Verani, *Inorg. Chim. Acta.*, 2004, **357**, 3803.
- 23 A. J. Blake, F. A. Devillanova, R. O. Gould, W.-S. Li, V. Lippolis, S. Parsons, C. Radek and M. Schroder, *Chem. Soc. Rev.* 1998, **27**, 195. P. H. Svensson and L. Kloo, *Chem. Rev.* 2003, **103** (5), 1649.
- Scheme 1** Donor molecules *R,R* and *S,S*-bis(2'-hydroxypropylthio)(ethylenedithio)tetrathiafulvalene, (BHPT-EDT-TTF).
- Fig. 1** Asymmetric unit of (*S,S*)-**1** viewed down the *a* axis.
- Fig. 2** Crystal structure of (*S,S*)-**1** viewed perpendicular to the *a* axis.
- Fig. 3** Face-to-face stacking of donor pairs showing close S...S contacts for (*S,S*)-**1**. "End on" view of donors (left), "side on" view of donors (right).
- Fig. 4** Asymmetric unit of (*S,S*)-**2**.
- Fig. 5** Face-to-face stacking of a donor pair showing close S...S contacts for (*S,S*)-**2**.
- Fig. 6** Crystal structure of (*S,S*)-**2** viewed down the *b* axis.
- Fig. 7** Crystal structure of (*S,S*)-**2** viewed down the *a* axis.
- Fig. 8** Asymmetric unit of (*S,S*)-**3**.

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**Fig. 9** Crystal structure of *(S,S)*-**3** viewed down the *b* axis.

**Fig. 10** Face-to-face stacking of a donor pair showing close S...S contacts for *(S,S)*-**3**.

5

**Fig. 11** Crystal structure of *(S,S)*-**3** viewed perpendicular to the *b* axis.

**Fig. 12** Crystal structure of *(S,S)*-**3** viewed perpendicular to the *c* axis showing the packing of the octaiodide anions parallel to the donor molecules.

10

**Fig. 13** Labelling of iodine atoms in the  $I_8^{2-}$  dianion of *(S,S)*-**3**.

**Fig. 14** Crystal structure of *(rac)*-**4** viewed perpendicular to the *b* axis.

15

## Supplementary Information.

### Enantiopure and racemic radical-cation salts of bis(2'-hydroxypropylthio)(ethylenedithio)TTF with polyiodide anions

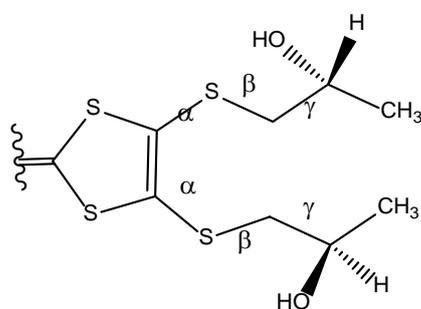
Lee Martin,<sup>\*a</sup> John D. Wallis,<sup>a</sup> Milena Guziak,<sup>a</sup> Peter Maksymiw,<sup>a</sup> Florence Konalian-Kempf,<sup>a</sup> Anthony Christian,<sup>a</sup> Shin'ichi Nakatsuji,<sup>b</sup> Jun'ichi Yamada<sup>b</sup> and Hiroki Akutsu<sup>b,c</sup>

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Table S1. Torsion angles for the donor cation side chains in *RR-1* / °, e.s.d.s in range 0.8-1.2°.



	Torsion $\alpha$	Torsion $\beta$	Torsion $\gamma$
DONOR 1, O1	-45.0	-78.2	-173.8
O2	63.3	63.3	57.3
DONOR 2 O3	39.5	55.6	55.4
O4	-72.3	-72.7	-165.8
DONOR 3 O5	-33.9	-90.5	81.6
O6	119.9	-155.7	-51.8
DONOR 4 O7	57.6	74.0	70.2
O8	-23.8	-178.8	66.0
DONOR 5 O9	-15.1	177.0	76.6
O10	55.2	75.4	66.4
DONOR 6 O11	34.9	69.0	70.9
O12	-98.3	133.8	173.5

Table S2. Torsion angles for the donor cation side chains in *S,S-2* / °, e.s.d.s 1-2°.

	Torsion $\alpha$	Torsion $\beta$	Torsion $\gamma$
DONOR 1, O1	40	64	172
O2	-67	-81	-171
DONOR 2 O3	-57	-113	54
O4	61	153	-168

Table S3. Torsion angles for the donor cation side chains in *SS-3* donor. / °, e.s.d.s 2-3°.

	Torsion $\alpha$	Torsion $\beta$	Torsion $\gamma$
DONOR 1, O1	58	57	-173
O2	-9	169	174
DONOR 2 O3	-97	69	175
O4	7	168	174

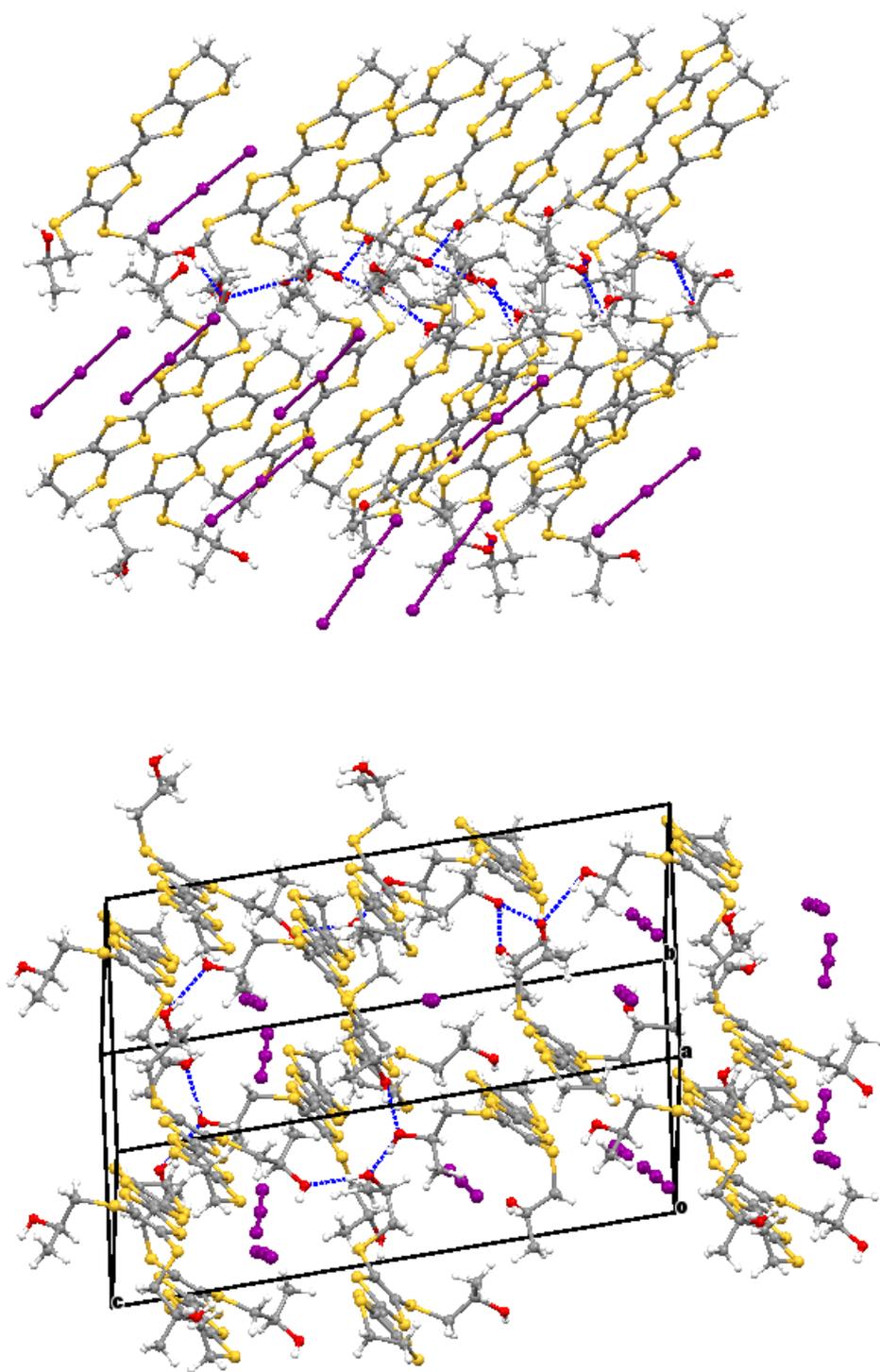
Table S4. Torsion angles for the donor cation side chains in *rac-4*. / °, e.s.d.s 0.5-0.8°, main conformation only.

	Torsion $\alpha$	Torsion $\beta$	Torsion $\gamma$
DONOR 1, O1	109.3	-82.4	-68.0
O2	12.6	-103.0	178.5

Table S5. Relative geometry of O atoms involved in hydrogen bonding for *R,R-1*, *S,S-2*, *S,S-3*, *rac-4*.

<i>R,R-1</i>	O(8)-H(8)⋯O(3)-H(3)(x-1, y, z)⋯O(6)-H(6)(x-1, y-1, z)⋯O(9)-H(9)(x, y-1, z)  O(11)-H(11)⋯O(2)-H(2)(x-1, y, z+1)⋯O(5)-H(5)(x, y, z+1)⋯O(4)-H(4)(x-1, y+1, z+1)  O(10)-H(10)⋯O(7)-H(7)(x, y+1, z)⋯O(12)-H(12)(x+1, y+1, z)	O(8)⋯O(3): 2.594(16) O(3)⋯O(6): 2.781(10) O(6)⋯O(9): 2.742(18) O(8)⋯O(3)⋯O(6): 98.6(5)° O(3)⋯O(6)⋯O(9): 125.4(3)°  O(11)⋯O(2): 2.940(13) O(2)⋯O(5): 2.832(16) O(5)⋯O(4): 2.914(13) O(11)⋯O(2)⋯O(5): 104.1(4)° O(2)⋯O(5)⋯O(4): 106.9(4)°  O(10)⋯O(7): 2.777(13) O(7)⋯O(12): 2.703(15) O(10)⋯O(7)⋯O(12): 117.1(4)°
<i>S,S-2</i>	O(3)-H(3)⋯O(4)-H(4)(x+1, y, z)⋯O(1)-H(1)(x+1, y+1, z-1)⋯O(2)-H(2)(x+1, y+1, z-1)	O(3)⋯O(4): 2.890(14) O(4)⋯O(1): 2.652(14) O(1)⋯O(2): 2.619(14) O(3)⋯O(4)⋯O(1): 94.2(5)° O(4)⋯O(1)⋯O(2): 114.1(5)°
<i>S,S-3</i>	O(3)-H(3)⋯O(2)(x, y, z+1) O(4)-H(4)⋯O(3)(x, y-1, z)	O(3)⋯O(2): 3.01(3) O(4)⋯O(3): 2.85(3) O(2)⋯O(3)⋯O(4): 121.3(9)
<i>rac-4</i>	O(1)-H(1)⋯O(2)(-x-1, -y, -z)	O(1)⋯O(2): 2.751(10)

Fig S1a-d Hydrogen bonding in *R,R*-1



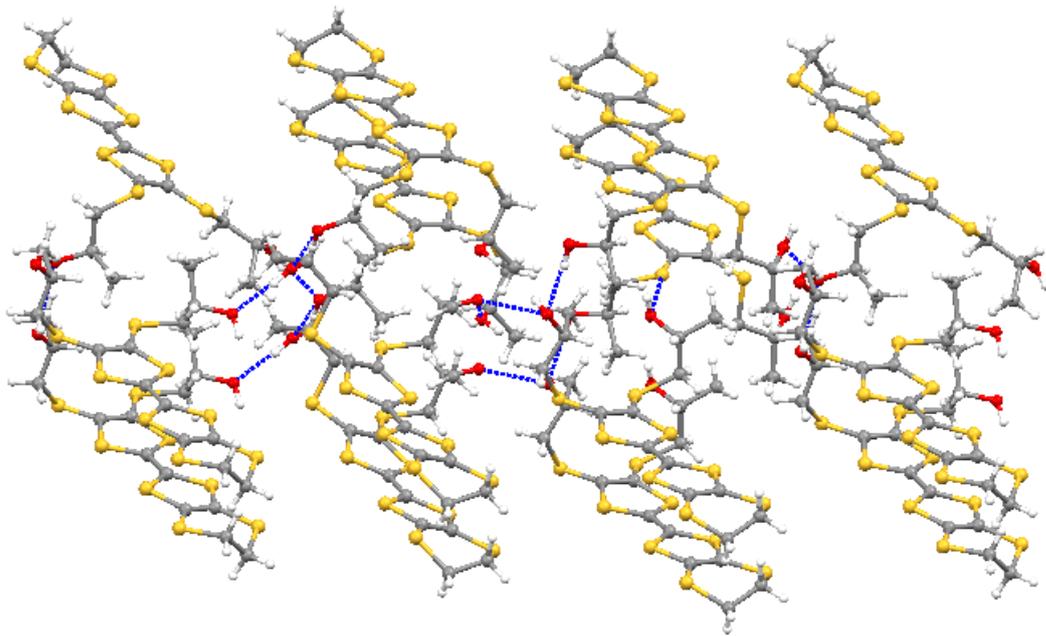
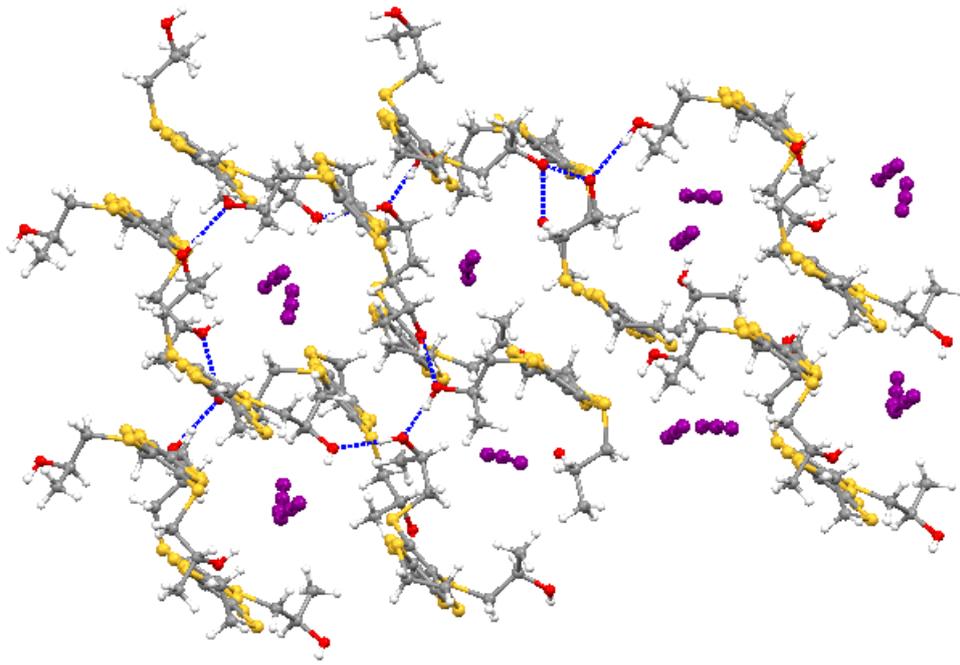


Fig S2. Hydrogen bonding in *rac-4*

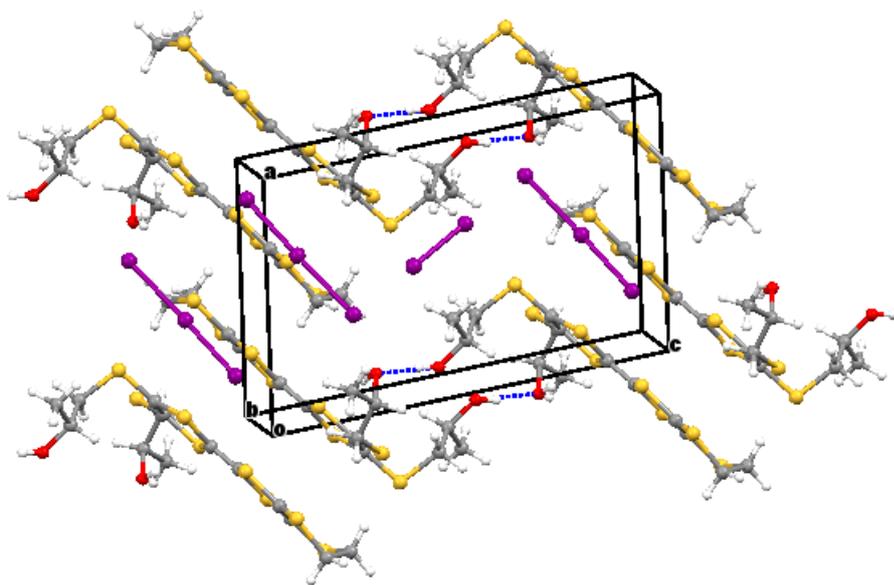


Fig S3a. Asymmetric unit of *S,S-1*.

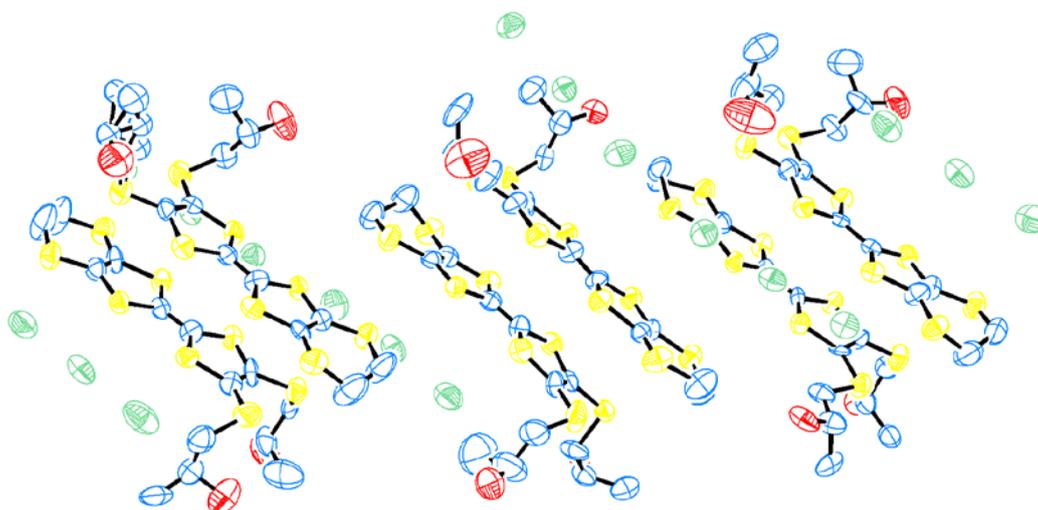


Fig S3b. Asymmetric unit of **S,S-2**.

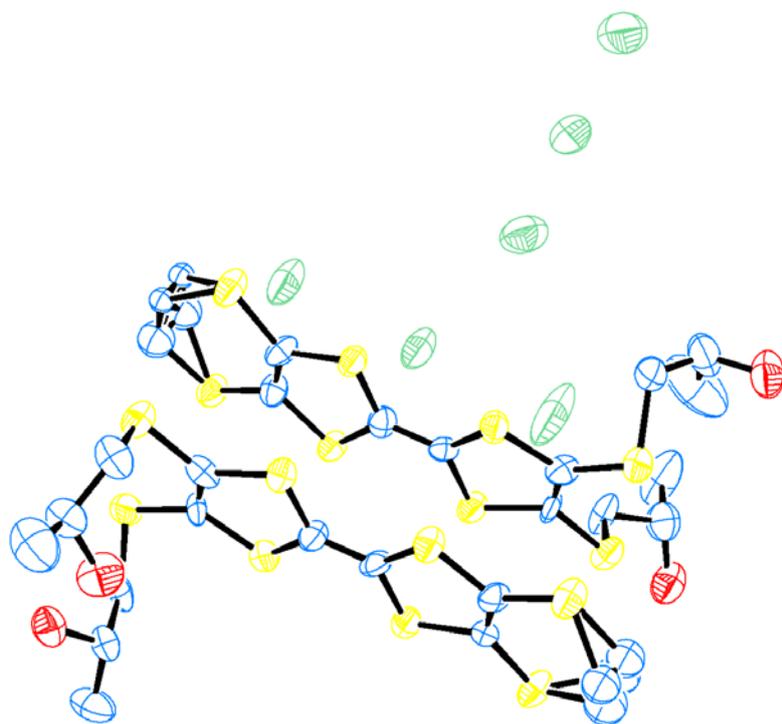


Fig S3c. Asymmetric unit of **S,S-3**.

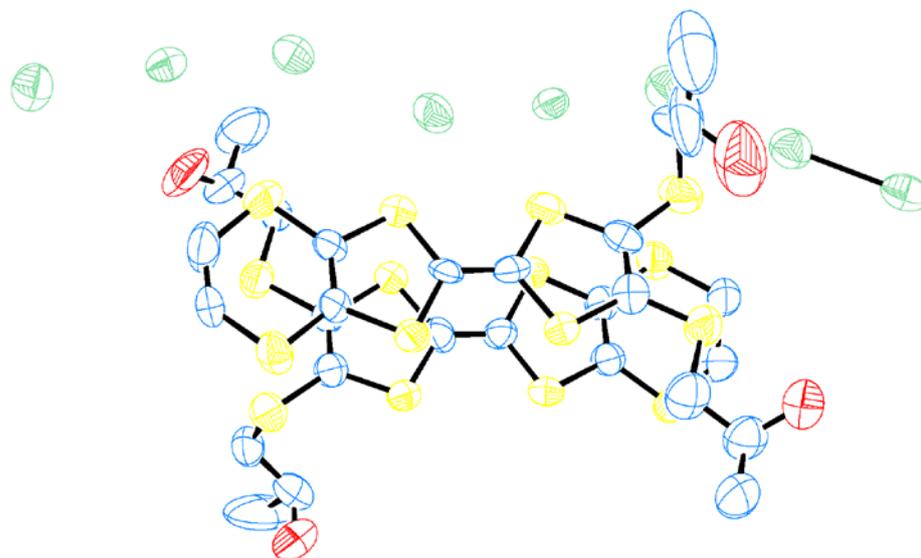


Fig S3d. Asymmetric unit of **rac-4**.

