Synthesis of New Chiral Organosulfur Donors with Hydrogen Bonding Functionality and Their First Charge Transfer Salts.

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Abstract.

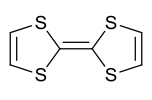
The syntheses of a range of enantiopure organosulfur donors with hydrogen bonding groups are described including TTF related materials with two, four, six and eight hydroxyl groups and multiple stereogenic centres and a pair of chiral N-substituted BEDT-TTF acetamides. Three charge transfer salts of enantiopure poly-hydroxy-substituted donors are reported, including a 4:1 salt with the *meso* stereoisomer of the dinuclear $[Fe_2(oxalate)_5]^{4-}$ anion in which both cation and anion have chiral components linked together by hydrogen bonding, and a semiconducting salt with triiodide.

Keywords: TTF, organosulfur donors, hydrogen bonding, chirality.

Introduction

TTF **1** and BEDT-TTF **2** have been at the forefront for the preparation of electrically conducting molecular systems, the former providing the first example of an organic metal in its complex with TCNQ,[1] and the latter providing a large number of salts with varying

electronic properties, including superconductivity.[2] Considerable numbers of substituted derivatives of TTF and BEDT-TTF have been reported,[3,4] and the former especially have found potential applications as molecular switches,[5,6] sensors,[5,7] field effect transistors[8] and molecular electronics[9] as well as in the preparation of conducting radical cation salts and fibres.[10] Two recent research themes in this area have been the installation of chirality into the donor molecules and the attachment of groups with hydrogen bonding potential. The former is of importance following the discovery of magneto-chiral



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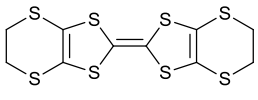

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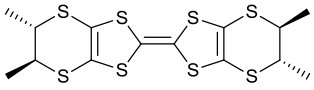

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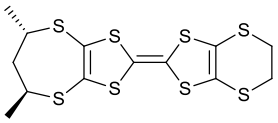

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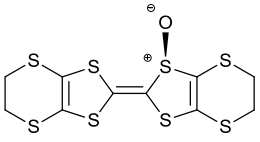

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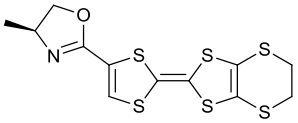

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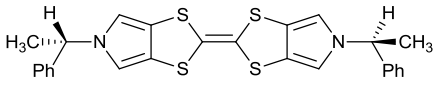

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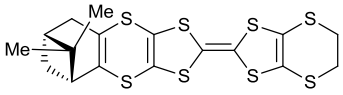

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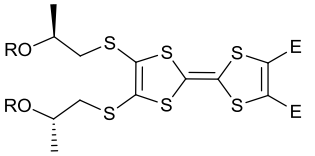

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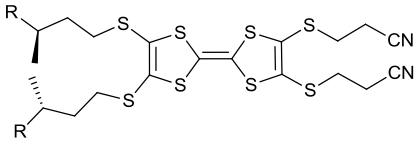

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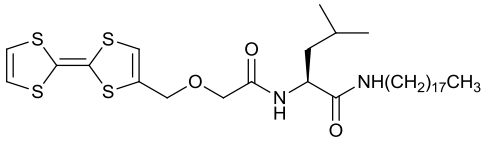

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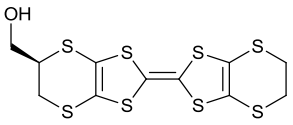

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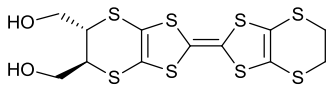

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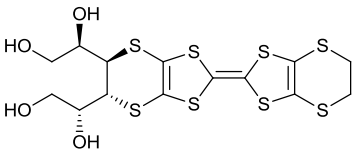

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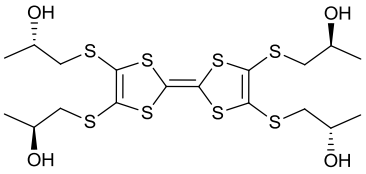
anisotropy in chiral conducting systems.[11] The latter is important since hydrogen bonding with the anion in a salt, or between donors, can offer new organisations in the crystalline state.[12] A range of enantiopure donors related to BEDT-TTF have been reported, including several with a stereogenic centre at a ring C or S atom e.g. **3**-**5**,[13,14] or external to the donor system as in **6**-**7**[15,16] as well as donors fused to a chiral pinene system e.g. **8**[17] or incorporating a stereogenic axis from a 1-,1'-binaphthyl system**.**[18] Examples of the latter have been investigated as redox sensitive chiroptical switches.[19] Several simple TTF derivatives with chiral side chains have also been reported, e.g. **9**-**10**[20] while Kato has combined **11** with an aromatic liquid crystal and an electron acceptor to provide fibrous conducting materials.[21] Progress in these areas has been reviewed.[22] A few



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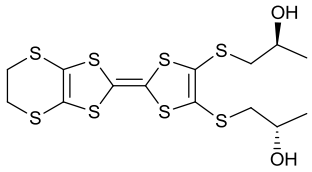

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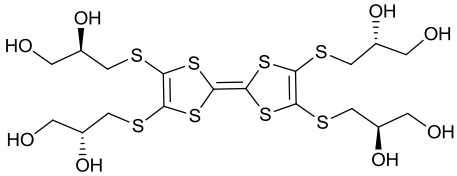

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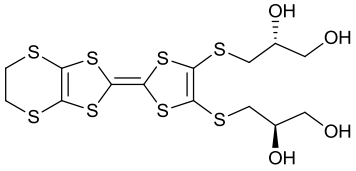

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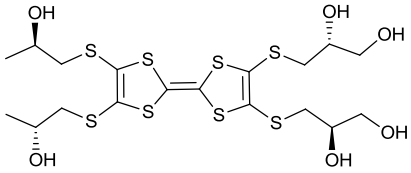

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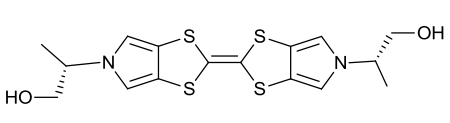

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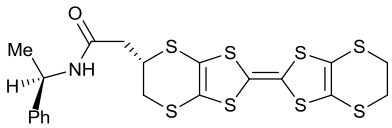

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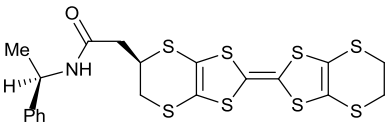

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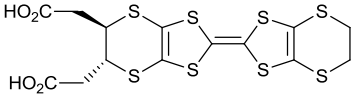
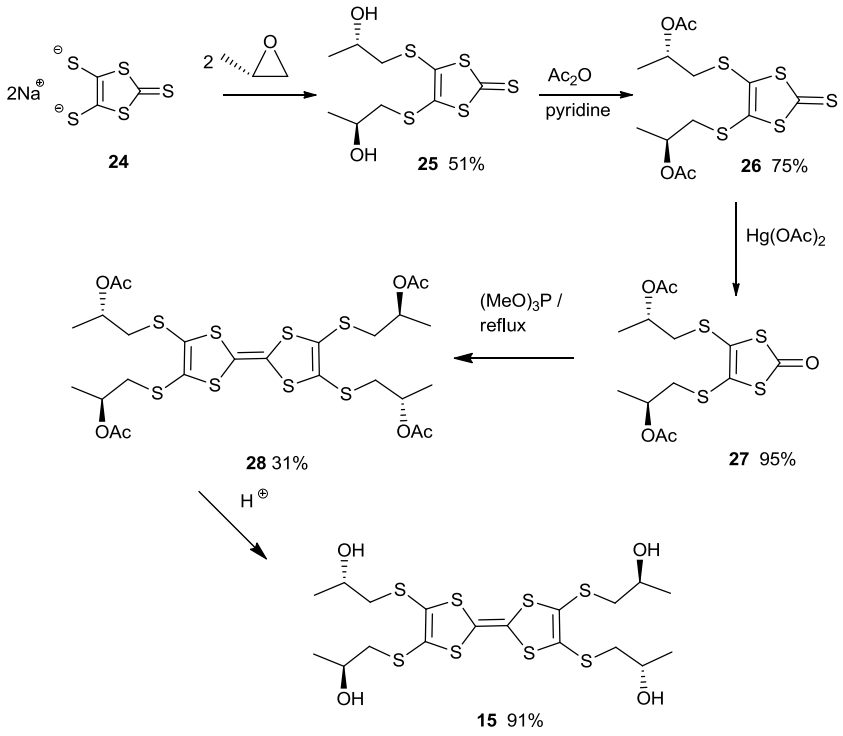


rac-**23**

enantiopure donors with hydrogen bonding functionality have been reported e.g. BEDT-TTF derivatives **12-14**,[23] as well as a series of peptide derivatives and a *D*-glucose derived material.[24] Here we report the preparation of new donors **15-22** which are both enantiopure and include hydroxyl or amide groups capable of forming hydrogen bonds, as well as progress towards making *trans*-BEDT-TTF diacid **23** as a racemate.

Results and Discussion.

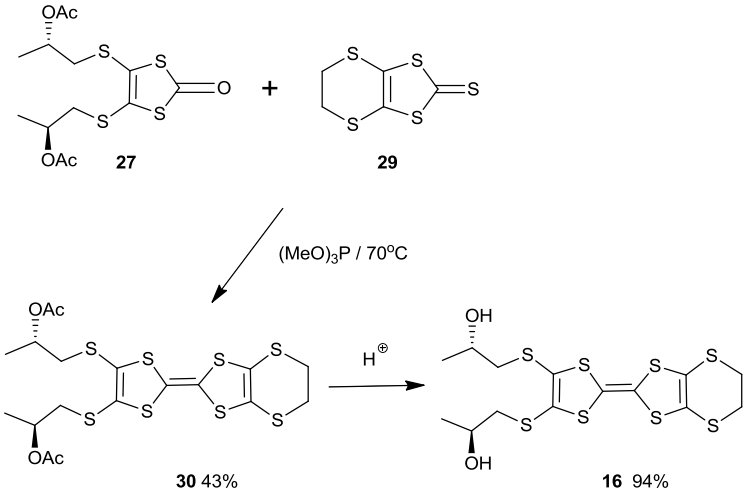
Synthesis of chiral TTF-related polyols 15-20.



Scheme 1.

As a first step to provide donors with both chirality and hydrogen bonding potential, two TTF derivatives with 2-hydroxypropylthio side-chains which had a hydroxyl group at a stereogenic centre were targeted (Scheme 1). Reaction of dithiolate **24**[25] with two equivalents of (*S*)-methyloxirane gave the thione **25** containing two chiral 2-hydroxypropylthio side-chains in 51% yield. The synthesis was continued by protection of the hydroxyl groups by acetylation to give **26** and exchange of the thione sulfur for oxygen using mercuric acetate to give the oxo compound **27** in 71% yield from thione **25**.

Homo-coupling of **27** in refluxing trimethyl phosphite for 24 hours gave the chiral O-protected donor **28** in 31% yield which was then hydrolysed to the chiral tetrol **15** in 91% yield. The chiral oxo compound **27** was also cross-coupled with the unsubstituted thione **29** to give the disubstituted donor **30** in 43% yield, which was subsequently hydrolysed to the diol **16** in 94% yield (Scheme 2). The *R,R* enantiomer of **16** was prepared in a similar way starting from (*R*)-methyloxirane. The attempted synthesis of the *meso*-(*R,S*)-isomer of **16** from *rac*-methyloxirane led to unseparable mixtures of *meso* and racemic (*R,R*) compounds at each step. The racemate is most easily made by mixing equimolar amounts of the two enantiomers. The crystal structure of donor **15** (Fig. 1) shows that one pair of chains form an internal hydrogen bond while both make further intermolecular interactions so that the donors and side-chains are more or less segregated in the crystal packing.[26]



Scheme 2.

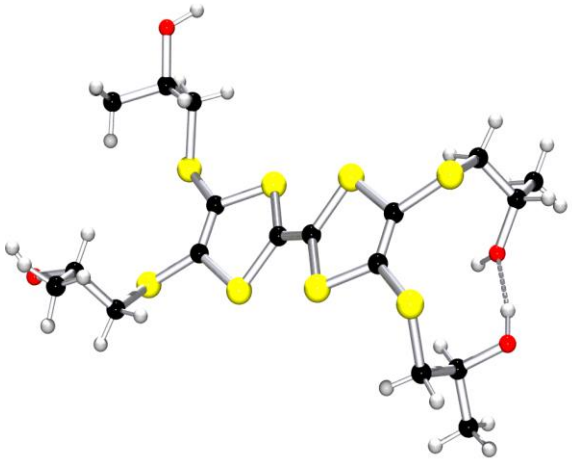
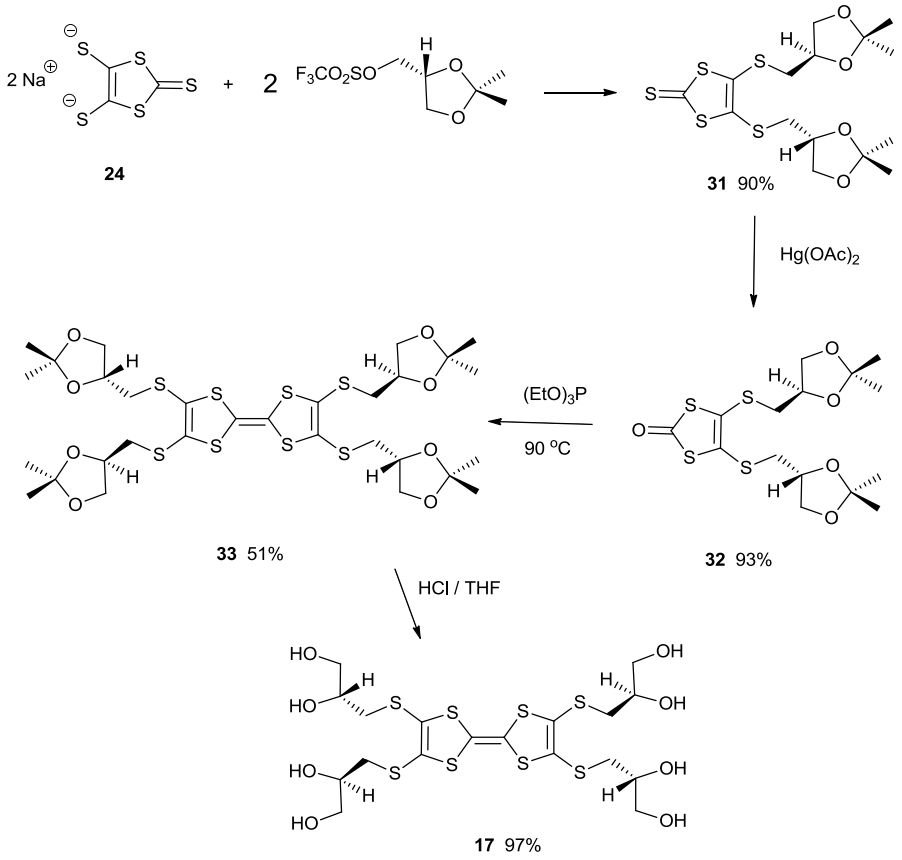
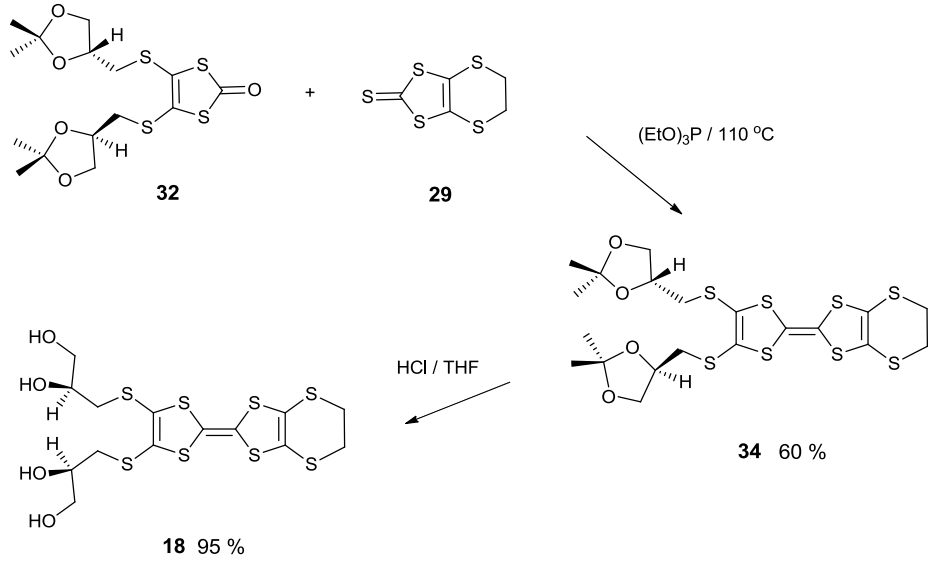


Figure 1. Molecular structure of **15**, showing the hydrogen bond between two side chains.



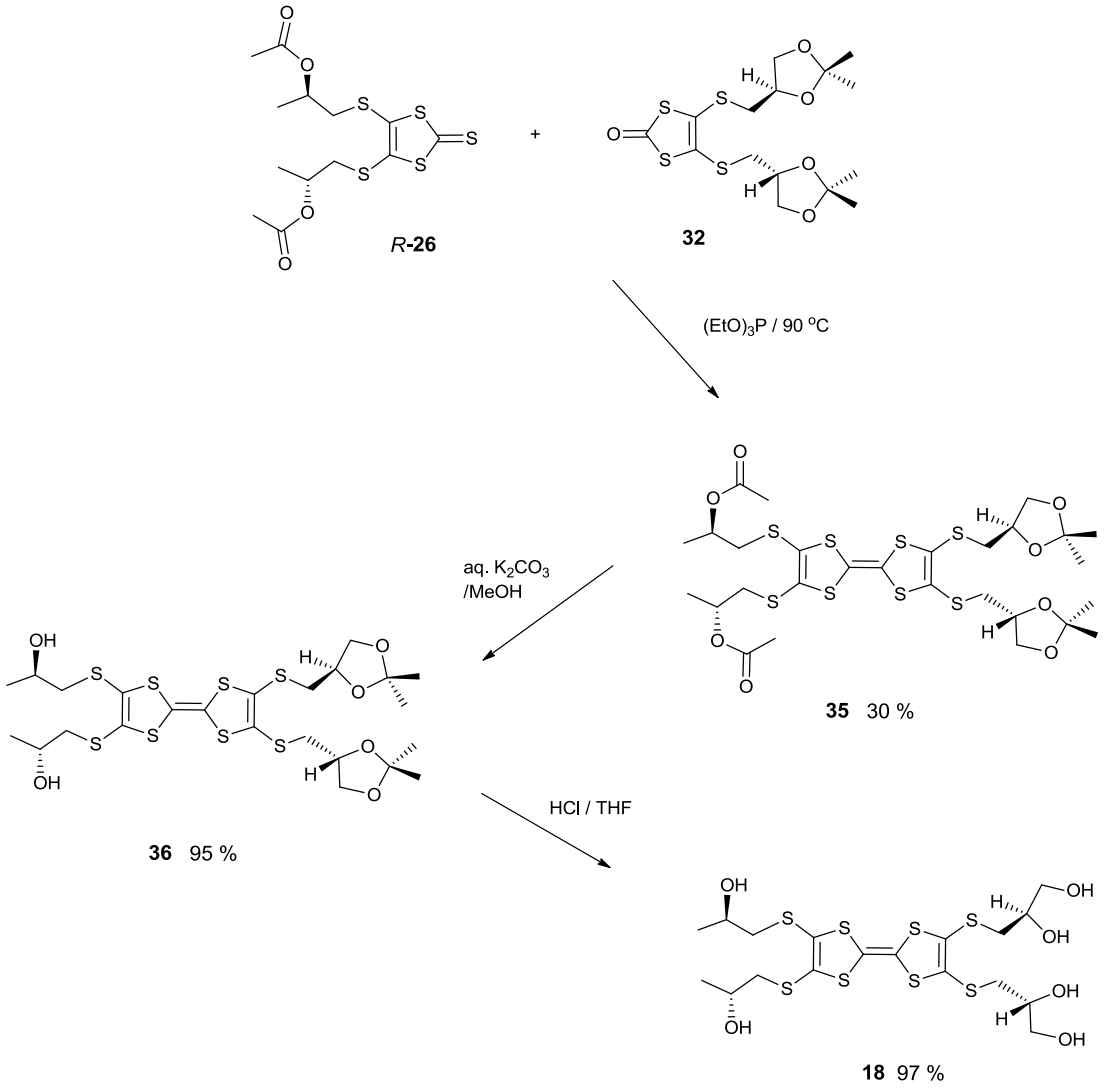
Scheme 3.

Introduction of hydroxyl groups on to the terminal methyl groups of these two would provide donors **17** and **18** with additional sites for hydrogen bonding or for extension of the side chains. The synthesis of these materials (Scheme 3) was achieved by reaction of the dithiolate **24** with two equivalents of the triflate of (*S*)-1,2-isopropylidene-glycerol to give the thione **31** in 90% yield. Neither the corresponding mesylate nor tosylate were effective for this reaction. The symmetrical donor **17** was then prepared in three steps by conversion of thione **31** to the oxo compound **32**, homo-coupling in triethyl phosphite to give the tetra(ketal) donor **33** in 51% yield and then almost quantitative deprotection of the diol groupings using HCl in THF. The unsymmetrical donor **18** was prepared by cross coupling of the oxo compound **32** with the thione **29** to give the donor **34** in 60% yield after chromatography, which was deprotected to give the tetrol **18** in 95% yield (Scheme 4). To provide a donor with different chirally disposed hydrogen bonding functionality at either end, the donor **19** was prepared which at one end had two (*R*)-2-hydroxypropylthio side chains and at the other end two (*R*)-2,3-dihydroxypropylthio side chains (Scheme 5). This was achieved by reacting the *R,R*-enantiomer of bis(acetoxy) thione **26** with the bis ketal-protected oxo compound **32** in triethyl phosphite to give the

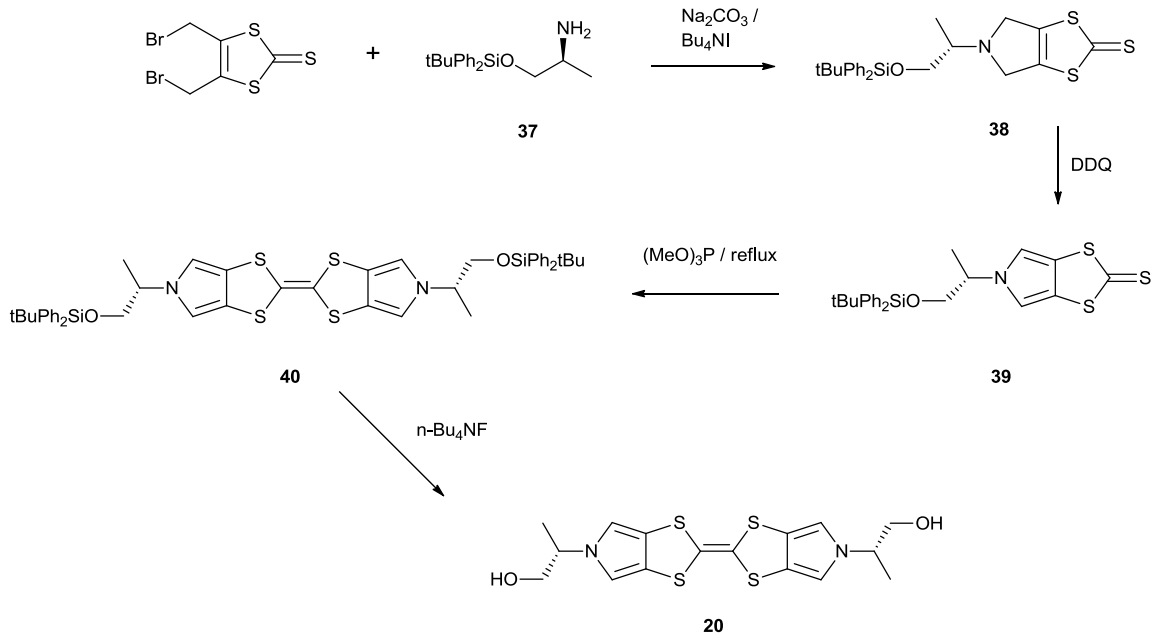


Scheme 4.

O-protected hexol **35** in 30% yield after chromatography to separate from homo-coupled species. Removal of the acetyl protecting groups with aqueous potassium carbonate gave the dihydroxy donor **36**, and the ketal groups were hydrolysed by subsequent treatment with HCl in THF to yield the unsymmetrical chiral hexol donor **18** with two different pairs of hydroxyl substituted stereogenic centres.



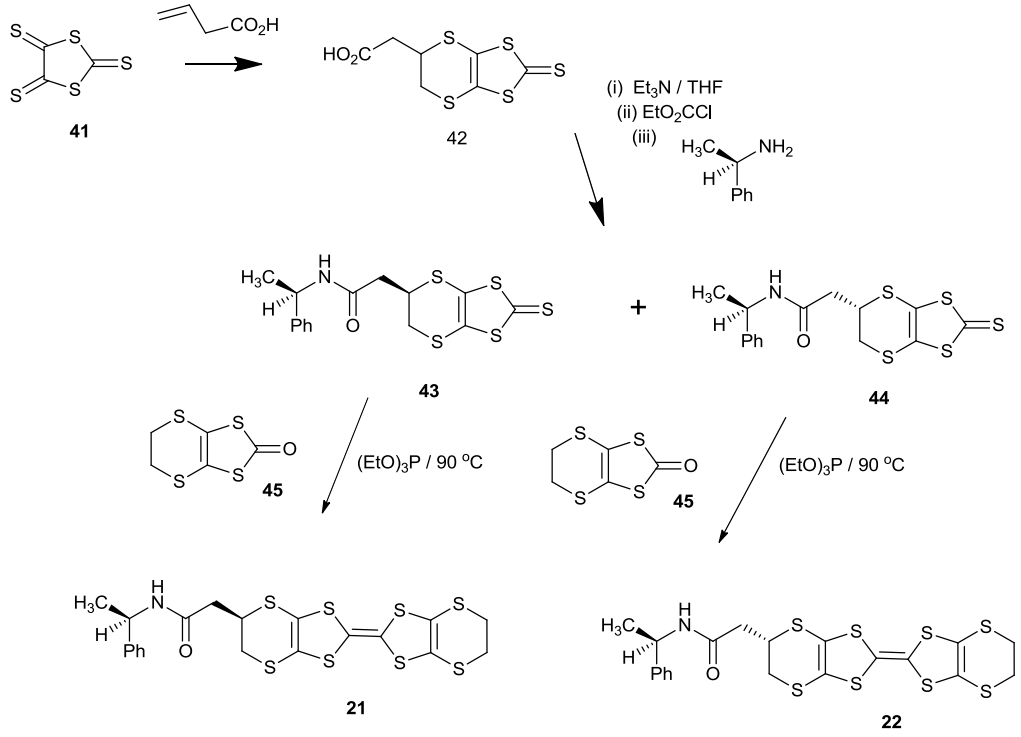
Scheme 5.



Scheme 6.

To prepare a donor with one chiral hydrogen bonding side chain at each end, the approach of Becher to make bis(pyrrolo)TTFs[27,28] was taken, an approach which has already yielded the chiral donor **7**.[16] Thus the donor **20**, a bis(pyrrolo)tetrathiafulvalene bearing *2S*-2-(1-hydroxy)propyl substituents attached to each nitrogen atom, was chosen as a target (Scheme 6). The synthesis started from (*S*)-(+)-2-amino-1-propanol, by *O*-protection with a t-butyldiphenylsilyl group to give amine **37**,[29] which was reacted with *bis*(bromomethyl)-1,3-dithiolethione[28] in the presence of sodium carbonate and tetrabutylammonium iodide to give the dihydropyrrole derivative **38** which was directly oxidized with DDQ in benzene at *ca* -10^{0}C to give the dithiolo(4,5-c)pyrrole thione **39** in 53% overall yield after chromatography. Prolonged reflux of thione **39** with freshly distilled trimethyl phosphite gave the corresponding bis(pyrrolo)tetrathiafulvalene **40** in 32% yield. Deprotection of the hydroxyl groups was carried out using tetrabutylammmonium fluoride in THF at room temperature to give the desired chiral donor **20** functionalised with two hydroxyl groups in 50% yield.

Synthesis of enantiopure amides 21 and 22.



Scheme 7.

There is only one monosubstituted BEDT-TTF which has been prepared as a pure enantiomer, the hydroxymethyl derivative, but the route is eight steps from (*S*)-1,2-isopropylideneglycerol. With a view to resolving the chirality at the stereogenic centre on a BEDT-TTF derivative in a shorter sequence we have taken an approach to deliberately prepare diastereomers which can then be separated, in this case by modification of our synthesis of the racemic BEDT-TTF derivatives bearing a functionalised acetamide side chain (-CH_2CONHR).[30] Trithione **41**[25] was reacted with vinylacetic acid to give the bicyclic carboxylic acid **42**, which was then converted to two diastereoisomeric amides **43** and **44** by formation of the mixed anhydride with ethyl chloroformate followed by reaction with the enantiopure amine *R*-α-phenylethylamine. The two isomeric amides were separated by chromatography and obtained in similar yields of *ca.* 28%, and the structure of **44** was confirmed by X-ray crystallography to have the *S* configuration at 5-C (Fig. 2). The main difference in their ^{1}H NMR spectra is

between the signals from the side chain methylene groups, which in **43** appears as a doublet at δ: 2.71 ppm, but in **44** appears as two doublet doublets at δ: 2.63 and 2.71 ppm. Both thiones were cross coupled with the unsubstituted oxo compound **45** in triethyl phosphite at 90°C to give the corresponding chiral donors **21** and **22** in 31 and 46% yields respectively. Attempts to convert these new donors to the enantiomers of primary amide BEDT-TTF-CH_2CONH_2 have been unsuccessful. However, these donors are likely to be better substrates for investigating the influence of chirality on conductivity since the two enantiomers of the primary amide can adopt similar shapes by the substituted dithiin ring adopting the particular envelope conformation which places the side chain in a pseudo-equatorial position.

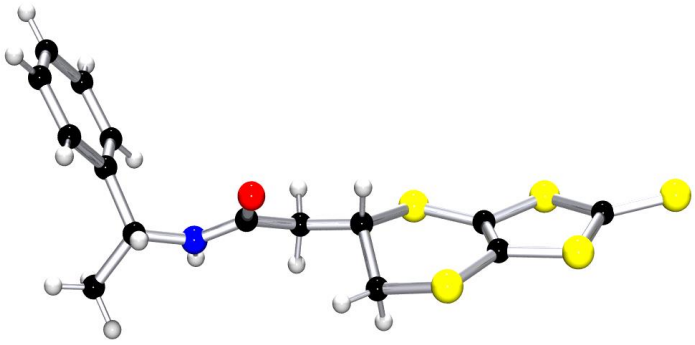
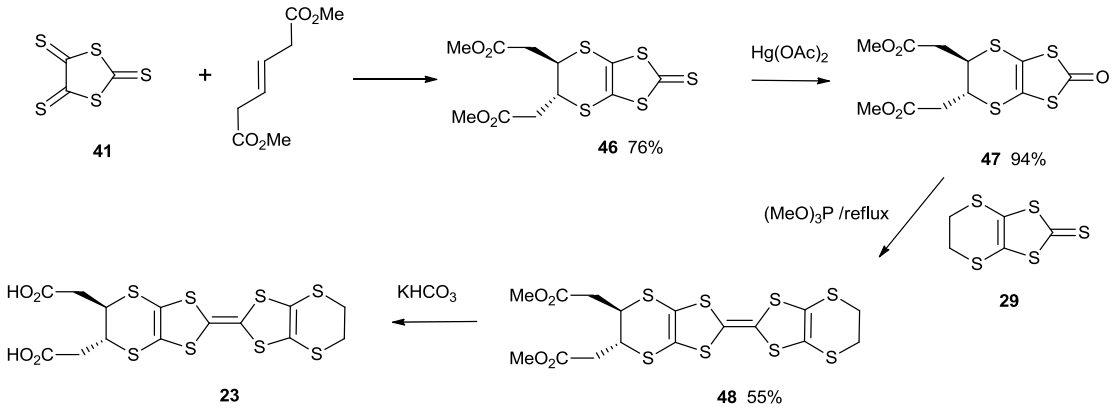


Figure 2. Molecular structure of diastereomer **44** with (*S*) stereochemistry at 5-C on the dithiin ring.

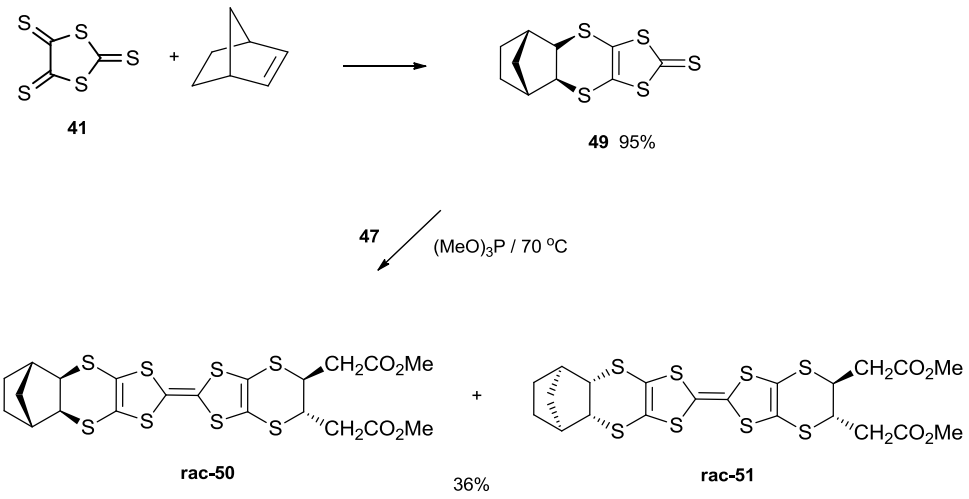
Synthesis of the racemic *trans*-diacid 23.



Scheme 8.

Carboxylic acid groups are also potential hydrogen bonding centres, as well as precursors of other functionalities. The only such BEDT-TTF derivative reported is the mono -CH_2CO_2H derivative, which has very limited solubility in typical organic solvents. So we examined routes to an enantiomer of the *trans* bis-acid **23**. Attempted synthesis from dimethyl 3,4-dihydroxyhexandioate failed when the derived cyclic sulfate ester could not be cyclised with the dithiolate **24**. The enantiomers of such *trans*-disubstituted BEDT-TTFs have been difficult to prepare, for example *trans*-BEDT-TTF-*bis*(methanol) was only prepared in enantiopure form by chiral chromatography.[13] We thus attempted the synthesis of the racemate of *bis*-acid **23**. Reaction of dimethyl *E*-hex-3-en-1,5-dioate with the trithione **41** in refluxing toluene gave the thione **46** with *trans* oriented side chains in 76 % yield. Reaction of the thione **46** with mercuric acetate gave the oxo compound **47** in 94% yield, the cross-coupling of which with the unsubstituted thione **29** gave the *trans* disubstituted donor **48** in 55 % yield. (Homo-coupling of **47** in trimethyl phosphite at 120 ^{o}C gave the tetrasubstituted BEDT-TTF in 81% yield as a mixture of a racemate and a *meso* compound.) Hydrolysis of the diester **48** with potassium hydrogen carbonate in a water/methanol/THF mixture followed by acidification give a solid the composition of which corresponds to a 1:1 mixture of the diacid **23** and its monopotassium salt.

To extend this chemistry, oxo compound **47** was cross-coupled with thione **49**, the adduct of norbornene and trithione **41**. The latter is formed very readily and exclusively as the *exo*-adduct in 95% yield, and its stereochemistry was confirmed by X-ray crystallography.[26] The cross coupled product was produced as a 1:1 mixture of two diastereomers **50** and **51**.



Scheme 9.

Charge Transfer Salts.

Table 1. Cyclic voltammetry data for electron donors[a].

Donor	E_1 (V)	E_2 (V)
15	0.50	0.76
16	0.48	0.80
17[b]	0.68	0.83
18[b]	0.71	0.85
19[b]	0.69	0.83
21	0.56	0.95
22	0.52	0.91
33	0.59	0.89
34	0.59	0.92
35	0.61	0.92
36	0.58	0.86
48	0.58	0.97
50/51	0.57	0.96

[a]Measured relative to Ag/AgCl at a platinum electrode in dichloromethane containing 0.1 M *n*-Bu_4NPF_6 as charge carrier and using a 100 mV s^{-1} scan, [b]THF used as solvent.

The oxidation potentials of the novel donors show two oxidation potentials similar to those of BEDT-TTF and tetra(methylthio)TTF (Table 1), though the donors with side-chains containing diols, **17-19**, are notably higher, possibly a reflection of a

non-reversible interaction with the electrode. Here we report the first results for preparing charge transfer materials from enantiopure donors **16** and **18**. Diol **16** forms a salt with the $Fe(III)_2(oxalate)_5$ tetraanion by electrocrystallisation with the ammonium salt of racemic iron(III)tris(oxalate) and a molecular complex with tetrafluoro-TCNQ. Tetrol **18** forms a 1:1 salt with triiodide. In the crystals of the oxalate salt (monoclinic, $P2_1$) the asymmetric unit contains four donor molecules and one $Fe(III)_2(oxalate)_5^{4-}$ species in which one oxalate bridges between the two iron atoms which thus retain coordination numbers of six (Fig. 3). The chirality at the two metal centres in the anion are opposite (Δ and Λ), nevertheless this is the first report of a charge transfer salt with a source of chirality in both the donor and the anion components. Charge transfer salts of this anion with TTF and BEDT-TTF have been reported.[31] The accuracy of the bond lengths is not sufficient for application of the empirical method for estimating each donor's oxidation state to determine whether the net charge of +4 is equally distributed or not.[32] The crystal structure contains alternate layers of donors and anions, with donors stacking within the layer. The eight terminal O atoms of the anion form seven hydrogen bonds to hydroxyl groups belonging to donor molecules, and there is just one crystallographically unique hydrogen bond between donor molecules, and it bridges between stacks. The bridging oxalate residue is not involved in any hydrogen bonding. Reproducible two probe resistivity measurements were not possible due to the fragility of the tiny crystals.

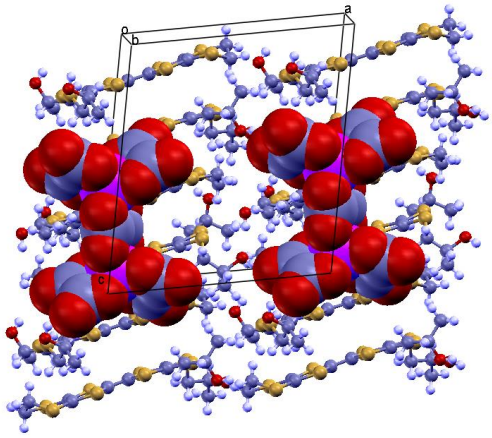


Figure 3. Crystal packing arrangement of $(\mathbf{16})_4Fe_2(oxalate)_5$ viewed along *b*, perpendicular to the successive layers of anions and donor cations.

The crystal structure of the 1:1 complex with TCNQ-F_4 is quite different (Fig. 4). The donors and acceptors are both packed in face-to-face pairs with one pair of donors and one pair of acceptors in the unit cell (triclinic, P1). The donor pairs are packed head to tail with four short S---S contacts between sulfur atoms of the opposing TTF units (3.339-3.354 Å), and the average bond lengths in the TTF cores indicate that the donor is a monocation.[32] The material is thus best considered as a salt. The pairs of donors and acceptors form layers in the *b.a-c* plane, with the best planes of the TTF cores of the donors and the TCNQ-F_4 acceptors lying at *ca* 65º to each other. There are O-H---F hydrogen bonds between the layers (Fig. 4). Although there is no stacking between the donor pairs, there are two S---S side to side contacts between donor pairs (3.545-3.579 Å). The material is an insulator: multiple crystals measured showed room temperature resistances higher than the measurement upper limit of the equipment (>1 x 10^7 Ohms).

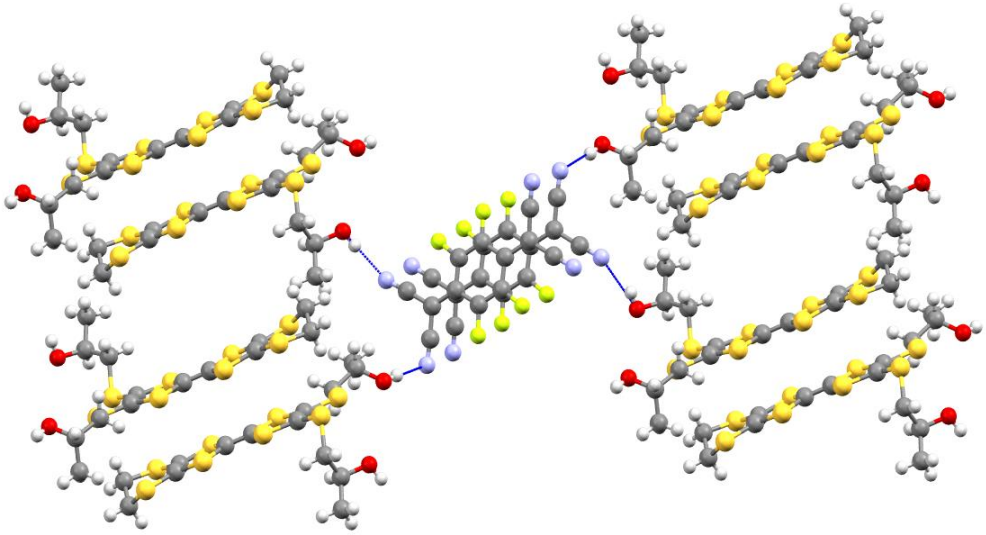
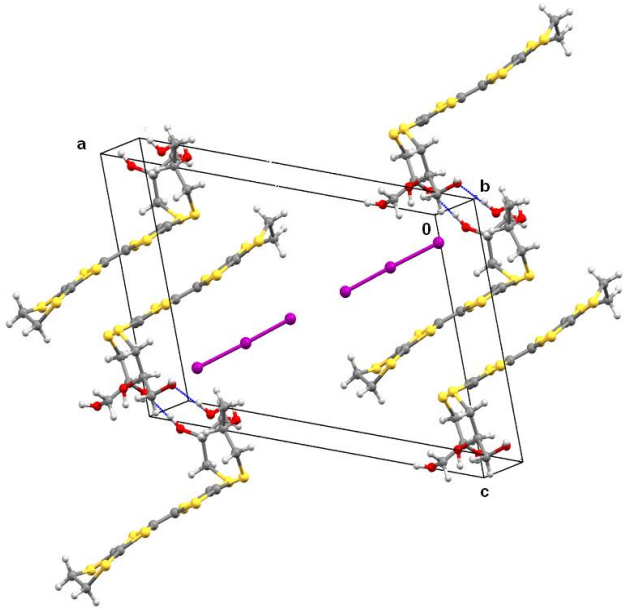


Figure 4. Hydrogen bonding between the TCNQ-F_4 molecules in one layer and molecules of donor **16** in adjacent layers, showing pairing of donor molecules. Donor pairs in the central layer are omitted for clarity.

Diffusion of iodine into a DCM solution of chiral tetrol **18** gave crystals of a 1:1 salt with I_3^- the structure of which was determined by X-ray crystallography at 150 K. Donor monocations are organised in 'face to face pairs' with side chains at opposite ends

of the pair and directed away from the other donor (Fig. 5). Triiodides are organised in 'end to end' linear pairs with the I···I contact between them being one of the shortest reported (3.422 Å). There are six short S···S contacts (3.365-3.480 Å) within the pair of donors, and two sets of intermolecular hydrogen bonds: one between secondary hydroxyl groups, and a roughly square array involving four primary hydroxyl groups with a 1:1 disorder in the positions of the hydrogen atoms around the square of oxygen atoms, with either arrangement breaking the symmetry of the two-fold axis which cuts the square. The salt is semiconducting with a room temperature resistivity of 3.61 ohm cm with an activation energy of 22.5 meV and show hysteresis in the range 60-250 K on cooling and rewarming (Fig. 6). This may be related to the disordered hydrogen bonding square arrangement which may prefer just one of the two possible arrangements at low temperature (< 60K), and this is maintained on warming until *ca* 250 K.



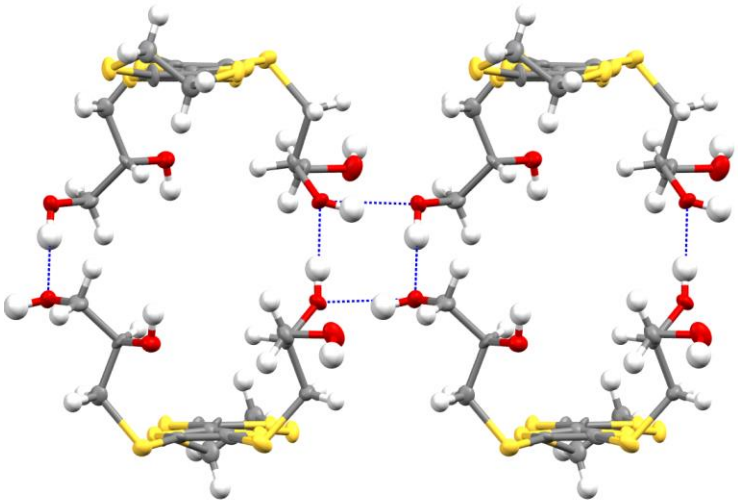


Figure 5. Crystal packing arrangement of **18**.I_3 showing the end to end triiodide pair and donor cation pairs (top), and four primary hydroxyl groups hydrogen bonding together in a square formation, in which just one of two sets of hydrogen atom positions is shown (below).

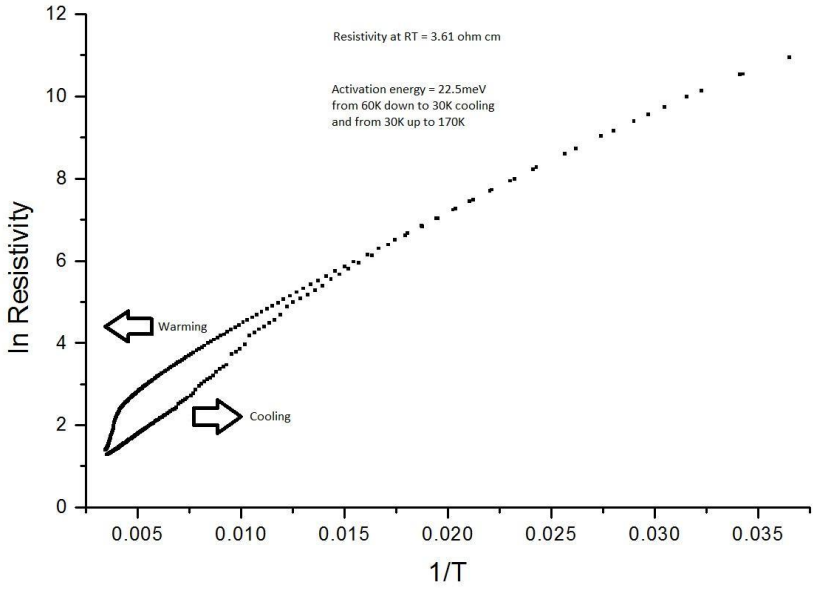


Figure 6. Plot of ln(Resistivity) vs 1/T for **18**.I_3 showing hysteresis between 60 and 250 K.

Conclusion.

A new range of symmetrically and unsymmetrically substituted enantiopure donors with hydrogen bonding potential are now available. The challenge now is to prepare conducting systems from them and see how their chirality moderates their electromagnetic properties by a comparison of the properties of products prepared from opposite enantiomers. Electrocrystallisation studies and diffusion experiments with electron deficient species are underway to build on the salts prepared here in which hydrogen bonding plays an important role in their physical properties.

Experimental. **General.** NMR spectra were measured on a JEOL ECLIPSE 400 spectrometer at 400 MHz for ^{1}H and at 100.6 MHz for ^{13}C using $CDCl_3$ as solvent and tetramethylsilane (TMS) as standard unless otherwise stated, and measured in p.p.m. downfield from TMS with coupling constants reported in Hz. IR spectra were recorded on Perkin Elmer Spectrum 100 FT-IR Spectrometer using an ATR window, and are reported in cm^{-1}. Raman measurements were made on a Foster and Freeman Foram 685-2 spectrometer, with excitation at 685 nm and are reported in cm^{-1}. Solid-state uv/visible spectra was measured using a JASCO V-670 instrument. Optical rotation data were measured on a PerkinElmer 241 polarimeter at the sodium D-line. Mass spectra were recorded at the EPSRC Mass Spectrometry Centre at the University of Swansea. Chemical analysis data were obtained from Mr Stephen Boyer, London Metropolitan University. X-ray diffraction datasets were measured by the EPSRC National Crystallography Service at Southampton University. Flash chromatography was performed on 40-63 silica gel (Merck).

Bis((*2'S*)-2'-hydroxylpropylthio)-1,3-dithiole-2-thione 25.

A solution of disodium dithiolate **24** in dry methanol (300 ml), prepared *in situ* from 4,5-bis(benzoylthio)-1,3-dithiol-2-thione (17.5 g, 43.0 mmol) and sodium methoxide (4.66 g, 86 mmol) under a nitrogen atmosphere,[25] was treated with (*S*)-(-)-propylene oxide (5.0 g, 86.0 mmol) at room temperature. The deep purple solution turned orange–red over several minutes, and the mixture stirred at room temperature for 5 h. Acetic acid (10 ml) was added. After stirring for 1 h, the reaction mixture was concentrated in *vacuo*, the methyl benzoate removed by Kugelrohr distillation, and the residue was purified by flash chromatography (SiO_2, eluting with cyclohexane:ethyl acetate 2:1) to yield **25** (6.90 g, 51.0%) as a red brown oil; R_f (cyclohexane:ethyl acetate 2:1) 0.26; δ_H (400 MHz, $CDCl_3$) 3.90 (2H, m, 2×C*H*OH), 3.23 (2H, br, 2×O*H*), 2.99 (2H, dd, J 3.6, 13.8 Hz, 2×CH_αS), 2.78 (2H, dd, J 8.4, 13.8 Hz, 2×CH_βS), 1.24 (6H, d, J 6.2 Hz, 2×CH_3); δ_C (100.6 MHz, $CDCl_3$) 210.6 (*C*=S), 136.6 (4-,5-*C*), 66.1 (2×*C*HOH), 45.4 (2×*C*H_2S), 22.0 (2×*C*H_3); ν_{max}: 3342, 2967, 2919, 1724, 1455, 1399, 1372, 1240, 1188, 1123, 1058, 1035, 934, 892,

816, 516, 451; *m/z*: (ES) 314 $[M]^+$; found C, 34.50; H, 4.55%, $C_9H_{14}O_2S_5$ requires C, 34.37; H, 4.49%; $^{293}[\alpha]_D = +61.7$ (c = 1.8, $CHCl_3$).

Bis((*2'S*)-2'-acetoxypropylthio)-1,3-dithiole-2-thione 26.

Acetic anhydride (5.0 ml, 52.9 mmol) was added to a solution of thione **25** (6.48 g, 20.6 mmol) in pyridine (70 ml) at 0 ^oC and then stirred overnight at room temperature. Water (300 ml) was added and the mixture extracted with CH_2Cl_2 (3 × 100 ml). The organic solution was washed consecutively with 0.5 M HCl solution (3 × 100 ml) and H_2O (100 ml), dried ($MgSO_4$) and evaporated. The residue was purified by flash chromatography (SiO_2, eluting with cyclohexane:ethyl acetate 4:1) to yield the protected thione **26** (6.16 g, 75.0%) as an orange brown oil; R_f (cyclohexane:ethyl acetate 4:1) 0.30; δ_H (400 MHz, $CDCl_3$) 4.99 (2H, m, 2×C*H*OAc), 2.99 (4H, d, J 5.8 Hz, 2×CH_2S), 1.98 (6H, s, 2×CH_3CO), 1.29 (6H, d, J 6.4 Hz, 2×CH_3); δ_C (100.6 MHz, $CDCl_3$) 210.2 (*C*=S), 169.9 (2×*C*=O), 136.2 (4-,5-*C*), 69.0 (2×*C*HOAc), 41.3 (2×*C*H_2S), 20.9 (2×*C*H_3CO), 19.0 (2×*C*H_3); ν_{max}: 2979, 2932, 1733, 1456, 1370, 1228, 1128, 1061, 1035, 955, 888, 632, 606, 516, 451, 412; *m/z*: (ES) 398 $[M]^+$; found C, 39.25; H, 4.58%, $C_{13}H_{18}O_4S_5$ requires C, 39.17; H, 4.55%; $^{293}[\alpha]_D = +45$ (c = 1.20, $CHCl_3$).

Bis((*2'S*)-2'-acetoxypropylthio)-1,3-dithiole-2-one 27, (Method A).

To a solution of the thione **26** (5.54 g, 13.9 mmol) in chloroform (130 ml) was added mercuric acetate (6.70 g, 21.0 mmol). After stirring for 2 h, the reaction mixture was filtered and the solid residue washed with chloroform. The combined filtrates were washed with sodium hydrogen carbonate solution and then water, dried over magnesium sulfate, and concentrated in *vacuo.* The residue was purified by flash chromatography (SiO_2, eluting with cyclohexane:DCM 3:1) to yield the oxo compound **27** as a brown oil (5.07 g, 95.4%); R_f (cyclohexane:DCM 3:1) 0.41; δ_H (400 MHz, $CDCl_3$) 4.97 (2H, m, 2×C*H*OAc), 2.94 (4H, d, J 5.8 Hz, 2×CH_2S), 1.96 (6H, s, 2×CH_3CO), 1.27 (6H, d, J 6.3 Hz, 2×CH_3); δ_C (100.6 MHz, $CDCl_3$) 188.7 (*C*=O), 169.9 (2×*C*OCH_3), 127.3 (4-,5-*C*), 69.1 (2×*C*HOAc), 41.2 (2×*C*H_2S), 20.9 (2×*C*H_3CO), 18.9 (2×*C*H_3); ν_{max}: 2980, 2933,

1734, 1667, 1613, 1448, 1370, 1229, 1128, 1092, 1037, 955, 883, 739, 632, 607, 551, 461; *m/z*: (ES) 382 $[M]^+$; found C, 40.81; H, 4.68%, $C_{13}H_{18}O_5S_4$ requires C, 40.82; H, 4.74%; $^{293}[\alpha]_D$ = +1.0 (c = 1.80, $CHCl_3$).

Tetrakis((*2S*)-2-acetoxypropylthio)TTF 28, (Method B).

A mixture of oxo compound **27** (3.30 g, 8.62 mmol) and freshly distilled trimethyl phosphite (60 ml) was heated to reflux for 24 h. The solvent was evaporated to dryness, and the residue was subjected to flash chromatography (SiO_2, eluting with cyclohexane:ethyl acetate 4:1) to yield the TTF derivative **28** as an orange oil (1.95 g, 30.9%); R_f (cyclohexane:ethyl acetate 4:1) 0.14; δ_H (400 MHz, $CDCl_3$) 5.01 (4H, m, 4×C*H*OAc), 2.97 (8H, d, J 5.7 Hz, 4×CH_2S), 2.03 (12H, s, 4×CH_3CO), 1.32 (12H, d, J 6.4Hz, 4×CH_3); δ_C (100.6 MHz, $CDCl_3$) 170.1 (4×*C*=O), 127.9 (4-,4'-,5-,5'-*C*), 110.6 (2-,2'-*C*), 69.4 (4×*C*HOAc), 40.9 (4×*C*H_2S), 21.1 (4×*C*H_3CO), 19.0 (4×*C*H_3); ν_{max}: 2979, 2932, 1733, 1447, 1369, 1227, 1128, 1091, 1034, 954, 890, 856, 772, 632, 606; *m/z*: (EI) 732 $[M]^+$; found C, 42.69; H, 4.90%, $C_{26}H_{36}O_8S_8$ requires C, 42.60; H, 4.95%; $^{293}[\alpha]_D$ = +60.2 (c = 1.5, $CHCl_3$).

Tetrakis((*2S*)-2-hydroxylpropylthio)TTF 15.

An aqueous solution (60 ml) of potassium carbonate (3.20 g, 23.2 mmol) was added to a solution of the tetra-acetate **28** (1.95 g, 2.66 mmol) in methanol (240 ml). After stirring overnight, the reaction mixture was concentrated and the solid was collected and washed with water to yield the chiral tetrol **15** as an orange solid (1.37 g, 91.2%); m.p. 91-93ºC; R_f (ethyl acetate:methanol 10:1) 0.47; δ_H (400 MHz, $CDCl_3$) 3.83 (4H, m, 4×C*H*OH), 2.98 (4H, dd, J 3.1, 13.7 Hz, 4×CH_αS), 2.95 (4H, br, d, J 3.0 Hz, 4×O*H*), 2.65 (4H, dd, J 8.9, 13.7 Hz, 4×CH_βS), 1.22 (12H, d, J 6.3 Hz, 4×CH_3); δ_C (100.6 MHz, $CDCl_3$) 128.3 (4-,4'-,5-,5'-*C*), 110.7 (2-,2'-*C*), 66.0 (4×*C*HOH), 45.2 (4×*C*H_2S), 21.8 (4×*C*H_3); ν_{max}: 3320, 2965, 2915, 1455, 1396, 1377, 1294, 1273, 1245, 1124, 1072, 1034, 932, 892, 875, 865, 823, 770, 725, 568, 465, 419, 410; *m/z*: (EI) 564 $[M]^+$; found C, 38.23; H, 5.04%, $C_{18}H_{28}O_4S_8$ requires C, 38.27; H, 5.00%; $^{293}[\alpha]_D$ = +212.5 (c = 0.24, $CHCl_3$).

Bis((2*S*)-2-acetoxypropylthio)(ethylenedithio)TTF 30, (Method C).

A mixture of oxo compound **27** (1.70 g, 4.44 mmol), thione **29** (3.00 g, 13.4 mmol) and freshly distilled trimethyl phosphite (70 ml) was heated to 70 ^{o}C for 30 h. The reaction mixture was cooled to room temperature then filtered and washed with chloroform. The solvent and trimethyl phosphite were removed *in vacuo*, the residue was subjected to flash chromatography (SiO_2, eluting with cyclohexane:ethyl acetate 4:1) to yield the donor **30** as an orange oil (1.07 g, 43.1%); R_f (cyclohexane:ethyl acetate 4:1) 0.26; δ_H (400 MHz, $CDCl_3$) 5.01 (2H, m, 2×C*H*OAc), 3.28 (4H, s, 5'-,6'-H_2), 2.97 (4H, d, J 5.8 Hz, 2×CH_2S), 2.03 (6H, s, 2×CH_3CO), 1.32 (6H, d, J 6.4 Hz, 2×CH_3); δ_C (100.6 MHz, $CDCl_3$) 170.0 (2×*C*=O), 127.8 (4-,5-*C*), 113.8 (3a'-,7a'-*C*), 112.3 & 109.7 (2-,2'-*C*), 69.3 (2×*C*HOAc), 40.8 (2×*C*H_2S), 30.0 (5'-,6'-*C*), 21.0 (2×*C*H_3CO), 18.9 (2×*C*H_3); ν_{max}: 2977, 2929, 1732, 1420, 1369, 1228, 1127, 1092, 1035, 955, 889, 857, 772, 632, 606, 395; *m/z*: (EI) 558 $[M]^+$; found C, 38.72; H, 4.06%, $C_{18}H_{22}O_4S_8$ requires C, 38.68; H, 3.97%; $^{293}[\alpha]_D$ = +29.3 (c = 0.74, $CHCl_3$).

Bis((*2S*)-2-hydroxylpropylthio)(ethylenedithio)TTF 16.

An aqueous solution (30 ml) of potassium carbonate (1.70 g, 12.3 mmol) was added to a solution of the di-acetate **30** (1.07 g, 1.91 mmol) in methanol (240 ml) and THF (20 ml). After stirring overnight, the reaction mixture was concentrated and the solid was collected and washed with water to yield the chiral diol **16** as a yellow solid (855 mg, 94.1%); m.p. 108-110^{o}C; R_f (ethyl acetate) 0.41; δ_H (400 MHz, $CDCl_3$) 3.79 (2H, m, 2×C*H*OH), 3.23 (4H, s, 5'-,6'-H_2), 2.97 (2H, dd, J 3.3, 13.8 Hz, 2×CH_αS), 2.84 (2H, br, s, 2×O*H*), 2.62 (2H, dd, J 9.0, 13.8 Hz, 2×CH_βS), 1.20 (6H, d, J 6.3 Hz, 2×CH_3); δ_C (100.6 MHz, $CDCl_3$) 128.3 (4-,5-*C*), 113.8 (3a'-,7a'-C), 112.3 & 109.7 (2-,2'-*C*), 65.9 (2×*C*HOH), 45.3 (2×*C*H_2S), 30.2 (5'-,6'-*C*), 21.8 (2×*C*H_3); ν_{max}: 3306, 2965, 2916, 1451, 1405, 1371, 1343, 1282, 1254, 1239, 1126, 1068, 1038, 1003, 934, 915, 878, 863, 812, 770, 720, 684, 472, 454, 442; *m/z*: (EI) 474 $[M]^+$; found C, 35.51; H, 3.84%, $C_{14}H_{18}O_2S_8$ requires C, 35.42; H, 3.82%; $^{293}[\alpha]_D$ = +146 (c = 0.42, $CHCl_3$).

Synthesis of bis((*2R*)-2-hydroxylpropylthio)(ethylenedithio)TTF.

This followed the procedure for the *S*-enantiomer but starting from (*R*)-(+)-propylene oxide to give a final product with optical rotation $^{293}[\alpha]_D$ = -148 (c =0.42, $CHCl_3$).

Preparation of 16.Fe_2(oxalate)$_5$.

$(NH_4)_3[Fe(C_2O_4)_3].3H_2O$ (120 mg) and 18-crown-6 (200 mg) in a 1:1 mixture of dichloromethane and acetonitrile (40 ml) was stirred for 6 h. and filtered into both sides of an electrochemical cell which contained donor **16** (10 mg) in the anode compartment. On applying a current of 1.0 μA across the cell, crystals began to grow in the first week and were harvested after 21 days. A large quantity of black plates of (**16**)$_4[Fe_2(C_2O_4)_5]$ were obtained and were found to be suitable for X-ray structure determination.

Preparation of complex of 16 withTCNQ-F_4.

TCNQ-F_4: A solution of TCNQ-F_4 (7 mg) in acetonitrile (3 ml) was gently layered over a solution of diol **16** (12 mg) in chloroform (3 ml) and left to slowly evaporate giving black crystals of a 1:1 complex whose composition was determined by X-ray crystallography.

4,5-*Bis*(((4'*R*)-2',2'-dimethyl-1',3'-dioxolan-4'-yl)methylthio)-1,3-dithiole-2-thione 31.

A solution of disodium dithiolate **24** in dry methanol (10 ml), prepared *in situ* from 4,5-bis(benzoylthio)-1,3-dithiol-2-thione (410 mg, 1.0 mmol) and sodium methoxide (0.48 ml, solution 25%wt, 2.0 mmol) under a nitrogen atmosphere,[25] was treated with a freshly prepared sample of the triflate of (*S*)-1,2-isopropylidene glycerol[33] (528 mg, 2.0 mmol) at room temperature. After 5 min an orange precipitate formed, which was collected, washed with methanol and dried to yield **31** as a yellow solid (390 mg, 90%); m.p. 124 ^oC; R_f (cyclohexane:ethyl acetate 5:1) 0.32; δ_H (400 MHz, $CDCl_3$) 4.26 (2H, quin, J 6.0 Hz, 2 x 4'-*H*), 4.11 (2H, dd, J 6.2, 8.4 Hz, 2 x 5'-H_α), 3.74 (2H, dd, J 5.4, 8.4 Hz, 2 x 5'-H_β), 3.09 (2H, dd, J 5.8, 13.4 Hz, 2 x 4'-CH_α-S), 2.92 (2H, dd, J 6.6, 13.4 Hz, 2 x 4'-CH_β-S), 1.40 (6H, s, 2 x -CH_3), 1.32 (6H, s, 2 x -CH_3); δ_C (100 MHz, $CDCl_3$) 210.0 (2-

C), 136.1 (4-, 5- *C*), 110.1 (2 x 2'-*C*), 74.5 (2 x 4'-*C*), 68.4 (2 x 5'-*C*), 39.6 (2 x 4'-*C*H_2-S), 26.9 (2 x -*C*H_3), 25.3 (2 x -*C*H_3); ν_{max}: 2990, 2876, 1370, 1214, 1051, 1036, 894, 864, 816, 421; *m/z:* (ESI) 449 $[M + Na]^+$, 413, 301; *HRMS* (ESI) found: 449.0008, $C_{15}H_{22}O_4S_5$ + Na requires 449.0014; $^{293}[\alpha]_D$ = - 41.6 (*c* = 0.24, THF).

4,5-Bis(((4'*R*)-2',2'-dimethyl-1',3'-dioxolan-4'-yl)methylthio)-1,3-dithiol-2-one 32.

From **31** (0.39 g, 9.1 mmol) using Method **A** gave **32** (0.35 g, 93%) as a yellow oil; R_f (cyclohexane:ethyl acetate 5:1) 0.42; δ_H (400 MHz, $CDCl_3$) 4.22 (2H, quin, J 6.0 Hz, 2 x 4'-*H*), 4.07 (2H, dd, J 6.2, 8.4 Hz, 2 x 5'-*H*α), 3.72 (2H, dd, J 5.4, 8.4 Hz, 2 x 5'-*H*β), 3.02 (2H, dd, J 5.8, 13.4 Hz, 2 x 4'-C*H*α-S), 2.87 (2H, dd, J 6.6, 13.4 Hz, 2 x 4'-C*H*β-S), 1.36 (6 H, s, 2 x C*H*$_3$), 1.28 (6 H, s, 2 x C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 188.6 (2-*C*), 127.1 (4-, 5- *C*), 109.8 (2 x 2'-*C*), 74.4 (2 x 4'-*C*), 68.3 (2 x 5'-*C*) 39.3 (2 x 4'-*C*H_2-S), 26.8 (2 x -*C*H_3), 25.2 (2 x - *C*H_3); $\nu_{max:}$ 2985, 1668, 1370, 1213, 1149, 1057, 884, 755; *m/z*: (ESI) 428 $[M + NH_4]^+$, 386, 353, 294, 217, 186; *HRMS* (ESI) found: 428.0686; [$C_{15}H_{22}O_5S_4$ + NH_4] requires 428.0688 $[M + NH_4]^+$; found C, 35.51; H, 3.84%, $C_{14}H_{18}O_2S_8$ requires C, 35.42; H, 3.82%; $^{293}[\alpha]_D$ = + 28.5 (*c* = 0.28, THF).

Tetrakis(((4'*R*)-2',2'-dimethyl-1',3'-dioxolan-4'-yl)methylthio)TTF 33.

A suspension of compound **32** (348 mg, 8.5 mmol) in freshly distilled triethyl phosphite (7 ml) was heated to 90 ^oC under nitrogen for 6 h. The resulting orange precipitate was filtered off, washed with n-hexane and dried to afford **33**. The triethyl phosphite was removed from the filtrate by Kugelrohr distillation, and residue was washed with hexane, filtered and dried to yield further donor **33**, an orange solid, total yield (169 mg. 51%); m.p. 146-147 ^oC; R_f (cyclohexane:ethyl acetate 5:1) 0.22; δ_H (400 MHz, $CDCl_3$) 4.28 (4 H, quin, J 6.0 Hz, 4 x 4'-*H*), 4.12 (4H, dd, J 6.2, 8.4 Hz, 4 x 5'-*H*α), 3.77 (4H, dd, J 5.4, 8.4 Hz, 4 x 5'-*H*β), 3.06 (4H, dd, J 5.8, 13.4 Hz, 4 x 4'-C*H*α-S), 2.87 (4H, dd, J 6.6, 13.4 Hz, 4 x 4'-C*H*β-S), 1.41 (12 H, s, 4 x C*H*$_3$), 1.32 (12 H, s, 4 x C*H*$_3$); δ_C (100 MHz, $CDCl_3$) 127.7 (4 x sp^2-*C*), 110.2 (2 x sp^2-*C*), 109.9 (4 x 2'-*C*), 74.8 (4 x 4'-*C*), 68.5 (4 x 5'-*C*) 39.1 (4 x 4'-*C*H_2-S), 26.9 (4 x -*C*H_3), 25.4 (4 x - *C*H_3); ν_{max}: 2985, 2938, 2883,

1369, 1224, 1202, 1150, 1052, 1020, 864, 841, 820, 770, 511, 408 cm^{-1}; *m/z*: (ESI) 806 $[M + NH_4]^+$, 613, 437, 351, 312, 219, 197; *HRMS*: (ESI) found: 806.1142, [$C_{30}H_{44}O_8S_8$ + NH_4] requires: 806.1140; found C, 45.77; H, 5.53%, $C_{30}H_{44}O_8S_8$ requires C, 45.66; H, 5.62%; $^{293}[\alpha]_D$ = + 77.5 (*c* = 0.40, THF).

Tetrakis((2'*R*)-2'-,3'-dihydroxypropyl-1'-thio)TTF 17, (Method D).

An aqueous solution of HCl (0.5 M, 7 ml) was added to a solution of tetra-ketal **33** (158 mg, 0.2 mmol) in methanol (10 ml) and tetrahydrofuran (3 ml) which was stirred under nitrogen for 12 h. Evaporation and drying *in vacuo* at room temperature afforded the octol **17** (122 mg, 97 %) as a brown solid; m.p. 164-166 ^oC; δ_H (400 MHz, $(CD_3)_2SO$) 4.30 (8H, br, 8 x O*H*), 3.56 (4H, m, 4 x 2'-*H*), 3.45 (8H, m, 4 x 3'-H_2), 2.93 (4H, m, 4 x 1'-H_α), 2.79 (4H, m, 4 x 1'-H_β); δ_C (100 MHz, $(CD_3)_2SO$) 126.9 (4-, 4'-, 5-, 5'-C), 109.4 (2-, 2'-*C*), 70.5 (4 x –*C*H(OH)), 64.2 (4 x –*C*H_2OH), 39.7 (4 x -*C*H_2S); ν_{max} 3243 br, 2916, 1395, 1229, 1063, 1018, 878, 770 cm^{-1}; *m/z*: (ESI) 627 [M - H]; *HRMS* (ESI) found: 626.9467, [$C_{18}H_{28}O_8S_8$ – H] requires 626.9468; found C, 34.30; H, 4.38%, $C_{18}H_{28}O_8S_8$ requires C, 34.37; H, 4.49 %; $^{293}[\alpha]_D$ = - 116.6 (*c* = 0.24, THF).

Bis(((4'*R*)-2',2'-dimethyl-1',3'-dioxan-4'-yl)methylthio)(ethylenedithio)TTF 34.

Reaction of **29** (0.35 g, 0.85mmol) and **32** (0.29 g, 1.27 mmol) in triethyl phosphite (7 ml) at 90 ^oC using Method **B** gave the protected donor **34** (301 mg. 60%) as a red brown solid; m.p. 69-71 ^oC; R_f (cyclohexane:ethyl acetate 5:1) 0.38; δ_H (400 MHz, $CDCl_3$) 4.22 (2 H, quin, J 6.0 Hz, 2 x 4'-*H*), 4.07 (2H, dd, J 6.2, 8.4 Hz, 2 x 5'-H_α), 3.72 (2H, dd, J 5.4, 8.4 Hz, 2 x 5'-H_β), 3.20 (4H, s, (SCH_2)$_2$), 2.99 (2H, dd, J 5.8, 13.4 Hz, 2 x 4'-CH_α-S), 2.81 (2H, dd, J 6.6, 13.4 Hz, 2 x 4'-CH_β-S), 1.35 (6 H, s, 2 x CH_3), 1.29 (6 H, s, 2 x CH_3); δ_C (100 MHz, $CDCl_3$) 127.6 (2 x sp^2C), 113.8 (2 x sp^2-*C*), 112.2 & 110.1 (2 x sp^2-C (central)), 109.8 (2- & 2'-*C*), 74.4 (2 x 4'-*C*), 68.3 (2 x 5'-*C*) 39.3 (2 x 4'-*C*H_2-S), 30.1 ((S*C*H_2)$_2$), 26.8 (2 x -*C*H_3), 25.2 (2 x - *C*H_3); ν_{max}: 2982, 2925, 2873, 1369, 1256, 1212,

1149, 1057, 842, 772; *m/z*: (ESI) 586 [M^+], 536, 502, 462, 391, 279, 217, 186; *HRMS*: (ESI) found: 586.9675, $C_{15}H_{26}O_4S_8$ + H requires 586.9670 found C, 41.03; H, 4.54%, $C_{15}H_{26}O_4S_8$ requires C, 40.93; H, 4.46%; N, 3.20%; $^{293}[\alpha]_D$ = + 28.0 (*c* = 0.25, THF).

Bis((2'*R*)-2',-3'-dihydroxypropyl-1'-thio)(ethylenedithio) TTF 18.

From **34** (0.14 g, 0.24 mmol) using Method **D**, afforded the tetrol **18** (114 mg, 95 %) as a brown solid; m.p. 94 ºC; δ_H (400 MHz, $(CD_3)_2SO$) 4.80 (4 H, br 4 x -O*H*), 3.50 (2H, m , 2 x C*H*-OH), 3.30 (4 H, m, 2 x -CH_2OH), 2.91 (2H, dd, J 6.2, 8.4 Hz, 2 x 1'-H_α), 2.75 (2H, dd, J 5.4, 8.4 Hz, 2 x 1'-H_β), 2.41 (4 H, s, (SCH_2)$_2$); δ_C (100 MHz, $(CD_3)_2SO$) 127.0 (2 x sp^2C), 112.8 (2 x sp^2C), 113.2 & 110.1 (2 x sp^2-C (central)), 70.5 (2 x –*C*H(OH)), 64.2 (2 x –*C*H_2OH), 39.7 (2 x –*C*H_2S), 29.5 ((S*C*H_2)$_2$); ν_{max}: 3244 br, 2919, 1395, 1290, 1259, 1182, 1109, 1061, 1016, 877, 767; *m/z*: (ESI) found: 505 [M - H], 503, 501, 491, 455, 364; *HRMS* (ESI) found: 504.8898, [$C_{14}H_{18}O_4S_8$-H] requires: 504.8889; found C, 33.16; H, 3.54%, $C_{14}H_{18}O_4S_8$ requires C, 33.18; H, 3.58%; $^{293}[\alpha]_D$ = - 390 (*c* = 0.40, MeOH).

***vic*-Bis(((4*R*)-2,2-dimethyl-1,3-dioxolan-4-yl)methylthio)-*vic*-bis((2'*R*)-2'-acetoxy)propylthio)TTF 35.**

From oxo compound **32** (1.10 g, 3.0 mml) and *R,R*-**26** (1.28 g, 3.0 mmol) and triethyl phosphite (10 ml) following Method C, but filtering off donor **33** at the end of the reaction, to yield the donor **35** as a brown oil (686 mg, 30 %); R_f (cyclohexane:ethyl acetate 3:1) 0.44; δ_H (400 MHz, $CDCl_3$): 4.97 (2H, m, 2 × 2'-*H*), 4.23 (2H, quin, J 6.0 Hz, 2 x 4-*H*), 4.10 (2H, dd, J 6.2, 8.4 Hz, 2 x 5-H_α), 3.72 (2H, dd, J 5.4, 8.4 Hz, 2 x 5-H_β), 3.15 (2H, dd, J 5.8, 13.4 Hz, 2 x 4-CH_α-S), 2.93 (4H, d, J 5.8 Hz, 2 ×1'-H_2), 2.80 (2H, dd, J 6.6, 13.4 Hz, 2 x 4-CH_β-S), 1.98 (6H, s, 2×CH_3CO), 1.35 (6H, s, 2 x 2-CH_3), 1.29 (6H, s, 2 x 2-CH_3), 1.28 (6H, d, J 6.4 Hz, 2× 3'-CH_3); δ_C (100 MHz, $CDCl_3$) 170.0 (2×*C*=O), 127.9 (2 x sp^2-*C*), 127.6 (2 x sp^2-*C*), 110.9 & 110.5 (2 x sp^2-*C*(central)), 109.8 (2 x 2-*C*), 74.4 (2 x 4-*C*), 69.3 (2 × 2'*C*), 68.3 (2 x 5-*C*), 40.9 (2 × 1'-*C*), 38.9 (2 x 4-

CH_2-S), 26.8 (2 x 2-*C*H_3), 25.4 (2 x 2-*C*H_3) 21.0 (2×*C*H_3CO), 19.0 (2 × 3'-*C*H_3); ν_{max}: 3324, 2927, 2850, 1737, 1625, 1517, 1370, 1310, 1229, 1088, 1055, 892, 642, 393; *HRMS* (ESI) found: 778.0827, $[C_{28}H_{40}O_8S_8 + NH_4]^+$ requires: 778.0827; $^{293}[\alpha]_D$ = + 11.6 (*c* = 0.345, THF).

vic-Bis(((4_R_)-2,2-dimethyl-1,3-dioxolan-4-yl)methylthio)-_vic_-bis((2'_R_)-2'-hydroxypropylthio)-TTF 36.

An aqueous solution (2.5 ml) of potassium carbonate (142 mg, 1.0 mmol) was added to a solution of **35** (100 mg, 0.13 mmol) in methanol (10 ml) and tetrahydrofuran (1.5 ml) which was stirred under nitrogen for 12 h. The solvents were evaporated under vacuum, and the orange solid collected, washed with water and dried to yield the chiral diol **29** as a light orange powder (84 mg, 95%); m.p. 92 – 93 ^oC; R_f (cyclohexane:ethyl acetate 1:1) 0.47; δ_H (400 MHz, CD_3OD): 4.26 (2H, m, 2 x 4-*H*), 4.14 (2H, t, J 6.6 Hz, 2 x 5-H_α), 3.88 (2H, m, 2 x 2'-H_β), 3.76 (2H, t, J 6.6 Hz, 2 x 5-H_β), 3.07 (2H, dd, J 5.8, 13.4 Hz) and 2.95 (6H, m), 4 x -CH_2S), 1.39 (6H, s, 2 x 2-CH_3), 1.31 (6H, s, 2 x 2-CH_3), 1.25 (6H, d, J 6.4 Hz, 2 x CHCH_3); δ_C (100 MHz, CD_3OD): 129.3 (4 x sp^2-*C*), 110.9 (2 x sp^2-*C*(central)), 109.8 (2 x 2-*C*), 76.4 (2 x 4-*C*), 69.5 (2 x 2´-*C*), 67.8 (2 x 5-*C*), 45.3 (2 x 1´-C), 40.1 (2 x 4-*C*H_2-S), 27.2 (2 x 2-*C*H_3), 25.7 (2 x 2-*C*H_3), 22.3 (2 x 3´-*C*H_3); ν_{max}: 3355, 2984, 1370, 1243, 1226, 1203, 1053, 864, 770 cm^{-1}; found 42.49; H, 5.36%, $C_{24}H_{36}O_6S_8$ requires C, 42.57; H, 5.36 %; $^{293}[\alpha]_D$ = + 266 (c = 0.015, methanol).

vic-Bis((2_R_)-2,3-dihydroxypropylthio)-_vic_-bis((2'_R_)-2'-hydroxypropylthio)-TTF 19.

Donor **36** (100 mg, 0.14 mmol) was hydrolysed following Method **D** to yield the chiral hexol **19** (85 mg, 96%) as a deep orange solid, m.p. 125-126 ^oC; R_f (ethyl acetate:methanol 9:1) 0.28; δ_H (CD_3OD): 3.87 (2H, m, 2 × 2-*H*), 3.73 (2H, m, 2 × 2'-*H*), 3.59 (4H, m, 2 x 3-H_2), 3.02 (2H, m) and 2.90 (6H, m) (2 x 1-H_2, 2 x 1'-H_2), 1.26 (6H, d, J 6.3 Hz, 2 × -CH_3); δ_C (CD_3OD) 129.5 (2 x sp^2-*C*), 129.4 (2 x sp^2-*C*), 110.3 & 109.7 (2 x sp^2-*C* (central)), 72.3 (2 × 2-*C*), 67.8 (2 x 2´-*C*), 65.8 (2 x 3-*C*), 44.3 (2 x 1´-*C*), 40.1 (2 x 1-*C*), 22.3 (2 x 3´-*C*); ν_{max}: 3293, 2966, 2918, 1395, 1372, 1066, 1033, 885, 771; found

C, 36.13; H, 4.68%, $C_{18}H_{28}O_6S_8$ requires C, 36.22; H, 4.73%; $^{293}[\alpha]_D$ = - 40.1 (c = 0.20, THF).

_S_-5-(1'-_tert_-Butyldiphenylsilyloxyprop-2'-yl)-1,3-dithiolo[4,5-c]pyrrolo-2-thione 39.

A mixture of (2*S*)-1-(*tert*-butyldiphenylsilyloxy)propyl-2-amine **37**[29] (3.51 g, 11.2 mmol), bis(dibromomethyl)-1,3-dithiol-2-thione[28] (3.50 g, 10.9 mmol), sodium carbonate (3.50 g, 33.0 mmol) and tetrabutylammonium iodide (1.00g, 2.7mmol) in THF (120ml) was refluxed under nitrogen overnight. After removal of solvent, the residue containing thione **38** was redissolved in chloroform (200 ml). After cooling to -15 ^oC, a solution of DDQ (3.20 g, 14.1 mmol) in benzene (80 ml) was added dropwise and resulted in the formation of a dark suspension. The mixture was stirred for another 2 h and then neutralised with 1M sodium carbonate solution. The mixture was extracted with DCM, and the combined organic solution was washed with 1M sodium carbonate solution and water before drying over magnesium sulfate. The filtrate was evaporated at 30 ^oC in *vacuo*, and the residue was purified by flash chromatography (SiO_2, eluting with cyclohexane:ethyl acetate 10:1) to yield the thione **39** as a yellow solid (2.86 g, 52.6%); m.p. 114-116 ^oC (dec.); R_f (cyclohexane:ethyl acetate 10:1) 0.28; δ_H (400 MHz, $CDCl_3$) 7.58 (2H, m, Ar-H_2), 7.52 (2H, m, Ar-H_2), 7.40 (6H, m, Ar-H_6), 6.77 (2H, s, 4-,6-*H*), 4.29 (1H, m, 2'-*H*), 3.87 (1H, dd, J 10.8, 4.1 Hz, 1'-H_α), 3.74 (1H, dd, J 10.8, 6.7 Hz, 1'-H_β), 1.52 (3H, d, J 6.9 Hz, CH_3), 1.08 (9H, s, C(CH_3)$_3$); δ_C (100.6 MHz, $CDCl_3$) 219.0 (2-*C*), 135.5, 135.4, 133.5, 129.6, 127.6 (Ar-C_{12}), 122.0 (3a-,6a-*C*), 110.5 (4-,6-*C*), 67.8 (*C*H_2OSi), 58.3 (*C*HN), 26.4 (C(*C*H_3)$_3$), 18.8 (*C*(CH$_3$)$_3$), 16.9 (*C*H$_3$); ν_{max}: 2930, 2855, 1485, 1471, 1427, 1389, 1302, 1138, 1102, 1074, 1051, 1019, 985, 872, 813, 760, 743, 701, 614, 600, 492; *m/z*: (EI) 469 $[M]^+$; found C, 61.42; H, 5.81; N, 2.89%, $C_{24}H_{27}NS_3Si$ requires C, 61.36; H, 5.79; N, 2.98%; $^{293}[\alpha]_D$ = -11.7 (c = 0.06, THF).

_S,S_-Bis(N-1''-_tert_-butyldiphenylsilyloxyprop-2''-yl)pyrrolo[3,4-d])tetrathiafulvalene 40

Reaction of **39** (2.84 g, 6.05 mmol) in trimethyl phosphite (70 ml) using Method B and refluxing for 51 h gave the donor **40** as a yellow solid (0.85 mg, 32.1%); m.p. 86-88 ^oC (dec.); R_f (cyclohexane:ethyl acetate 10:1) 0.39; δ_H (400 MHz, $CDCl_3$) 7.45 (4H, m, Ar-

H_4), 7.39 (4H, m, Ar-H_4), 7.30 (12H, m, Ar-H_{12}), 6.40 (4H, s, 4-,6-,4'-,6'-*H*), 3.99 (2H, m, 2×2''-*H*), 3.63 (2H, dd, J 10.2, 4.5 Hz, 2×1''-H_α), 3.55 (2H, dd, J 10.2, 6.4 Hz, 2× 1''-H_β), 1.35 (6H, d, J 6.8 Hz, 2×CH_3), 0.94 (18H, s, 2×C(CH_3)$_3$); δ_C (100.6 MHz, $CDCl_3$) 135.6, 135.5, 133.0, 132.7, 129.9, 129.7, 127.8 (Ar-C_{20}), 120.0 (2-,2'-*C*), 118.6 (3a-,3a'-,6a-,6a'-*C*), 110.9 (4-,4'-,6-,6'-*C*), 68.3 (2×1''-*C*), 57.9 (2×2''-*C*), 26.7 (2×C(*C*H$_3$)$_3$), 19.1 (2×*C*(CH$_3$)$_3$), 17.2 (2×3''-*C*); ν_{max}: 2930, 2856, 1488, 1471, 1427, 1368, 1301, 1104, 1071, 1021, 824, 759, 740, 699, 609, 501, 485; *m/z*: (EI) 874 $[M]^+$; found C, 65.75; H, 6.18; N, 3.12%, $C_{48}H_{54}O_2N_2S_4Si$ requires C, 65.86; H, 6.22; N, 3.20%; $^{293}[\alpha]_D$ = +5.0 (c = 0.2, $CHCl_3$).

_S,S_-Bis(N-(1''-hydroxyprop-2''-yl)pyrrolo[3,4-d])tetrathiafulvalene 20.

A mixture of the *bis*-protected donor **40** (0.85 g, 1.0 mmol) and tetrabutylammonium fluoride solution (1.0 M in THF, 5.0 ml, 5.0 mmol) in THF (60 ml) was stirred at room temperature for 6 h. After adding water (5 ml), the solvent was removed. The residue was washed with ether and then purified by flash chromatography (SiO_2, eluting with ethyl acetate:methanol 9:1) to yield a yellow solid (283 mg). The solid was stirred with DCM (20 ml) overnight to give the chiral diol **20** as a yellow solid (193 mg, 49.9%); m.p. 176-178 ^oC (dec.); R_f (ethyl acetate:methanol 9:1) 0.15; δ_H (400 MHz, $CDCl_3$) 6.54 (4H, s, 4-,4'-,6-,6'-*H*), 4.08 (2H, m, 2×2''-*H*), 3.67 (4H, m, 2×1''-H_2), 1.53 (2H, br, 2×O*H*), 1.41 (6H, d, J 7.0 Hz, 2×CH_3); δ_C (100.6 MHz, $CDCl_3$) 120.4 (2-,2'-*C*), 119.3 (3a-,3a'-,6a-,6a'-*C*), 110.6 (4-,4'-,6-,6'-*C*), 67.4 (2x1''-*C*), 58.4 (2×2''-*C*), 17.4 (2×3''-*C*); ν_{max}: 3385, 1489, 1366, 1301, 1135, 1125, 1114, 1059, 1025, 992, 974, 757,606; *m/z*: (EI) 398 $[M]^+$; found C, 48.29; H, 4.44; N, 6.95%, $C_{16}H_{18}N_2O_2S_4$ requires C, 48.21; H, 4.55; N, 7.03%; $^{293}[\alpha]_D$ = +27.6 (c =0.2, THF).

Diastereoisomers of *N*-(1'-Phenyl-ethyl)-2-thioxo-5,6-dihydro-[1,3]dithiolo[4,5-*b*][1,4]dithiin-5-yl-acetamide, 43 and 44.

A stirred solution of the acid **41**[30] (2.90 g, 10.3 mmol) and triethylamine (1.70 ml, 12.2 mmol) in dry THF (100 ml) under a nitrogen atmosphere was cooled to 0 ^oC and ethyl

chloroformate (1.34 g, 12.3 mmol) was added. After stirring for 10 min a solution of (*R*)-(+)-alpha-methylbenzylamine (2.50 g, 20.6mmol) in THF (10 ml) was added. The solution was allowed to warm to room temperature and then stirred overnight. Removal of the solvent and column chromatography (cyclohexane/ethyl acetate 3:1) gave, after elution of unreacted chiral amine, two yellow fractions:

(5*R*,1'*R*) isomer) **43**, (1.12g, 28.3%), yellow feathery needles, m.p. 135-137 ^{o}C, R_f (cyclohexane:ethyl acetate 3:1) 0.26; δ_H(400 MHz, $CDCl_3$) 7.26 (5H, m, Ar-H_5), 5.94 (1H, d, J 7.7 Hz, N-*H*), 5.04 (1H, quin, J 7.1 Hz, N-C*H*), 4.11 (1H, m, 5-*H*), 3.34 (1H, dd, J 2.8, 13.5 Hz, 6-H_α), 3.06 (1H, dd, J 5.3, 13.5 Hz, 6-H_β), 2.67 (2H, d, J 7.1 Hz, (O=C)CH_2), 1.43 (3H, d, J 6.8 Hz, CH_3); δ_C (100.6 MHz, $CDCl_3$) 207.65 (*C*=S), 167.67 (*C*=O), 142.47, 128.76, 127.63 & 126.09 (Ar-C_6), 122.55 & 120.85 (3a-,7a-*C*), 49.21 (N-*C*H), 41.39 (O=C-*C*H_2), 38.24 (5-*C*), 34.07 (6-*C*), 21.66 (*C*H_3); ν_{max}: 3144, 3072, 2960, 2888, 1648, 1552, 1500, 1456, 1420, 1372, 1240, 1060; *m/z*: (CI): 403 ($[M+NH_4]^+$), 388, 387, 386 ($[M+H]^+$), 385, 356, 312, 280; *HRMS* (CI): found 384.9750, $C_{15}H_{15}NOS_5$ requires: 384.9752; $^{297}[\alpha]_D$: +122 (c = 0.46, DCM).

(5*S*,1'*R*) isomer) **44**, (1.10g, 27.8%), yellow plates, m.p. 161-163 ^{o}C, R_f (cyclohexane:ethyl acetate 3:1) 0.14; δ_H(400 MHz, $CDCl_3$) 7.26 (5H, m, Ar-H_5), 5.84 (1H, d, J 7.4 Hz, N*H*), 5.05 (1H, quin, J 7.1 Hz, N-C*H*), 4.11 (1H, m, 5-*H*), 3.41 (1H, dd, J 2.7, 13.5 Hz, 6-H_α), 3.20 (1H, dd, J 5.3, 13.5 Hz, 6-H_β), 2.71 (1H, dd, J 7.1, 15.4 Hz, (O=C)CH_α), 2.63 (1H, dd, J 7.1, 15.4 Hz, (O=C)CH_β), 1.44 (3H, d, J 7.1 Hz, CH_3); δ_C: 207.63 (*C*=S), 167.63 (*C*=O), 142.71, 128.74, 127.56 & 126.01 Ar-C_6), 122.62 & 121.00 (3a-,7a-*C*), 49.28 (N-*C*H), 41.42 (O=C-*C*H_2), 38.32 (5-*C*), 33.92 (6-*C*), 21.77 (*C*H_3); ν_{max}: 3108, 2936, 2864, 1636, 1552, 1504, 1456, 1348, 1318, 1300, 1264, 1060; *m/z*: (CI): 403($[M+NH_4]^+$), 386 ($[M+H]^+$), 385, 387, 312, 280; *HRMS* (CI) found: 384.9756, $C_{15}H_{15}NOS_5$ requires: 384.9752; $^{297}[\alpha]_D$: - 176 (c = 0.39, DCM).

***(1'R,5R)- N*-(1'-Phenyl-ethyl)-(BEDT-TTF)-acetamide 21.**

A solution of thione **43** (573 mg, 1.923 mmol) and the unsubstituted oxo compound **45** (620 mg, 3.846 mmol) in triethyl phosphite (10 ml) was stirred overnight at 90 ^{o}C. After cooling, the volatiles were removed under vacuum and the crude material purified by

column chromatography (eluting with cyclohexane:ethyl acetate 3:1) to afford the donor **21** (253 mg, 31 %) as an orange-red glassy solid, m.p. 125-127 ^{o}C dec.; R_f (cyclohexane:ethyl acetate 3:1) 0.24; δ_H (400 MHz, $CDCl_3$): 7.22 (5H, m, Ar-H_5), 5.93 (1H, d, *J* 7.8 Hz, N-*H*), 5.03 (1H, quin, *J* 7.4 Hz, N-C*H*), 4.02 (1H, m, 5-*H*), 3.24 (1H, dd, *J* 3.1, 13.4 Hz, 6-H_α), 3.21 (4H, s, 5'-,6'-H_2), 2.94 (1H, dd, *J* 4.8, 13.3 Hz, 6-H_β), 2.57 (2H, d, *J* 7.2 Hz, (O=C)CH_2), 1.42 (3H, d, *J* 6.9 Hz, CH_3); δ_C (100.6 MHz, $CDCl_3$): 168.1 (*C*=O), 142.9, 128.7, 127.4 &126.0 (Ar-C_6), 113.8, 113.7, 112.7, 112.1, 112.0 & 111.2 (6 x sp^2-*C*), 49.2 (N-*C*H), 41.6 (O=C-*C*H_2), 38.5 (5-*C*), 34.6 (6-*C*), 30.1 (5'-,6'-*C*), 21.8 (*C*H_3); ν_{max}: 3300, 2970, 2924, 1713, 1650, 1543, 1449, 1366, 1263; *m/z* (CI): 563 ($[M+NH_4]^+$), 546 ($[M+H]^+$), 462, 391, 279, 217; *HRMS* (CI)*:* found 545.9298, ($C_{20}H_{19}NOS_8$ + H) requires 545.9305; found C, 43.85; H, 3.38; N, 2.64%, $C_{20}H_{19}NOS_8$ requires C, 43.87; H, 3.40; N, 2.64%; $^{293}[\alpha]_D$: +2.1 (c = 0.147, DCM).

***(1'R,5S)*-*N*-(1'-Phenyl-ethyl)-(BEDT-TTF)-acetamide 22.**

Following the procedure for **21**, thione **44** (600 mg, 1.56 mmol) and oxo compound **45** (810 mg, 3.89 mmol) in triethyl phosphite (14 ml) afforded the donor **22** (185 mg, 46 %) as a pink solid, m.p. 148-158 ^{o}C dec. R_f (cyclohexane:ethyl acetate 3:1) 0.22; δ_H (400 MHz, $CDCl_3$) 7.29 (5H, m, Ar-H_5), 6.09 (1H, d, J 7.8 Hz, N-*H*), 5.07 (1H, quin, J 7.3 Hz, N-C*H*), 4.03 (1H, m, 5-*H*), 3.33 (1H, dd, J 3.0, 13.3 Hz, 6-H_α), 3.26 (4H, s, 5'-,6'-H_2), 3.11 (1H, dd, J 4.9, 13.3 Hz, 6-H_β), 2.66 (1H, dd, J 6.8, 15.1 Hz, (O=C)CH_α), 2.59 (1H, dd, J 7.2, 15.1 Hz, (O=C)CH_β), 1.45 (3H, d, J 6.8 Hz, CH_3); δ_C (100.6 MHz, $CDCl_3$) 168.2 (*C*=O), 142.6, 128.7, 127.5& 126.1 (Ar-C_6), 113.8, 112.6, 112.2, 111.7 & 111.3 (6 x sp^2-*C*), 49.1 (N-*C*H), 41.6 (O=C-*C*H_2), 38.4 (5-*C*), 34.7 (6-*C*), 30.1 (5'-,6'-*C*), 21.7 (*C*H_3); ν_{max}: 3297, 3050, 2976, 2925, 1642, 1542, 1448, 1410, 1373, 1263, 1159, 1127, 1018; *m/z:* 568($[M+NH_4]^+$), 546($[M+H]^+$), 443, 357, 217; *HRMS* (CI) found: 545.9299, ($C_{20}H_{19}NOS_8$ + H) requires: 545.9305; found C, 43.83; H, 3.40; N, 2.70%, $C_{20}H_{19}NOS_8$ requires C, 43.92; H, 3.40; N, 2.64%; $^{297}[\alpha]_D$: - 68 (c = 0.17, CH_2Cl_2).

Dimethyl *trans*-5,6-dihydro-2-thioxo-1,3-dithiolo[4,5-b]dithiin-5,6-diacetate 46.

A suspension of trithione **41** (3.10 g, 15.8 mmol) and dimethyl *E*-hex-3-enedioate (2.75g, 16.0 mmol) in toluene (100 mL) was heated to reflux for 48 h under nitrogen. After evaporation of toluene, the residue was dissolved in chloroform, warmed with charcoal for 10 min, filtered and evaporated. The residue was purified by flash chromatography (SiO_2, eluting with cyclohexane:ethyl acetate 2:1), and the main fraction evaporated and stirred with hexane for 2 days to remove alkene starting material. Filtration and evaporation solution afforded thione **46** (4.41 g, 75.8%) as a yellow powder; m.p. 90-92 ^oC; R_f (cyclohexane:ethyl acetate 3:1) 0.36; δ_H (400 MHz, $CDCl_3$): 3.83 (2H, m, 5-,6-*H*), 3.73 (6H, s, 2×OCH_3), 2.86 (4H, m, 5-,6-CH_2); δ_C (100.6 MHz, $CDCl_3$): 206.9 (*C*=S), 170.3 (2×*C*=O), 118.8 (3a-,7a-*C*), 52.3 (2 × O*C*H_3), 40.9 (2 × 5-,6-*C*H_2), 40.7 (5-,6-*C*); ν_{max}: 2949, 1719, 1486, 1437, 1369, 1249, 1206, 1158, 1062, 1031, 1016, 973, 921, 886, 810, 574, 516; found C, 35.91; H, 3.23%, $C_{11}H_{12}O_4S_5$ requires C, 35.85; H, 3.28%.

Dimethyl *trans*-5,6-dihydro-2-oxo-1,3-dithiolo[4,5-b]dithiin-5,6-diacetate 47.

From **46** (1.84 g, 5.03 mmol) using Method **A** afforded **47** (1.67 g, 94.3%) as a pale orange solid; m.p. 79-81 ^oC; R_f (cyclohexane:ethyl acetate 3:1) 0.40; δ_H (400 MHz, $CDCl_3$): 3.75 (2H, m, 5-,6-*H*), 3.67 (6H, s, 2×OCH_3), 2.87 (4H, m, 5-,6-CH_2); δ_C (100.6 MHz, $CDCl_3$): 170.5 (*C*=O), 109.5 (3a-,7a-*C*), 52.2 (2×O*C*H_3), 42.0 (5-,6-*C*), 40.9 (2 × 5-,6-*C*H_2); ν_{max}: 3001, 2944, 1733, 1716, 1684, 1647, 1626, 1505, 1435, 1398, 1363, 1258, 1204, 1170, 1150, 1055, 978, 927, 778, 554; found C, 37.38; H, 3.34%, $C_{11}H_{12}O_5S_4$ requires C, 37.49; H, 3.42%.

Dimethyl *vic-trans*-BEDT-TTF-diacetate 48.

From **47** (1.97 g, 5.61 mmol) and **29** (3.14 g, 14.0 mmol) and trimethyl phosphite (60 ml) using Method **C** gave the *trans* diester **48,** as an orange solid (1.64 g, 55.3%,); m.p. 136-138°C; R_f (cyclohexane:ethyl acetate 2:1) 0.62; δ_H (400 MHz, $CDCl_3$): 3.73 (2H, m, 5-,6-*H*), 3.69 (6H, s, 2×OCH_3), 3.25 (4H, s, 5'-,6'-H_2), 2.77 (4H, m, 2 x 5-,6-CH_2);

δ_C (100.6 MHz, $CDCl_3$): 170.6 (2×*C*=O), 113.8, 112.0, 110.3, 110.0 (2-,2'-,3a-,3a'-, 7a-,7a'-*C*), 52.1 (2×O*C*H_3), 41.0 (2 × 5-,6-*C*H_2), 40.7 (5,6-*C*), 30.1 (5'-,6'-*C*); ν_{max}: 2956, 2918, 1732, 1436, 1414, 1367, 1338, 1308, 1288, 1258, 1239, 1214, 1191, 1138, 1152, 1093, 1031, 1011, 988, 912, 873, 848, 772; found C, 36.41; H, 2.95%, $C_{16}H_{16}O_4S_8$ requires C, 36.34; H, 3.05%.

***vic-trans*-BEDT-TTF-di(acetic acid) 23.**

Diester **48** (200 mg, 0.38 mmol) and potassium hydrogen carbonate (300 mg, 3.00 mmol) were dissolved in a mixture of methanol (9 ml), THF (10 ml) and water (5 ml) and refluxed together for 2 h. The filtered mixture was evaporated and extracted between water and dichloromethane. The aqueous layer was carefully acidified with 1M hydrochloric acid and the suspension produced stirred in an ice bath for 1 h and filtered to give a product with a 1:1 composition of **23** and its monopotassium salt, as a yellow brown powder (80 mg, 41%) which was insoluble in organic solvents; m.p. 170-173 ^oC (dec.); ν_{max}: 2916 br, 1702, 1437, 1404, 1288, 1248, 1222, 1163, 1001, 884. Found C: 32.7 H: 2.1% $C_{14}H_{12}O_4S_8$. $C_{14}H_{11}O_4S_8K$ requires C: 32.3 H: 2.2 % .

***exo*- 5,8-Methano-4a,5,6,7,8,8a-hexahydro-1,3-dithiolo[4,5- b]benzo-1,4-dithiin-2-thione 49.**

Norbornene (4.00 g, 42.4 mmol) and trithione **41** (8.30 g, 42.4 mmol) were refluxed together in toluene (500 ml) for 27 h and filtered. The filtrate was evaporated to dryness and the residue refluxed in methanol (50 ml) for 30 min. After cooling to room temperature, filtration gave thione **49** (11.69 g, 95%) as thin yellow plates, m.p. 172-174 ^oC; R_f (cyclohexane: ethyl acetate 4:1) 0.78; δ_H (400 MHz, $CDCl_3$): 3.39 (2H, s, 4a-,8a-*H*), 2.37 (3H, br, 5-,8-,10$_\alpha$-*H*), 1.66 (2H, d*, J 8.8 Hz, 6$_\alpha$-,7$_\alpha$-*H*), 1.33 (1H, d, J 10.8 Hz, 10$_\beta$-*H*), 1.27 (2H, d*, J 8.8 Hz, 6$_\beta$-,7$_\beta$-*H*) *some further coupling; δ_C (100.6 MHz, $CDCl_3$): 209.9 (*C*=S), 136.5 (3a-,9a-*C*), 60.3 (4a-,8a-*C*), 44.3 (5-,8-*C*), 35.3 (10-*C*), 29.1 (6-,7-*C*); ν_{max}: 2951, 2870, 1466, 1449, 1300, 1180, 1145, 1057, 1005, 928, 887, 783, 510, 492, 465, 448; found: C, 41.29; H, 3.43%, $C_{10}H_{10}S_5$ requires: C, 41.35; H, 3.47%.

Dimethyl *trans-exo*-(cyclopentan-1'',3''-BEDT-TTF-5,6-diacetate diastereomers 50-51.

Oxo compound **47** (1.50 g, 4.26 mmol) and thione **49** (3.14 g, 10.81 mmol) in trimethyl phosphite following Method **C** gave, after chromatography, a 1:1 mixture of **50** and **51** (0.90 g, 35.7%,) as an orange solid, m.p. 164-168 °C; R_f (cyclohexane:ethyl acetate 4:1) 0.34; two diastereomers showing very similar ^{1}H & ^{13}C NMR signals: δ_H (400 MHz, $CDCl_3$) 3.73 (2H, m, 5-,6-*H*), 3.66 and 3.56 (6H, s , 2 xOCH_3, 2 isomers), 3.32 (2H, s, 5'-,6'-*H*), 2.75 (4H, m, 5,6-CH_2CO), 2.32 (2H, s, 1''-,3''-*H*), 2.30 (1H, d, J 11 Hz, 2''$_\alpha$-*H*), 1.61 (2H, d, J 8 Hz, 4''$_\alpha$-,5''$_\alpha$-*H*), 1.24 (1H, d, J 11 Hz, 2''$_\beta$-*H*), 1.23 (2H, d, J 8 Hz, 4''$_\beta$-,5''$_\beta$-*H*); δ_C ($CDCl_3$): 170.7 (2×*C*=O), 126.9 (3a'-,7a'-*C*), 112.7, 110.7, 110.4, 108.5 (2-,2'-,3a-,7a-*C*), 59.7 (5'-,6'-*C*), 52.2 & 52.1 (2×O*C*H_3), 44.3, 41.5, 40.8, 40.2 (5-,6-*C*, 5,6-*C*H_2CO, 1''-3''-*C*, two isomers), 35.1 (2''-*C*), 29.1 (4''-,5''-*C*); ν_{max}: 2947, 2869, 1729, 1435, 1396, 1357, 1300, 1215, 1197, 1165, 1143, 1003, 971, 920, 893, 877, 771, 651, 603, 493; *m/z*: (EI) 528 $[M]^+$; *HRMS* (ES, with ammonium acetate) found: 594.9351, $[M+H]^+$, $C_{21}H_{22}O_4S_8$+H requires: 594.9357; found C, 42.50; H, 3.56%, $C_{21}H_{22}O_4S_8$ requires C, 42.40; H, 3.73%.

X-ray Crystallography.

Crystal structures were measured using MoKα radiation at 120 K, solved with SHELXS-97 and refined with SHELXL-97[34] using the X-SEED interface.[35] Molecular illustrations are made with ORTEP-3[36] and Mercury[37] using POVRAY.[38] Data is deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ with reference numbers CCDC 924767 – 924772.

Crystal data for **15**: $C_{18}H_{28}O_4S_8$, M_r = 564.88, orthorhombic, a = 9.7257(3), b = 9.8612(4), c = 26.3649(11) Å, V = 2528.58(17) Å^3, Z = 4, $P2_12_12_1$, D_c = 1.48 g cm^{-3}, μ(MoKα) = 0.073 mm^{-1}, T = 120(2) K, 5533 unique reflections, 4269 with $F > 4\sigma(F)$, R = 0.049, wR = 0.090.

Crystal data for **44**: $C_{15}H_{15}NOS_5$, M_r = 385.58, monoclinic, a = 5.1301(3), b = 9.2119(5), c = 17.9448(10) Å, α = 90.0, β = 94.715(5), γ = 90.0°, V = 845.715(5) Å ^{3}, Z = 2, $P2_1$, D_c = 1.52 g cm^{-3}, μ(MoKα) = 0.685 mm^{-1}, T = 120(2) K, 3866 unique reflections, 3703 with F > 4σ(F), R = 0.033, wR = 0.088, Flack parameter: 0.02(8).

Crystal data for **49**: $C_{10}H_{10}S_5$, M_r = 290.48, monoclinic, a = 6.3435(1) b = 7.3999(2) c = 12.5755(4) Å, β = 90.915(2)°, V = 590.23 Å^3 , Z = 2, $P2_1$, D_c = 1.634 g cm^{-3}, μ(MoKα) = 0.94 cm^{-1}, T = 120(2) K, 2488 unique reflections, 2415 with F > 4σ(I), R = 0.042, wR = 0.108.

Crystal data for (**16**)$_4$[Fe_2(oxalate)$_5$]: $4C_{14}H_{18}O_2S_8.C_{10}O_{20}Fe_2$, M_r = 2450.86, monoclinic, a = 13.8685(4), b = 21.8745(8), c = 15.4879(5) Å, β = 100.678(2)°, V = 4617.1(3) Å ^{3}, Z = 2, $P2_1$, D_c = 1.76 g cm^{-3}, μ(MoKα) = 1.114 mm^{-1}, T = 120(2) K, 19353 unique reflections, 14466 with F > 4σ(F), R = 0.071, wR = 0.136.

Crystal data for **16.**TCNQ-F_4: $C_{14}H_{18}O_2S_8.C_{12}N_4F_4$, M_r = 750.92, triclinic, a = 8.8930(2), b = 12.4995(2), c = 13.9897(3) Å, α = 89.2960(10), β = 74.2240(10), γ = 86.8580(10)°, V = 1494.24(5) Å ^{3}, Z = 2, P1, D_c = 1.67 g cm^{-3}, μ(MoKα) = 0.066 mm^{-1}, T = 120(2) K, 13037 unique reflections, 11743 with F > 4σ(F), R = 0.033, wR = 0.081.

Crystal data for **18**.I_3: $C_{14}H_{18}O_4S_8.I_3$, M_r = 887.46, monoclinic, *a* = 19.1095(7), *b* = 10.1013(3), *c* = 13.8161(6) Å, β = 110.103(4)°, *V* = 2504.45(16) Å ^{3}, *Z* = 4, *C2*, D_c = 2.35 g cm^{-3}, μ = 4.43 mm^{-1}, *T* = 150 K, 3845 unique reflections (R_{int} = 0.0249), 3282 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.038, $R_w(F^2$, all data) = 0.084.

Conductivity measurements.

Two-probe DC transport measurements were made on several crystals of **16**.Fe(III)$_2$(oxalate)$_5$ and **18**.I_3, respectively, using a HUSO HECS 994C multi-channel conductometer. Gold wires (15 μm diameter) were attached to the crystal, and the attached wires were connected to an eight-pin integrated circuit plug with gold conductive cement.

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Graphical Abstract.