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New Chiral Organosulfur Donors Related To Bis(ethylenedithio)tetrathiafulvalene.

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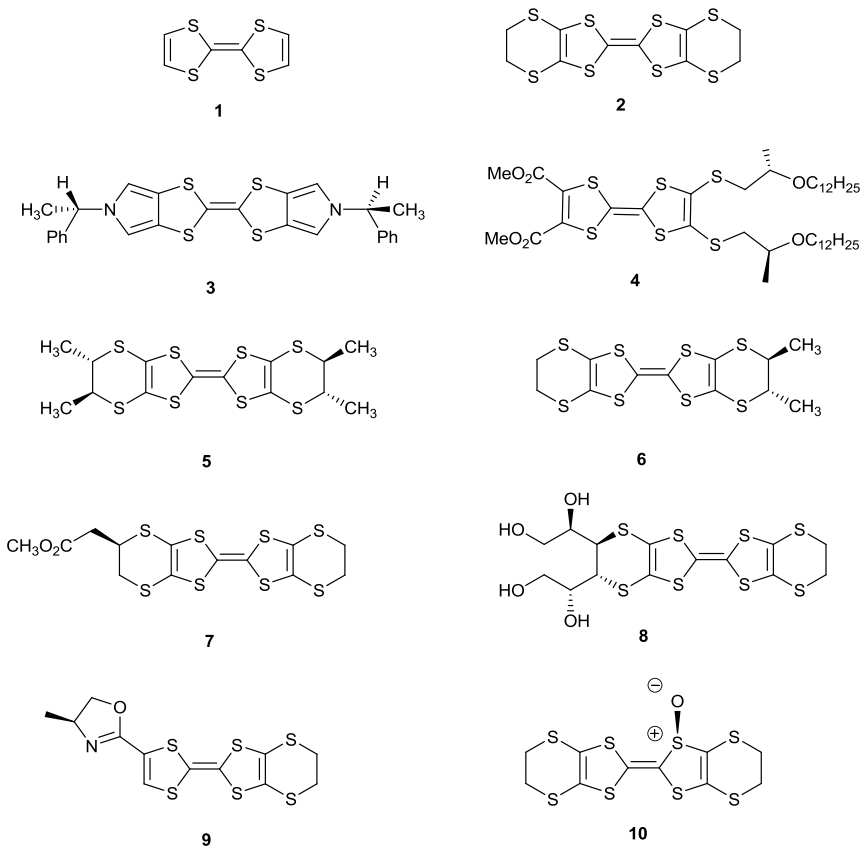
Abstract. Six new enantiopure chiral organosulfur donors, with structures related to BEDT-TTF, have been synthesised for use in the preparation of organic metals, starting either by double nucleophilic substitutions on the bis-mesylate of *2R,4R*-pentane-2,4-diol or by a cycloaddition with subsequent elimination of acetic acid on the enol acetate of (+)-nopinone. Crystal structures of some of their radical cation triiodides salts and TCNQ complexes are reported.

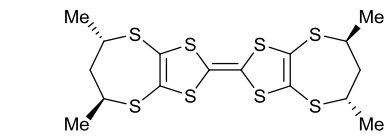
Introduction

The radical cation salts and charge transfer molecular complexes of TTF **1** and BEDT-TTF **2** show a wide range of electrical behaviour, and have found use in a range of systems including metallic systems, semiconductors and low-temperature superconductors.[1] Introduction of chirality into the system may be expected to introduce further effects. Indeed, Rikken has demonstrated the phenomenon of magneto-chiral anisotropy in carbon nanotubes, i.e. that in a coaxial magnetic field the resistance to current flow along nanotubes with enantiomeric structures are different.[2] Furthermore, one could anticipate that chirality may modulate the Hall effect, in which the path of an electric current travelling in a perpendicular magnetic field is displaced in a direction perpendicular to both that of the current and the magnetic field. The challenge is to prepare molecular materials in which the current can flow in a chiral environment, and the state of progress has been



reviewed recently.[3] In one approach several enantiopure organosulfur donors have been prepared, including donors with chiral sidechains e.g. **3**–**4**,[4] BEDT-TTF

derivatives with stereogenic carbon atoms in the molecular skeleton, e.g. **5**–**8**[5–10], EDT-TTF derivatives containing a chiral oxazoline group such as **9**,[11] and an enantioenriched donor **10** containing a stereogenic sulfur atom.[12] A small number of radical cation salts of enantiopure donors have now been characterised and in two cases, $(\mathbf{6})_2PF_6$ and $(\mathbf{9})_2AsF_6$, a comparison made between enantiomeric and racemic materials.[7,10] In the former, stacks of donors on either side of the anions are related by a centre of symmetry in the racemate and by a two-fold rotation axis in the enantiopure salt but the salts have similar conductivities;[8] however, in the latter the enantiopure material shows a room-temperature conductivity an order of magnitude higher than for the racemate, due to disorder in the racemate, [11] however no suitable system has been found so far in which chirality is strongly expressed in the packing arrangement. Other approaches for incorporating chirality into such salts are to use either a chiral anion such as tris(oxalato)Cr(III)[13] or $[Sb_2(L\text{-tartrate})_2]$[2–14] or to introduce an enantiopure solvent molecule in the salt's crystal structure.[15] The arrangement of donors in a helical arrangement is a particularly attractive goal, and has been partially achieved by supramolecular organisation of donor pairs in the TTF mellitate salt.[16]



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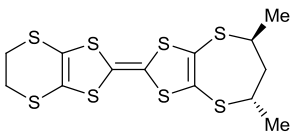

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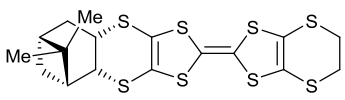

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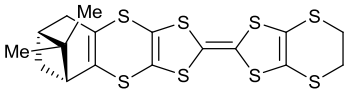

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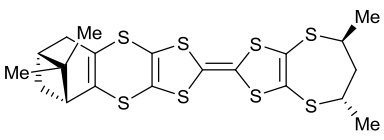

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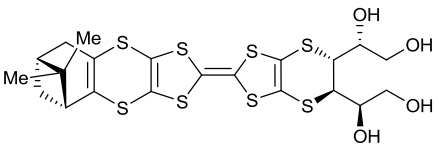

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Here we report the synthesis of a group of novel chiral organosulfur donors, **11**–**16**, in which chirality is provided by one or more hydrocarbon groupings. The structures of products from initial experiments to form charge transfer complexes are also described.

Discussion

Synthesis of 11 and 12

Electrocrystallisation of the enantiopure donor (*S*,*S*,*S*,*S*)-tetramethylBEDT-TTF **5** has given a series of radical cation salts, but their crystal structures were pseudocentrosymmetric, with the methyl groups adopting equatorial orientations.[6] However, we reasoned that insertion of a methylene group between each pair of stereogenic centres to give **11** would provide a more promising system. The outer seven-membered rings of donor **11** would be expected to adopt chair conformations and give two possible molecular conformations, A and B (Fig. 1), in analogy with the structures of **17–19**.[17] The *trans* orientation of the methyl groups on the propylene bridge would force one into an axial position and the other into an equatorial position. Molecules in conformation B could be envisaged to stack in a helix.

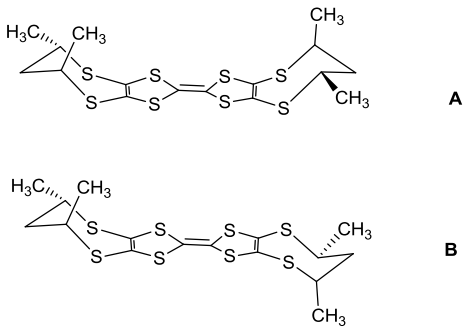
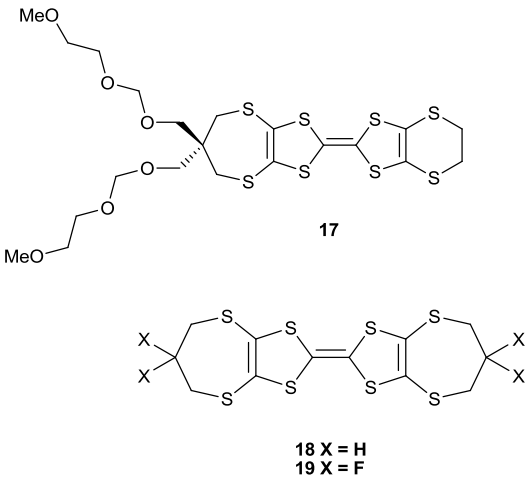
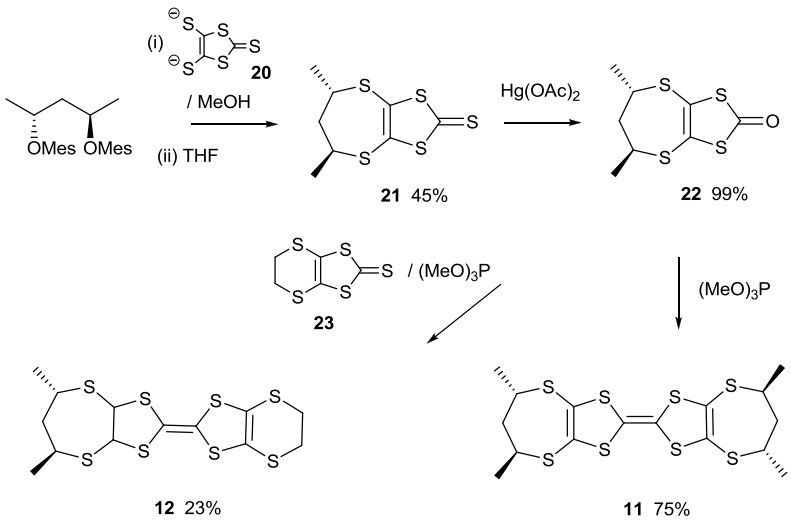


Figure 1. Possible chair conformation of **11** showing the axial and equatorial dispositions of the methyl groups.



The synthesis of donor **11** started with the cyclisation of the dithiolate **20**, prepared in three steps from carbon disulfide,[18] with the bis-mesylate of *R*,*R*-pentane-

2,4-diol (Scheme 1). The first mesylate group is substituted by reaction in methanol at room temperature, but it was necessary to replace the methanol with THF and heat to reflux to complete the cyclisation to give the thione **21** in 45% yield. The thione was converted to oxo compound **22** using mercuric acetate in quantitative yield, and this was then homocoupled in refluxing trimethyl phosphite over 24 hours to give **11** in 75% yield. Cross-coupling, under similar conditions, of oxo compound **22** with a three-fold excess of the unsubstituted thione **23** yielded the cross-coupled donor **12** in 22% yield after chromatography. The low yield of **12** is a consequence of the faster homocoupling of thione **23** to give BEDT-TTF.



Scheme 1

The molecular structures of donors **11** and **12** were determined by X-ray crystallography. For both donors the seven-membered rings adopt chair conformations with one methyl group in an axial position and one in an equatorial position. For the homocoupled donor **11** (Fig. 2) the structure of the organosulfur system deviates very strongly from planarity, with the plane of the central $S_2C{=}CS_2$ grouping lying at 31.8° and 35.2° to the planes defined by the S–C=C–S groupings of the outer dithiepine rings, to give the molecule a strongly bowed structure. The structure of the cross-coupled donor **12** (Fig. 3) is not so bowed, with the plane of the central $S_2C{=}CS_2$ grouping lying at 19.2° to the dithiepine S–C=C–S plane and at 19.7° to the dithiin S–C=C–S plane. All bond angles in the seven-membered rings of **11** and **12** are widened: at sp^2 C atoms: [**11**: 127.47(10)–127.84(10), **12**: 125.90(9)–126.23(9)°], at S atoms [**11**: 102.94(6)–105.93(6), **12**: 103.65(5)–105.43(5)°], at

methine C atoms [**11**: 113.33(9)–115.62(9), **12**:113.54(8)–114.90(8)°], and especially at the methylene C atoms [**11**: 117.33(11)–117.64(10), **12**: 117.92(10)°]. However, there is no indication of significant strain on the bond lengths in this ring, e.g. sp^3C–sp^3C [**11**: 1.5244(18)–1.5292(18), **12**: 1.5278(16)–1.5304(17) Å], and as expected C–S bonds to sp^3C [**11**: 1.8259(13)–1.8400(12), **12**: 1.8301(12)–1.8327(13) Å] are longer than those to sp^2C [**11**: 1.7438(13)–1.7459(13), **12**:1.7441(11)–1.7451(12) Å]. Despite the non-planarity of these donors, it is envisaged that, on formation of radical cation salts, the organosulfur region of the molecule will be closer to planarity.

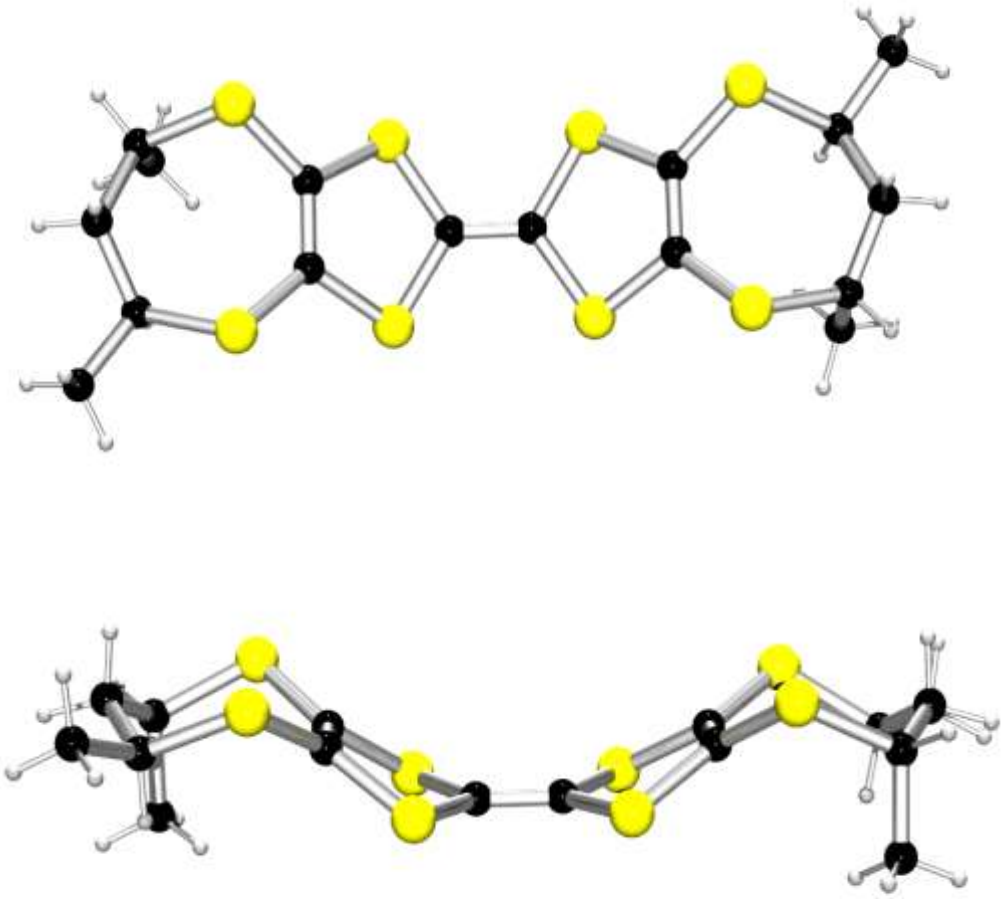


Figure 2. Two views of the molecular structure of donor **11**.

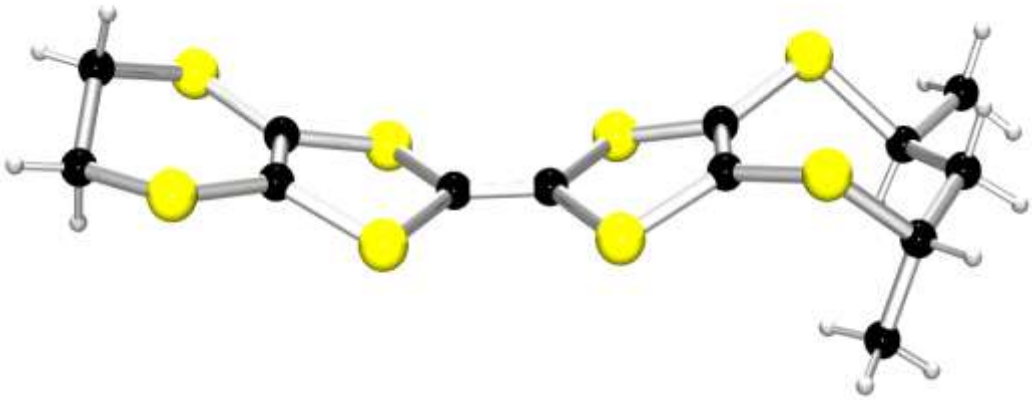
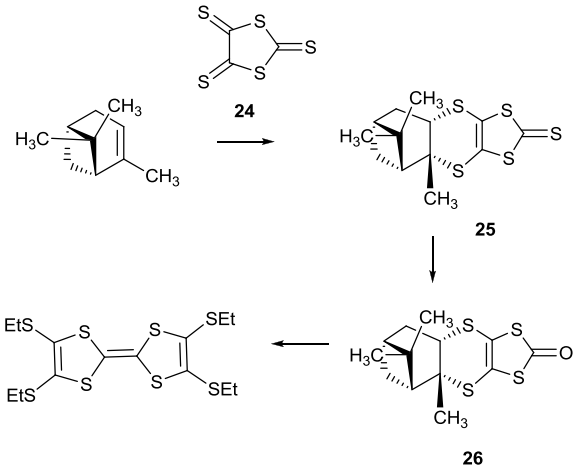


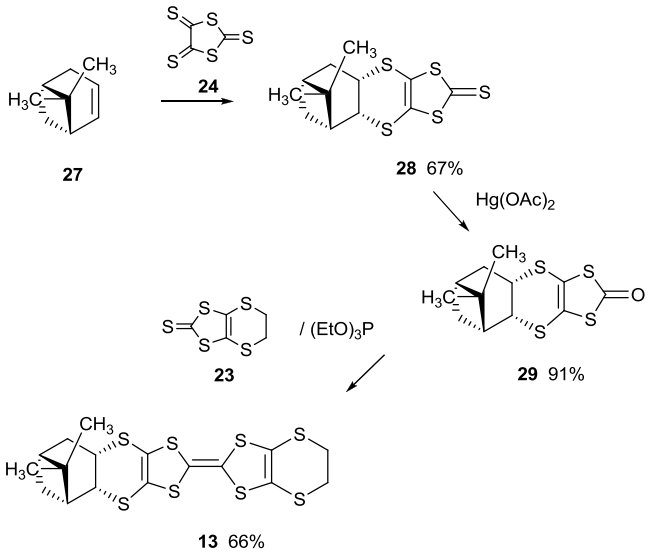
Figure 3. Molecular structure of **12**.

Synthesis of donors 13–16

We have already shown that (–)-α-pinene undergoes diastereoselective addition to the trithione **24** to give the thione **25** but, after conversion to the oxo compound **26**, attempted self-coupling in triethyl phosphite gave only tetra(ethylthio)TTF (Scheme 2).[9] The X-ray crystal structure of **25** indicated strain at the quarternary carbon atom at the fusion with the dithiin ring, and it is probably this factor in the oxo compound which facilitates ring opening with triethyl phosphite. A sensible step would be to make the material without the methyl group at the strained centre, for which apopinene **27** is required as starting material. Indeed, reaction of apopinene with trithione **24**[18] by a hetero Diels Alder reaction gave thione **28** in 67% yield. Conversion of this thione to the oxo compound **29** with mercuric acetate proceeded satisfactorily and the product was cross-coupled with the unsubstituted thione **23** to give the donor **13** (Scheme 3). Subsequent crystal structure measurements of the donor in a TCNQ molecular complex[19] and in a triiodide salt (Fig 10) confirmed the stereochemistry of the addition reaction of trithione **24** to the less hindered face of apopinene. However, it is difficult to obtain the starting material (-)-apopinene from (-)-mytenal with high enantiopurity, not least because the enantiomers are interconverted by a shift in position of the double bond. Thus, our starting material had an e.e. of only 42% estimated from its optical rotation.



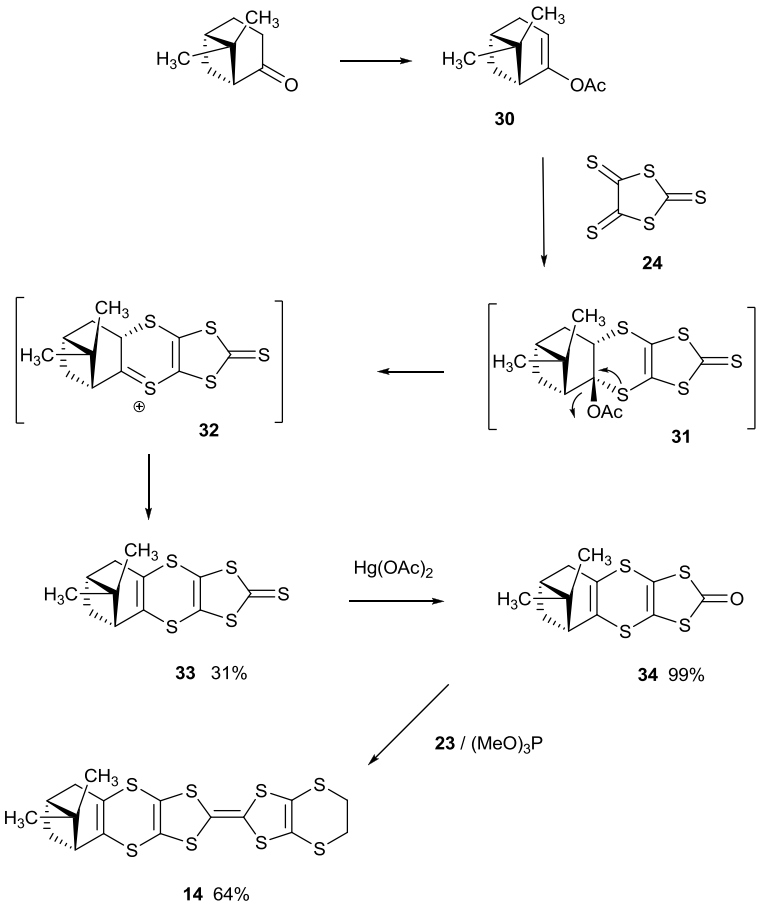
Scheme 2



Scheme 3

The rather acute orientation of the bicyclo[3.1.1]heptyl group relative to the rest of the molecule is not ideal for the close packing of the organosulfur residues. To obtain fusion of the chiral grouping to the BEDT-TTF system at a carbon-carbon double bond rather than a single one, the reaction of the (+)-nopinone enol acetate **30** with trithione **24** was attempted. It was reasoned that, after cycloaddition to give intermediate **31**, the acetate group might be eliminated by nucleophilic displacement by the α-S atom to give cation **32** which could then lose a proton to give the desired product (Scheme 4). Indeed, this reaction was carried out by refluxing the enol acetate **30** with the trithione **24**, and gave the desired fused thione **33** in 31% yield after

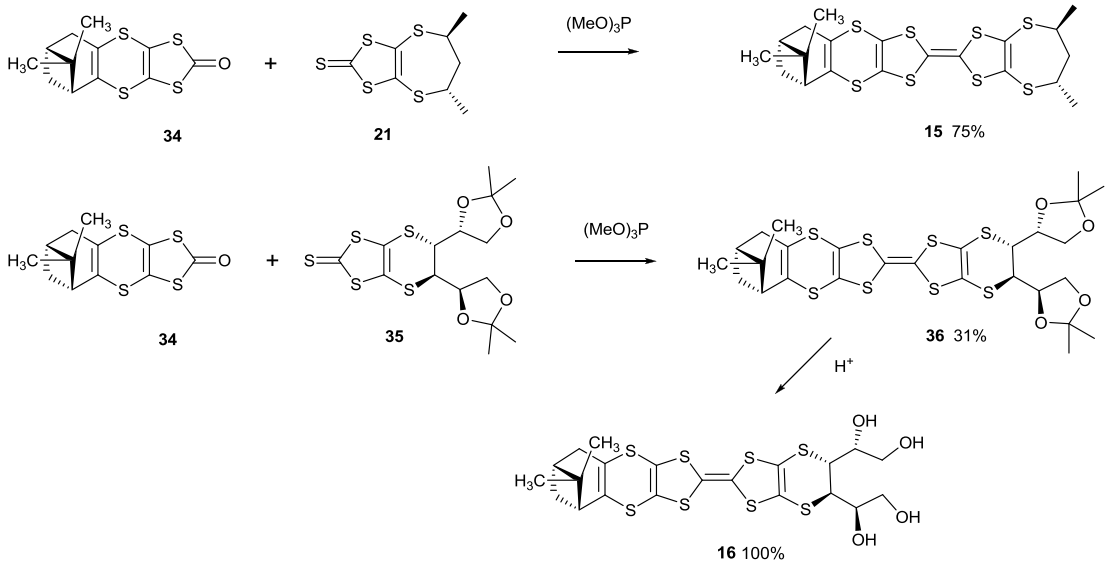
purification. The thione **33** was converted in the usual manner to the oxo compound **34** in quantitative yield, which was cross-coupled with the unsubstituted thione **23** by reaction in trimethyl phosphite at 70 °C for 20 hours to give the chiral donor **14** in 63% yield.



Scheme 4

The molecular structure of donor **14** has been determined by X-ray crystallography, and one of the two crystallographically unique molecules is disordered between two orientations.[19] The similar shapes of the two orientations of such a donor could be avoided if chirality were introduced at the other end of the donor. The most convenient way is to include two substituents related by a C_2 axis, which means there is only one stereoisomer for the cross-coupled material. We thus decided to make two further donors, **15** and **16**, by cross-coupling of oxo compound **34** with (a) thione **21** to give the cross-coupled donor **15** in 64% yield, and (b) the

chiral thione derived from D-mannitol **35**[10] to give the cross-coupled donor **36** in 31% yield, which was deprotected with aqueous HCl in THF to give the tetrol **16** (Scheme 5).



Scheme 5

Charge transfer salts and complexes

The c.v. data for donors **11**–**16** are given in Table 1. All donors show the usual two oxidation processes expected of BEDT-TTF-like molecules. The inclusion of seven- rather than six-membered rings in the donor made almost no difference to the oxidation potentials of **11** and **12**. Donor **13** showed slightly lower oxidation potentials but in **14** the change in the fusion between the apopinene unit and the dithiin from a single bond to a double bond led to an increase in the first two oxidation potentials by *ca* 0.08 V. This feature is retained in the related cross-coupled donors **15** and **16** whose oxidation potentials are slightly higher than for **14**. We have carried out some initial electrocrystallisation experiments with donors **11**–**15** as well as the diffusion of iodine vapour into solutions of donors. From these we have been able to structurally characterise two triiodides salts: a 1:1 salt with donor **12** (Figure 4–6) and a 3:3 + chlorobenzene salt with donor **13** (Figure 7–10).

Table 1. Half wave potentials for donors from cyclic voltammetry measurements.[a]

Donor	$E_1^{1/2}$(V)	$E_2^{1/2}$ (V)
2	0.51	0.94
11	0.50	0.96
12	0.51	0.93
13	0.48	0.89
14	0.56	0.97
15	0.59	0.99
16	0.59	0.98

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

The structure of salt **12**·I_3 , prepared from the donor and iodine, contains two crystallographically unique donor monocations and two triiodide anions (Figs. 4–6). The two donor cations are packed together, face to face, with a dithiepine and a dithiin ring opposite one other. The TTF units lie almost directly opposite each other, and there are four S---S contacts between these two groups in the range 3.288–3.331 Å. This pair is surrounded by four triodides, two lying close to and parallel with a pair of donor edges containing sulfur atoms (twenty I---S contacts in the range 3.678–4.307 Å) and two further triiodides lying above and below the faces of the donor cation pair, but in each case nearer to one edge of sulfur atoms (ten I---S contacts in the range 3.661–4.464 Å). The organosulfur region of cation **12** is much closer to planar than in the neutral donor. The organosulfur cores are just slightly bowed, one more so than the other, such that the angles between the plane containing the four sulfur atoms of the TTF group and the planes defined by the two sets of four sulfur atoms at either side of the molecule are 2.0° and 2.5° for one donor cation and 6.2 and 11.4° for the other cation, compared to 19.2–19.7° for the neutral donor. There are notable differences in the (averaged) bond lengths of the central TTF unit of the cations of **12** compared to the neutral donor: the central C=C bond is longer at 1.38 Å (cf 1.349 Å), but the two C–S bonds are shorter (1.724 Å cf 1.759Å and 1.733 Å cf 1.763 Å). Furthermore, these bond lengths are similar to those observed in the BEDT-TTF monocation in the (BEDT-TTF)HCl_2 salt.[20] Use of the established empirical correlation between bond lengths and charge for BEDT-TTF and its salts[21] gives values for the charge on each cation of **12** as +1.16(10) and +1.18(10). The Raman spectrum on this salt shows signals at 1462 and 1408 cm^{-1} (compared to 1555,

1507, 1491, 1478 cm^{-1} in the pure donor), which support the donor's +1 oxidation state by comparison with the correlation between Raman C=C signals and oxidation state for BEDT-TTF.[22] Measurement of resitivity showed the material to be an insulator.[23]

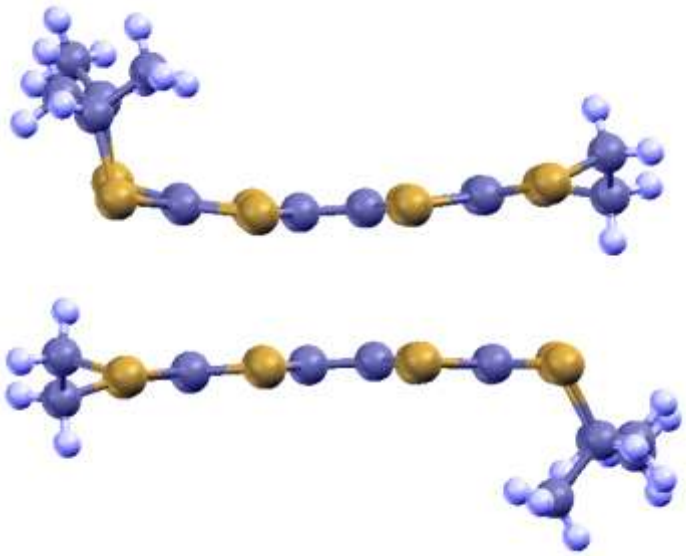


Figure 4. Packing of a pair of cations of **12** in crystal structure of **12**·I_3.

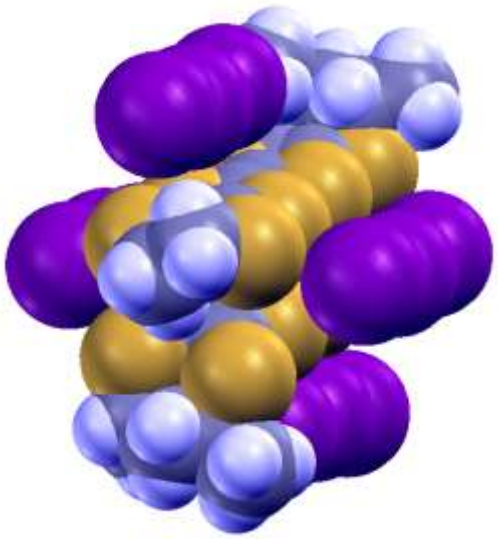


Figure 5. Local packing arrangement of cations of $\mathbf{12}^{\cdot+}$ surrounded by four triiodide ions.

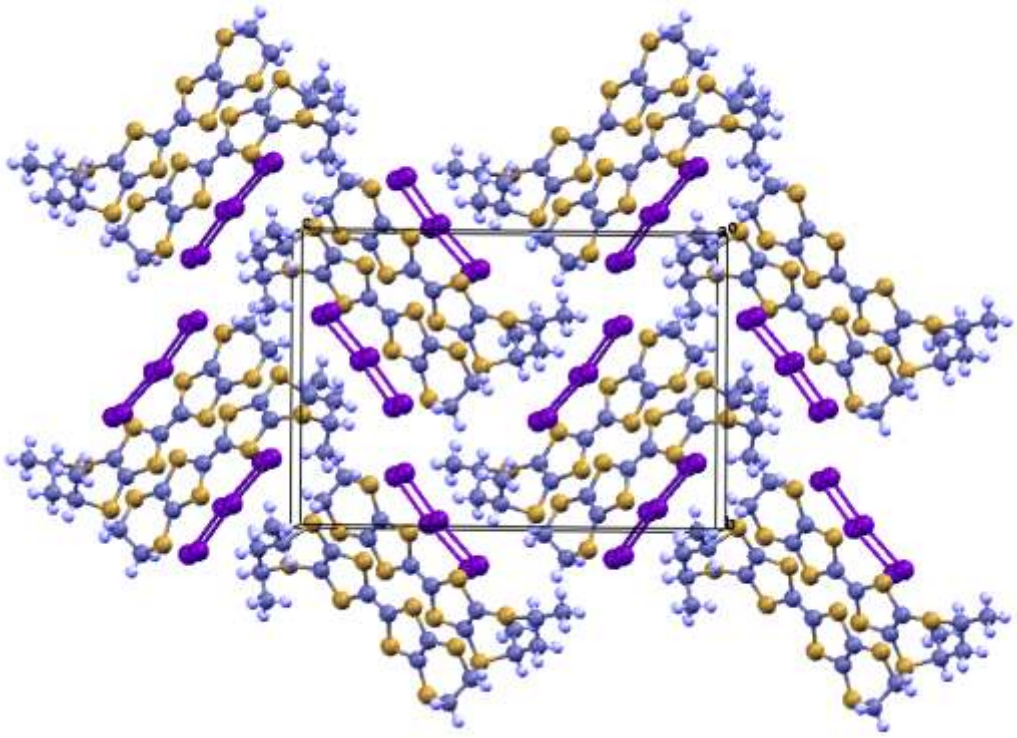


Figure 6. Crystal packing arrangement in **12**·I_3 viewed down the *a* axis, with the *c* axis horizontal.

Electrocrystallisation of donor **13** in chlorobenzene yielded a 3:3 salt with triodide which included one molecule of chlorobenzene whose structure was measured by single crystal X-ray diffraction at the Daresbury Laboratory Synchrotron Radiation Source. The crystal packing arrangement is presented in Figs. 7–10. Within the monoclinic unit cell (space group $P2_1$) there are two pairs of donor cations and two isolated donor cations, all of which have their main axes oriented roughly parallel to the *c* axis. Four triiodides lie between the donor cations and parallel to their axes. This block extends in the *a* and *b* axis directions to form a layer, and layers are separated by another narrower layer composed of further triodides and also chlorobenzene molecules, in which the triiodides lie roughly perpendicular to the other triiodides in the structure. The organosulfur cores of each donor are close to planar, with rms deviations for the three independent molecules in the range 0.07–0.11 Å, consistent with a cation structure. The C–S bond lengths are rather imprecise in the presence of triiodides but, using bond lengths of the TTF grouping averaged over all three donor cations, an average charge of +1.18 was estimated using the

empirical correlation approach. Within a pair the two donor cations are oriented *trans* with their sulfur atoms opposite each other, and four S---S separations between their TTF units of 3.365(8)–3.453(8) Å (Fig. 10). The Raman spectrum is also supportive of the monocation donor structure. Donor **13** also gave some solid black materials on electrocrystallisation from 1,1,1-trichloroethane and from THF. Both showed Raman shifts typical of a donor monocation (1454 and 1402, 1453 and 1406 cm^{-1}). Resistivity measurements on the former[24] showed the material to be an insulator. There was insufficient materials for such a measurement on $(\mathbf{13})_3(I_3)_3.C_6H_5Cl$.

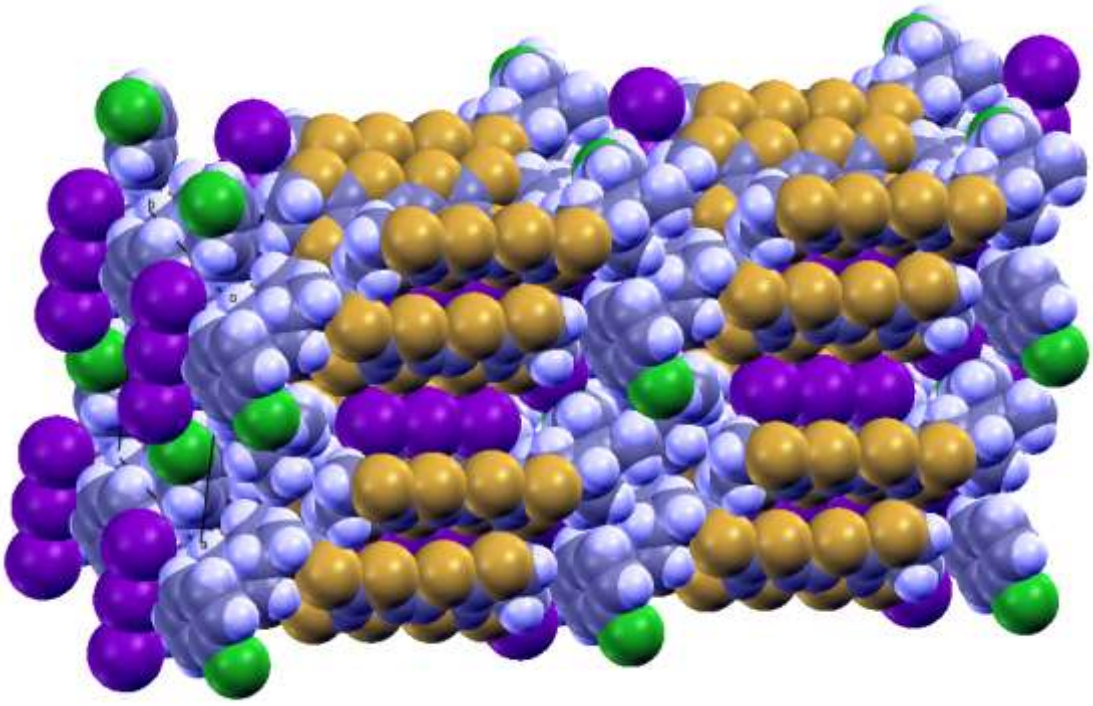


Figure 7. Space-filling packing diagram of $\mathbf{13}_3(I_3)_3{\cdot}C_6H_5Cl$ with the *c* axis horizontal and *a* axis vertical.

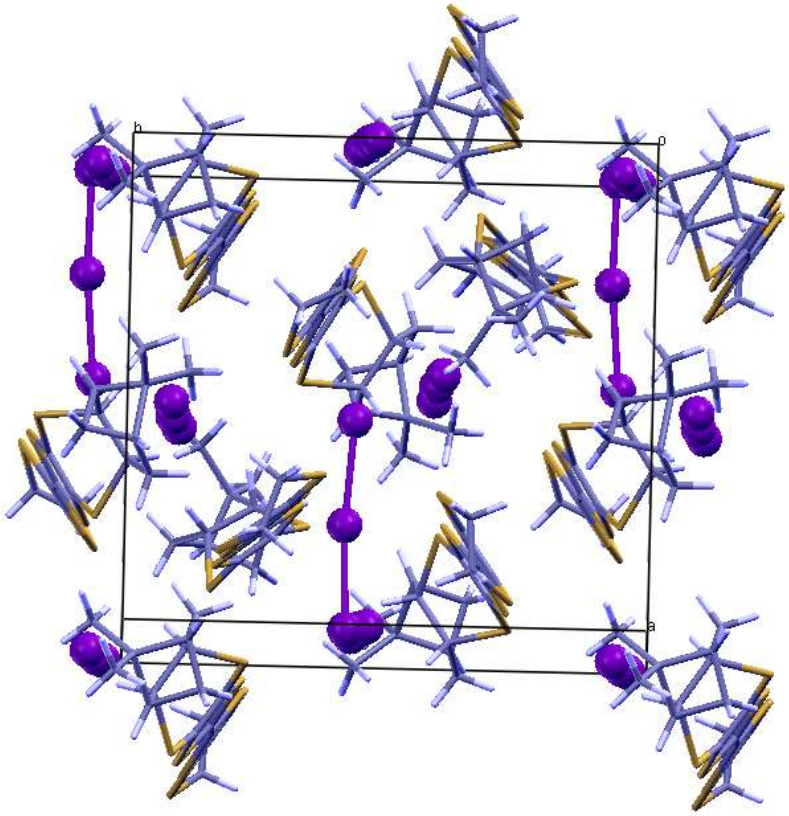


Figure 8. View of the mutual arrangements of the donor cations and triiodide anions in $\mathbf{13}_3(I_3)_3{\cdot}C_6H_5Cl$, viewed down the *c* axis, with chlorobenzene molecules omitted. Two donor cation pairs and two isolated donors complete the unit cell.

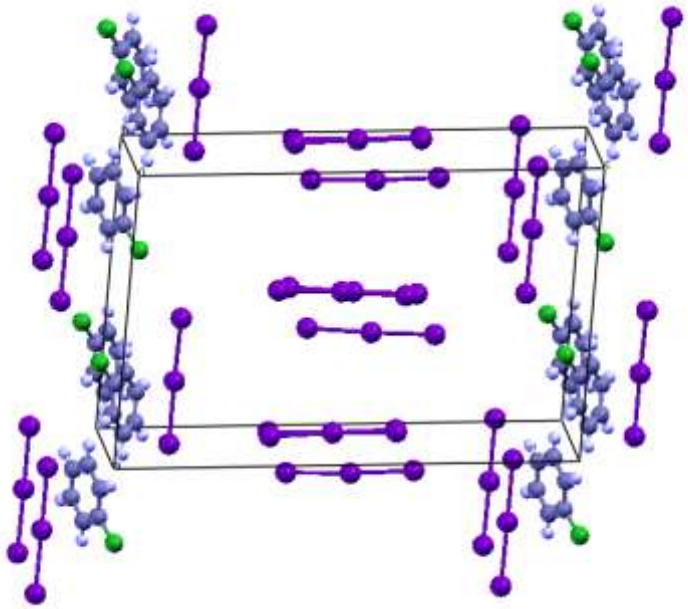


Figure 9. View of the crystal packing of $\mathbf{13}_3(I_3)_3{\cdot}C_6H_5Cl$ with donor cations omitted, showing the formation of layers by chlorobenzene molecules and triiodides.

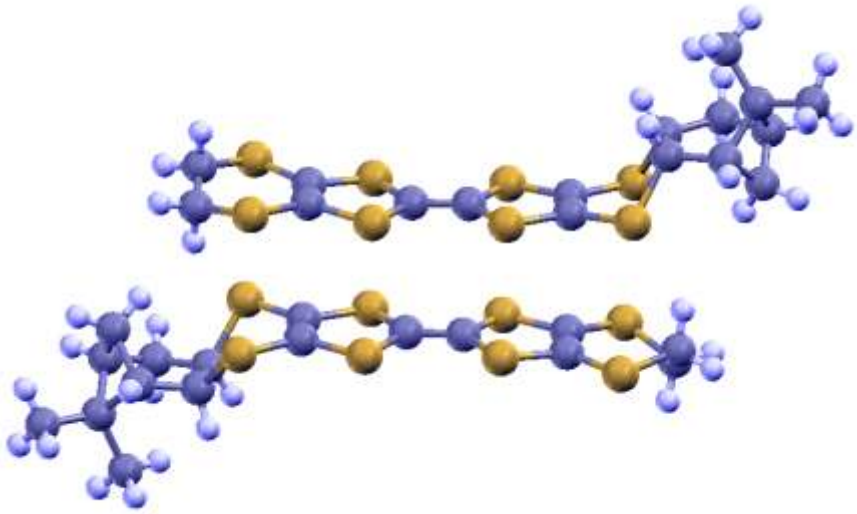


Figure 10. Donor cation pair from the crystal structure of $\mathbf{13}_3(I_3)_3 \cdot C_6H_5Cl$.

TCNQ complexes

Three 1:1 molecular complexes between BEDT-TTF and TCNQ have been reported, and crystallographic studies have shown them to have very distinctive packing arrangements.[25] Thus, we have attempted to prepare TCNQ complexes from some of the new donors reported here, and obtained 1:1 TCNQ complexes from donors **13**, **14** and **15**. The solid-state uv/visible spectra for these compounds all showed a charge transfer band centred in the range 689–701 nm. The X-ray diffraction data were measured and the structures solved for all three complexes and showed that they have formed mixed stacks containing alternate donor and acceptor molecules. The stacks are aligned side by side so that there are lines of donors or acceptors running perpendicular to the stacking direction. The measurement of structure of **15**.TCNQ was the most accurate, and is shown in Fig 11. X-ray diffraction data for **14**.TCNQ, from a very small crystal, was collected at the new Diamond Light Source single-crystal diffraction beamline I19 as part of the commissioning phase in collaboration with the National Crystallography Service, using procedures that are still under development. Further details of each structure are provided in the Supplementary Information.

The bond lengths of the TTF portion of the donor in **15**.TCNQ are typical of an unoxidised donor,[26] and this is supported by an empirical calculation of the charge based on the bond lengths,[21] suggesting very little charge transfer from donor to acceptor. Thus, the donor is not flattened as observed in the structure of the cation **12**$^{+}$. The charge on the TCNQ molecule can also be estimated from its molecular geometry,[27] and analysis of the average geometry of the two TCNQ acceptors indicate that the charge is close to zero. Resistivity measurements on all three TCNQ complexes showed these materials to be insulators.[23]

Measurements of the Raman and infra-red spectra also provide methods for assessing the degree of charge transfer in donors and acceptors.[22,28] The Raman spectra for these complexes each show a prominent signal at *ca* 1600 cm^{-1} and another one in the range 1434–1450 cm^{-1} which would be consistent with neutral TCNQ.[29,30] In contrast, the infra-red spectra of the TCNQ complexes of **13**–**15** show cyanide stretches in the range 2217–2213 cm^{-1}, which from the correlation of anionic charge with stretching frequency corresponds to a net negative charge of *ca* 0.35e.[28] However, the range in stretching frequencies between neutral and monoanionic TCNQ is just 44 cm^{-1}, so other effects from the crystal environment on the CN stretching frequency may easily upset the correlation between charge and stretching frequency. Bernstein has commented on a comparison of the crystallographic and spectroscopic data for TCNQ complexes in his recent comprehensive review[30] and elsewhere.[27] In summary, the data from the X-ray and Raman studies support the donor and acceptor being in their uncharged state in the TCNQ complex.

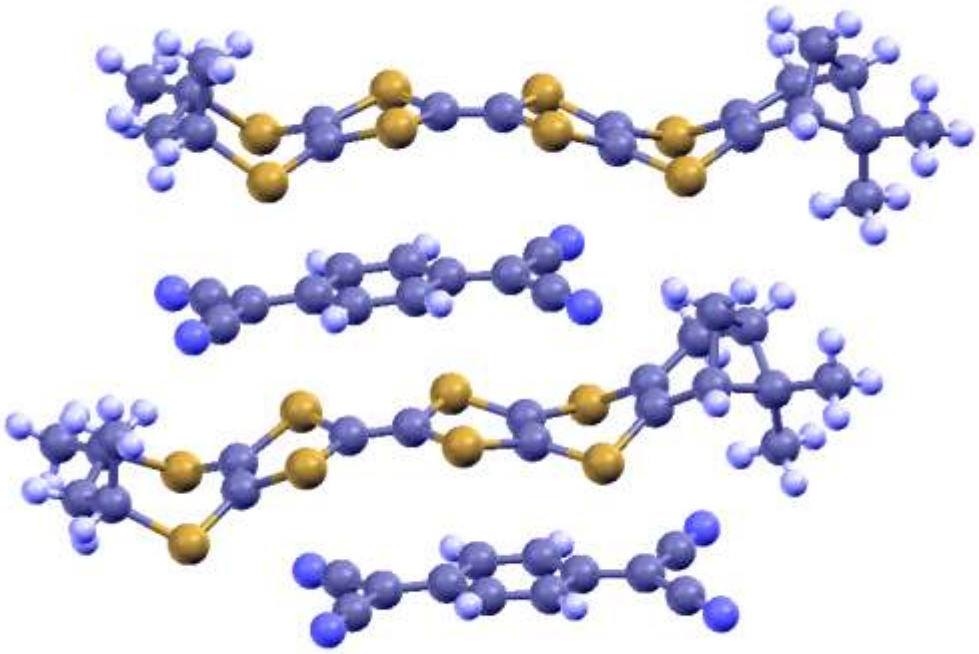


*Figure 11***.** The four crystallographically unique molecules in a stack of **15**·TCNQ**.**

Conclusions

Six new chiral donors have been prepared, and studies to prepare conducting materials initiated, though to date only 1:1 radical cation salts have been prepared. It is notable how the flexed organosulfur ring system of the donor **12** flattens out when it is oxidised to its +1 oxidation state. To form 2:1 salts, which are more likely to be conducting, there are two approaches. One is to use ET-derived donors which are only substituted at one end, so that they can stack head to tail, and such structures have been observed in achiral cases.[31] An alternative approach is to use mixtures of the chiral donors with an unsubstituted donor which can more readily adopt a planar structure even in their unoxidised state. Despite the reported electronic properties of BEDT-TTF·TCNQ complexes, it appears that more oxidising acceptors are needed for reaction with donors **13**–**15** to obtain electroactive materials. Further studies on the conversion of these chiral donors into conducting systems are currently underway. From the synthetic chemistry point of view, with chiral thiones and oxo compounds **21**–**22** and **33**–**34** in hand, many further donors can be prepared by cross-coupling reactions.

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. IR spectra were recorded on Perkin Elmer Spectrum 100 FT-IR Spectrometer, and are reported in cm^{-1}. Raman measurements were made on a Foster and Freeman Raman spectrometer, Foram 685-2, with excitation at 685 nm and are reported in cm^{-1}. Solid-state uv/visible spectra were measured using a JASCO V-670. Optical rotation data were measured on a Perkin Elmer 241 polarimeter. 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 (NCS) at Southampton University, except for (**13**)$_3$(I_3)$_3$·C_6H_5Cl which was investigated at Daresbury Laboratory Synchrotron Radiation Source and **14**·TCNQ which was investigated at Diamond Light Source, both of these through the synchrotron component of the NCS run from Newcastle University. Flash chromatography was performed on 40–63 silica gel (Merck).

(2*R*,4*R*)-Pentanediyl-bis(methanesulfonate)[32]

Triethylamine (7.50 mL, 53.8 mmol) was added to a solution of (2*R*,4*R*)-(−)-pentanediol (2.00 g, 19.2 mmol) in dichloromethane (70 mL). The resulting mixture was cooled to 0 °C, and methanesulfonyl chloride (4.00 mL, 51.7 mmol) was added dropwise over 10 min. The mixture was stirred at 0 °C for 2 h and then poured into 40 mL of cold 1 *N* HCl. The aqueous layer was extracted with dichloromethane (2 × 40 mL) and the combined organic phases were washed with saturated $NaHCO_3$ solution, dried with $MgSO_4$, filtered, and concentrated. The bis(methanesulfonate) was obtained in quantitative yield (5.00 g, 100%) as a colourless oil and used without further purification. δ_H (400 MHz, $CDCl_3$) 4.93 (2H, m, 2-,4-*H*), 3.06 (6H, s, 2 × C*H*$_3$SO$_2$), 1.89 (2H, dd, *J* 5.5, 7.4 Hz, 3-*H*$_2$), 1.47 (6H, d, *J* 6.0 Hz, 1,5-*H*$_3$); δ_C (100.6 MHz, $CDCl_3$) 75.5 (2-,4-*C*), 43.4 (3-*C*), 38.7 (2 × *C*H$_3$SO$_2$), 21.7 (2 × *C*H$_3$).

(*5S,7S*)-5,7-Dimethyl-6,7-dihydro-5*H*-1,3-dithiolo[4,5-b]-1,3-dithiepine-2-thione 21

A solution of dithiolate **20** was generated by reaction of 4,5-bis(benzoylthio)-1,3-dithiole-2-thione (7.80 g, 19.2 mmol) with two equivalents of sodium methoxide in dry methanol (300 mL) under a nitrogen atmosphere and then treated with (2*R*,4*R*)-pentanediyl-bis(methanesulfonate) (5.00 g, 19.2 mmol) at room temperature. The deep purple solution turned orange–red over several minutes, and the mixture was stirred at room temperature overnight. The solvent was removed *in vacuo* at room temperature, and replaced with dry THF (300 mL), and the resulting solution heated to reflux for 24 h. The mixture was filtered and the solids washed with further THF, and the combined filtrates evaporated. The residue was partitioned between dichloromethane and water, the organic layer separated, and washed again with water, and dried with magnesium sulfate. Flash chromatography (cyclohexane:DCM 4:1) gave the product **21** (2.48 g, 44.9%) as a yellow solid; m.p. 65–67 °C; R_f (cyclohexane:DCM 4:1) 0.36; δ_H (400 MHz, $CDCl_3$) 3.35 (2H, m, 5-,7-*H*), 2.32 (2H, t, *J* 5.5 Hz, 6-H_2), 1.35 (6H, d, *J* 7.1 Hz, 2×CH_3); δ_C (100.6 MHz, $CDCl_3$) 211.6 (*C*=S), 136.9 (3a-,8a-*C*), 48.4 (6-*C*), 38.2 (5-,7-*C*), 20.5 (2×*C*H_3); ν_{max} (ATR): 2957, 2918, 1443, 1412, 1380, 1239, 1050, 1023, 994, 881, 852, 779, 654, 593, 511, 473, 456, 390; *m/z*: (ES) 266 $[M]^+$; found C, 36.14; H, 3.70%, $C_8H_{10}S_5$ requires C, 36.06; H, 3.78%; $^{20}[\alpha]_D$ = +10.0 (c = 0.8, $CHCl_3$).

(*5S,7S*)-5,7-Dimethyl-6,7-dihydro-5*H*-1,3-dithiolo[4,5-b]-1,3-dithiepine-2-one 22

Mercuric acetate (4.40 g, 13.8 mmol) was added to a solution of the thione **21** (2.42 g, 9.08 mmol) in chloroform (100 mL). After stirring for 2 h, the reaction mixture was filtered and the solid residue washed with chloroform. The combined filtrates were concentrated *in vacuo* and the residue purified by flash chromatography (cyclohexane:DCM 4:1) to yield the oxo compound **22** as a reddish oil (2.25 g, 99.0%); R_f (cyclohexane:DCM 4:1) 0.33; δ_H (400 MHz, $CDCl_3$) 3.28 (2H, m, 5-,7-*H*), 2.26 (2H, t, *J* 5.5 Hz, 6-H_2), 1.32 (6H, d, *J* 7.1 Hz, 2×CH_3); δ_C (100.6 MHz, $CDCl_3$) 189.9 (*C*=O), 127.4 (3a-,8a-*C*), 47.8 (6-*C*), 37.9 (5-,7-*C*), 20.3 (2×*C*H_3); ν_{max} (ATR): 2961, 2922, 2868, 1667, 1615, 1487, 1446, 1418, 1380, 1243, 1192, 1106, 1076, 1034, 998, 883, 751, 551, 470; *m/z*: (EI) 250 $[M]^+$; found C, 38.30; H, 3.93%, $C_8H_{10}OS_4$ requires C, 38.37; H, 4.02%; $^{20}[\alpha]_D$ = –50.7 (*c* = 1.70, $CHCl_3$).

Bis((*2S*,*4S*)-pentane-2,4-dithio)tetrathiafulvalene 11

A mixture of oxo compound **22** (451 mg, 1.80 mmol) and freshly distilled trimethyl phosphite (20 mL) was heated to reflux for 24 h. The reaction mixture was cooled to room temperature, and the yellow solid collected by filtration, washed with ethyl acetate and dried in *vacuo* to give donor **11** (318 mg, 75.3%); m.p. 195–197 °C; R_f (cyclohexane:DCM 4:1) 0.22; δ_H (400 MHz, $CDCl_3$) 3.16 (4H, m, 2-,2′-,4-,4′-*H*), 2.24 (4H, t, *J* 5.4 Hz, 3-,3′-H_2), 1.30 (12H, d, *J* 7.1 Hz, 4×CH_3); δ_C (100.6 MHz, $CDCl_3$) 127.4 (4 × sp^2-*C*(dithiepine)), 112.8 (2 × sp^2-*C*(central)), 48.7 (3-,3′-*C*), 37.9 (2-,2′-,4-,4′-*C*), 20.5 (4×CH_3); ν_{max} (ATR): 2958, 1441, 1375, 1241, 1189, 1104, 1076, 1034, 993, 881, 768, 653, 590, 530, 488, 455, 388; *m/z*: (EI) 468 $[M]^+$; *HRMS* (EI) found: 467.9320, $C_{16}H_{20}S_8$ requires: 467.9325; found C, 41.03; H, 4.24%, $C_{16}H_{20}S_8$ requires C, 40.99; H, 4.30%; $^{20}[\alpha]_D = -153.0$ (*c* = 0.2, $CHCl_3$).

(Ethylenedithio)((*2S*,*4S*)-pentane-2,4-dithio)tetrathiafulvalene 12

A mixture of oxo compound **22** (0.69 g, 2.76 mmol), unsubstituted thione **23** (2.00 g, 8.90 mmol) and freshly distilled trimethyl phosphite (50 mL) was heated to 70°C for 30 h. The reaction mixture was cooled to room temperature then filtered and washed with chloroform. The solvent was evaporated to dryness and the residue purified by chromatography (cyclohexane:ethyl acetate 4:1) to give donor **12** (265 mg, 22.5%); m.p. 131–133 °C; R_f (cyclohexane:ethyl acetate 8:1) 0.29; δ_H (400 MHz, $CDCl_3$) 3.22 (4H, s, CH_2CH_2), 3.12 (2H, m, 2-,4-*H*), 2.22 (2H, t, *J* 5.4 Hz, 3-H_2), 1.26 (6H, d, *J* 7.0 Hz, 2 × CH_3); δ_C (100.6 MHz, $CDCl_3$) 127.9 (2 × sp^2-*C*(dithiepine), 115.4 (2 × sp^2-*C*(dithiin)), 113.8 and 109.1 (2 × sp^2*C*(central)), 48.7 (3-*C*), 37.5 (2-,4-*C*), 30.2 (CH_2CH_2), 20.5 (2 × CH_3); ν_{max} (ATR): 2954, 2915, 2866, 1442, 1373, 1288, 1241, 1192, 1125, 1073, 1031, 996, 902, 890, 849, 770, 514, 490, 442, 406, 389; *m/z*: (EI) 426 $[M]^+$; found C, 36.68; H, 3.23%, $C_{13}H_{14}S_8$ requires C, 36.59; H, 3.31%; $^{20}[\alpha]_D$ = –80.5 (*c* = 0.2, $CHCl_3$).

(1*S*, 5*R*)-6,6-Dimethylbicyclo[3.1.1]hept-2-ene 27[33a]

A slurry of (–)-myrtenal (8.00 g, 53.0 mmol) and freshly made palladium hydroxide on barium sulfate (1.00 g) was heated slightly above 140 °C with magnetic stirring for 1.5 h. A Dean-Stark trap collected 6 mL (83%) of the desired apopinene. δ_H (400

MHz, $CDCl_3$) 6.08 (1H, m, 2-*H*), 5.48 (1H, m, 3-*H*), 2.30 (1H, m, 7-H_α), 2.20 (2H, m, 4-H_2), 2.04 (2H, m, 1-,5-*H*), 1.20 (3H, s, CH_3), 1.13 (1H, d, *J* 8.2 Hz, 7-H_β), 0.82 (3H, s, CH_3); δ_C (100.6 MHz, $CDCl_3$) 136.5 and 124.1 (2-,3-*C*), 41.9 and 41.2 (1-,5-*C*), 38.0 (6-*C*), 32.5 and 32.0 (4-,7-*C*), 26.4 and 21.3 (2 × CH_3); $^{20}[\alpha]_D$ = –19.4 (neat). Estimated e.e. 42%, from value of $[\alpha]_D$ = –45.1 for material with e.e. of 98%.[33b]

***(4aR,5R,7R,8aS)*-6,6-Dimethyl-4a,5,6,7,8,8a-hexahydro-5,7-methano-benzo[b]1,3-dithiolo[4,5-e]1,4-dithiin-2-thione 28**

A suspension of trithione **24** (4.00 g, 20.0 mmol) in a mixture of apopinene **27** (1.48 g, 12.0 mmol) and toluene (120 mL) was refluxed for 24 h. The reaction mixture was filtered hot and the solid residue was washed with chloroform. The combined filtrates were evaporated and the residue purified by column chromatography (cyclohexane:chloroform 4:1) to yield the thione **28** (2.58 g, 66.8%) as a yellow solid; m.p. 60–62 °C; R_f (cyclohexane:chloroform 4:1) 0.30; δ_H (400 MHz, $CDCl_3$) 4.05 (1H, d, *J* 8.2 Hz, 4a-*H*), 3.64 (1H, m, 8a-*H*), 2.64 (1H, m, 8-H_α), 2.44 (1H, m, 10-H_α), 2.15 (1H, s, 7-*H*), 2.14 (1H, s, 5-*H*), 1.93 (2H, d*, *J* 12.6 Hz, 8-H_β, 10-H_β), 1.36 (3H, s, α-CH_3), 0.98 (3H, s, β-CH_3); δ_C (100.6 MHz, $CDCl_3$) 210.6 (*C*=S), 138.4 and 138.1 (3a-,9a-*C*), 56.8 (4a-*C*), 46.3 (5-*C*), 45.3 (8a-*C*), 41.3 (6-*C*), 39.1 (7-*C*), 33.4 (10-*C*), 26.2 (8-*C*), 26.0 (α-*C*H_3), 20.7 (β-*C*H_3); ν_{max} (KBr): 1466, 1447, 1384, 1369, 1314, 1275, 1244, 1201, 1059, 1032, 1025, 926, 912, 888, 782, 511; *m/z*: (EI) 319 $[M]^+$; *HRMS* (EI) found: 317.9693, $C_{12}H_{14}S_5$ requires: 317.9694; found C, 45.33; H, 4.59%, $C_{12}H_{14}S_5$ requires C, 45.24; H, 4.43%; $^{20}[\alpha]_D$ = +8.3 (*c* = 0.2, $CHCl_3$). N.B.: this is a scalemic mixture. * denotes further small splittings.

***(4aR,5R,7R,8aS)*-6,6-Dimethyl-4a,5,6,7,8,8a-hexahydro-5,7-methano-benzo[b]1,3-dithiolo[4,5-e]1,4-dithiin-2-one 29**

Mercuric acetate (4.30 g, 13.5 mmol) was added to a solution of the thione **28** (2.86 g, 8.97 mmol) in chloroform (85 mL). After stirring for 2 h, the reaction mixture was filtered and the solid residue washed with chloroform. The combined filtrates were concentrated *in vacuo* and the residue was purified by flash chromatography (cyclohexane:chloroform 4:1) to yield the oxo compound **29** as a yellow solid (2.48 g, 91.4%); m.p. 100–102 °C; R_f (cyclohexane:chloroform 4:1) 0.26; δ_H (400 MHz,

$CDCl_3$) 4.03 (1H, d, *J* 8.0 Hz, 4a-*H*), 3.61 (1H, m, 8a-*H*), 2.54 (1H, m, 8-H_α), 2.37 (1H, m, 10-H_α), 2.07 (2H, m, 5-,7-*H*), 1.84 (2H, m, 8-H_β, 10-H_β), 1.30 (3H, s, α-CH_3), 0.92 (3H, s, β-CH_3); δ_C (100.6 MHz, $CDCl_3$) 190.3 (*C*=O), 129.0 and 128.9 (3a-,9a-*C*), 57.4 (4a-*C*), 46.3 (5-*C*), 45.7 (8a-*C*), 41.3 (6-*C*), 39.1 (7-*C*), 33.5 (10-*C*), 26.1 (8-*C*), 26.0 (α-*C*H_3), 20.6 (β-*C*H_3); ν_{max} (KBr): 2900, 1710, 1464, 1370, 1246, 1164, 1064, 1021, 926, 888, 782; *m/z*: (EI) 302 $[M]^+$; *HRMS* (EI) found: 301.9924, $C_{12}H_{14}OS_4$ requires: 301.9922; found C, 47.77; H, 4.57%, $C_{12}H_{14}OS_4$ requires C, 47.65; H, 4.66%; $^{20}[\alpha]_D$ = +7.2 (*c* = 1.00, $CHCl_3$). N.B.: this is a scalemic mixture. * denotes further small splittings.

(Ethylenedithio)((*1R,2R,3S,5R*)-6,6-dimethyl-bicyclo[3.1.1]heptane-2,3-dithio)tetrathiafulvalene 13

A mixture of oxo compound **29** (163 mg, 0.450 mmol), unsubstituted thione **23** (330 mg, 1.47 mmol) and freshly distilled trimethyl phosphite (10 mL) was heated to 70 °C for 22 h. The reaction mixture was cooled to room temperature, then filtered and washed with chloroform. The solvent was evaporated to dryness, and the residue purified by flash chromatography (cyclohexane:chloroform 4:1) to give donor **13** (170 mg, 66.0%); m.p. 156–158 °C (dec.); R_f (cyclohexane:chloroform 4:1) 0.30; δ_H (400 MHz, $CDCl_3$) 3.94 (1H, d, *J* 8.4 Hz, 2-*H*), 3.45 (1H, m, 3-*H*), 3.30 (4H, m, CH_2CH_2), 2.54 (1H, m, 4-H_α), 2.33 (1H, m, 7-H_α), 1.98 (1H, s, 5-*H*), 1.97 (1H, s, 1-*H*), 1.79 (2H, m, 4-H_β, 7-H_β), 1.30 (3H, s, α-CH_3), 0.93 (3H, s, β-CH_3); δ_C (100.6 MHz, $CDCl_3$) 129.0, 128.9, 128.8, 113.7, 113.5 (6 × sp^2-*C*), 55.9 (2-*C*), 46.3 (1-*C*), 44.8 (3-*C*), 41.0 (6-*C*), 39.3 (5-*C*), 33.5 (7-*C*), 26.1 (4-*C*), 26.0 and 20.6 (2 × -*C*H_3); ν_{max} (KBr): 2916, 1636, 1470, 1450, 1410, 1385, 1368, 1319, 1283, 1192, 1136, 1048, 995, 924, 910, 882, 770; *m/z*: (EI) 478 $[M]^+$; *HRMS* (EI) found: 477.9165, $C_{17}H_{18}S_8$ requires: 477.9169; found C, 42.48; H, 3.70%, $C_{17}H_{18}S_8$ requires C, 42.64; H, 3.79%; $^{20}[\alpha]_D$ = +17.6 (c = 0.44, $CHCl_3$). N.B.: this is a scalemic mixture. * denotes further small splittings.

Enol acetate of *1R*-(+)-nopinone 30[34]

(+)-(*1R*)-Nopinone (2.50 g, 18.1 mmol) and *p*-toluenesulfonic acid (0.50 g, 2.60 mmol) in isopropenyl acetate (50.0 mL, 454 mmol) were heated to reflux and the

acetone formed in the reaction fractionally distilled from the system through a 12-in. column packed with glass helices. After 5 h, the remaining isopropenyl acetate was removed under reduced pressure. The residue was diluted with diethyl ether (100 mL) and washed with water. After drying over magnesium sulfate, ether was removed to yield the nopinone enol acetate as a colourless oil (3.18 g, 97.5%). δ_H (400 MHz, $CDCl_3$) 5.15 (1H, m, 3-*H*), 2.46 (1H, m, 7-H_α), 2.28 (1H, d, *J* 16.0 Hz, 4-H_α), 2.20 (1H, dt, *J* 16.0 Hz, 2.5Hz, 4-H_β), 2.09 (2H, m, 1-,5-H_2), 2.08 (3H, s, COCH_3), 1.42 (1H, d, *J* 8.7 Hz, 7-H_β), 1.28 (3H, s, 6-CH_3), 0.93 (3H, s, 6-CH_3); δ_C (100.6 MHz, $CDCl_3$) 169.1 (*C*=O), 156.1 (2-*C*), 106.3 (3-*C*), 46.0 (1-*C*), 40.4 (5-*C*), 38.9 (6-*C*), 31.5 (7-*C*), 28.0 (4-*C*), 25.8 (6-*C*H_3), 21.0 (6-*C*H_3), 20.9 (*C*H_3CO).

***(5R,7R)*-6,6-Dimethyl-5,6,7,8-tetrahydro-5,7-methano-benzo[b]1,3-dithiolo[4,5-e]1,4-dithiin-2-thione 33**

Enol acetate **30** (3.18 g, 17.6 mmol) and trithione **24** (4.50 g, 22.9 mmol) were refluxed together in toluene (120 mL) for 44 h. The reaction mixture was filtered and the solid residue washed with chloroform. The combined filtrates were concentrated in *vacuo* and the residue was purified by flash chromatography (cyclohexane) to yield thione **33** as an orange oil (1.75 g, 31.3%); R_f (cyclohexane) 0.14; δ_H (400 MHz, $CDCl_3$) 2.60 (1H, dd, *J* 17.6, 2.8 Hz, 8-H_α), 2.51 (1H, m, 10-H_α), 2.45 (1H, dd, *J* 17.6, 2.8 Hz, 8-H_β), 2.38 (1H, t, *J* 5.5 Hz, 5-*H*), 2.20 (1H, m, 7-*H*), 1.35 (1H, d, *J* 9.6 Hz, 10-H_β), 1.30 (3H, s, 6-CH_3), 0.77 (3H, s, 6-CH_3); δ_C (100.6 MHz, $CDCl_3$) 214.0 (*C*=S), 138.9 (4a-*C*), 127.9, 127.5 and 124.6 (3a-, 4a-, 8a-*C*), 49.5 (5-*C*), 40.5 (7-*C*), 40.4 (6-*C*), 36.9 (8-*C*), 32.1 (10-*C*), 25.4 (6-*C*H_3), 20.8 (6-*C*H_3); ν_{max} (ATR): 2970, 2931, 2867, 1487, 1465, 1443, 1383, 1366, 1113, 1058, 1012, 899, 755, 617, 506, 476, 451, 386; *m/z*: (EI) 316 $[M]^+$; found C, 45.62; H, 3.70%, $C_{12}H_{12}S_5$ requires C, 45.53; H, 3.82%; $^{20}[\alpha]_D = -61.4$ (*c* = 0.4, $CHCl_3$).

(5*R*,7*R*)-6,6-Dimethyl-5,6,7,8-tetrahydro-5,7-methano-benzo[b]1,3-dithiolo[4,5-e]1,4-dithiin-2-one 34

Mercuric acetate (2.26 g, 7.09 mmol) was added to a solution of the thione **33** (1.50 g, 4.74 mmol) in chloroform (50 mL). The reaction mixture was stirred overnight, filtered and the solid residue washed with chloroform. The combined filtrates were concentrated in *vacuo* and the residue was purified by flash chromatography

(cyclohexane:ethyl acetate 20:1) to yield the oxo compound **34** as a pale yellow solid (1.40 g, 98.5%); m.p. 92–94 °C; R_f (cyclohexane:ethyl acetate 20:1) 0.55; δ_H (400 MHz, $CDCl_3$) 2.62 (1H, dd, *J* 17.2, 2.8 Hz, 8-H_a), 2.52 (1H, m, 10-H_α), 2.46 (1H, dd, *J* 17.2, 2.5 Hz, 8-H_β), 2.40 (1H, t, *J* 5.5 Hz, 5-*H*), 2.21 (1H, m, 7-*H*), 1.38 (1H, d, *J* 9.2 Hz, 10-H_β), 1.31 (3H, s, 6-CH_3), 0.74 (3H, s, 6-CH_3); δ_C (100.6 MHz, $CDCl_3$) 192.5 (*C*=O), 139.1 (4a-*C*), 124.5 (8a-*C*), 118.1 (3a-*C*), 117.5 (9a-*C*), 49.5 (5-*C*), 40.6 (7-*C*), 40.5 (6-*C*), 37.0 (8-*C*), 32.1 (10-*C*), 25.4 (6-*C*H_3), 20.7 (6-*C*H_3); ν_{max} (ATR): 2970, 2927, 2903, 1744, 1674, 1607, 1592, 1421, 1363, 1115, 1094, 1018, 963, 899, 875, 748, 619, 542, 470, 460, 451; *m/z*: (EI) 300 $[M]^+$; found C, 47.96; H, 4.06%, $C_{12}H_{12}OS_4$ requires C, 47.96; H, 4.03%; $^{20}[\alpha]_D = -54.2$ (*c* = 0.8, $CHCl_3$).

(Ethylenedithio)((1*R*,5*R*)-6,6-dimethyl-bicyclo[3.1.1]heptene-2,3-dithio)-tetrathiafulvalene 14

A mixture of oxo compound **34** (1.44 g, 4.79 mmol), unsubstituted thione **23** (2.70 g, 12.0 mmol) and freshly distilled trimethyl phosphite (70 mL) was heated to 70 °C for 20 h. The reaction mixture was cooled to room temperature, then filtered and washed with chloroform. The solvent was evaporated to dryness and the residue purified by flash chromatography (cyclohexane:DCM 4:1) to give donor **14** as a yellow powder (1.46 g, 63.9%); m.p. 205–207 °C (dec.); R_f (cyclohexane:DCM 4:1) 0.34; δ_H (400 MHz, $CDCl_3$) 3.22 (4H, m, CH_2CH_2), 2.48 (1H, dd, *J* 17.2, 2.8 Hz, 4-H_α), 2.43 (1H, m, 7-H_α), 2.35 (1H, dd, *J* 17.2, 2.6 Hz, 4-H_β), 2.26 (1H, t, *J* 5.6 Hz, 1-*H*), 2.12 (1H, m, 5-*H*), 1.30 (1H, d, *J* 9.4 Hz, 17-H_β),1.24 (3H, s, 6-CH_3), 0.74 (3H, s, 6-CH_3); δ_C (100.6 MHz, $CDCl_3$) 139.1 (2-*C*), 124.9 (3-*C*), 119.9, 119.5, 117.3, 113.7, 112.9 (6 × sp^2-*C*), 49.2 (1-C), 40.6 (5-*C*), 40.5 (6-*C*), 36.8 (4-*C*), 32.1 (7-*C*), 30.1 (*C*H_2*C*H_2), 25.5 (6-*C*H_3), 20.8 (6-*C*H_3); ν_{max} (ATR): 2973, 2908, 1601, 1465, 1445, 1423, 1382, 1365, 1263, 1111, 1091, 1014, 909, 896, 766, 617, 508, 445, 397; *m/z*: (EI) 476 $[M]^+$; found C, 42.73; H, 3.33%, $C_{17}H_{16}S_8$ requires C, 42.82; H, 3.38%; $^{20}[\alpha]_D = -53.5$ (*c* = 0.4, $CHCl_3$).

((*2S*,*4S*)-Pentane-2,4-dithio)((1′*R*,5′*R*)-6′,6′-dimethyl-bicyclo[3.1.1]heptene-2′,3′-dithio)tetrathiafulvalene 15

A mixture of oxo compound **34** (0.80 g, 2.66 mmol), thione **21** (1.80 g, 6.75 mmol) and freshly distilled trimethyl phosphite (70 mL) was heated to 70 °C for 26 h. The

reaction mixture was concentrated and the components separated by flash chromatography (cyclohexane:DCM 4:1) to give donor **15** as a yellow powder (1.04 g, 75.3%); m.p. 161–163 °C (dec.); R_f (cyclohexane:DCM 4:1) 0.35; δ_H (400 MHz, $CDCl_3$) 3.17 (2H, m, 2-,4-*H*), 2.52 (1H, dd, *J* 17.2, 2.8 Hz, 4′-H_α), 2.46 (1H, m, 7-H_α), 2.39 (1H, dd, *J* 17.2, 2.6 Hz, 4-H_β), 2.30 (1H, t, *J* 5.6 Hz, 1-*H*), 2.25 (2H, t, *J* 5.4 Hz, 3-H_2), 2.12 (1H, m, 5-*H*), 1.34 (1H, d, *J* 9.5 Hz, 7-H_β), 1.30 (6H, dd, *J* 7.1, 4.8 Hz, 2-,4-CH_3), 1.28 (3H, s, 6′-CH_3), 0.79 (3H, s, 6′-CH_3); δ_C (100.6 MHz, $CDCl_3$) 139.1 (2′-*C*), 127.8, 127.7 (2 × sp^2*C*(dithiepine)), 124.8 (3′-*C*), 119.8, 119.4, 116.7, 114.7 (4 × sp^2-*C*), 49.2 (1′-C), 48.7 (3-*C*), 40.6 (5′-*C*), 40.5 (6′-*C*), 37.7 (br), 37.6 (br, 2-,4-*C*), 36.8 (4′-*C*), 32.1 (7′-*C*), 25.5 (6′-*C*H_3), 20.8 (6′-*C*H_3), 20.6, 20.3 (2-,4-*C*H_3); ν_{max} (ATR): 2970, 2955, 2921, 1601, 1464, 1442, 1428, 1416, 1378, 1364, 1237, 1113, 1074, 1014, 997, 897, 769, 651, 618, 597, 513; *m/z*: (EI) 518 $[M]^+$; found C, 46.30; H, 4.17%, $C_{20}H_{22}S_8$ requires C, 46.29; H, 4.27%; $^{20}[\alpha]_D$ = –94.3 (*c* = 0.3, $CHCl_3$).

***(2R,3R,4R,5R-)*(Bis(*O*,*O*-isopropylidene)-1,2,5,6-tetrahydroxyhexan-3,4-dithio ((1′*R*,5′*R*)-6′,6′-dimethylbicyclo[3.1.1]heptene-2′,3′-dithio)tetrathiafulvalene 37**

A mixture of oxo compound **34** (0.624 g, 2.08 mmol), thione **35** (0.528 g, 1.24 mmol) and freshly distilled trimethyl phosphite (35 mL) was heated to 70°C for 48 h. The reaction mixture was concentrated and the components separated by flash chromatography (cyclohexane:ethyl acetate 20:1) to give donor **36** as an orange powder (0.258 g, 30.6%); m.p. 95–97 °C (dec.); R_f (cyclohexane:ethyl acetate 20:1) 0.21; δ_H (400 MHz, $CDCl_3$) 4.36 (2H, m, 2-,5-*H*), 4.13 (2H, dd, *J* 8.5, 6.3 Hz, 1-,6-H_α), 3.99 (2H, m, 1-,6-H_β), 3.66 (2H, m, 3-,4-*H*), 2.50 (1H, dd, *J* 17.2, 2.9 Hz, 4′-H_a), 2.44 (1H, m, 7′-H_α), 2.36 (1H, dd, *J* 17.2, 2.4 Hz, 4′-H_β), 2.28 (1H, t, *J* 5.5 Hz, 1′-*H*), 2.14 (1H, m, 5′-*H*), 1.39 (6H, s, 2 × *C*H_3), 1.32 (d, partially obscured, 7-H_β), 1.30 (6H, s, 2 × CH_3), 1.26 (3H, s, 6′-CH_3) , 0.76 (3H, s, 6′-CH_3); δ_C (100.6 MHz, $CDCl_3$) 139.1 (2′-*C*), 124.7 (3′-*C*), 119.8, 119.3, 117.8, 111.5, 109.9, 109.3 (6 × sp^2-*C*), 110.2 (2 × –O_2*C*), 76.0, 75.8 (2-,5-*C*), 67.9, 67.8 (1-,6-*C*), 49.1 (1′-C), 44.9, 44.7 (3-,4-*C*), 40.5 (5′-*C*), 40.4 (6′-*C*), 36.7 (4′-*C*), 32.0 (7′-*C*), 27.0 (2 × *C*H_3), 25.4 (6′-*C*H_3), 25.3 (2 × *C*H_3), 20.7 (6′-*C*H_3); ν_{max} (ATR): 2983, 2933, 1453, 1380, 1369, 1244, 1210, 1146, 1061, 1020, 969, 901, 834, 770, 617, 511; *m/z*: (EI) 676 $[M]^+$; found C, 47.84; H, 4.70%, $C_{27}H_{32}O_4S_8$ requires C, 47.90; H, 4.76%; $^{20}[\alpha]_D$ = +4.5 (*c* = 0.2, $CHCl_3$).

((*2R,3R,4R,5R*)-1,2,5,6-Tetrahydroxy-3,4-dithio)((*1′R,5′R*)-6′,6′-dimethyl-bicyclo[3.1.1]heptene-2′,3′-dithio)tetrathiafulvalene 16

Diketal **36** (0.120 g, 0.180 mmol) was stirred with a mixture of aq. HCl (4 *M*, 8 mL) and THF (20 mL) under nitrogen for 12 h. Evaporation and drying *in vacuo* gave the donor **16** (0.105 g, 100%) as a buff powder, m.p. 140–142 °C; δ_H (400 MHz, DMSO-d_6) 5.20 (2×O*H*), 4.66 (2×O*H*), 3.89 (2H, m, 2-,5-H), 3.65 (2H, m, 1-,6-H_α), 3.58 (2H, m, 1-,6-H_β), 3.51 (2H, m, 3-,4-*H*), 2.61 (1H, dd, *J* 17.2, 2.8 Hz, 4′-H_a), 2.51 (1H, m, partially obscured, 7′-H_a), 2.35 (2H, m, 1′-,4′-H_b), 2.16 (1H, m, 5′-*H*), 1.27 (3H, s, 6′-CH_3), 1.24 (1H, d, partially obscured, 7′-H_b), 0.73 (3H, s, 6′-CH_3); δ_C (100.6 MHz, DMSO-d_6) 138.4 (2′-*C*), 124.9 (3′-*C*), 119.6, 119.2, 115.3, 112.5, 110.7, 109.9, (6 × sp^2-*C*), 72.0, 71.6 (2-,5-*C*), 63.2 (1,6-*C*), 48.6 (1′-C), 42.8, 42.6 (3-,4-*C*), 36.3 (4′-*C*), 31.5 (7′-*C*), 25.0 (6′-*C*H_3), 20.5 (6′-*C*H_3), Expected peaks 40.5 (5′-*C*), 40.4 (6′-*C*) are obscured by the peak due to d_6-DMSO; ν_{max} (ATR): 3264, 2983, 2930, 1451, 1425, 1381, 1369, 1212, 1148, 1101, 1063, 1018, 924, 900, 876, 834, 769, 617, 512; *m/z*: (EI) 676 $[M]^+$; found C, 42.35; H, 3.95%, $C_{21}H_{24}O_4S_8$ requires C, 42.25; H, 4.05%; $^{20}[\alpha]_D$ = +81.2 (*c* = 0.24, THF).

Electrocrystallisations

With donor **13**

(a) Electrocrystallisation of donor **13** (10 mg) in a solution of tetrabutylammonium triiodide (57 mg) in chlorobenzene (20 mL) at room temperature, using a constant current of 0.1 μA over 3 weeks, afforded black crystals of (**13**)$_3$(I_3)$_3$·C_6H_5Cl. Raman: 1443, 1426, 1395.

(b) Electrocrystallisation of donor **13** (10 mg) in a solution of tetrabutylammonium triiodide (120 mg) in 1,1,1-trichloroethane (40 mL) at room temperature, using a constant current of 1.0 μA over 2 weeks, afforded black needle crystals of (**13**)$_2$(I_3)$_2$·Cl_3CCH_3. Raman: 1402 and 1453 (Raman for donor **13**: 1548, 1510 1488). A similar experiment in THF, conducted at 3.0 μA over 15 days gave a black material exhibiting Raman signals at 1406 and 1453, indicating a 1:1 donor cation:triodide ratio.

Reaction of 12 with iodine

A solution of donor **12** (10 mg) in 1,1,2-trichloroethane (5 mL) was placed in a tank containing iodine vapour and left for 3 days, and gave black crystals of the **12**·I_3 salt. ν_{max} (ATR): 2955, 2912, 2854, 2823, 1409, 1322 1235, 1168, 1016, 998 882, 487, 476, 457; Raman: 1462, 1408, 572 **(**Raman for pure **12**: 1555, 1507, 1491, 1478, 493).

Preparation of TCNQ complexes

13·TCNQ

To a hot solution (90°C) of TCNQ (5 mg, 0.024 mmol) in 1,1,2-trichloroethane (3 mL) was added a hot solution (90°C) of donor **13** (11 mg, 0.023 mmol) in 1,1,2-trichloroethane (2 mL), and the mixture was heated at 90°C for 2 h. The solvent was left to evaporate slowly to precipitate **13**·TCNQ as black crystals, ν_{max} (ATR): 2914, 2214 (CN), 1668, 1533, 1506, 1450, 921, 909, 885, 837, 772, 495, 472, 398; Raman 1597, 1533, 1434, 1187 (Raman of pure **13**: 1549, 1510, 1488); λ_{max} (solid state): 213, 294, 350, 650, 689.

14·TCNQ

To a hot solution (90°C) of TCNQ (5 mg, 0.023 mmol) in 1,1,2-trichloroethane (3 mL) was added a hot solution (90°C) of donor **14** (11 mg, 0.023 mmol) in 1,1,2-trichloroethane (2 mL), and the mixture was heated at 90°C for 2 h. 1,1,2-Trichloroethane was removed *in vacuo* and some acetonitrile was added to dissolve all solid material and then evaporated slowly to precipitate **14**·TCNQ as black microcrystals, found C, 51.1; H, 3.0; N, 8.1%, $C_{29}H_{20}N_4S_8$ requires C, 51.2; H, 3.0; N, 8.2%; ν_{max} (ATR): 2217 (CN), 1536, 1516, 1412, 903, 840, 770, 473; Raman: 1600, 1546 (weak), 1501 (weak), 1450, 1190, 989 (Raman of pure **14**: 1549, 1498); λ_{max} (solid state):212, 304, 405, 522, 701.

15·TCNQ

To a hot solution (65°C) of donor **15** (10 mg, 0.019 mmol) in a mixture of acetonitrile (5 mL) and chloroform (1.5 mL) was added a hot solution (65°C) of TCNQ (5 mg, 0.024 mmol) in acetonitrile (3 mL), and the mixture was heated at 65°C for 2 h. The

solvent evaporated slowly to produce **15**·TCNQ as a black crystalline solid, ν_{max} (ATR): 2974, 2938**,** 2213 (CN), 1536, 1497, 1442, 1378, 1352, 1040, 877, 838, 770, 472; Raman: 1600, 1490, 1443 (Raman of pure **15**: 1552, 1514, 1488); λ_{max} (solid state): 213, 301, 335, 399, 479 sh, 693.

X-Ray Crystallography

Data were collected with Mo*K*α radiation at 100–150K, except for (**13**)$_3$(I$_3$)$_3$.C$_6$H$_5$Cl and **14**·TCNQ, for which the synchrotron X-ray wavelengths were 0.6710 and 0.6889 Å respectively. The structures were solved with SHELXS-97 and refined with SHELXL-97.[35] Molecular illustrations are made with ORTEP-3[36] and Mercury[37]. Data have been deposited at the Cambridge Crystallographic Data Centre, 12 Union Road, Cambridge, CB2 1EZ with reference numbers CCDC 749271–749278.

Crystal data for **11**: $C_{16}H_{20}S_5$, M_r = 468.80, orthorhombic, a = 7.7282(3), b = 12.4310(5), c = 21.2863(8) Å, V = 2044.96(14) Å^3, Z = 4, $P2_12_12_1$, D_c = 1.52 g cm^{-3}, μ = 0.087 mm^{-1}, T = 100 K, 5095 unique reflections, 5045 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.017, $R_w(F^2$, all data) = 0.043.

Crystal data for **12**: $C_{13}H_{14}S_5$, M_r = 426.72, triclinic, a = 6.8624(5), b = 7.0519(5), c = 9.5071(7) Å, α = 80.453(4), β = 83.676(4), γ = 75.465(3)°, V = 438.05(5) Å^3, Z = 1, $P\bar{1}$, D_c = 1.62 g cm^{-3}, μ = 1.01 mm^{-1}, T = 150 K, 6275 unique reflections, 5989 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.020, $R_w(F^2$, all data) = 0.048.

Crystal data for **14**: $C_{17}H_{16}S_8$, M_r = 476.78, monoclinic, a = 7.7420(4), b =14.2133(8), c = 18.0225(11) Å, β = 90.418(3)°, V = 1983.13(19) Å^3, Z = 4, $P2_1$, D_c = 1.60 g cm^{-3}, μ = 0.90 mm^{-1}, T = 120 K, 4594 unique reflections, 3746 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.044, $R_w(F^2$, all data) = 0.101. One of the two independent molecules is disordered about the long molecular axis, so that there are two positions (in a ratio ~3:2) for the 6,6-dimethylbicyclo[3.1.1]heptene-2,3-dithio) unit.[19]

Crystal data for **12**·I_3: $C_{13}H_{14}S_8{\cdot}I_3$, M_r = 807.42, monoclinic, a = 8.2507(6), b = 13.8305(13), c = 20.3877(18) Å, β = 99.998(4)°, V = 2291.1(3) Å^3, Z = 4, $P2_1$, D_c = 2.34 g cm^{-3}, μ = 4.82 mm^{-1}, T = 120 K, 5987 unique reflections, 5392 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.044, $R_w(F^2$, all data) = 0.141.

Crystal data (synchrotron) for (**13**)$_3$(I_3)$_3$·chlorobenzene: $(C_{13}H_{14}S_8)_3{\cdot}(I_3)_3{\cdot}C_6H_5Cl$, M_r = 2793.03, monoclinic, a = 13.441(3), b = 14.338(8), c = 21.160(4) Å, β = 95.39(3)°, V = 4059.8(14) Å^3, Z = 2, $P2_1$, D_c = 2.20 g cm^{-3}, μ = 4.12 mm^{-1}, T = 120 K, 11613 unique reflections, 7909 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.052, $R_w(F^2$, all data) = 0.110.

Crystal data for **13**·TCNQ: $C_{17}H_{18}S_8{\cdot}C_{12}H_4N_4$, M_r = 683.0, triclinic, a =7.2400(7) , b = 7.8327(6), c = 27.247(3) Å, α = 87.572(5), β = 87.761(3), γ = 76.405(2)°, V = 1499.8(2) Å^3, Z = 2, $P\bar{1}$, D_c = 1.51 g cm^{-3}, μ = 0.62 mm^{-1}, T = 120 K, 6530 unique reflections, 3707 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.12, $R_w(F^2$, all data) = 0.23. The structure is modelled with a 72:28 disorder between enantiomers. [19]

Crystal data (synchrotron) for **14**·TCNQ: $C_{17}H_{16}S_8{\cdot}C_{12}H_4N_4$, M_r = 680.97, orthorhombic, a = 7.877(6) , b = 13.630(10), c = 27.69(2) Å, V = 2973(4) Å^3, Z = 4, $P2_12_12_1$, D_c = 1.52 g cm^{-3}, μ = 0.57 mm^{-1}, T = 120 K, 3638 unique reflections, 1760 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.058, $R_w(F^2$, all data) = 0.129.[19]

Crystal data for **15**·TCNQ: $C_{20}H_{22}S_8{\cdot}C_{12}H_4N_4$, M_r = 723.05, orthorhombic, a = 7.8793(8) , b = 27.888(3), c = 29.721(3) Å, V = 6530.8(12) Å^3, Z = 8, $P2_12_12_1$, D_c = 1.47 g cm^{-3}, μ = 0.58 mm^{-1}, T = 120 K, 13554 unique reflections, 9479 with $F^2 > 2\sigma$, $R(F, F^2>2\sigma)$ = 0.097, $R_w(F^2$, all data) = 0.199.[19]

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23. Resistance greater than 200MOhms.

24. A partial solution of X-ray diffraction data collected for the material from 1,1,1-trichloroethane showed that the donor cations are arranged in face-to-face pairs, and triiodides are integrated into the donor packing arrangement. There is also one molecule of trichloroethane for each two donors and two triodides, packed among the hydrocarbon residues of the donors. Unit cell: triclinic, a = 9.8926(12), b = 12.8696(15), c = 22.078(3) Å, α = 92.212(4), β = 95.39(3), γ =90.591(5)°.

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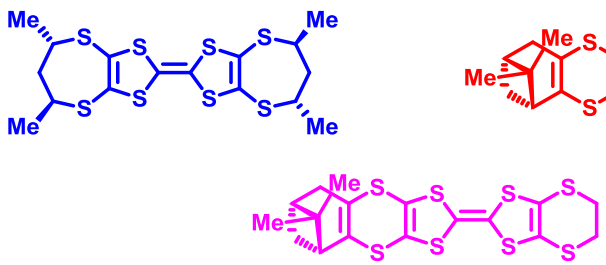
Graphical Abstract.



The syntheses of six new chiral donors related to BEDT-TTF are described, along with some of the structures of the donors, electocrystallisation products and TCNQ complexes.