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# 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.



## 1. 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 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 enantiopure donors with hydrogen bonding functionality have been reported, e.g., BEDT-TTF derivatives **12**–**14**,[4b,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.

## 2. Results and discussion

### 2.1. Synthesis of chiral TTF-related polyols 15–20

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

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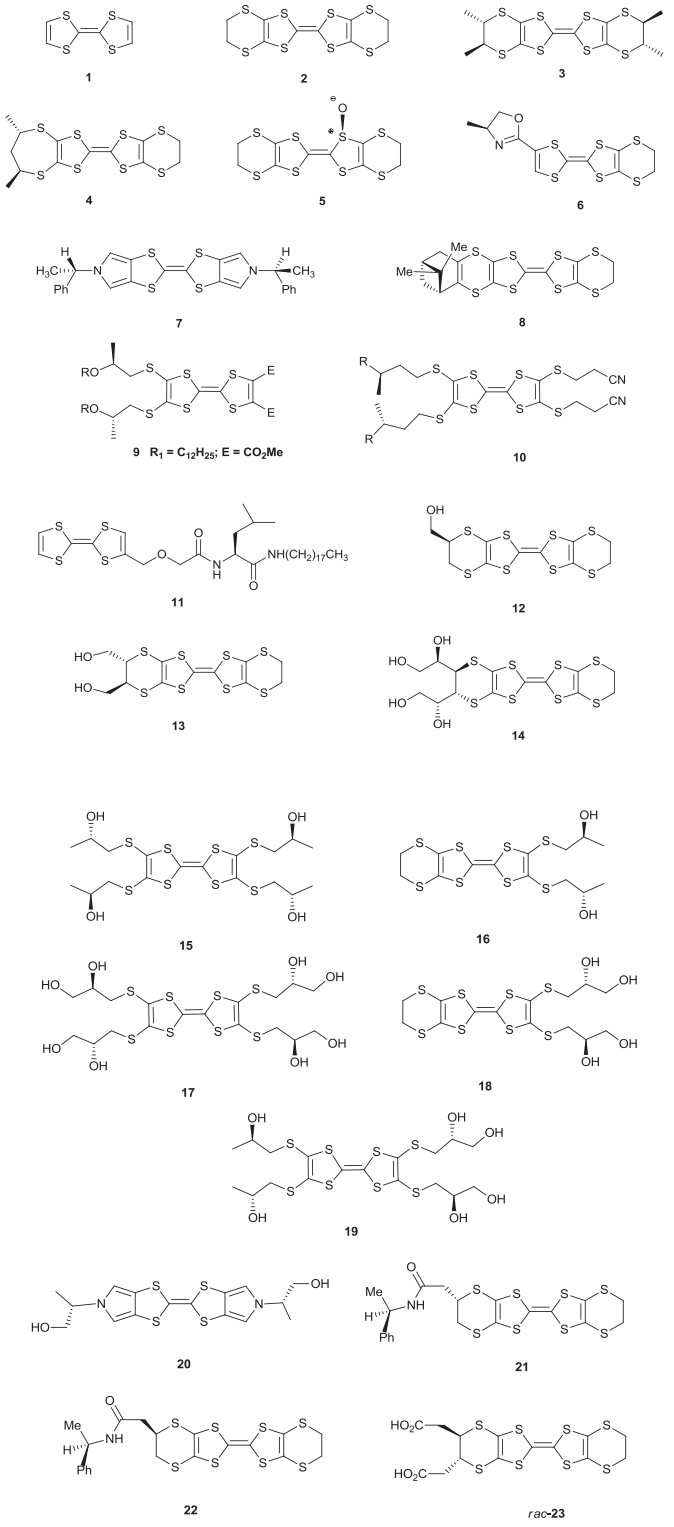
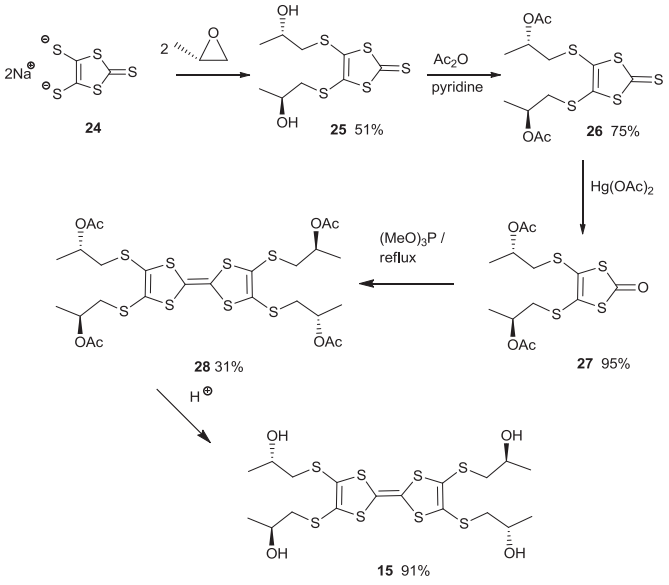
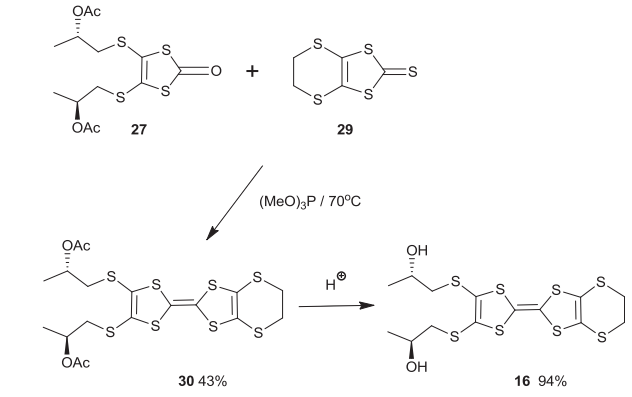



**Scheme 1.**

dithiolate **24**[25] with 2 equiv 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 h 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.**

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 2 equiv 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