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LETTERS

Synthesis of bis(ethylenedithio)tetrathiafulvalene derivatives with metal ion ligating centres

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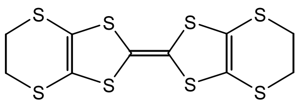
Abstract—The syntheses of eight derivatives of BEDT-TTF (ET) containing pyridine, 2,2′-bipyridine or 2,4′-pyridylpyrimidine binding sites on a side chain are reported, for use in the preparation of organic/inorganic hybrid materials. The intermediate hydroxyethyl derivative of BEDT-TTF is prepared in an efficient five-step procedure. © 2003 Elsevier Science Ltd. All rights reserved.

Bis(ethylenedithio)tetrathiafulvalene, BEDT-TTF or ET, **1**, a readily oxidisable organosulfur donor, has played a major role in the field of organic conductors over the last ten years.[1] Of particular importance is the observation of superconductivity at low temperatures in radical cation salts such as $ET_2[Cu(N(CN)_2)Br]$.[2] However, only a few substituted derivatives of ET have been prepared, e.g. the tetramethyl[3] and tetraethyl[4] derivatives. Charge transfer salts of the latter are under investigation as 'molecular rulers' in nanotechnology.



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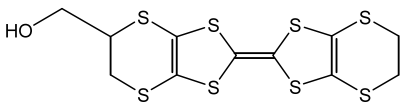

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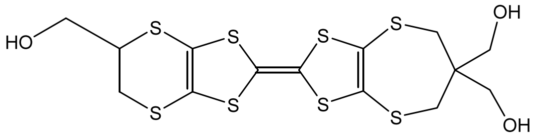

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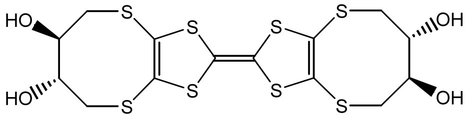

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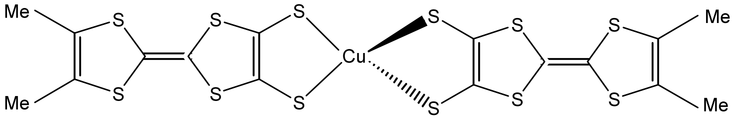

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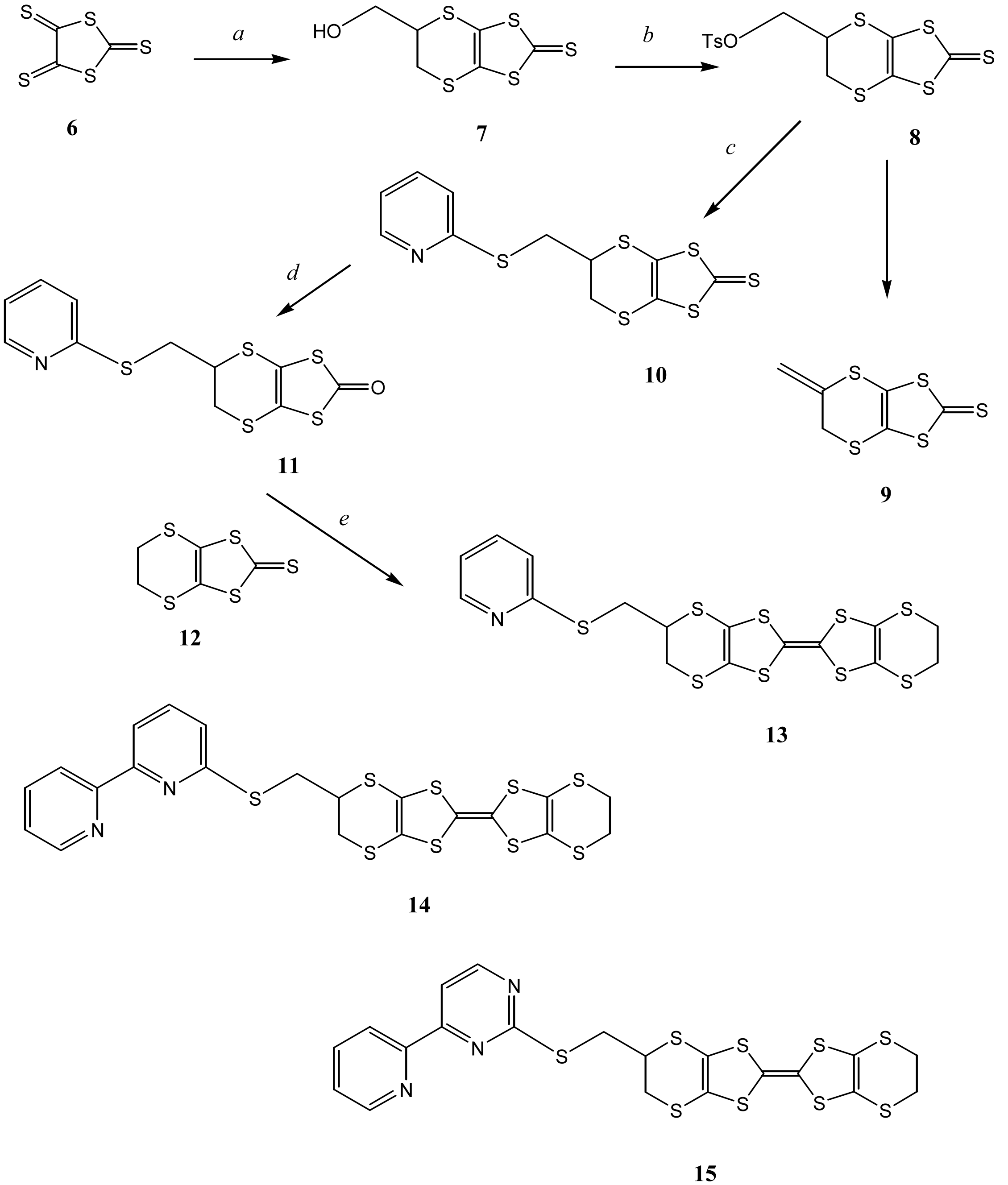
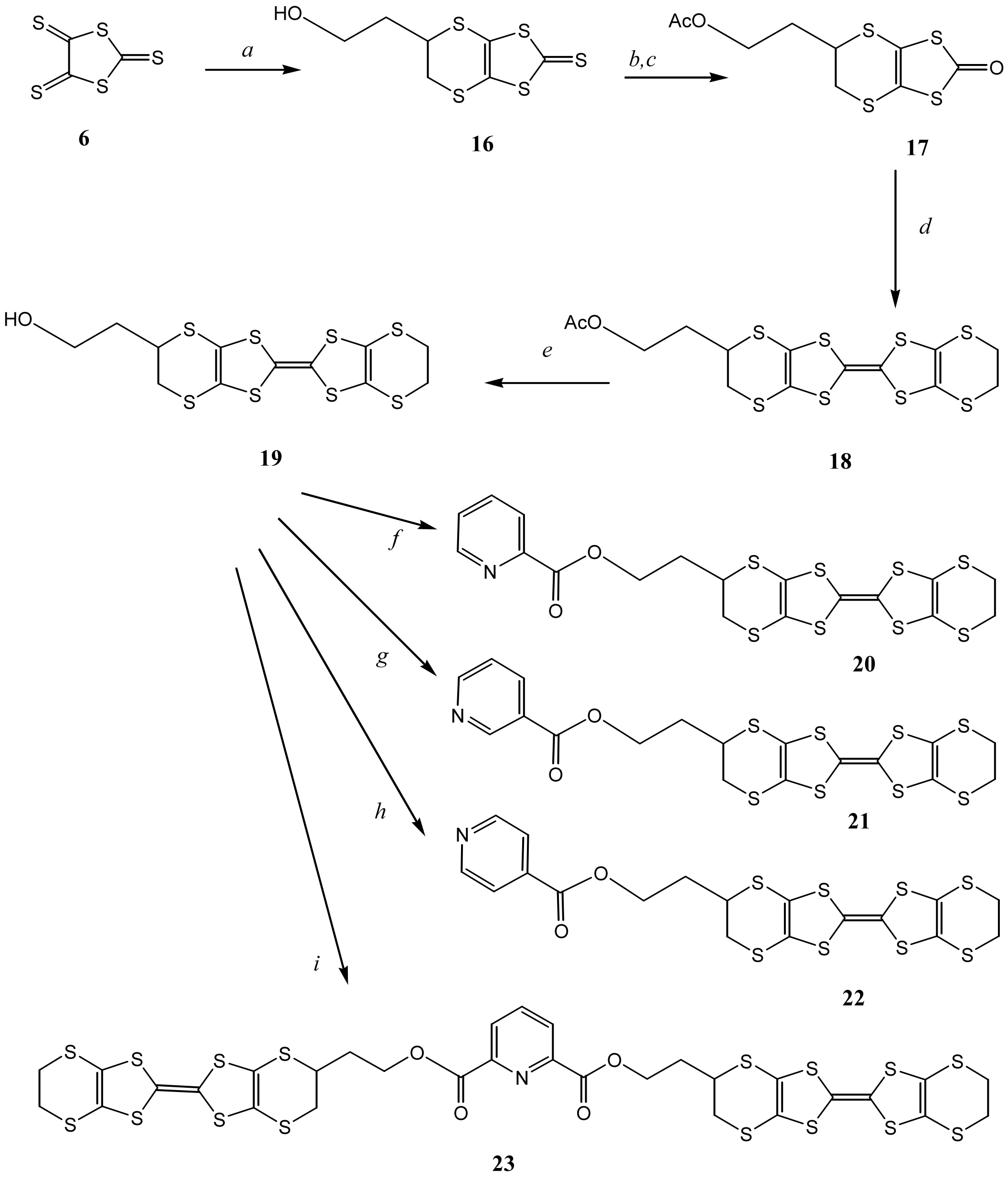
Formigue has prepared poly-chloro and -fluoro analogues as isomeric mixtures,[5] and we have prepared both racemic and enantiopure versions of the hydroxymethyl derivative HMET **2**,[6] polysubstituted materials such as **3** and hydroxy derivatives with expanded outer rings such as **4**[7] which all have the potential for attachment to other molecular systems.

There is increasing interest in bifunctional materials which combine the electrical conducting properties of organosulfur donors with the magnetic effects of transition metal ions, and in which these properties may interact in novel ways. Day prepared a paramagnetic superconductor from ET and Fe(III) oxalates,[8] and Coronado reported a material with independent electrical conductivity and ferromagnetism containing ET and a mixed metal oxalate network.[9] Interplay of magnetic and electrical effects was demonstrated in κ-(BETS)$_2$FeBr$_4$ and λ-(BETS)$_2$FeCl$_4$ which changed from an insulator to a metal and then to a superconductor by increasing the external magnetic field.[10] Recently, Day has reported radical cation salts of metal complex anions containing a heterocyclic ligand, e.g. (ET)$_2$Fe(phen)(NCS)$_4$ which is a paramagnetic semiconductor, and (ET)$_2$Cr(isoquin)$_2$(NCS)$_4$ which is a ferromagnetic semiconductor.[11] The organosulfur donor and the complex anion are separate species in these systems. In order to gain some control over the relative



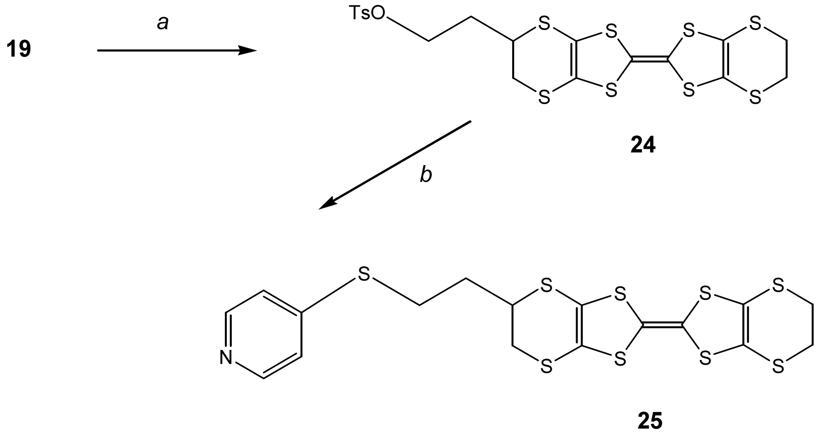
Scheme 1. *Reagents and conditions*: (a) allyl alcohol, toluene, reflux; (b) 2 equiv. tosyl chloride, pyridine, rt; (c) pyridyl-2-thiolate$^-$ Na$^+$, THF or DMF; (d) mercuric acetate, acetic acid, chloroform; (e) 2 equiv. **12**, triethyl phosphite, 80°C, 5 h.



Scheme 2. *Reagents and conditions*: (a) but-3-en-1-ol, toluene, reflux; (b) acetic anhydride, pyridine, rt; (c) mercuric acetate, acetic acid, chloroform; (d) 2 equiv. **12**, triethyl phosphite, 90°C, 5 h; (e) 2 M HCl, THF; (f) picolinoyl chloride hydrochloride, THF, Et_3N; (g) nicotinoyl chloride hydrochloride, THF, Et_3N; (h) isonicotinoyl chloride hydrochloride, THF, Et_3N; (i) 2,6-pyridine dicarbonyl dichloride, THF, Et_3N.

orientations of these moieties we set out to attach the metal binding ligand to the ET system. Here we report efficient syntheses of systems **13**–**15**, **20**–**23** and **25** in which the ET group is covalently bound to pyridine, 2,2′-bipyridine or 2,4′-pyridylpyrimidine ligands for use in the construction of new organic/inorganic hybrid materials. This approach contrasts with the recent report of the conducting paramagnetic molecule **5** in which the organosulfur donor itself coordinates the metal.[12]

The trithione **6**, an oligomeric material in the solid state, undergoes Diels–Alder reactions with a variety of functionalised alkenes, though the reported yields are variable (10–70%).[13] However, we were able to obtain thione **7** in 71% yield from reaction of **6** with allyl alcohol using refluxing toluene as the solvent. The alcohol **7** was converted to the corresponding tosylate **8** in 94% yield. This material slowly eliminates tosic acid to give alkene **9**, but nevertheless can be used when freshly prepared or, if stored, it can be purified by chromatography before use. The tosylate can be readily displaced by pyridine-2-thiolate to give thione **10** in 78% yield (Scheme 1). The synthesis is completed by standard procedures: conversion of the thione to oxo compound **11**, and then cross coupling with excess of thione **12** in triethyl phosphite gives the pyridine substituted ET derivative **13** in an overall yield of 35% from **8**. In an analogous way tosylate **8** can be substituted with 2,2′-bipyridine-6-thiolate[14] or 2,4′-pyridylpyrimidine-2′-



Scheme 3. *Reagents and conditions*: (a) 4 equiv. tosyl chloride, pyridine; (b) pyridyl-4-thiolate$^-$Na$^+$, THF/DMF (1:2).

thiolate[14] and the products converted to ET derivatives **14** and **15** which bear bidentate metal ion binding groups in overall yields of 30 and 35%, respectively, from **8**.

The second series of ET derivatives **20**–**23** was prepared by an alternative route in which the metal binding group is installed at the end of the synthesis (Scheme 2). Hydroxyethyl-ET, HEET, **19**, was prepared in a very convenient fashion starting from trithione **6** and but-3-en-1-ol. The latter two substances react in refluxing toluene to give thione **16** in a yield of 83%. Protection of the hydroxyl function as an acetate, followed by the standard procedure for exchange of thione sulfur for oxygen using mercuric acetate gave the oxo compound **17** in 87% yield from the thione **16**. Cross coupling with the unsubstituted thione **12** in triethyl phosphite gave the protected ET derivative **18** in 60% yield after chromatography to separate from homocoupled material. Finally, HEET, **19** was generated by hydrolysis with 2 M HCl in THF. By this route a functionalised ET, which will facilitate the attachment of the ET grouping to many other molecular systems via ester, ether and other linkages, was accessed in 43% overall yield from trithione **6**.

HEET **19** reacted smoothly with a variety of pyridine acid chlorides to provide compounds **20**–**23** in moderate to high yields (50–90%). Of particular interest was **23** where two ET moieties were linked in the same molecule. This compound was expected to be a mixture of racemic and *meso* compounds, though unsurprisingly there is no difference discernable in the ^{1}H and ^{13}C NMR spectra. Finally, the hydroxy derivative HEET was also converted to its tosylate **24**, which was substituted with the sodium salt of pyridine-4-thiolate to give the donor **25** (Scheme 3). All the donors reported here are racemic, but access to enantiopure HMET **2**[6] and ET-CH_2CO_2Me,[15] a precursor to enantiopure HEET, means that in principle single enantiomers can be obtained.

The cyclic voltammetry data for seven of the new donors show the expected two reversible oxidations with almost no variation in the potentials ($\sim$0.50 and $\sim$0.90 V) at which they occur (Table 1). In contrast, compound **23** which bears two ET moieties shows two reversible half wave potentials at 0.43 and 0.55 V, which together correspond to loss of two electrons, and a further irreversible oxidation process at 0.82 V (Fig. 1). Since the molecular structure allows the two ET moieties to lie close to one another, the first two oxidations are assigned to conversion of $(\text{-ET})_2$ to $(\text{-ET})_2^+$ and then to $(\text{-ET}^+)_2$, and interestingly the first of these takes place at a lower potential than for oxidation of ET itself. We speculate that the irreversibility of the oxidation at 0.82 V may be due an intramolecular reaction between the further oxidised ET moieties. This is under further investigation.

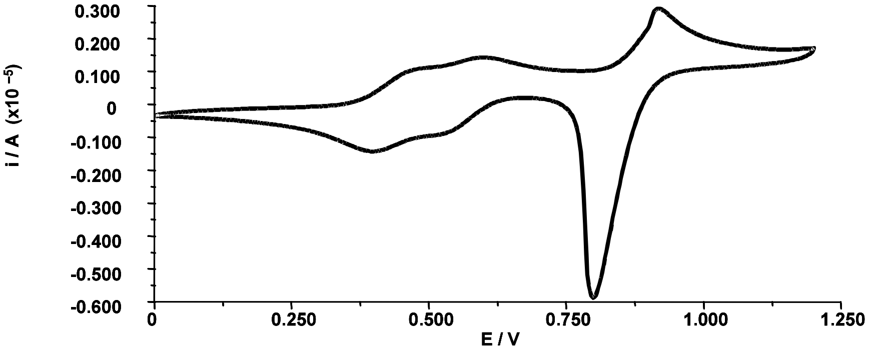
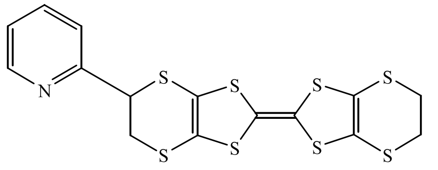


Figure 1. Cyclic voltammogram of **23** in CH_2Cl_2 containing 0.1 M n-Bu_4NPF_6, scan rate of 100 mV s^{-1}, E (V) relative to Ag/AgCl.



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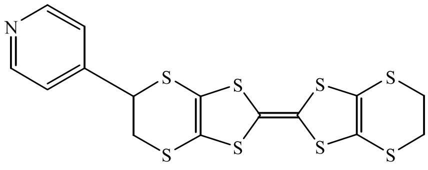

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Table 1. Oxidation potentials (V, relative to the AgCl/Ag electrode) measured by cyclic voltammetry[a] for oxidation of ET and novel derivatives

	E_1 (V)	E_2 (V)
1	0.48	0.87
13	0.48	0.89
14	0.49	0.90
15	0.50	0.91
20	0.49	0.90
21	0.50	0.90
22	0.50	0.90
23	0.43, 0.55	0.82[b]
25	0.50	0.89

[a] Measured in dichloromethane containing 0.1 M tetrabutylammonium hexafluorophosphate with a scan rate of 100 mV s^{-1} relative to Ag/AgCl using a μ-Autolab type II apparatus.

[b] Irreversible.

Thus, we have demonstrated simple preparative routes to ET derivatives containing metal binding groups, which should be applicable not only to the installation of the many alternative metal ligating groups but also to other functionalities to provide novel materials and building blocks in supramolecular chemistry. The coordination chemistry and electrocrystallisation of the molecules reported in this work are under current study. Other workers[16] have reported the synthesis of related pyrid-2-yl and pyrid-4-yl derivatives of ET, **26** and **27**, though these were only obtained in low yields, and the general approach is less flexible requiring vinyl derivatives of the pyridines. Ouahab et al. have reported a TTF bound to the 4-position of a pyridine, and have prepared a copper complex[17] and Bryce has prepared Langmuir Blodgett films of related derivatives of ethylenedithio-TTF.[18]

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