Synthetic strategies for preparing BEDT-TTF derivatives functionalised with metal ion binding groups

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The syntheses of BEDT-TTF (ET) derivatives with potential metal ion binding pyridyl, bipyridyl and terpyridyl groups is achieved either by stepwise construction of the organosulfur core or *via* reactions of hydroxymethyl-ET for which a cheap and efficient four step route is reported. The tosylate of hydroxymethyl-ET, reported for the first time, undergoes nucleophilic substitutions with pyridyl, bipyridyl- and terpyridyl-thiolates to give new donors. The X-ray crystal structures of two substituted ET derivatives show considerable deviation of the organosulfur donor system from planarity by bending about the short molecular axis of the ET group.

Introduction

The radical cation salts of bis(ethylenedithio)tetrathiafulvalene (BEDT-TTF or ET) **1**, have been extensively studied because of their wide variety of electrical properties,[1] including the occurrence of superconductivity in salts such as $ET_2[Cu(SCN)_2]$ and $ET_2(ICl_2)$.[2] Substituted derivatives of ET are more difficult to prepare, however a number of mono-, di- and tetrasubstituted materials are now reported,[3] and some of their radical cation salts have been studied.[4] Materials with novel combinations of electrical and magnetic properties are a current theme of research in which a transition metal ion provides a magnetic centre.[5] The latter may feature in the anion, as in Day's paramagnetic superconductor $(ET)_4[Fe(oxalate)_3]\cdot H_2O\cdot C_6H_5CN$,[6] the Kobayashis' radical cation salts of BETS **2** with FeX_4^- (X = Cl, Br) whose electrical properties can be changed by an external magnetic field,[7] and Coronado's salts of partially oxidized layers of ET[8] or BETS[9] with chromium(III)/manganese(II) oxalate networks as anions, which shows almost independent conducting and ferromagnetic behaviour. Complex anions such as $[Cr(III)(phen)(NCS)_4]^-$ and $[trans\text{-}M(isoquinoline)_2(NCS)_4]^-$ (M = Cr(III) or Fe(III)) have also been used[10] with TTF[11,12] and ET[12,13] and other donors.[14] In contrast, attachment of the metal binding group, notably pyridine or bipyridine centres, to the donor has been developed in a number of cases. For example, Ouahab has reported radical cation salts of **3**,[15] a TTF conjugated to a pyridine through an alkene; Batail and Avarvari have reported a series of *N*-pyridyl- and *N*-2,2′-bipyridyl-TTF and EDT-TTF-carboxamides such as **4** and **5**,[16] and Pilkington has included bipyridyl metal binding sites as bridges in molecules such as **6** which link a TTF to a verdazyl radical.[17] Other metal binding centres utilised include phosphines,[18] as in the molybdenum complex **7** which has been electrocrystallised to a radical cation salt,[19] both phosphine and nitrogen centres in **8**,[20] and dithiolates as in neutral paramagnetic systems such as **9**.[21]

We have been involved in attaching the metal binding ligand to the ET framework and we have communicated the syntheses of donors such as donors **10–12**.[22] Here we describe the synthetic approaches to racemic donors **13–18** either by stepwise construction of the molecule, or from hydroxymethyl-ET which can be functionalised by either tosylation and substitution or by ester formation. An efficient four step synthesis of racemic hydroxymethyl-ET is also described. Several donors with pyridine rings directly attached to an ET or EOET framework **19–21** have been reported.[23,24]

Synthesis of ET derivatives

The ligands **13**[22] and **14** were prepared initially by syntheses involving typically five steps according to the general scheme developed earlier in this laboratory and illustrated in Scheme 1. The mercaptobipyridine groups were introduced at the third step of the synthesis. Trithione **22**[25] was cyclised with allyl alcohol to give the hydroxymethyl thione **23**, which was tosylated using 1.5 equivalents of tosyl chloride in pyridine to give **24** in an overall yield of 62% from **22**. The 6-mercapto- and 4-mercaptobipyridines **25** and **26** were synthesized in several steps *via* the corresponding halobipyridines. 6-Bromo-2,2′-bipyridine was prepared by reaction of 6-bromo-2-lithiopyridine with ethyl 2-pyridylsulfoxide.[26] 2,2′-Bipyridine was converted in two steps to 4-nitro-2,2′-bipyridine-*N*-oxide which was reacted with acetyl chloride and phosphorus trichloride[27] to give 4-chlorobipyridine, which was found to be superior to the chlorination of the *N*-oxide of 2,2′-bipyridine which requires a tedious separation of 4- and 6-chloro isomers.[28] The mercaptobipyridines were obtained by heating the halobipyridine with sodium hydrogen sulfide, potassium hydroxide and DMF which, compared with the earlier procedure using hydrogen sulfide as the source of sulfur,[28] was much more reproducible, took much less time and doubled the yield to typically 80% for this step. Reaction of tosylate **24** with the sodium salt of each mercaptobipyridine in DMF furnished thiones **27** and **28** in yields of 70–73%. Subsequent

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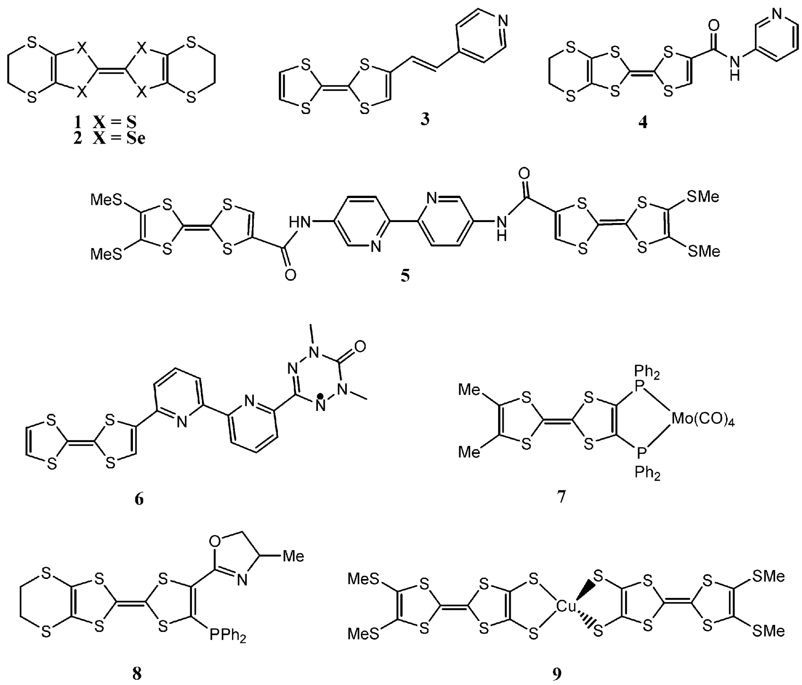


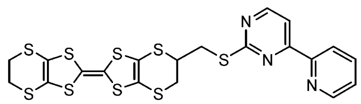
exchange of thione sulfur for oxygen using mercuric acetate gave oxo compounds **29** (93%) and **30** (97%), which were cross coupled with the unsubstituted thione **31**[25] in triethyl phosphite at 90–100 °C to give ligands **13** (46%) and **14** (54%) after separation from homo-coupled products by chromatography. The overall yields of each ligand from the trithione **22** were 18% (**13**) and 24% (**14**).

This synthetic route provides oxo compounds **29** and **30** which can be cross-coupled with alternative thiones to give further bipyridine-substituted donors. Nevertheless, it could be more convenient to be able to introduce the metal binding group right at the end of the synthesis, especially if the metal binding moiety is expensive, or difficult to make. In addition, when we tried to make the ligand **15** containing a 4′-mercapto-2,2′: 6′,2″-terpyridine group by the route above, the final step of the synthesis was problematic. 4′-Mercaptoterpyridine **33** was prepared from the commercially available chloro compound **32** and sodium hydrogen sulfide in DMF in quantitative yield. Constable reported the first details of this compound recently.[29] Reaction of the tosylated thione **24** with the sodium salt of the mercaptoterpyridine **33** gave the thione **34** in 69% yield and this product was converted to the oxo compound **35** in 67% yield. However, purification of the donor **15**, from the reaction of oxo compound **35** with the unsubstituted thione **31** in triethyl phosphite, required several chromatographic separations and gave a very low yield of the donor. Thus, we developed a different approach (Scheme 2) involving nucleophilic substitution on tosyloxymethyl-ET **40** to prepare donor **15**.

Synthesis of HMET and its tosylate

We have developed a method of preparing hydroxymethyl-ET, HMET, in four steps from trithione **22** in an overall yield of 44% utilising an acetyl protecting group (Scheme 2). Thus, cycloaddition of trithione **22** with allyl acetate gives the thione **36** (72%) which is converted to the oxo compound **37** in 90% yield. Cross coupling with unsubstituted thione **31** gave acetyloxymethyl-ET **38** in 70% yield after separation from homocoupled products. Finally, hydrolysis of the acetate gave HMET **39** in 96% yield. This represents the most efficient synthesis of racemic HMET reported to date. The preparation of HMET **39** has been reported by Zhu[30] and ourselves[31] in five step syntheses in which the hydroxyl group is protected with a TBDMS group. The new route is shorter and considerably cheaper, and full experimental details are provided.

Tosylation of HMET was only possible by use of a large excess of tosyl chloride in pyridine over 20 h which gave the product **40** in 85% yield. Use of just two equivalents of tosyl chloride gave no product after 24 h, and at least seven equivalents are necessary for this reaction to succeed. We measured the X-ray crystal structure of this tosylate to look for any feature which might give clues to the difficulty in the tosylation. In fact the structure is particularly unusual, since it shows that the tosyl group is bent back over the ET system (Fig. 1); the closest intramolecular contacts between the ET and tosyl group (*ca.* 3.5–3.6 Å) involve the methyl carbon and sp^2 carbon atoms of the unsubstituted "half" of the ET system. However, there is no charge transfer interaction; the crystal colour is typical of an ET derivative, and in solution the UV/visible spectrum shows no remarkable features. Both tosyl and ET units are involved in the molecular stacking (Fig. 2): the phenyl rings stack face to face (separation 3.44 Å) and these pairs then stack with some overlap between adjacent ET moieties (separation 3.80 Å). There is one rather close intermolecular S···S contact between dithiole rings of 3.3884(17) Å. The ET moiety is significantly non-planar even in the heterocyclic core of the molecule. Thus, the best planes defined by the sulfur and sp^2 carbon atoms of the two



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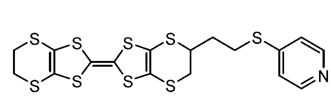

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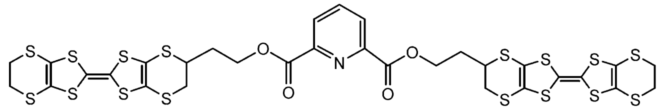

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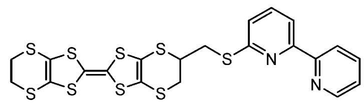

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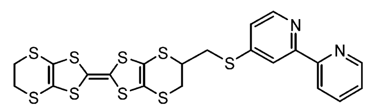

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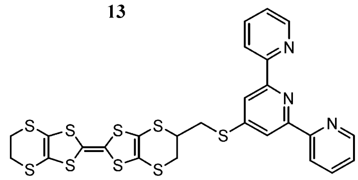

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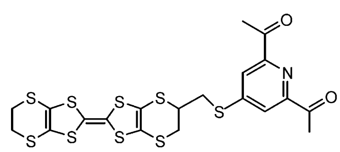

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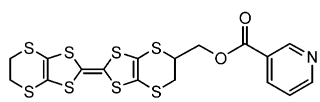

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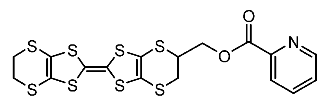

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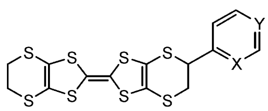
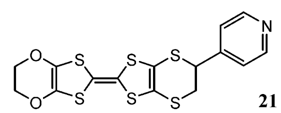


19 **X = N, Y = CH**
20 **X= CH, Y = N**



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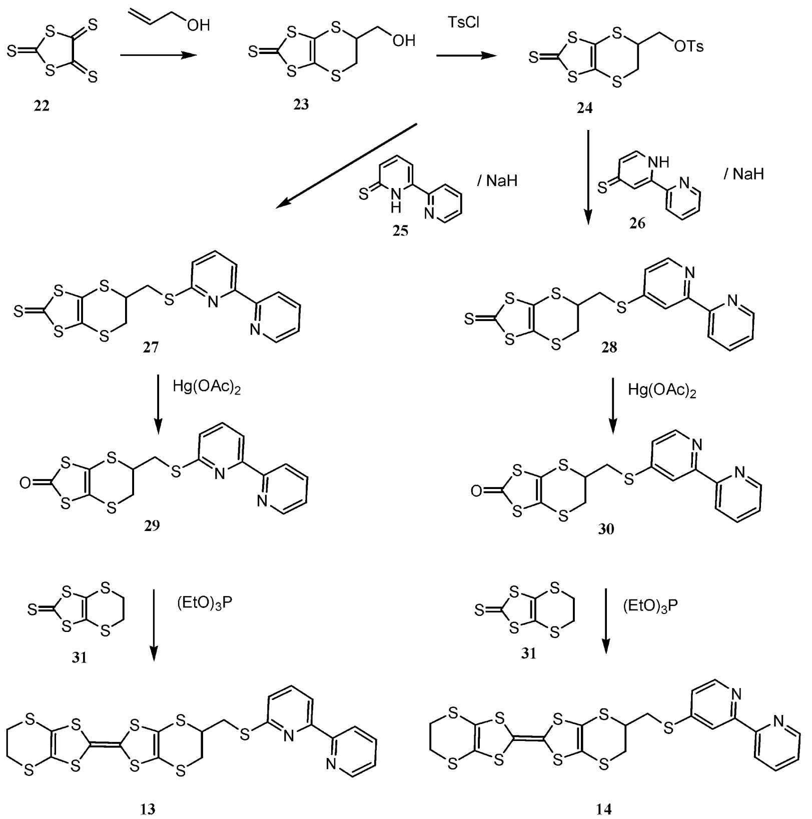
dithiolodithiin units lie at 33.75(5)° to each other. The substituted dihydrodithiin ring adopts a half chair conformation while for the unsubstituted ring both sp^3 carbon atoms deviate to the same side of the ring plane. There is some disorder in the structure with *ca.* 13% of molecules preferring a slightly different conformation; the ET and methylphenyl groups occupy similar positions, but in the minor component the tosyloxymethyl sidechain is attached to the other carbon of the ethylene bridge. In both structures the sidechain adopts a pseudoaxial orientation with respect to the ET group. The sluggishness of the reaction between HMET and tosyl chloride may just be due to the HMET molecules being stacked in solution and so access to the hydroxyl group is hindered. There is no similar difficulty in tosylation the hydroxymethyl thione **23**.

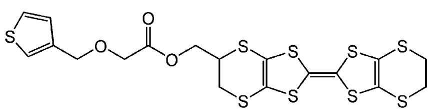
Reaction of the sodium salt of 4′-mercaptoterpyridine **33** with the tosylated donor **40** in DMF over 48 h at room temperature gave the terpyridyl-ET derivative **15** in 65% yield after chromatography, and thus avoiding the difficulties of the previous synthesis. Ligand **14** was also prepared by reaction of the appropriate bipyridinethione **26** with the tosylated HMET in a yield of 65%. The overall yields of **14** from trithione by this route or the stepwise route discussed earlier are very similar. However, when a range of derivatives is being made, it may be simpler to make a large amount of the tosylated donor, and then react it with the required nucleophiles. The tosylated donor was also reacted with the sodium salt of 2,6-diacetyl-4-mercaptopyridine, to give the pyridyl substituted donor **16** in 70% yield. The X-ray structure of **16** is shown in Fig. 3. The pyridyl group is not bent back over the ET moiety as in the tosylate, but the sidechain is extended away from the ET to which it attaches by a pseudo-axial connection. The pyridyl substituent remains roughly parallel to the ET grouping. The latter shows some deviations from planarity (Fig. 4); the planes of the two dithiolodithiin sections, as defined by their four sulfur atoms, lie at 24.18(1)°. In the substituted dihydrodithiin ring both sp^3 carbon atoms are displaced to the same side of the plane defined by the other four atoms, the substituted atom carbon by less than the methylene carbon atom (0.543 *cf.* 1.151 Å). In the unsubstituted dihydrodithiin ring only one of the sp^3 carbon atoms is strongly displaced from the plane of the four other atoms (by 0.711, *cf.* −0.107 Å). Further substitution reactions on tosylated HMET will find applications for preparing a range of substituted ET derivatives.

The facile synthesis of HMET **39** now opens up access to further functionalised derivatives *e.g.* by esterification. Thus, DCC coupling of HMET with pyridinecarboxylic acids gave new donors substituted with binding groups, **17** and **18**, in reasonable yields (*ca.* 50%), with considerable potential for preparation of further materials. Furthermore, this route was taken to attach other heterocyclic moieties *e.g.* a thiophene in



Scheme 1

41 which could also be used to bring additional electrical properties on polymerisation.



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In summary, routes to the synthesis of a number of ET derivatives with metal binding groups are described. The approach *via* HMET in particular has the potential for preparing substrates for multifunctional materials by attachment of the ET unit to molecular systems bringing additional properties. We are currently studying the coordination chemistry of the new donors reported here.

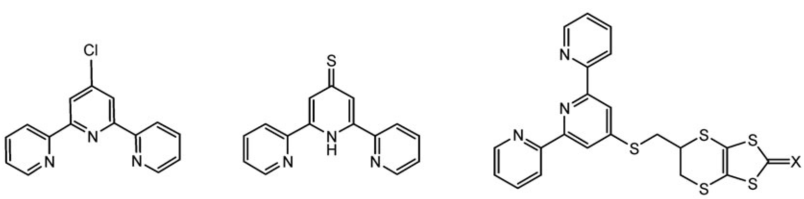
Experimental

General

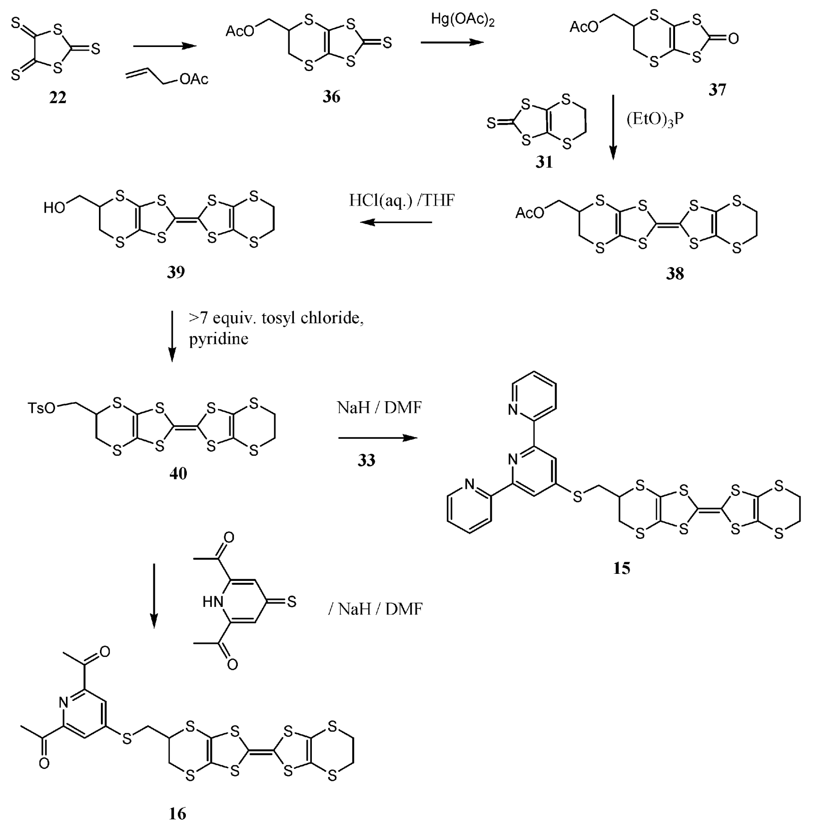
NMR spectra were measured on a JEOL JNM-EX270 spectrometer at 270 MHz for ^{1}H and at 67.8 MHz for ^{13}C using $CDCl_3$ as solvent, and measured in p.p.m. downfield from TMS, unless otherwise stated. IR spectra were recorded on a PerkinElmer Spectrum RX 1 FT-IR spectrometer in cm^{-1}. Mass spectra were recorded at the EPSRC National Mass Spectrometry Centre at Swansea University. X-ray diffraction datasets were measured by the EPSRC National Crystallography Service at Southampton University. Chemical analysis data were obtained from the Microanalytical Laboratory, University of Nottingham. Flash chromatography was performed on 40–63 silica gel (Merck).

5,6-Dihydro-5-(hydroxymethyl)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-thione 23[30]

A suspension of allyl alcohol (15 ml, 0.22 mol) and trithione **22**[25] (27.8 g, 0.14 mol) in toluene (600 ml) was heated to reflux



32 **33** **34** X = S **35** X = O



Scheme 2

for 4 h. After cooling to room temperature the reaction mixture was filtered, and the solid washed with ethanol. Combined washings and filtrate were evaporated and the residue purified by flash chromatography (SiO_2, EtOAc) to furnish **23** as an yellow oil (26.7 g, 73%) which solidified on standing, δ_H: 3.96 (2H, m, CH_2OH), 3.84 (1H, m, 5-*H*), 3.39 (1H, dd, J = 13.4, 2.8 Hz, 6-H_α), 3.32 (1H, dd, J = 13.4, 6.7 Hz, 6-H_β), 1.80 (1H, br, O*H*), δ_C: 210.2 (*C*=S), 125.5, 123.7 (3′a- & 7′a-*C*), 64.4 (CH$_2$OH), 39.8 (5-*C*), 33.1 (6-*C*).

5,6-Dihydro-5-(4′-methybenzenesulfonyloxy)-methyl-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-thione 24

Alcohol **23** (10.00 g, 39.4 mmol), tosyl chloride (11.23 g, 59 mmol) and dry pyridine (40 ml) were stirred overnight under nitrogen. The solution was added to ice water (200 ml) and filtered. The solid was dissolved in DCM and washed with water (200 ml), 4 M HCl (3 × 200 ml) and brine (100 ml) before being dried over $MgSO_4$. Concentration *in vacuo* yielded the product **24** as a brown solid, (13.65 g, 85%), mp 114–116 °C, δ_H: 7.80 (2H, d, J = 8.2 Hz, 2′-,6′-*H*), 7.32 (2H, d, J = 8.2 Hz, 3′-,5′-*H*), 4.30 (1H, dd, J = 10.4, 9.7 Hz, CH_αO), 4.12 (1H, dd, J = 10.4, 6.2 Hz, CH_βO), 3.91 (1H, m, 5-*H*), 3.28 (2H, d, J = 3.7 Hz, 6-H_2), 2.41 (3H, s, CH_3); δ_C: 207.0 (2-*C*), 145.3 (1′-*C*), 132.0 (4′-*C*), 130.1 (2′-, 6′-*C*), 128.0 (3′-, 5′-*C*), 122.2, 121.1 (3a, 7a-*C*), 68.5 (CH$_2$O), 40.2 (5-*C*), 30.5 (6-*C*), 21.7 (CH_3); ν_{max} (KBr): 1594, 1482, 1359, 1191, 1122, 1001, 999, 965, 824, 809, 790, 665, 567, 549, 516; found C: 38.4, H: 3.0%, $C_{13}H_{12}O_3S_6$ requires C: 38.2, H: 3.0%.

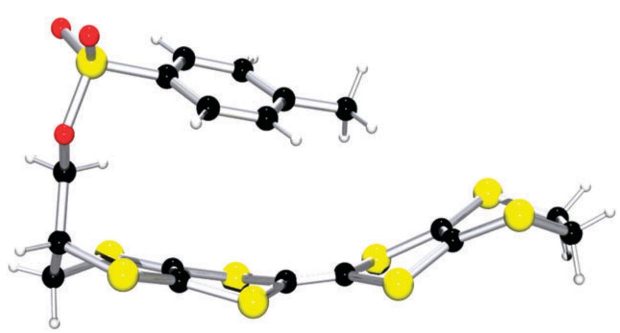


Fig. 1 Molecular structure of tosyloxymethyl-ET **40**.

6-Mercapto-2,2′-bipyridine 25

6-Bromo-2,2′-bipyridine[26] (1.24 g, 5.28 mmol) and solid KOH (0.87 g, 15.5 mmol) were added to a suspension of sodium hydrogen sulfide (3.1 g, 55.2 mmol) in DMF (80 ml). The mixture was heated to reflux under nitrogen atmosphere overnight. After cooling to RT, the mixture was filtered and the filtrate was concentrated under reduced pressure to give a yellow residue. The residue was dissolved in 50 ml H_2O, and neutralised with diluted HCl (2 M). The yellow precipitate was collected and re-dissolved in CH_2Cl_2, and washed twice with H_2O. The organic phase was separated and dried over $MgSO_4$. Removal of solvent afforded 6-mercapto-2,2′-bipyridine[28] as a yellow solid (0.77 g, 78%). δ_H: 12.28 (1H, br, N*H*), 8.61 (1H, d,

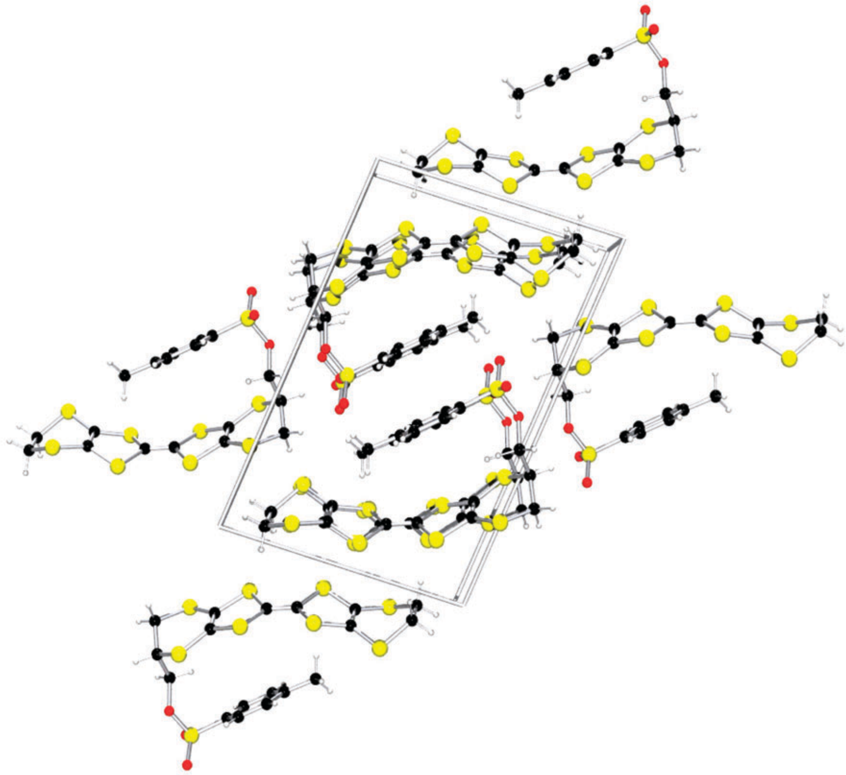


Fig. 2 Crystal packing for tosyloxymethyl-ET **40** looking down the *a* axis.

J = 4.7 Hz, 6′-*H*), 7.79 (2H, m, 4-,4′-*H*), 7.48 (1H, d, J = 8.7 Hz, 3′-*H*), 7.28 (2H, m, 3-,5′-*H*), 7.14 (1H, d, J = 8.2 Hz, 5-*H*); δ_C: 179.5 (6-*C*), 149.5 (2-*C*), 146.7 (2′-*C*), 144.3 (6′-*C*), 138.3 (4′-*C*), 137.8 (4-*C*), 133.3 (3-*C*), 125.7 (3′-*C*), 121.3 (5′-*C*), 110.8 (5-*C*).

5,6-Dihydro-5-(2′,2″-bipyridin-6′-ylthiomethyl)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-thione 27

Sodium hydride (0.31 g, 50% dispersion in oil, 6.5 mmol) was added to a solution of 6-mercapto-2,2′-bipyridine (1.23 g, 6.5 mmol) in dry DMF (20 ml). After 40 min of stirring a solution of tosylate **24** (2.60 g, 6.5 mmol) in dry DMF (10 ml) was added and the resulting mixture was stirred under nitrogen for 25 h. The solution was concentrated *in vacuo*, and the residue partitioned between DCM and water. The organic layer separated and dried over $MgSO_4$. Purification by flash chromatography on silica (8 : 1 cyclohexane : EtOAc) yielded **27** as a red solid, (1.88 g, 70%), mp 117–120 °C, δ_H (400 MHz): 8.58 (1H, d, J = 4.7 Hz 6″-*H*), 8.20 (1H, d, J = 7.9 Hz, 3″-H), 8.06 (1H, d, J = 7.8 Hz, 3′-*H*), 7.76 (1H, dt, J = 7.8, 1.7 Hz, 4″-*H*), 7.52 (1H, t, J = 7.8 Hz, 4′-*H*), 7.18 (1H, dd, J = 7.4, 5.0 Hz, 5″-*H*), 7.13 (1H, d, J = 7.9 Hz, 5′-*H*), 4.07 (1H, m, 5-*H*), 3.84 (1H, dd, J = 14.1, 4.7 Hz, 6-H_α), 3.48 (1H, dd, J = 14.1, 9.6 Hz, 6-H_β), 3.40 (2H, m, 5-CH_2Sbipy); δ_C (100 MHz): 207.4 (2-*C*), 155.7 (2′-,6′-*C*), 155.1 (2″-*C*), 149.1 (6″-*C*), 137.2 (4′-*C*), 136.9 (4″-*C*), 123.9 (3a-*C*), 122.5 (5″-*C*), 122.4 (7a-*C*), 121.6 (5′-*C*), 120.7 (3″-*C*), 117.3 (3′-*C*), 41.9 (5-*C*), 33.7 (5-*C*), 32.7 (CH_2Sbipy); ν_{max} (KBr): 1576, 1555, 1480, 1443, 1419, 1140, 1061, 983, 773, 740; *m*/*z*: (EI) 425 ([M + H]$^+$, 100%); *HRMS*: (EI) found [M + H]$^+$ 424.9403, $C_{16}H_{12}N_2S_6$ requires 424.9402.

5,6-Dihydro-5-(2′,2″-bipyridine-6′-thiomethyl)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-one 29

To a solution of thione **27** (0.30 g, 0.71 mmol) in chloroform (5 ml) was added glacial acetic acid (2 ml) and then mercury(II)

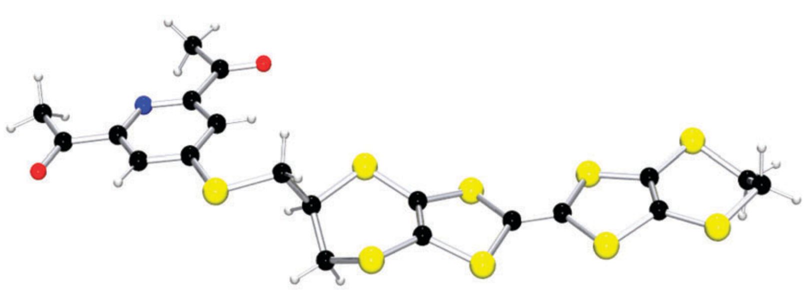


Fig. 3 X-ray structure of **16**.

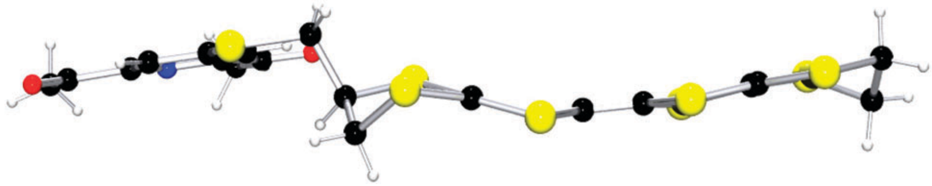


Fig. 4 X-ray structure of **16**.

acetate (0.57 g, 1.78 mmol). This was stirred for 2 h before being filtered. The filtrate was collected and diluted with water (20 ml). The solution was neutralised with sodium bicarbonate and the organic layer separated and dried over $MgSO_4$. Concentration *in vacuo* yielded **29** as a beige solid, (0.27 g, 93%), mp 120–123 °C, δ_H (400 MHz): 8.61 (1H, dm, J = 4.6 Hz, 6″-*H*), 8.27 (1H, dd, J = 7.9, 1.0 Hz, 3″-*H*), 8.11 (1H, dd, J = 7.6, 1.0 Hz, 3′-*H*), 7.78 (1H, dt, J = 7.8, 1.7 Hz, 4″-*H*), 7.59 (1H, dt, J = 7.9, 1.0 Hz, 4′-*H*), 7.26 (1H, ddd, J = 7.6, 5.0, 1.3 Hz, 5″-*H*), 7.17 (1H, d, J = 7.8 Hz, 5′-*H*), 4.11 (1H, m, 5-*H*), 3.97 (1H, dd, J = 14.0, 4.4 Hz, 6-H_α), 3.55 (3H, m, 6-H_β, CH_2Sbipy); δ_C (100 MHz): 188.5 (2-*C*), 155.9 (6′-*C*), 155.8 (2′-*C*), 155.3 (2″-*C*), 149.2 (6″-*C*), 137.3 (4′-*C*), 136.9 (4″-*C*), 123.9 (5″-*C*), 122.5 (5′-*C*), 120.7 (3″-*C*), 117.3 (3′-*C*), 112.2, 112.1 (sp^2 *C*), 43.6 (5-*C*), 33.8 (6-*C*, *C*H_2Sbipy); ν_{max} (KBr): 1656, 1618, 1558, 1556, 1529, 1506, 1433, 1384, 1260, 1212, 1145, 1097, 1020, 861, 804, 774, 462; *m*/*z*: (CI) 409 ([M]$^+$, 100%); *HRMS*: (CI) found [M + H]$^+$ 408.963, $C_{16}H_{12}NOS_5$ requires 408.963.

(2″,2‴-Bipyridin-6″-ylthiomethyl)-ET 13

A suspension of oxo compound **29** (0.34 g, 0.83 mmol) and unsubstituted thione **31**[25] (0.36 g, 1.60 mmol) in dry triethyl phosphite (15 ml) was heated to 90 °C under nitrogen for 6 h. The solution was allowed to cool and concentrated *in vacuo*. The residue was purified by flash chromatography on silica (1 : 6 EtOAc : cyclohexane) to yield **13** as an orange solid, (0.53 g, 46%), mp 100–103 °C, δ_H (400 MHz): 8.60 (1H, ddd, J = 5.0, 1.7, 1.0 Hz, 6‴-*H*), 8.28 (1H, td, J = 7.9. 1.0 Hz, 3‴-*H*), 8.10 (1H, dd, J = 7.8, 1.0 Hz, 5″-*H*), 7.78 (1H, dt, J = 7.7, 1.7 Hz, 4‴–*H*), 7.58 (1H, t, J = 7.8 Hz, 4″-*H*), 7.25 (1H, ddd, J = 7.5, 4.7, 1.2 Hz, 5‴-*H*), 7.12 (1H, dd, J = 7.9, 0.7 Hz, 3″-*H*), 4.02 (1H, m, 5-*H*), 3.86 (1H, dd, J = 13.9, 4.5 Hz, 6-H_α), 3.39 (1H, dd, J = 14.0 9.7 Hz, 6-H_β), 3.33 (1H, dd, J = 13.5, 5.2 Hz, CH_αSbipy), 3.24 (1H, dd, J = 13.5, 3.2 Hz, CH_βSbipy), 3.22 (4H, s, 5′-,6′-H_2); δ_C (100 MHz): 156.2 (2″-*C*), 156.0 (6″-*C*), 155.5 (2‴-*C*), 149.2 (6‴-*C*), 137.3 (4‴-*C*), 137.1 (4″-*C*), 124.0 (3″-*C*), 122.5 (3‴-*C*), 120.9 (5″-*C*), 117.2 (5‴-*C*), 113.9, 113.9, 113.3, 112.8 (sp^2 *C*), 42.5 (5-*C*), 33.9 (6-*C*), 33.4 (*C*H_2Sbipy), 30.2 (5′-,6′-*C*); ν_{max} (KBr): 2920, 1654, 1575, 1508, 1410, 1246, 1137, 770; *m*/*z*: (APCI) 585 [M + H]$^+$ (57%), 425 (45%), 156 (100%). *HRMS*: (EI) found [M + H]$^+$ 584.8881, $C_{21}H_{16}N_2S_9$ requires 584.8878.

4-Mercapto-2,2′-bipyridine 26

Sodium hydrogen sulfide (4.95 g, 88.4 mmol) was suspended in DMF (50 ml), to it was added 4-chloro-2,2′-bipyridine[27] (1.61 g, 8.43 mmol) and solid KOH (1.39 g, 24.8 mmol). The mixture was heated to reflux under nitrogen atmosphere overnight. After cooling to RT, the mixture was filtered and the filtrate was concentrated under reduced pressure to give a yellow residue. The residue was dissolved in 50 ml H_2O, and neutralised with diluted HCl (2 M). The yellow precipitate was collected and re-dissolved in CH_2Cl_2, and washed twice with H_2O. The organic phase was separated and dried over $MgSO_4$. Removal of solvent afforded **26**[28] as a yellow solid (1.27 g, 80%), mp 162–164 °C, δ_H (400 MHz): 11.20 (1H, br, N*H*), 8.62 (1H, dd, 5.0, 0.9 Hz, 6′-*H*), 8.09 (1H, d, J = 1.8 Hz, 3-*H*), 7.92 (1H, d, J = 7.8 Hz, 3′-*H*), 7.85 (1H, dt, J = 1.3, 7.8 Hz, 4′-*H*), 7.53 (1H, d, J = 6.4 Hz, 6-*H*), 7.46 (1H, dd, J = 6.4, 1.8 Hz, 5-*H*), 7.40 (1H, dd, J = 7.3, 5.1 Hz, 5-*H*); δ_C (DMSO-d$_6$, 100 MHz): 191.3 (C=S), 149.5 (6′-*C*), 148.3 (2′-*C*), 139.8 (2-*C*), 138.2 (4′-*C*), 133.7 (6-C), 129.6 (5-C), 126.4 (3-C), 125.6 (5′-C), 121.3 (3′-C); ν_{max} (KBr): 3413 br, 3053 br, 1606, 1564, 1458, 1411, 1353, 1300, 1210, 1115, 1088, 1051, 993, 824, 781, 713, 606; *m*/*z*: (ES$^+$) 189 [M + H]$^+$; found C: 63.3, H: 4.1, N: 14.8%, $C_{10}H_8N_2S$ requires C: 63.8, H: 4.3, N: 14.9%.

5,6-Dihydro-5-(2′,2″-bipyridine-4′-ylthiomethyl)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-thione 28

Sodium hydride (0.26 g, 50% dispersion in oil, 5.40 mmol) was added to a solution of 4-mercapto-2,2′-bipyridine **26** (0.95 g, 5.05 mmol) in dry DMF (20 ml). After stirring for 40 min, a solution of tosylate **24** (2.06 g, 5.05 mmol) in dry DMF (20 ml) was added and the mixture was stirred under nitrogen for 27 h. The solvent was removed under vacuum and the residue was portioned between CH_2Cl_2 and water. The organic phase was separated and dried over $MgSO_4$. Purification by flash chromatography on silica (CH_2Cl_2/MeOH: 9.5/0.5) gave the product **28** as a yellow solid (1.57g, 73%) mp 73–75 °C, δ_H: 8.61 (1H, td, J = 4.9, 0.8 Hz, 6″-*H*), 8.45 (1H, d, J = 5.2 Hz, 6′-*H*), 8.33 (1H, d, J = 7.9 Hz, 3″-*H*), 8.28 (1H, d, J = 1.7 Hz, 3′-*H*), 7.75 (1H, dt, 7.4, 1.6 Hz, 4″-*H*), 7.25 (1H, m, 5″-*H*), 7.11 (1H, dd, J = 5.2, 2.0 Hz, 5′-*H*), 3.80 (1H, m, 5-*H*), 3.39 (4H, m, 5-CH_2S, 6-H_2); δ_C: 207.4 (*C*=S), 156.4 & 155.2 (2′-,2″-*C*), 149.2 & 149.1 (6′-,6″-*C*), 147.3 (4′-*C*), 137.0 (4″-*C*), 124.2 (5″-*C*), 121.9 & 121.5 (3a-,7a-*C*), 121.4 & 121.3 (3″-,5′-*C*), 118.4 (3′-*C*), 41.2 (5-*C*), 35.0 & 32.7 (5-*C*H_2, 6-*C*); ν_{max} (KBr): 1569, 1559, 1532, 1442, 1379, 1056 787, 729, 702, 512; *m*/*z*: (EI) 424 ([M]$^+$, 100%); *HRMS*: (CI) found 423.9315 [M]$^+$, $C_{16}H_{12}N_2S_6$ requires 423.9319.

5,6-Dihydro-5-(2′,2″-bipyridine-4′-ylthiomethyl)-1,3-dithiolo-[4,5-*b*]-1,4-dithiin-2-one 30

Mercuric acetate (2.17 g, 6.81 mmol) was added to a solution of thione **28** (1.15 g, 2.72 mmol) in $CHCl_3$ (20 ml) and glacial acetic acid (10 ml) and the mixture stirred for 4 h. The yellow filtrate was diluted with water (50 ml), and saturated aqueous $NaHCO_3$ was added to bring the pH to 8–9. The organic phase was separated and washed with water, followed by drying over $MgSO_4$. The product **30** was obtained as a yellow waxy solid (1.08 g, 97%), δ_H: 8.61 (1H, td, J = 4.9, 0.9 Hz, 6″-*H*), 8.44 (1H, d, 5.2 Hz, 6′-*H*), 8.32 (1H, d, J = 8.2 Hz, 3″-*H*), 8.27 (1H, d, J = 2.0 Hz, 3′-*H*), 7.76 (1H, m, 4″-*H*), 7.27 (1H, m, 5″-*H*), 7.11 (1H, dd, J = 5.2, 1.9 Hz, 5′-*H*), 3.81 (1H, m, 5-*H*), 3.41 (2H, m) & 3.51 (2H, m) (5-CH_2, 6-H_2); δ_C: 189.0 (2-*C*), 156.3 & 155.2 (2′-,2″-*C*), 149.2 & 149.1 (6′-,6″-*C*), 147.5 (4′-*C*), 137.0 (4″-*C*), 124.2 (5″-*C*), 121.4 (3″-,5′-*C*), 118.5 (3′-*C*), 112.4 & 112.3 (3a-,7a-*C*), 42.8 (5-*C*), 35.1 & 33.8 (5-CH_2 & 6-*C*); ν_{max} (KBr): 1675, 1568, 1552, 1444, 1377, 785; *m*/*z*: (EI) 408 $[M]^+$; *HRMS*: (EI) found 407.9550 $[M]^+$, $C_{16}H_{12}N_2OS_5$ requires 407.9548.

(2″,2‴-Bipyridine-4″-ylthiomethyl)-ET 14

A suspension of oxo compound **30** (1.08 g, 2.65 mmol) and the unsubstituted thione **31**[25] (1.19 g, 5.30 mmol) in dry triethyl phosphite (20 ml) was heated at 100 °C under nitrogen for 8 h. The mixture was allowed to cool and concentrated *in vacuo*. The residue was purified by flash chromatography on silica (CH_2Cl_2/MeOH: 9.5/0.5) to yield the product **14** as a yellow solid (0.84 g, 54%), mp 137–139 °C, δ_H (400 MHz): 8.67 (1H, ddd, J = 5.1, 1.8, 0.9 Hz, 6‴-*H*), 8.43 (1H, dd, J = 5.2, 0.6 Hz, 6″-*H*), 8.37 (1H, d, J = 7.8 Hz, 3‴-*H*), 8.33 (1H, d, J = 1.6 Hz, 3″-*H*), 7.82 (1H, dt, J = 7.8, 1.8 Hz, 4‴-*H*), 7.32 (1H, ddd, J = 7.8, 5.1, 1.1 Hz, 5‴-*H*), 7.17 (1H, dd, J = 5.2, 1.8 Hz, 5″-*H*), 3.80 (1H, m, 5-*H*), 3.37 (4H, m, 6-H_2, 5-CH_2), 3.28 (4H, s, 5′-,6′-H_2); δ_C (100 MHz): 156.3 & 156.2 (2″-,2‴-*C*), 149.2 (6‴-*C*), 149.1 (6″-*C*), 147.8 (4″-*C*), 137.0 (4‴-*C*), 124.1 (5‴-*C*), 121.5 (3‴-*C*), 121.3 (5″-*C*), 118.5 (3″-*C*), 41.5 (5-C), 35.0 & 33.3 (5-CH_2, 6-*C*), 30.2 (5′-,6′-*C*); ν_{max} (KBr): 1571, 1555, 1534, 1446, 1410, 1379, 787; *m*/*z*: (ES) 585 $[M + H]^+$; found C: 43.2, H: 2.6, N: 4.6%, $C_{21}H_{16}N_2S_9$ requires C: 43.1, H: 2.8, N: 4.8%.

5-Acetyloxymethyl-5,6-dihydro-[1,3]dithiolo[4,5-*b*][1,4]dithiine-2-thione 36

A suspension of trithione **22** (4.97 g, 25.3 mmol) and allyl acetate (4.10 g, 41 mmol) in toluene (100 ml) was heated to reflux for 12 h then cooled and filtered. The solid residue was washed with chloroform and the combined filtrates collected, decolourised with charcoal then purified by flash chromatography on silica gel eluting with 1 : 1 cyclohexane : ethyl acetate to yield **36** (5.4 g, 72%) as a red oil; δ_H: 4.36 (m, 2H, CH_2O), 3.94 (m, 1H, 5-*H*), 3.34 (dd, 1H, J = 13.6, 3.2 Hz, 6-H_α), 3.26 (dd, 1H, J = 13.6, 5.7 Hz, 6-H_β), 2.08 (s, 3H, COCH_3); δ_C: 207.5 (*C*=S), 170.3 (*C*=O), 122.2, 122.1 (3a-, 7a-*C*) 64.3 (CH_2O), 42.4 (5-*C*), 31.3 (6-*C*), 20.7 (CH_3); ν_{max} (film): 2923, 2848, 1738, 1487, 1379, 1219, 1057, 8921, 786; *m*/*z*: (EI^+) 296 ($[M]^+$, 100%); *HRMS*: (EI) found 295.9134 $[M]^+$, $C_8H_8O_2S_5$ requires 295.9127.

5-Acetyloxymethyl-5,6-dihydro-[1,3]dithiolo-[4,5-*b*][1,4]dithiine-2-one 37

To a solution of thione **36** (3.37 g, 11.4 mmol) in chloroform (40 ml) was added glacial acetic acid (10 ml) and mercuric acetate (9.11 g, 28.5 mmol). A white precipitate could be seen to form almost immediately. The mixture was stirred for 2 h, filtered and the solid residue washed with chloroform. The combined filtrates were collected and neutralised with sodium hydrogen carbonate. The organic layer was collected, washed with water, dried over $MgSO_4$ and concentrated to yield **37** (2.88 g, 90%) as a beige solid; mp 76–79 °C; δ_H: 4.34 (m, 2H CH_2O), 3.92 (m, 1H, 5-*H*), 3.32 (dd, 1H, J = 13.6, 3.2 Hz, 6-H_α), 3.18 (dd, 1H, J = 13.6, 5.9 Hz, 6-H_β), 2.04 (s, 3H, COCH_3); δ_C: 188.4 (O=*C*S_2), 170.3 (O*C*(O)CH_3), 113.5, 113.0 (3a-, 7a-*C*), 64.5 (CH_2O), 43.2 (5-*C*), 32.4 (6-*C*), 20.7 (C(O)CH_3); ν_{max} (KBr): 2917, 1743, 1670, 1634, 1382, 1361, 1250, 1216, 906, 894, 855, 764, 646, 467; *m*/*z*: (EI^+) 280 ($[M]^+$, 100%); *HRMS*: (EI) found 279.9362 $[M]^+$, $C_8H_8O_3S_4$ requires 279.9356.

Acetyloxymethyl-ET 38

A mixture of oxo compound **37** (2.83 g, 10.1 mmol) and unsubstituted thione **31**[25] (4.51 g, 20.1 mmol) was heated in triethyl phosphite (50 ml) to 80 °C under N_2 for 20 h to give an orange solution. Triethyl phosphite was removed by distillation *in vacuo* and the residue purified by flash chromatography on silica gel eluting with 5 : 1 cyclohexane : ethyl acetate to yield a red solid which was recrystallised from methanol to yield **38** (3.21 g, 70%) as a orange solid; mp 111–112 °C; δ_H (400 MHz): 4.26 (2H, d, J = 7.3 Hz, −CH_2O), 3.81 (1H, m, 5-*H*), 3.22 (4H, s, 5′-, 6′-H_2), 3.17 (1H, dd, J = 13.2, 3.2 Hz, 6-H_α), 3.09 (1H, dd, J = 13.2, 5.8 Hz, 6-H_β), 2.01 (3H, s, CH_3); δ_C (100 MHz): 170.4 (*C*=O), 113.9, 113.8, 112.0, 111.2 (sp^2-*C*), 64.6 (CH_2O), 41.9 (5-*C*), 32.1 (6-*C*), 30.1 (5′-, 6′-*C*), 20.7 (CH_3); ν_{max} (KBr): 2917, 1743, 1670, 1634, 1382, 1361, 1250, 1216, 906, 894, 855, 764, 646; *m*/*z*: (ES) 456 ($[M]^+$, 25%), 88 (100%); *HRMS*: (ES) found 456.8676 $[M + H]^+$, $C_{13}H_{12}O_2S_8$ requires 456.8678.

Hydroxymethyl-ET (HMET) 39

A solution of ester **38** (0.65 g, 1.40 mmol) in THF (10 ml) and 20% HCl solution (5 ml) was stirred under N_2 for 24 h. The solution was neutralised by the addition of solid $NaHCO_3$. The organic layer was collected, washed with brine and dried over Na_2SO_4. Removal of solvent yielded **39**[30.31] (0.56 g, 96%) as an orange solid, mp 178–181 °C (dec.); δ_H: 3.74 (3H, m, CH_2OH & 5-*H*), 3.32 (4H, s, 5′-, 6′-H_2), 3.30 (1H, dd, J = 13.5, 5.0 Hz, 6-H_α), 3.22 (1H, dd, J = 13.5, 3.4 Hz, 6-H_β), 1.58 (1H, s, O*H*); δ_C: 114.5, 113.5, 113.0, 111.2, 111.1 (sp^2-*C*), 63.9 (CH_2OH), 45.5 (5-*C*), 31.7 (6-*C*), 30.1 (5′-, 6′-*C*); ν_{max} (KBr): 2918, 1409, 1284, 1259, 1055, 1000, 909, 886, 772; *m*/*z*: (EI) 414 $[M]^+$.

Tosyloxymethyl-ET 40

Hydroxymethyl-ET **39** (0.28 g, 0.68 mmol) and tosyl chloride (1.21 g, 6.30 mmol) were dissolved in dry pyridine (15 ml), and the solution stirred for 20 h under nitrogen. The solution was added to iced water (40 ml) and the yellow precipitate collected by filtration, and washed with H_2O and MeOH. The solid was redissolved in CH_2Cl_2, and washed with aqueous HCl (2 M) and then H_2O. The organic phase was dried over $MgSO_4$, and the solution evaporated to give the product **40** as an orange solid (0.33 g, 85%), mp 60–62 °C, δ_H: 7.71 (2H, d, J = 8.5 Hz, Ar-H_2), 7.29 (2H, d, J = 8.5 Hz, Ar-H_2), 4.22 (1H, t, J = 10.1 Hz, CH_βO), 4.07 (1H, dd, J = 10.1, 5.1 Hz, CH_αO), 3.82 (1H, m, 5-H), 3.22 (4H, s, 5′-,6′-H_2), 3.18 (2H, m, 6-H_2), 2.40 (3H, s, CH_3); δ_C: 145.4 (4″-C), 132.2 (1″-C), 130.1 (3″-,5″-C), 128.0 (2″-,6″-C), 113.9, 113.5 & 112.8 (sp^2-C), 68.9 (CH$_2$O), 40.8 (5-C), 31.2 (6-C), 30.1 (5′-,6′-CH$_2$), 21.7 (CH$_3$); ν_{max} (KBr): 1358, 1187, 1171, 1088, 953, 912, 808, 767, 668, 569, 549; m/z: (EI) 568 ([M]$^+$, 100%); Found C: 37.9, H: 2.7%, $C_{18}H_{16}O_3S_9$ requires C: 38.0, H: 2.8%.

4′-Mercapto-2,2′:6′,2″-terpyridine 33

The compound was prepared quantitatively from 4′-chloro-2,2′:6′,2″-terpyridine **32** following the procedure used for 4-mercapto-2,2′-bipyridine, to give the product **33**[29] as a bright yellow solid (99%) , mp 230–235 °C, δ_H (400 MHz): 12.46 (1H, br, NH), 8.73 (2H, br d, J = 4.4 Hz, 6-,6″-H), 8.06 (2H, s, 3′-,5′-H), 7.98 (2H, d, J = 7.9 Hz, 3-,3″-H), 7.83 (2H, dt, J = 7.7, 1.1 Hz, 4-,4″-H), 7.40 (2H, dd, J = 7.0, 5.1 Hz, 5-,5″-H); δ_C (100 MHz): 193.5 (C=S), 149.8 (6-,6″-C) , 147.7 (2-,2″-C), 139.0 (2′-,6′-C), 137.7 (4-,4″-C), 126.6 (3′-,5′-C), 125.4 (5-,5″-C), 120.5 (3-,3″-C); ν_{max} (KBr): 3249, 1607, 1566, 1483, 1462, 1451, 1327, 1265, 1115, 1099, 1077, 1062, 990, 881, 845, 782, 730, 699, 678, 616, 585, 466; m/z: (ES) 266 ([M + H]$^+$, 100%).

(2″,2‴:6‴,2⁗-Terpyridine-4‴-ylthiomethyl)-ET 15

Sodium hydride (0.037 g, 50% dispersion in oil, 0.77 mmol) was added to a solution of 4′-mercapto-2,2′:6′,2″-terpyridine **33** (0.20 g, 0.76 mmol) in dry DMF (8 ml). After stirring for 40 min, a solution of tosyloxymethyl-ET **40** (0.46 g, 0.80 mmol) in dry DMF (10 ml) was added and the mixture was stirred under nitrogen for 48 h. Solvent was removed under vacuum and the residue was portioned between CH_2Cl_2 and water. The organic phase was separated and dried over $MgSO_4$. Removal of solvent afforded a brown residue which was purified by flash chromatography on silica (CH_2Cl_2/MeOH: 19/1) to give the product **15** a yellow solid (0.33 g, 65%), mp 200–202 °C, δ_H (400 MHz): 8.62 (2H, ddd, 4.7, 1.8, 0.9 Hz, 6″-,6⁗-H), 8.51 (2H, dd, J = 7.9, 1.0 Hz, 3″-,3⁗-H), 8.31 (2H, s, 3‴-5‴-H), 7.78 (2H, dt, J = 7.8, 1.8 Hz, 4″-,4⁗-H), 7.28 (2H, ddd, J = 7.8, 4.7, 1.0 Hz, 5″-,5⁗-H), 3.81 (1H, m, 5-H), 3.58 (1H, dd, J = 14.3, 5.0 Hz, 5-CH_αSterpy), 3.45 (1H, dd, J = 14.3, 9.7 Hz, 5-CH_βSterpy), 3.35 (1H, dd, J = 13.2, 5.1 Hz, 6-H_α), 3.27 (1H, dd, J = 13.2, 3.2 Hz, 6-H_β), 3.21 (4H, s, 5′-,6′-H_2); δ_C (100 MHz): 155.4 (2″-,2‴-,6‴-,2⁗-C), 149.1 (6″-,6⁗-C), 148.9 (4‴-C), 137.0 (4″-,4⁗-C), 124.1 (5″-,5⁗-C), 121.4 (3″-,3⁗-C), 118.4 (3‴-,5‴-C), 113.8, 113.0, 112.8, 112.0 & 111.4 (sp^2-C), 41.6 (5-C), 34.8 (5-CH$_2$Sterpy), 33.3 (6-C), 30.2 (5′-,6′-C); ν_{max} (KBr): 1576, 1550, 1467, 1405, 1389, 1259, 808, 782, 730, 673; m/z: (CI) 662 [M + H]$^+$. Found C 45.9, H 2.7, N 5.9%, $C_{26}H_{19}N_3S_9 \cdot H_2O$ requires C 45.9, H 3.1, N 6.2%.

(2″,2‴-Bipyridine-4″-ylthiomethyl)-ET 14 (from 40)

Sodium hydride (0.058 g, 50% dispersion in oil, 1.21 mmol) was added to a solution of 4-mercapto-2,2′-bipyridine (0.22 g, 1.17 mmol) in dry DMF (10 ml). After stirring for 40 min, a solution of tosyloxymethyl-ET (0.68 g, 1.20 mmol) in dry DMF (15 ml) was added and the mixture was stirred under nitrogen for 48 h. Solvent was removed under vacuum and the residue was portioned between CH_2Cl_2 and water. The organic phase was separated and dried over $MgSO_4$. Removal of solvent afforded a brown residue which was purified by flash chromatography on silica (CH_2Cl_2/MeOH: 9.5/0.5) to give the product as a yellow solid. Yield, 0.44 g, 65%.

4-Mercapto-2,6-diacetylpyridine

4-Chloro-2,6-diacetylpyridine[32] (0.57 g, 2.88 mmol) and solid KOH (0.48 g, 8.6 mmol) were added to a suspension of sodium hydrogen sulfide (1.56 g, 28.0 mmol) in DMF (50 ml). The mixture was heated to reflux under nitrogen atmosphere for 62 h. After cooling to room temperature, the mixture was filtered and the filtrate was concentrated under reduced pressure to give a brown residue. The residue was dissolved in H_2O (15 ml), and neutralised with diluted HCl (2 M). The yellow precipitate was collected by filtration and re-dissolved in CH_2Cl_2, and the bright yellow solution was washed with H_2O and brine, respectively. The organic phase was separated and dried over $MgSO_4$. Removal of solvent afforded the title product as a brown solid which was used for next step without further purification (0.40 g, 70%). mp 92–95 °C. δ_H(400 MHz): 7.95 (2H, s, 3-,5-H), 3.80 (1H, s, SH), 2.70 (6H, s, 2 × CH_3); δ_C (100 MHz): 199.0 (2 × C=O), 152.5 (2-,6-C), 147.1 (4-C), 123.3 (3-,5-C), 25.6 (2 × CH_3); ν_{max} (KBr): 1699, 1571, 1412, 1360, 1308, 1230, 892, 806, 608, 499; m/z: (ES$^+$) 196 [M + H]$^+$, 218 [M + Na]$^+$; *HRMS*: (CI) found 196.0428 [M + H]$^+$, $C_9H_{10}NO_2S$ requires 196.0427.

(2″,6″-Diacetylpyridine-4″-ylthiomethyl)-ET 16

Sodium hydride (0.023 g, 50% dispersion in oil, 0.48 mmol) was added to a solution of 4-mercapto-2,6-diacetylpyridine (0.09 g, 0.46 mmol) in dry DMF (4 ml). After stirring overnight, a solution of tosyloxymethyl-ET **40** (0.27 g, 0.48 mmol) in dry DMF (7 ml) was added and the mixture was stirred under nitrogen for 6 d. Solvent was removed under vacuum and the brown residue was partitioned between CH_2Cl_2 and water. The organic phase was separated and washed with brine, dried over $MgSO_4$. Removal of solvent afforded a brown oily residue which was purified by flash chromatography on silica eluted with CH_2Cl_2 and **16** was obtained as an orange solid (0.19 g, 70%), mp 180–183 °C, δ_H (400 MHz): 8.00 (2H, s, 3″-,5″-H), 3.75 (1H, m, 5-H), 3.52 (1H, dd, J = 12.8, 5.0 Hz, 6-H_α), 3.45 (1H, dd, J = 12.8, 7.8 Hz, 6-H_β), 3.32 (2H, d, J = 4.2 Hz, CH_2S), 3.28 (4H, s, 5′-,6′-H_2), 2.75 (6H, s, 2 × CH_3); δ_C (100 MHz): 199.0 (2 × C=O), 152.6 (2″-,6″-C), 150.5 (4″-C), 121.4 (3″-,5″-C), 113.8, 112.9, 112.6, 112.5, 101.8 (sp^2-C), 41.1 (5-C), 34.9 (6-C), 33.4 (CH$_2$S), 30.1 (5′-,6′-C), 25.6 (2 × CH$_3$); ν_{max} (KBr): 1696, 1570, 1408, 1359, 1304, 1260, 1228, 800, 732, 606; m/z: (ES) 591 [M]$^+$; found C: 38.9, H: 2.8, N: 2.1%. $C_{20}H_{17}NO_2S_9 \cdot 0.5CH_2Cl_2$ requires: C: 38.9, H: 2.8, N: 2.2%.

Nicotinic acid, HMET ester 17

N,N'-dicyclohexylcarbodiimide (0.12 g, 0.6 mmol) was added to a solution of HMET **39** (0.19 g, 0.46 mmol), picolinic acid

(0.10 g, 0.6 mmol) and 4-dimethylaminopyridine (5 mg) in dry dichloromethane (10 ml). The mixture was stirred for 20 h at RT, after which the mixture was concentrated and purified by silica gel column chromatography eluting with 5 : 1 cyclohexane : ethyl acetate to yield **17** (0.12 g, 50%) as an orange solid, mp 175–176 °C; δ_H (400 MHz, DMSO-d$_6$): 9.12 (1H, dd, J = 2.1, 0.6 Hz, 2″-*H*), 8.82 (1H, dd, J = 4.8, 1.7 Hz, 6″-*H*), 8.33 (1H, dt, J = 7.9, 2.0 Hz , 4″-*H*), 7.58 (1H, ddd, J = 7.9. 4.9, 0.8 Hz, 5″-*H*), 4.55 (1H, dd, J = 11.2, 7.2 Hz, CH_αO), 4.49 (1H, dd, J = 11.2, 6.3 Hz, CH_βO), 4.33 (1H, m, 5-*H*), 3.52 (1H, dd, J = 13.6, 5.5 Hz, 6-H_α), 3.44 (1H, dd, J = 13.6, 3.4 Hz, 6-H_β), 3.39 (4H, s, 5′-,6′-H_2); δ_C (100 MHz, DMSO-d$_6$): 164.3 (*C*=O), 153.9 (6″-C), 150.2 (2″-*C*), 137.0 (4″-*C*), 125.2 (3″-*C*), 123.9 (5″-*C*), 113.2, 112.9, 110.8, 110.0 (sp^2-*C*), 65.1 (*C*H$_2$O), 41.6 (5-*C*), 31.5 (6-*C*), 29.5 (5′-.6′-*C*); ν_{max} (KBr): 1723, 1636, 1617 1384, 1276, 1109, 1023 738, 618; *m*/*z*: (ES) 520 [M + H]$^+$; *HRMS*: (ES) found 519.8780 [M + H]$^+$. $C_{17}H_{13}NO_2S_8$ + H requires 519.8785.

Picolinic acid, HMET ester 18

Reaction of HMET **39** and picolinic acid, following to the procedure for **17** above gave **18** (0.13 g, 54%) as an orange solid; mp 163–165 °C, δ_H (400 MHz, DMSO-d$_6$): 8.73(1H, d, J = 4.6 Hz, 6″-*H*), 8.08 (1H, d, J = 7.8 Hz, 3″-*H*), 8.00 (1H, dt, J = 7.7, 1.2 Hz, 4″-*H*), 7.66 (1H, dd, J = 7.8, 4.6 Hz, 5″-*H*), 4.49 (1H, dd, J = 11.2, 7.1 Hz, CH_αO), 4.42 (1H, dd, J = 11.2, 6.7 Hz, CH_βO), 4.32 (1H, m, 5-*H*), 3.47 (1H, dd, J = 13.5, 5.3 Hz, 6-H_α), 3.42 (1H, dd, J = 13.5, 3.7 Hz, 6-H_β); 3.38 (4H, s, 5′-,6′-H_2); δ_C (100 MHz, DMSO-d$_6$): 164.1 (*C*=O), 149.9 (6″-*C*), 147.0 (2″-*C*), 137.5 (4″-*C*), 127.6 (5″-*C*), 125.2 (3″-*C*), 113.3, 113.2, 112.9, 110.8, 110.0 (sp^2-*C*), 65.3 (*C*H$_2$O), 41.7 (5-*C*), 31.6 (6-*C*), 29.5 (5′-.6′-*C*); ν_{max} (KBr): 1741, 1723, 1306, 1280, 1277, 1243, 1133, 1087, 771, 740, 699; *m*/*z*: (ES) 520 [M + H]$^+$; *HRMS*: (ES) found 519.8781 [M + H]$^+$. $C_{17}H_{13}NO_2S_8$ + H requires 519.8785.

3-Thienylmethoxyacetic acid, HMET ester 41

To a solution of HMET **39** (0.19 g, 0.46 mmols), (thiophen-3-yl) methoxyacetic acid (0.10 g, 0.6 mmols) and 4-dimethylaminopyridine (0.005 g) in dry dichloromethane (10 ml) was added *N*,*N*′-dicyclohexylcarbodiimide (0.12 g, 0.6 mmols). The mixture was stirred for 20 h at RT, after which the mixture was concentrated and purified by silica gel column chromatography eluting with 5 : 1 cyclohexane : ethyl acetate to yield **41** (0.19 g, 73%) an oily orange solid; δ_H: 7.26 (1H, dd, J = 3.0, 5.0 Hz, 5″-*H*), 7.19 (1H, br m, 2″-*H*), 7.03 (1H, dd, J = 1.1, 5.0 Hz, 4″-*H*), 4.58 (2H, s, OCH_2Ar), 4.32 (2H, d, J = 7.2 Hz, CH_2O), 4.05 (2H, s, C(=O)CH_2O), 3.82 (1H, m, 5-*H*), 3.21 (4H, s, 5′-,6′-H_2), 3.16 (1H, dd, J = 3.5 13.5 Hz, 6-H_α), 3.06 (1H, dd, J = 5.5, 13.5 Hz, 6-H_β); δ_C: 169.8 (*C*=O), 137.9 (3″-*C*), 127.4 (2″-*C*), 126.4 (5″-*C*), 123.8 (4″-*C*), 113.7 (sp^2-*C*), 68.4 (O*C*H$_2$Ar), 66.7 (C(O)*C*H$_2$O), 64.7 (*C*H$_2$O), 41.7 (5-*C*), 32.5 (6-*C*), 30.1 (5′-, 6′-*C*); ν_{max} (KBr): 2910, 2848, 1744, 1697, 1656, 1401, 1277, 1183, 1158, 1116, 991, 903, 851, 768, 727, 691, 628, 566, 499; *m*/*z*: (EI) 569 ([M + H]$^+$, 10%), 230 (100%); *HRMS*: (EI) found 567.8575 [M]$^+$, $C_{18}H_{16}O_3S_9$ requires 567.8580.

X-Ray crystallography for 16 and 40

Data was collected by the EPSRC National Crystallography Service on a Bruker-Nonius FR591 diffractometer equipped with a rotating anode source and CCD camera using Mo Kα radiation at 120 K, and structures were solved and refined with SHELXS-97 and refined with SHELXL-97.[33]

Crystal data for 16. $C_{20}H_{17}NO_2S_9.0.5CH_2Cl_2$, M_r = 634.35, triclinic, a = 7.8542(1), b = 11.9820(2), c = 14.1992(3) Å, α = 90.439(1), β = 92.745(1), γ = 101.822(1)°, V = 1306.2 Å^3, Z = 2, $P\bar{1}$, D_c = 1.61 g cm^{-3}, μ(Mo Kα) = 0.89 mm^{-1}, T = 120 K, 5986 unique reflections, 5172 with $F_o > 4\sigma(F_o)$, R = 0.038, wR = 0.084. Orange X-ray quality single crystals were obtained by layering hexane onto a concentrated solution of the compound in dichloromethane. A molecule of the latter solvent is included in the crystal structure, and lies near the centre of symmetry which relates the two chlorine atoms, but the position of the methylene group is disordered.

Crystal data for 40. $C_{18}H_{16}O_3S_9$, M$_r$ = 568.85, triclinic, a = 6.2490(1), b = 11.0486(3), c = 16.4757(4) Å, α = 82.167(2), β = 82.328(2), γ = 87.627(2)°, V = 1116.5 Å^3, Z = 2, $P\bar{1}$, D_c = 1.69 g cm^{-3}, μ (Mo Kα) = 0.91 mm^{-1}, T = 120 K, 5118 unique reflections, 4486 with $F_o > 4\sigma(F_o)$, R = 0.039, wR = 0.107. Light brown X-ray quality single crystals were obtained by layering hexane onto a concentrated solution of the compound in CH_2Cl_2. The structure is disordered 87 : 13 between two structures in which the ET and 4-$CH_3C_6H_4$ fragments occupy very similar positions, but with the different points of attachment of the tosyloxymethyl sidechain to the ethylene bridge of the ET moiety.

CCDC reference numbers 616013 and 616014. For crystallographic data in CIF or other electronic format see DOI: 10.1039/b606715h

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