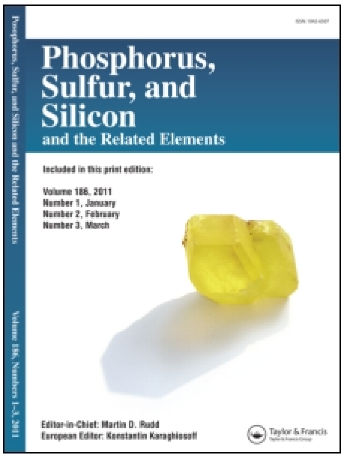

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Synthesis and Properties of New Functionalised Tetrathiafulvalene (TTF) π-Electron Donors

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SYNTHESIS AND PROPERTIES OF NEW FUNCTIONALISED TETRATHIAFULVALENE (TTF) π-ELECTRON DONORS

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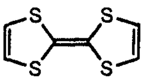
Abstract The synthesis, solution electrochemistry, and X-ray crystal structures of a wide range of highly-functionalised TTF derivatives are presented.

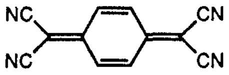
INTRODUCTION

There is currently considerable interest in organic materials that possess special solid state properties, notably high electrical conductivity. The first organic metal was the charge-transfer complex formed by the donor tetrathiafulvalene (TTF) **1** and the acceptor tetracyano-*p*-quinodimethane (TCNQ) **2**.[1] A large number of metallic organic charge-transfer solids are now known. They are composed of highly ordered arrays of donor and acceptor species, one or both of which must be a radical ion which is thermodynamically stable. The materials can be either single-chain conductors, *eg*. salts of tetramethyltetraselenafulvalene of general formula $(TMTSF)_2^{+\cdot}$ X^-, where the anion is a closed shell species, or two-chain conductors, *eg*. $TTF^{+\cdot}$-$TCNQ^{-\cdot}$ charge-transfer complexes, in which both components are open-shell species. The presence of a supermolecular orbital extending throughout the crystal lattice provides a mechanism for metallic delocalisation of electrons, with the width of the conduction band dependent upon interactions between molecular orbitals of neighbouring molecules. Planarity (or near planarity) of the radical ion species is, in general, a prerequisite for efficient intermolecular delocalisation of charge carriers. Transport properties in organic conductors are usually highly anisotropic (hence, they are termed 'one-dimensional metals'). An increase in the dimensionality of these materials, which can be achieved by close interstack chalcogen-chalcogen interactions, is known to stabilise the metallic state by suppressing lattice instabilities (Peierls distortions). For some materials, especially salts of the cation radical of BEDT-TTF **3** with inorganic anions, a superconducting state is attained at very low temperatures (<12 K).[2]

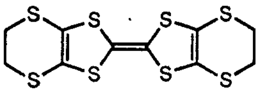
The global challenge for chemists working on conducting charge-transfer materials is the preparation of new molecular systems which meet the stringent requirements, both at the intra- and inter-molecular level, for high conductivity or superconductivity. Since our ability to induce molecules to pack within a crystal lattice in a prescribed manner (*eg*. in sheets, stacks or dimer pairs) is still very limited, the rational design of organic metals is essentially restricted to controlling the key properties of the individual component molecules which can be deduced *a priori*, *eg*. planarity, ionisation potential / electron affinity, extent of conjugation *etc*. The field has been reviewed regularly over the last few years.[3-9]



1 TTF



2 TCNQ



3 BEDT-TTF

NEW TETRATHIAFULVALENE (TTF) DONORS

Our recent work has concerned modification of the TTF framework in two distinct ways. These are:

(i) extending the π–electron conjugation between the two 1,3-dithiole rings by incorporation of cyclic or vinylogous 'spacer' groups;

(ii) attachment of functional groups to the periphery of the TTF molecule.

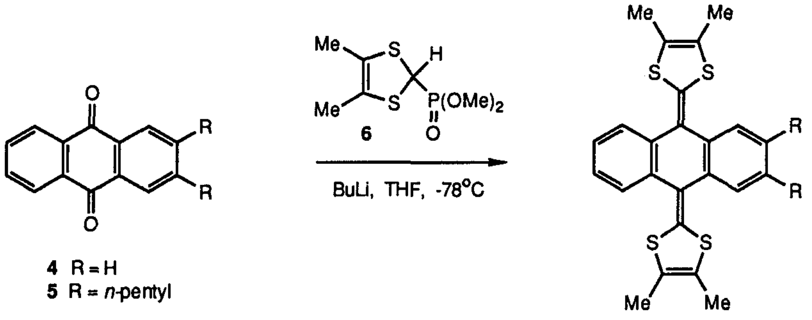
These two topics will now be considered in turn. We will emphasise the new synthetic methodology that has underpinned this work, and describe the solution electrochemistry and X-ray crystal structures of several of the new TTF donors. Complexation studies, *eg*. with TCNQ **2**, will also be mentioned for selected materials.

Extended TTF Systems Possessing Cyclic 'Spacer' Groups.

Several donor molecules in this family have been synthesised in our laboratory[10-15] and by other workers.[16-19] Interest in these systems stems from the significantly different redox and conformational properties they should display, compared to TTF **1**. 1,3-Dithiole Horner-Wittig reagents, *eg*. compound **6**, are key intermediates in many of the syntheses. Anthracenediylidene derivatives **7** and **8** have been prepared in one step from the corresponding anthraquinones **4** and **5**, respectively, and reagent **6**.[12,14,15]

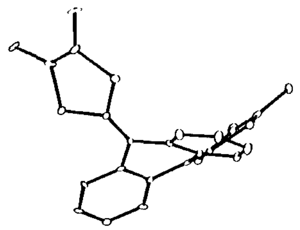
The X-ray crystal structures of both donors **7**[13] (Figure 1) and **8**[15] have been obtained. The molecules are butterfly-shaped with the central quinonoid ring severely distorted into a boat form. Compound **7** forms a highly conductive 1:4 complex with TCNQ **2**, the electronic, magnetic and structural properties of which have been studied.[13]

Static susceptibility data establish that the donor is present as the dication in the complex 7^{2+} $[(TCNQ)_4]^{2-\cdot}$. The X-ray crystal structure of the complex reveals a remarkable packing arrangement (Figure 2). Donor 7, in the dication form, adopts a dramatically different conformation from that of the neutral species, with dihedral angles of 86.0° between the planar anthracene group and the two 1,3-dithiolium cation rings. This conformation effectively removes the conjugation between the two heterocyclic rings. The TCNQ molecules stack plane-to-plane, parallel to *a*, with typical ring-over-bond overlap and a uniform intermolecular spacing of 3.36 Å. The room temperature conductivity value of the complex, σ_{rt} = 60 Scm^{-1}, varies only slightly upon cooling to 90 K, but then decreases abruptly, presumably due to a structural transition. The high conductivity is attributed to delocalised electrons on the TCNQ stacks.



SCHEME 1

7 R=H
8 R = *n*-pentyl



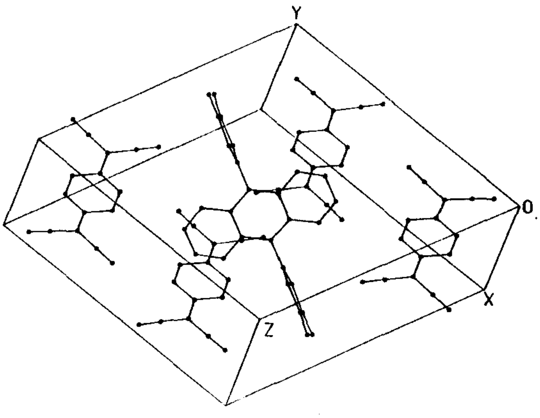


FIGURE 1. X-Ray molecular structure of neutral compound 7.

FIGURE 2. X-Ray crystal structure of the complex 7^{2+} $[(TCNQ)_4]^{2-\cdot}$

The dipentyl derivative **8** was prepared to enable the solution redox properties of the system to be investigated by cyclic voltammetry;* the presence of the alkyl side-chains considerably increases the solubility of the cationic redox states, especially at low temperatures where the most informative data are obtained. At -70°C three distinct oxidation waves are seen (Figure 3).[15] The first redox wave (E_{ox} = +0.28 V) is a quasi-reversible two-electron transfer to yield the dication species 8^{2+}; subsequently there are two further, sequential, one-electron oxidations of the anthracene system. The first anthracene oxidation ($E_3{}^{1/2}$ = +1.64 V) is cleanly reversible, whereas the second anthracene oxidation ($E_4{}^{1/2}$ = *ca.* +2.2 V) is at the limit of the solvent 'window' and is thus irreversible.

The first two-electron transfer step for system **8** has been examined carefully in an attempt to detect the radical cation species. However, even at -80°C using scan rates varying from 20 mV-50 Vsec^{-1}, there is still only one observable wave. The potential of this oxidation is temperature independent; however, the reduction peak of dication 8^{2+} -> neutral **8** in the back sweep is shifted progressively to more negative potentials with decreasing temperature (Figure 3). This is undoubtedly a reflection of the stability of the planar, anthracene system, together with the additional stabilisation within the 6π, 1,3-dithiolium rings at the dication redox stage. The marked conformational change that accompanies reduction of the dication to the buckled, neutral anthraquinodimethane structure accounts for the temperature dependence and the irreversibility of this step.

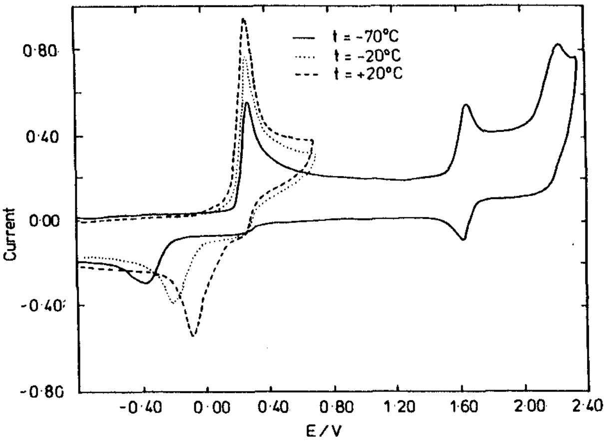


FIGURE 3. Cyclic voltammograms of compound **8** at various temperatures.

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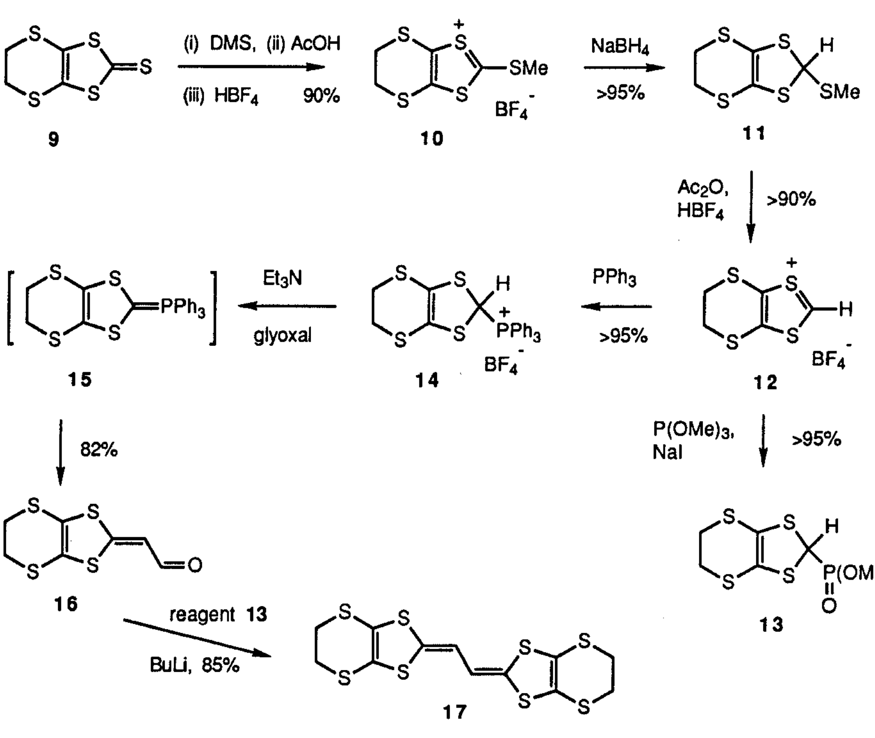
* All cyclic voltammetric data reported in this paper are *versus* Ag/AgCl.

Vinylogous TTF and BEDT-TTF Derivatives

These systems have been studied extensively in recent years.[20-26] Separation of the 1,3-dithiole rings by vinyl groups reduces on-site Coulombic repulsion in the dication state, and, hence, a non-correlated type of conductivity may be possible. The vinylogues are conformationally flexible (in contrast to compounds **7** and **8**) and may, therefore, adopt planar conformations, favouring close packing in the solid state.

We synthesised the vinylogue **17** of BEDT-TTF[22] concurrently with two other groups.[23,24] The synthetic route to **17** is shown in Scheme 2.[14,22] Pivotal steps involve the use of the novel Horner-Wittig and Wittig reagents **13** and **14**.



SCHEME 2

Cyclic voltammetry has established the solution redox behaviour of vinylogue **17**. Figure 4 shows the voltammogram of compound **17** along with those of TTF **1** and BEDT-TTF **3**, obtained under identical conditions, for comparison. All three molecules undergo two reversible, single-electron oxidations. Two important consequences of 'stretching' the conjugated π-system are observed: (i) both the first and second oxidation potentials of **17** are lowered in comparison with BEDT-TTF **3**, *ie*. molecule **17** is a stronger donor than BEDT-TTF, and (ii) the difference between the two redox waves, $\Delta E^{1/2}$, is reduced in the vinylogue. This is evidence of reduced intramolecular Coulombic repulsion in the dication. However, unlike compound **8** (Figure 3) for which the waves for $E_1{}^{1/2}$ and $E_2{}^{1/2}$ coalesce, the radical cation of compound **17** is observed.

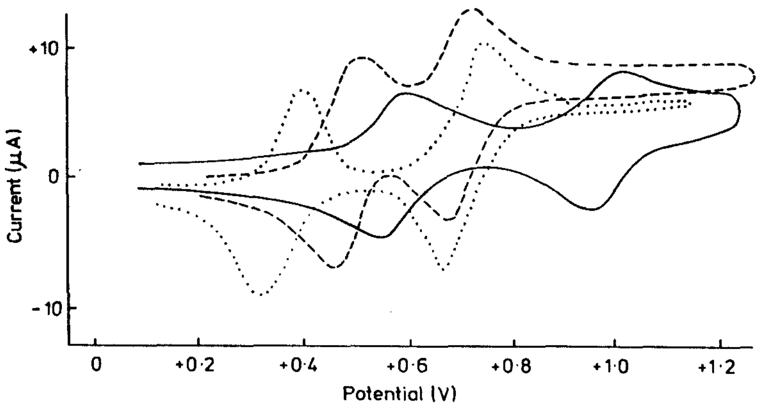
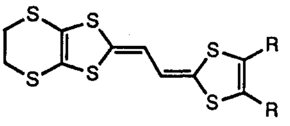
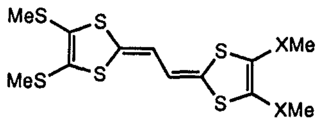


FIGURE 4. Cyclic voltammograms of compounds **1** (····), **3** (——) and **17** (----).

We have applied the route outlined in Scheme 2 to the synthesis of a range of vinylogues, *eg*. **18** and **19**.[22,25,26] The X-ray crystal structure of the unsymmetrical derivative **18**[22] and the symmetrical derivative **20**[27] are shown in Figures 5 and 6, respectively. Compound **21**, which has peripheral methylseleno groups is isostructural with compound **20**.[25] The 2,2'-ethanediylidenebis(1,3-dithiole) framework of the neutral compounds **18**, **20** and **21** is planar. The molecules of compound **20** and **21** stack uniformally with several intermolecular S---S(Se) contacts close to the sum of the van der Waals radii.



18 R = Me
19 R - R = S-$(CH_2)_3$-S



20 X = S
21 X = Se

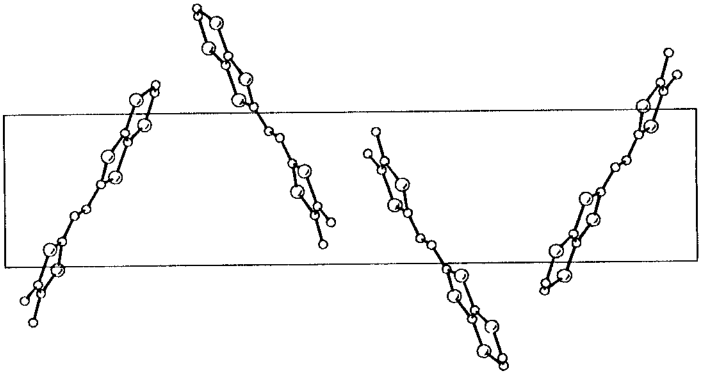


FIGURE 5. X-Ray crystal structure of compound **18**.

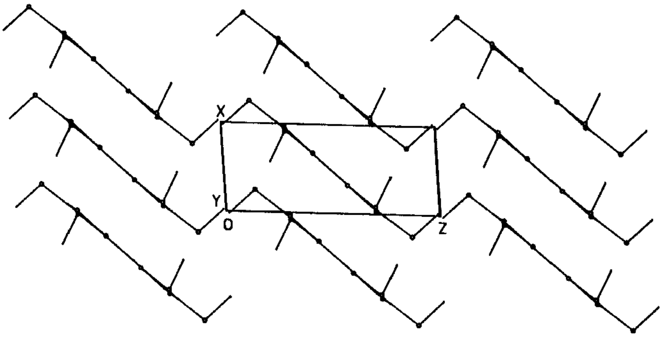


FIGURE 6. X-Ray crystal structure of compound **20**.

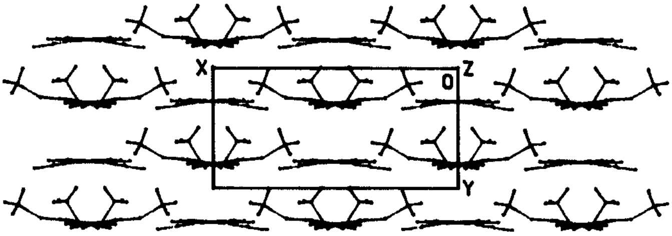


FIGURE 7. X-Ray crystal structure of a 1:1 complex of compound **20** and TCNQ **1**, viewed down the long axes of the molecules.

Donor **20** forms a 1:1 charge-transfer complex with TCNQ **2**, the X-ray crystal structure of which is shown in Figure 7.[27] Both the radical cation and radical anion species have crystallographic C_2 symmetry; the former is non-planar with a dihedral angle of *ca.* 19° between the two 1,3-dithiole rings (Figure 8). The complex has a mixed stack structure (Figure 7) and, therefore, has low conductivity. Attempts to electrocrystallise salts of **18-20**, and related vinylogous TTF and BEDT-TTF systems,[26] with inorganic anions have been unsuccessful.

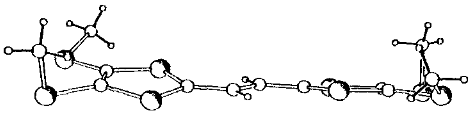


FIGURE 8. Structure of the cation radical $20^{+\cdot}$ in the TCNQ complex.

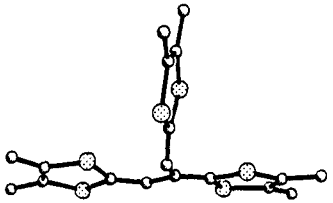
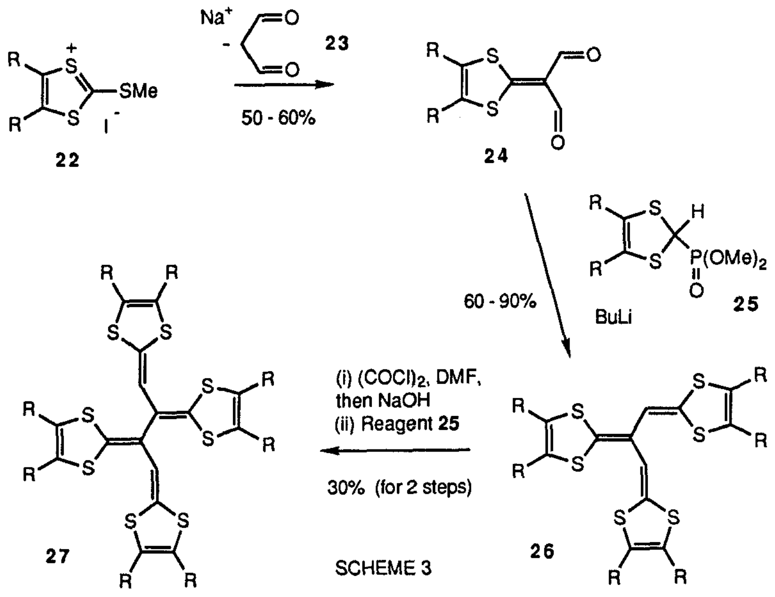


FIGURE 9. X-Ray molecular structure of compound **26** (R = Me).

We have used 1,3-dithiole Horner-Wittig reagents to obtain extended TTF donors comprising three and four 1,3-dithiole rings, *eg*. molecules of general formulae **26** and **27** (Scheme 3).[28] The synthesis of dialdehyde **24** is based on the work of Gompper *et*



SCHEME 3

al.[29] Tris(1,3-dithiole) derivatives analogous to **26** have been prepared recently by other workers using a different approach.[30] Our methodology (Scheme 3) has unprecedented potential for the construction of extensively conjugated multi-1,3-dithiole systems.

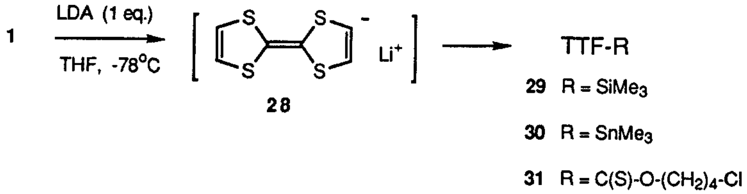
The X-ray crystal structure of the hexamethyl-tris(1,3-dithiole) derivative **26** (R=Me) is shown in Figure 9.[28] A striking feature of the molecular structure is that one of the dithiole rings is almost orthogonal to the other two rings. This non-planar structure prevents the formation of ordered stacks in the crystal lattice.

Attachment of Functionalised Side-Chains to TTF

The most widespread modifications to TTF have been the replacement of the sulfur atoms by selenium (*eg*. tetramethyltetraselenafulvalene, TMTSF) and the fusion of heterocyclic rings (*eg*. BEDT-TTF, **3**). In contrast, scant attention has been paid to the attachment of *functionalised* substituents to the TTF framework.[31-34] When suitable substituents are attached, such compounds can act as building blocks for the following classes of materials, all of which are largely unexplored:

(i) salts and complexes with increased intermolecular interactions, *eg*. hydrogen bonding;
(ii) Langmuir-Blodgett films;
(iii) macrocyclic TTF derivatives;
(iv) oligomeric and polymeric TTF derivatives.

Our approach to TTF derivatives endowed with one functionalised side-chain has utilised reactions of monolithio-TTF **28**, a species which was first generated by Green.[31] Anion **28** can be trapped with reasonable efficiency (typically 25-45%) by reactive electrophiles, *eg*. carbon dioxide,[31] acid chlorides[35] and Eschenmoser's salts.[34] The yield of mono-substituted products is frequently reduced due to multi-substitution, which arises from disproportionation of the mono-anion **28**.[31] We have developed new reactions of anion **28** to synthesise amphiphilic TTF derivatives bearing one long chain which form highly conducting Langmuir-Blodgett films.[35,36] During the course of this work, trimethylsilyl-TTF **29** was found to be a shelf-stable equivalent of anion **28**,[35] although it seems that the trimethylstannyl analogue **30**, subsequently reported by Japanese workers, may be a more efficient reagent.[37]



The X-ray crystal structure of TTF-thioester derivative **31** (obtained from reaction of anion **28** with the corresponding chlorothioformate) is of particular interest as very few crystal structures of functionalised TTF derivatives have been reported.[35,38,39] The side-chain of compound **31** lies in the same plane as the TTF ring, with the C=S group in conjugation with the TTF π-electron system. The molecules of **31** stack along the *z* direction in a head-to-tail fashion (TTF moiety over side-chain) with no stacking interaction between the TTF rings (Figure 10).[40] The separation between the mean molecular planes of neighbouring molecules is *ca.* 3.7Å.

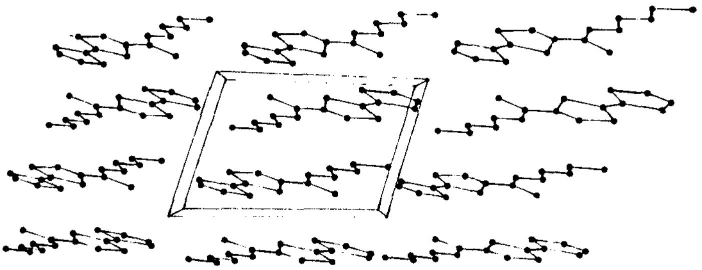


FIGURE 10. X-Ray crystal structure of compound **31**.

Preparation and Reactions of the TTF-thiolate Anion **32**.

Monolithio-TTF **28** reacts with elemental sulfur at -78°C to afford the thiolate anion **32** which has been trapped *in situ* with a range of electrophiles.[35,41,42] An important advantage of thiolate anion **32** over anion **28** is that the former will react efficiently not only with acid chlorides, but also with alkyl halides. Reaction of anion **32** with benzoyl chloride gave thioester **33** (*ca.* 75% yield) from which the thiolate anion **32** can be efficiently regenerated (as the sodium salt) by treatment with sodium ethoxide in ethanol at -10°C. Compound **33** is, therefore, a convenient shelf-stable source of anion **32**.[42]

Reaction of **32** with 2-bromoethanol yields TTF derivative **34** (65% yield from TTF). Compound **34**, which can be prepared in *ca.* 2 gram batches, is proving to be a most versatile TTF derivative for the elaboration of side-chain functionality. For example, standard reactions of the alcohol group of **34** with methacryloyl chloride and mesyl chloride, in the presence of triethylamine, yield methacrylate and mesylate derivatives **35** and **36**, respectively, in high yield. Reaction of mesylate derivative **36** with base affords vinylthio derivative **37**,[41] and sequential reaction of **36** with sodium azide and lithium aluminium hydride affords the shelf-stable amine **38** in good yield.[43]

$$\underset{\mathbf{33}}{\mathrm{TTF\text{-}S\text{-}C(O)Ph}} \underset{\mathrm{NaOEt}}{\overset{\mathrm{PhC(O)Cl}}{\rightleftarrows}} \underset{\mathbf{32}}{\left[\mathrm{TTF\text{-}S^{-}\ Li^{+}}\right]} \longrightarrow \mathrm{TTF\text{-}S\text{-}R}$$

34 R = $(CH_2)_2$-OH

35 R = $(CH_2)_2$-O-C(O)-C(Me)=CH_2

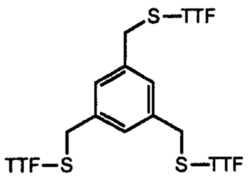
36 R = $(CH_2)_2$-O-SO_2Me

37 R = CH=CH_2

38 R = $(CH_2)_2$-NH_2

Several bis- and tris-TTF derivatives have been prepared by reactions of both thiolate anion **32** and alcohol **34**.[42] Representative examples are as follows: anion **32** reacts with 1,3,5-tri(bromomethyl)benzene to give tris-TTF system **39** (17%). Addition of anion **32** (generated from reagent **33**) to 1,4-diiodopropane gave iodide **40** (50%) from which the bis-TTF derivative **41** was obtained in 26% yield. Alcohol **34** reacts with TTF-carbonylchloride, benzene-1,3,5-tri(carbonyl-chloride) and malonyl dichloride to yield products **42** (34%, based on TTF-carboxylic acid), **43** (72%) and **44** (84%).

Bis(tetrathiafulvalenyl)sulfide **45** has been synthesised (14% yield) by reaction of monolithio-TTF **28** with di(phenylsulfonyl)sulfide. The X-ray crystal structure of **45** is shown in Figure 11.[44] The molecule is bent about the bridging sulfur atom with a fold angle of *ca.* 100°. A feature of the molecular packing is that there are several intermolecular S---S contacts that are significantly shorter than the van der Waals distance (the shortest contact is 3.45Å). Such tight packing of a neutral TTF donor is observed in only a few other structures, *eg*. BEDT-TTF **3**, for which the shortest intermolecular S---S distance is 3.48Å.[45]



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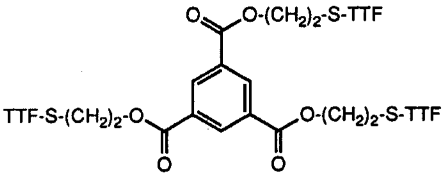


43

40 TTF-S-$(CH_2)_3$-I

41 TTF-S-$(CH_2)_3$-S-TTF

42 TTF-S-$(CH_2)_2$-O-C(O)-TTF

44 TTF-S-$(CH_2)_2$-O-C(O)-CH_2-C(O)-O-$(CH_2)_2$-S-TTF

45 TTF-S-TTF

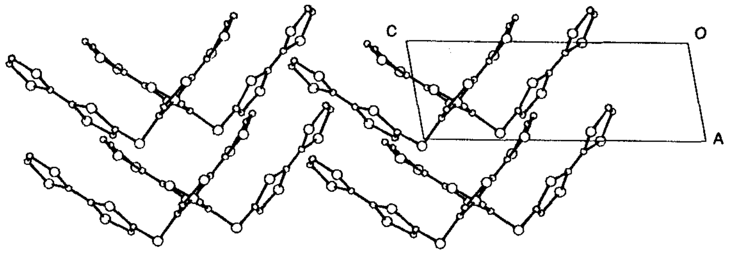
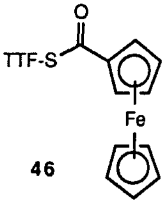


FIGURE 11. X-Ray crystal structure of compound **45**.

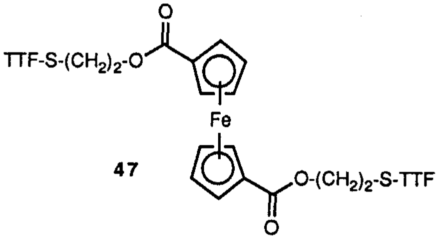
Cyclic voltammetric studies on the multi-TTF systems **39** and **41**-**44** suggest that there are no inter- or intra-molecular Coulombic effects between charged TTF moieties in solution, and that the individual TTF units are electronically isolated by the 'spacer' groups.[42] The symmetrical dimers **41** and **43**, and the symmetrical trimers **39** and **41** each show two reversible redox waves at very similar potentials to related TTF monomers, due to simultaneous oxidation of the two or three TTF units at the same potentials. Thus the dimers sequentially form dications and tetracations, and the trimers form trications and tetracations, with no intermediate oxidation states being detected. For the unsymmetrical TTF dimer **42**, three distinct oxidation waves are observed: the first oxidation of each of the TTF groups is separated by 0.11V, which is consistent with the known higher oxidation potential of TTF-ester derivatives. The second oxidation of both TTF groups of **42** occurs at the same potential.

However, there is evidence for intra- and/or inter-molecular Coulombic repulsion in system **45**, where the first oxidation of each TTF unit occurs at a different potential.[45] Three distinct oxidation waves are observed. The first two oxidations ($E_1{}^{1/2} = 0.49V$ and $E_2{}^{1/2} = 0.61V$) are both reversible one-electron processes (sequential formation of the mono- and di-cationic species, TTF-S-$TTF^{+\cdot}$ and $TTF^{+\cdot}$-S-$TTF^{+\cdot}$, respectively) while further oxidation to tri- and tetra-cationic species, $(TTF)_2S^{3+\cdot}$ and $(TTF)_2S^{4+}$, respectively, is observed as a single, irreversible, two-electron wave at $E^{1/2} = 0.86V$.

The high reactivity of both thiolate anion **32** and alcohol **34** with acid chlorides has enabled us to link organometallic groups to TTF. For example, reactions with ferrocene-carbonyl chloride and -dicarbonyl chloride have furnished the fascinating redox systems **46** (30%) and **47** (12%) respectively.[46] Complexation studies of these TTF-ferrocene derivatives with TCNQ, TCNE and other acceptors will be of special interest, in view of the remarkable magnetic properties observed in certain ferrocene complexes.[47]

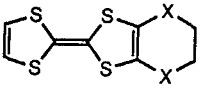


46

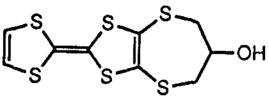


47

Dichalcogenation of lithiated TTF has been explored for the first time.[49] Under precisely controlled conditions [TTF (1 equiv.), LDA (1.1 equiv.), elemental sulfur or selenium (1.5 equiv.) at -78°C, followed by addition of the dihalo reagent (1.1 equiv.)] products **48** (25%), **49** (26%) and **50** (15%) are obtained. This new, one-pot route to the unsymmetrical donors **48-50**, is preferable to phosphite-mediated cross-coupling of the two half units.[48]



48 X = S
49 X = Se



50

The X-ray crystal structure of compound **49** presents, we believe, a novel type of packing for a TTF system (Figure 12).[49] Pairs of molecules, related *via* an inversion centre, can be regarded as dimers with typical ring-over-bond overlap. Within the dimer, the interplanar separation between the tetrathioethene fragments is short (3.35Å). Dimers of **49**, with molecular planes orthogonal to each other, are arranged in a chess-board fashion. This packing is reminiscent of the κ-phases of $(BEDT\text{-}TTF)_2X$ salts, although in the κ-phases, the molecules are aligned with the long axis perpendicular to a layer (and parallel to each other) while in the present structure they lie within the layer and perpendicular to each other.

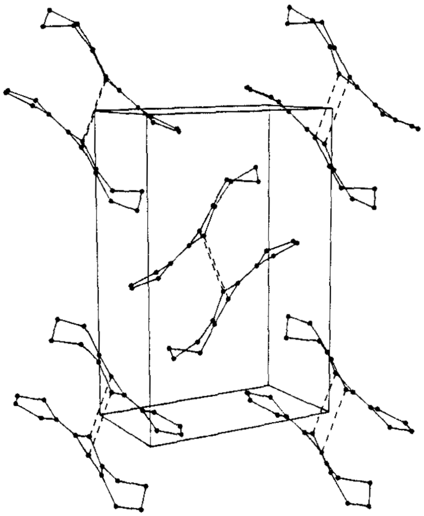


FIGURE 12. X-Ray crystal structure of compound **49**.

CONCLUSIONS

We have described a wide range of tetrathiafulvalene derivatives that have recently been synthesised in our laboratory during the course of studies on organic conductors. The combination of unusual multi-stage redox chemistry and interesting structural properties is a notable feature of many of these molecules. The presence of reactive functional groups on the TTF system offers unique potential for the development of new organic materials with unconventional solid-state properties.

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