Covalently Attached Ferrocene and Tetrathiafulvalene Redox Systems

Adrian J. Moore,[a] **Peter J. Skabara,**[a] **Martin R. Bryce,***[a] **Andrei S. Batsanov,**[a] **Judith A. K. Howard**[a] **and Stephen T. A. K. Daley**[b]

[a] *Department of Chemistry, University of Durham, Durham, UK DH1 3LE*
[b] *ICI FCMO, PO Box A38, Leeds Road, Huddersfield, Yorkshire, UK HD2 1FF*

The synthesis and solution redox properties of several covalently attached ferrocene and tetrathiafulvalene units are reported, together with the X-ray crystal structure of a 1,1′-bis(1,3-dithiole-2-ylidene)-substituted ferrocene derivative.

The study of molecules comprising two different redox centres that are covalently linked is a burgeoning topic within supramolecular chemistry, with applications in molecular electronic devices, sensors, electrocatalysis and energy conversion.[1] Current research in this area focuses on gaining control over charge-transfer interactions between combinations of organic and organometallic species, *e.g.*, bipyridinium cations, quinones, metallocenes and metal-coordinated macrocycles.[2]

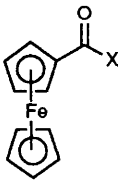
The *covalent* incorporation of tetrathiafulvalene (TTF) units into multistage redox assemblies[3] presents a fascinating prospect for the following reasons: (*i*) oxidation of TTF to the radical cation species occurs reversibly at a relatively low potential (*ca.* 0.34 V, *vs.* Ag/AgCl for unsubstituted TTF) which can be finely tuned by the attachment of appropriate substituents; (*ii*) $TTF^{+\bullet}$ is thermodynamically a very stable species; (*iii*) oxidised TTF units readily form highly ordered arrays with close intermolecular interactions involving both π–π overlap and S···S contacts. However, the chemistry of functionalised TTF derivatives which are needed to construct such assemblies is virtually unexplored.[4–6] There are two main reasons for this: (*i*) direct substitution onto the TTF ring is frequently an inefficient process, yielding a mixture of products which are difficult to separate[7] (*ii*) very few methods are available whereby the TTF system can be built up from functionalised components, and these are invariably lengthy procedures involving a capricious coupling reaction of two 1,3-dithiole units as the final step.[8]

We report here the synthesis of prototype systems comprising covalently linked ferrocene and TTF moieties. Additionally, we describe the solution electrochemical properties of the new materials, an X-ray crystal structure and preliminary data on complex formation with tetracyano-*p*-quinodimethane (TCNQ). Two distinct structural combinations of ferrocene and TTF are described, utilising functionalised TTF and 1,3-dithiole building blocks that we have recently developed in the context of studies on organic metals. Ferrocene has been attached both to the periphery of TTF (compounds **1b–1d**, **3b**, **4b** and **5**) and incorporated as a spacer unit between two 1,3-dithiole-2-ylidene rings (compounds **6a** and **6b**).

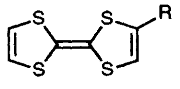
Systems **1b–1d**, comprising one ferrocene and one TTF unit separated by one, two and five atom spacer groups, respectively, were prepared as follows. Ferrocenecarbonyl chloride **1a** reacted with tetrathiafulvalenyllithium **2a**[7] (−78 °C in diethyl ether) to yield compound **1b** (12% yield).† Reaction of compound **1a** with TTF-thiolate anion **2b** (generated from thiobenzoate derivative **2c** and sodium ethoxide in ethanol at −10 °C)[5] gave thioester derivative **1c** (27% yield). The reaction of acid chloride **1a** with TTF-alcohol **2d**[4] (triethylamine, dichloromethane, 20 °C) was particularly efficient, affording ester **1d** in 80% yield. Directly analogous reactions have provided bis-TTF and bis-ferrocene derivatives **3b** and **4b**, respectively. Thus the reaction of 1,1′-ferrocenedicarbonyl dichloride **3a** and TTF-alcohol **2d** gave the product **3b** (20% yield, based on 1,1′-ferrocenedicarboxylic acid), and TTF-dialcohol **4a**[9] and compound **1a** gave product **4b** (60% yield).

Ferrocene–TTF system **5**, with a *trans*-ethene linkage, was obtained (58% yield, after separation from a mixture of *trans*- and *cis*-isomers) from the reaction of TTF–carboxaldehyde **2e**[10] and the Wittig reagent generated from ferrocene–CH_2–PPh_3^+ iodide (butyllithium, tetrahydrofuran, −78 °C).[11]

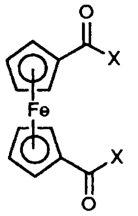
The incorporation of conjugated acyclic and cyclic units (*e.g.* ethene, anthracene and thiophene groups) between two 1,3-dithiole rings, to form 'stretched' TTF derivatives with unusual structural and redox properties, has been the subject of extensive studies in our laboratory[12] and elsewhere.[13] Hitherto, the use of an organometallic spacer group, which is



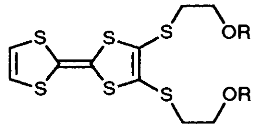
1a; X = Cl
b; X = TTF
c; X = S–TTF
d; X = O–$(CH_2)_2$–S–TTF



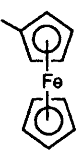
2a; R = Li
b; R = S^-Na^+
c; R = S–C(O)–Ph
d; R = S–$(CH_2)_2$–OH
e; R = CHO

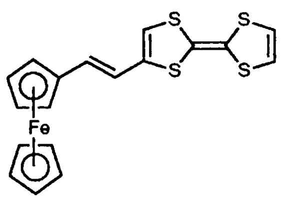


3a; X = Cl
b; X = O–$(CH_2)_2$–S–TTF

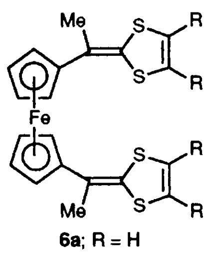


4a; R = H
b; R = (O)C

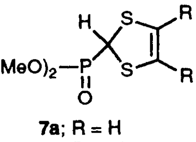




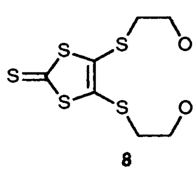
5



6a; R = H
b; R = Me



7a; R = H
b; R = Me



8 R = (O)C

---

† Satisfactory elemental analysis, mass spectra and ^1H NMR spectra were obtained for all new compounds.

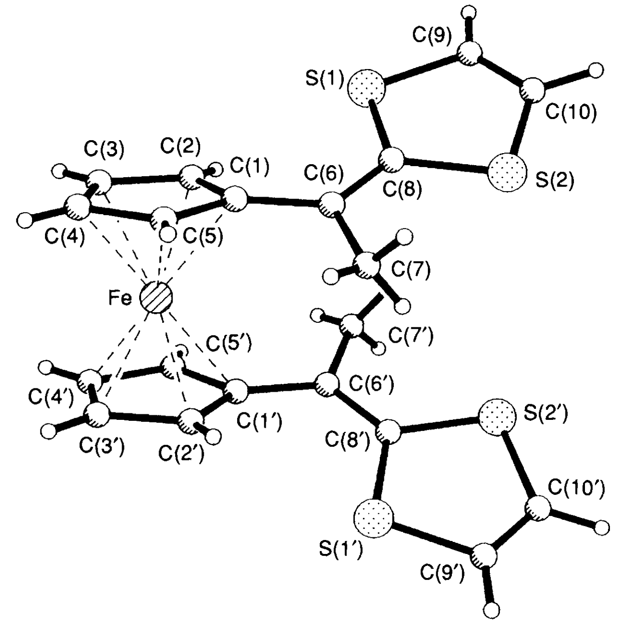


Fig. 1 Molecular structure of [Fe($C_5H_4CMe=C_3S_2Me_2$)$_2$] **6a**. Selected bond lengths (Å): Fe–C(1) 2.073(5), Fe–C(2) 2.049(7), Fe–C(3) 2.042(8), Fe–C(4) 2.049(5), Fe–C(5) 2.046(7), Fe–Cp-plane 1.65, C(1)–C(6) 1.463(6), C(6)–C(8) 1.356(7), C(8)–S(1) 1.760(6), C(8)–S(2) 1.770(4), S(1)–C(9) 1.744(7), S(2)–C(10) 1.723(10), C(9)–C(10) 1.307 (12)

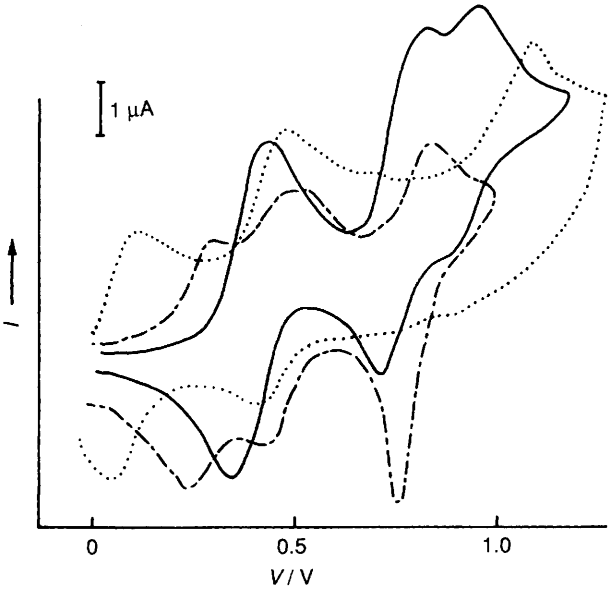


Fig. 2 Cyclic voltammograms of compounds **3b** (——), **5** (– · · –) and **6a** (······)

Table 1 Cyclic volatmmetric data[a]

Compound	$E_1^{\frac{1}{2}}$	$E_2^{\frac{1}{2}}$	$E_3^{\frac{1}{2}}$
TTF	0.34	0.71	
Ferrocene	0.36		
1b	0.38	0.73	0.88
1c	0.45	0.73[b]	
1d	0.35	0.61	0.75
3b	0.37[c]	0.71[c]	0.85
4b	0.45	0.62[c]	0.82
5	0.26	0.44	0.77
6a	0.10	0.56	1.15[d]
6b	0.06	0.51	1.05[d]

[a] Data are in volts, recorded using a Pt working electrode, Pt gauze counter electrode, Ag/AgCl reference electrode, 0.2 mol dm^{-3} $Bu^t_4N^+PF_6^-$, 10^{-4} mol dm^{-3} compound in dry acetonitrile under nitrogen at 20 °C, with iR compensation. All waves represent a reversible, one electron process except where indicated. [b] Broad two electron wave. [c] Two electron wave. [d] Irreversible wave.

itself a redox species, has not been reported in this context. Compounds **6a** and **6b** have now been prepared in 60–70% yield by the twofold reaction of 1,1′-diacetylferrocene and the 1,3-dithiole Horner–Wittig reagents **7a** and **7b**,[12b] respectively (butyllithium, tetrahydrofuran, −78 °C).

The structure of compound **6a** was determined by X-ray diffraction‡ (Fig. 1). The molecule is situated around a twofold crystallographic axis, with the cyclopentadienyl rings parallel to within 1.3° and staggered by 17.6°. The entire ligand is remarkably non-planar, being twisted by 26.0° around the C(1)–C(8) axis and by *ca.* 3.4° around the C(6)=C(8) double bond. The dithiole ring adopts an envelope conformation, folding by 11° along S(1)···S(2).

The electrochemical redox properties of the ferrocene–TTF systems have been studied by cyclic voltammetry; the data are collated in Table 1 and the cyclic voltammograms of compounds **3b**, **5** and **6a** are shown in Fig. 2. In all the compounds where ferrocene and TTF are linked by a bridge (*viz.* **1b–1d**, **3b**, **4b** and **5**) three reversible electron transfer oxidations are observed within the range *ca.* 0.3–0.85 V. These correspound to TTF → $TTF^{+\bullet}$, $TTF^{+\bullet}$ → TTF^{2+} and ferrocene → ferrocinium. In all cases the first oxidation is assigned to TTF → $TTF^{+\bullet}$, whereas the second oxidation is assigned to $TTF^{+\bullet}$ → TTF^{2+} for compounds **1d** and **3b**, and to the ferrocene unit for compound **4b**. This interpretation is supported by data obtained for the model compound **8**[9] which does not contain the TTF system. For compounds **1b**, **1c** and **5** the assignment of the second and third oxidations is unclear. Both compounds **6a** and **6b** display two, reversible single-electron oxidations and a third irreversible oxidation at a higher potential. A striking feature of the data for **6a** and **6b** is that the first oxidation occurs at a remarkably low potential (*ca.* 0.1 V); we, therefore, assign this wave to the oxidation of the entire delocalised system involving significant interaction between the two 1,3-dithiole rings and ferrocene.

Compounds **6a** and **6b** yield charge-transfer complexes with TCNQ (40% yield, from dichloromethane solution) which have high room temperature conductivity values (σ_{rt} = 0.2 and 0.1 S cm^{-1}, respectively, using two-probe techniques on compressed pellets). The stoichiometry of both complexes, as judged by elemental analysis, is 1 donor : 2 TCNQ.

---

‡ *Crystal data* for **6a**: $C_{20}H_{18}FeS_4$, M = 442.4, monoclinic, space group $C2/c$ (No. 15), a = 17.847(2), b = 10.191(2), c = 12.849(2) Å, β = 126.01(1)°, U = 1890.4(6) Å, Z = 4, D_c = 1.56 g cm^{-3}, μ(Mo-Kα) = 12.4 cm^{-1}, $F(000)$ = 912, crystal size 0.15 × 0.25 × 0.40 mm. 2170 independent intensity data were collected at 23 °C on a Rigaku AFC-6S diffractometer using graphite-monochromated Mo-Kα radiation (λ = 0.71073 Å) and 2θ/ω scan mode (2θ < 55°). The structure was solved by direct methods. All non-hydrogen atoms were refined in anisotropic approximation and all H atoms in isotropic approximation by full-matrix least-squares to R = 0.056 (R_w = 0.065, goodness-of-fit 1.90) for 1592 reflections with $|F| > 4\sigma(F)$, corrected for absorption by semi-empirical methods (108 azimuthal scans of 3 reflections used, min. to max. transmission ratio 0.687). Atomic coordinates, bond lengths and angles, and thermal parameters have been depostied at the Cambridge Crystallographic Data Centre. See Notice to Authors, Issue No. 1.

We thank the SERC and ICI FCMO for funding this work, and The Royal Society for financial support (to A. S. B.).

Received, 21st December 1992; Com. 2/06746C

References

1 Reviews: J.-M. Lehn, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1304; *Frontiers in Supramolecular Organic Chemistry and Photochemistry*, ed. H.-J. Schneider and H. Dürr, VCH, Weinheim, 1991.

2 P. L. Anelli, P. R. Ashton, R. Ballardini, V. Balzani, M. Delgado, M. T. Gandolfi, T. T. Goodnow, A. E. Kaifer, D. Philp, M. Pietraszkiewicz, L. Prodi, M. V. Reddington, A. M. Z. Slawin, N. Spencer, J. F. Stoddart, C. Vincent and D. J. Williams, *J. Am. Chem. Soc.*, 1992, **114**, 193; R. W. Wagner, P. A. Brown, T. E. Johnson and J. S. Lindsey, *J. Chem. Soc., Chem. Commun.*, 1991, 1463; D. N. Blauch and J.-M. Savéant, *J. Am. Chem. Soc.*, 1992, **114**, 3323.

3 D. Philp. A. M. Z. Slawin, N. Spencer, J. F. Stoddart and D. J. Williams, *J. Chem. Soc., Chem. Commun.*, 1991, 1584.

4 A. J. Moore and M. R. Bryce, *J. Chem. Soc., Chem. Commun.*, 1991, 1638.

5 M. R. Bryce, G. J. Marshallsay and A. J. Moore, *J. Org. Chem.*, 1992, **57**, 4859.

6 R. Gasiorowski, T. Jørgensen, J. Møller, T. K. Hansen, M. Pietraszkiewicz and J. Becher, *Adv. Mater.*, 1992, **4**, 568.

7 D. C. Green, *J. Org. Chem.*, 1979, **44**, 1476.

8 A. Krief, *Tetrahedron*, 1986, **42**, 1209.

9 P. J. Skabara, A. J. Moore and M. R. Bryce, unpublished data.

10 Compound **2e** was prepared by a modification of the literature procedure (ref. 7). We thank J. Garin for providing us with details.

11 P. L. Pauson and W. E. Watts, *J. Chem. Soc.*, 1963, 2990.

12 (*a*) M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Fraser, W. Clegg, M. B. Hursthouse and A. I. Karaulov, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 1450; (*b*) A. J. Moore and M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1991, 157; (*c*) A. J. Moore and M. R. Bryce, *Tetrahedron Lett.*, 1992, **33**, 1373.

13 Z. Yoshida and T. Sugimoto, *Angew. Chem., Int. Ed. Engl.*, 1988, **27**, 1573; U. Schöbel, J. Salbeck and J. Daub, *Adv. Mater.*, 1992, **4**, 41; T. K. Hansen, M. V. Lakshmikantham, M. P. Cava, R. E. Niziurski-Mann, F. Jensen and J. Becher, *J. Am. Chem. Soc.*, 1992, **114**, 5035; A. S. Benahmed-Gasmi, P. Frere, B. Garrigues, A. Gorgues, M. Jubault, R. Carlier and F. Texier, *Tetrahedron Lett.*, 1992, **33**, 6457.