Functionalised Oligoenes with Unusual Topologies: Synthesis, Electrochemistry and Structural Studies on Redox-Active [3]- and [4]-Dendralenes

Martin R. Bryce,* Malcolm A. Coffin, Peter J. Skabara, Adrian J. Moore, Andrei S. Batsanov, and Judith A. K. Howard[a]

Abstract: New [3]- and [4]-dendralenes bearing electron-donor 1,3-dithiole and ferrocene substituents have been synthesised. Compounds **8**, **15** and **17** have been characterised by single-crystal X-ray diffraction. Two of the dithiole rings of **8** are conjugated (dihedral angle 9°), while the third dithiole ring is almost orthogonal to this plane, and hence its π-electron system is isolated. For the dendralene precursor molecule **15**, the substituted cyclopentadienyl ring, two C=C bonds and fused dithiole and dithiine rings comprise an extended π-conjugated system. In molecule **17** the potential conjugation path C(6)C(3)C(4)C(5)-C_5H_5 is distorted by an 8° twist around the C(3)−C(4) bond and a 7° twist around the C(5)−C(21) bond, and the delocalisation along the chain is insignificant. Solution electrochemical data demonstrate that the dendralenes are strong π-electron donors, which give rise to dication, radical trication or tetracation species. Spectroelectrochemical studies on compounds **7** and **10** suggest that the radical species are situated within the linear 1,2-ethylenediylidene moieties and that a conformational change may occur at the dication redox stage. UV/Vis spectroscopic data are consistent with poor cross-conjugation in these systems.

Keywords: dendralenes • electrochemistry • ferrocene • radicals • structure elucidation

Introduction

The structural, electronic and optical properties of conjugated organic molecules and their derived oligomers and polymers continues to attract widespread attention.[1] Linearly conjugated species, for example polyacetylene,[2] and polythiophene derivatives[3] are representative, and the electronic and spectroscopic properties of their charged states, generated by chemical or electrochemical means, have been the subject of extensive investigations. The importance of studying well-defined oligomers of these and related polymeric species has recently been emphasised by several authors;[4] the benefits include precisely defined structures, ease of purification, solubility and tractability.

Dendralenes are a class of cross-conjugated materials which have received relatively scant attention.[5] They are the simplest one-dimensional π systems with non-degenerate ground states, a topological feature which may give rise to unusual physical properties not found in their linear counterparts. In particular, redox-active dendralenes which readily give rise to open-shell species are very rare.[6] Although very few detailed electrochemical, spectroscopic or structural studies have been reported on dendralenes, novel applications have been envisaged for the stable cross-conjugated radicals which they may form. For example, they have possible applications as soliton valves and switches in molecular electronic devices.[7]

Herein we report our studies on the synthesis and characterisation of a series of prototype redox-active [3]- and [4]-dendralenes. The redox properties are imparted by the donor 1,3-dithiole[8] and ferrocene[9] substituents. These molecules enable us to study π-electron delocalisation in dendralenes.

Results and Discussion

Synthesis: Our first targets[10] were tris- and tetra-1,3-dithiole derivatives, and their synthesis is shown in Scheme 1. The 1,3-dithiolium cation salts **1**[11] and **2**[12] reacted with the sodium salt of malonaldehyde, following the procedure of Gompper et al.,[13] to yield compounds **3** and **4** (24–50% yields). Twofold reaction of these dialdehydes with the phosphorus-stabilised carbanion generated from the appropriate reagents **5**[11] and **6**[12] proceeded cleanly to afford the [3]-dendralene systems **7** and **8** (62–67% yields). Formylation of compound **7** was achieved by a Vilsmeier reaction[6] to yield compound **9** (53% yield) which underwent a further olefination reaction using reagent **5** to provide the [4]-dendralene system **10** (57% yield).

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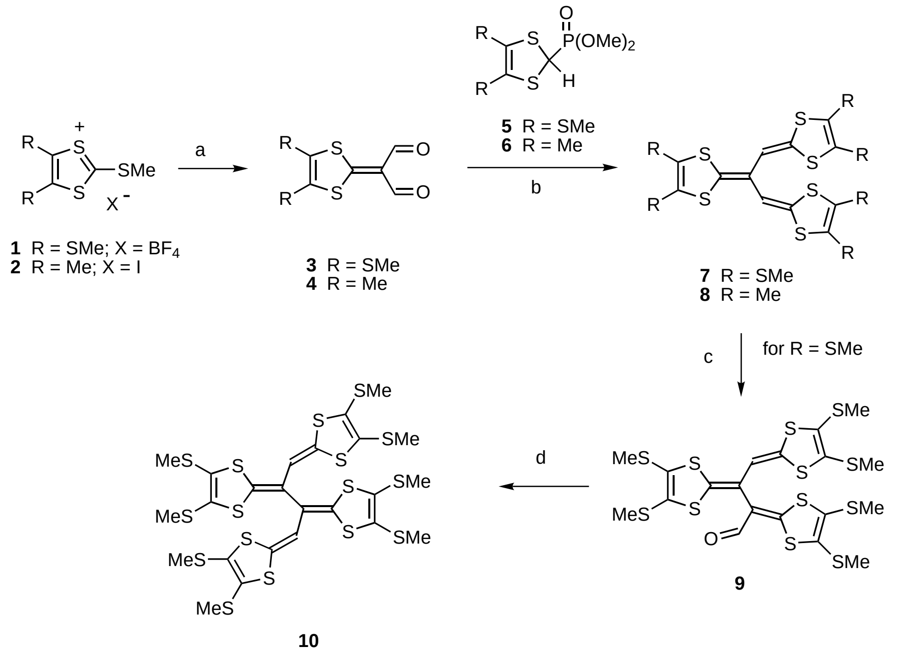
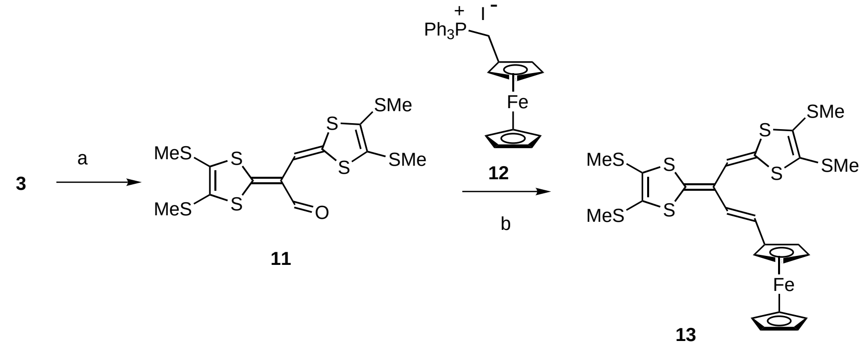
[a] Prof. M. R. Bryce, Dr. M. A. Coffin, Dr. P. J. Skabara, Dr. A. J. Moore, Dr. A. S. Batsanov, Prof. J. A. K. Howard
Department of Chemistry
University of Durham, Durham DH1 3LE (UK)
Fax: (+44) 191-384-4737
E-mail: m.r.bryce@durham.ac.uk



Scheme 1. Reagents and conditions: a) NaOCH=CH−CH=O, MeCN, 20 °C; b) **5** or **6** in THF, *n*BuLi, −78 °C; then add **3** or **4**, −78 → 20 °C; c) oxalyl chloride, DMF, −5 °C then 20 °C; then add **7**; d) **5** in THF, *n*BuLi, −78 °C, then add **9**, −78 → 20 °C.

We have also synthesised a complementary series of compounds with ferrocene units replacing one or two of the dithiole rings (Schemes 2 and 3). Reaction of dialdehyde **3** with one equivalent of the phosphonate anion derived from **5** gave compound **11**, in an optimised 30 % yield, after separation from compound **7** and unreacted compound **3**. Aldehyde **11** then reacted with the ylide formed by treatment of phosphonium salt **12**[14] with butyllithium to afford the 2:1 dithiole:ferrocene system **13** in 54 % yield (Scheme 2).



Scheme 2. Reagents and conditions: a) **5** in THF, *n*BuLi, −78 °C, then add **3**, −78 → 20 °C; b) **12**, THF, *n*BuLi, −78 °C; then add **11**, −78 → 20 °C.

To circumvent the low-yielding mono-functionalisation of **3**, we developed an alternative, more efficient route to analogues of **13**. In this series we focused on the ethylenedithio-substituted 1,3-dithiole derivatives (rather than methylsulfanyl analogues) for reasons of increased crystallinity. Compound **14**[15] reacted with the ylide derived from Wittig reagent **12** to give diene **15** as a highly-crystalline solid in 64 % yield (Scheme 3). The ^{1}H NMR data for **15** were entirely consistent with the s-*trans* (*E*) structure, which was further confirmed by X-ray analysis. Functionalisation of **15**, to afford aldehyde **16** in 74 % yield, was readily achieved by the same method used for the transformation of **7** into **9**. Aldehyde **16** was then converted into the 2:1 ferrocene:dithiole system **17** (72 % yield) and the 2:1 dithiole:ferrocene system **19** (a direct analogue of **13**) (83 % yield) using reagents **12** and **18**,[15] respectively. Iterative procedures then converted **19** into aldehyde derivative **20** (71 % yield) and finally the [4]-dendralene structure **21** (65 % yield).

X-ray crystal structures of compounds 8, 15 and 17: Compounds **8**, **15** and **17** were characterised by single-crystal X-ray diffraction. The structure of **8** (Figure 1) has previously been reported.[10] The molecule contains three 1,3-dithiole-methylene moieties, two of which (A and B) form a dihedral angle of 9° and constitute a single conjugated system. The double bonds C(1)=C(2) and C(7)=C(8) are therefore elongated to 1.365(10) and 1.381(10) Å, while the intervening single bond C(1)−C(7) is shortened to 1.409(8) Å (cf. 1.455 Å in planar 1,3-butadienes)[16] and has a bond order of approximately 1.4. The third 1,3-dithiol-2-ylidene moiety (C) is inclined by 80° to A and by 82° to B, hence its π-electron system is completely isolated: the C(7)−C(13) bond remains essentially single (1.499(12) Å).

Molecule **15** (Figure 2) has *trans* configuration about both C(1)−C(2) and C(2)−C(3)

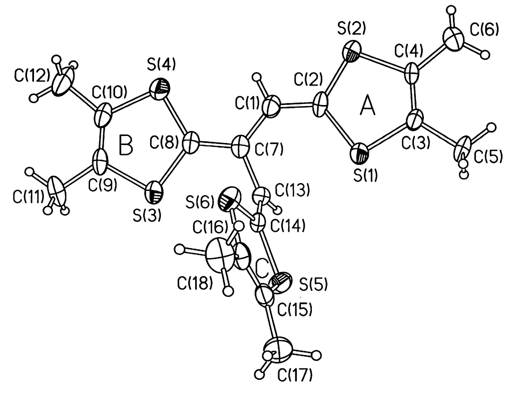
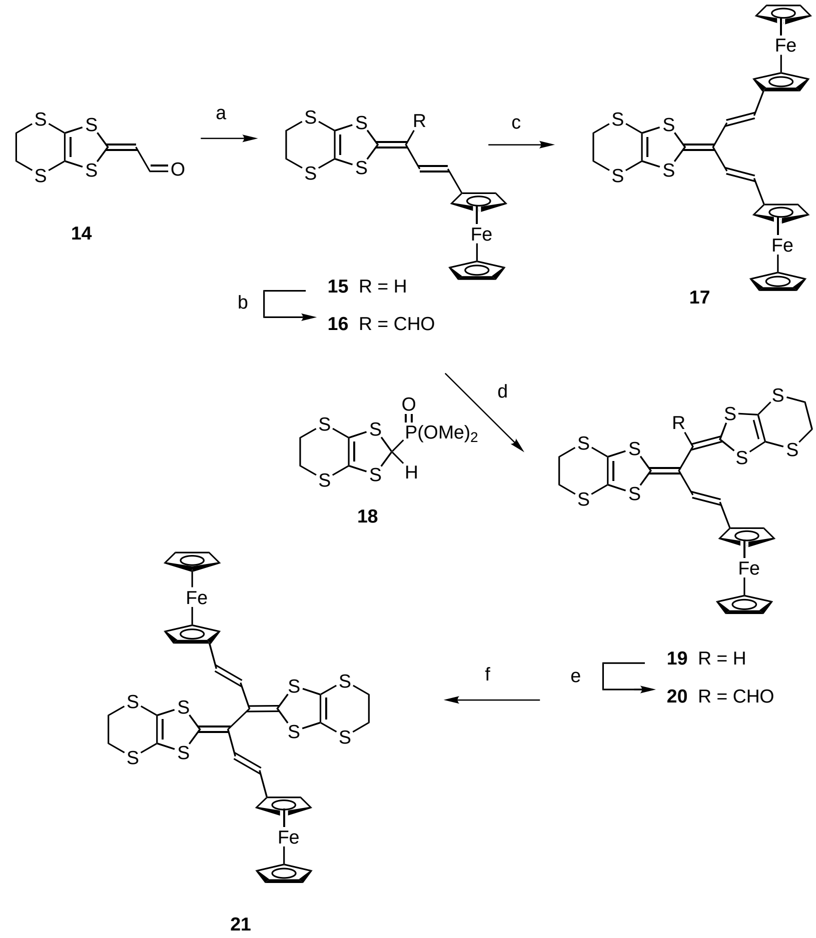


Figure 1. Molecular structure of **8** (30 % displacement ellipsoids).



Scheme 3. Reagents and conditions: a) **12**, THF, *n*BuLi, 20 °C; then add **14**, 20 °C; b) oxalyl chloride, DMF, 0 °C then 20 °C; then add **15**, NaOH; c) **12**, THF, *n*BuLi, 20 °C; then add **16**, 20 °C; d) **18**, THF, *n*BuLi, −78 °C; then add **16**, −78 °C to 20 °C; e) oxalyl chloride, DMF, 0 °C then 20 °C; then add **19**, NaOH; f) **12**, THF, *n*BuLi, 20 °C; then add **20**, 20 °C.

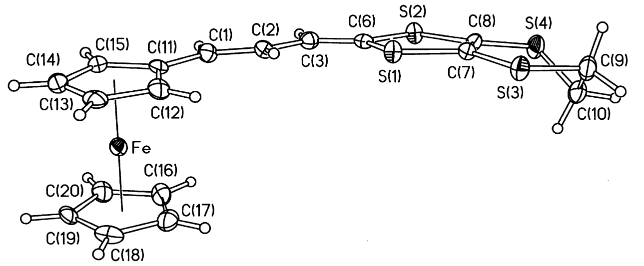


Figure 2. Molecular structure of **15** (50 % displacement ellipsoids). Bond lengths [Å]: C(1)−C(11) 1.448(6), C(1)−C(2) 1.356(6), C(2)−C(3) 1.436(6), C(3)−C(6) 1.345(6), C(6)−S(1) 1.770(5), C(6)−S(2) 1.758(5).

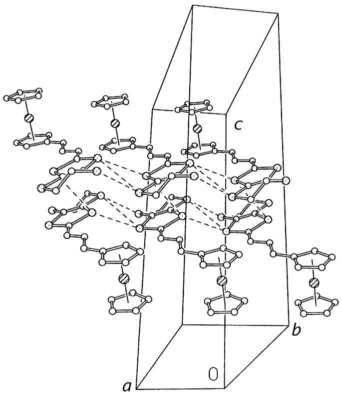


Figure 3. Crystal packing of **15**, showing S⋯S contacts ≤3.66 Å.

bonds. The substituted cyclopentadienyl ring, two C=C bonds and fused dithiole and dithiine rings comprise an extended π-conjugated system, which is slightly twisted about the C(1)−C(11), C(1)=C(2) and C(2)−C(3) bonds, by 10.5(7), 4.8(4) and 5.2(4)°, respectively. The dithiine ring adopts an envelope conformation: the C(10) atom deviates by 0.78 Å from the plane of the rest. The latter plane is inclined by 5.4° to the planar dithiole ring. The degree of π-delocalisation can be roughly measured by "bond alternation" D. This value represents the average difference between the lengths of (formally) single and double bonds, which can vary from 0.12 Å in localised all-*trans* polyenes to 0 Å in fully delocalised systems.[17] The degree of delocalisation in **15** ($\Delta = 0.09(1)$ Å) is therefore much lower than in **8** ($\Delta = 0.036(12)$ Å). Molecules in the crystal form pseudo-dimers, wherein the conjugated parts of the molecules are in face-to-face contact with a mean interplanar separation of approximately 3.5 Å. Translationally related dimers then form a double ribbon (Figure 3), where each molecule forms two particularly short S⋯S contacts (3.38 Å, cf. the standard van der Waals contact[18] of 3.60 Å) through dithiine sulfur atoms S(3) and S(4).

Molecule **17** (Figure 4) has a *trans* configuration about the C(1)=C(2) and C(4)=C(5) bonds. The fused dithiole-dithiine system is much more puckered than in **15**. The planarity of the potential conjugation path C(6)C(3)C(4)C(5)-C_5H_5 is slightly distorted, as in **15**. The C(1)=C(2) bond is inclined by 50° to the C(3)=C(6) bond and by 26° to the cyclopentadienyl ring with atoms labelled C(11⋯15). The ferrocenyl−ethene fragment takes no part in the conjugation.

Electrochemical and spectroscopic studies: The redox chemistry of the new compounds has been studied by cyclic voltammetry and the data are collated in Table 1, along with data for model bis(1,3-dithiol-2-ylidene)ethane derivatives **22**–**24**[19] obtained under the same conditions for comparison. The [3]-dendralenes **7** (Figure 5) and **8** display two, reversible,

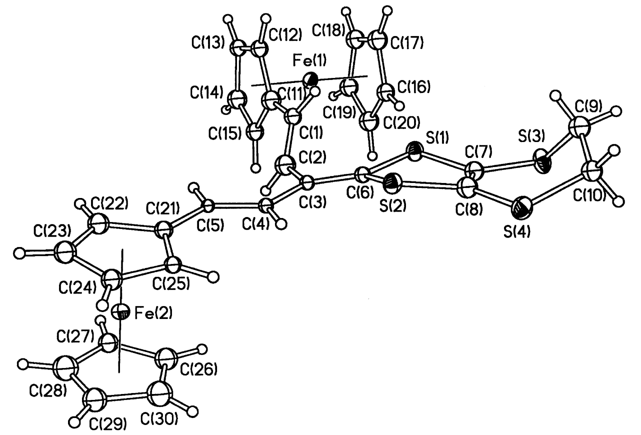


Figure 4. Molecular structure of **17** (50% displacement ellipsoids). Bond lengths [Å, $\sigma = 0.02$]: C(1)–C(11) 1.45, C(1)–C(2) 1.34, C(2)–C(3) 1.47, C(3)–C(6) 1.35, C(6)–S(1) 1.80, C(6)–S(2) 1.76, C(3)–C(4) 1.43, C(4)–C(5) 1.33, C(5)–C(21) 1.47.

Table 1. Cyclic voltammetric data.[a]

Compound	$E_1^{1/2}$ [V]	$E_2^{1/2}$ [V]	$E_3^{1/2}$ [V]
7	0.36	0.49	1.20 (q)
8	0.08	0.33	1.25 (q)
10	0.28	0.43	0.83 (2e)
11	0.61 (ir.)	0.81 (ir.)	–
13	0.35	0.48	0.66
15	0.33	0.49	–
16	0.38	0.86 (ir.)	–
17	0.26	0.40	0.55
19	0.35	0.50	0.65
21	0.37 (2e)	0.61	0.76
22[b]	0.19	0.34	–
23	0.50	0.63	–
24	0.48	0.65	–
27[b]	0.22 (2e)	–	–

[a] Data were recorded using a platinum disc working electrode, platinum gauze counter electrode, ca. 10^{-4} M solution of compound, 0.2 M tetrabutylammonium hexafluorophosphate in dry dichloromethane under a nitrogen or argon atmosphere at 20 °C, versus silver wire quasi-reference electrode (corrected versus ferrocene/ferrocene$^+$ as $E^{1/2} = +0.36$ V versus Ag/AgCl) using IR compensation, scan rate 100 mV s^{-1}. All waves represent a reversible, one-electron process except where indicated: 2e: a two-electron wave; ir.: an irreversible wave; q: a quasi-reversible wave. [b] Data taken from ref. [20b)].

single-electron waves leading to sequential formation of the cation radical and dication species, which corresponds to the electrochemical behaviour of the simpler vinylogous TTF systems **22**[20] and **23**,[19] respectively. The third oxidation process for **7** and **8** occurs at a considerably more positive potential (approximately 1.2 V) which is consistent with values for an isolated (non-conjugated) 1,3-dithiol-2-ylidene system.[21] This last oxidation is, therefore, unambiguously assigned to the orthogonal 1,3-dithiole ring of **7** and **8** (i. e. ring C, Figure 1) and this suggests a solution-state structure similar to that in the solid state.

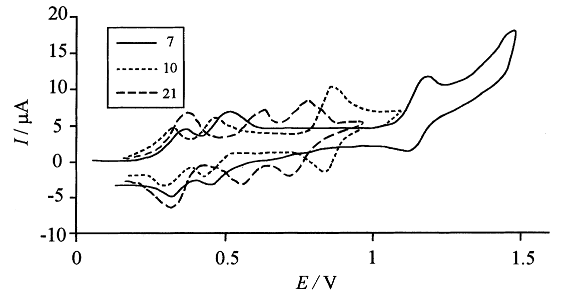
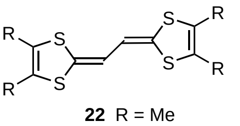
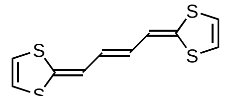


Figure 5. Cyclic voltammograms of compounds **7**, **10** and **21**. (For conditions see Table 1.)

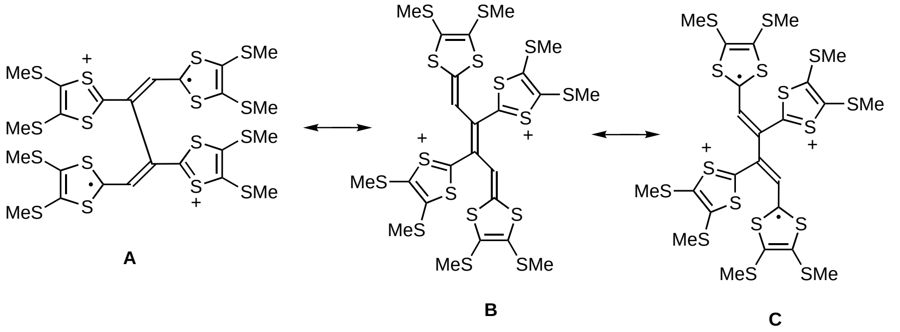


22 R = Me
23 R = SMe
24 R-R = S(CH$_2$)$_2$S
25 R = H
26 R = CO$_2$Me



27

The [4]-dendralene compound **10** exhibits quite similar $E_1^{1/2}$ and $E_2^{1/2}$ values, but the third oxidation wave is negatively shifted by approximately 500 mV, compared to analogue **7**, and represents a two-electron process (Figure 5). This coalescence of the third and fourth oxidation waves of **10** and the relatively low potential at which they occur suggests that the dication actually exists as the bis(cation radical) represented by structure **A** in Scheme 4. The intermediate **A** constitutes a σ-bonded pair of half-units behaving as two independent 1,2-ethylenebis(1,3-dithiol-2-ylidene) moieties. This species possibly undergoes a structural rearrangement to **B**, such that the uncharged 1,3-dithiole rings become linear in relation to one another. Intermediate **B** represents a vinylogous TTF system substituted at the central atoms by 1,3-dithiolium units. The simultaneous two-electron oxidation of **10**, corresponding to $E_{3,4}^{1/2}$ is directly analogous to the one-step, two-electron oxidation of 1,4-butenediylidene-2,2′-bis(1,3-dithiole)s. For example, compound **27** is oxidised to the dication at +0.22 V[20] since the polyene spacer group is sufficiently long to eliminate the Coulombic repulsion between the terminal 1,3-dithiolium rings. The potential for the simultaneous two-electron process is positively shifted in **10**$^{2+}$ (+0.83 V) compared to **27**, which can be attributed to the strongly electron-withdrawing nature of the dithiolium cations, togeth-



Scheme 4.

er with some degree of Coulombic repulsion in the multicharged systems.

Both 2:1 dithiole:ferrocene systems **13** and **19** display essentially identical redox behaviour. The first two oxidation processes occur at very similar potentials to **7**, and are, therefore, assigned with confidence to oxidation of the conjugated bis(1,3-dithiol-2-ylidene)ethane framework, while the third oxidation at 0.65–0.66 V is assigned to the ferrocene/ferrocenium redox couple of the pendant ferrocenylethene moiety.

A comparison of the CV data for **15** with that for **17**, reveals a negative shift of 70–90 mV in the $E_1^{1/2}$ and $E_2^{1/2}$ values for the latter compound, consistent with increased delocalisation (reduced coulombic repulsion) in **17**. It is also notable that these values for **17** are negatively shifted relative to those for **13** and **19** (by ca. 90 mV) which probably reflects the increased spacer length between the redox centres in **17**, which would again decrease the Coulombic repulsion.

The redox behaviour of the 2:2 dithiole:ferrocene system **21** is significantly different from that of the tetrakis(1,3-dithiole) system **10** already discussed. The first redox wave of **21** is a two-electron process, while the second and third waves are each one-electron processes (Figure 5). It appears, therefore, that the waves corresponding to oxidation of the bis(1,3-dithiol-2-ylidene)ethane framework of **21** to the radical cation and dication coalesce in this molecule (cf. the model compound **24**[19a] for which $\Delta E = 170$ mV). This is possibly due to some decrease in Coulombic repulsion arising from delocalisation of the charges onto the ferrocenylethene moieties. We note that similar coalescence of the two redox waves is known to occur for systems where two dithiole rings are separated by three double bonds.[17, 20] The third and fourth waves seen for **21** are consistent with ferrocene/ferrocenium redox couples, taking place separately at 0.61 and 0.76 V. Both these values are positively shifted by 0.21 V compared to the values for compound **17**, which seemingly reflects increased Coulombic repulsion associated with formation of the tri- and tetra-cations of **21**, as opposed to the di- and trications of **17**.

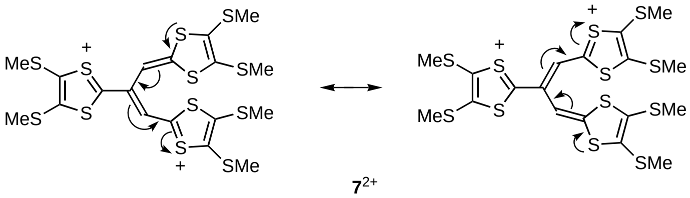
A comment on the CV behaviour of aldehyde derivatives **11** and **16** is worthwhile. Irreversible oxidation waves were recorded for these compounds (for both waves for **11**) probably as a consequence of close intramolecular O···S contacts perturbing the π-conjugation.[22]

Sugimoto et al. initially established that an increase in the number of sp^2 carbons in the spacer group between two 1,3-dithiole rings leads to a red shift of the lowest energy band (λ_{max} 368 nm for TTF, and 404 nm and 432 nm for **25** and **27**, respectively, in chloroform).[20b] Substitution of electron-withdrawing and electron-donating groups onto the dithiole rings leads to blue and red shifts, respectively (for example 389 nm for **26**; 415 nm for **22**).[20a] We observe only a small red shift of the absorption maxima for the series **23**[19b] ($\lambda_{max} = 404$ nm), **7** ($\lambda_{max} = 408$ nm) and **10** ($\lambda_{max} = 412$ nm) implying that the additional 1,3-dithiol-2-ylidene groups do not significantly extend the π-conjugation in the system. This is consistent with the X-ray data for **8** and the CV data. These data are similar for the dithiole:ferrocene derivatives. The lowest energy absorption band is seen for compound **17** ($\lambda_{max} = 394$ nm): this is red shifted by 20 nm relative to the bands for **13** and **15** (both $\lambda_{max} = 374$ nm). Diederich and co-workers have also shown that in dendralenic acetylene systems there is no red shift in comparison with the corresponding linear half-units, which is consistent with poor cross-conjugation through the molecule.[5c]

In spectroelectrochemical experiments in dichloromethane on the series of compounds **23**, **7** and **10** the cation radicals are characterised by the following absorption bands: **23**$^{+\bullet}$, $\lambda_{max} =$ 580 and 750 nm; **7**$^{+\bullet}$, 578 and 740 nm; **10**$^{+\bullet}$, 577 and 750 nm. For the spectra obtained at 0.60 V, that is the spectra of the dication species, a significant red shift was observed in the lowest energy absorption for **7**$^{2+}$ (500 and 645 nm) and **10**$^{2+}$ (570 and 710 nm) relative to **23**$^{2+}$ (400 nm). We tentatively suggest that a conformational change may occur at the dication redox stage, with an additional dithiole ring interacting with the 2,2′-(ethanediylidene)bis(1,3-dithiole) chromophore.

These results provide evidence for the structures shown in Scheme 5. The similarities in λ_{max} for the cation radicals **23**$^{+\bullet}$, **7**$^{+\bullet}$ and **10**$^{+\bullet}$, suggest that the soliton species in the dendralene systems are situated within the linear 1,2-ethylenediylidene fragments. However, in each of the dicationic intermediates the absorption maxima represent different electronic behaviour: in **23**$^{2+}$ delocalisation of the π electrons between the 1,3-dithiole rings is not possible, hence there is a large shift in λ_{max} to the blue. The lowest energy absorption maxima for **7**$^{2+}$ are markedly higher than the value of λ_{max} for neutral compound **7** (408 nm). This behaviour is attributed to an intramolecular charge transfer (ICT) process within **7**$^{2+}$, represented by the push-pull sequence in Scheme 5. However, the values for **10**$^{2+}$ strongly suggest that the intermediate must exist as structure **C** (Scheme 4) since if **B** predominated we would expect: i) absorption maxima corresponding to fragments analogous to **23**$^{2+}$ and **27**, at about 400 and 432 nm, respectively; and/or ii) an ICT band (at ca. 645 nm, similar to **7**$^{2+}$) arising from the donation of π electrons from an uncharged dithiole ring to a dithiolium cation three sp^2 carbon atoms away; this pathway of π-electron movement also precludes the possibility of ICT between the remaining two 1,3-dithiole rings. The values of λ_{max} are significantly higher than would be expected for these processes, and they are not much lower than the values for the cation radical **10**$^{+\bullet}$ These data therefore imply that the intermediate dication **10**$^{2+}$ exists as the bis(cation radical) **C**, rather than **B** as suggested in the CV study above.

To explore this matter further, SEEPR data in acetonitrile were obtained for compounds **7** and **10**. Oxidation at 0.40 V led to a a strong EPR signal from the cation radicals, by analogy with data reported previously for compound **23**.[19b]



7^{2+}

Scheme 5.

Further oxidation of **10** at 0.60 V resulted in a considerable reduction in the intensity of the EPR signal, suggesting a predominant ground state structure **B** for the dication, rather than **C**. Structure **C**, which is implied by the UV/Vis absorption spectra discussed above may be a low-lying photoexcited state which is accessible under the conditions of irradiation in the spectrometer beam.

Conclusion

These molecules are among the first redox-active dendralenes to be characterised. Efficient routes for their synthesis have been developed and cyclic voltammetric studies establish that they are strong π-electron donor molecules. Cyclic voltammetric and UV/Vis spectroscopic data are consistent with poor cross-conjugation in these systems, in agreement with previous theoretical studies on dendralenes. For example, only small red shifts are observed in the values of λ_{max} for the series **23**, **7** and **10.** X-ray structural data reveal that two of the dithiole rings of **8** are conjugated, while the third dithiole ring is almost orthogonal to this plane, and hence its π-electron system is isolated. A comparison of the crystal structures of **15** and **17** shows a more effective conjugation of the substituted cyclopentadienyl ring, two C=C bonds and fused dithiole and dithiine rings, in the former compound. In molecule **17**, delocalisation along this conjugation path is reduced by twisting of the chain. Unravelling the subtle interplay of steric and electronic demands in the varied oxidation states of these systems is clearly a complex issue! The study of new analogues with a pendant electron-acceptor unit, for example a dicyanomethylene group, is being explored.[23] To date, no salts of dendralenes have been characterised crystallographically. It would be of considerable interest to establish the conformational changes which accompany the redox reactions in dendralenes of this family.

Experimental Section

General details: Elemental analyses were performed on a Carlo–Erba Strumentazione. ^{1}H NMR spectra were obtained on a Bruker AC 250 spectrometer operating at 250.134 MHz. ^{13}C NMR spectra were obtained on a Varian 400 spectrometer operating at 100.581 MHz. Mass spectra were recorded on a VG7070E spectrometer operating at 70 eV. IR spectra were recorded on a Perkin–Elmer 1615 FTIR spectrometer operated from a Grams Analyst 1600. UV spectra were obtained on a Kontron Uvicon 930 spectrophotometer using quartz cells; extinction coefficients (ε) are quoted in $\text{M}^{-1}\,\text{cm}^{-1}$. Melting points were obtained on a Kofler hot-stage microscope apparatus and are uncorrected. Cyclic voltammetric data were obtained on a BAS 50 W electrochemical analyser under the conditions reported in Table 1. Spectroelectrochemical measurements were made on a Perkin–Elmer Lambda 19 spectrophotometer using a Pyrex cell, with ITO thin layer working electrode, silver wire reference electrode and a platinum wire counter electrode in CH_2Cl_2/0.1M $Bu_4N^+ClO_4^-$. All solutions were purged with argon and retained under an inert atmosphere while the data were recorded. TLC analyses were performed using Merck pre-coated silica (0.2 mm) aluminium backed sheets. Column chromatography was carried out using Merck silica gel (70–230 mesh). Solvents were distilled prior to use in chromatography. All reagents were of commercial quality and used as supplied unless otherwise stated; solvents were dried where necessary using standard procedures.

X-ray crystallography: X-ray diffraction experiments were carried out on a Rigaku AFC6S 4-circle diffractometer ($Mo_{K\alpha}$ radiation, $\lambda = 0.71073$ Å) with a Cryostream (Oxford Cryosystems) open-flow N_2 gas cryostat, using teXsan software.[24] The empirical (φ scans) absorption corrections were negligible. The structures were solved by direct methods and refined by full-matrix least-squares against F^2 of all data, using SHELXTL software[25] (**15**: non-H atoms anisotropic, H atoms ”riding”; **17**: Fe, S atoms anisotropic, C isotropic, H ”riding”). Crystal data and experimental details are listed in Table 2. Crystallographic data (excluding structure factors) have been deposited with the Cambridge Crystallographic Data Centre as supplementary publications nos. CCDC-133930 (**15**) and 133931 (**17**). Data for **8** had been deposited earlier (ref. WAGHER). Copies of the data can be obtained free of charge on application to CCDC, 12 Union Road, Cambridge CB2 1EZ, UK (fax: (+44)1223-336-033; e-mail: deposit@ccdc.cam.ac.uk.

Table 2. Crystal data and experimental details.

Compound	15	17
formula	$C_{18}H_{16}FeS_4$	$C_{30}H_{26}Fe_2S_4$
formula weight	416.4	626.5
T [K]	120	150
crystal system	monoclinic	triclinic
space group	$P2_1/c$ (no. 14)	$P\bar{1}$ (no. 2)
a [Å]	5.985(4)	7.274(2)
b [Å]	12.487(5)	10.122(3)
c [Å]	22.780(9)	19.168(5)
α [°]	90	77.49(2)
β [°]	96.57(4)	80.94(2)
γ [°]	90	71.57(2)
V [Å^3]	1691.3(1.4)	1301.0(6)
Z	4	2
ρ[g cm^{-3}]	1.635	1.599
$\mu(Mo_{K\alpha})$ [mm^{-1}]	1.38	1.46
scan mode	ω	$2\theta/\omega$
max. 2θ [°]	55	50
reflections collected	4218	4817
unique reflections	3801	4415
R_{int}	0.044	0.073
reflections with $F^2 > 2\sigma(F^2)$	2235	2384
refined parameters	224	174
$R[F^2 > 2\sigma(F^2)]$	0.045	0.115
$wR(F^2)$ all data	0.113	0.298
residual max., min. $\Delta\rho$ [e Å^{-3}]	0.54, −0.46	1.03, −0.95

1,3-Propanedial-2-(4,5-dimethyl-1,3-dithiole-2-ylidene) (4): Compound **4** was prepared analogously to compound **3**[13] from salt **2**[12] (0.9 g, 3 mmol), the sodium salt of malonaldehyde (0.3 g, 3.2 mmol) in acetonitrile (100 mL) and isolated, after purification on a neutral alumina column (eluent: dichloromethane/hexane 1:1 v/v), as a pale yellow solid (0.20 g, 34%). M.p. 150 °C (sublimation); ^{1}H NMR ($CDCl_3$): $\delta = 9.74$ (s, 2H), 2.42 (s, 6H); IR (nujol): $\tilde{\nu}_{max} = 1620$ cm^{-1} (C=O); MS (EI): m/z: 200 [M^+]; $C_8H_8O_2S_2$ calcd: C 48.0, H 4.0; found: C 47.7, H 3.9.

Propane-1,2,3-tris[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene] (7) and propane-1,2-bis[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-3-al (11): To a solution of phosphonate ester **5**[11] (0.70 g, 2.3 mmol) in THF (50 mL) at −78 °C under nitrogen was added nBuLi (1.6M in hexane, 1 mL, 1.6 mmol). After 1 h, compound **3**[13] (0.30 g, 1.1 mmol) in THF (50 mL) was added and the solution was stirred at −78 °C for 2 h. The solution was then allowed to warm to room temperature overnight, then the solvent was evaporated and the residue extracted into dichloromethane (100 mL), which was washed with water (2 × 100 mL) and dried ($MgSO_4$). Evaporation of the organic phase yielded an orange solid which was a mixture of products. Purification was achieved on a neutral alumina column (eluent: dichloromethane/hexane 1:2 v/v) to yield **7** as a yellow oil (0.47 g, 67%). ^{1}H NMR ($CDCl_3$): $\delta = 5.65$ (s, 2H), 2.35 (s, 6H), 2.34 (s, 6H), 2.33 (s, 6H); MS (DCI): m/z: 621 [MH^+]; $C_{18}H_{20}S_{12}$ calcd: C 34.8, H 3.3; found: C 34.4, H 3.6. Continued elution with hexane/dichloromethane (1:1 v/v) afforded **11** as a red solid (0.15 g, 30%). M.p. 126–127 °C; ^{1}H NMR ($CDCl_3$): $\delta = 9.42$ (s, 1H), 5.98

(s, 1H), 2.54 (s, 3H), 2.49 (s, 3H), 2.43 (s, 3H), 2.37 (s, 3H); IR (nujol): $\tilde{\nu}_{max} = 1618\ cm^{-1}$ (C=O); MS (DCI): m/z: 443 [MH^+]; $C_{13}H_{14}OS_8$ calcd: C 35.3, H 3.2; found: C 35.2, H 3.2.

Propane-1,2,3-tris(4,5-dimethyl-1,3-dithiol-2-ylidene) (8): Compound **8** was prepared analogously to **7** from reagent **6**[12] (0.36 g, 1.5 mmol) in THF (50 mL), nBuLi (1.6 M in hexane, 1 mL, 1.6 mmol) and compound **4** (0.15 g, 0.75 mmol) in THF (10 mL), and purified on a neutral alumina column (eluent: hexane/dichloromethane 2:1 v/v) to yield **8** as a yellow solid (0.20 g, 62 %). M.p. >230 °C; ^1H NMR ($CDCl_3$): $\delta = 5.72$ (s, 2H), 1.92 (s, 6H), 1.89 (s, 12H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 502 (2.8×10^3), 404 nm (3.1×10^4); MS (EI): m/z: 428 [M^+]; $C_{18}H_{20}S_6$ calcd: C 50.4, H 4.7; found: C 50.6, H 5.0.

Butane-1,2,3-tris[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene]-4-al (9): Oxalyl chloride (0.1 mL) was added to anhydrous dimethylformamide (DMF) (5 mL) at −5 °C and the mixture stirred at room temperature for 0.5 h under nitrogen. A solution of compound **7** (200 mg, 0.32 mmol) in anhydrous DMF (5 mL) was then added and after 3 h the solution was hydrolysed with NaOH (5 M, 2 mL), slowly turning the colour from brown to red. Dichloromethane (50 mL) was added and the organic phase was washed with water (3 × 100 mL), dried ($MgSO_4$) and evaporated. The resulting red solid was purified on a neutral alumina column (eluent: hexane/dichloromethane 2:1 v/v) to yield **9** as a red solid (110 mg, 53 %). M.p. 172–174 °C; ^1H NMR ($CDCl_3$): $\delta = 9.08$ (s, 1H), 5.90 (s, 1H), 2.55 (s, 3H), 2.48 (s, 3H), 2.43 (s, 3H), 2.36 (s, 3H), 2.34 (s, 3H), 2.27 (s, 3H); UV/Vis (CH_2Cl_2): λ_{max} (ε): 408 nm (2.5×10^4); MS (DCI): m/z 649 [MH^+]; $C_{19}H_{20}OS_{10}$ calcd: C 35.2, H 3.1; found: C 35.3, H 3.2.

Butane-1,2,3,4-tetrakis[4,5-bis(methylsulfanyl)-1,3-dithiol-2-ylidene] (10): To a solution of phoshonate ester **5** (150 mg, 0.5 mmol) in dry THF (50 mL) under nitrogen at −78 °C, was added nBuLi (1.6 M in hexane, 0.31 mL, 0.5 mmol). After 1 h a solution of compound **9** (260 mg, 0.4 mmol) in dry THF (10 mL) was added and the mixture stirred at −78 °C for 1 h before being allowed to warm to room temperature overnight. The solvent was then evaporated, water added (100 mL) and the product extracted with dichloromethane (3 × 50 mL). Drying ($MgSO_4$), evaporation and column chromatography on neutral alumina (eluent: hexane/dichloromethane 2:1 v/v) yielded **10** as a yellow solid (190 mg, 57 %). M.p. 87–92 °C ; ^1H NMR ($CDCl_3$): $\delta = 5.68$ (s, 2H), 3.47 (s, 6H), 3.45 (s, 6H), 3.43 (s, 6H), 3.40 (s, 6H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 502 (2.8×10^3), 404 nm (3.1×10^4); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 512 (8.3×10^3), 412 nm (3.8×10^4); MS (DCI): m/z: 827 (MH^+); $C_{24}H_{26}S_{16}$ calcd: C 34.8, H 3.2; found: C 34.9, H 3.2.

1-[3,4-Bis(4,5-dimethylsulfanyl-1,3-dithiol-2-ylidene)but-1-enyl]ferrocene (13): To a solution of compound **12**[14] (600 mg, 1.02 mmol) in THF (60 mL), was added butyllithium (1.6 M in hexane, 0.7 mL, 1.12 mmol) and the ylide left to form for 15 min. After this time compound **11** (170 mg, 0.38 mmol) was added, and the mixture stirred at 20 °C for 16 h, then evaporated under reduced pressure, and the residue extracted with dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Purification by column chromatography, using neutral alumina with hexane-dichloromethane (3:1 v/v) as the eluent, afforded **13** as a red solid, which was recrystallized from dichloromethane–hexane (1.30 g, 54 % yield). M. p. 54-56 °C; ^1H NMR ($CDCl_3$): $\delta = 6.19$ (s, 2H), 5.89 (s, 1H), 4.43 (m, 2H), 4.30 (m, 2H), 4.17 (s, 5H), and 2.46–2.38 (m, 12H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 374 (3.2×10^4), 288 (3.9×10^4), 261 nm (1.7×10^4); MS (EI): m/z: 624 ([M^+]); $C_{24}H_{24}FeS_8$ calcd: C 46.2, H 3.9; found: C 46.5, H 4.1.

1-[3-(5,6-Dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)diallyl]ferrocene (15): To a solution of **12** (4.00 g, 6.81 mmol) in THF (100 mL) at 20 °C, was added butyllithium (4.3 mL, 1.6 M, 6.88 mmol) and the ylide was left to form for 15 min at 20 °C. Compound **14**[15] (1.40 g, 5.98 mmol) was then added, and the reaction was stirred at 20 °C for 24 h. The reaction mixture was evaporated under reduced pressure, and the residue extracted with dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Purification using column chromatography on silica gel with hexane–dichloromethane (3:1 v/v) as the eluent, afforded **15** as a dark red solid, which was recrystallised from dichloromethane–hexane (1.60 g, 64 % yield). M.p. 148–150 °C; ^1H NMR ($CDCl_3$): $\delta = 6.53–5.66$ (m, 3H), 4.27 (m, 2H), 4.18 (m, 2H), 4.03 (s, 5H), and 3.22 (s, 4H); ^{13}C NMR [$(CD_3)_2C(O)$]: $\delta = 129.8$, 127.1, 123.4, 117.4, 111.3, 84.0, 70.0, 69.9, 67.5, and 30.0; UV/Vis (CH_2Cl_2): λ_{max} (ε) = 374 (2.0×10^4), 288 (1.2×10^4), 261 nm (1.5×10^4); MS (DCI): m/z: 417 [MH^+]; $C_{18}H_{16}FeS_4$ calcd: C 51.9, H 3.9; found: C 52.3; H 3.9.

1-[4-oxo-3-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)but-1-enyl]-ferrocene (16): To anhydrous dimethylformamide (15 mL, excess) cooled to 0 °C, oxalyl chloride (0.6 mL, 6.87 mmol) was added slowly dropwise and the mixture stirred for 5 min at 0 °C, and then warmed to 20 °C, remaining so for a further 30 min. Compound **15** (1.4 g, 3.37 mmol) was then added and the mixture stirred at 20 °C for 16 h. The reaction was quenched at 0 °C with aqueous sodium hydroxide (50 mL, 1 M), and then with water (200 mL). Dichloromethane was added (75 mL), and the organic layer separated, dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography on silica gel, with dichloromethane as the eluent, afforded **16** as a bright red solid, which was recrystallised from dichloromethane–hexane (1.1 g, 74 % yield). M.p. 169–172 °C; ^1H NMR ($CDCl_3$): $\delta = 9.63$ (s, 1H), 6.70 (d, $J = 16.1$ Hz, 1H), 6.48 (d, $J = 16.1$ Hz, 1H), 4.44 (m, 2H), 4.30 (m, 2H), 4.14 (s, 5H), and 3.39 (s, 4H); IR (KBr): $\tilde{\nu}_{max} = 1616\ cm^{-1}$; MS (DCI): m/z: 445 [MH^+]; $C_{19}H_{16}FeOS_4$ calcd: C 51.4, H 3.6; found: C 51.3, H 3.8.

1,1′-Bis[3-(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)penta-1,4-diene-1,5-diyl]diferrocene (17): To a suspension of **12** (1.00 g, 1.70 mmol) in THF (60 mL), at room temperature, was added butyllithium (1.6 M in hexane, 1.1 mL, 1.76 mmol), and the reaction stirred for 15 min before **16** (500 mg, 1.13 mmol) was added and the reaction stirred for 16 h. The reaction mixture was evaporated under reduced pressure, and extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Column chromatography on silica gel with toluene as the eluent afforded **17** as an orange solid, which was recrystallised from dichloromethane-hexane (510 mg, 72 % yield). M.p. 189 °C (decomp); ^1H NMR ($CDCl_3$): $\delta = 6.37$ (s, 4H), 4.44 (m, 4H), 4.31 (m, 4H), 4.18 (s, 10H), and 3.35 (s, 4H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 394 (2.4×10^4), 288 (3.5×10^4), 270 nm (sh); MS (DCI): m/z: 627 [MH^+]; $C_{30}H_{26}Fe_2S_4$ calcd: C 57.5, H 4.2; found: C 57.5; H 4.4.

1-[3,4-Bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4-dithiin-2-ylidene)but-1-enyl]-ferrocene (19): To a solution of **18**[15] (1.00 g, 3.03 mmol) in THF (100 mL), was added butyllithium (1.9 mL, 1.6 M, 3.04 mmol) at −78 °C, and the reaction stirred at this temperature for 15 min. Compound **16** (1.00 g, 2.25 mmol) was then added and the reaction was warmed slowly to room temperature with stirring for a further 16 h. The reaction mixture was evaporated under reduced pressure, and extracted into dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$), and evaporated. Column chromatography on silica gel with dichloromethane–hexane (1:1 v/v) as the eluent afforded **19** as an orange solid, which was recrystallised from dichloromethane–hexane (1.16 g, 83 % yield). M.p. 187–189 °C; ^1H NMR ($CDCl_3$): $\delta = 6.20$ (s, 2H), 5.97 (s, 1H), 4.41 (m, 2H), 4.28 (m, 2H), 4.16 (s, 5H), and 3.31 (m, 8H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 384 (2.2×10^4), 291 (3.7×10^4), 219 nm (5.9×10^4); MS (DCI): m/z: 621 [MH^+]; $C_{24}H_{20}FeS_8$ calcd: C 46.4, H 3.3; found: C 46.1, H 3.2.

1-[5-Oxo-3,4-bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-pent-1-enyl]ferrocene (20): Anhydrous dimethylformamide (10 mL, excess) was cooled to 0 °C, and oxalyl chloride (0.2 mL, 2.29 mmol) added slowly dropwise. The mixture was stirred for 5 min at 0 °C, and then warmed to 20 °C and stirred for a further 30 min. After this time, **19** (500 mg, 0.81 mmol) was added and the mixture stirred at 20 °C for 3 h. The reaction was quenched at 0 °C with aqueous sodium hydroxide (50 mL, 1 M), and finally with water (200 mL). Dichloromethane was added (75 mL), and the organic layer separated, dried ($MgSO_4$), and evaporated under reduced pressure. Column chromatography on silica gel with dichloromethane as the eluent afforded **20** as an unstable red solid, which was recrystallised from dichloromethane–hexane (370 mg, 71 % yield). M.p. 175 °C (decomp); ^1H NMR ($CDCl_3$): $\delta = 9.14$ (s, 1H), 6.32 (m, 1H), 6.89 (m, 1H), 4.35 (m, 2H), 4.27 (m, 2H), 4.10 (s, 5H), and 3.31 (m, 8H); IR (KBr): $\tilde{\nu}_{max} =$ 1610, 1410, 1261, 1103, 1024, and 802 cm^{-1}; MS (DCI): m/z: 649 [MH^+].

***trans*-1,1′-Bis[3,4-bis(5,6-dihydro-1,3-dithiolo[4,5-*b*][1,4]dithiin-2-ylidene)-hexa-1,5-diene-1,6-diyl]diferrocene (21)**: To a suspension of **12** (1.00 g, 1.70 mmol) in THF (60 mL), at room temperature, was added butyllithium (1.6 M, 1.1 mL, 1.76 mmol), and the reaction stirred for 15 min. Compound **20** (300 mg, 0.46 mmol) was then added and the reaction stirred at 20 °C for 16 h. The reaction mixture was evaporated under reduced pressure and extracted with dichloromethane. Water was added, the organic layer separated, dried ($MgSO_4$) and evaporated. Column chromatography on silica gel with toluene as the eluent afforded **21** as a red solid which was recrystallised from dichloromethane (250 mg, 65 % yield). M.p. 182 °C (decomp); ^1H NMR ($CDCl_3$): $\delta = 6.26$ (d, $J = 15.2$ Hz, 2H), 5.96 (d, $J =$

15.5 Hz, 2H), 4.39 (m, 4H), 4.24 (m, 4H), 4.11 (s, 10H), and 3.31 (s, 8H); UV/Vis (CH_2Cl_2): λ_{max} (ε) = 384 (7.4×10^4), 290 nm (7.4×10^4); MS (DCI): *m/z*: 831 [*MH*$^+$]; $C_{36}H_{30}Fe_2S_8$ calcd: C 52.0, H 3.6; found: C 52.3, H 3.7.

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[1] a) *Handbook of Conducting Polymers* (Eds.: T. A. Skotheim, R. L. Elsenbaumer, J. R. Reynolds), 2nd ed., Marcel Dekker, New York, **1998**; b) *Handbook of Organic Conductive Molecules and Polymers, Vol. 1–4* (Ed.: H. S. Nalwa), Wiley, Chichester, **1997**.

[2] Review: H. Shirakawa, see ref. [1a], **1998**, 197–208.

[3] Reviews: R. D. McCullough, *Adv. Mater.* **1998**, *10*, 93–116; b) *Handbook of Oligo and Polythiophenes* (Ed.: D. Fichou), Wiley-VCH, Weinheim, **1998**; c) M. R. Andersson, O. Thomas, W. Mammo, M. Svensson, M. Theander, O. Inganäs, *J. Mater. Chem.* **1999**, *9*, 1933–1940.

[4] Reviews: a) *Electronic Materials: The Oligomer Approach* (Eds.: K. Müllen, G. Wegner), Wiley-VCH, Weinheim, **1998**; b) J. Roncali, *J. Mater. Chem.* **1997**, *7*, 2307–2321; c) G. Horowitz, *J. Mater. Chem.* **1999**, *9*, 2021–2026.

[5] a) Review: H. Hopf, *Angew. Chem.* **1984**, *96*, 947–958; *Angew. Chem. Int. Ed. Engl.* **1984**, *23*, 948–959; b) N. Tyutyulkov, F. Dietz, K. Müllen, M. Baumgarten, S. Karabunarliev, *Chem. Phys.* **1994**, *189*, 83–97; c) A. M. Boldi, J. Anthony, V. Gramlich, C. B. Knobler, C. Boudon, J.-P. Gisselbrecht, M. Gross, F. Diederich, *Helv. Chim. Acta* **1995**, *78*, 779–796; d) R. T. Tykwinski, F. Diederich, *Liebigs Ann. Chem.* **1997**, 649–661; e) M. H. Palmer, J. A. Blair-Fish, P. Sherwood, *J. Mol. Struct.* **1997**, *412*, 1–18; f) R. R. Tykwinski, *Chem. Commun.* **1999**, 905–906; g) Y. Zhao, R. R. Tykwinski, *J. Am. Chem. Soc.* **1999**, *121*, 458–459.

[6] Y. Misaki, Y. Matsumura, Y. Sugimoto, Z. Yoshida, *Tetrahedron Lett.* **1990**, *30*, 5289–5292.

[7] a) F. L. Carter in *Computer Applications in Chemistry* (Eds.: S. R. Heller, R. Potenzone, Jr.), Elsevier, Amsterdam, **1983**, 225–262; b) F. L. Carter, R. E. Siatkowski in *From Atoms to Polymers* (Eds.: J. F. Liebman, A. Greenberg), VCH, Weinheim, **1989**, 307–392.

[8] T. K. Hansen, J. Becher, *Adv. Mater.* **1993**, *5*, 288–292.

[9] *Ferrocene* (Eds.: A. Togni, T. Hayashi), VCH, Weinheim, Germany, **1995**.

[10] Preliminary communication: M. A. Coffin, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, *J. Chem. Soc. Chem. Commun.* **1993**, 552–554.

[11] A. J. Moore, M. R. Bryce, *Tetrahedron Lett.* **1992**, *33*, 1373–1376.

[12] A. J. Moore, M. R. Bryce, *J. Chem. Soc. Perkin Trans. 1* **1991**, 157–168.

[13] F. Adams, R. Gompper, A. Hohenester, H.-U. Wagner, *Tetrahedron Lett.* **1988**, *29*, 6921–6924.

[14] P. L. Pauson, W. E. Watts, *J. Chem. Soc.* **1963**, 2990–2996.

[15] A. J. Moore, M. R. Bryce, *Synthesis* **1991**, 26–28.

[16] F. H. Allen, O. Kennard, D. G. Watson, L. Brammer, A. G. Orpen, R. Taylor, *J. Chem. Soc. Perkin Trans. 2* **1987**, S1–S19.

[17] A. J. Moore, M. R. Bryce, A. S. Batsanov, A. Green, J. A. K. Howard, M. A. McKervey, P. McGuigan, I. Ledoux, E. Ortí, R. Viruela, P. M. Viruela, B. Tarbit, *J. Mater. Chem.* **1998**, *8*, 1173–1184.

[18] R. S. Rowland, R. Taylor, *J. Phys. Chem.* **1996**, *100*, 7384–7391.

[19] a) A. J. Moore, M. R. Bryce, D. J. Ando, M. B. Hursthouse, *J. Chem. Soc. Chem. Commun.* **1991**, 320–321; b) M. R. Bryce, A. J. Moore, B. K. Tanner, R. Whitehead, W. Clegg, F. Gerson, A. Lamprecht, S. Pfenninger, *Chem. Mater.* **1996**, *8*, 1182–1188.

[20] a) Z. Yoshida, T. Kawase, H. Awaji, I. Sugimoto, T. Sugimoto, S. Yoneda, *Tetrahedron Lett.* **1983**, *24*, 3469–3472; b) T. Sugimoto, H. Awaji, Y. Misaki, T. Kawase, S. Yoneda, Z. Yoshida, *Chem. Mater.* **1989**, *1*, 535–547.

[21] a) A. J. Moore, P. J. Skabara, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, S. T. A. K. Daley, *J. Chem. Soc. Chem. Commun.* **1993**, 417–419; b) A. J. Moore, M. R. Bryce, P. J. Skabara, A. S. Batsanov, L. M. Goldenberg, J. A. K. Howard, *J. Chem. Soc. Perkin Trans. 1*, **1997**, 3443–3449; see also c) A. Togni, M. Hobi, G. Rihs, G. Rist, A. Albinati, P. Zanello, D. Zech, H. Keller, *Organometallics* **1994**, *13*, 1224–1234.

[22] a) E. H. Elandaloussi, P. Frère, A. Benahmed–Gasmi, A. Riou, A. Gorgues, J. Roncali, *J. Mater. Chem.* **1996**, *6*, 1859–1863; b) T. K. Hansen, M. R. Bryce, J. A. K. Howard, D. S. Yufit, *J. Org. Chem.* **1994**, *59*, 5324–5327.

[23] A. Green, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, *J. Organomet. Chem.* **1999**, *590*, 180–183.

[24] TEXSAN: Single crystal structure analysis software, Version 5.0, Molecular Structure Corporation, TX, USA, **1989**.

[25] G. M. Sheldrick, SHELXTL, Version 5.10, Bruker Analytical X-ray Systems, Madison, WI, USA, **1997**.

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