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Aryl ester dendrimers incorporating tetrathiafulvalene units: convergent synthesis, electrochemistry and charge-transfer properties

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The convergent synthesis of a range of aryl ester dendrimers with peripheral tetrathiafulvalene (TTF) units is reported. 4-(Hydroxymethyl)-TTF and 4,5-(2-hydroxymethylpropane-1,3-diyldithio)-TTF have been used as the starting TTF reagents. The core reagents are benzene-1,3,5-tricarbonyl trichloride, terephthaloyl chloride, biphenyl-4-4′-dicarbonyl chloride and 4,4′-oxybis(benzenecarbonyl chloride). Dendrimers comprising up to 12 TTF units have been characterised by elemental analysis, plasma desorption mass spectrometry, ^{1}H NMR spectroscopy and solution electrochemistry. Cyclic voltammetry (CV) and ultra microelectrode CV studies show that the TTF dendrimers display nearly ideal redox behaviour for the TTF system with no significant interaction between the TTF units. Thin layer cyclic voltammetric studies show that all the TTF units of these systems undergo two, single-electron oxidations. The dendrimers form charge-transfer complexes upon reaction with iodine in solution. Intermolecular interactions of the TTF radical cations are observed in the UV–VIS spectra of some of the oxidised derivatives.

The synthesis and characterisation of dendrimers, cascade molecules and related hyper-branched systems is a rapidly-expanding topic in polymer science.[1] These materials comprise a multifunctionalised core, from which radiate repeating layers of monomers with a branch occurring at each monomer unit. They possess well-defined, three-dimensional structural order, and their size and architecture can be precisely controlled in their synthesis, providing unique molecular frameworks for the disposition of functional groups in predetermined spatial arrangements. Initial research into dendrimers focused on the synthesis of higher generation systems with large molecular weights and dense surface packing.[2] As synthetic methodology has developed, the emphasis has clearly changed towards systems which incorporate more elaborate functional groups[3] at the exterior surface of, or embedded within, the dendrimer framework, *e.g.* crown ethers,[4] chiral units,[5] polynuclear metal complexes,[6] liquid crystal groups[7] and saccharide units,[8] which impart special properties to these macromolecules. In the context of functional dendrimers, a variety of redox-active organic and organometallic groups[9] have been incorporated into the structures with several long-term aims in mind. These include: (i) new electron-transfer catalysts; (ii) studies on the dynamics of electron transport at surfaces and within restricted reaction spaces; (iii) new materials for energy conversion; (iv) organic semiconductors; (v) organic magnets; and (vi) mimics of biological redox processes.

Some dendrimers contain a single redox-active unit (*e.g.* a metalloporphyrin) at the core, and the solution redox behaviour of this central 'encapsulated' group is modulated by the shielding effect of the outer spheres of the dendrimer structure.[10] More commonly, however, organometallic redox units, *e.g.* ferrocene and related metal sandwiches[11] or metal(bipyridyl),[6] are emplaced at peripheral sites and/or within the branches. The redox groups may behave independently in multi-electron processes (*n* identical electroactive centres giving rise to a single *n*-electron wave) or they may interact intra- or inter-molecularly, in which case overlapping or closely-spaced redox waves are observed at different potentials.

We recognised that advances in the synthesis of mono-functionalised tetrathiafulvalene (TTF) derivatives[12] offered the possibility of constructing dendrimers bearing TTF units. The incorporation of TTF into dendrimers presents a fascinating prospect for the following reasons: (i) oxidation of TTF to the cation radical and dication species occurs sequentially and reversibly at low potentials in a range of organic solvents (see Table 1); (ii) the oxidation potentials can be finely tuned by substituents on the TTF ring system; (iii) TTF cation radicals are thermodynamically very stable; (iv) oxidised TTF units have a high propensity to form dimers or ordered stacks, along which there can be high electron mobility, and (v) TTF is stable to many synthetic transformations, although it is important to avoid strongly acidic conditions and strong oxidising agents. Most multi-TTF derivatives[13] are dimers,[14] although some trimers,[15] pentamers,[16] higher oligomers,[17] and main-chain and side-chain polymeric TTFs[18] are known. A feature of these multi-TTF systems is that in general they readily yield multiply-charged species upon electrochemical oxidation in solution. Our aim was to synthesise structurally well-defined multi-electron redox systems, exploiting the known solubility enhancement in highly-branched macromolecules, compared to their linear counterparts.

Results and Discussion

Synthesis

We now describe in detail the synthesis of aryl ester dendrimers[19] functionalised with peripheral TTF groups.[20] 4-(Hydroxymethyl)-TTF **1**[12] has served as a convenient starting material. A convergent strategy, based on a repetitive coupling/deprotection sequence, has furnished dendrimer **12** comprising a 1,3,5-benzene triester core, surface-functionalised with 12 TTF units (Scheme 1). In a convergent synthesis,[21] dendrimer construction begins at what will become the surface of the molecule, and progresses inwards *via* a series of dendron wedges of increasing size, several of which are attached to the core unit in the final step. The functionalised reagent which we used for the esterification reactions that built up successive generations is 5-(*tert*-butyldimethylsilyloxy)isophthaloyl chloride **4**.[19] A conceptually similar synthesis, using a new TTF derivative **20**, is shown in Scheme 2. A series of bifunctional cores have also been used, as shown in Schemes 3–5.

At the outset of this work, we established that 4-(hydroxymethyl)-TTF **1** readily formed esters under mild conditions, and that the products were stable to silica gel chromatography,

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Table 1 Solution electrochemical data obtained by CV and UV–VIS spectroscopy[a]

compound	$E_1^{1/2}$/V	$E_2^{1/2}$/V	λ_{max}/nm	λ_{max}/nm after addition of I_2
TTF	0.34	0.71	228, 312, 320, 365, 450	232, 295, 366, 442, 590
3	0.42	0.84	220, 307, 365	225, 363, 439, 590
6	0.42	0.81	222, 306	222, 306, 591
7	0.45	0.86	220, 263, 305, 360	222, 294, 363, 590
9	0.42	0.81	223, 299, 364, 433	222, 299, 364, 433, 590
12	0.43	0.86	220, 295, 363	223, 262, 291, 363, 590
20	0.50	0.82	265, 334	293, 335, 367, 800
21	0.52	0.83	227, 263, 332, 443	233, 290, 359, 815
23	0.50	0.82	233, 263, 335, 395	233, 290, 338, 812
24	0.52	0.83	233, 263, 311, 335, 440	230, 296, 335, 827
25a	0.41	0.84	222, 242, 302, 370	222, 295, 362, 516
26a	0.42	0.83	222, 250, 300, 362	221, 294, 365, 433, 516
27a	0.44	0.86	222, 250, 300, 362	221, 294, 365, 433, 516
25b	0.40	0.81	223, 291, 363	221, 291, 365, 516
26b	0.43	0.85	293, 365, 398	262, 318, 363, 438, 528, 831
27b	0.41	0.82	229, 306, 370	233, 296, 368, 545, 836
25c	0.40	0.83	222, 270, 308, 363	222, 280, 363, 437, 578, 820
26c	0.40	0.84	223, 307, 364	233, 281, 314, 530, 830
27c	0.41	0.82	233, 281, 362	233, 281, 362, 525, 830
28	0.41	0.83	232, 312, 320, 364, 444	230, 295, 363, 444, 590

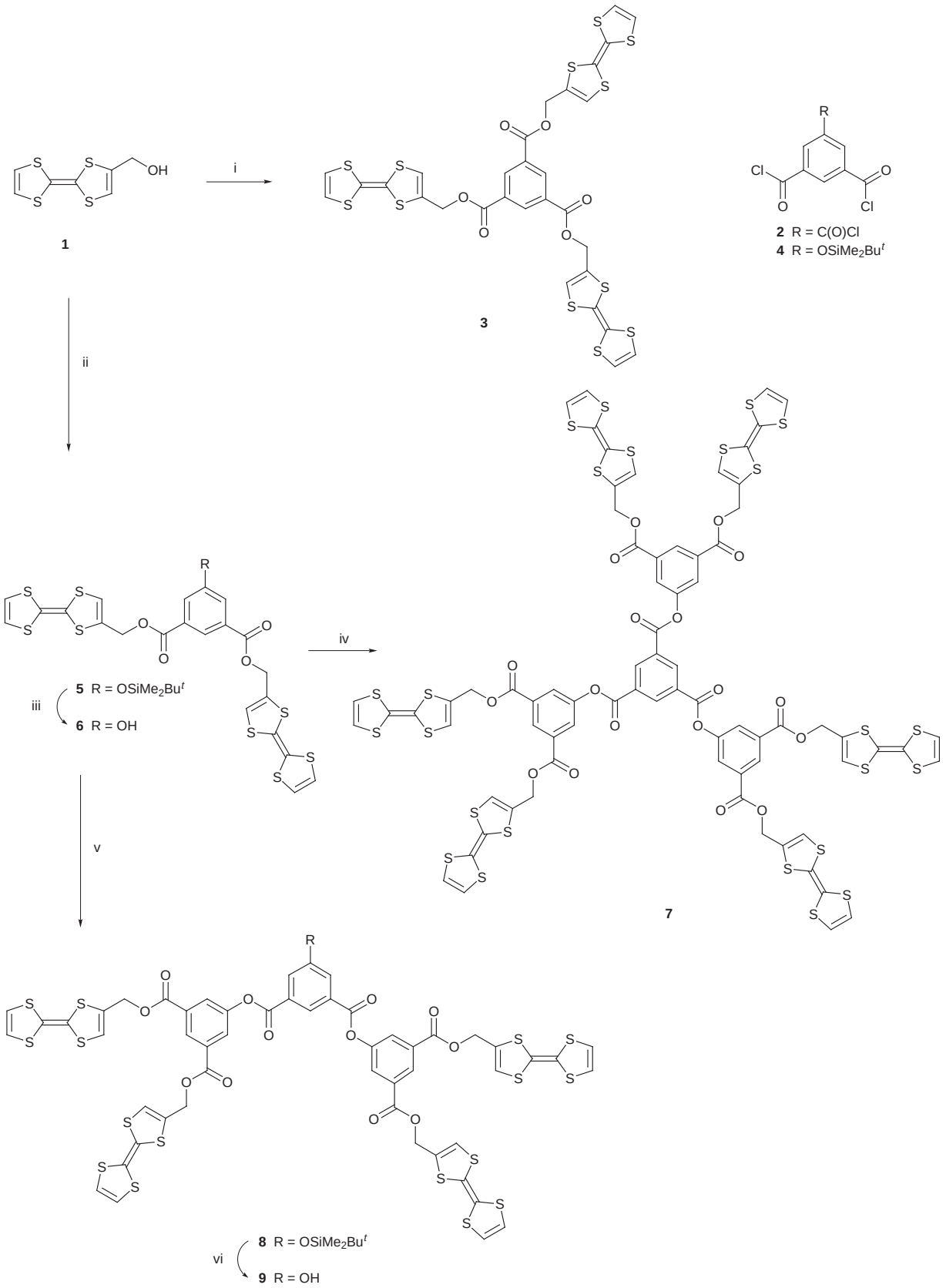
[a]CV data were obtained at 20 °C *vs.* Ag/AgCl, under argon using a platinum working electrode (1.6 mm diameter) and a platinum wire counter electrode, *ca.* 5×10^{-4} M compound, electrolyte 0.1 M $Bu_4N^+PF_6^-$, scan rate 100 mV s^{-1}. CV data were obtained in MeCN–CH_2Cl_2 (1:1 v/v); UV–VIS data obtained in CH_2Cl_2 at 20 °C, except for compounds **25a**, **26a**, **27a**, **25b**, **26b** and **27b**, for which all data (CV and UV–VIS) were obtained in DMSO.

but not to acidic media.[12] In an initial model experiment for dendrimer synthesis, compound **1** reacted with benzene-1,3,5-tricarbonyl trichloride **2**, using triethylamine as base in dichloromethane at room temperature, to afford the tris(TTF) derivative **3** in 85% yield. The analogous reaction of **1** with the silyl-protected diacid chloride **4** gave compound **5** (83% yield), deprotection of which [tetra-*n*-butylammonium fluoride (TBAF) in tetrahydrofuran (THF) at room temperature] afforded the bis(TTF) derivative **6** (85% yield) as a first generation dendron wedge containing the phenolic group as a reactive handle for further functionalisation. The hexakis(TTF) dendrimer **7** was obtained in 75% yield from reaction of **6** with triacid chloride **2**, in the presence of 4-dimethylaminopyridine (DMAP) as base (dichloromethane, room temperature). This reaction required DMAP as base: no reaction occured when triethylamine (the base used in the synthesis of **3**) was used instead. Following the same procedures that gave compounds **5** and **6**, reaction of two equivalents of alcohol **6** with reagent **4** yielded the silyl protected derivative **8** (76% yield) and hence dendron wedge **9** in 95% yield. By iterative procedures, compounds **9** and **4** reacted in the presence of a mixture of *N,N*-dimethylaniline and 4-dimethylaminopyridine (optimum ratio *ca.* 1:1 v/v) to yield octakis(TTF) derivative **10** in 76% yield. It was notable that no product was obtained using either triethylamine, *N,N*-dimethylaniline, or DMAP as the sole base: there is precedent for this in the work of Miller *et al.*, who noted that careful selection of the correct base was necessary for the synthesis of each generation of aryl ester dendrimers.[19] Compound **10** was desilylated, as before, to yield phenol derivative **11** (50% yield). Compound **9** reacted with benzene-1,3,5-tricarbonyl trichloride **2** to give the dodeca(TTF) dendrimer **12** in 48% yield.

Molecule **3** was stable for several months at room temperature, whereas **7** and **12** were stable only when stored at <0 °C; when stored at room temperature, even in the dark and under an argon atmosphere, they decomposed after a few days. Stability of the dendrimers and the dendron wedges decreased with increasing generation, so no attempts were made to assemble molecules of higher generation by reactions of **11**. These TTF macromolecules were purified by chromatography on silica gel and they were isolated as yellow–orange solids (compounds **3** and **5**–**8**) or as oils (compounds **9**–**12**), all of which were soluble in polar organic solvents. They were >98% pure as judged by ^{1}H NMR spectroscopy, and their plasma desorption mass spectra (PDMS) were consistent with the proposed structures. Solids were pure by combustion analysis.

We next sought to vary the structure of the TTF unit in these macromolecules, and to this end we chose the new derivative 4,5-(2-hydroxymethylpropane-1,3-diyldithio)TTF **20**. The methylthio substituents were attached as they are known to enhance the solubility of TTF derivatives, without significantly affecting the redox properties.[22] We envisaged that the hydroxymethyl substituent in compound **20** would function as a reactive alcohol (similar to compound **1**) in esterification reactions, and be less sterically hindered than the hydroxy analogue, 4,5-(2-hydroxypropane-1,3-diyldithio)TTF, which we had synthesised previously.[22]

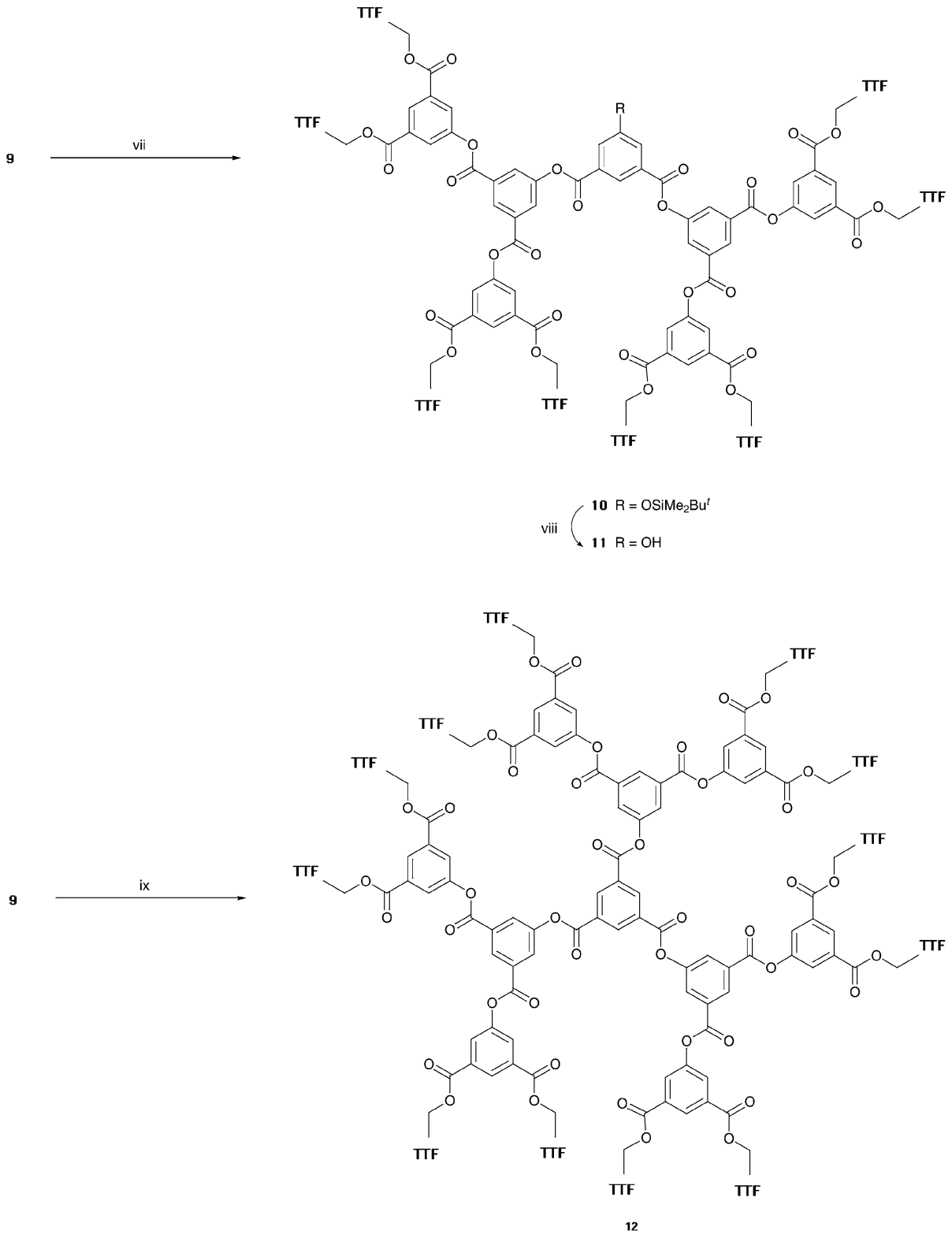
The synthesis of compound **20** and its esterification reactions are shown in Scheme 2. Thione **15** was prepared by reaction of alcohol **13**[23] with zincate salt **14**[24] in refluxing acetonitrile in 85% yield. The hydroxymethyl functionality was protected as its *tert*-butyldiphenylsilyl ether derivative **16**, in 84% yield, by reaction with *tert*-butyldiphenylsilyl chloride in the presence of imidazole in DMF.[25] The thione group was then oxidised to the corresponding ketone **17** under standard conditions (mercuric acetate in chloroform–acetic acid)[24b,26] in 88% yield. Ketones **17** and **18**[27] were then cross-coupled in the presence of triethyl phosphite at 130 °C,[28] to yield TTF derivative **19**, which was not separated from self-coupled products. After treatment of the mixture of TTF derivatives with TBAF in THF, alcohol **20** was isolated in 31% overall yield for the two steps. ^{1}H NMR spectroscopy revealed that alcohol **20** exists as a mixture of two conformational isomers, where the hydroxymethyl group at C-2 can be axial or equatorial with respect to the locked conformation of the seven-membered ring.[22] As a model reaction, three-fold esterification of **20** was achieved by reaction with reagent **2,** using DMAP as base, to afford compound **21** as an orange solid in 57% yield. Dendrimer **24** was then synthesised as shown in Scheme 2 *via* compounds **22** and **23**. In contrast to the silyl deprotection reactions in Scheme 1, the reaction of **22** with TBAF in THF was not straightforward and unless very dilute reaction conditions were used, the formation of **23** was accompanied by decomposition to form brown, oily products. Nonetheless, alcohol **23** could be isolated as an orange solid in an optimised yield of 66%. Esterification of **23** required far harsher conditions than the comparable reactions of alcohols **6** or **20**. Deprotonation of alcohol **23** was achieved using sodium



Scheme 1 *Reagents and conditions*: i, Et_3N, compound **2**, CH_2Cl_2, 20 °C; ii, Et_3N, compound **4**, CH_2Cl_2, 20 °C; iii, TBAF, THF, 20 °C; iv, DMAP, compound **2**, CH_2Cl_2, 20 °C; v, DMAP, compound **4**, CH_2Cl_2, 20 °C; vi, TBAF, THF, 20 °C; vii, DMAP–*N,N*-dimethylaniline, compound **4**, CH_2Cl_2, 35 °C; viii, TBAF, THF, 20 °C; ix, DMAP–*N,N*-dimethylaniline, compound **2**, CH_2Cl_2, 35 °C.

hydride in refluxing THF (no reaction was observed using DMAP in refluxing dichloromethane) and the resulting alkoxide reacted with reagent **2** to afford dendrimer **24** as an orange oil in 58% yield. Compounds **23** and **24** were harder to purify and were less stable than their analogues **6** and **7**, so we did not develop further the chemistry of TTF derivative **20** in this context.[29]

Instead, in attempts to improve dendrimer stability, we opted to change from trifunctional to bifunctional core units, with a view to obtaining more open structures. Thus, using

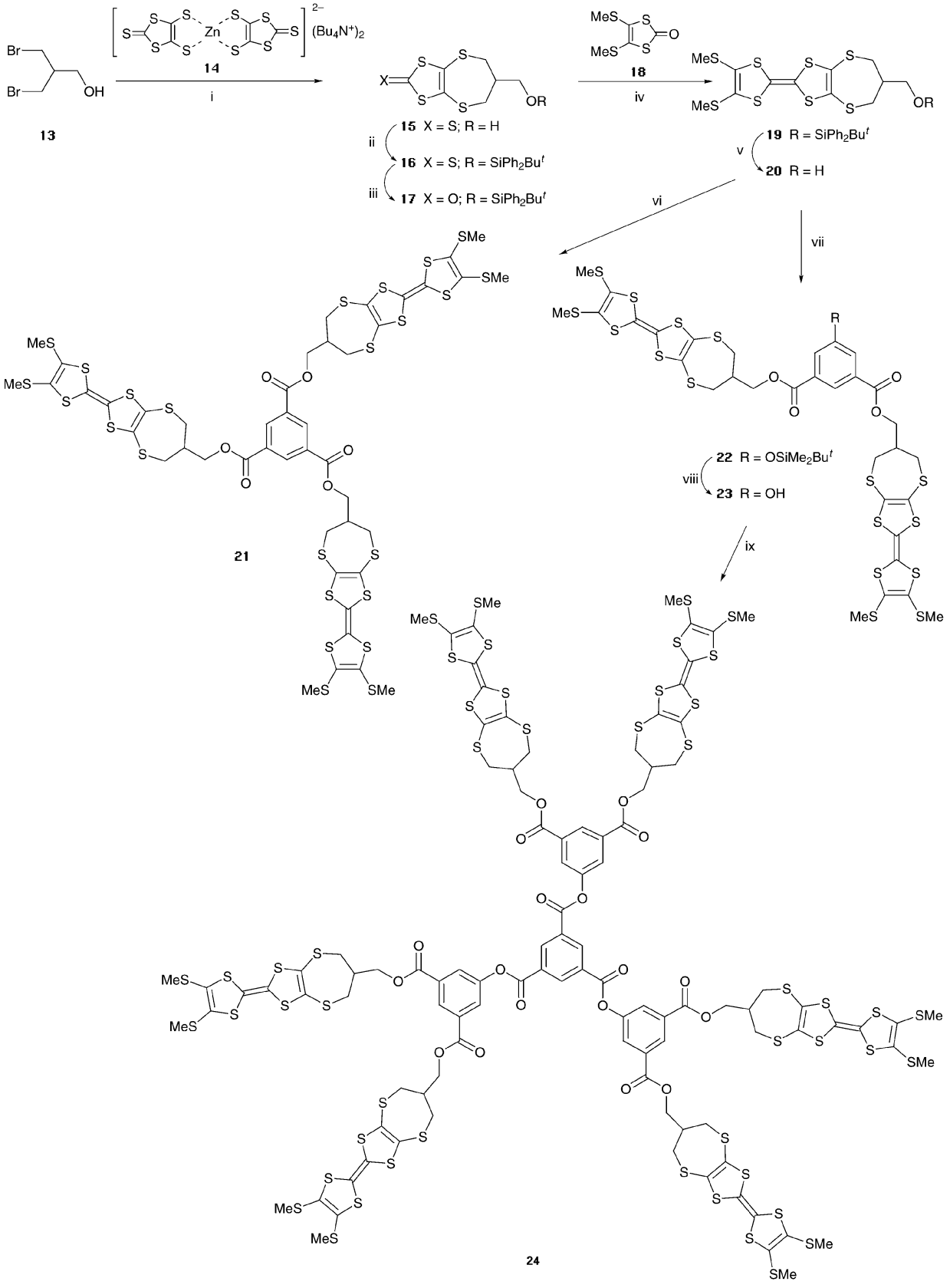


Scheme 1 (continued)

reagent **1** as the TTF derivative, terephthaloyl chloride, biphenyl-4,4′-dicarbonyl dichloride and 4,4′-oxybis(benzenecarbonyl chloride) gave the oligoester systems **25**–**27**, respectively (Schemes 3–5).[30] As in Scheme 1, it was necessary to choose carefully the base for the esterification reactions of alcohols **1**, **6** and **9**. The compounds containing the benzene and biphenyl cores, *viz*. **25a**,[31] **25b**, **26a**, **26b**, **27a** and **27b**, were only sparingly soluble in organic solvents, whereas analogues **25c**, **26c** and **27c**, with the more flexible diphenyl ether core unit, showed good solubility in polar organic solvents (*e.g.* acetone and dichloromethane). The three series of compounds **25a–c**, **26a–c** and **27a–c** were all stable upon storage at room temperature in air and daylight for at least one year, which is in marked contrast to the analogues in Schemes 1 and 2, which are built around the benzene triester core, where the high density of ester groups in the interior of the molecule appear to be responsible for the instability.

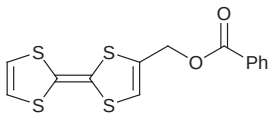
Electrochemical redox properties

An important aspect of this work was to evaluate the solution redox properties of the materials synthesised. A variety of



Scheme 2 *Reagents and conditions*: i, MeCN, reflux; ii, *tert*-butyldiphenylsilyl chloride, imidazole, DMF, 20 °C; iii, mercuric acetate, $CHCl_3$–glacial AcOH, 20 °C; iv, triethyl phosphite, 130 °C; v, TBAF, THF, 20 °C; vi, DMAP, compound **2**, CH_2Cl_2, 20 °C; vii, DMAP, compound **4**, CH_2Cl_2, 20 °C; viii, TBAF, THF, 20 °C; ix, NaH, compound **2**, THF, reflux

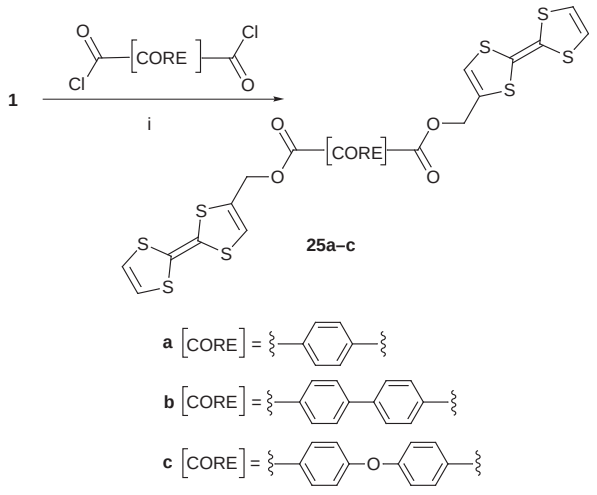
electrochemical techniques were used, *viz*. cyclic voltammetry (CV) using platinum electrodes, and CV using platinum ultramicroelectrodes (UME CV), chronoamperometry (CA) and thin layer cyclic voltammetry (TLCV). An initial study was made using CV. Data are collated in Table 1 for a selection of the new compounds, together with TTF and the model TTF phenyl ester derivative **28** (prepared by reaction of compound **1**[12] with benzoyl chloride, 92% yield) for comparison. Experiments were performed in a mixture of acetonitrile and dichloromethane (1 : 1 v/v) except for derivatives **25a**, **25b**, **26a**,



28

26b, **27a** and **27b**, where insolubility forced us to use dimethyl sulfoxide as the solvent. These experiments established that all the compounds exhibited two redox couples typical of the TTF system (*i.e.* the sequential formation of the TTF cation radical and the TTF dication).[32] It was noted that the silyl ether derivatives tended to adsorb onto the electrode, resulting in narrower waves: data for these compounds, are, therefore, not included in Table 1. The attachment of alkylthio substituents to TTF is known to raise the oxidation potential[32,33] (an additive effect has been noted for one, two and four alkylthio substituents)[33] and this effect is manifested in a small anodic shift in the values of E_1 (but not E_2) for compounds **19**, **21**, **23** and **24**, which contain four alkylthio groups, relative to the other compounds in Table 1. For compound **28** and the bis-TTF systems **6**, **23** and **25a–c**, the redox waves were reversible, at least up to scan rates of 500 mV s^{-1}: the criterion applied for reversibility was a ratio of 1.0 ± 0.1 for the intensities of the cathodic and anodic currents I_c/I_a, and no shift of the half wave potentials with varying scan rates. For oligomers containing more than two TTF groups, slightly increased peak separations at higher scan rates were observed, consistent with quasi-reversible behaviour.

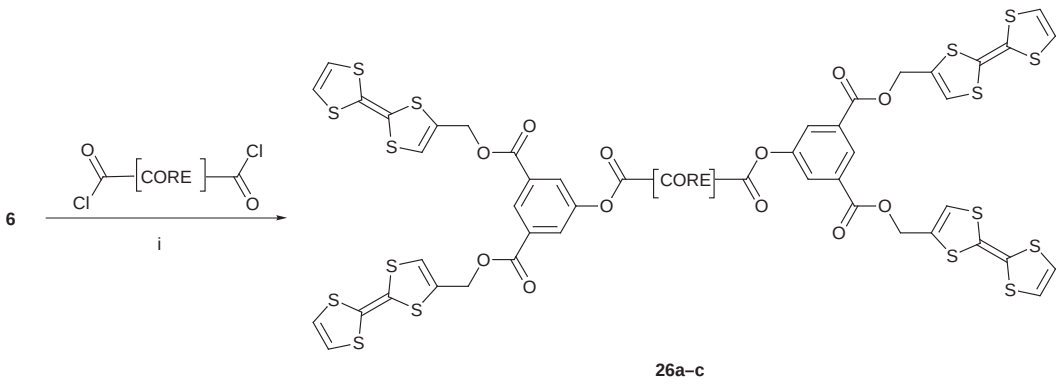
We performed extensive CV and UME CV studies[34] in attempts to determine the number of electrons involved in the two redox waves of the TTF dimers, wedges and dendrimers.



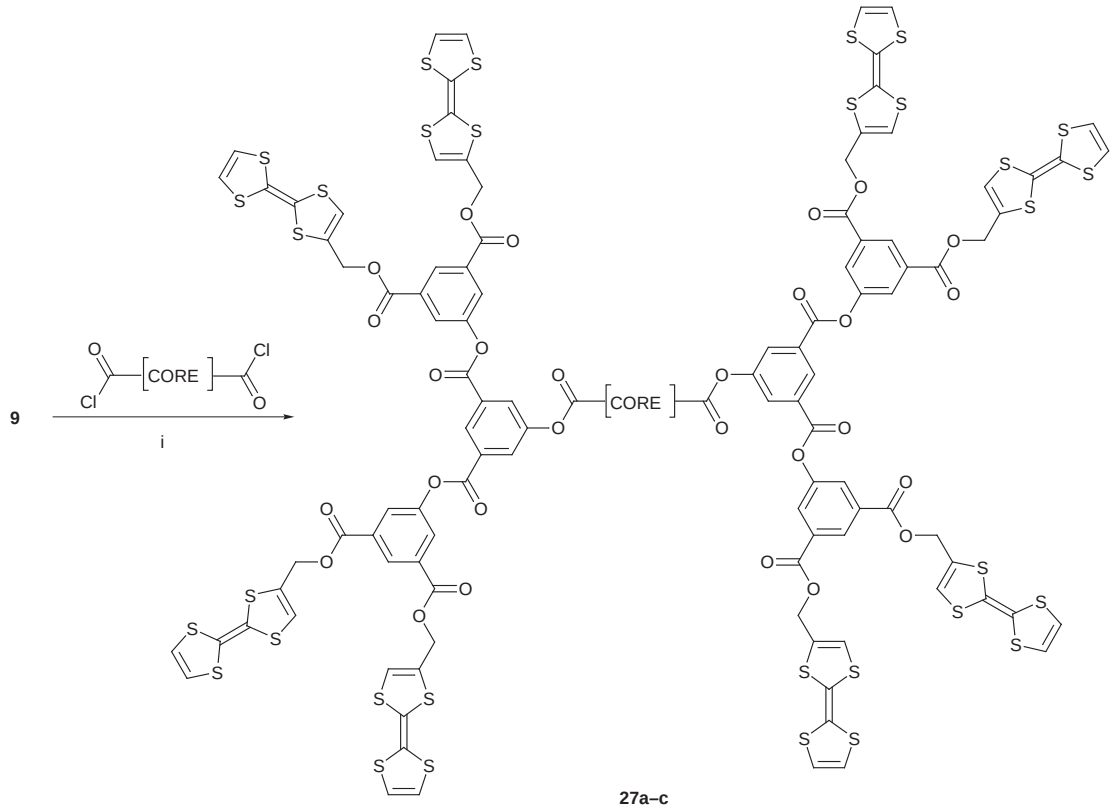
Scheme 3 *Reagents and conditions*: i, NEt_3 (for **25a**), DMAP (for **25b** and **25c**) CH_2Cl_2, 20 °C

The study revealed that accurate data could be obtained only for TTF itself, for which calculations[34a] gave values of 1 ± 0.07 electrons (e) for each wave. For dimeric TTF system **6**, calculations suggested that the first and second waves corresponded to 2.1 ± 0.1 and 1.8 ± 0.1 e, respectively, which was in reasonable agreement with the expected value of 2.0 e for each wave. For the higher TTF oligomers, calculations of the number of electrons transferred at each redox wave, using the combined data of CV and CA to eliminate unknown diffusion coefficients,[35] or UME CV and CV/CA[34a] gave irreproducible results between different experiments. Possible reasons for this are: (i) adsorption and electrode passification, and/or (ii) errors in determining the concentration of the dendrimers due to their low solubility and the very small amounts of material used. [The concentration of our dendrimers was *ca.* two orders of magnitude lower than in ref. 34(*a*).] For other dendrimers and branched systems containing multiples of structurally very similar (or identical) redox groups (*e.g.* ferrocene[11c] and related iron sandwiches[11a]) the extent of oxidation of the system has been calculated using formulae which take into account the different diffusion coefficients of a reference compound and the dendrimer. However, applying these methods[34a] to our TTF derivatives gave inconclusive results.[36] Assuming full oxidation, from the limiting currents at the ultra-microelectrode, diffusion coefficients of the TTF oligomers were, as expected, lower than those of TTF itself,[37] but the values did not correlate with the molecular weights of the oligomers, so this method could not be used reliably with this series of compounds. A general trend, for all the series of compounds in Schemes 1–5, was that with increasing molecular size (*i.e.* increased numbers of TTF units), the first redox wave broadened, whereas the second wave sharpened. Similar behaviour has been reported previously for TTF amides immobilised on RuO_2 or PtO electrode surfaces,[38] and the data can be explained by adsorption or precipitation on the UME. The CV and UME CV of dendrimer **12** are shown in Figs. 1(*a*) and (*b*), respectively.

The electrochemistry of the stable bis-, tetra- and octa-TTF derivatives **25c**, **26c** and **27c** was studied using TLCV techniques.[39] Integrating the voltammetric waves against the one-electron reduction peak of the internal standard 2,3-dichloronaphthoquinone (DCNQ) provided clear evidence that complete oxidation occurs for all the TTF units in these compounds, and we suggest that this is likely to be the case for all the compounds in Schemes 1–5. We note that for compound **27c** the second TTF oxidation wave was slightly narrower than the first wave, which was probably due to adsorption phenomena. Fig. 1(*c*) shows the TLCV of compound **27c** in the presence of DCNQ. These TLCV data are qualitatively similar to those we have reported recently for a structurally very different family of TTF dendrimers, where complete oxidation of all the TTF groups was also observed.[40] We suggest, therefore, that TLCV is the most reliable method for assessing the extent of oxidation of multi-TTF derivatives in solution.



Scheme 4 *Reagents and conditions*: i, DMAP, CH_2Cl_2, 20 °C (**a**–**c** as Scheme 3)



Scheme 5 *Reagents and conditions*: i, DMAP–*N,N*-dimethylaniline, CH_2Cl_2, 35 °C (**a**–**c** as Scheme 3)

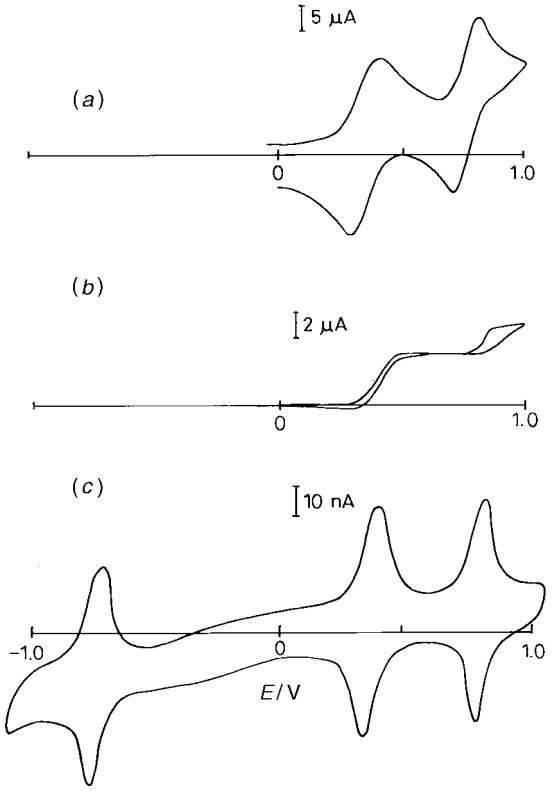


Fig. 1 Solution electrochemistry: (*a*) CV of dendrimer **12** (solvent MeCN, electrolyte $Bu_4N^+PF_6^-$, Pt electrode, *vs.* Ag/AgCl, scan rate 100 mV s^{-1}); (*b*) UME CV of dendrimer **12** [solvent MeCN–CH_2Cl_2 (1 : 1 v/v), electrolyte $Bu_4N^+PF_6^-$, Pt electrode, *vs.* Ag/AgCl, scan rate 50 mV s^{-1}]; (*c*) TLCV of compound **27c** (0.5×10^{-4} M) and 2,3-dichloronaphthoquinone (4.0×10^{-4} M) as internal reference (which gives rise to the wave at negative potential) in 1 M $Bu_4N^+PF_6^-CH_2Cl_2$ solution, *vs.* Ag/Ag^+, scan rate 10 mV s^{-1}

Charge-transfer complexes

TTF is famous for its ability to form charge-transfer complexes[41] with electron acceptors, *e.g.* halogens.[42] UV–VIS Spectroscopy is a convenient method for monitoring the formation of TTF cation radicals, which have a characteristic absorption band at $\lambda_{max} = 580$ nm for unsubstituted TTF.[43] As mentioned earlier, oxidised TTF units can form dimers or stacks, and they display lower energy absorptions, *e.g.* 830 nm for $(TTF^{+\cdot})_2$ dimers.[43b,44] To assess the ability of our TTF dendrimers to undergo chemical oxidation, UV–VIS spectra were obtained in dichloromethane or DMSO solution before and after the addition of iodine (Table 1). There were significant changes in the spectra upon addition of iodine. All the compounds derived from 4-(hydroxymethyl)TTF **1** showed a new band with a λ_{max} value between 516 and 590 nm. Additionally for compounds **21**, **23**, **24**, **25c**, **26b**, **26c**, **27b** and **27c** a low intensity, broad absorption band was present with a λ_{max} value between 810 and 836 nm. The higher energy band is consistent with the formation of isolated (non-interacting) TTF cation radicals, while the lower energy band suggests the existence of interacting cation radical dimers. Addition of iodine to solutions of compounds **21**, **23** and **24**, *i.e.* those derived from 4,5-(2-hydroxymethylpropane-1,3-diyldithio)TTF **20**, resulted in no absorption in the 500–600 nm region; the lower energy band with a λ_{max} value between 812–827 nm was, however, clearly observed, suggesting that dimerisation is especially favoured with these derivatives. Dilution studies for the stable dendrimers **26b**, **26c**, **27b** and **27c** established that the absorption coefficient of this band decreased with increasing dilution, which is, therefore, assigned to an intermolecular dimer band. These data provide evidence that the oxidised dendrimers self-associate in solution, by virtue of intermolecular interactions of their peripheral TTF cation radicals. It is not clear why the low energy dimer absorption is not seen for some of the compounds in Table 1 (indeed, we did not observe it for TTF itself under these conditions); subtle conformational factors at the periphery of the macromolecules appear to be important in determining whether or not dimer formation is energetically

favourable. The relatively rigid and short aryl ester units in our systems presumably disfavour intramolecular dimerisation. These observations are timely in the light of studies of intramolecular interactions of naphthalene diimide anion radicals at the periphery of flexible poly(amidoamine) dendrimers.[45] Intermolecular self-association of dendrimers by hydrogen-bonding[46] or coordinative bonds[47] has also been reported recently.

Molecular modelling studies

Molecular modelling studies were performed on selected compounds. We first found the energetically most favourable conformer of subunit **28** to provide an appropriate conformation for use in the minimisation of the dendrimer structures. The energy-minimised conformations of compounds **12** and **27b** are shown in Fig. 2(*a*) and (*b*), respectively. The electrochemical and UV–VIS spectrophotometric data discussed above are consistent with these conformations, with the important proviso that the preferred conformation may be very solvent dependent.[48] There are two points to note: (i) all the TTF groups of **12** and **27b** are exposed and, therefore, are available to participate in redox processes: there are no TTF groups buried within the macromolecular structure; (ii) the juxtaposition of the TTF groups, enforced by the aryl ester branch units, does not favour intramolecular interactions; rather, intermolecular interactions (as seen in the UV–VIS spectra) should be preferable.

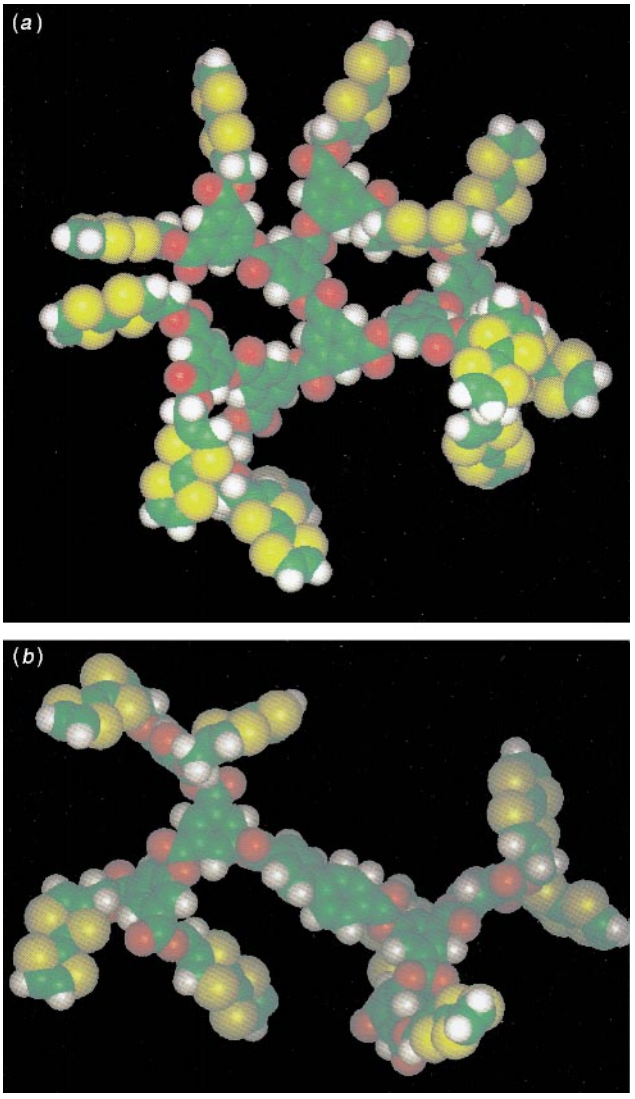


Fig. 2 Energy minimised conformations of (*a*) compound **12** and (*b*) compound **27b**. Green = carbon; white = hydrogen; red = oxygen; yellow = sulfur.

Conclusions

This investigation has combined two different topics in contemporary materials chemistry, namely the study of functionalised TTF systems and dendritic macromolecules. Convergent methodology has provided aryl ester dendrimers with peripheral TTF groups, and established that these compounds possess well-defined redox activity, affording highly-charged cationic species. The higher generation TTF dendrimers containing the benzene triester core were stable only when stored at $<0\,^{\circ}C$, whereas the analogues with a diphenyl ether core enjoy good shelf stability and are soluble in organic solvents. Several new functionalised TTF and multi-TTF derivatives have been synthesised during the course of this work, and those possessing reactive alcohol substituents, *e.g.* compounds **6**, **9**, **20** and **23**, are available in synthetically useful quantities and should be suitable for other synthetic transformations for the incorporation of TTF units into new materials.

Experimental

General

Column chromatography was carried out using Merck silica gel (70–230 mesh) and solvents were distilled prior to use in column chromatography. All reactions were performed in dry, distilled solvents under an atmosphere of nitrogen which was dried by passage through a column of phosphorus pentoxide. Melting points were recorded on a Reichert-Kofler hot-stage microscope apparatus and are uncorrected. Solution state electronic spectra were obtained on a Unicam UV2 instrument. ^{1}H NMR spectra were recorded on Varian Gemini-200, XL-200, Varian VXR-200 and Varian 400 instruments; chemical shifts (δ) are quoted in ppm, relative to tetramethylsilane as an internal reference (0 ppm), and coupling constants (J) are quoted in Hz. Mass spectra were obtained on a VG 7070E instrument, with ionisation modes as indicated; ammonia was used as the impingent gas for chemical ionisation mode. Plasma desorption mass spectrometry was carried out on a BioIon 10 K time of flight instrument (Biosystems, Uppsala, Sweden) over 5×10^5 fissions (^{252}Cf) at the Department of Molecular Biology, University of Odense, Denmark. Elemental analyses were obtained on a Carlo-Erba Strumentazione instrument. Cyclic voltammetry (CV) and UME CV experiments were performed in a one-compartment cell with platinum working and counter electrodes: the microelectrodes were 10 μm diameter (from BAS). The reference electrode was Ag/AgCl. Electrochemical measurements were carried out with a BAS 100 electrochemical analyser or an EG & G Princeton Applied Research potentiostat/galvanometer, model no. 273 using iR compensation. The TLCV cell used in this work was constructed as described previously.[39b] All solutions were purged with argon and retained under the inert atmosphere whilst measurements were carried out.

A Silicon Graphics Indigo workstation, running Biosym Technologies Insight II (version 2.3.5) molecular modelling package was used to determine the minimum energy conformation of the compounds. Molecules were built using the 'Builder' program, then studied using the 'Discover' program. Initially the molecules were contorted for 10 000 iterations at a temperature of 750 K. The structure was minimised using the VA09A minimisation algorithm for 10 000 iterations.

Tris(tetrathiafulvalen-4-ylmethyl) benzene-1,3,5-tricarboxylate 3

To a solution of alcohol **1**[12,49] (100 mg, 0.43 mmol) in dichloromethane (100 cm^3) was added compound **2** (34 mg, 0.13 mmol)

and triethylamine (0.14 cm^3, 1 mmol) and the solution stirred at 20 °C for 18 h. The solvent was removed *in vacuo* and column chromatography of the residue, eluent dichloromethane, afforded compound **3** (94 mg, 85%) as an orange solid, mp 53–54 °C (Analysis found: C, 40.7; H, 2.3; $C_{30}H_{18}O_6S_{12}$ requires: C, 41.9; H, 2.1%); *m/z* (PDMS) 859.3 (M^+); δ_H ($CDCl_3$) 8.85 (3 H, s), 6.45 (3 H, s), 6.29 (6 H, s), 5.10 (6 H, s).

Bis(tetrathiafulvalen-4-ylmethyl) 5-*tert*-butyldimethylsiloxybenzene-1,3-dicarboxylate 5

To a solution of alcohol **1** (100 mg, 0.43 mmol) in dichloromethane (50 cm^3) was added compound **4**[19] (64 mg, 0.19 mmol) and triethylamine (0.2 cm^3, 1.43 mmol) and the solution stirred at 20 °C for 18 h. Workup as described for compound **3**, afforded compound **5** (116 mg, 83%) as a yellow solid, mp 45–46 °C (Analysis found: C, 45.9; H, 3.9; $C_{28}H_{28}O_5S_8Si$ requires: C, 46.1; H, 3.9%); *m/z* (PDMS) 729.1 (M^+); δ_H [$(CD_3)_2CO$] 8.26 (1 H, t, *J* 1.5), 7.74 (2 H, d, *J* 1.5), 6.84 (2 H, s), 6.62 (4 H, s), 5.21 (4 H, s), 1.03, (9 H, s), 0.30 (6 H, s).

Bis(tetrathiafulvalen-4-ylmethyl) 5-hydroxybenzene-1,3-dicarboxylate 6

To a solution of compound **5** (5.67 g, 7.78 mmol) in THF (75 cm^3) was added tetrabutylammonium fluoride (TBAF) (7.5 cm^3, 1.1 M in THF, 8.25 mmol) and the solution stirred at 20 °C for 18 h. Workup as described for compound **3** afforded compound **6** (4.1 g, 85%) as a yellow solid, mp 76–77 °C (Analysis found: C, 43.4; H, 2.7; $C_{22}H_{14}O_5S_8$ requires: C, 43.0; H, 2.3%); *m/z* (PDMS) 614.7 (M^+); δ_H [$(CD_3)_2CO$] 9.24 (1 H, s, exch.), 8.16 (1 H, t, *J* 1.5), 7.73 (2 H, d, *J* 1.5), 6.85 (2 H, s), 6.62 (4 H, s), 5.19 (4 H, s).

Tris[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)phenyl] benzene-1,3,5-tricarboxylate 7

To a solution of alcohol **6** (155 mg, 0.25 mmol) in dichloromethane (60 cm^3) was added compound **2** (20 mg, 0.075 mmol) and DMAP (75 mg, 0.61 mmol) and the solution stirred at 20 °C for 18 h. Workup as descibed for compound **3** [eluent dichloromethane–acetone (5:1 v/v)] afforded compound **7** (113 mg, 75%) as a yellow solid, mp 80–81 °C; *m/z* (PDMS) 2000.6 (M^+); δ_H [$(CD_3)_2SO$] 9.10 (3 H, s), 8.44 (3 H, t, *J* 1.5), 8.32 (6 H, d, *J* 1.5), 7.00 (6 H, s), 6.70 (12 H, s), 5.20 (12 H, s).

Bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)phenyl 5-*tert*-butyldimethylsilyloxybenzene-1,3-dicarboxylate 8

To a solution of alcohol **6** (100 mg, 0.16 mmol) in dichloromethane (50 cm^3) was added compound **4** (24 mg, 0.072 mmol) and DMAP (70 mg, 0.58 mmol) and the solution stirred at 20 °C for 18 h. Workup as described for compound **3** afforded compound **8** (91 mg, 76%) as a yellow solid, mp 85–86 °C (Analysis found: C, 46.5; H, 2.9; $C_{58}H_{44}O_{13}S_{16}Si$ requires: C, 46.7; H, 3.2%); *m/z* (PDMS) 1490.0 (M^+); δ_H [$(CD_3)_2CO$] 8.61 (1 H, t, *J* 1.5), 8.55 (2 H, t, *J* 1.5), 8.25 (4 H, d, *J* 1.5), 7.95 (2 H, d, *J* 1.5), 6.84 (4 H, s), 6.58 (8 H, s), 5.22 (8 H, s), 1.04 (9 H, s), 0.32 (6 H, s).

Bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)phenyl 5-hydroxybenzene-1,3-dicarboxylate 9

To a solution of compound **8** (5.76 g, 3.9 mmol) in THF (60 cm^3) was added TBAF (7 cm^3, 1.1 M in THF, 7.7 mmol) and the solution stirred at 20 °C for 18 h. Workup as described for compound **3** afforded compound **9** as a yellow oil (5.1 g, 95%); *m/z* (PDMS) 1375.8 (M^+); δ_H [$(CD_3)_2CO$] 9.30 (1 H, br s, exch.), 8.15 (3 H, t, *J* 1.5), 7.73 (6 H, d, *J* 1.5), 6.68 (4 H, s), 6.63 (8 H, s), 5.20 (8 H, s).

Bis{3,5-bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)-phenoxycarbonyl]phenyl} 5-*tert*-butyldimethylsilyloxybenzene-1,3-dicarboxylate 10

To a solution of alcohol **9** (110 mg, 0.08 mmol) in dichloromethane (60 cm^3) was added compound **4** (13 mg, 0.039 mmol), DMAP (40 mg, 0.33 mmol) and *N,N*-dimethylaniline (0.05 cm^3, 0.39 mmol) and the resultant mixture stirred at 35 °C for 54 h. Workup as for compound **3** afforded compound **10** (90 mg, 76%) as an orange oil; *m/z* (PDMS) 1505.0 (M^{2+}/2); δ_H [$(CD_3)_2CO$] 8.62 (1 H, t, *J* 1.5), 8.56 (2 H, t, *J* 1.5), 8.25 (12 H, d, *J* 1.5), 7.94 (6 H, d, *J* 1.5), 6.81 (8 H, s), 6.58 (16 H, s), 5.18 (16 H, s), 1.03 (9 H, s), 0.30 (6 H, s).

Bis{3,5-bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)-phenoxycarbonyl]phenyl} 5-hydroxybenzene-1,3-dicarboxylate 11

To a solution of compound **10** (90 mg, 0.029 mmol) in THF (60 cm^3) was added TBAF (0.2 cm^3, 1.1 M, 0.22 mmol) and the solution stirred at 20 °C for 18 h. Workup as described for compound **3** [eluent dichloromethane–acetone (5:1 v/v)] afforded compound **11** (42 mg, 50%) as an orange oil; *m/z* (PDMS) 2897.6 (M^+); δ_H [$(CD_3)_2CO$] 9.30 (1 H, br s, exch.), 8.14 (7 H, t, *J* 1.5), 7.78 (14 H, d, *J* 1.5), 6.83 (8 H, s), 6.58 (16 H, s), 5.15 (16 H, s).

Tris{3,5-bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)-phenoxycarbonyl]phenyl} benzene-1,3,5-tricarboxylate 12

To a solution of alcohol **9** (50 mg, 0.036 mmol) in dichloromethane (60 cm^3) was added compound **2** (2.0 mg, 0.0075 mmol), DMAP (30 mg, 0.25 mmol) and *N,N*-dimethylaniline (0.05 cm^3, 0.39 mmol) and the solution stirred at 35 °C for 54 h. Workup as described for compound **3** [eluent dichloromethane–acetone (5:1 v/v)] afforded compound **12** (15 mg, 48%) as an orange oil; *m/z* (PDMS) 2141.7 (M^{2+}/2); δ_H [$(CD_3)_2CO$] 8.54 (3 H, s), 8.17 (9 H, t, *J* 1.5), 7.73 (18 H, d, *J* 1.5), 6.84 (12 H, s), 6.61 (24 H, s), 5.19 (24 H, s).

4,5-[2-(Hydroxymethyl)propane-1,3-diyldithio]-1,3-dithiole-2-thione 15

To a stirred solution of alcohol **13**[23] (4.51 g, 19.44 mmol) in acetonitrile (100 cm^3) was added zincate salt **14**[24] (6.97 g, 9.73 mmol) and the mixture was refluxed for 4.5 h to afford an orange-coloured solution. Workup as described for compound **3** [eluent dichloromethane–acetone (5:1 v/v)] afforded compound **15** (4.41 g, 85%) as an orange solid, mp 128–130 °C (Analysis found: C, 31.6; H, 3.0; $C_7H_8OS_5$ requires: C, 31.3; H, 3.0%); *m/z* (CI) 269 ($M^+ + 1$); δ_H [$(CD_3)_2CO$] 4.07 (1 H, t, *J* 5.2, exch.), 3.71 (2 H, m), 3.16 (2 H, m), 2.81 (2 H, m), 2.47 (1 H, m).

4,5-[2-(*tert*-Butyldiphenylsilyloxymethyl)propane-1,3-diyldithio]-1,3-dithiole-2-thione 16

To a solution of thione **15** (400 mg, 1.5 mmol) in DMF (80 cm^3) was added *tert*-butyldiphenylsilyl chloride (830 mg, 3.0 mmol) and imidazole (1.1 g, 16 mmol) and the mixture stirred at 20 °C for 18 h. After evaporation *in vacuo*, the residue was dissolved in dichloromethane (50 cm^3), washed with water (2 × 50 cm^3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo*. Column chromatography of the residue, eluent dichloromethane–hexane (1:1 v/v) afforded compound **16** (630 mg, 84%) as a viscous orange oil; *m/z* (CI) 507 ($M^+ + 1$); δ_H ($CDCl_3$) 7.63 (4 H, m), 7.38 (6 H, m), 3.73 (2 H, d, *J* 6.1), 2.96 (2 H, m), 2.66 (2 H, m), 2.52 (1 H, m), 1.06 (9 H, s).

4,5-[2-(*tert*-Butyldiphenylsiloxymethyl)propane-1,3-diyldithio]-1,3-dithole-2-one 17

To a solution of thione **16** (1.43 g, 2.8 mmol) in chloroform–glacial acetic acid (100 cm^3, 3:1 v/v) was added mercuric

acetate (1.0 g, 3.1 mmol) and the reaction stirred at 20 °C for 18 h. Water (100 cm^3) was added and the reaction mixture was stirred for a further 1 h, after which time the resulting white precipitate was removed by filtration through a Celite bed. The organic phase was separated and washed with saturated aqueous sodium hydrogen carbonate (100 cm^3), dried ($MgSO_4$), filtered and the solvent removed *in vacuo* to afford compound **17** (1.22 g, 88%) as a viscous colourless oil; *m/z* (CI) 508 ($M+NH_3^+$); δ_H ($CDCl_3$) 7.64 (4 H, m), 7.39 (6 H, m), 3.73 (2 H, d, *J* 5.9), 2.93 (2 H, m), 2.62 (2 H, m), 2.46 (1 H, m), 1.06 (9 H, s).

4,5-Di(methylthio)-4′,5′-[2-(*tert*-butyldiphenylsiloxymethyl)-propane-1,3-diyldithio]tetrathiafulvalene 19 and 4,5-di(methylthio)-4′,5′-[2-(hydroxymethyl)propane-1,3-diyldithio]tetrathiafulvalene 20

A stirred suspension of ketone **17** (430 mg, 2.0 mmol) and ketone **18**[26] (1.0 g, 2.0 mmol) in triethyl phosphite (5 cm^3) was heated to 130 °C, and the reaction maintained at that temperature for 2 h, after which time the solution had turned dark red. Column chromatography of the crude reaction mixture (eluent hexane) removed triethyl phosphite, then continued elution with a mixture of dichloromethane–hexane (3:1 v/v) afforded an orange oil consisting of an inseparable mixture of the cross-coupled product **19** and self-coupled products. This mixture was dissolved in THF (100 cm^3), TBAF (2.0 cm^3, 1·1 M in THF, 2.2 mmol) was added and the mixture was stirred at 20 °C for 18 h. The solvent was removed *in vacuo* and column chromatography of the residue, eluent dichloromethane–acetone (1:1 v/v) afforded an orange oil which crystallised from dichlomethane–hexane to yield compound **20** (300 mg, overall yield 31% from ketone **17**) as a yellow solid, mp 128–130 °C (Analysis found: C, 33.0; H, 3.2; $C_{12}H_{14}OS_8$ requires: C, 33.5; H, 3.3%); *m/z* (CI) 431 ($M^+ +1$); δ_H ($CDCl_3$) 3.78 (2 H, d, *J* 6.0), 2.89 (2 H, m), 2.58 (2 H, m), 2.45 (1 H, m), 2.41 (6 H, s), OH not observed.

Tris{1,3-[4-5-di(methylthio)tetrathiafulvalene-4′,5′-diyldithio]propan-2-ylmethyl} benezene-1,3,5-tricarboxylate 21

To a solution of alcohol **20** (100 mg, 0.23 mmol) in dichloromethane (50 cm^3) was added compound **2** (18.5 mg, 0.07 mmol) and DMAP (59 mg, 0.48 mmol) and the reaction mixture stirred at 20 °C for 18 h. The solvent was removed *in vacuo* and column chromatography of the residue, eluent dichloromethane–hexane (5:1 v/v), afforded compound **21** (66 mg, 57%) as an orange solid, mp 133–135 °C (Analysis found: C, 37.3; H, 3.0; $C_{45}H_{42}O_6S_{24}$ requires: C, 37.3; H, 2.9%); *m/z* (PDMS) 1448.4 (M^+); δ_H ($CDCl_3$) 8.78 (3 H, s), 4.57 (6 H, br s), 2.96 (6 H, m), 2.78–2.66 (9 H, m), 2.40 (18 H, s).

Bis{1,3-[4-5-di(methylthio)tetrathiafulvalene-4′,5′-diyldithio]propan-2-ylmethyl} 5-*tert*-butyldimethylsilyloxybenzene-1,3-dicarboxylate 22

To a solution of alcohol **20** (110 mg, 0.26 mmol) in dichloromethane (50 cm^3) was added compound **4** (39 mg, 0.12 mmol) and DMAP (59 mg, 0.48 mmol) and the reaction mixture stirred at 20 °C for 18 h. Workup as described for compound **3** afforded compound **22** (126 mg, 96%) as an orange solid, mp 66–67 °C (Analysis found: C, 41.3; H, 4.2; $C_{38}H_{44}O_5S_{16}Si$ requires: C, 40.7; H, 4.0%); *m/z* (PDMS) 1120.9 (M^+); δ_H ($CDCl_3$) 8.15 (1 H, t, *J* 1.5), 7.65 (2 H, d, *J* 1.5), 4.50 (4 H, br s), 2.90 (2 H, m), 2.75 (8 H, m), 2.40 (12 H, s), 1.03 (9 H, s), 0.25 (6 H, s).

Bis{1,3-[4-5-di(methylthio)tetrathiafulvalene-4′,5′-diyldithio]propan-2-ylmethyl} 5-hydroxybenzene-1,3-dicarboxylate 23

To a solution of compound **22** (100 mg, 0.09 mmol) in THF (50 cm^3) was added TBAF (0.2 cm^3, 1.1 M in THF, 0.22 mmol) and the reaction mixture stirred at 20 °C for 18 h. Workup as described for compound **3** [eluent dichloromethane–acetone (1:1 v/v)] afforded compound **23** as an orange solid (59 mg, 66%), mp 238–239 °C (Analysis found: C, 38.8; H, 3.3; $C_{32}H_{30}O_5S_{16}$ requires: C, 38.1; H, 3.0%); *m/z* (PDMS) 1007.6 (M^+); δ_H [$(CD_3)_2SO$] 10.18 (1 H, s, exch.), 7.90 (1 H, t, *J* 1.5), 7.61 (2 H, d, *J* 1.5), 4.45 (4 H, m), 3.11 (2 H, m), 2.72 (8 H, m), 2.42 (12 H, s).

Tris(3,5-bis{1,3-[4,5-di(methylthio)tetrathiafulvalene-4′,5′-diyldithio]propan-2-ylmethoxycarbonyl}phenyl) benzene-1,3,5-tricarboxylate 24

To a solution of alcohol **23** (50 mg, 0.05 mmol) in THF (50 cm^3) was added compound **2** (4 mg, 0.015 mmol) and sodium hydride (30 mg, 1.25 mmol) and the reaction mixture was then stirred at reflux for 18 h. Workup as described for compound **3** [eluent dichloromethane–hexane (5:1 v/v)] afforded compound **24** (28 mg, 58%) as an orange oil; *m/z* (PDMS) 1579.0 ($M^{2+}/2$); δ_H ($CDCl_3$) 8.73 (3 H, s), 8.25 (3 H, t, *J* 1.5), 7.95 (6 H, d, *J* 1.5), 4.57 (12 H, br s), 2.96 (6 H, m), 2.78–2.66 (24 H, m), 2.40 (36 H, s).

Bis(tetrathiafulvalen-4-ylmethyl) benzene-1,4-dicarboxylate 25a

To a solution of compound **1** (156 mg, 0.67 mmol) in dichloromethane (60 cm^3) was added terephthaloyl chloride (67 mg, 0.33 mmol) and triethylamine (0.3 cm^3, 2.2 mmol) and the solution stirred at 20 °C for 18 h. Workup as described for compound **3** [eluent dichloromethane–acetone (5:1 v/v)] afforded compound **25a** (117 mg, 59%) as a salmon coloured solid, mp 188–189 °C (Analysis found: C, 44.0; H, 2.2; $C_{22}H_{14}O_4S_8$ requires: C, 44.1; H, 2.4%); *m/z* (EI) 599 (M^+); δ_H [$(CD_3)_2SO$] 8.14 (4 H, s), 7.01 (2 H, s), 6.75 (4 H, s), 5.19 (4 H, s).

Bis(tetrathiafulvalen-4-ylmethyl) biphenyl-4,4′-dicarboxylate 25b

To a solution of compound **1** (105 mg, 0.45 mmol) in dichloromethane (60 cm^3) was added biphenyl-4,4′-dicarbonyl dichloride (61 mg, 0.22 mmol) and DMAP (220 mg, 1.80 mmol) and the solution stirred at 20 °C for 48 h. Workup as described for compound **3** afforded compound **25b** (81 mg, 55%) as an orange solid, mp 219–222 °C (Analysis found: C, 48.1; H, 2.7; $C_{28}H_{18}O_4S_8$ requires: C, 47.8; H, 2.7%); *m/z* (CI) 675 (M^+); δ_H [$(CD_3)_2SO$] 8.06 (4 H, d, *J* 8.0), 7.91 (4 H, d, *J* 8.0), 6.97 (2 H, s), 6.71 (4 H, s), 5.16 (4 H, s).

Bis(tetrathiafulvalen-4-ylmethyl) 4,4′-oxybis(benzenecarboxylate) 25c

To a solution of alcohol **1** (105 mg, 0.45 mmol) in dichloromethane (60 cm^3) was added 4,4′-oxybis(benzenecarbonyl chloride) (66 mg, 0.22 mmol) and DMAP (110 mg, 0.9 mmol) and the solution stirred at 20 °C for 18 h. Workup as described for compound **3** [eluent dichloromethane–acetone (5:1 v/v)] afforded compound **25c** (130 mg, 84%) as a yellow solid, mp 154–156 °C (Analysis found: C 48.9; H, 2.6; $C_{28}H_{18}O_5S_8$ requires: C, 48.7; H, 2.6%); *m/z* (DCI) 691 (M^+); δ_H [$(CD_3)_2CO$] 8.04 (4 H, d, *J* 9.0), 7.17 (4 H, d, *J* 9.0), 6.80 (2 H, s), 6.59 (4 H, s), 5.13 (4 H, s).

Bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)phenyl] benzene-1,4-dicarboxylate 26a

To a solution of compound **4** (100 mg, 0.16 mmol) in dichloromethane (60 cm^3) was added terephthaloyl choride (16 mg, 0.08 mmol) and DMAP (40 mg, 0.32 mmol) and the solution stirred at 20 °C for 18 h. Workup as described for compound **3** [eluent dichloromethane–acetone (5:1 v/v)] afforded com-

pound **26a** (117 mg, 59%) as a salmon coloured solid, mp 113–114 °C (Analysis found: C, 46.1; H, 2.3; $C_{52}H_{30}O_{12}S_{16}$ requires: C, 45.9; H, 2.2%); *m/z* (PDMS) 1359.7 (M^+); δ_H [$(CD_3)_2SO$] 8.59 (2 H, t, *J* 1.5), 8.28 (4 H, d, *J* 1.5), 8.12 (4 H, s), 6.89 (4 H, s), 6.65 (8 H, s), 5.24 (8 H, s).

Bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)phenyl] biphenyl-4,4′-dicarboxylate 26b

To a solution of compound **4** (100 mg, 0.16 mmol) in dichloromethane (60 cm^3) was added biphenyl-4-4′-dicarbonyl dichloride (22 mg, 0.08 mmol) and DMAP (156 mg, 1.28 mmol) and the solution stirred at 20 °C for 18 h. The solution was filtered and the residue washed sequentially with water (25 cm^3), dichloromethane (50 cm^3), isopropyl alcohol (25 cm^3) and diethyl ether (50 cm^3) to afford compound **26b** (94 mg, 83%) as an orange solid, mp >250 °C (Analysis found: C, 48.7; H, 2.5; $C_{58}H_{34}O_{12}S_{16}$ requires: C, 48.5; H, 2.4%); *m/z* (PDMS) 1435.8 (M^+); δ_H [$(CD_3)_2SO$] 8.57 (2 H, t, *J* 1.5), 8.29 (4 H, d, *J* 8.8), 8.24 (4 H, d, *J* 1.5), 8.03 (4 H, d, *J* 8.8), 7.01 (4 H, s), 6.72 (8 H, s), 5.21 (8 H, s).

Bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)phenyl] 4,4′-oxydibenzoate 26c

To a solution of compound **4** (75 mg, 0.12 mmol) in dichloromethane (60 cm^3) was added 4,4'-oxybis(benzenecarbonyl chloride) (17 mg, 0.06 mmol) and DMAP (117 mg, 0.96 mmol) and the solution stirred under nitrogen at 20 °C for 18 h. Workup as described for compound **3** afforded compound **26c** (43 mg, 52%) as an orange solid, mp 110–112 °C (Analysis found: C, 47.9; H, 2.4; $C_{58}H_{34}O_{13}S_{16}$ requires C, 48.0; H, 2.4%); *m/z* (PDMS) 1451.7 (M^+); δ_H [$(CD_3)_2CO$] 8.57 (2 H, t, *J* 1.5), 8.30 (4 H, d, *J* 8.2), 8.24 (4 H, d, *J* 1.5), 7.32 (4 H, d, *J* 8.2), 6.88 (4 H, s), 6.62 (8 H, s), 5.25 (8 H, s).

Bis{3,5-bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)-phenoxycarbonyl]phenyl} benzene-1,3-dicarboxylate 27a

To a solution of compound **9** (132 mg, 0.096 mmol) in dichloromethane (60 cm^3) was added terephthaloyl chloride (8.5 mg, 0.042 mmol), DMAP (190 mg, 1.56 mmol) and *N,N*-dimethylaniline (0.2 cm^3, 1.56 mmol) and the solution stirred at 35 °C for 72 h. The solution was washed with cold acetic acid (1 M, 15 cm^3), and addition of saturated aqueous sodium carbonate (15 cm^3) precipitated compound **27a** (21 mg, 15%) as a salmon coloured solid which was collected by filtration, mp >250 °C (Analysis found: C, 46.1; H, 2.3; $C_{112}H_{62}O_{28}S_{32}$ requires: C, 46.7; H, 2.2%; *m/z* (PDMS) 1440.8 ($M^{2+}/2$); δ_H [$(CD_3)_2CO$] 8.59 (6 H, t, *J* 1.5), 8.27 (12 H, d, *J* 1.5), 8.23 (4 H, s), 6.88 (8 H, s), 6.62 (16 H, s), 5.24 (16 H, s).

Bis{3,5-bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)-phenoxycarbonyl]phenyl} biphenyl-4,4′-dicarboxylate 27b

To a solution of compound **9** (85 mg, 0.062 mmol) in dichloromethane (60 cm^3) was added biphenyl-4,4′-dicarbonyl dichloride (7.5 mg, 0.027 mmol), DMAP (190 mg, 1.56 mmol), and *N,N*-dimethylaniline (0.2 cm^3, 1.56 mmol) and the solution stirred at 35 °C for 54 h. The solution was washed sequentially with cold acetic acid (1 M, 15 cm^3), saturated aqueous sodium carbonate (15 cm^3) and brine (15 cm^3), and the organic layer dried ($MgSO_4$). The solvent was removed *in vacuo* and column chromatography of the residue, eluent dichloromethane–hexane (5:1 v/v), afforded compound **27b** (28 mg, 35%) as an orange oil; *m/z* (PDMS) 2954.7 (M^+); δ_H [$(CD_3)_2CO$] 8.33 (2 H, t, *J* 1.5), 8.29 (4 H, d, *J* 1.5), 8.14 (4 H, t, *J* 1.5), 8.02 (8 H, d, *J* 1.5), 7.80 (4 H, d, *J* 7.0), 7.77 (4 H, d, *J* 7.0), 6.85 (8 H, s), 6.62 (16 H, s), 5.22 (16 H, s).

Bis{3,5-bis[3,5-bis(tetrathiafulvalen-4-ylmethoxycarbonyl)-phenoxycarbonyl]phenyl} 4,4′-oxydibenzoate 27c

To a solution of compound **9** (108 mg, 0.078 mmol) in dichloromethane (60 cm^3) was added 4,4′-oxybis(benzenecarbonyl chloride) (10.9 mg, 0.037 mmol), DMAP (190 mg, 1.56 mmol) and *N,N*-dimethylaniline (0.2 cm^3, 1.56 mmol) and the solution stirred at 35 °C for 72 h. Workup as described for compound **27b** [eluent dichloromethane–acetone (5:1 v/v)] afforded compound **27c** (18 mg, 16%) as an orange oil; *m/z* (PDMS) 2971.1 (M^+); δ_H [$(CD_3)_2CO$] 8.57 (4 H, t, *J* 1.5), 8.29 (4 H, d, *J* 9.0), 8.24 (8 H, d, *J* 1.5), 8.14 (2 H, t, *J* 1.5), 7.72 (4 H, d, *J* 1.5), 7.30 (4 H, d, *J* 9.0), 6.88 (8 H, s), 6.62 (16 H, s), 5.24 (16 H, s).

Tetrathiafulvalen-4-ylmethyl benzoate 28

To a solution of compound **1**[12] (500 mg, 2.14 mmol) in dichloromethane (50 cm^3) was added benzoyl chloride (0.25 cm^3, 2.18 mmol) and triethylamine (1 cm^3, excess) and the solution stirred at 20 °C for 12 h. After evaporation of the solvent, the residue was chromatographed, eluting with hexane–dichloromethane (1:1 v/v) to afford compound **28** (665 mg, 92%) as a yellow solid, mp 68 °C (Analysis found: C, 49.8; H, 3.1; $C_{14}H_{10}O_2S_4$ requires: C, 49.7; H, 3.0%); *m/z* (DCI) 339($M^+ + 1$); δ_H ($CDCl_3$) 8.05 (2 H, d, *J* 7.8), 7.56 (1 H, t, *J* 7.0), 7.44 (2 H, m), 6.40 (1 H, s), 6.21 (2 H, s), 5.05 (2 H, s).

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