Synthesis and electrochemistry of new tetrathiafulvalene (TTF) dendrimers: X-ray crystal structure of a tetrafunctionalised TTF core unit

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A new synthetic approach to tetrathiafulvalene (TTF) dendrimers is reported. Tetrakis(4-chloromethylbenzylthio)tetrathiafulvalene **7** is a functionalised core unit which reacts with four equivalents of the thiolate ion generated from compound **16** to afford the trisdeca-TTF derivative **3**. Compound **3** is a shelf-stable solid which has been characterised by elemental analysis, MALDI-TOF mass spectrometry, ^{1}H NMR spectroscopy and solution electrochemistry. Thin layer cyclic voltammetry studies on pentakis-TTF and trisdeca-TTF derivatives **11** and **3** in dichloromethane solution in the presence of 2,3-dichloronaphthoquinone as an internal reference, show that all the TTF units undergo two single-electron oxidations. The single crystal X-ray structure of compound **7** is reported: the molecules have crystallographic C_i symmetry and form chair-like stacks parallel to the crystallographic *y* axis.

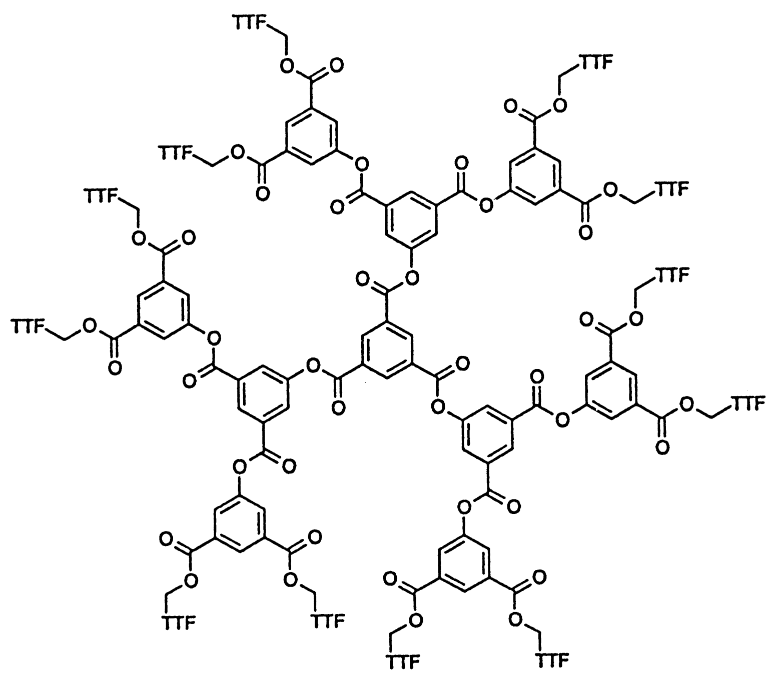
A bourgeoning topic within the arena of nanochemistry[1] is the study of dendritic and hyperbranched macromolecules.[2] Of particular interest is the fact that these materials possess a high degree of structural order, and their size and architecture can be precisely controlled in their synthesis, providing unique molecular scaffolds for the emplacement of functional groups in predetermined spatial arrangements.[2d,3] A range of substituents (*e.g.* crown ethers,[4] chiral units,[5] polynuclear metal complexes[6] and liquid crystal groups[7]) have recently been appended to, or embedded within, dendrimer frameworks to impart special properties to these macromolecules.[8,9] A variety of redox-active organic and organometallic groups have been incorporated into dendritic and hyperbranched systems[10] 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; (iii) organic semiconductors; (iv) organic magnets; and (v) mimics of biological redox processes.

Some dendrimer systems contain a single redox-active unit (*e.g.* a metalloporphyrin)[11] at the core, for which the key issue is generally to observe how the redox behaviour of this central 'encapsulated' group is modulated by the shielding effect of the rest of the dendrimer structure, which should provide a more compact insulating layer than would an analogous linear polymer. The majority of studies, however, concern multiple redox units (*e.g.* polynuclear metal complexes)[6] emplaced within the branches and/or at peripheral sites, where the redox groups may act independently in multi-electron processes (*n* identical electroactive centres which undergo electron transfer in a single *n*-electron wave) or they may interact intra- or inter-molecularly (overlapping or closely-spaced redox waves at different potentials).

We first recognised[12] that tetrathiafulvalene (TTF) units offered considerable potential as components of novel redox-active dendrimers. The incorporation of TTF into dendrimers presents a fascinating prospect for the following reasons: (i) oxidation of the TTF ring system to the cation radical and dication species occurs sequentially and reversibly at very accessible potentials in a range of organic solvents (for unsubstituted TTF, $E_1^{1/2} = +0.34$ and $E_2^{1/2} = +0.78$ V, *vs.* Ag/AgCl in acetonitrile); (ii) the oxidation potentials can be finely tuned by the attachment of appropriate substituents; (iii) the TTF cation radical is thermodynamically very stable; and (iv) oxidised TTF units are key components of molecular conductors,[13] because of their propensity to form highly-ordered stacks along which there is high electron mobility. The stacks are stabilised by intermolecular p–p interactions and non-bonded sulfur , sulfur interactions. Most multi-TTF derivatives reported to date[14] are dimers,[15] although some trimers,[16] pentamers,[17] higher oligomers[18] and main-chain and side-chain polymeric TTFs[19] are now known. A key feature of these multi-TTF systems is that they generally yield multiply-charged species upon electrochemical oxidation in solution.

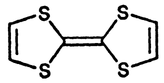
In our initial work on TTF dendrimers, a convergent strategy based on a repetitive coupling/deprotection sequence, using 4-(hydroxymethyl)-TTF as the starting monomer, furnished dendrimer **1** comprising a benzene-1,3,5-triester core, and surface-functionalised with twelve TTF units.[12] A conceptually similar synthesis using a 4,4′-biphenyl ether diester core gave the octakis-TTF system **2** possessing a more open structure than analogue **1**.[20] The solution electrochemical redox behaviour of systems **1** and **2** was studied by classical cyclic voltammetry (CV), cyclic voltammetry with ultramicroelectrodes (UME CV) and chronoamperometry.[12,20,21] For compound **1**, the CV waves were quasi-reversible, with slight broadening, which became more noticable with repeated scans, when the second TTF oxidation peak became irreversible and deposition of material on the electrode surface was observed: each wave represented a multi-electron transfer with essentially no interaction between the charged TTF units. We were unable to establish unambiguously the number of electrons involved in each redox wave for compounds **1** and **2**: the different diffusion rates of the internal standard (2,3-dichloronaphthoquinone) and the dendrimer could readily account for the apparent incomplete oxidation of all the TTF units. (Scanning to higher potentials showed no further oxidation waves, precluding the presence of any TTF groups buried within the dendrimer structure.)

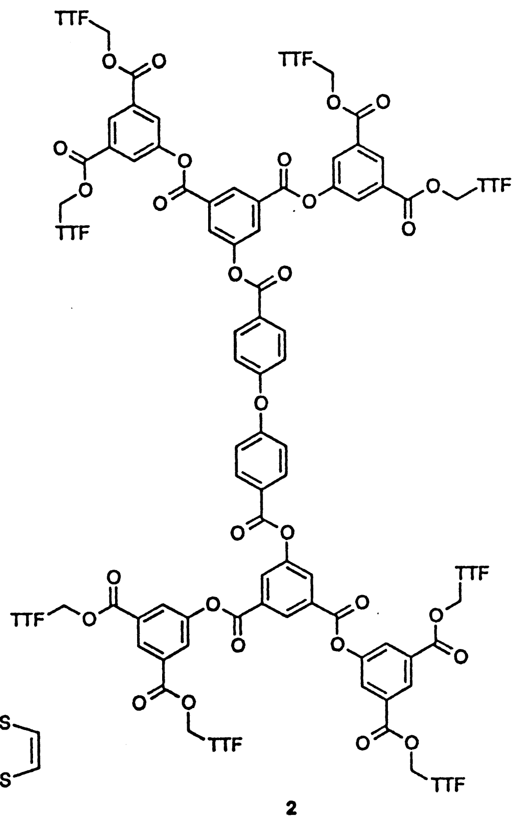
Herein we report an entirely different approach to TTF dendrimers which has culminated in the synthesis of macromolecule **3** comprising thirteen TTF units. There are several novel features of this work: (i) TTF units are emplaced at all layers of the structural hierarchy (unlike compounds **1** and **2**); (ii) compound **7** is presented as a new, versatile building block for macromolecular TTF assemblies, and its single crystal structure is described; (iii) thin layer cyclic voltammetry (TLCV) has been applied to redox-active dendrimer systems for the first time, and it is clear that all the TTF groups of **3** are involved in the solution electrochemical redox processes.



1

TTF =





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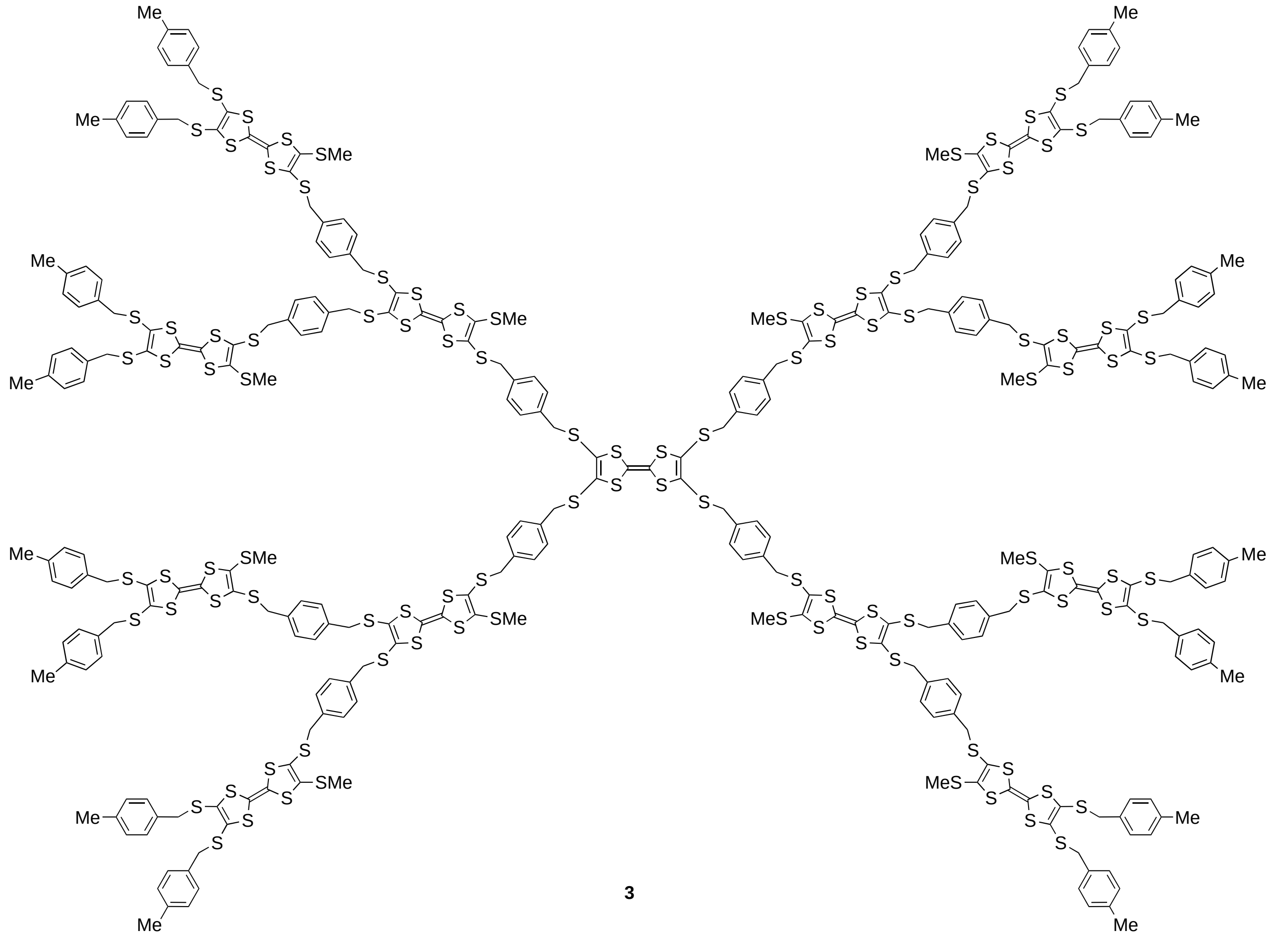


3

Results and Discussion

Synthesis

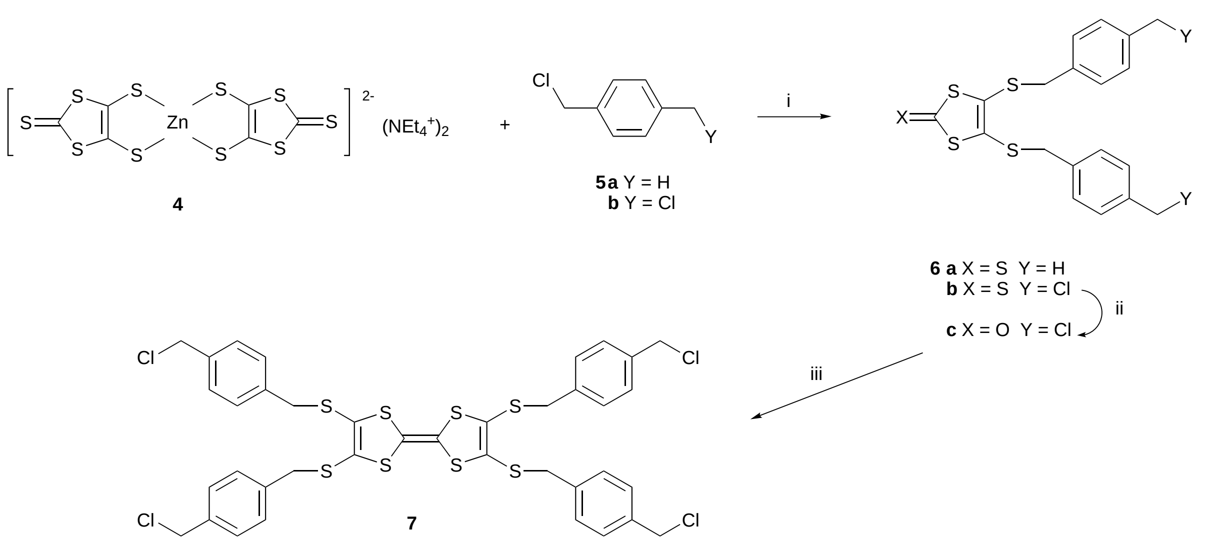
Zincate salt **4**[22] reacted with a-chloro-*p*-xylene **5a** or with a,a′-dichloro-*p*-xylene **5b** to yield 4,5-disubstituted 1,3-dithiole-2-thione derivatives **6a** (90% yield) and **6b** (60% yield), respectively. The latter was converted to the ketone **6c** (84% yield) using the standard mercuric acetate procedure (Scheme 1). Compound **7** was synthesised in 78% yield by self-coupling of **6c** in the presence of triethyl phosphite under standard conditions,[23] and isolated as orange crystals suitable for X-ray analysis (see below). Compound **7** is our key core unit and displacement of the benzylic chlorines by thiolate anions proved to be a facile process. We identified **10** as a promising building block from which a reactive thiolate anion could be generated, following the protocol developed by Becher and coworkers for related cyanoethyl-protected TTF-thiolate systems.[24] Accordingly, compound **6a** was cross-coupled with ketone **8** to furnish TTF derivative **9** in 67% yield (Scheme 2). Sequential deprotection of **9** allowed unsymmetrical substitution reactions. Initial treatment of **9** with caesium hydroxide (1.05 equiv.), followed by methylation of the resulting monothiolate anion, afforded **10** (96% yield) which was deprotected using a second equivalent of caesium hydroxide to yield the caesium salt of the thiolate anion of **10**, four equivalents of which reacted with **7** to yield the pentakis-TTF derivative **11** in almost quantitative yield. Compound **11** was purified by column chromatography and isolated as a yellow–brown solid. The parent molecular ion of **11** was observed in the matrix-assisted laser desorption time-of-flight (MALDI TOF) mass spectrum at *m*/*z* 2964 (M^+, calc. for $C_{130}H_{116}S_{40}$; 2956).

An analogous synthetic protocol enabled assembly of the trisdeca-TTF derivative **3**, which can be viewed as a second generation dendrimer. For this synthesis we needed the monothiolate derivative of **16** as the reactive 'wedge' to undergo four-fold reaction with core reagent **7**. The synthesis of **3** is shown in Scheme 3. Compound **13** was prepared in high yield by the literature route from **12**,[24b] and converted into ketone **14** (98% yield) using mercuric acetate. Cross-coupling of equimolar amounts of thione **6b** and ketone **14**, in the presence of triethyl phosphite, gave compound **15** in an optimised yield of 45%. By direct analogy with the preparation of **11**, compound **15** was converted into **16** in 74% yield. The caesium thiolate salt of **16** (4 equiv.) reacted cleanly with compound **7** to furnish compound **3** in 66% yield as an air-stable yellow–brown solid. Compound **3** was characterised unambiguously by a combination of elemental analysis, MALDI TOF mass spectrometry and ^{1}H NMR spectroscopy. In particular, the MALDI TOF spectrum of **3**, showed a parent ion peak at *m*/*z* 7377 (M^+, calc. for $C_{314}H_{276}S_{104}$, 7372) with several other peaks observed in the spectrum due to fragmentation of the parent molecule.

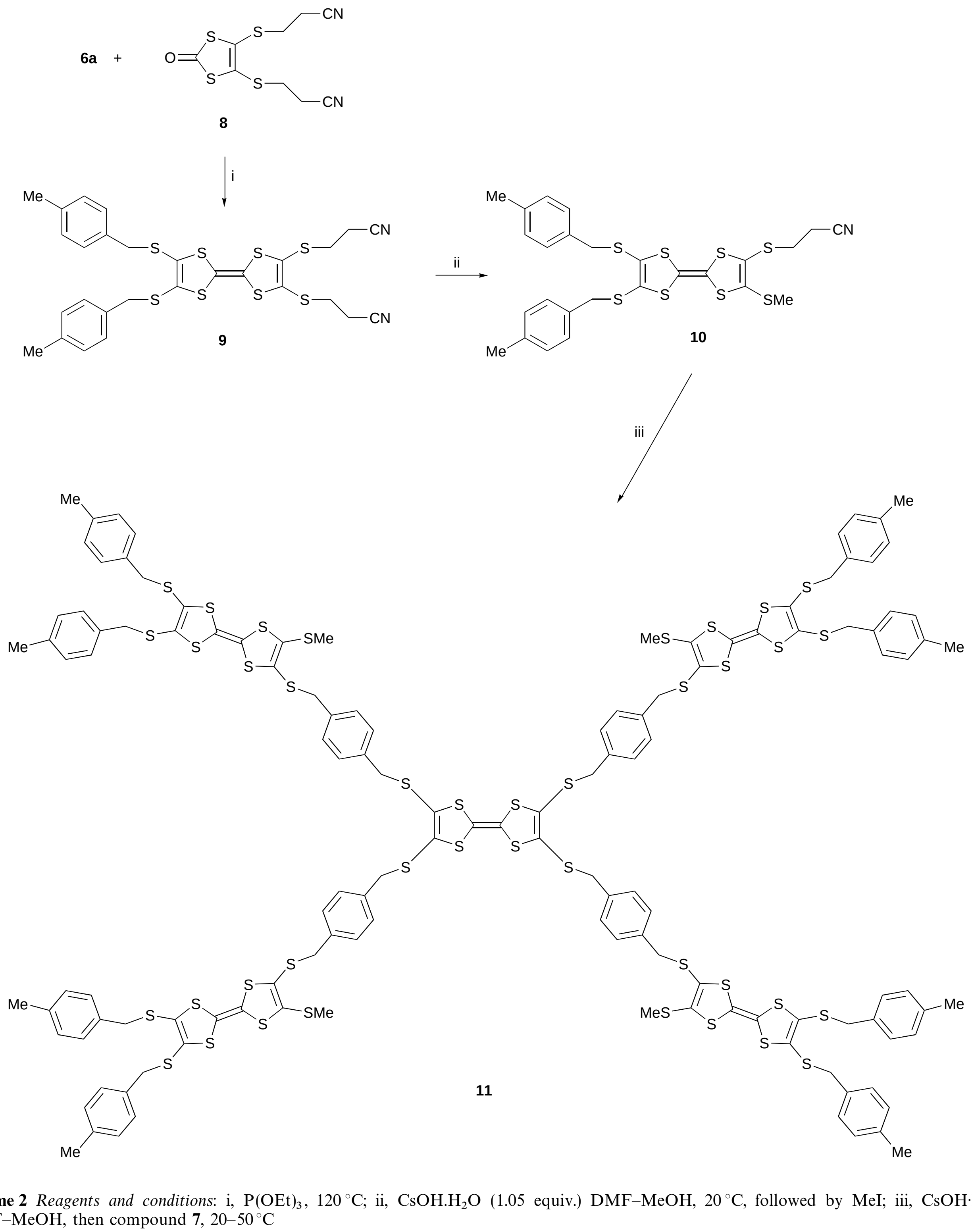
Solution electrochemistry

The solution redox properties of compounds **3,7,9–11,15** and **16** in benzonitrile are collated in Table 1, together with data for TTF for comparison. All these new compounds exhibited two redox couples typical of the TTF system[25] and for the multi-TTF derivatives there was no apparent interaction between the different TTF units. 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 ± 0.5 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. The attachment of thioalkyl substituents to the TTF ring is known to raise the oxidation potential[25,26] (an additive effect has been noted for one, two and four thioalkyl substituents)[26] and the new compounds in Table 1 follow this trend. It is notable that the values of both the first and second redox potentials appear to be further raised slightly by the presence of the cyanoethyl groups (*viz.* compounds **9**, **10** and **15**), although for compound **16** inequivalence of the TTF groups (only one of which carries a cyanoethyl group) was not observed.

More significant are the results of thin layer cyclic voltammetric (TLCV) studies on compounds **11** and **3**, which contain five and thirteen TTF units, respectively. In contrast to conventional cyclic voltammetry, in TLCV[27] the current is not limited by the kinetics of mass transfer to the electrode. TLCV has been applied recently to the detection of mixed valence states in TTF and its derivatives.[28] However, we are not aware of any reports of this technique being applied to multi-TTF systems or to redox-active dendrimers. As mentioned above, classical CV, UME CV and chronoamperometry had previously given inconclusive results concerning the number of electrons involved in the redox waves of compounds **1**[12,21] and **2**.[20,21] For other multi-TTF systems (*e.g.* pentamers) oxidation of all the TTF units had been assumed, based on the shapes of the CV waves, but not rigorously established.[17] For other dendrimers and branched systems containing multiples of structurally very similar (or identical) redox groups (*e.g.* ferrocene[29] and related iron sandwiches[30]) the extent of oxidation of the system can be calculated using formulae which take into



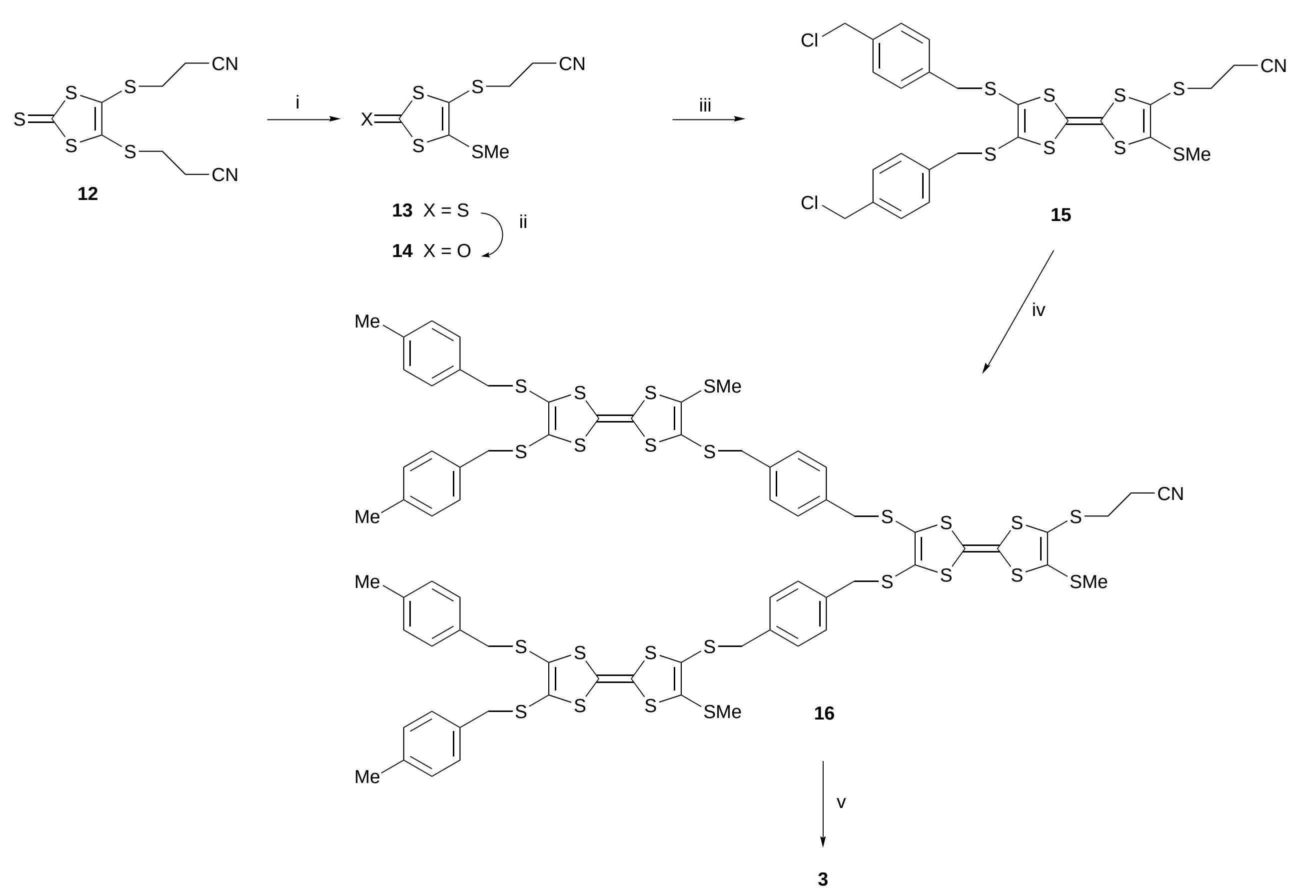
Scheme 1 *Reagents and conditions*: i, acetone, reflux; ii, $Hg(OAc)_2$, $CHCl_3$–$MeCO_2H$, 20 °C; iii, $P(OEt)_3$, 120 °C



Scheme 2 *Reagents and conditions*: i, P(OEt)$_3$, 120 °C; ii, CsOH.H$_2$O (1.05 equiv.) DMF–MeOH, 20 °C, followed by MeI; iii, CsOH·H$_2$O, DMF–MeOH, then compound **7**, 20–50 °C

account the different diffusion coefficients of a model compound and the dendrimer.[31] A very elegant alternative method is provided by certain macromolecules which contain within their structure two (or more) different redox units in a known ratio, which are oxidised or reduced at different potentials, thereby providing a covalently-bound internal reference.[6,32] However, this is not the case with the compounds herein where all the TTF units are tetrathio-substituted.

TLCV studies were conducted on known concentrations of compounds **11**, **3** and 2,3-dichloronaphthoquinone (DCNQ) in dichloromethane solution. The one-electron reduction peak of DCNQ provided the internal reference, and by integrating the voltammetric waves, the number of electrons exchanged per oxidation wave was calculated to be five for compound **11** (which contains five TTF units) and 12–14 (E_1) and 11–12 (E_2) for compound **3** (which contains 13 TTF units). These data clearly suggest that complete oxidation occurs for all the TTF units in compounds **11** and **3**. For compound **3**, the small variation in the number of electrons calculated for different experiments is within reasonable experimental limits, given the very small quantities of the compound used and the large number of TTF groups present. We note that for both compounds **11** and **3** the second TTF oxidation wave was slightly narrower than the first wave, which was probably due to



Scheme 3 *Reagents and conditions*: i, CsOH.H_2O (1 equiv.), DMF–MeOH, 20 °C, followed by MeI; ii, Hg(OAc)$_2$, $CHCl_3$–MeCO$_2$H, 20 °C; iii, compound **6b**, P(OEt)$_3$, 125 °C; iv, compound **10**, CsOH·H_2O (1 equiv.), DMF–MeOH, then compound **15**, 20 °C; v, CsOH.H_2O, DMF–MeOH, then compound **7**, 20–80 °C

Table 1 Solution redox properties of compounds **3**,**7**,**9**–**11**,**15** and **16**[a]

compound	$E_1^{1/2}$/V	$E_2^{1/2}$/V
TTF	0.34	0.78
3	0.57	0.90
7	0.58	0.92
9	0.67	1.01
10	0.63	0.97
11	0.56	0.89
15	0.64	0.98
16	0.57	0.90

[a] Platinum electrodes, supporting electrolyte Bu_4NPF_6 (0.1 M) in benzonitrile, scan rate 100 mV s^{-1} *versus* Ag/AgCl.

adsorption phenomena. Fig. 1 shows the TLCV of compound **3** in the presence of DCNQ.

X-Ray crystal structure of compound 7

Compound **7** is a functionalised, four-directional core unit which offers considerable potential for future studies. It was of interest, therefore, to establish the structure of **7** in the solid state. The single crystal X-ray structure reveals that the molecule has a crystallographic C_i symmetry (Fig. 2). The TTF moiety displays a chair-like distortion, the dithiole rings folding by 6.4° along the S , S vectors. One of the two independent 4-(chloromethyl)benzyl substituents is ordered, while the other one is disordered over two positions (A and B) with approximately equal occupancies, differing in the torsion angles around the S(3)–C(2), S(3)–C(4), C(4)–C(5) and C(8)–C(11) bonds (by 30, 27, 81 and 27°, respectively) and consequently in the orientation of the benzene ring plane (by 44°), but basically occupying the same area of space (the positions of the terminal chlorine atom differ by only 0.67 Å). In any case, the conformation of all the substituents in **7** is profoundly out-of-(the TTF)plane. Thus the overall molecular conformation is similar to those in other TTF derivatives with long linear-chain substituents,[33] and so is the crystal packing. The molecules form a stair-like stack in the direction parallel to the crystallographic *y* axis, in which the TTF planes are parallel with interplanar separations of *ca.* 3.6 Å. The adjacent TTF moieties in the stack overlap through only one dithiole ring each. Apparently, the more effective (and more common) ring-over-bond (*i.e.* the central C=C bond) overlap is prevented by the steric bulk of the substituents.

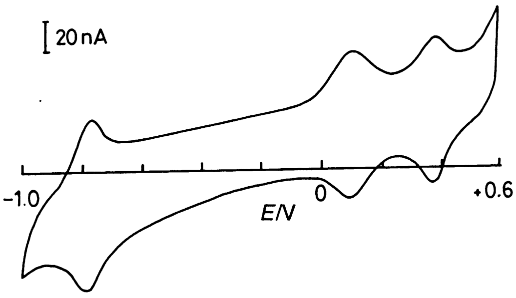


Fig. 1 TLCV of dendrimer **3** (0.5 × 10^{-4} M) and 2,3-dichloronaphthoquinone (6.4 × 10^{-4} M) as internal reference, in Bu_4NClO_4 (1 M)–CH_2Cl_2 solution, reference *vs.* Ag/Ag$^+$, scan rate 5 mV s^{-1}

It is noteworthy that in the crystal the disordered side-chain of **7** is surrounded by such chains of other molecules on three sides (the ordered chain of the same molecule being on the fourth side) *viz.* two parallel chains of the neighbours within the stack and one antiparallel chain of the inversion-equivalent molecule of another stack. Thus the structure contains a vast area of disorder, in the form of a wide (*ca.* 10 × 10 Å) infinite

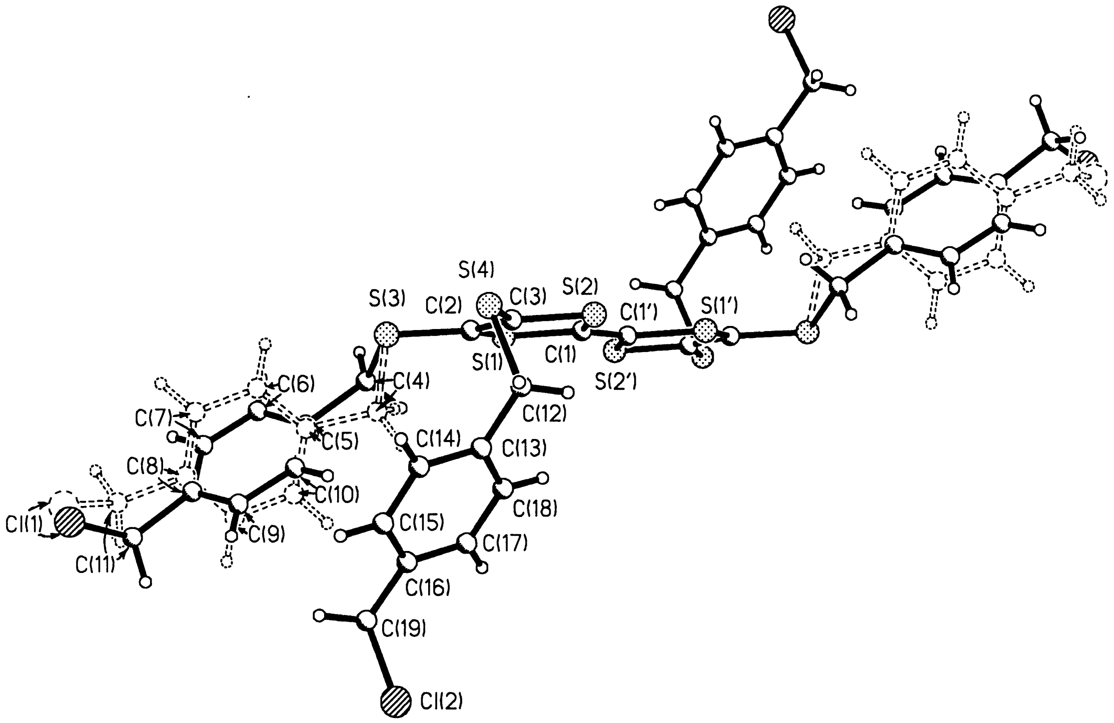


Fig. 2 Molecular structure of **7**. Position A of the disordered chain is shown solid, position B dashed. Primed atoms are symmetry-related *via* the inversion centre. Selected bond distances (Å): C(1)–S(1) 1.752(7), C(1)–S(2) 1.754(8), S(1)–C(2) 1.759(7), S(2)–C(3) 1.761(7), C(1)–C(1′) 1.345(13), C(2)–C(3) 1.342(9), C(2)–S(3) 1.755(7), C(3)–S(4) 1.738(7).

channel parallel to the *y* axis. It is not clear whether the choice between the A and B positions of a chain is affected by that of the adjacent chains or can be independent from them. The shortest intermolecular contacts between these positions, interstack C(4A) , C(6A) 3.43 and C(6A) , C(6A) 3.36 Å and intrastack C(7B) , C(10B) 3.36 Å, are not prohibitively short.

Conclusions

We have developed new expedient methodology for the synthesis of TTF-based dendrimers which possess well-defined redox activity, notably the trisdeca-TTF derivative **3**. The methodology should be applicable to higher generation TTF systems. Thin layer cyclic voltammetry has demonstrated that the electrochemical oxidation of these macromolecules involves all of the TTF units, and in these experiments there was no observable interaction between the redox sites. These data support our earlier suggestion[10] that the TLCV technique should be well-suited to electrochemical studies on dendritic macromolecules containing multiple redox centres. Several new functionalised TTF and multi-TTF reagents, *e.g.* compounds **7** and **16**, synthesised during the course of this work are now readily-available in synthetically useful quantities, and they offer great potential as reactive building blocks in the assembly of supramolecular[34] and polymeric TTF systems. In particular, by virtue of the four reactive benzylic halide groups at the periphery of **7** this molecule is a very attractive core unit for future studies, and the facile deprotection of **16**, to generate a reactive thiolate anion, makes this system eminently suited to a range of further synthetic transformations.

Experimental

General

All reagents and solvents were of commercial quality and were dried where necessary using standard procedures. ^{1}H NMR Spectra were obtained on a VXR 200 spectrometer operating at 200.14 MHz. MALDI TOF Mass spectra were obtained on a Kratos IV instrument in the reflection mode, operating with irradiation from a nitrogen laser at 337 nm. The matrix was 2,5-dihydroxybenzoic acid and spectra were averaged over 100 pulses whilst scanning across the sample: peak half-widths were between 6–10 amus. Melting points were obtained on a Reichert hot-stage microscope apparatus and are uncorrected. Electrochemical data were obtained on a BAS CV-50W Voltammetric Analyser. The counter, working and reference electrodes were Pt wire, Pt disc (1.6 mm diameter from BAS) and Ag/AgCl, respectively. Cyclic voltammetry was performed under argon using IR compensation. The thin layer cyclic voltammetry cell used in this work was constructed as described previously.[27b]

4,5-Bis(4-methylbenzylthio)-1,3-dithiole-2-thione 6a†

A mixture of zincate salt **4**[22] (7.2 g, 10 mmol) and a-chloro-*p*-xylene **5a** (11.25 g, 80 mmol) in acetone (60 ml) was refluxed for 1 h. The red solid which precipitated during the reaction was removed by filtration, then the filtrate was concentrated *in vacuo* affording a bright yellow solid, recrystallisation of which from ethanol yielded yellow needles of **6a** (7.50 g, 90%), mp 85–86 °C (Found: C, 55.85; H, 4.42. $C_{19}H_{18}S_5$ requires C, 56.11; H, 4.46%); d_H(CDCl$_3$) 2.33(s, 6H), 3.89 (s, 4H), 7.12 (s, 8H).

4,5-Bis(4-chloromethylbenzylthio)-1,3-dithiole-2-thione 6b

By analogy with **6a**, compound **4** (3.6 g, 5 mmol) and a,a′-dichloro-*p*-xylene **5b** (10.5 g, 60 mmol) in acetone (150 ml) gave yellow needles of **6b** (2.86 g, 60%) after purification by column chromatography [silica, eluent: dichloromethane–light petroleum (bp 40–60 °C), 1:1 (v/v)], mp 123.5–124.5 °C (Found: C, 48.03; H, 3.39; $C_{19}H_{16}Cl_2S_5$ requires C, 48.00; H, 3.39 d_H(CDCl$_3$) 3.91 (s, 4H), 4.57 (s, 4H), 7.23 (d, 4H, *J* 8.2), 7.35 (d, 4H, *J* 8.2).

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† Compound **6a** has recently been prepared independently in 75% yield by a similar route in Professor Becher's laboratory (R. P. Clausen and J. Becher, *Tetrahedron*, 1996, **52**, 3171). We thank Professor Becher for bringing this reference to our attention.

4,5-Bis(4-chloromethylbenzylthio)-1,3-dithiol-2-one 6c

To a solution of compound **6b** (3.5 g, 7.36 mmol) in a mixture of chloroform and acetic acid (80 ml; 3 : 1, v/v), mercuric acetate (7.0 g, 22 mmol) was added and the mixture was stirred at 20 °C overnight. Filtration of the product through Celite and evaporation of the filtrate yielded a yellow oil, which was washed with 5% aqueous $NaHCO_3$ (100 ml) and filtered to give a pale yellow solid, which was chromatographed on a silica column [eluent: light petroleum (bp 40–60 °C)–dichloromethane, 1 : 1 (v/v)] affording **6c** as off-white crystals (2.85 g, 84%), mp 67–68.5 °C (Found: C, 49.59; H, 3.46; $C_{19}H_{16}Cl_2OS_4$ requires C, 49.66; H, 3.51%); d_H($CDCl_3$) 3.87 (s, 4H), 4.56 (s, 4H), 7.22 (d, 4H, *J* 8.2), 7.34 (d, 4H, *J* 8.2).

Tetrakis(4-chloromethylbenzylthio)tetrathiafulvalene 7

Compound **6c** (2.8 g, 6.09 mmol) in triethyl phosphite (25 ml) was stirred under argon and heated at 120 °C for 1 h. The mixture was cooled to 20 °C and methanol (70 ml) was added. The precipitate was collected by filtration and washed with a large volume of methanol, followed by purification by column chromatography (silica, eluent: dichloromethane), affording compound **7** as orange crystals (2.1 g, 78%), mp 181–183 °C, which after recrystallisation from carbon disulfide gave red needles which were suitable for X-ray analysis (Found: C, 51.40; H, 3.63. $C_{38}H_{32}Cl_4S_8$ requires C, 51.46; H, 3.64%); d_H($CDCl_3$) 3.84 (s, 8H), 4.56 (s, 8H), 7.24 (d, 8H, *J* 8.2), 7.34 (d, 8H, *J* 8.2).

4,5-Bis(2-cyanoethylthio)-4′,5′-bis(4-methylbenzylthio)tetrathiafulvalene 9

A mixture of compound **8**[22b] (2.88 g, 10 mmol), compound **6a** (6.10 g, 15 mmol) and triethyl phosphite (50 ml) was heated with stirring at 120 °C for 75 min under argon. Ethanol (50 ml) was added to the reaction mixture which was then cooled to 20 °C. The orange solid which precipitated was collected by filtration, washed with a large volume of ethanol and then chromatographed (silica column, eluent: dichloromethane) to afford compound **9** (4.36 g, 67%) as orange needles, mp 142–143.5 °C (from ethanol–dichloromethane) (Found: C, 52.05; H, 3.99; N, 4.37. $C_{28}H_{26}N_2S_8$ requires C, 51.98; H, 4.05; N, 4.33%); d_H($CDCl_3$) 2.32 (s, 6H), 2.75 (t, 4H, *J* 7.0), 3.09 (t, 4H, *J* 7.0), 3.85 (s, 4H), 7.13 (s, 8H).

4-(2-Cyanoethylthio)-5-methylthio-4′,5′-bis(4-methylbenzylthio)tetrathiafulvalene 10

To a stirred solution of compound **9** (3.0 g, 4.64 mmol) in dimethylformamide (30 ml) under argon at 20 °C, a solution of $CsOH·H_2O$ (0.82 g, 4.88 mmol) in methanol (25 ml) was added dropwise over 2 h. Stirring was continued for 1 h at 20 °C, then methyl iodide (4.5 ml) was added and the mixture was stirred for a further 1 h. Evaporation of the reaction mixture *in vacuo* gave an orange residue, which was dissolved in dichloromethane (50 ml) and washed with water, then the organic layer was separated and dried over $MgSO_4$. Column chromatography of the concentrated solution (silica, eluent: dichloromethane) yielded an orange solid which crystallised from ethanol–chloroform as orange needles (2.24 g, 92%) mp 135–136.5 °C (Found: C, 51.15; H, 4.07; N, 2.08. $C_{26}H_{25}NS_8$ requires C, 51.36; H, 4.14; N, 2.03%); d_H($CDCl_3$) 2.32 (s, 6H), 2.48 (s, 3H), 2.71 (t, 2H, *J* 7.2), 3.03 (t, 2H, *J* 7.2), 3.84 (s, 4H), 7.13 (s, 8H).

4,4′,5,5′-Tetrakis(4-{[4′,5′-bis(4-methylbenzylthio)-5-methylthiotetrathiafulvalen-4-yl]thiomethyl}benzylthio)tetrathiafulvalene 11

To the stirred solution of **10** (358 mg, 0.589 mmol) in degassed DMF (20 ml) under argon, $CsOH·H_2O$ (99.4 mg, 0.59 mmol) in methanol (2 ml) was added in one portion. The mixture was stirred at 20 °C overnight to obtain a brown–red solution. Compound **7** (130 mg, 0.146 mol) was then added in one portion and the mixture was aggitated with ultrasound for 10 min, followed by stirring at 20 °C for 1 h and then at 50 °C for 4 h, to afford a precipitate. The reaction mixture was evaporated *in vacuo* and water (20 ml) was added to the residue. A brown–yellow solid was collected by filtration and washed with a large amount of methanol. Column chromatography of the solid [silica, eluent: dichloromethane–light petroleum (bp 40–60 °C), 2 : 1 (v/v)] gave compound **11** (430 mg, 99.5%) as an amorphous yellow–brown solid, mp *ca.* 150 °C (Found: C, 52.45; H, 3.93. $C_{130}H_{116}S_{40}$ requires C, 52.73; H, 3.95%); *m/z* (MALDI-TOF) 2964 (M^+ calc. 2956); d_H($CDCl_3$) 2.22 (s, 12H), 2.31 (s, 24H), 3.81 (s, 8H), 3.83 (s, 8H), 3.85 (s, 8H), 3.97 (s, 8H), 7.1–7.3 (m, 48H).

4-(2-Cyanoethylthio)-5-methylthio-1,3-dithiole-2-thione 13

Following the reported method,[24b] reaction of compound **12**[22b] (1.5 g, 4.93 mmol) in DMF (30 ml) with $CsOH·H_2O$ (0.83 g, 4.94 mmol) in methanol (30 ml) at 20 °C followed by addition of methyl iodide (1.5 ml) gave a product which was purified by column chromatography (silica, eluent: dichloromethane) to yield **13** as yellow crystals (1.2 g, 92%), mp 88–89 °C (Found: C, 31.56; H, 2.62; N, 4.91. $C_7H_7NS_5$ requires C, 31.67; H, 2.66; N, 5.28%); d_H($CDCl_3$) 2.56 (s, 3H), 2.76 (t, 2H, *J* 7.0), 3.09 (t, 2H, *J* 7.0).

4-(2-Cyanoethylthio)-5-methylthio-1,3-dithiol-2-one 14

To the solution of **13** (1.2 g, 4.52 mmol) in a mixture of chloroform and acetic acid [3 : 1 (v/v), 40 ml], mercuric acetate (4.0 g, 12.6 mmol) was added and the mixture was stirred at 20 °C overnight. Filtration of the product mixture through Celite and evaporation of the filtrate yielded a yellow residue, which was dissolved in dichloromethane and washed with saturated $NaHCO_3$ solution. The organic phase was separated, dried over $MgSO_4$, concentrated and chromatographed (silica column, eluent: dichloromethane), affording white needles of **14** (1.1 g, 98%), mp 57.5–58.5 °C (Found: C, 33.42; H, 2.78; N, 5.24. $C_7H_7NOS_4$ requires C, 33.71; H, 2.83; N, 5.62%); d_H ($CDCl_3$) 2.52 (s, 3H), 2.75 (t, 2H, *J* 7.0), 3.08 (t, 2H, *J* 7.0).

4-(2-Cyanoethylthio)-5-methylthio-4′,5′-bis(4-chloromethylbenzylthio)tetrathiafulvalene 15

A mixture of **14** (125 mg, 0.5 mmol) and **6b** (238 mg, 0.5 mmol) in triethyl phosphite (5 ml) was heated to 125 °C and stirred under argon for 1.5 h. The mixture was evaporated *in vacuo* and the orange oily residue was chromatographed on a silica column (eluent: dichloromethane), affording **15** as an orange solid (153 mg, 45%), mp 146.5–148.5 °C (Found: C, 46.15; H, 3.38; N, 1.64. $C_{26}H_{23}Cl_2NS_8$ requires C, 46.13; H, 3.42; N, 2.07%); d_H($CDCl_3$) 2.48 (s, 3H), 2.72 (t, 2H, *J* 7.0), 3.04 (t, 2H, *J* 7.0), 3.85 (s, 4H), 4.57 (s, 4H), 7.25 (d, 4H, *J* 8.2), 7.34 (d, 4H, *J* 8.2).

4,5-Bis(4-{[4′,5′-bis(4-methylbenzylthio)-5-methylthiotetrathiafulvalen-4-yl]thiomethyl}benzylthio)-4′-(2-cyanoethylthio)-5’-methylthiotetrathiafulvalene 16

By analogy with the preparation of compound **11**, compound **16** was synthesized from **10** (277 mg, 0.456 mmol) in DMF (20 ml), $CsOH·H_2O$ (76.5 mg, 0.456 mmol) in methanol (4 ml) and compound **15** (154 mg, 0.227 mmol) at 20 °C with stirring for 6 h. Purification was achieved by vacuum evaporation, washing with water and chromatography on a silica column (eluent: chloroform) to yield **16** (298 mg, 74%) as an orange solid, mp 55 °C (Found: C, 49.77; H, 3.77; N, 0.72. $C_{72}H_{65}NS_{24}$ requires C, 50.46; H, 3.83; N, 0.82%); *m/z* 1710.84200 (M^+ calc. 1710.84142); d_H($CDCl_3$) 2.22 (s, 6H), 2.30 (s, 12H), 2.44

(s, 3H), 2.56 (t, 2H, *J* 6.7), 2.97 (t, 2H, *J* 6.7), 3.81 (s, 4H), 3.83 (s, 4H), 3.85 (s, 4H), 3.96 (s, 4H), 7.1–7.3 (m, 24H).

4,4′,5,5′-Tetrakis(4-{[4′,5′-bis(4-{[4′,5′-bis(4-methylbenzylthio)-5-methylthiotetrathiafulvalen-4-yl]thiomethyl}benzylthio)-5-methylthiotetrathiafulvalen-4-yl]thiomethyl}benzylthio)tetrathiafulvalene 3

By analogy with the synthesis of compound **11**, compound **3** was synthesized from compound **16** (178 mg, 0.104 mmol) in DMF (10 ml), $CsOH \cdot H_2O$ (20 mg, 119 mmol) in methanol (1.5 ml) and compound **7** (23 mg, 0.0259 mmol) with stirring for 3 h, both at 20 °C and at 80 °C. After work-up, the dark yellow filtrate was filtered through alumina 90 using a short column (eluent: chloroform). The resultant solid was then triturated with DMF (2 × 10 ml) to give compound **3** as a light brown tar, which solidified into an amorphous solid (126 mg, 66%), mp *ca.* 75 °C, upon trituration with a large amount of methanol (Found: C, 50.81; H, 3.79. $C_{314}H_{276}S_{104}$ requires C, 51.07; H, 3.77%); *m/z* (MALDI-TOF) 7377 (M^+ calc. 7372); $d_H(CDCl_3)$ 2.21 (s, 36H), 2.30 (s, 48H), 3.82 (s, 56H), 3.95 (s, 24H), 7.11(s) and 7.21 (m, 112H).

Crystal structure determination of compound 7

The X-ray diffraction experiment was performed on a Siemens 3-circle diffractometer with a CCD area detector, using graphite-monochromated Mo-Ka radiation, l = 0.71073 Å. *Crystal data:* $C_{38}H_{32}Cl_4S_8$, $M = 886.9$, monoclinic, space group $P2_1/c$ (No.14), $a = 12.706(2)$, $b = 5.789(1)$, $c = 28.159(3)$ Å, b = 99.69(1)°, $V = 2041.7(5)$ Å^3, $Z = 2$, $D_c = 1.44$ g cm^{-3}, $F(000) = 912$, m = 7.3 cm^{-1}, crystal size 0.32 × 0.18 × 0.08 mm, v scan mode, 2h ≤ 52°, 10429 total, 3515 unique, 1978 observed $[|F| > 4s(F)]$ data, $R_{int}(F^2) = 0.060$. The structure was solved by direct methods and refined by full-matrix least squares against F^2 of all data, using SHELXTL software.[35] The C(4) to C(11) and Cl(1) atoms were refined as disordered over two positions (A and B) with equal occupancies and their geometries restrained to similarity. The refinement (ordered non-H atoms anisotropic, disordered ones isotropic, H atoms 'riding', 217 variables, 145 restraints) converged at $wR(F^2$, all data$) = 0.247$, $R(F$, obs. data$) = 0.079$, goodness-of-fit 1.07. Residual electron density features: $Dr_{max} = 0.64$, $Dr_{min} = -0.74$ eÅ^{-3}.

Atomic coordinates, thermal parameters, and bond lengths and angles have been deposited at the Cambridge Crystallographic Data Centre (CCDC). See Information for Authors, *J. Mater. Chem.*, 1997, Issue 1. Any request to the CCDC for this material should quote the full literature citation and the reference number 1145/30.

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