Arborol-Functionalised Tetrathiafulvalene Derivatives: Synthesis and Thin-Film Formation

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The syntheses of a series of novel tetrathiafulvalene derivatives substituted with four side-chains terminating in hydrophilic amidoalcohol (arborol) groups are reported, for example the tetrathiafulvalene derivative **15**. Some of these arborol derivatives formed thin films by spin-coating from methanol solution onto solid supports such as glass, ITO-coated glass and gold. The quality of the films improved markedly with an increasing number of alcohol substituents at the periphery of the molecule. Optical absorption spectroscopy showed that oxidative doping of these films could be achieved chemically and electrochemically. The observation of low-energy bands in the UV/Vis absorption spectra (λ_{max} = 820 nm tailing to ca. 1300 nm) and the moderate levels of conductivity ($\sigma_{rt} \approx 10^{-4}$ S cm^{-1}) in these doped films strongly suggest that a significant degree of supramolecular order is present, with π-π stacking of the TTF cores. To the best of our knowledge this is the first time that semiconducting behaviour has been achieved in molecular arborol systems that possess an electroactive core unit. This work offers the prospect of using spin-coated films of TTF-arborols as semiconducting charge-transport layers in optoelectronic devices.

Introduction

Arborols are branched polyalcohol units with a tree-like topology (e.g. prototype compound **1**). Newkome et al. have developed their syntheses and established that the attachment of these hydrophilic substituents to a hydrocarbon core imparts unusual chemical and physical properties to the molecules, notably they form aqueous gels in a thermally reversible process.[1] Very few arborols with "functional" cores have been studied. Recently, Kuroda and Swager synthesised arborol-substituted poly(phenyleneethynylene) derivatives such as **2**, which are non-ionic water-soluble fluorescent polymers.[2] Of particular relevance to the present work is a report by Jørgensen et al. that the bis(arborol)TTF derivative **3** (TTF = tetrathiafulvalene) forms a gel containing "molecular wires" believed to derive from stacking of the TTF units.[3] UV/Vis absorption spectra suggested that these TTF aggregates could be chemically oxidised to the radical-cation species and, although the possibility of conductive stacks was discussed, no conductivity data were reported. Compound **3** suffers the drawback of being an inseparable mixture of *cis* (i.e. 4,4′) and *trans* (i.e. 4,5′) isomers at the TTF core. In view of the widespread interest in new TTF derivatives in materials and supramolecular chemistry[4] we sought to synthesise new tetrakis(arborol)- and 4,5-bis(arborol)-TTF derivatives which, unlike **3**, should not present isomer problems. Herein we report our studies in this area.[5] As a basis for our synthetic protocol we have previously established an efficient methodology for the synthesis of TTF derivatives containing four side-chains, each bearing one terminal hydroxy group.[6]

Results and Discussion

Synthesis of Materials

At the outset of this work we expected that problems of isolation and purification of the products would be encountered with the increasing number of peripheral hydroxy groups, and this indeed proved to be the case. We initially opted to synthesise the bis(arborol) system **6**. Our strategy (which is different from that used by Jørgensen et al. to synthesise **3**[3]) involved reaction of TTF-thiolate anions (which were generated by deprotection of their cyanoethylthio precursors)[6a,7] with 1-haloalkyl esters followed by conversion of the esters into terminal hydroxyalkylamide substituents. Accordingly, the synthesis of compound **6** is shown in Scheme 1. Deprotection of compound **4** using so-

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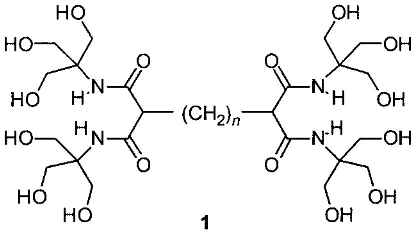

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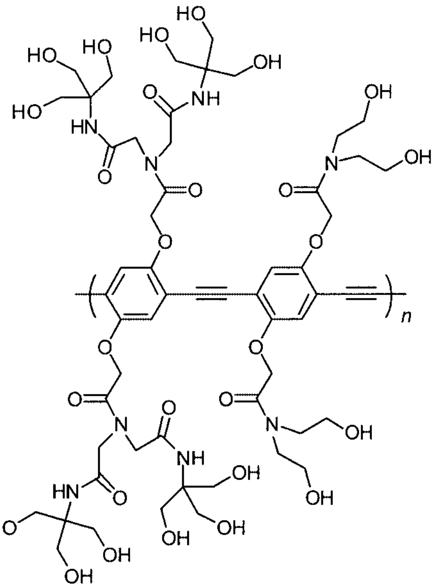

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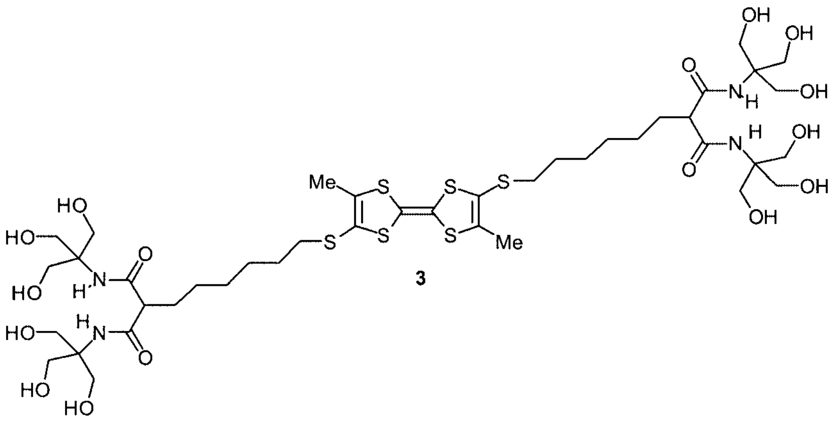

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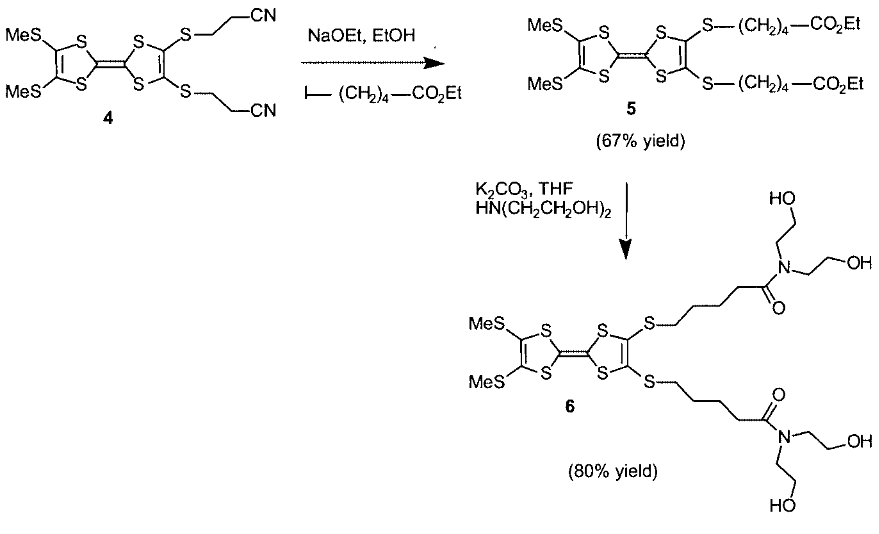
dium ethoxide in ethanol followed by twofold alkylation of the dithiolate anion thereby generated gave the TTF-diester derivative **5** in 67% yield. Reaction of **5** with potassium carbonate and diethanolamine in THF gave the tetrahydroxy derivative **6** in 80% yield. The analogous synthesis of tetrakis(arborol)TTF derivative **9** is shown in Scheme 2. Reaction of **8** with tris(hydroxymethyl)aminomethane (Tris) in DMSO in the presence of K_2CO_3 gave compound **10** bearing twelve peripheral hydroxy substituents. Compounds **6**, **9** and **10** are viscous oils.

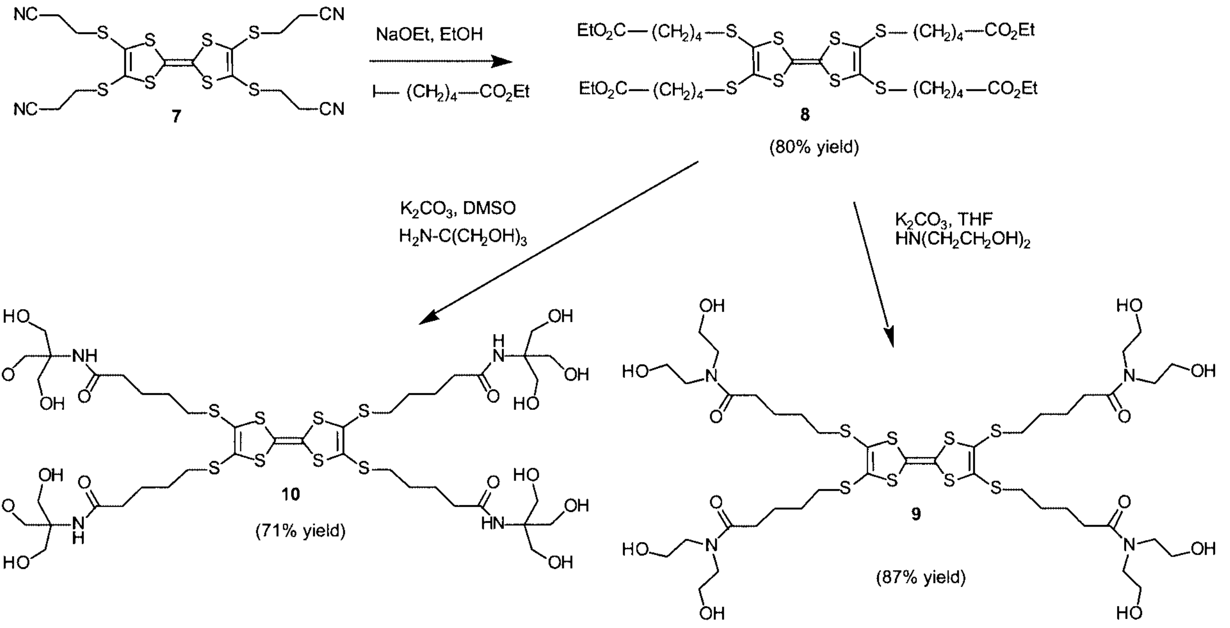
To obtain the more extensively branched arborol structure **15** bearing 24 peripheral hydoxy groups we used the route shown in Scheme 3. The dithiolate dianion derived from reagent **11** was alkylated with reagent **12** to afford the product **13** in 86% yield. Phosphite-induced self-coupling of **13** under standard conditions[8] gave the TTF derivative **14** in 61% yield. The target arborol **15** was obtained as a viscous orange oil (58% yield from **14**) by analogy with the synthesis of **10**. Compound **15** was especially difficult to purify as it readily formed emulsions during extraction and workup. Nonetheless, plasma desorption mass spectra (PDMS) and ^{1}H NMR spectroscopy unambiguously confirmed that essentially pure compound **15** had been isolated. Cooling a warm solution of **15** in an ethanol/water solvent mixture (1:3, v/v) led to opaque very viscous solutions ; stiff gels suitable for microscopy studies could not be obtained.

Cyclic Voltammetry

Cyclic voltammetric (CV) data for the new TTF derivatives **5**, **6**, **8**−**10**, **14** and **15** in dichloromethane or methanol solution showed the two sequential oxidation waves typical of TTF derivatives[9] (Table 1). Both these waves are reversible for all the derivatives except arborol **15** (Figure 1), for which they are quasi-reversible (especially the second oxidation wave) probably due to deposition of the dication species on the electrode which was observed visually after a few scans to 1.0 V. If scanning was restricted to the potential window between 0 and +600 mV (i.e. scanning through the $TTF^0/TTF^{+\cdot}$ couple) good reversibility of this first wave



Scheme 1

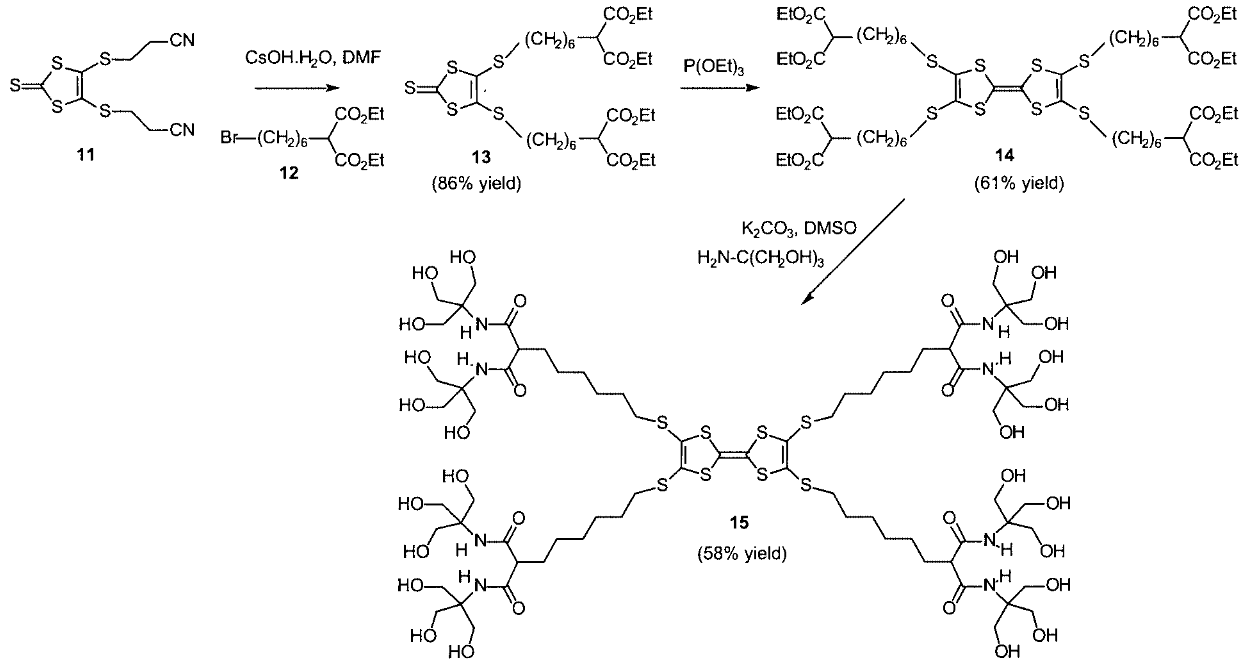


Scheme 2

was achieved for **15**. (The criterion applied for reversibility was a ratio of 1.0±0.05 for the intensities of the anodic and cathodic currents and no shift of the half-wave potentials with varying scan rates between 50 and 250 mV s^{-1}.) It is known that alkylsulfanyl substituents raise the oxidation potential of the TTF system[9b][9c] and the potential for the first wave in compounds **5**, **6**, **8**–**10**, **14** and **15** (0.52–0.57 V vs. Ag/AgCl) is entirely consistent with literature values for $TTF(SR)_4$ derivatives under these conditions. It is notable that for compounds **6**, **9** and **10**, which contain terminal hydroxy substituents, the potential of the second oxidation wave (the $TTF^{+\cdot}/TTF^{2+}$ couple) is significantly lower (by 120–160 mV) in methanol than in dichloromethane whereas the first wave is unchanged (within 10 mV). Compound **9** is representative: in CH_2Cl_2 $E_1^{1/2} = 0.53$, $E_2^{1/2} = 0.89$ V; in MeOH $E_1^{1/2} = 0.52$, $E_2^{1/2} = 0.73$ V. For compound **15** ΔE (i.e. $E_2^{ox} - E_1^{ox}$) is reduced to only 180 mV. These data reflect an increased stability of the dication state in methanol possibly due to specific hydrophilic interactions with the solvent. It is known that the ionisation potentials of TTF vary markedly depending on the solvating power of the solvent.[9b] Literature data for compound **3**[3] are included in Table 1 for comparison; the lower oxidation potentials of **3** can be readily explained by the presence of the electron-donating methyl substituents on the TTF core.

Thin-Film Formation by Spin Coating

Films of arborols **9**, **10** and **15** were prepared by spin-coating a methanolic solution of the compound. Optimum conditions were found to be 2000 rpm for 2 min. Different



Scheme 3

Table 1. Cyclic voltammetric data

Compound	Solvent	$E_1^{1/2}$ [V][a]	$E_2^{1/2}$ [V]	ΔE /V[b]
3[c]	MeCN	0.46 (E^{ox})	0.78 (E^{ox})	0.32
5	CH_2Cl_2	0.57	0.94	0.37
5	MeOH	0.56	0.90	0.34
6	CH_2Cl_2	0.55	0.92	0.37
6	MeOH	0.55	0.80	0.25
8[d]	CH_2Cl_2	0.56	0.90	0.34
9	CH_2Cl_2	0.53	0.89	0.36
9	MeOH	0.52	0.73	0.21
10	CH_2Cl_2	0.53	0.90	0.37
10	MeOH	0.52	0.76	0.24
14	CH_2Cl_2	0.52	0.84	0.32
15	MeOH	0.53 (E^{ox})	0.71 (E^{ox})	0.18

[a] Versus Ag/AgCl. See Exp. Sect. for further details. [b] $\Delta E = E_2^{1/2} - E_1^{1/2}$ except for **3** and **15** for which it is $E_2^{ox} - E_1^{ox}$. [c] Versus standard calomel electrode: data taken from ref.[3] [d] Low solubility resulted in unreliable data in MeOH.

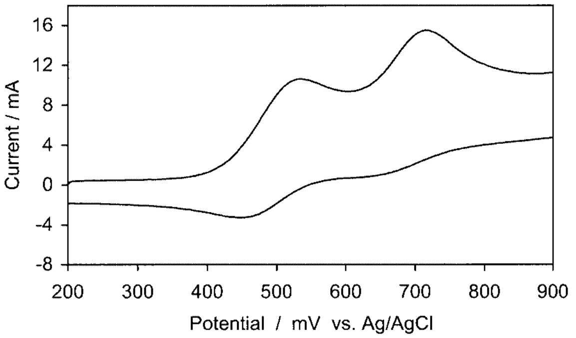


Figure 1. CV of compound **15** in MeOH; scan rate 100 mV s^{-1}, electrolyte 0.1 M Bu_4NClO_4, 20 °C

substrates were tested (e.g. glass, indium, tin oxide coated glass and gold) and the best-quality films were obtained on glass. The quality of the films improved markedly with an increasing number of alcohol groups at the periphery of the molecule: arborol **15** gave better quality films than **10** whereas **9** gave only very patchy films. Compounds **6** and the ethyl ester precursors **5**, **8** and **14** did not give any films under these conditions. This emphasises the important structural requirement of the arborol branches for film formation presumably due to intermolecular hydrogen-bonding interactions and hydrophobic interactions with the substrate. The films were pale yellow in appearance and had thicknesses of ca. 50 nm. The film quality for **10** and **15** was improved by admixture of the solution with 15−20 mol % of 16-hexanediol prior to spin coating. The subsequent discussion of characterisation data is restricted to films of compound **15**.

Optical Absorption Spectra

The UV/Vis spectrum of spun films of **15** on glass shows bands at λ_{max} = 280, 345 (shoulder) and 400 nm (shoulder). Chemical doping of the films (neat or with added hexanediol) was achieved by exposure to iodine vapour for 2 min in a sealed container. The UV/Vis spectra confirm the formation of TTF cation radicals: in particular, the appearance of a broad band at λ_{max} = 820 nm tailing into the red (ca. 1300 nm) is diagnostic of $TTF^{+\cdot}$ species.[10] A marked increase in the intensity of the absorption bands relative to the undoped sample has been noted previously for Langmuir−Blodgett films of other TTF derivatives.[11] Figure 2 shows the UV/Vis spectra of compound **15** on glass slides before and after iodine doping.

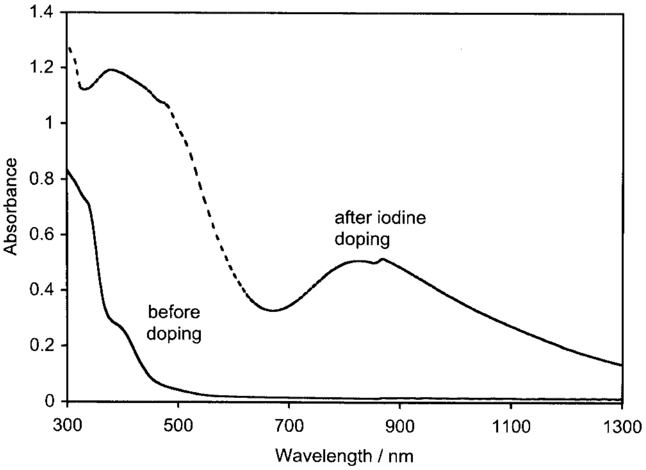


Figure 2. UV/Vis/NIR spectra of thin films of **15** spin-coated of MeOH solution onto glass before and after exposure to iodine vapour

Conductivity Studies

For all samples ohmic current-voltage characteristics were observed over the range 0−10 V. The in-plane dc conductivity values on the spin-coated films of **15** were $\sigma_{rt} \approx 10^{-6}$ S·cm^{-1}. By varying the distance between the electrodes it was established that the effect of contact resistance was negligible. The conductivity increased by ca. two orders of magnitude upon iodine doping to reach a maximum value of $\sigma_{rt} \approx 10^{-4}$ S·cm^{-1} for the best-quality film samples. No anisotropy of conductivity was found in the film plane. Electrical measurements using interdigitated electrode arrays (20 µm gap 4 cm track length) gave similar values. Electrochemical doping with tetrabutylammonium perchlorate or hexafluorophosphate as the electrolyte raised the conductivity by one to two orders of magnitude to $\sigma_{rt} \approx 10^{-5}$−$10^{-4}$ S·cm^{-1}. Partial dissolution of the films upon application of an electrochemical potential could account for the variability of this value between different samples. Nonetheless, the observation of low-energy bands in the UV/Vis spectra and, more convincingly, the moderate levels of conductivity in these doped films strongly suggest that a significant degree of supramolecular order is present, with π-π stacking of the TTF cores. We note that Khodorkovsky et al. have recently demonstrated that the presence of low-energy absorption bands alone is not reliable evidence of dimer formation in TTFs substituted with thioalkyl groups.[10b]

The structural properties of the films of arborol **15** were examined by low-angle X-ray diffraction (LXRD), scanning electron microscopy (SEM) and atomic force microscopy (AFM). LXRD showed weak structural features but no discernible features could be observed in the SEM or AFM studies.

Conclusions

During the past decade thin films of TTF derivatives have been obtained by the Langmuir−Blodgett technique,[11,12] thermal evaporation,[13] electropolymerisation[14] and by self-assembly of thiol-substituted derivatives onto solid supports[15] for purposes of obtaining new molecular conductors, cation sensors and smart surfaces. However, we are not aware of any previous work on thin films of TTF derivatives formed by simple spin-coating techniques. The key role played by the arborol substituents in **15** in facilitating film formation has been established by comparison with other less hydrophilic TTF derivatives. This work establishes for the first time that semiconducting behaviour can be achieved in molecular arborol systems that possess an electroactive core unit. The observation of low-energy bands in the UV/Vis spectra and the moderate levels of conductivity in the doped films strongly suggest that a significant degree of supramolecular order is present. This work opens up the possibility of using spin-coated films of these novel TTF-arborols as semiconducting charge-transport layers in optoelectronic devices.[16]

Experimental Section

General: Details of the electrochemical conductivity and spectroscopic techniques and equipment are the same as those reported previously.[11b,17] Cyclic voltammetric data are reported for solutions in dichloromethane or methanol (as stated in Table 1) with 0.1 M tetrabutylammonium perchlorate as electrolyte using Pt electrodes versus Ag/AgCl at 20 °C. The interdigitated electrode arrays were produced as described previously.[18] Film thicknesses were measured using a surface-profiling Tencor Instruments Alpha-Step 200. All synthetic reagents were used as supplied. Solvents were dried and distilled using standard procedures. All reactions were performed under a nitrogen or argon atmosphere.

4,5-Bis(ethoxycarbonylbutylthio)-4′,5′-bis(methylthio)tetrathiafulvalene (5): A solution of sodium (0.25 g, 11 mmol), dissolved in ethanol (20 mL), was added in one batch to compound **4**[6a] (1.0 g, 2.1 mmol), suspended in dry ethanol (30 mL). After stirring at 20 °C for 4 h, ethyl 5-iodopentanoate[19] (2.59 g, 11 mmol) was added in one batch. After 1 h, the solution had turned orange. The solution was stirred at 20 °C overnight, ammonium chloride (1 g) was added with stirring and the mixture was filtered through Celite, which was then washed with ethanol. The filtrate was concentrated to give **5** as an orange solid (0.89 g, 67%); m.p. 37−38 °C. $C_{22}H_{32}O_4S_8$ (617.0): calcd. C 42.83, H 5.23; found C 42.93, H 5.27. MS (EI): *m/z* = 616 [M$^+$]. ^{1}H NMR (CDCl$_3$): δ = 4.13 (q, *J* = 7.2 Hz, 4 H), 2.83 (t, *J* = 7.0 Hz, 4 H), 2.43 (s, 6 H), 2.32 (s, 4 H), 1.72 (m, 8 H), 1.25 (t, *J* = 7.2 Hz, 6 H) ppm. ^{13}C NMR (CDCl$_3$): δ = 173.05, 127.73, 127.4, 110.79, 110.31, 60.26, 37.77, 33.68, 29.10, 23.75, 19.08, 14.20 ppm.

4,5-Bis[(*N*,*N*-bis(2-hydroxyethyl)butaneamidothio]4′,5′-bis(methylthio)tetrathiafulvalene (6): Diethanolamine (0.5 mL) and potassium carbonate (0.1 g) were added to a solution of compound **5** (0.35 g 0.57 mmol) in tetrahydrofuran (25 mL). The mixture was heated at reflux for 24 h, cooled, filtered and the filtrate concentrated to leave **6** as a viscous orange oil (0.33 g 80%). $C_{26}H_{42}N_2O_6S_8$ (735.1): calcd. C 42.48, H 5.76, N 3.81; found C 42.66, H 5.55, N 3.52. HRMS: found 734.08080; $C_{26}H_{42}N_2O_6S_8$ requires 734.08085. ^{1}H NMR ([D$_6$]DMSO): δ = 3.54−3.31 (m, 16 H), 2.85 (s, 4 H), 2.44 (s, 4 H), 2.35 (s, 4 H), 1.59 (m, 8 H) ppm. ^{13}C NMR ([D$_6$]DMSO): δ = 172.02, 172.01, 126.93, 126.37, 109.20, 59.98, 59.08, 58.77, 51.36, 50.43, 48.27, 48.05, 35.27, 31.51, 28.84, 23.50, 18.38 ppm.

4,4′,5,5′-Tetrakis(ethoxycarbonylbutylthio)tetrathiafulvalene (8): A solution of sodium (0.42 g 19 mmol), dissolved in ethanol (20 mL), was slowly added to compound **7**[6a] (1.0 g 1.84 mmol), suspended in dry ethanol (10 mL). After stirring at 20 °C for 4 h, ethyl 5-iodopentanoate (2.35 g 9.2 mmol) was added and the solution was stirred at 20 °C for 4 h. The solution was then filtered and the solid was washed with ethanol and petroleum ether (b.p. 80−100 °C) to give a solid which was sufficiently pure for further reaction or could be recrystallised from ethanol to afford **8** as small orange needles (1.24 g, 80%); m.p. 71−72 °C. $C_{34}H_{52}O_8S_8$ (845.3): calcd. C 48.31, H 6.20; found C 47.86, H 6.28. MS (EI): m/z = 844 [M^+]. ^1H NMR ($CDCl_3$): $\delta = 4.13$ (q, J = 7.2 Hz, 8 H), 2.83 (t, J = 6.9 Hz, 8 H), 2.33 (t, J = 6.9 Hz, 8 H), 1.78−1.67 (m, 16 H), 1.26 (t, 12 H, J = 7.2 Hz) ppm. ^{13}C NMR ($CDCl_3$): $\delta = 172.95$, 127.61, 109.96, 60.16, 35.65, 33.57, 28.98, 23.64, 14.09 ppm.

Tetrathiafulvalene Derivative 9: By analogy with the preparation of **6** from **5**, compound **8** (2.0 g 2.4 mmol) in THF (50 mL), diethanolamine (2.0 g 19.0 mmol) and potassium carbonate (0.33 g) gave compound **9** as a very viscous oil (2.24 g 87%). $C_{42}H_{72}N_4O_{12}S_8$ + 3 H_2O (1135.6): calcd. C 44.42, H 6.92, N 4.93; found C 44.47, H 7.06, N 5.41. MS (PDMS): m/z = 1081.7 [M^+]. ^1H NMR ([D_6]DMSO): $\delta = 4.85$ (br. s, 8 H), 3.52−3.32 (q of t, 32 H), 2.87 (t, J = 7.0 Hz, 8 H), 2.36 (t, J = 7.0 Hz, 8 H), 1.59 (m, 16 H) ppm. ^{13}C NMR ([D_6]DMSO): $\delta = 171.96$, 169.93, 127.00, 109.00, 58.99, 58.88, 58.71, 58.68, 51.30, 50.38, 48.22, 47.99, 35.22, 31.48, 28.78, 23.48 ppm.

Tetrathiafulvalene Derivative 10: Tris(hydroxymethyl)aminomethane (72 mg 0.60 mmol) and potassium carbonate (82 mg 0.60 mmol) were added to a solution of compound **8** (100 mg 0.12 mmol) in dimethyl sulfoxide (10 mL) and the mixture was stirred at 20 °C for 48 h. After filtration, the solvent was removed in vacuo and the residue was washed and triturated with dichloromethane and hexane to yield product **10** as an orange-brown oil (97 mg 71%). $C_{42}H_{72}N_4O_{16}S_8$ + 2 H_2O (1181.6): calcd. C 42.69, H 6.48, N 4.74; found C 42.90, H 6.58, N 4.54. MS (PDMS): m/z = 1146.5 [M^+]. ^1H NMR ([D_6]DMSO): $\delta = 7.95$ and 7.24 (both br. s, NH), 4.93 (br. s, OH), 3.52 (m, 24 H), 2.84 (t, J = 7.0 Hz, 8 H), 2.33 (t, J = 7.0 Hz, 8 H), 1.56 (m, 16 H) ppm.

4,5-Bis(6,6-diethoxycarbonylhexylthio)-1,3-dithiol-2-thione (13): Cesium hydroxide monohydrate (0.77 g 4.64 mmol) was added to a stirred solution of 4,5-bis(2′-cyanoethylthio)-1,3-dithiole-2-thione (**11**)[6a] (0.70 g 2.32 mmol) in dry dimethylformamide (10 mL) and the stirring continued for 2 h. Diethyl 6-(bromohexyl)malonate (**12**)[2] (1.5 g 4.64 mmol) was then added and the mixture was stirred at 20 °C overnight. The solvent was removed in vacuo and the resulting oily product was dissolved in CH_2Cl_2 and washed with H_2O. The combined organic phases were dried with $MgSO_4$ and the solvents evaporated. The residue was chromatographed on a silica column eluting with CH_2Cl_2 to afford compound **13** (1.35 g 86%) as an orange oil. $C_{29}H_{46}O_8S_5$ (683.0): calcd. C 51.00, H 6.79; found C 51.50, H 6.60. MS (EI): m/z = 682 [M^+]. HRMS found 682.17955; $C_{29}H_{46}O_8S_5$ requires 682.17962. ^1H NMR ($CDCl_3$): $\delta_H = 4.18$ (q, J = 7.2 Hz, 8 H), 3.29 (t, J = 8.1 Hz, 2 H), 2.85 (t, J = 7.3 Hz, 4 H), 1.87 (m, 4 H), 1.50−1.30 (m, 16 H), 1.26 (t, 18 H, J = 7.2 Hz) ppm. IR (KBr): $\tilde{\nu}$ = 1747, 1731, 1368, 1067 cm^{-1}.

Tetrathiafulvalene Derivative 14: Compound **13** (0.5 g 0.73 mmol) was dissolved in triethyl phosphite (15 mL) and the mixture was heated at reflux for 10 h. The solvent was evaporated under vacuum and the resulting oil was chromatographed on a silica column, eluting first with hexane to remove traces of starting materials and then with CH_2Cl_2 to afford **14** as a dark orange oil (0.58 g 61%). $C_{58}H_{92}O_{16}S_8$ (1301.8): calcd. C 53.51, H 7.12; found C 53.21, H 6.80. MS (PDMS): m/z = 1302 [M^+]. ^1H NMR ($CDCl_3$): $\delta = 4.22$ (q, 16 H, J = 7.1 Hz), 3.30 (t, J = 8.2 Hz, 4 H), 2.85 (m, 8 H), 1.87 (m, 8 H), 1.50−1.40 (m, 32 H), 1.33 (t, 24 H, J = 7.1 Hz) ppm.

Tetrathiafulvalene Derivative 15: According to the procedure for the preparation of compound **10**, compound **14** (0.5 g 0.38 mmol), DMSO (10 mL), tris(hydroxymethyl)aminomethane (0.23 g 1.90 mmol) and K_2CO_3 (0.26 g 1.9 mmol) gave a residue which was triturated with CH_2Cl_2 and hexane to afford **15** as an orange oil (0.42 g 58%). $C_{74}H_{132}N_8O_{32}S_8$ + 5 H_2O (1192.5): calcd. C 44.61, H 7.18, N 5.62; found C 44.30, H 7.48, N 5.29. MS (PDMS): m/z = 1902 [M^+]. ^1H NMR ([D_6]DMSO): $\delta = 7.77$ and 7.19 (both br. s, NH), 4.90 (br. s, NH), 3.52 (m, 48 H, CCH_2OH), 3.30 [4 H, t, J = 8.0 Hz, $CHC(O)$], 2.85 (t, J = 7.2 Hz, 8 H, CH_2S), 1.57 (m, 40 H, CH_2CH_2) ppm.

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