New Multi(tetrathiafulvalene) Dendrimers

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Received 29 March 2000

Dedicated to Professor Fred Wudl on the occasion of his 60th birthday

Abstract: The convergent synthesis of multi(TTF) dendrimers with glycol chains as the branches is reported. Key methodology in the iterative steps involves nucleophilic displacement of reactive halides by transient TTF-thiolate anions. Core units in the dendrimers are 1,3,5-trisubstituted benzene, TTF and hexa-substituted benzene, providing three-, four- and six-directional cores, respectively. Cyclic voltammetry (CV) and thin layer CV studies establish that the TTF redox chemistry is retained in the dendrimer structures, with clean sequential formation of multi(cation radical) and multi(dication) species upon electrochemical oxidation.

Key words: dendrimer, tetrathiafulvalene, cesium hydroxide, nucleophilic displacements, coupling, cyclic voltammetry

The synthesis and characterisation of new dendrimers continues to attract considerable attention.[1] These macromolecules possess well-defined, three-dimensional structural order, and they provide unique frameworks for placing functional groups in predetermined spatial arrangements in a polymeric structure. The aim of early research into dendrimers[1a] was to obtain higher generation systems with large molecular weights and dense surface packing.[2] As this topic has developed, the emphasis has changed towards systems which incorporate more elaborate functional groups at the periphery of, or embedded within, the dendrimer framework, to impart special properties to the molecules. In this context, a variety of redox-active organic and organometallic groups have been incorporated into the structures with several long-term aims in mind.[3] 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.

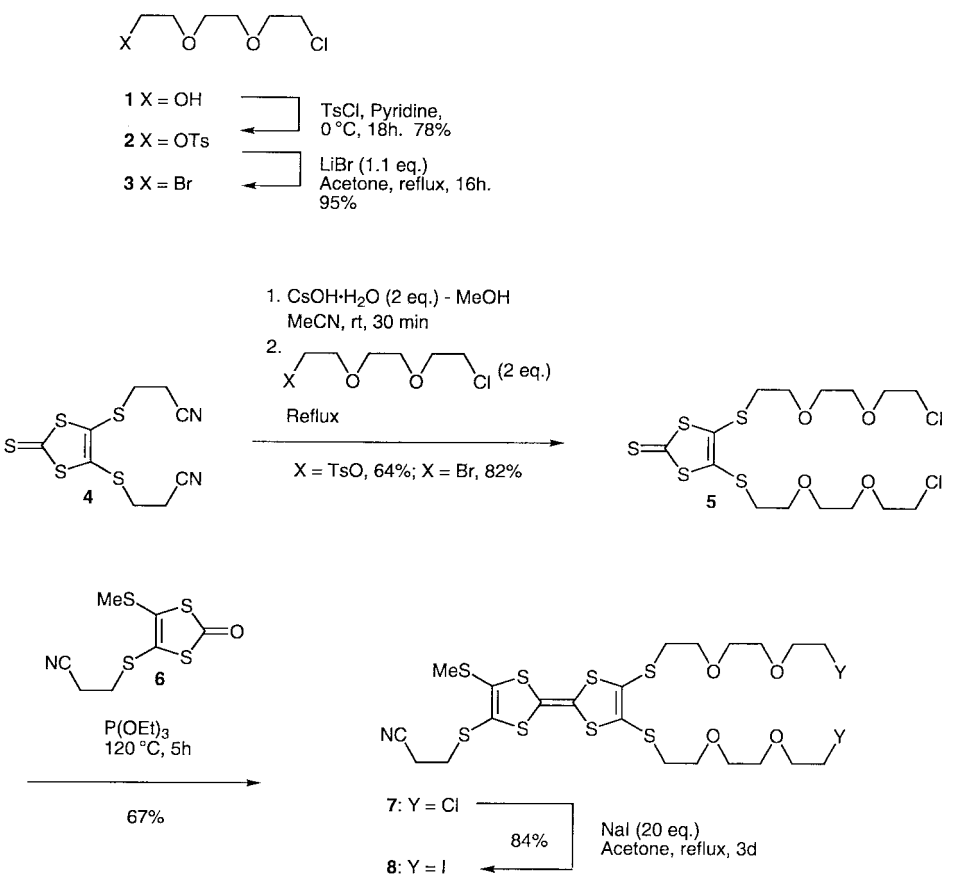
Some dendrimers contain a single redox-active unit at the core [e.g. metalloporphyrin,[4] ruthenium(II)bis(terpyridyl) complex,[5] ferrocene,[6] C_{60}[7] or an iron-sulfur cluster[8]] and for some systems the solution redox behaviour of this central 'encapsulated' group is modulated by the shielding effect of the dendrimer hierarchy, which hinders access of the redox site to the electrode surface.[9] Alternatively, the redox units, e.g. ferrocene and related metal sandwiches,[10] metal(bipyridyl),[11] fullerenes,[12] naphthalene diimides,[13] or tetrathiafulvalenes[14] 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 have exploited recent advances in the synthesis of functionalised tetrathiafulvalene (TTF) derivatives to assemble dendrimers bearing TTF units.[14] The incorporation of TTF into dendrimers presents a fascinating prospect for the following reasons:[15] (i) oxidation of TTF to the cation radical and dication species occurs sequentially and reversibly at low potentials in a range of organic solvents; (ii) the oxidation potentials can be finely tuned by substituents on the TTF ring system; (iii) TTF cation radicals are thermodynamically very stable; and (iv) oxidised TTF units have a high propensity to form dimers or ordered stacks, along which there can be high electron mobility. Most multi-TTF derivatives[16] are dimers,[17] although some trimers,[18] higher oligomers,[19] and main-chain and side-chain polymeric TTFs[20] are known. A feature of these multi-TTF systems is that in general they readily yield multiply-charged species upon electrochemical oxidation in solution.

In a previous communication[14d] we described TTF dendrimers incorporating glycol chains as the branches to impart good solubility in a wide range of solvents, and air-stability, thereby facilitating their characterisation. We now describe this work in full, and extend these studies to new TTF-glycol dendrimers.

We chose a convergent approach to multi-TTF dendrimers, with the cesium salts of TTF thiolate anions[21] as key intermediate species in the iterative steps, and identified compound **8** as a versatile branch monomer unit. Glycol chains were constructed from compound **1**, which was cleanly converted via tosyl derivative **2** into the corresponding bromo derivative **3**. Compound **4**[22] was deprotected by reaction with cesium hydroxide, and the resulting dithiolate species was trapped with either tosylate **2** or bromide **3** to afford product **5**. The latter reaction proceeded more rapidly and was higher yielding (82 *vs* 64%). Cross-coupling of thione **5** with ketone **6**[23] in the presence of triethyl phosphite, under standard conditions, gave TTF derivative **7** in 67% yield. Halogen exchange using sodium iodide in acetone yielded the more reactive diiodo analogue **8** (84%) (Scheme 1).

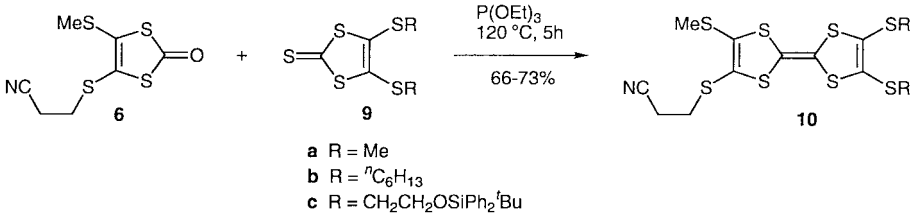
TTF derivatives **10a–c** were synthesised in 66–73% yields by cross-coupling of **6** and compounds **9a**,[24] **9b**[25]



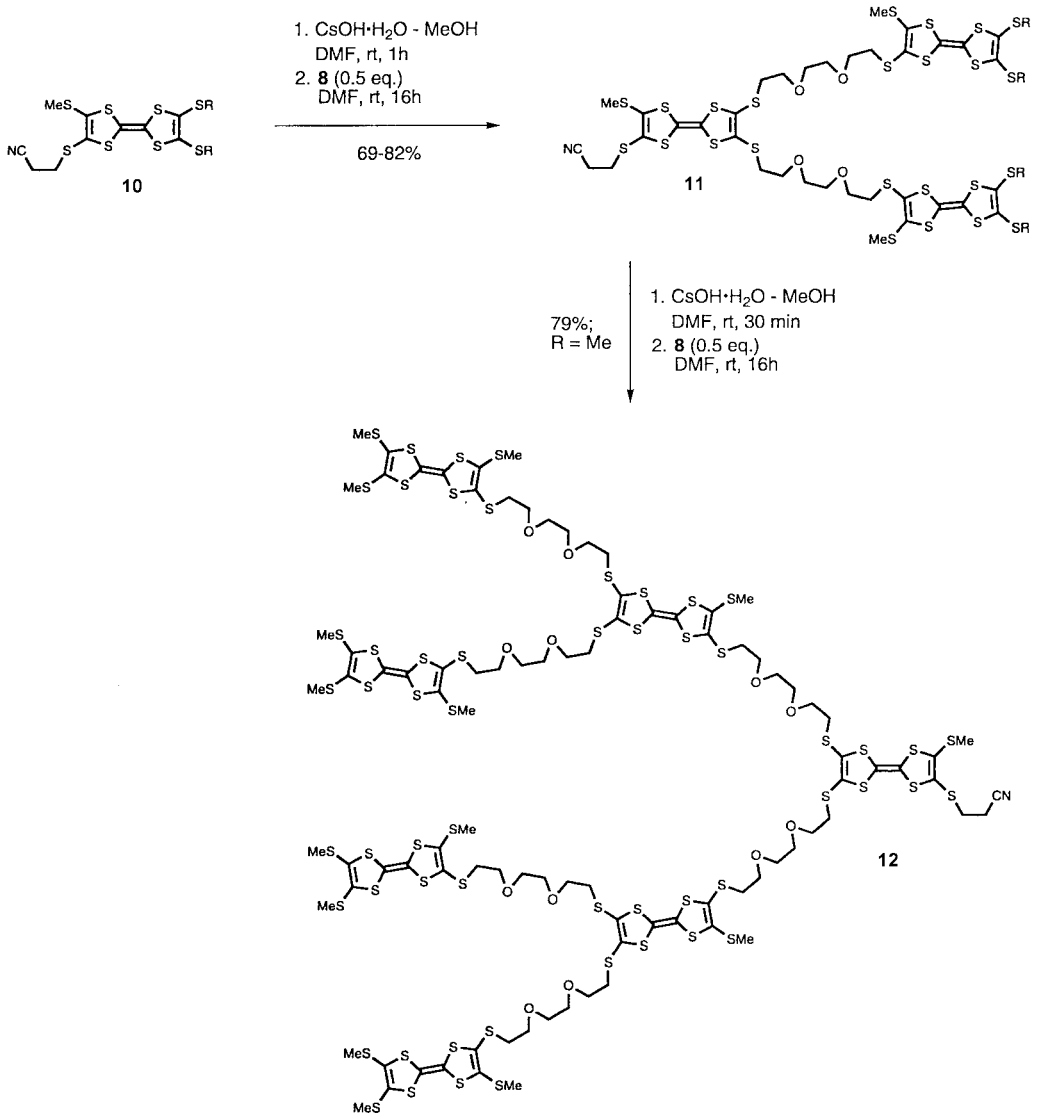
Scheme 1

and **9c**,[26] respectively (Scheme 2). As the next step, assembly of the tris-TTF dendron wedges **11a–c** proceeded smoothly by reaction of two equivalents of the thiolate anions of **10a–c** with the difunctional reagent **8**. Following analogous procedures to those described above, compound **11a** (2 equiv) reacted with **8** to yield compound **12** (79%) containing TTF units at the focal point, at branch sites and at the periphery (Scheme 3). Three-fold reactions of the thiolates of compounds **11a–c** and **12** with the trifunctional core reagent **13**[27] gave the multi-TTF dendrimers **14a–c** (Scheme 4) and **16** (Scheme 5), respectively. The formation of **14a**, **b** and **16** proceeded in remarkably high yield (75–95%) whereas the formation of **14c** was less efficient (28%) with several, more polar, minor products also formed (TLC evidence). Two of these minor products were isolated and identified (by ^{1}H NMR) as **14c** minus one and two of the silyl protecting groups, i.e. defect dendrimers. Apparently, cesium hydroxide was cleaving some of the protecting groups as well as generating the thiolate. (This effect was also seen in the synthesis of the series of wedges **11**, where **11c** was formed in the lowest yield.) Removal of the TBDPS protecting group of **14c** with fluoride ion in THF afforded compound **15** in 47% yield.

We have used two other core units for reactions involving the transient thiolate anion obtained from **11a**. The benzylic chlorides of the four-directional TTF core reagent **17**[14b] were readily displaced to yield the TTF_{13} dendrimer **18**, (Scheme 6) containing TTF units at the core, at branch points and at the periphery. Analogous six-fold reaction of



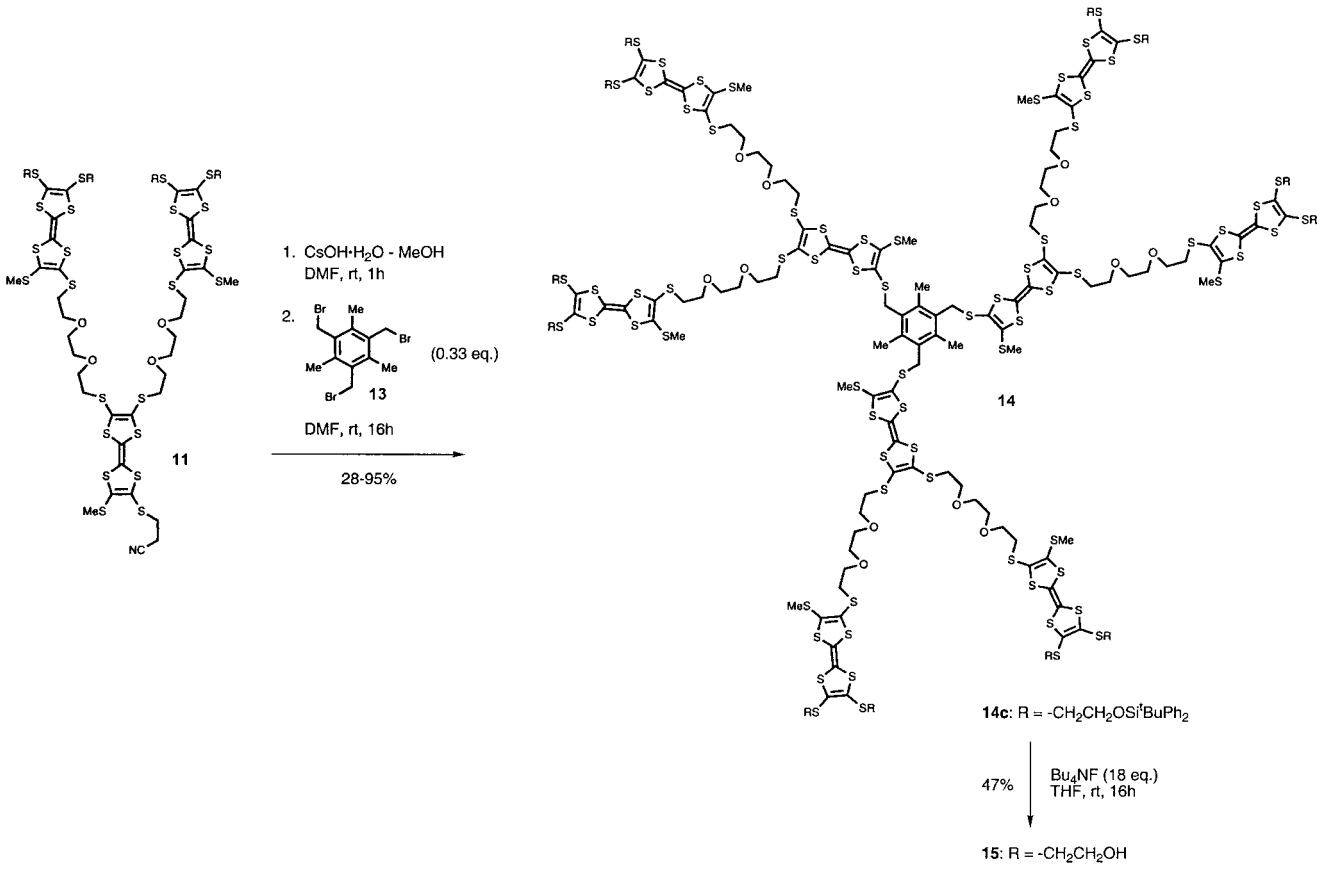
Scheme 2



Scheme 3

the hexa-functional core **19**[28] gave the beautiful TTF_{18} structure **20**, comprising 12 peripheral and 6 inner TTF units constructed around a benzene core (Scheme 7).

Dendrimers **14**, **15**, **16**, **18** and **20** are all air-stable compounds, which possess good solubility in a wide range of organic solvents. In this respect they are considerably easier to isolate and characterise than the arylester dendrimers with TTF functionality which we studied previously.[14a,c] Their structures were unambiguously established by a combination of elemental analysis, mass spectrometry (plasma desorption, MALDI and electrospray) and ^{1}H NMR spectroscopy. Their oxidised states were generated in conventional cyclic voltammetry (CV) and thin layer CV experiments in organic solvents. The dendrimers and their precursor wedges all display the two-stage redox behaviour typical of tetra(alkylsulfanyl)TTF derivatives.[29] (It is known that alkylsulfanyl substitution raise the oxidation potential of the TTF system). We demonstrated[14b] that TLCV is a reliable method for determining the extent of oxidation of multi(TTF) derivatives. Using the same procedures with **14a**, **16**, **18** and **20** as those described previously[14b] (i.e. integrating the voltammetric waves against the one-electron reduction peak of the internal standard 2,3-dichloronaphthoquinone) provided clear evidence that complete oxidation occurs for all the TTF units. Thus for **16** the redox waves represent the sequential formation of $\mathbf{16}^{21+\cdot}$ and $\mathbf{16}^{42+}$, while for **20** they represent the formation of $\mathbf{20}^{18+\cdot}$ and $\mathbf{20}^{36+}$ species. As noted previously for various multi-TTF systems,[14b,c,d,19b,30] the second TTF oxidation wave tends to be slightly narrower than the first wave, which is probably due to adsorption phenomena of the highly oxidised species on the electrode surface. There is no evidence from the CV data for any shielding of the inner TTF units in these dendrimers.



Scheme 4

By analogy with crown-annulated TTF systems,[31] we considered the possibility that these dendrimers could display a voltammetric response in the presence of metal cations,[32] due to metal coordination to the glycol units. However, no significant change (i.e. < ±20 mV) was observed in the potentials of the redox waves in the CV response of dendrimer **16** in the presence of Li, Na, K and Ag cations.

In summary, we have exploited the versatility of TTF-thiolate chemistry to develop expedient syntheses of a range of new dendritic TTF macromolecules which enjoy good air-stability and solubility in organic solvents, thereby offering significant advantages over previous polymeric TTFs.

^{1}H and ^{13}C spectra were obtained on Varian Unity 300, Oxford 200 and Varian VXR 400s spectrometers; chemical shifts are quoted in ppm, relative to TMS as an internal reference (0 ppm). Mass spectra (EI and CI) were recorded on a Micromass Autospec spectrometer operating at 70 eV with the ionisation mode as indicated. Plasma desorption mass spectra (PDMS), MALDI mass spectra and electrospray mass spectra were obtained on Bio-Ion 10K, Kratos IV and Finnigan MAT SSQ 710 instruments, respectively. Melting points were recorded on a Reichert-Kofler hot-stage microscope and are uncorrected. Elemental analyses were obtained on a Carlo-Erba Strumentazione instrument. Column chromatography was carried out using Prolabo silica (70−230 mesh). Solvents were distilled prior to use for chromatography, with the exception of CH_2Cl_2 and $CHCl_3$, which were used as supplied. CV data were measured with iR compensation using either a BAS CV50 electrochemical analyser or an EGG 263 potentiostat. TLCV data were obtained using methods described previously.[14b]

2-[2-(2-Chloroethoxy)ethoxy]ethyl Tosylate (2)

A solution of **1** (18.49 g, 110 mmol) in anhyd pyridine (80 mL) was stirred at 0 °C under argon and freshly recrystallised tosyl chloride (23.00 g, 121 mmol) was added in small portions during 2 h. The reddish solution was stirred for another 6 h at 0 °C, whereupon the reaction was allowed to attain r.t. over 12 h. The mixture was carefully poured onto a mixture of concd HCl (80 mL) and crushed ice (300 mL) whilst stirring vigorously. The aqueous phase was extracted with CH_2Cl_2 (3 × 150 mL) and the combined organic phases washed with H_2O (200 mL). The solution was dried ($MgSO_4$), concentrated in vacuo and the residue was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc, 95:5 v/v) affording **2**[33] as a colourless oil; (27.62 g, 78%).

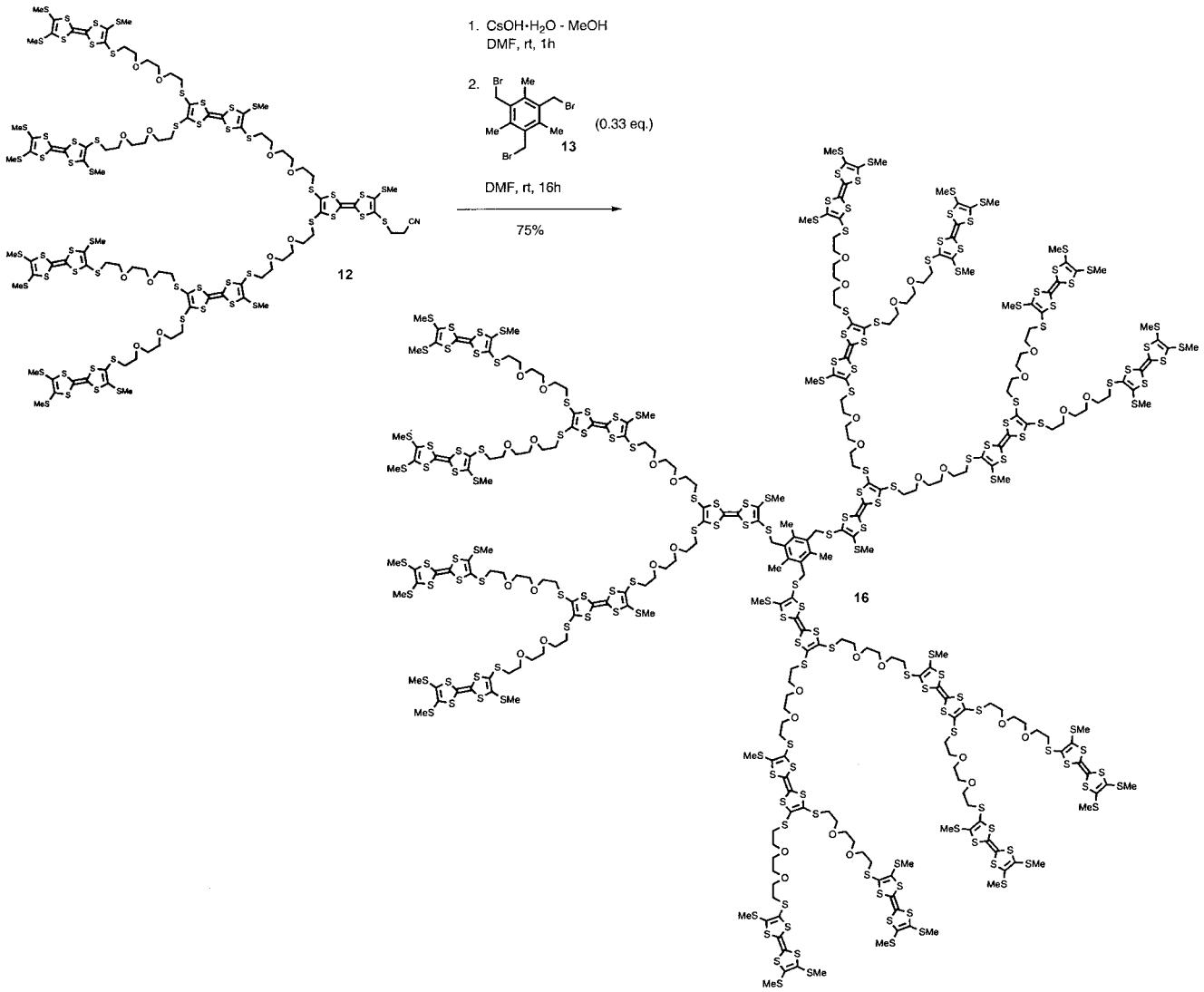
^{1}H NMR ($CDCl_3$/TMS): δ = 7.80 (d, 2 H, *J* = 8.4 Hz), 7.35 (d, 2 H, *J* = 7.9 Hz), 4.17 (t, 2 H, *J* = 4.7 Hz), 3.70 (m, 4 H), 3.61 (m, 6 H), 2.45 (s, 3 H).

^{13}C NMR ($CDCl_3$/TMS): δ = 144.91, 133.00, 129.87, 127.98, 71.28, 70.63, 70.49, 69.16, 68.66, 42.62, 21.47.

MS(EI): *m/z* (%) = 322 (M^+, 0.25), 229 (18), 199 (92), 155 (100), 91 (88).

1-(2-Bromoethoxy)-2-(2-chloroethoxy)ethane (3)

To a solution of **2** (29.0 g, 89.8 mmol) in anhyd acetone (200 mL) was added LiBr (8.58 g, 98.8 mmol) and the solution was refluxed



Scheme 5

for 16 h in which time a colourless salt precipitated. The salt was filtered off and the solution concentrated in vacuo. The residue was redissolved in CH_2Cl_2 (300 mL), washed with H_2O (3 × 150 mL) and dried ($MgSO_4$). The solvent was removed under reduced pressure and the residue purified by column chromatography (silica gel, CH_2Cl_2/hexane, 1:1 v/v) affording **3**[34] as a colourless oil; (19.7 g, 95%).

^{1}H NMR ($CDCl_3$/TMS): δ = 3.81 (t, 2 H, *J* = 6.4 Hz), 3.75 (t, 2 H, *J* = 5.8 Hz), 3.67 (s, 4 H), 3.62 (t, 2 H, *J* = 5.8 Hz), 3.46 (t, 2 H, *J* = 6.4 Hz).

^{13}C NMR ($CDCl_3$/TMS): δ = 71.27, 71.10, 70.50, 70.38, 42.64, 30.24.

MS(CI): *m*/*z* (%) = 250 (MNH_4^+, 100).

4,5-Bis{2-[2-(2-chloroethoxy)ethoxy]ethylthio}-1,3-dithiole-2-thione (5)

Method A: To a solution of **4**[22] (3.54 g, 11.6 mmol) in anhyd degassed MeCN (140 mL) was added a solution of $CsOH•H_2O$ (4.29 g, 25.9 mmol) in anhyd degassed MeOH (25 mL), whereupon the colour changed from orange to dark red. The solution was stirred under argon at r.t. for 30 min before **2** (7.50 g, 23.2 mmol) was added via a syringe, and the mixture was refluxed for 16 h to give back an orange solution. The solvent was removed in vacuo and the residue redissolved in CH_2Cl_2 (300 mL). The solution was washed with H_2O (3 × 150 mL), dried ($MgSO_4$) and concentrated in vacuo. The product was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc, 97:3 v/v) which afforded **5** as a yellow oil; (3.66 g, 64%).

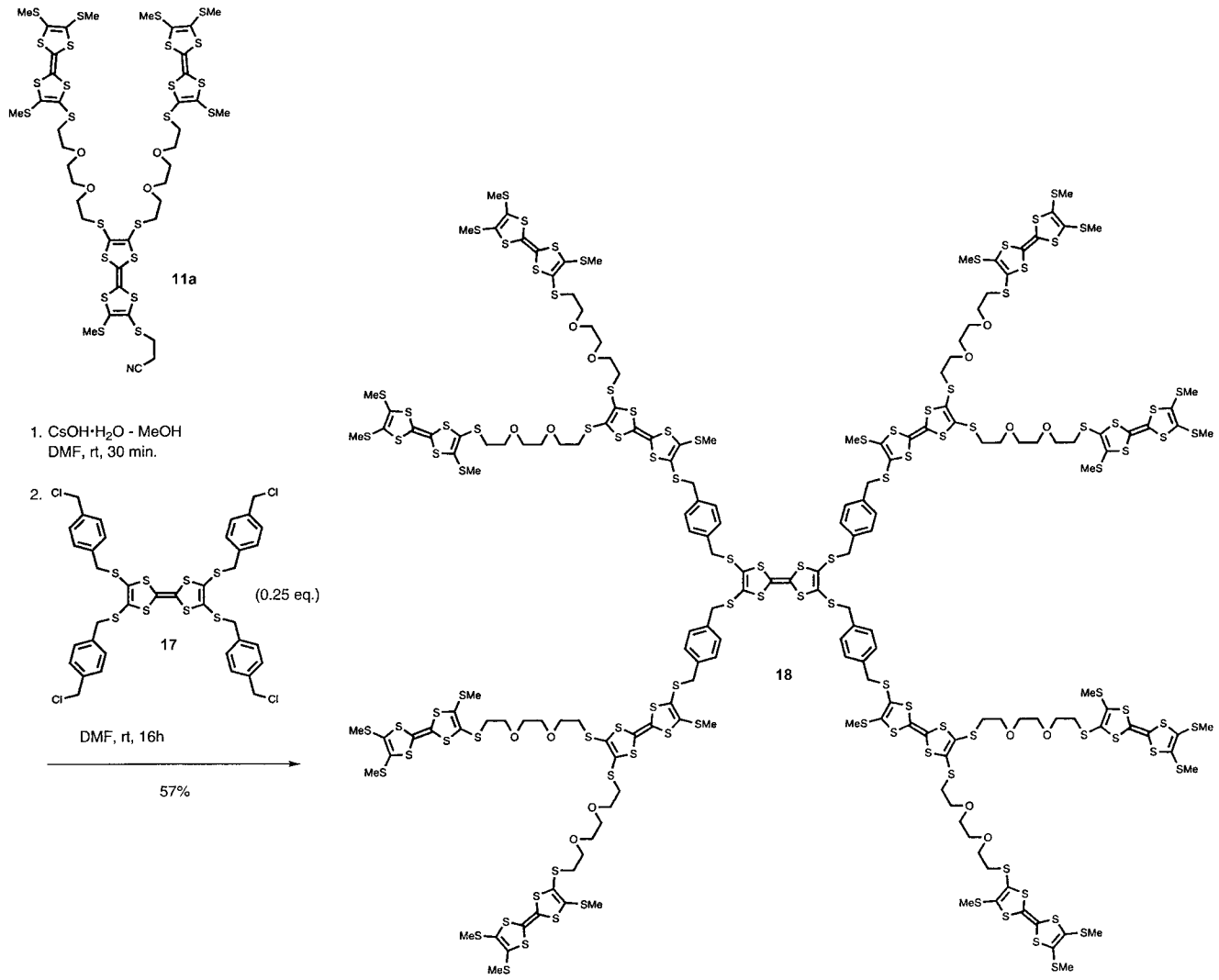
Method B: The method was similar to Method A. Compound **4** (4.78 g, 15.7 mmol) was deprotected using $CsOH•H_2O$ (5.54 g, 33.0 mmol), and then reacted with **3** (8.00 g, 34.6 mmol). It was necessary for the reaction to reflux for only 2 h. Workup similar to Method A afforded **5** as a yellow oil; (6.46 g, 82%).

^{1}H NMR ($CDCl_3$/TMS): δ = 3.72 (m, 8 H), 3.63 (m, 12 H), 3.06 (t, 4 H, *J* = 6.4 Hz).

^{13}C NMR ($CDCl_3$/TMS): δ = 210.88, 136.47, 71.29, 70.49, 70.45, 69.79, 42.74, 36.04.

MS(PDMS): *m*/*z* = 498.0 (M^+, calcd: 499.6).

Anal. $C_{15}H_{24}Cl_2O_4S_5$ (499.6): calcd C 36.07, H 4.84; found C 35.93, H 4.86.



Scheme 6

2,3-Bis{2-[2-(2-chloroethoxy)ethoxy]ethylthio}-6-(2-cyanoethylthio)-7-methylthiotetrathiafulvalene (7)

A mixture of **5** (5.00 g, 10.0 mmol) and **6**[23] (5.00 g, 20.0 mmol) was suspended in degassed $(OEt)_3P$ (45 mL) and stirred at 120 °C for 5 h. The solution was cooled to r.t. and concentrated in vacuo, affording a very dark red residue which was chromatographed (silica gel, CH_2Cl_2 until the first band was off the column, then CH_2Cl_2/EtOAc, 95:5 v/v). The fractions containing the middle band were combined and concentrated in vacuo to give **7** as an orange solid; (4.68 g, 67%), mp 44–45 °C.

^{1}H NMR ($CDCl_3$/TMS): δ = 3.77 (t, 4 H, *J* = 5.6 Hz), 3.68 (m, 16 H), 3.03 (m, 6 H), 2.72 (t, 2 H, *J* = 7.2 Hz), 2.48 (s, 3 H).

^{13}C NMR ($CDCl_3$/TMS): δ = 135.14, 128.07, 127.72, 119.93, 117.54, 111.96, 109.51, 71.37, 70.57, 70.47, 70.02, 42.76, 35.45, 31.16, 19.10, 18.71.

MS(CI): *m*/*z* (%) = 700 (MH^+, 3.41).

Anal. $C_{22}H_{31}Cl_2NO_4S_8$ (700.9): calcd C 37.70, H 4.46, N 2.00; found C 37.64, H 4.33, N 1.97.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.60 V, $E_2^{1/2}$ = 0.92 V.

2,3-Bis{2-[2-(2-iodoethoxy)ethoxy]ethylthio}-6-(2-cyanoethylthio)-7-methylthiotetrathiafulvalene (8)

To a solution of **7** (4.60 g, 6.56 mmol) in anhyd degassed acetone (150 mL) was added NaI (20.0 g, 133 mmol) and the mixture was refluxed under argon for 3 d. The solvent was removed in vacuo and the dark red residue redissolved in CH_2Cl_2 (200 mL). The solution was washed with H_2O (3 × 150 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (silica gel, CH_2Cl_2/EtOAc, 94:6 v/v) afforded **8** as an orange-red solid; (4.87 g, 84%), 62–63 °C.

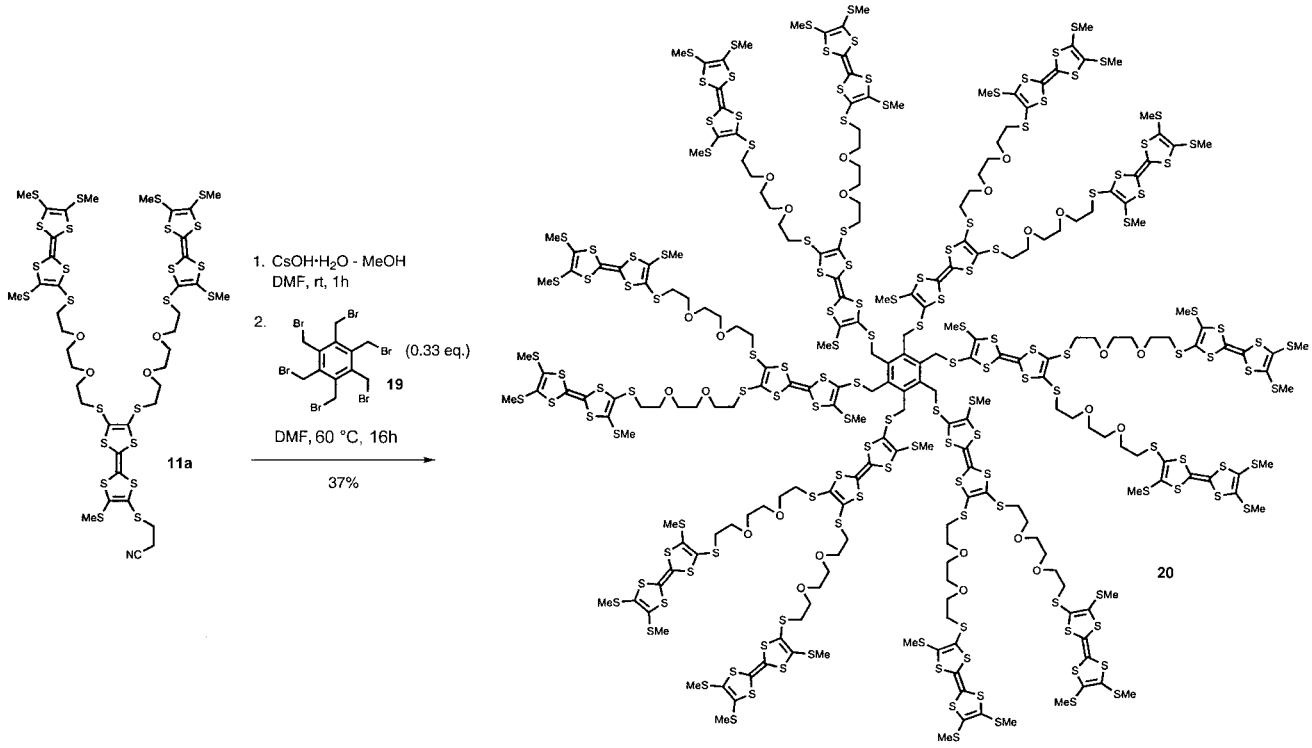
^{1}H NMR ($CDCl_3$/TMS): δ = 3.75 (t, 4 H, *J* = 6.8 Hz), 3.69 (t, 4 H, *J* = 6.8 Hz), 3.65 (s, 8 H), 3.26 (t, 4 H, *J* = 6.8 Hz), 3.02 (t, 6 H, *J* = 6.4 Hz), 2.71 (t, 2 H, *J* = 7.2 Hz), 2.47 (s, 3 H).

^{13}C NMR ($CDCl_3$/TMS): δ = 135.10, 128.02, 127.67, 119.84, 117.48, 111.94, 109.44, 71.86, 70.40, 70.08, 69.99, 35.41, 31.10, 19.07, 18.68, 3.01.

MS(PDMS): *m*/*z* = 883.7 (M^+, calcd: 883.8).

Anal. $C_{22}H_{31}I_2NO_4S_8$ (883.8): calcd C 29.90, H 3.54, N 1.58; found C 29.88, H 3.54, N 1.64.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.60 V, $E_2^{1/2}$ = 0.92 V.



Scheme 7

2-(2-Cyanoethylthio)-3,6,7-trimethylthiotetrathiafulvalene (10a); General Procedure for 10a–c

Compounds **9a**[24] (3.17 g, 14.0 mmol) and **6** (1.75 g, 7.00 mmol) were dissolved in degassed $(OEt)_3P$ (25 mL) and stirred at 120 °C for 4 h. The very dark red solution was cooled to 0 °C and MeOH (150 mL) was added, which caused formation of an orange precipitate. The precipitate was filtered, washed with MeOH (4 × 25 mL) and dried in vacuo. The crude product was chromatographed (silica gel, CH_2Cl_2/hexane, 3:1 v/v) and the fractions containing the middle band were combined and concentrated to give **10a** as an orange powder; (1.97 g, 66%); mp 102–103 °C (Lit.[35] 102–104 °C).

2-(2-Cyanoethylthio)-3-methylthio-6,7-bis(hexylthio)tetrathiafulvalene (10b)

Prepared like **10a** from compound **9b**[25] (2.93 g, 8.00 mmol) and **6** (2.00 g, 8.00 mmol) except that the reaction mixture was concentrated in vacuo. The very dark red residue was chromatographed (silica gel, CH_2Cl_2/hexane, 2:1 v/v) and the fractions containing the middle band were combined and concentrated in vacuo to give **10b** as an orange powder; (3.07 g, 68%); mp 88–89 °C.

^{1}H NMR ($CDCl_3$/TMS): δ = 3.01 (t, 2 H, *J* = 7.2 Hz), 2.81 (t, 4 H, *J* = 7.2 Hz), 2.70 (t, 2 H, *J* = 7.3 Hz), 2.46 (s, 3 H), 1.62 (m, 4 H), 1.41 (m, 4 H), 1.28 (m, 8 H), 0.88 (t, 6 H, *J* = 6.6 Hz).

^{13}C NMR ($CDCl_3$/TMS): δ = 135.09, 127.88, 127.61, 119.91, 117.53, 112.81, 108.13, 36.30, 31.26, 31.14, 29.64, 28.14, 22.50, 19.05, 18.70, 14.00.

MS(PDMS): *m*/*z* = 567.1 (M^+, calcd: 568.0).

Anal. $C_{22}H_{33}NS_8$ (568.0): calcd C 46.52, H 5.86, N 2.47; found C 46.54, H 5.89, N 2.40.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.58 V, $E_2^{1/2}$ = 0.92 V.

2-(2-Cyanoethylthio)-3-methylthio-6,7-bis[2-(*tert*-butyldiphenylsilyloxy)ethylthio]tetrathiafulvalene (10c)

Prepared like **10a** from **9c**[26] (7.00 g, 9.17 mmol) and **6** (2.00 g, 8.00 mmol) except that the mixture was concentrated in vacuo. The very dark red residue was chromatographed (silica gel, CH_2Cl_2/hexane, 1:1) and the fractions containing the middle band were combined and concentrated in vacuo to give **10c** as an orange syrup; (5.63 g, 73%).

^{1}H NMR ($CDCl_3$/TMS): δ = 7.67 (dd, 8 H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.40 (m, 12 H), 3.81 (t, 4 H, *J* = 6.4 Hz), 3.01 (t, 2 H, *J* = 7.2 Hz), 2.93 (t, 4 H, *J* = 7.2 Hz), 2.67 (t, 2 H, *J* = 7.4 Hz), 2.48 (s, 3 H), 1.06 (s, 18 H).

^{13}C NMR ($CDCl_3$/TMS): δ = 135.52, 135.14, 133.24, 129.74, 127.77, 127.72, 127.49, 120.00, 117.49, 112.91, 108.46, 63.05, 63.02, 38.40, 38.34, 31.19, 26.77, 19.17, 19.16, 19.12, 18.68.

MS(PDMS): *m*/*z* = 963.3 (M^+, calcd: 964.6).

Anal. $C_{46}H_{53}NO_2S_8Si_2$ (964.6): calcd C 57.28, H 5.54, N 1.45; found C 57.21, H 5.67, N 1.38.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.60 V, $E_2^{1/2}$ = 0.95 V.

Wedge 11a; Typical Procedure for 11a–c, 12

To a solution of **10a** (1.03 g, 2.41 mmol) in anhyd degassed DMF (50 mL) was added a solution of $CsOH{\bullet}H_2O$ (0.424 g, 2.53 mmol) in anhyd degassed MeOH (10 mL). The mixture was stirred for 1 h in which it changed colour from orange to dark red. Addition of a solution of **8** (1.06 g, 1.20 mmol) in anhyd degassed DMF (15 mL), followed by stirring for 16 h, afforded an orange mixture which was concentrated in vacuo. The residue was redissolved in CH_2Cl_2 (200 mL), washed with H_2O (2 × 150 mL), dried ($MgSO_4$) and concentrated in vacuo. The product was purified by column chromatography (silica gel, CH_2Cl_2/EtOAc, 98:2 v/v) which afforded **11a** as a sticky dark red oil (1.28 g, 77%).

^{1}H NMR ($CDCl_3$/TMS): δ = 3.69 (t, 8 H, *J* = 6.8 Hz), 3.65 (s, 8 H), 3.01 (m, 10 H), 2.72 (t, 2 H, *J* = 7.2 Hz), 2.48 (s, 3 H), 2.43 (s, 18 H).

MS(PDMS): *m*/*z* = 1375.3 (M^+, calcd: 1377.3).

Anal. $C_{40}H_{49}NO_4S_{24}$ (1377.3): calcd C 34.88, H 3.59, N 1.02; found C 34.65, H 3.49, N 1.01.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.57 V, $E_2^{1/2}$ = 0.89 V.

Wedge 11b

Prepared like **11a** from **10b** (0.954 g, 1.68 mmol), CsOH•H_2O (0.296 g, 1.76 mmol) and **8** (0.707 g, 0.800 mmol). Chromatographic purification (silica gel, CH_2Cl_2) afforded **11b** as a red-orange oil (1.09 g, 82%).

^{1}H NMR ($CDCl_3$/TMS): δ = 3.68 (t, 8 H, *J* = 6.6 Hz), 3.64 (s, 8 H), 3.02 (m, 10 H), 2.81 (t, 8 H, *J* = 7.2 Hz), 2.71 (t, 2 H, *J* = 7.2 Hz), 2.47 (s, 3 H), 2.43 (s, 6 H), 1.62 (m, 8 H), 1.40 (m, 8 H), 1.29 (m, 16 H), 0.88 (t, 12 H, *J* = 6.8 Hz).

MS(PDMS): *m*/*z* = 1658.1 (M^+, calcd: 1657.9).

Anal. $C_{60}H_{89}NO_4S_{24}$ (1657.9): calcd C 43.47, H 5.41, N 0.84; found C 43.52, H 5.50, N 0.81.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.57 V, $E_2^{1/2}$ = 0.89 V.

Wedge 11c

Prepared like **11a** from **10c** (2.41 g, 2.50 mmol), CsOH•H_2O (0.441 g, 2.63 mmol) and **8** (1.05 g, 1.19 mmol). Chromatographic purification (silica gel, CH_2Cl_2) afforded **11c** as an orange syrup (2.01 g, 69%).

^{1}H NMR ($CDCl_3$/TMS): δ = 7.66 (dd, 16 H, J_1 = 7.6 Hz, J_2 = 1.2 Hz), 7.39 (m, 24 H), 3.79 (t, 8 H, *J* = 6.4 Hz), 3.68 (t, 8 H, *J* = 6.8 Hz), 3.63 (s, 8 H), 3.01 (m, 10 H), 2.92 (t, 8 H, *J* = 7.2 Hz), 2.67 (t, 2 H, *J* = 7.2 Hz), 2.46 (s, 3 H), 2.44 (s, 6 H), 1.05 (s, 36 H).

MS(PDMS): *m*/*z* = 2451.2 (M^+, calcd: 2451.1).

Anal. $C_{108}H_{129}NO_8S_{24}Si_4$ (2451.1): calcd C 52.92, H 5.30, N 0.57; found C 53.13, H 5.62, N 0.58.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.57 V, $E_2^{1/2}$ = 0.90 V.

Wedge 12

Prepared like **11a** from wedge **11a** (0.382 g, 0.277 mmol), CsOH•H_2O (0.0489 g, 0.291 mmol) and **8** (0.123 g, 0.139 mmol). Chromatographic purification (silica gel, CH_2Cl_2/EtOAc, 97:3) afforded **12** as an orange-red oil (0.358 g, 79%).

^{1}H NMR ($CDCl_3$/TMS): δ = 3.68 (t, 24 H, *J* = 6.4 Hz), 3.63 (s, 24 H), 3.01 (m, 26 H), 2.71 (t, 2 H, *J* = 7.2 Hz), 2.47 (s, 3 H), 2.43 (s, 42 H).

MS(PDMS): *m*/*z* = 3273.1 (M^+, calcd: 3276.4).

Anal. $C_{96}H_{121}NO_{12}S_{56}$ (3276.4): calcd C 35.19, H 3.72, N 0.43; found C 35.67, H 2.93, N 0.31.

CV (CH_2Cl_2/MeCN 9:1, vs. Ag/AgCl): $E_1^{1/2}$ = 0.57 V, $E_2^{1/2}$ = 0.87 V.

Dendrimer 14a; General Procedure for 14a–c, 16, 18 and 20

To a solution of wedge **11a** (0.732 g, 0.531 mmol) in anhyd degassed DMF (50 mL) was added a solution of CsOH•H_2O (0.0982 g, 0.585 mmol) in anhyd degassed MeOH (1.0 mL). The solution was stirred for 1 h, in which the colour changed from orange to red-brown. A solution of **13**[27] (0.0707 g, 0.177 mmol) in anhyd degassed DMF (3 mL) was added dropwise to the mixture over 5 min. The colour changed back to orange and the reaction was stirred for 16 h in which a red oil precipitated. The solvent was removed in vacuo and the residue redissolved in CH_2Cl_2 (150 mL). The solution was washed with H_2O (2 x 150 mL), dried ($MgSO_4$) and concentrated in vacuo. Purification by column chromatography (silica gel, CH_2Cl_2/EtOAc, 95:5 v/v) afforded **14a** as an orange toffee (0.650 g, 89%).

^{1}H NMR ($CDCl_3$/TMS): δ = 4.14 (s, 6 H), 3.68 (m, 24 H), 3.64 (s, 24 H), 3.00 (m, 24 H), 2.55 (s, 9 H), 2.42 (m, 63 H).

MS(PDMS): *m*/*z* = 4128.6 (M^+, calcd: 4128.9).

Anal. $C_{123}H_{150}O_{12}S_{72}$ (4128.9): calcd C 35.78, H 3.66; found C 35.69, H 3.63.

CV (CH_2Cl_2/MeCN 5:1 v/v, vs. Ag/AgCl): $E_1^{1/2}$ = 0.55 V, $E_2^{1/2}$ = 0.85 V.

Dendrimer 14b

Prepared like **14a** from wedge **11b** (0.663 g, 0.400 mmol), CsOH•H_2O (0.0705 g, 0.420 mmol) and **13** (0.0519 g, 0.130 mmol). Chromatographic purification (silica gel, CH_2Cl_2/EtOAc, 99:1 v/v) afforded **14b** as a red oil (0.614 g, 95%).

^{1}H NMR ($CDCl_3$/TMS): δ = 4.14 (s, 6 H), 3.69 (m, 24 H), 3.64 (s, 24 H), 3.01 (m, 24 H), 2.80 (t, 24 H, *J* = 7.2 Hz), 2.56 (s, 9 H), 2.43 (s, 18 H), 2.42 (s, 9 H), 1.62 (quintet, 24 H, *J* = 7.6 Hz), 1.40 (quintet, 24 H, *J* = 7.6 Hz), 1.29 (m, 48 H), 0.88 (t, 36 H, *J* = 6.8 Hz).

MS(MALDI): *m*/*z* = 4969.9 (M^+, calcd: 4970.8).

Anal. $C_{183}H_{270}O_{12}S_{72}$ (4970.8): calcd C 44.22, H 5.48; found C 44.28, H 5.67.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.56 V, $E_2^{1/2}$ = 0.88 V.

Dendrimer 14c

Prepared like **14a** from wedge **11c** (1.13 g, 0.461 mmol), CsOH•H_2O (0.0813 g, 0.484 mmol) and **13** (0.0598 g, 0.150 mmol). Chromatographic purification (silica gel, CH_2Cl_2/EtOAc, 98:2 v/v) afforded **14c** as an orange glass (0.307 g, 28%).

^{1}H NMR ($CDCl_3$/TMS): δ = 7.65 (d, 48 H, *J* = 7.6 Hz), 7.38 (m, 72 H), 4.14 (s, 6 H), 3.79 (t, 24 H, *J* = 6.4 Hz), 3.67 (m, 24 H), 3.62 (s, 24 H), 3.01 (m, 24 H), 2.91 (t, 24 H, *J* = 7.2 Hz), 2.55 (s, 9 H), 2.42 (s, 18 H), 2.40 (s, 9 H), 1.04 (s, 108 H).

MS(MALDI): *m*/*z* = 7395 $(M + K)^+$, (calcd: 7389).

Anal. $C_{327}H_{390}O_{24}S_{72}Si_{12}$ (7350.4): calcd C 53.43, H 5.35; found C 53.40, H 5.58.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.58 V, $E_2^{1/2}$ = 0.90 V.

Dendrimer 15

To a solution of dendrimer **14c** (0.354 g, 0.048 mmol) in THF (50 mL) was added a solution of Bu_4NF (0.90 mL, 0.90 mmol of a 1.0 M solution in THF) and the mixture was stirred for 16 h in which a dark red oil precipitated. Addition of H_2O (5 mL) made the oil go into solution before the mixture was concentrated in vacuo. The residue was purified twice by column chromatography. First (silica gel, CH_2Cl_2/MeOH, 9:1 v/v) then a second column (silica gel, CH_2Cl_2/MeOH, 95:5 v/v) which afforded **15** as a viscous dark red oil (0.102 g, 47%).

^{1}H NMR ($CDCl_3$/TMS): δ = 4.16 (s, 6 H), 3.76 (t, 24 H, *J* = 5.3 Hz), 3.70 (t, 24 H, *J* = 6.7 Hz), 3.65 (s, 24 H), 3.11 (br s, 12 H), 3.01 (m, 48 H), 2.56 (s, 9 H), 2.44 (s, 18 H), 2.43 (s, 9 H).

MS(ES): *m*/*z* = 1495.7, 1122.1, 897.6 (calcd: 1496.5 $[M^{3+}]$, 1122.4 $[M^{4+}]$, 897.9 $[M^{5+}]$).

Anal. $C_{135}H_{174}O_{24}S_{72}$ (4489.5): calcd C 36.12, H 3.91; found C 36.20, H 3.76.

CV (CH_2Cl_2/MeCN 3:1, vs. Ag/AgCl): $E_1^{1/2}$ = 0.55 V, $E_2^{1/2}$ = 0.85 V.

Dendrimer 16

Prepared like **14a** from wedge **12** (0.345 g, 0.105 mmol), CsOH•H_2O (0.0186 g, 0.111 mmol) and **13** (0.0140 g, 0.0350 mmol). Purification by column chromatography (silica gel,

CH_2Cl_2/EtOAc, 94:6 v/v) afforded **16** as an orange toffee (0.257 g, 75%).

^{1}H NMR ($CDCl_3$/TMS): δ = 4.10 (s, 6 H), 3.68 (m, 72 H), 3.63 (s, 72 H), 3.01 (m, 72 H), 2.55 (s, 9 H), 2.42 (m, 135 H).

MS(MALDI): *m*/*z* = 9874 $(M + K)^+$, (calcd: 9865).

Anal. $C_{291}H_{366}O_{36}S_{168}$ (9826.2): calcd C 35.57, H 3.75; found C 35.50, H 3.70.

CV (CH_2Cl_2/MeCN 3:1 v/v, vs. Ag/AgCl): $E_1^{1/2}$ = 0.56 V, $E_2^{1/2}$ = 0.86 V.

Dendrimer 18

Prepared like **14a** from wedge **11a** (0.606 g, 0.440 mmol) and CsOH•H_2O (0.0776 g, 0.462 mmol), but this time alkylation was carried out using **17**[14b] (0.0887 g, 0.100 mmol) dissolved in anhyd degassed DMF (15 mL). Purification by column chromatography (silica gel, CH_2Cl_2/EtOAc, 97:3 v/v) afforded **18** as a red toffee (0.346 g, 57%).

^{1}H NMR ($CDCl_3$/TMS): δ = 7.27 (d, 8 H, *J* = 8.2 Hz), 7.22 (d, 8 H, *J* = 8.2 Hz), 3.99 (s, 8 H), 3.88 (s, 8 H), 3.68 (m, 32 H), 3.64 (s, 32 H), 3.01 (m, 32 H), 2.42 (s, 72 H), 2.25 (s, 12 H).

MS(MALDI): *m*/*z* = 6070 $(M + K)^+$, (calcd: 6077).

Anal. $C_{186}H_{212}O_{16}S_{104}$ (6038.0): calcd C 37.00, H 3.54; found C 37.26, H 3.57.

CV (CH_2Cl_2, vs. Ag/AgCl): $E_1^{1/2}$ = 0.56 V, $E_2^{1/2}$ = 0.87 V.

Dendrimer 20

Prepared like **14a** from wedge **11a** (0.551 g, 0.400 mmol) and CsOH•H_2O (0.0739 g, 0.440 mmol), except that this time alkylation was carried out using **19**[28] (0.0381 g, 0.0600 mmol) and the dendrimer core was added as a solid, against a positive pressure of argon, and the mixture stirred for 16 h at 60 °C. Purification by column chromatography (silica gel, CH_2Cl_2/EtOAc, 95:5 v/v) afforded **20** as a dark red glass; (0.181 g, 37%).

^{1}H NMR ($CDCl_3$/TMS): δ = 4.46 (br s, 12 H), 3.69 (m, 48 H), 3.65 (s, 48 H), 3.01 (m, 48 H), 2.48 (s, 18 H), 2.43 (m, 108 H).

MS(ES): *m*/*z* = 2698.0, 2024.4, 1619.4 (calcd: 2698.7 $[M^{3+}]$, 2024.0 $[M^{4+}]$, 1619.2 $[M^{5+}]$).

Anal. $C_{234}H_{282}O_{24}S_{144}$ (8096.06): calcd C 34.72, H 3.51; found C 35.24, H 3.44.

CV (CH_2Cl_2/MeCN 4:1 v/v, vs. Ag/AgCl): $E_1^{1/2}$ = 0.57 V, $E_2^{1/2}$ = 0.86 V.

Acknowledgement

We thank the EPSRC for funding, and ESF/SMARTON for a travel grant (C.A.C.) and Dr. L. M. Goldenberg for TLCV experiments.

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Article Identifier:
1437-210X,E;2000,0,12,1695,1704,ftx,en;P02900SS.pdf