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Highly-charged organic nanoparticles: redox-active dendrimers incorporating 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene units†

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The incorporation of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene units into dendritic structures has been achieved by convergent routes. The key starting material is the 4-(hydroxymethyl) derivative **3**. The branches contain aryl ester and aryl ether groups and the core reagent is benzene-1,3,5-tricarbonyl chloride. Dendrimers **10**, **15** and **18** with 6 and 12 redox units at the periphery have been characterised by ^{1}H NMR spectroscopy, elemental analysis, mass spectrometry, UV-vis spectroscopy and solution electrochemistry. The 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene redox chemistry is retained in the dendrimer structures: clean formation of hexa(dication) and dodeca(dication) species is observed upon electrochemical oxidation. These highly-charged species enjoy remarkable electrochemical stability as their reduction to the neutral species is thwarted by the loss of aromaticity and the marked conformational change which accompanies this process. Molecular modelling studies were performed on **10**, $\mathbf{10}^{12+}$, **18** and $\mathbf{18}^{24+}$ by molecular mechanics.

Introduction

The study of structurally-ordered monodisperse oligomers as new materials which possess interesting optoelectronic properties is of contemporary interest.[1] In this context dendrimers and related hyper-branched macromolecules continue to attract considerable attention by virtue of their well-defined, three-dimensional frameworks in which functional groups can be placed in predetermined positions thereby imparting special properties to the molecules.[2] From this viewpoint, redox-active organic and organometallic groups have been built into the structures with several long-term aims in mind,[3] such as (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.

Dendrimers have been synthesised which contain a redox-active unit at the core [*e.g.* metalloporphyrin,[4] ruthenium(II)-bis(terpyridyl) complex,[5] ferrocene,[6] C_{60},[7] an iron–sulfur cluster[8] or bipyridinium[9]] and some of these display solution redox behaviour which is modulated by the outer layers of the structure hindering access of the redox site to the electrode surface.[10] Alternatively, the redox units, *e.g.* ferrocene and related metal sandwiches,[11] metal(bipyridyl),[12] fullerenes,[13] naphthalene diimides,[14] tetrathiafulvalenes[15] or phenothiazines[16] are situated at peripheral sites and/or within the branches. These redox groups may behave independently in multi-electron processes (*n* identical electroactive centres giving rise to a single *n*-electron wave at the same potential as the monomer unit) or they may interact intra- or inter-molecularly, giving rise to overlapping or closely-spaced redox waves at different potentials.

Consider the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system. The parent compound **1**[17] and its derivatives, *e.g.* **2** and **3**,[18] undergo a single, quasi-reversible, two-electron oxidation wave to yield a thermodynamically stable dication at E^{ox} *ca.* +0.4 V (in MeCN *vs.* Ag/AgCl) in the CV.[19] X-Ray crystal structures have shown that a major structural change accompanies this oxidation to the dication: the central anthracenediylidene ring which is boat shaped in the neutral molecule, becomes a planar and fully aromatic anthracene system, with the 6π 1,3-dithiolium cations almost orthogonal to this plane.[20] The extended π-conjugation between the dithiolium rings and the twisted structure serves to remove intramolecular Coulombic repulsion.[21] *System 1 is, therefore, very different from those redox species mentioned above, for which there is very little structural change upon oxidation or reduction.* Theoretical calculations have deduced that the saddle-shape of neutral **1** arises from steric hindrance between the sulfur atoms and the hydrogen atoms at the *peri* sites of the anthracenediylidene system, and this is completely relieved in the dication.[22] This interplay of unusual structural and redox properties has led to the use of monomeric derivatives of **1** as components of intermolecular[20,23] and intramolecular[24] charge-transfer systems.

We now present the first incorporation of 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene units into dendritic structures using convergent methodology and discuss their UV-vis spectroscopic, redox and structural properties. At the outset we reasoned that highly-charged redox states should be attainable, and with dense surface packing intradendrimer interactions might be manifest. Prior to this work only a very few dimers, *e.g.* **4**,[18,25] and one trimer **5**[18] of system **1** were known.

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†Molecular Saddles Part 8: For part 7 of this series see: C. A. Christensen, A. S. Batsanov, M. R. Bryce and J. A. K. Howard, *J. Org. Chem.*, 2001, **66**, 3313.

‡Electronic supplementary information (ESI) available: molecular models of **10** and $\mathbf{10}^{12+}$ viewed along the plane of the benzene core (Fig. S1) and **18** and $\mathbf{18}^{24+}$ viewed perpendicular to the plane of the benzene core (Fig. S2). See http://www.rsc.org/suppdata/jm/b1/b106010b/

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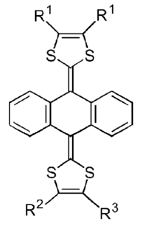
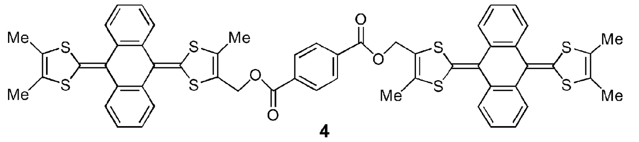


R^1	R^2	R^3	
H	H	H	**1**
Me	Me	$CH_2O(CO)Ph$	**2**
Me	Me	CH_2OH	**3**



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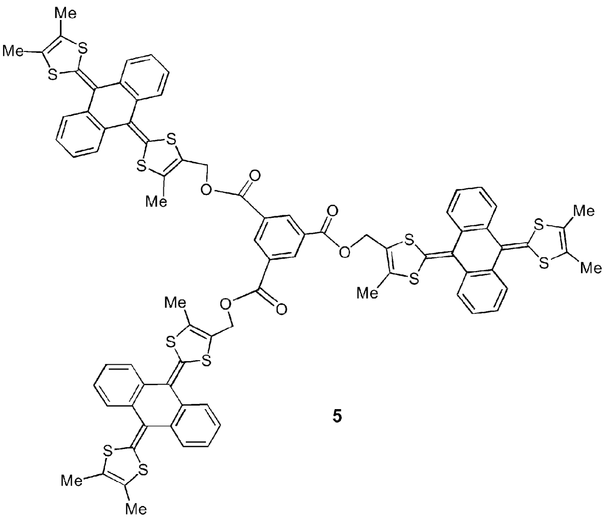

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Results and discussion

Synthesis

Recent synthetic developments have made **3** readily available in 2–3 g batches,[18] and we established that aryl ester derivatives could be obtained under mild conditions, *e.g.* reaction with 1,3,5-benzenetricarbonyl chloride (**9**) afforded trimer **5** in 78% yield.[18] We, therefore, considered **3** to be a convenient starting reagent for a convergent synthesis of dendritic structures.

The reaction of **3** with the silyl-protected diacid chloride **6**,[26] using triethylamine as base in dichloromethane at room temperature, gave **7** (97% yield), deprotection of which [tetra-*n*-butylammonium fluoride (TBAF) in tetrahydrofuran (THF) at room temperature] afforded the dendron wedge **8** (99% yield) containing the phenolic group as a reactive handle for further functionalisation. By analogy with the preparation of **7**, the hexakis[anthracenebis(dithiole)] derivative **10** was obtained in 77% yield from reaction of **8** with **9** (Scheme 1). Similarly, reaction of **8** with reagent **6** gave the protected second generation wedge **11** (72% yield). Repeated attempts at desilylation of **11** unexpectedly led to fragmentation of the molecule and essentially quantitative conversion back to **8**. We were, therefore, unable to synthesise higher generation analogues of **10**.

To circumvent this problem we incorporated more robust ether linkages into the dendritic scaffold, using the strategy developed by Fréchet for poly(arylether) systems.[27] Compound **3** was converted into the chloromethyl derivative **12** in 95% yield by treatment with triphenylphosphine–carbon tetrachloride. Two-fold reaction of **12** with 3,5-dihydroxybenzyl alcohol **13**, using potassium carbonate as base, afforded **14**, albeit in only 28% yield. The disappointing yield for this reaction is due to the heterogeneous mixture and poor reactivity of **12**. Compound **14** was smoothly converted into **15** (57%) and **16** (65%), by direct analogy with the preparation of **10** and **11**. Unlike **11**, **16** was cleanly deprotected (TBAF, THF) to yield alcohol derivative **17** (70% yield) (Scheme 2). Three-fold esterification of **17** with core reagent **9** gave the dodeca[anthracenebis(dithiole)] derivative **18** (54% yield) (Scheme 3). Dendrimers **10**, **15** and **18** were isolated as air-stable orange solids and their structures were unambiguously established by a combination of ^{1}H NMR spectroscopy, mass spectrometry and elemental analysis. The ^{1}H NMR spectra of **10** and **18** are shown in Figs. 1 and 2, respectively.

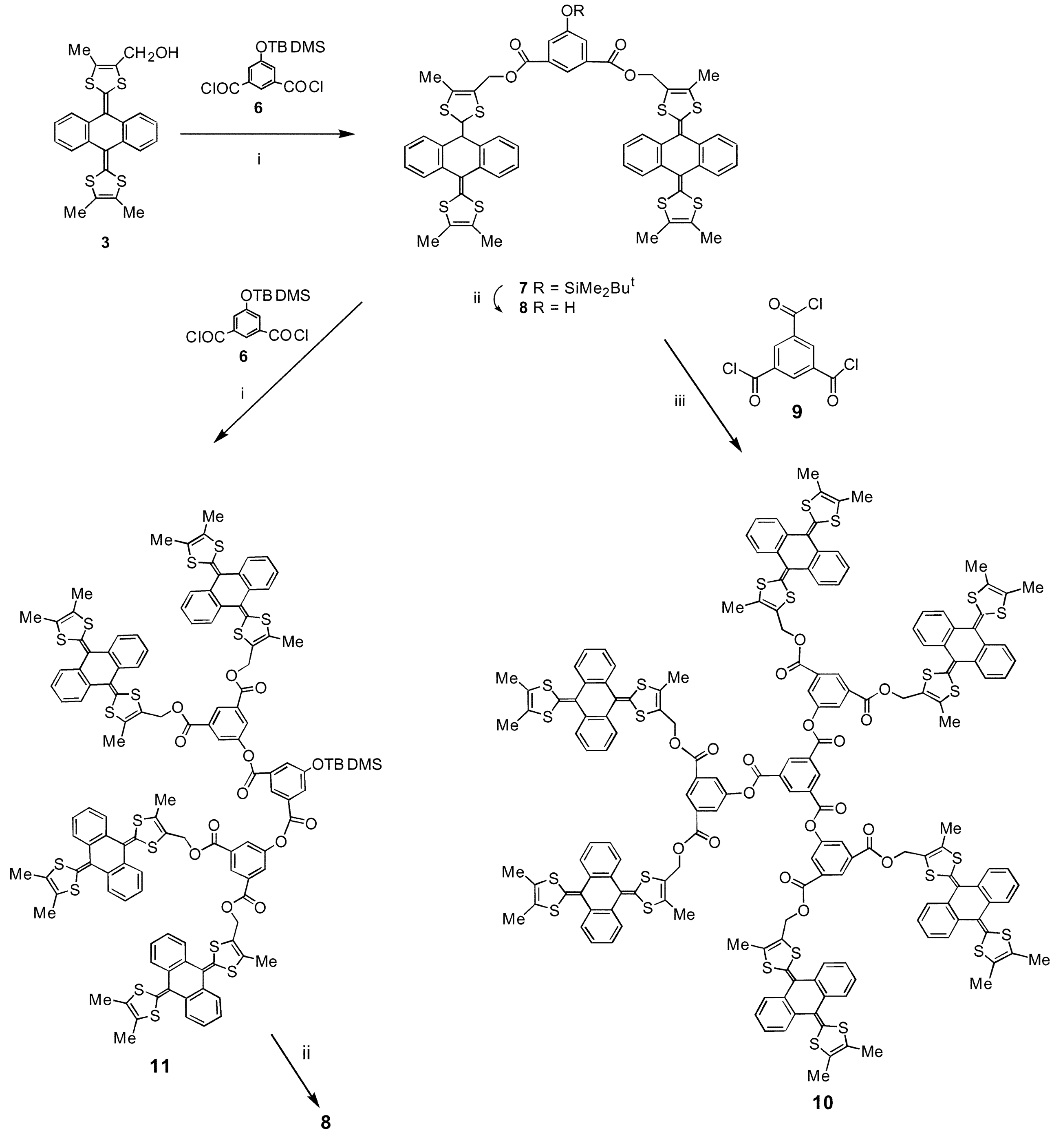
Solution electrochemistry

Solution electrochemical data, obtained by cyclic voltammetry (CV) are collated in Table 1. The benzoyl ester **2** shows the typical quasireversible two-electron redox wave (neutral → dication species) observed for 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene derivatives.[19,20b] A comparison of the model compound **2** with the dendritic molecules **5**, **10**, **15** and **18** reveals some interesting trends. The oxidation potential (E^{ox}_{pa}) is almost identical for all the compounds [*ca.* 500 mV in dichloromethane–acetonitrile (2 : 1 v/v) and 600 mV in THF (Figs. 3 and 4)]. All the peripheral redox units are independent and oxidised at the same time. A slight broadening of the oxidation peak can be noticed with increasing generation. This feature has already been reported with certain other dendrimers containing redox moieties at the periphery.[3]

A striking feature of these data is that as the generation increases there is a decrease in the reversibility of the redox wave in THF, leading to a complete electrochemical irreversibility for **18** ($\Delta E = 1150$ mV). However, in a mixture of DCM–MeCN, where the charged species are more soluble, this irreversibility is less pronounced. This is consistent with precipitation of the charged species occurring on the surface of the Pt electrode in THF, which does not take place in DCM–MeCN. This was confirmed by the electrode being completely blocked after a few scans around E^{ox}_{pa} for **10** and **18** in THF which prevents their use as modified electrodes, *cf.* the ferrocenyl dendrimers reported recently by Astruc *et al.*[11e] and Cuadrado *et al.*[11d] which are useful in this regard. Consequently, the decrease of reversibility for **10** and **15** in DCM–MeCN (ΔE increased by 100 mV and 160 mV, respectively) can be attributed to the dramatic change of conformation which must occur on reduction of the oxidised forms of $\mathbf{10}^{12+}$ and $\mathbf{15}^{12+}$ back to their neutral forms. This represents an interesting dendritic effect on the solution redox chemistry.

Chemical oxidation and reduction

Addition of iodine to a dichloromethane solution of **10**, **15** and **18** gave red–purple precipitates of the iodide salts of $\mathbf{10}^{n+}$, $\mathbf{15}^{n+}$ and $\mathbf{18}^{n+}$. These precipitates could be reduced back to the neutral species by adding sodium hydrosulfite and heating the mixture. The ^{1}H NMR spectra recorded before oxidation and after reduction were identical, showing that the chemical redox processes in these dendrimers are reversible without any significant decomposition of the oxidised species. Evidence for complete oxidation to $\mathbf{10}^{12+}$ was provided by ^{1}H NMR data in dry DMF in which both the neutral and oxidised species are soluble: in particular, the methyl and CH_2 protons (shown as Me_1, Me_2 and H_d in Fig. 1) shifted downfield from δ 2.19, 1.88 and 5.23 to δ 3.36, 3.10 and 6.28, respectively, consistent with each unit being oxidised to the bis(1,3-dithiolium) cation, as



Scheme 1 *Reagents and conditions*: i, Et_3N, CH_2Cl_2, 20 °C; ii, TBAF, THF, 20 °C; iii, Et_3N, CH_2Cl_2, 20 °C.

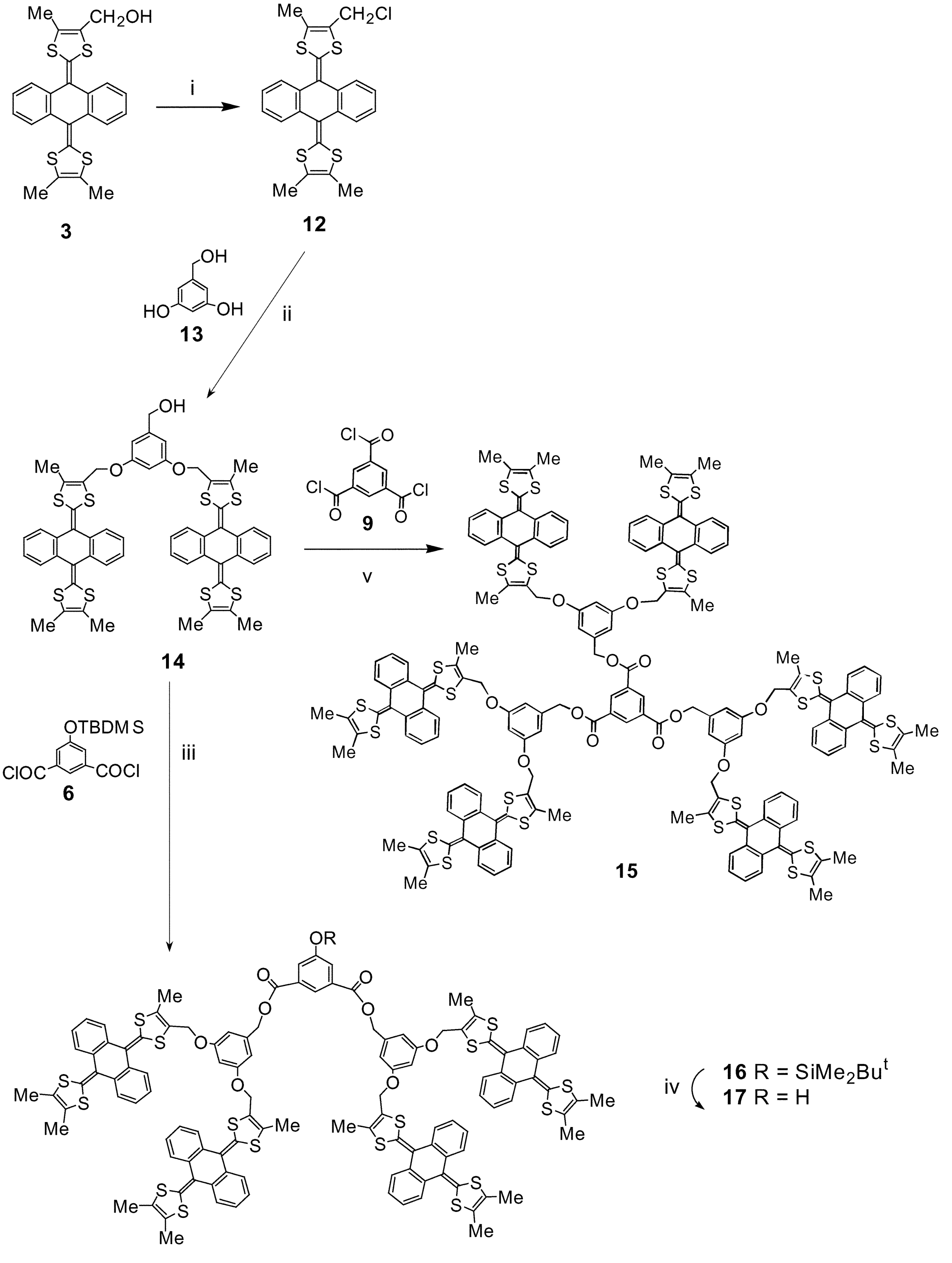
shown previously in monomeric derivatives.[28] No paramagnetic broadening of the NMR spectra was observed, confirming that no cation radical species derived from **10** were present.

UV-Vis spectroscopy

UV-Vis spectra were obtained in DCM solution. The benzoyl ester **2** served as a model compound, and showed the two characteristic absorption bands at $\lambda_{max} = 368$ and 436 nm for the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system.[20c] The spectra are shown in Fig. 5. UV-Vis spectra of **2** were recorded for a range of concentrations varying from C to $20 \times C$ (where $C = 6.31 \times 10^{-6}$ M). The absorbances at $\lambda_{max} =$ 368 and 436 nm vary as a linear function of the concentration (Fig. 5 inset). UV-Vis spectra of **10**, **15** and **18** were recorded at the same concentration $C = 6.31 \times 10^{-6}$ M. The spectra obtained for **10** and **15** (curves II and III, respectively) are equivalent to a $6 \times C$ spectrum of **2**, and for **18** (curve I) equivalent to a $12 \times C$ spectrum of **2**. Consequently, the extinction coefficient of each dendrimer corresponds to the extinction coefficient of one chromophore unit multiplied by the number of units in the dendrimer. This confirms that each chromophore unit is acting independently, with no dendritic effect observed in the optical spectra. Therefore, this spectroscopic technique could also be used to quantify the number of units present for a new dendrimer.

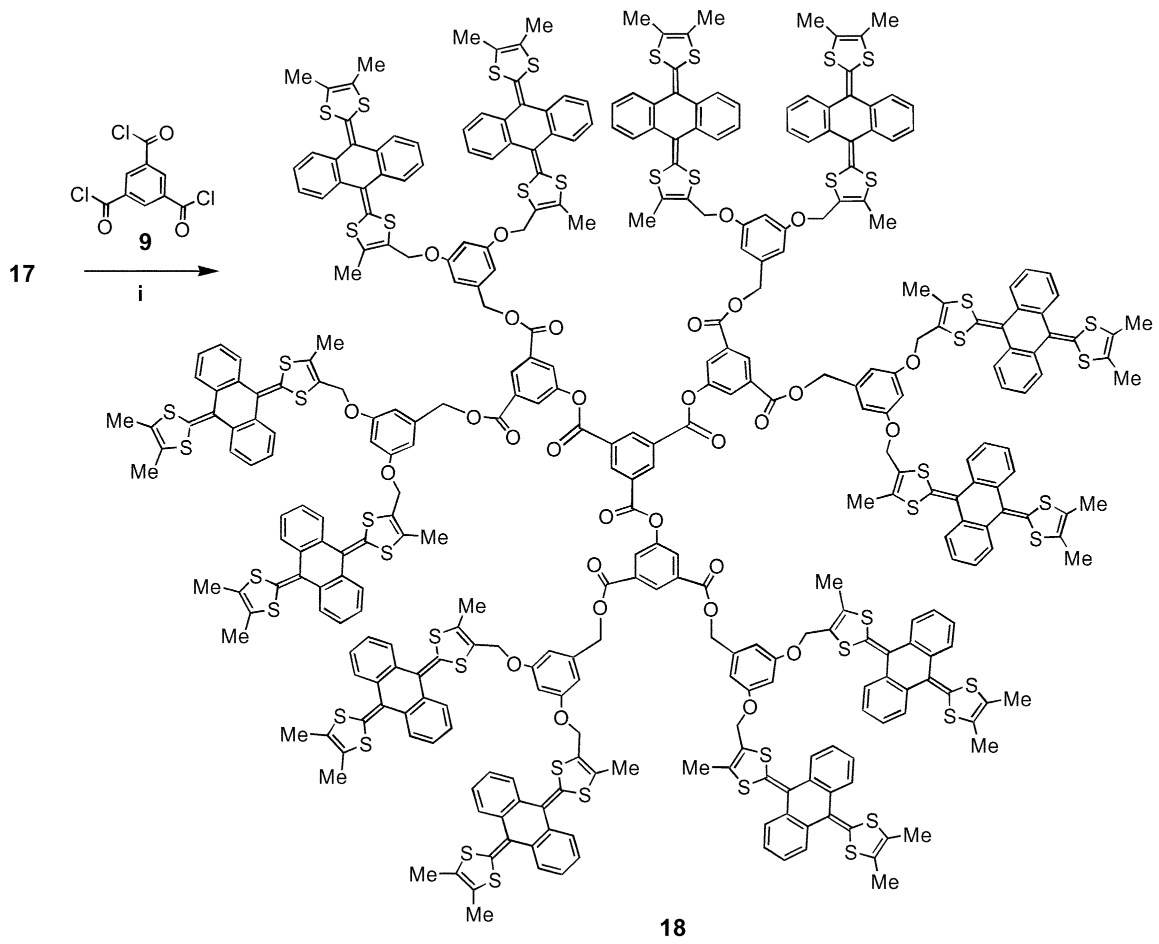
Molecular modelling studies

In order to visualise the change in conformation occurring during oxidation, molecular modelling studies were performed on **10**, $\mathbf{10}^{12+}$, **18** and $\mathbf{18}^{24+}$ by molecular mechanics. Energy



Scheme 2 *Reagents and conditions*: i, PPh_3, CCl_4, MeCN, reflux; ii, K_2CO_3, 18-crown-6, THF, reflux; iii, Et_3N, CH_2Cl_2, 20 °C; iv, TBAF, THF, 20 °C; v, Et_3N, CH_2Cl_2, 20 °C.

minimisation of the 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene unit in the neutral state showed the most favourable saddle-shape conformation which is in agreement with previous X-ray crystal structures,[20] variable temperature solution ^{1}H NMR data[18] and theoretical calculations on monomeric derivatives.[22] Energy minimisation of the core was then performed before the addition of the energy-minimised units at its periphery. Geometry optimisation of the dendrimers **10** and **18** was then calculated and the resulting converged structures are shown in Figs. 6 and 7. The energy-minimised conformations of $\mathbf{10}^{12+}$ and $\mathbf{18}^{24+}$ were obtained by adding to the energy-minimised conformation of **10** and **18**, a positive charge on the C(2) atom of each dithiole ring (*i.e.* 12 and 24 positive charges in total for **10** and **18**, respectively). The structures obtained for $\mathbf{10}^{12+}$ and $\mathbf{18}^{24+}$ show that each unit adopts the characteristic dicationic shape wherein the anthracene moiety is planar with the two dithiolium units perpendicular to it, which is in accord with theoretical calculations and



Scheme 3 *Reagents and conditions*: i, Et_3N, CH_2Cl_2, 20 °C.

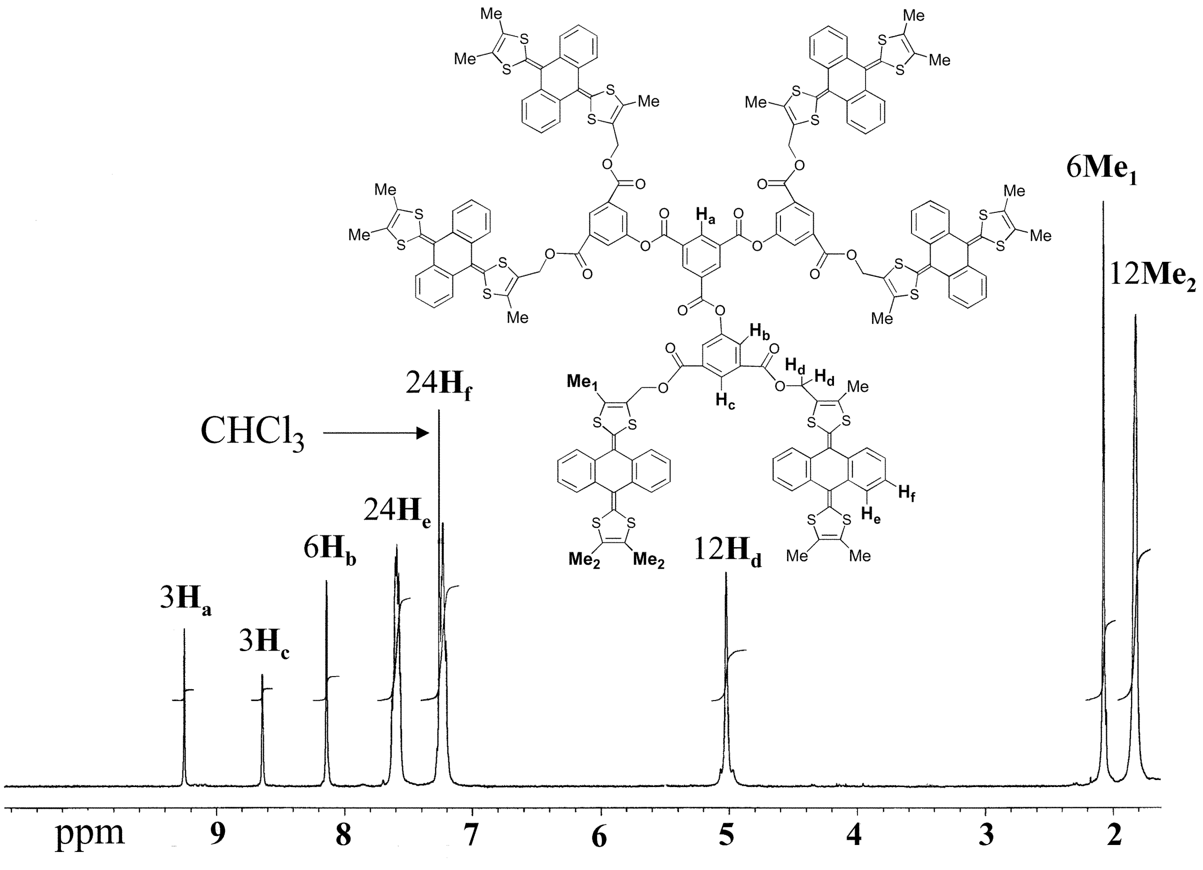


Fig. 1 ^{1}H NMR spectrum of **10** in $CDCl_3$.

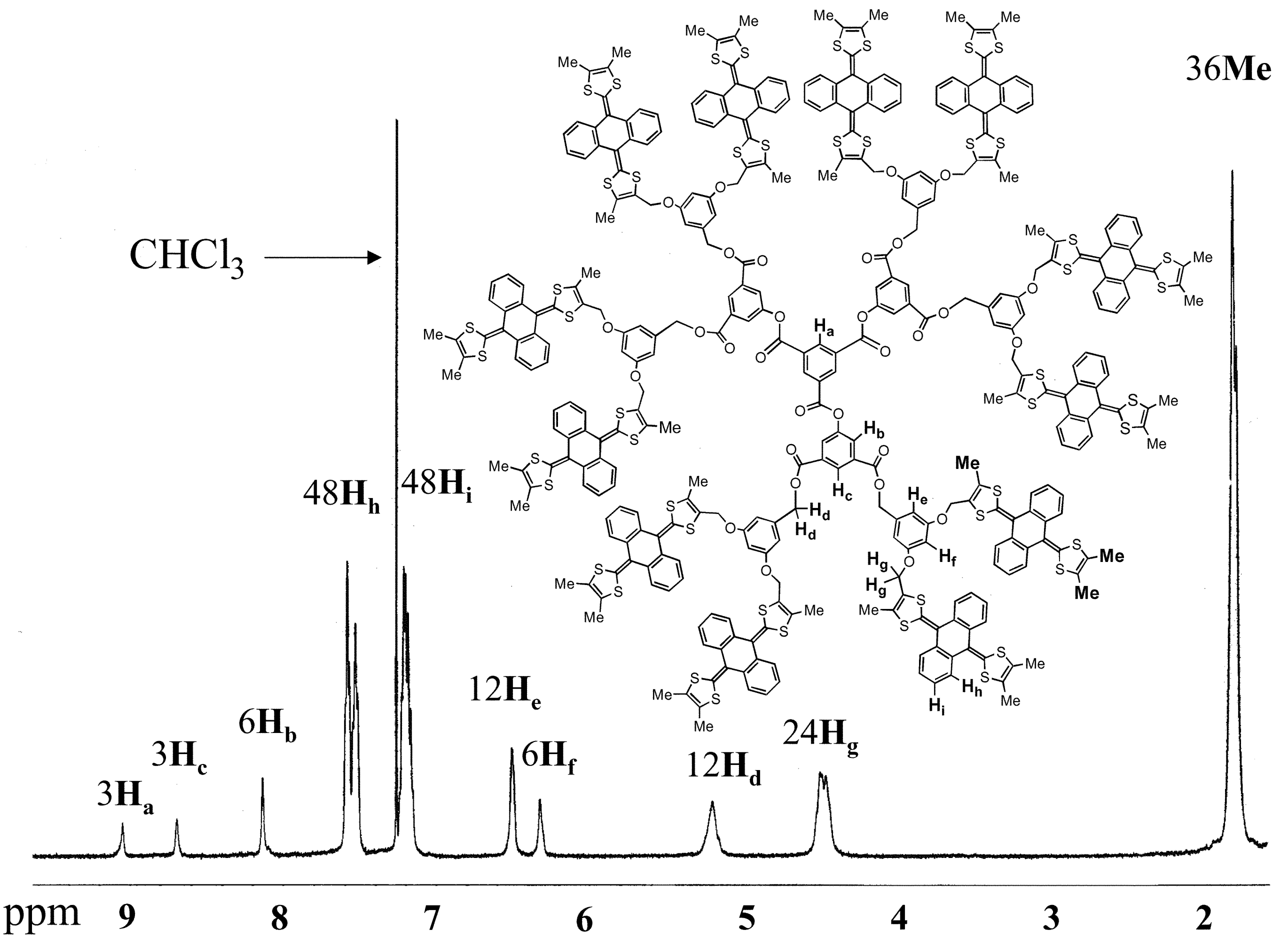


Fig. 2 ^1H NMR spectrum of **18** in $CDCl_3$.

Table 1 Cyclic voltammetric data[a]

	THF			DCM–acetonitrile (2 : 1 v/v)		
Compound	E^{ox}/V	E^{red}/V	ΔE/V[b]	E^{ox}/V	E^{red}/V	ΔE/V[b]
2	0.60 (2e)	0.18	0.42	0.46 (2e)	0.16	0.30
5	0.62 (6e)	0.16	0.46	*n.d.*[c]	*n.d.*[c]	*n.d.*[c]
10	0.66 (12e)	−0.13	0.79	0.51 (12e)	0.11	0.40
15	0.64 (12e)	0.02	0.62	0.54 (12e)	0.08	0.46
18	0.61 (24e)	−0.54	1.15	Not soluble		

[a] *Versus* Ag/AgCl, electrolyte $Bu_4N^+PF_6^-$, 20 °C, scan rate 100 mV s^{-1}. [b] $\Delta E = E^{ox} - E^{red}$. [c] Not determined.

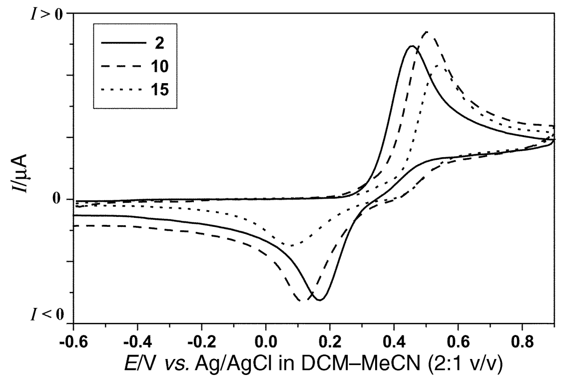


Fig. 3 Cyclic voltammograms of **2**, **10** and **15** under the conditions stated in Table 1.

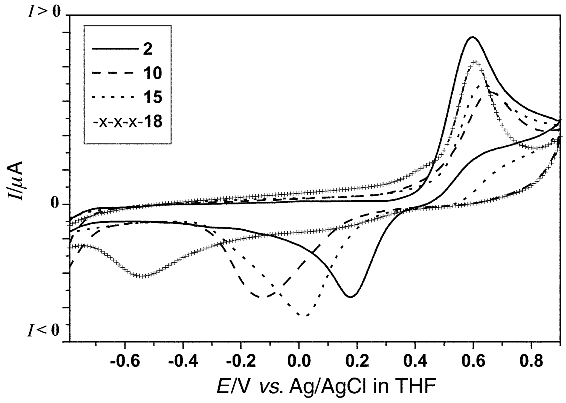


Fig. 4 Cyclic voltammograms of **2**, **10**, **15** and **18** under the conditions stated in Table 1.

X-ray crystal structures.[20] It also complies with a maximum space expansion between the units arising from Coulombic repulsion between the positively charged dithiolium rings.

It should be noted that for the neutral form of dendrimer **10** other unsymmetrical local minima of comparable energy can be reached where π–π interactions occur between the units. The proximity of the 12 units of dendrimer **18** leads also to π–π interactions between the units and consequently to several converged unsymmetrical structures, but also to a symmetrical one of lowest energy presented in Fig. 7. On the contrary, starting from different non-optimised geometries of $\mathbf{10}^{12+}$ and $\mathbf{18}^{24+}$, only one converged structure for each species was observed, in which all the charged units are as far as possible

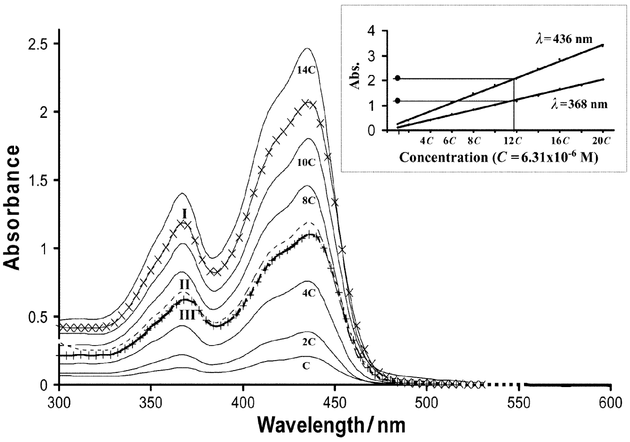


Fig. 5 UV-Vis spectra of **2** at varying concentrations C to $14 \times C$, **10** (concentration C, curve II), **15** (concentration C, curve III) and **18** (concentration C, curve I); $C = 6.31 \times 10^{-6}$ M in CH_2Cl_2. The inset shows the correlation of the maxima of absorption for **18** at concentrations C to $20 \times C$ (black circles) to the linear variation of absorbance as a function of the concentration of **2**, for wavelengths λ_{max} 368 and 436 nm.

from each other. The structures shown for **10** and **18** provide a good comparison between the shape of the neutral and oxidised forms of the dendrimers. The average molecular diameter of their spherical shapes is 40 Å for **10** and 46 Å for $\mathbf{10}^{12+}$. This is representative of the compact form of **10** imposed by the saddle-shape conformation of the units, compared to the more extended shape of $\mathbf{10}^{12+}$ imposed by the Coulombic repulsion. In the case of dendrimer **18**, this feature is even more pronounced especially due to the π–π interactions occurring inside the dendritic structure. Consequently, dendrimer **18** presents a cylindrical shape (*ca.* 52 Å × 30 Å) and its oxidised form the expected spherical shape with an average molecular diameter of 61 Å. It is also noteworthy that there are cavities inside the neutral and oxidised forms that could offer some interesting host–guest properties which are currently under investigation.

Conclusions

In this work we have synthesised the first dendrimers to incorporate the anthracene-bis(dithiole) system: macromolecules with 6 and 12 of these redox units at the periphery have been obtained by convergent methodology with aryl ester and aryl ether units in the branches, joined to a 1,3,5-benzene triester core unit. These compounds possess well-defined redox activity, and the two-electron oxidation of each of the redox units affords species with a high charge: molecular weight ratio. Charged organic nanoparticles of this type are relevant to the miniaturisation of electronic materials.[29] The dendritic wedges synthesised during the course of this work, *e.g.* **8**, **14** and **17**, which possess reactive alcohol substituents, are available in synthetically useful quantities and should be amenable to other synthetic transformations, *e.g.* to yield dendronised polymers[30] or new systems which undergo multi-electron charge-transfer processes.

Experimental

General methods and procedures

^1H and ^{13}C NMR spectra were obtained on Oxford 200, Varian Unity 300 and Varian VXR 400S spectrometers operating at 199.992 (^1H) and 50.293 (^{13}C), 299.908 (^1H) and 75.420 (^{13}C), and 400.0 (^1H) and 100.6 (^{13}C) MHz, respectively. Mass spectra were recorded on a Micromass Autospec spectrometer operating at 70 eV. 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. Infra-red spectra were recorded using KBr disks on a Perkin Elmer 1600 FTIR, spectrometer operated from a Grams Analyst 1600. Electronic absorption spectra were obtained using a Perkin Elmer II UV-vis spectrophotometer operating with 1 ml quartz cells. Melting points were obtained on a Philip Harris melting point apparatus and are uncorrected. Cyclic voltammetric data were measured with iR compensation using a BAS CV50 electrochemical analyser. The experiments were carried out with 5 cm^3 of a *ca.* 10^{-4} M solution of the compound in DCM containing 0.1 M tetrabutylammonium perchlorate as the electrolyte, at scan rate 100 mV s^{-1}. The oxidation potentials (which represent a two-electron process) were measured *versus* a platinum wire quasi-reference electrode and corrected *versus* decamethylferrocene/decamethylferrocenium$^+$ by adding decamethylferrocene to the studied solution after the experiment, and referenced *versus* Ag/AgCl. Structures were modeled and optimised in the gas phase without consideration of the counterions using the MM$^+$ programme Hyperchem 5.0 (Hyperchem, Hypercube Inc., 1115 NW 4th Street, Gainsville FL 32601, USA) following the technique of other workers.[31]

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 under an inert atmosphere of nitrogen in pre-dried glassware.

Dimer 7

To a stirred solution of alcohol **3**[18] (800 mg, 1.77 mmol) in dry DCM (100 cm^3) at 20 °C was added diacid chloride **6**[26] (320 mg, 0.885 mmol) and triethylamine (0.5 cm^3, 3.54 mmol). The resultant mixture was stirred overnight. After evaporation of the solvents *in vacuo*, the residue was purified by chromatography eluting with DCM to afford **7** (1.00 g, 97%) as an orange solid, mp 215 °C; δ_H ($CDCl_3$) 8.26 (s, 1 H), 7.6 (m, 10 H), 7.2 (m, 8 H), 5.01 (s, 4 H), 2.09 (s, 6 H), 1.88 (s, 12 H), 0.98 (s, 9 H), 0.20 (s, 6 H); ν_{max} (KBr) 1727, 1521, 1445, 1219, 755, 675, 644 cm^{-1}; λ_{max} (lg ε) (CH_2Cl_2) 368 (4.33), 436 (4.58); *m/z* (MALDI-TOF) 1164 (M^+); [Analysis found: C, 63.76; H, 5.01; $C_{62}H_{56}O_5S_8Si$ (1164.17) requires: C, 63.88; H 4.84%].

Dimer 8

To a stirred solution of **7** (200 mg, 0.17 mmol) in dry THF (50 cm^3) at 20 °C was added tetrabutylammonium fluoride (1 M in THF, 0.17 cm^3, 0.17 mmol). The resultant mixture was stirred for 1 h. The solvents were removed by evaporation *in vacuo* and the residue was purified by chromatography with DCM containing 2% of MeOH as eluent, to afford **8** (178 mg, 99%) as an orange solid, mp > 250 °C; δ_H ($CDCl_3$) 8.24 (s, 1 H), 7.6 (m, 10 H), 7.2 (m, 8 H), 5.01 (s, 4 H), 2.09 (s, 6 H), 1.89 (s, 12 H); ν_{max} (KBr) 3500 (br), 1727, 1521, 1445, 1219, 755, 675, 645 cm^{-1}; λ_{max} (lg ε) (CH_2Cl_2) 368 (4.39), 436 (4.63); *m/z* (MALDI-TOF) 1050 (M^+); [Analysis found: C, 63.72; H, 4.04; $C_{56}H_{42}O_5S_8$ (1051.46) requires: C, 63.97; H, 4.03%].

Dendrimer 10

By analogy with the preparation of **7**, alcohol **8** (100 mg, 0.1 mmol), 1,3,5-benzenetricarbonyl trichloride (**9**) (8.4 mg, 0.033 mmol) and triethylamine (26 μl, 0.2 mmol) in dry DCM (20 cm^3) were stirred at 20 °C. Chromatography eluting with DCM afforded **10** (81 mg, 77%) as an orange solid, mp > 250 °C; δ_H ($CDCl_3$) 9.26 (s, 3 H), 8.64 (s, 3 H), 8.14 (s, 6 H), 7.6 (m, 24 H), 7.2 (m, 24 H), 5.03 (s, 12 H), 2.08 (s, 18 H), 1.83 (s, 36 H); ν_{max} (KBr) 1729, 1520, 1444, 1213, 754, 675, 644 cm^{-1}; λ_{max} (lg ε) (CH_2Cl_2) 368 (5.03), 436 (5.27); *m/z*

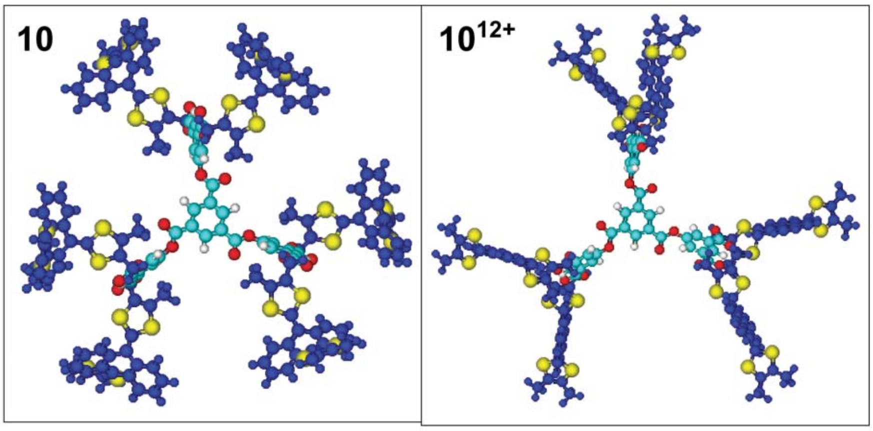


Fig. 6 Molecular model of **10** (left view) and **10^{12+}** (right view) perpendicular to the plane of the core benzene ring. Colour code: 9,10-bis(1,3-dithiol-2-ylidene)-9,10-dihydroanthracene system (purple); sulfur (yellow); oxygen (red); remaining carbon scaffold (light blue).

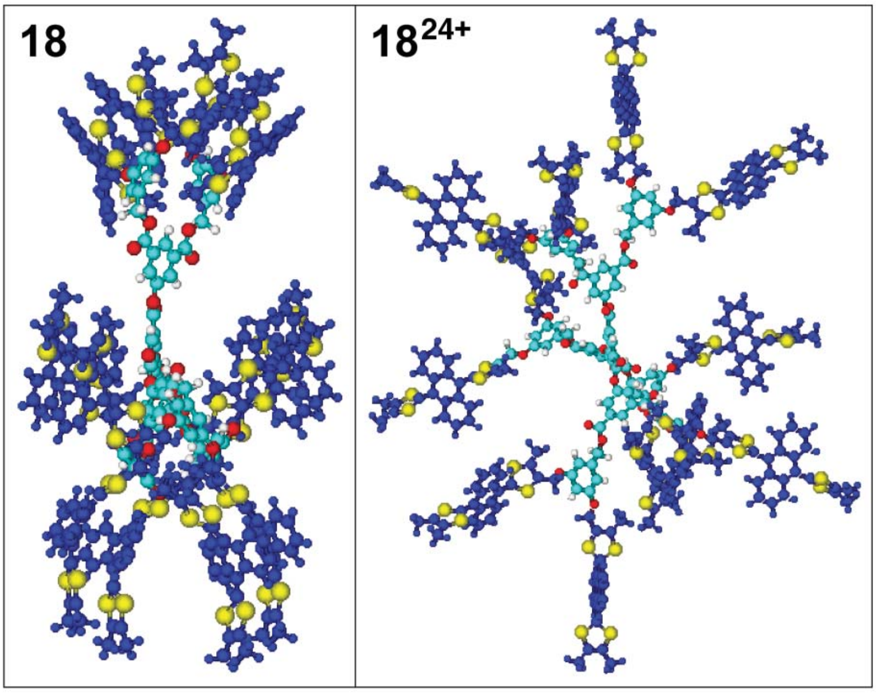


Fig. 7 Molecular model of **18** (left view) and **18^{24+}** (right view) along the plane of the benzene ring. Colour codes are the same as Fig. 6.

(MALDI-TOF) 3308 (M^+); [Analysis found: C 63.81, H 4.05; $C_{177}H_{126}O_{18}S_{24}$, (3310.47) requires: C, 64.22; H 3.84%].

Dendron wedge 11

Following the same procedure as **7**, alcohol **8** (550 mg, 0.52 mmol), diacid chloride **6** (100 mg, 0.26 mmol) and triethylamine (0.14 cm^3, 1.04 mmol) afforded **11** (450 mg, 72%) as an orange solid, mp 230 °C (decomp.: black powder at >200 °C); δ_H (CDCl$_3$) 8.62 (m, 3 H), 8.11 (d, *J* 1.4, 4 H), 7.89 (d, *J* 1.2, 4 H), 7.6 (m, 16 H), 7.2 (m, 16 H), 5.02 (s, 8 H), 2.09 (s, 12 H), 1.85 (s, 24 H), 1.03 (s, 9 H), 0.29 (s, 6 H); ν_{max} (KBr) 1728, 1519, 1444, 1215, 756, 675, 644 cm^{-1}; λ_{max} (lg ε) (CH$_2$Cl$_2$) 368 (4.85), 436 (5.12); *m*/*z* (MALDI-TOF) 2362 (M^+); $C_{126}H_{100}O_{13}S_{16}Si$ requires 2363.28.

10-(4,5-Dimethyl-1,3-dithiol-2-ylidene)-9,10-dihydro-9-(4-chloromethyl-5-methyl-1,3-dithiol-2-ylidene)anthracene 12

To a stirred solution of **3** (2.00 g, 4.4 mmol) in dry acetonitrile (50 cm^3) was added triphenylphosphine (1.25 g, 4.8 mmol) and carbon tetrachloride (20 cm^3). After 1 h at reflux the colour changed from orange to dark brown and TLC monitoring showed the reaction was complete. The mixture was filtered through a plug of silica gel, eluting with EtOAc and then concentrated *in vacuo*. Flash chromatography of the residue eluting with EtOAc–hexane (1 : 2 v/v) afforded **12** (2.00 g, 95%) as an orange solid, mp 225 °C (decomp. to a black powder); δ_H (CDCl$_3$) 7.66–7.59 (m, 4 H), 7.29–7.25 (m, 4 H), 4.27 (s, 2 H), 2.03 (s, 3 H), 1.93 (s, 6 H); ν_{max} (KBr) 1512, 1456, 1445, 755, 675, 644 cm^{-1}; λ_{max} (lg ε) (EtOAc) 364 (4.24), 428 (4.49). [Analysis found: C, 61.26; H, 4.13; $C_{24}H_{19}ClS_4$ (471.12) requires C, 61.18; H, 4.06%].

(N.B. This compound is easily decomposed on silica and especially in solvents like DCM, or in acid conditions).

Dendron wedge 14

To a stirred solution of **12** (2.00 g, 4.2 mmol) in dry THF (50 cm^3) was added 3,5-dihydroxybenzyl alcohol (298 mg, 2.1 mmol), K$_2$CO$_3$ (640 mg, 4.2 mmol) and 18-crown-6 (112 mg, 0.4 mmol). The resulting mixture was heated at reflux and vigorously stirred for 24 h. The solvent was evaporated *in vacuo*. Water (100 cm^3) was added to the residue and the crude product extracted with chloroform (3×50 cm^3). The combined organic layers were dried over $MgSO_4$ and evaporated to dryness. The residue was chromatographed (eluent: dichloromethane) to afford **14** (600 mg, 28%) as an orange solid, mp *ca.* 240 °C; δ_H ($CDCl_3$) 7.65–7.61 (m, 8 H), 7.28–7.23 (m, 8 H), 6.56 (s, 2 H), 6.42 (s, 1 H). 4.64 (s, 4 H), 4.61 (s, 2 H). 1.98 (s, 6 H), 1.90 (s, 12 H); ν_{max} (KBr) 3450 (br) 1595, 1520, 1456, 1444, 1281, 1144, 755, 675, 644 cm^{-1}; λ_{max} (lg ε) (CH_2Cl_2) 368 (4.56), 436 (4.80); *m*/*z* (MALDI-TOF) 1009 (M^+); [Analysis found: C, 64.77; H, 4.35; $C_{55}H_{44}O_3S_8$ (1009.5) (+0.5 mol of H_2O) requires: C, 64.86; H 4.45%].

Dendrimer 15

By analogy with the preparation of **7**, alcohol **14** (100 mg, 0.1 mmol), 1,3,5-benzenetricarbonyl trichloride (**9**) (8.4 mg, 0.03 mmol) and triethylamine (26 µl, 0.2 mmol) in dry DCM (10 cm^3) were stirred at room temperature. Chromatography on silica gel eluting with dichloromethane afforded dendrimer **15** (60 mg, 57%) as an orange solid, mp 245 °C, δ_H ($CDCl_3$) 8.92 (s, 3 H), 7.62–7.54 (m, 24 H), 7.26–7.21 (m, 24 H), 6.52 (s, 6 H), 6.37 (s, 3 H), 5.22 (s, 6 H), 4.51 (s, 12 H), 1.84 (br s, 54 H); λ_{max} (lg ε) (CH_2Cl_2) 368 (4.99), 436 (5.24); *m*/*z* (MALDI-TOF) 3184 (M^+); [Analysis found: C, 65.42; H, 4.03; $C_{174}H_{132}O_{12}S_{24}$ (3184.49) requires C, 65.63; H 4.18%].

Dendron wedge 16

Following the same procedure as for **7**, alcohol **14** (300 mg, 0.3 mmol), diacid chloride **6** (54 mg, 0.15 mmol) and triethylamine (80 µL, 0.6 mmol) afforded **16** (220 mg, 65%) as an orange solid, mp *ca.* 245 °C; δ_H ($CDCl_3$) 8.34 (br s, 1 H), 7.73 (s, 2 H), 7.65–7.54 (m, 16 H), 7.29–7.22 (m, 16 H), 6.54 (br s, 4 H), 6.37 (br s, 2 H), 5.20 (br s, 4 H), 4.51 (br s, 8 H), 1.84 (br s, 36 H), 0.99 (s, 9 H), 0.23 (s, 6 H); ν_{max} (KBr) 1725, 1595, 1520, 1444, 1216, 1144, 754, 675, 644 cm^{-1}; λ_{max} (lg ε) (CH_2Cl_2) 368 (4.81), 436 (5.03); *m*/*z* (MALDI-TOF) 2278 (M^+); [Analysis found: C, 65.43; H, 4.73; $C_{124}H_{104}O_9S_{16}Si$ (2279.3) requires C, 65.34; H, 4.60%].

Dendron wedge 17

Following the same procedure as for **8**, dendron **16** (200 mg, 0.09 mmol) was dissolved in dry THF (50 cm^3). Tetrabutylammonium fluoride (1 M in THF, 0.09 cm^3, 0.09 mmol) was added and the resultant mixture was stirred for 1 h. The solvent was removed by evaporation *in vacuo* and the residue was purified by chromatography with DCM as eluent, to afford **17** (133 mg, 70%) as an orange solid, mp 245 °C (decomp.); δ_H ($CDCl_3$) 8.30 (br s, 1 H), 7.71 (s, 2 H), 7.65–7.54 (m, 16 H), 7.27–7.17 (m, 16 H), 6.52 (br s, 4 H), 6.37 (br s, 2 H), 5.20 (br s, 4 H), 4.52 (br s, 8 H) 1.84 (br s, 36 H); ν_{max} (KBr) 3450 (br), 1726, 1596, 1520, 1445, 1222, 1146, 755, 675, 644 cm^{-1}; λ_{max} (lg ε) (CH_2Cl_2) 368 (4.85), 436 (5.09); *m*/*z* (MALDI-TOF) 2164 (M^+); [Analysis found: C, 64.15; H, 4.23; $C_{118}H_{90}O_9S_{16}$ (2165.0) (+2 mol of H_2O) requires: C, 64.39; H 4.30%].

Dendrimer 18

By analogy with the preparation of **7**, alcohol **17** (130 mg, 0.06 mmol), 1,3,5-benzenetricarbonyl trichloride (**9**) (5.3 mg, 0.02 mmol) and triethylamine (16 µl, 0.12 mmol) in dry DCM (10 cm^3) were stirred at 20 °C. Chromatography eluting with DCM afforded **18** (72 mg, 54%) as an orange solid, mp 240 °C (decomp.); δ_H ($CDCl_3$) 9.05 (s, 3 H), 8.69 (s, 3 H), 8.14 (s, 6 H), 7.59–7.46 (m, 48 H), 7.28–7.18 (m, 48 H), 6.51 (s, 12 H), 6.33 (s, 6 H), 5.22 (br s, 12 H), 4.50 (m, 24 H), 1.82–1.79 (br s, 108 H); ν_{max} (KBr) 1731, 1596, 1520, 1444, 1222, 1146, 753, 675, 644 cm^{-1}; λ_{max} (lg ε) (CH_2Cl_2) 368 (5.27), 436 (5.51); *m*/*z* (MALDI-TOF) 6648 (M^+); [Analysis found: C, 65.37; H, 4.23; $C_{363}H_{270}O_{30}S_{48}$ (6651.2) requires: C 65.55, H 4.09%].

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References

1 (*a*) Reviews: *Electronic Materials: The Oligomer Approach*, Eds. K. Müllen and G. Wegner, Wiley-VCH, Weinheim, 1998; (*b*) R. E. Martin and F. Diederich, *Angew. Chem., Int. Ed.*, 1999, **38**, 1350; (*c*) Y. Shirota, *J. Mater. Chem.*, 2000, **10**, 1; (*d*) D. Fichou, *J. Mater. Chem.*, 2000, **10**, 571; (*e*) J. L. Segura and N. Martín, *J. Mater. Chem.*, 2000, **10**, 2403.

2 (*a*) Reviews: D. A. Tomalia, A. M. Naylor and W. A. Goddard, III, *Angew. Chem., Int. Ed. Engl.*, 1990, **29**, 138; (*b*) G. R. Newkome, C. N. Moorefield and F. Vögtle, *Dendritic Molecules: Concepts, Synthesis, Perspectives*, VCH, Weinheim, 1996; (*c*) O. A. Matthews, A. N. Shipway and J. F. Stoddart, *Prog. Polym. Sci.*, 1998, **23**, 1; (*d*) M. Fischer and F. Vögtle, *Angew. Chem., Int. Ed.*, 1999, **38**, 884; (*e*) S. Hecht and J. M. J. Fréchet, *Angew. Chem., Int. Ed.*, 2001, **40**, 74; (*f*) *Dendrimers II: Architecture, Nanostructure and Supramolecular Chemistry*, Ed. F. Vögtle, Springer, London, 2000.

3 For a review of redox-active dendrimers see: M. R. Bryce and W. Devonport, in *Advances in Dendritic Macromolecules*, Ed. G. R. Newkome, JAI Press, London, 1996, Volume 3, p. 115.

4 P. Weyermann, J.-P. Gisselbrecht, C. Boudon, F. Diederich and M. Gross, *Angew. Chem., Int. Ed.*, 1999, **38**, 3215.

5 M. Kimura, T. Shiba, T. Muto, K. Hanabusa and H. Shirai, *Chem. Commun.*, 2000, 11.

6 C. M. Cardona and A. E. Kaifer, *J. Am. Chem. Soc.*, 1998, **120**, 4023.

7 X. Camps, E. Dietel, A. Hirsch, S. Pyo, L. Echegoyen, S. Hackbarth and B. Röder, *Chem. Eur. J.*, 1999, **5**, 2362.

8 C. B. Gorman, J. C. Smith, M. W. Hager, B. L. Parkhurst, H. Sierzputowska-Gracz and C. A. Haney, *J. Am. Chem. Soc.*, 1999, **121**, 9958.

9 R. Toba, J. M. Quintela, C. Peinador, E. Román and A. E. Kaifer, *Chem. Commun.*, 2001, 857.

10 For a review of encapsulated redox centres in dendrimers and other structures, see: C. M. Cardona, S. Mendoza and A. E. Kaifer, *Chem. Soc. Rev.*, 2000, **29**, 37.

11 (*a*) C. Valério, E. Alonso, J. Ruiz, J.-C. Blais and D. Astruc, *Angew. Chem., Int. Ed.*, 1999, **38**, 1747; (*b*) Review: M. A. Hearshaw and J. R. Moss, *Chem. Commun.*, 1999, 1; (*c*) S. Nlate, J. Ruiz, J.-C. Blais and D. Astruc, *Chem. Commun.*, 2000, 417; (*d*) S. Nlate, J. Ruiz, V. Sartor, R. Navarro, J.-C. Blais and D. Astruc, *Chem. Eur. J.*, 2000, **6**, 2544; (*e*) Review: C. M. Casado, I. Cuadrado, M. Morán, B. Alonso, B. García, B. González and J. Losada, *Coord. Chem. Rev.*, 1999, **185–186**, 53.

12 (*a*) S. Serroni, A. Juris, M. Venturi, S. Campagna, I. R. Resino, G. Denti, A. Credi and V. Balzani, *J. Mater. Chem.*, 1997, **7**, 1227; (*b*) G. R. Newkome, A. K. Patri and L. A. Godínez, *Chem. Eur. J.*, 1999, **5**, 1445.

13 N. Armaroli, C. Boudon, D. Felder, J.-P. Gisselbrecht, M. Gross, G. Marconi, J.-F. Nicoud, J.-F. Nierengarten and V. Vicinelli, *Angew. Chem., Int. Ed.*, 1999, **38**, 3731.

14 I. Tabakovic, L. L. Miller, R. G. Duan, D. C. Tully and D. A. Tomalia, *Chem. Mater.*, 1997, **9**, 736.

15 (*a*) M. R. Bryce, W. Devonport, L. M. Goldenberg and C. Wang, *Chem. Commun.*, 1998, 945; (*b*) M. R. Bryce, *J. Mater. Chem.*, 2000, **10**, 589; (*c*) C. A. Christensen, M. R. Bryce and J. Becher, *Synthesis*, 2000, 1695.

16 J. B. Christensen, M. F. Nielsen, J. A. E. H. van Haare, M. W. P. L. Baars, R. A. J. Janssen and E. W. Meijer, *Eur. J. Org. Chem.*, 2001, 2123.

17 A. J. Moore and M. R. Bryce, *J. Chem. Soc., Perkin Trans. 1*, 1991, 157.

18 N. Godbert, M. R. Bryce, S. Dahaoui, A. S. Batsanov, J. A. K. Howard and P. Hazendonk, *Eur. J. Org. Chem.*, 2001, 749.

19 (*a*) For discussions of redox processes in derivatives of the title system see: M. R. Bryce, M. A. Coffin, M. B. Hursthouse, A. I. Karaulov, K. Müllen and H. Scheich, *Tetrahedron Lett.*, 1991, **32**, 6029; (*b*) S.-G. Liu, I. Pérez, N. Martín and L. Echegoyen, *J. Org. Chem.*, 2000, **65**, 9092.

20 (*a*) M. R. Bryce, A. J. Moore, M. Hasan, G. J. Ashwell, A. T. Fraser, W. Clegg, M. B. Hursthouse and A. I. Karaulov, *Angew.*

Chem., Int. Ed. Engl., 1990, **29**, 1450; (*b*) M. R. Bryce, T. Finn, A. S. Batsanov, R. Kataky, J. A. K. Howard and S. B. Lyubchik, *Eur. J. Org. Chem.*, 2000, 1199; (*c*) A. E. Jones, C. A. Christensen, D. F. Perepichka, A. S. Batsanov, A. Beeby, P. J. Low, M. R. Bryce and A. W. Parker, *Chem. Eur. J.*, 2001, **7**, 973.

21 (*a*) For discussions of Coulombic effects in multi-stage redox systems see: K. Deuchert and S. Hünig, *Angew. Chem., Int. Ed. Engl.*, 1978, **17**, 875; (*b*) S. Hünig and H. Berneth, *Top. Curr. Chem.*, 1980, **92**, 1.

22 N. Martín, L. Sánchez, C. Seoane, E. Ortí, P. M. Viruela and R. Viruela, *J. Org. Chem.*, 1998, **63**, 1268.

23 S. Triki, L. Ouahab, D. Lorcy and A. Robert, *Acta Crystallogr., Sect. C: Cryst. Struct. Commun.*, 1993, **C49**, 1189.

24 (*a*) M. A. Herranz, N. Martín, L. Sánchez, J. Garín, J. Orduna, R. Alcalá, B. Villacampa and C. Sánchez, *Tetrahedron*, 1998, **54**, 11651; (*b*) M. A. Herranz and N. Martín, *Org. Lett.*, 1999, **1**, 2005; (*c*) C. A. Christensen, M. R. Bryce, A. S. Batsanov, J. A. K. Howard, J. O. Jeppesen and J. Becher, *Chem. Commun.*, 1999, 2433; (*d*) N. Martín, L. Sánchez and D. M. Guldi, *Chem. Commun.*, 2000, 113.

25 N. Martín, I. Pérez, L. Sánchez and C. Seoane, *J. Org. Chem.*, 1997, **62**, 870.

26 T. M. Miller, E. W. Kwok and T. X. Neenan, *Macromolecules*, 1992, **25**, 3143.

27 C. J. Hawker and J. M. J. Fréchet, *J. Am. Chem. Soc.*, 1990, **112**, 7638.

28 N. Godbert, A. S. Batsanov, M. R. Bryce and J. A. K. Howard, *J. Org. Chem.*, 2001, **66**, 713.

29 U. Simon, *Adv. Mater.*, 1998, **10**, 1487.

30 Review: A. D. Schlüter and J. P. Rabe, *Angew. Chem., Int. Ed.*, 2000, **39**, 864.

31 S. Heinen and L. Walden, *Angew. Chem., Int. Ed.*, 2000, **39**, 806.