Redox-switchable polyester dendrimers incorporating both π-donor (tetrathiafulvalene) and π-acceptor (anthraquinone) groups

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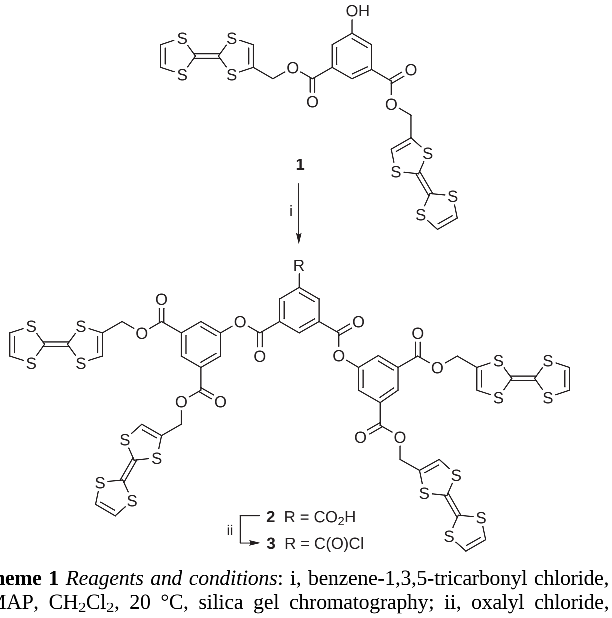
Received (in Liverpool, UK) 9th September 1998, Accepted 16th October 1998

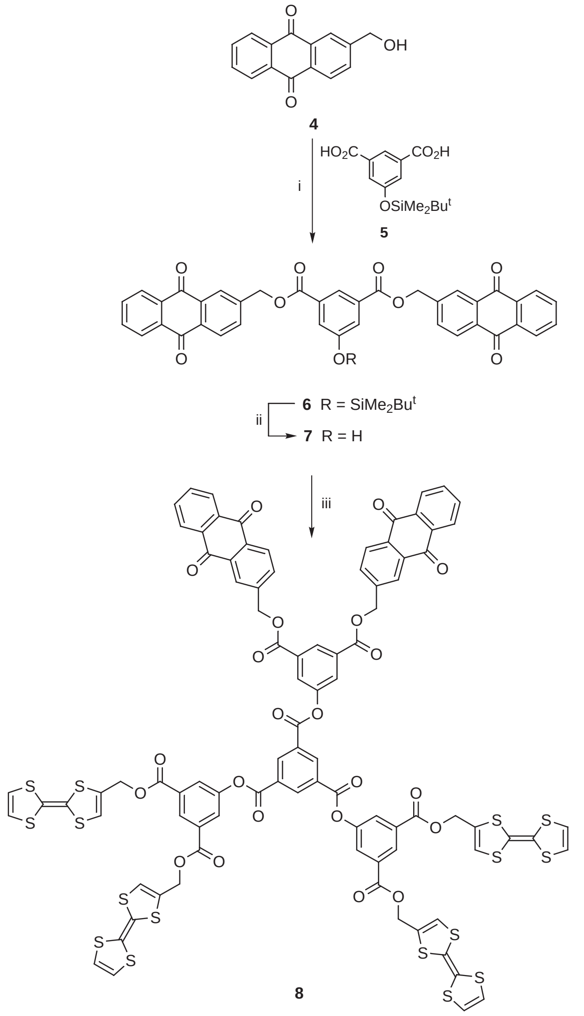
The convergent synthesis of $(TTF)_x(AQ)_y$ (TTF = tetrathiafulvalene; AQ = anthraquinone) polyester dendrimers is reported; the molecules undergo clean amphoteric redox behaviour with reversible switching between cationic and anionic states being achieved under electrochemical control; the higher generation system $(TTF)_8(AQ)_4$ displays an intradendrimer charge-transfer interaction in solution.

Dendritic molecules[1] which possess functional groups at the exterior surface and/or embedded within their structure[2] are of current interest. In this context, dendrimers which carry multiple cationic or anionic sites are attracting attention, due to their potential applications as macromolecular polyelectrolytes, catalysts and charge transfer materials. The charged sites may be introduced into the structure in two conceptually different ways: (i) during the synthesis, *e.g.* by using quaternary ammonium linkages,[3] by incorporating transition metals,[4] or by attaching polyanionic surfaces;[5] or (ii) by electrochemical redox processes or chemical doping of a neutral dendrimer which contains redox-active groups.[6] For these systems, the redox centres may behave independently in multi-electron processes (*n* identical non-interacting 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. Representative electron donor groups are ferrocene,[7] metal-(bipyridyl)[8] and tetrathiafulvalene (TTF),[9] while interior anthraquinone (AQ)[10] and peripheral naphthalene diimide[11] groups have been used as electron acceptor units. Dendritic systems containing both strong π-donor and π-acceptor groups covalently bonded into their framework[12] are especially attractive targets as they should possess amphoteric redox properties under electrochemical control,[8b] and may engage in inter- and/or intra-molecular charge-transfer interactions.

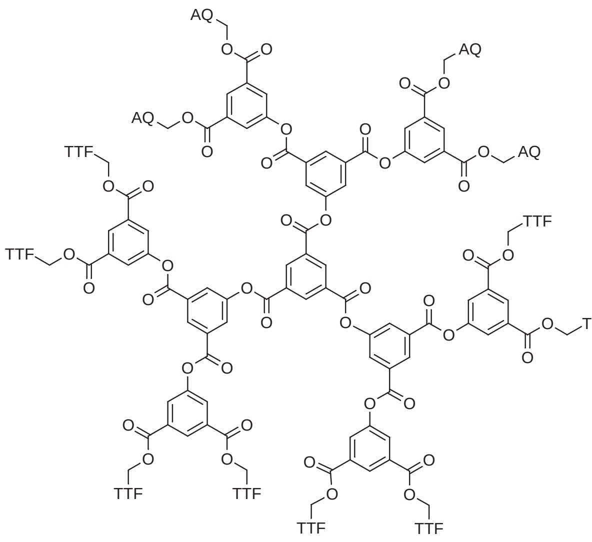


Scheme 1 *Reagents and conditions*: i, benzene-1,3,5-tricarbonyl chloride, DMAP, CH_2Cl_2, 20 °C, silica gel chromatography; ii, oxalyl chloride, toluene 80 °C.

Herein we report the prototype systems **8** and **9** containing both TTF and AQ units, built around a benzene 1,3,5-triester core. The synthesis of the $(TTF)_4$ dendron **3** is shown in Scheme 1.† The reaction of phenol derivative **1**[9a,d] (2.1 equiv.) with benzene-1,3,5-tricarbonyl chloride (1.0 equiv.) in the presence of DMAP as base (CH_2Cl_2, 20 °C) afforded the carboxylic acid derivative **2** (56% yield) after hydrolysis of the unreacted acid chloride group during workup. Reaction of **2** with oxalyl chloride in toluene afforded acid chloride derivative **3** (82% yield). The synthesis of the $(AQ)_2$ reagent **7** is shown in Scheme 2. 2-(Hydroxymethyl)anthraquinone **4** reacted with 5-(*tert*-butyldimethylsiloxy)isophthalic acid **5**[13] using the DMAP-catalysed DCC method[14] to form compound **6** in 55% yield. Attempted desilylation of **6** using TBAF in THF resulted in cleavage of the ester linkages;[15] however, heating a solution of **6** in a mixture of THF–aq. HCl (1 M) gave the alcohol derivative **7** (81% yield) which was only sparingly soluble in most organic



Scheme 2 *Reagents and conditions*: i, DCC, DMAP, CH_2Cl_2, 0–20 °C; ii, HCl (1 M)–THF (7:1 v/v), 50 °C; iii, **3**, DMAP, 1,4-dioxane, reflux.



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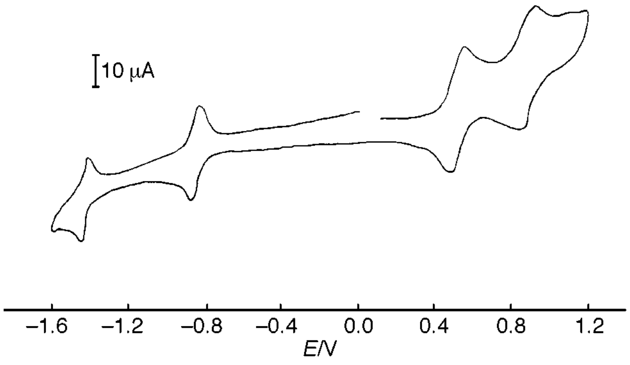

Fig. 1 Cyclic voltammogram of **8** (MeCN, 20 °C, $Bu_4N^+PF_6^-$ electrolyte, Pt electrode, *vs.* Ag/AgCl, scan rate 50 mV s^{-1}).

solvents. Esterification of **7** to afford G1 dendrimer **8** (60% yield, after column chromatography on silica gel) was achieved by reaction with acid chloride derivative **3** in the presence of DMAP in refluxing 1,4-dioxane. Analogous iterative procedures, starting with the known octa-TTF building block,[9d] gave the $(TTF)_8(AQ)_4$ G2 system **9**. Compounds **8** and **9** are soluble in a range of organic solvents (*e.g.* CH_2Cl_2, $CHCl_3$, THF, dichlorobenzene and CS_2): they darken on storage in air, and can be stored for several weeks under vacuum in the dark at 0 °C.

The solution electrochemistry of **8** and **9** has been studied by cyclic voltammetry (CV) in MeCN solution (Fig. 1). Scanning anodically, **8** exhibits two reversible four-electron oxidation waves to form, sequentially, the radical cation and dication of each of the TTF moieties;[16] scanning cathodically, two reversible two-electron waves are observed, corresponding to the reduction of each anthraquinone unit to the radical anion and the dianion.[17] Thus, **8** demonstrates clean amphoteric redox behaviour with reversible switching between the +8, +4, 0, −2 and −4 charged states being achieved. The CV of **9** is very similar (the +16, +8, 0, −4 and −8 states are clearly observed) although the second TTF wave was slightly narrower than the first wave, which was probably due to adsorption phenomena, as observed previously with some higher generation systems.[9d]

An important difference between the G1 and G2 systems **8** and **9** is manifested in their UV–VIS spectra. Compound **9** shows a very weak (ε < 250) broad absorption band in the λ 460–750 nm region in MeCN, which is not present in **8**. The solvent dependency of this band and experiments at various concentrations of **9** suggest that this low energy band arises from intramolecular (rather than intermolecular) π–π charge-transfer from TTF to anthraquinone units. Based on the different redox potentials of these donor and acceptor moieties, the degree of charge-transfer is expected to be small (< 0.1)[18] and that it is observed only in **9** appears to be an interesting consequence of the more densely packed structure of the higher generation molecule.

In summary, an efficient route has been established to polyester 'co-block' dendrimers containing both π-donor and π-acceptor moieties at the periphery. A future direction will be the incorporation into these structures of stronger π-acceptor groups,[18,19] in conjunction with TTF, enabling the study of intramolecular charge-transfer interactions within a dendritic microenvironment. Such materials could find applications in the development of electrooptical switches.

This work was funded by EPSRC (W. D.) and Universidad Complutense de Madrid (P. de. M.).

Notes and references

† All new compounds gave ^1H NMR spectra, mass spectra (FAB or plasma desorption) and analytical data which were entirely consistent with their structures. *Selected data* for **8**: $\delta_H(CDCl_3)$ 9.16 (3 H, s), 8.42 (3 H, t, *J* 1.5), 8.39 (6 H, d, *J* 1.5), 8.22–7.85 (14 H, m), 7.06 (4 H, s), 6.72 (8 H, s), 5.54 (4 H, s) and 5.20 (8 H, s).

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Communication 8/07062H