COMMUNICATION

Branched ferrocene derivatives: using redox potential to probe the dendritic interior †

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Dendritically functionalised ferrocene derivatives have been prepared, their electrochemical properties investigated, and comparison with literature results leads to the conclusion that the precise structure of dendritic branches plays a pivotal role in controlling molecular properties.

Recently, much attention has focused on the way in which dendritic encapsulation [1] of redox-active moieties alters their redox properties.[2] Although it is well established that encapsulation leads to a decrease in electrochemical reversibility, the effect of dendritic structure on redox potential has not been so easy to define. For example, the dendritic porphyrins of Diederich and co-workers have half potentials shifted relative to their non-dendritic analogues,[3] whilst in contrast, the dendritic porphyrins of Fréchet and co-workers do not.[4] Recently, Cardona and Kaifer published a series of ferrocenes functionalised with dendritic branching constructed from aliphatic amide groups in which the presence of even relatively small quantities of dendritic branching markedly affected the metallocene redox potential.[5] Ferrocene is an interesting and suitable redox-active probe of the dendritic environment due to its electrochemical simplicity. In this communication, bis-functionalised dendritic ferrocenes (**G1** and **G2**) with a different type of branched superstructure are reported and their behaviour is contrasted with that of Kaifer's system.

Dendritic ferrocenes **G1** and **G2** (Fig. 1) were targeted by the convergent approach,[6] with modified 'Fréchet-style' dendritic branches **2** and **4** being appended to 1,1′-bis(chlorocarbonyl)-ferrocene respectively. The dendritic branches were modified with oligo-ether solubilising groups at the periphery in order to

† Characterisation data for **G1** and **G2** are available as supplementary data. For direct electronic access see http://www.rsc.org/suppdata/p2/1999/1563, otherwise available from BLDSC (SUPPL. NO. 57582, pp. 1) or the RSC Library. See Instructions for Authors available *via* the RSC web page (http://www.rsc.org/authors).

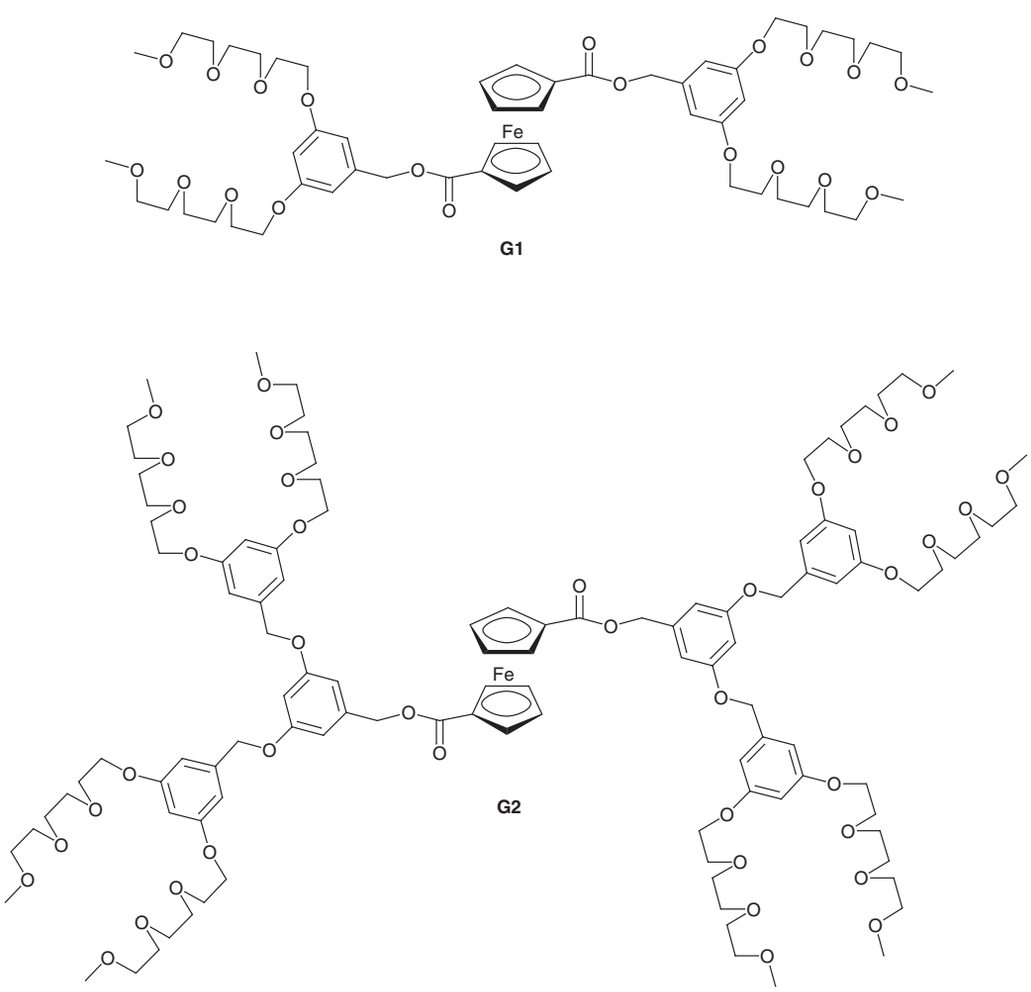
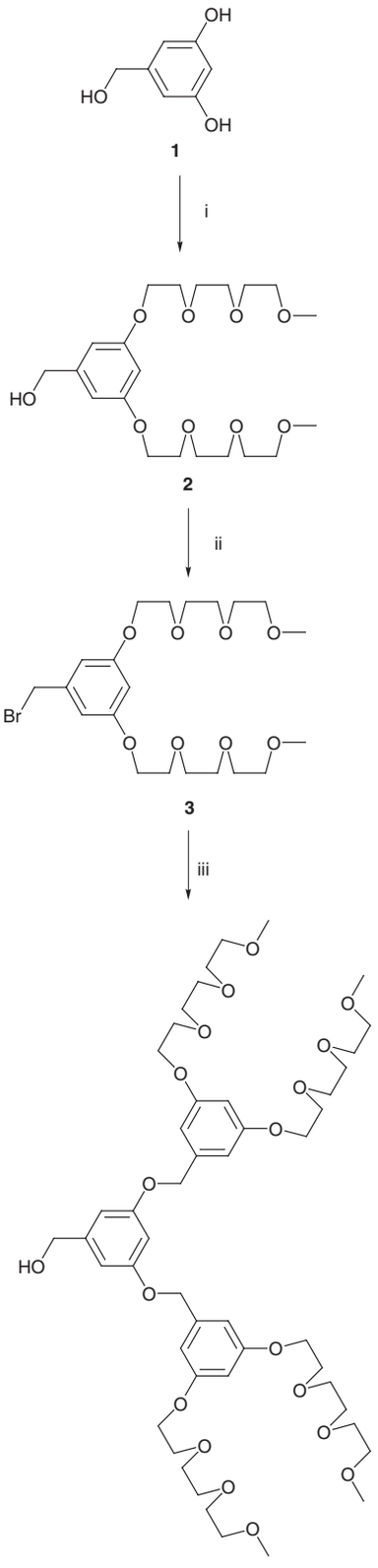


Fig. 1 Dendritically modified bis-functionalised ferrocene derivatives (**G1** and **G2**).



Scheme 1 Synthesis of novel Fréchet-style dendritic wedges modified for enhanced solubility properties. *Reagents and conditions*: i, $CH_3O(CH_2)_2O(CH_2)_2O(CH_2)_2OTs$,[7] K_2CO_3, 18-crown-6, acetone, 85%; ii, PPh_3, CBr_4, THF, 67%; iii, compound **1**, K_2CO_3, 18-crown-6, acetone, 94%.

yield high solubility in a range of different solvents, whilst maintaining electroneutrality. These solubilised dendritic wedges, the physical properties of which should make them of wide-ranging interest, were synthesised as outlined in Scheme 1. This synthesis was also extended to yield third generation branches. The new dendritic branches (**2** and **4**) were coupled with 1,1′-bis(chlorocarbonyl)ferrocene using dichloromethane as solvent in the presence of base. As the dendritic wedge increased in size, however, the coupling became progressively less efficient: in fact the third generation wedge (not illustrated in Scheme 1) would only couple once with the ferrocene core. This is presumably a result of the combination of steric hindrance caused by the branch and the relatively low reactivity of the acid chloride core. First and second generation dendrimers **G1** and **G2** were, however, readily obtained and characterised.‡

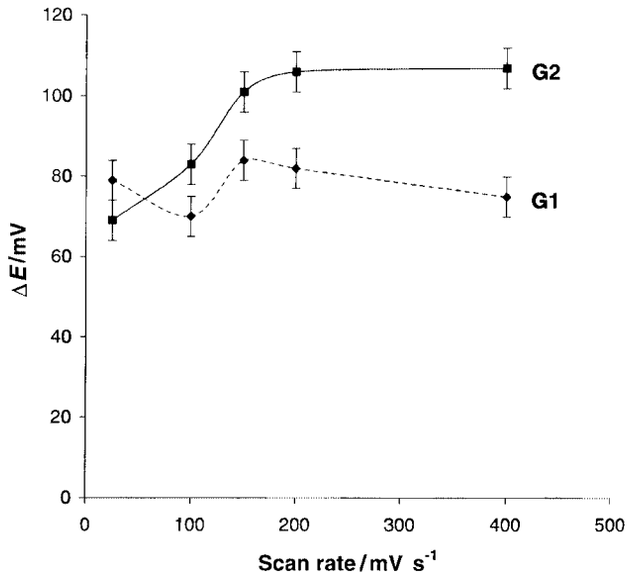


Fig. 2 Effect of increasing scan rate (mV s^{-1}) on cyclic voltammogram peak separation ($\Delta E = E_{ox} - E_{red}$ (mV)) for **G1** and **G2** in CH_2Cl_2 solution.§

Cyclic voltammetry was used to investigate the electrochemical properties of these novel, dendritically functionalised ferrocenes.§ Initially, they were investigated in dichloromethane solution at a range of different scan rates. Compound **G1** ($M_r = 1103.0$) exhibited reversible cyclic voltammograms at scan rates between 25 and 400 mV s^{-1} with the peak separation constant at around 80 mV. Compound **G2** ($M_r = 2176.3$), however, showed a small increase in peak separation with increasing scan rate, from 70 mV at 25 mV s^{-1} to 110 mV at 400 mV s^{-1}. This is indicative of a slight decrease in reversibility for the larger dendrimer **G2** due to impeded access of the redox active unit to the electrode surface. This is in agreement with previous observations of dendritically functionalised redox centres.[3–5]

Of key interest, however, was the effect of dendritic generation on redox potential. Dendrimers **G1** and **G2** had $E_{1/2}$ values of 0.460 V and 0.466 V (relative to Fc/Fc^+) respectively, within error range of the same value. It is consequently concluded that in this case, in CH_2Cl_2 solution, the extra layer of dendritic branching has *no effect on the redox potential of the core*. Dendrimers **G1** and **G2** were also investigated in methanolic solution, and whilst showing poor reversibility at low scan rates (indicative of EC mechanistic behaviour with the electron transfer being followed by a chemical process), the redox potentials were once again unaffected by the extra layer of dendritic branching. Dendrimer **G1** had an $E_{1/2}$ value of 0.481 V, whilst that of compound **G2** was 0.482 V (relative to Fc/Fc^+ at 200 mV s^{-1}).

It is therefore clear that in this case, the dendritic shell does not create a microenvironment for the redox probe at the core, or at least not one which the ferrocene moiety is capable of detecting. This forms an interesting contrast to the work of Cardona and Kaifer, who investigated the effect of aliphatic-amide dendritic branching appended to a mono-functionalised ferrocene nucleus.[5] They observed that even relatively small amounts of branching gave rise to cathodic shifts in $E_{1/2}$ of 30 mV (difference between first and second generation dendritic ferrocenes, $M_r = 627.6$ and 1652.0 amu, respectively).¶ It was initially surprising that these dendrimers should exhibit such an effect because the ferrocene probe is only mono-substituted,

unlike **G1** and **G2** in which it is bis-substituted and might be expected to be more deeply buried. The dendritic branching of Cardona and Kaifer, however, has greater flexibility due to its aliphatic nature, and the first branching point is located close to the ferrocene nucleus, which might explain the greater degree of apparent encapsulation. Clearly, considering this result, and taking into account other reports from the literature,[3,4] different types of dendritic branching can have markedly different effects on encapsulated core units.

The importance of the structure of the branched shell is, of course, a result which most chemists might expect, but this observation highlights the importance of not viewing all dendrimers as simply equivalent branched molecules. Furthermore, it emphasises the diversity of properties that might be expected in the future for structures with relatively subtle differences. It is only by careful investigation with simple environmental probes, such as ferrocene, that the unique properties which can be generated within these branched macromolecules will be fully understood, and this work is currently in progress.

Acknowledgements

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Notes and references

‡ For characterisation see supplementary information.

§ Cyclic voltammetry performed at 25 °C with either 0.1 M (MeOH) or 0.2 M (CH_2Cl_2) tetra-*n*-butylammonium hexafluorophosphate as background electrolyte. Glassy carbon electrode as working, platinum wire as counter, and Ag/Ag^+ (in acetonitrile) as reference. All redox potentials are quoted referenced to unfunctionalised Fc/Fc^+ under the same conditions.

¶ Cardona and Kaifer's electrochemical measurements were also made in CH_2Cl_2 containing 0.2 M tetra-*n*-butylammonium hexafluorophosphate. Their third generation dendritic system (M_r = 4725.0) exhibited a further cathodic shift of 60 mV (as compared to the 2nd generation analogue).

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