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Preliminary communication

New lipophilic macrocyclic host molecules containing multiple ferrocenyl redox-active centres

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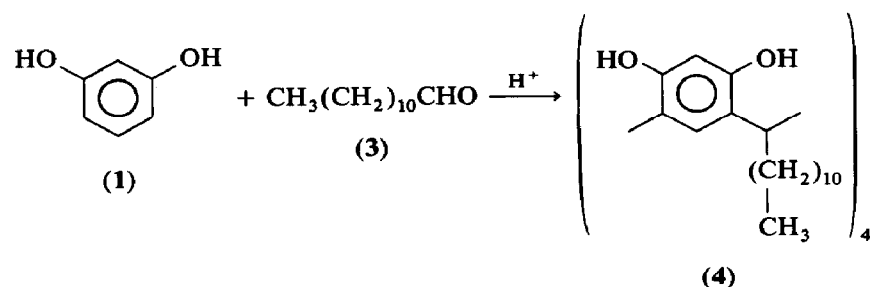
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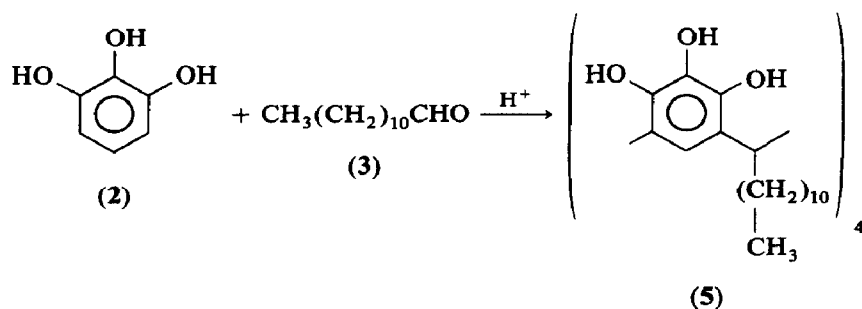
Abstract

The syntheses and electrochemistry of two novel lipophilic macrocyclic host molecules containing eight and twelve ferrocene redox-active centres are described.

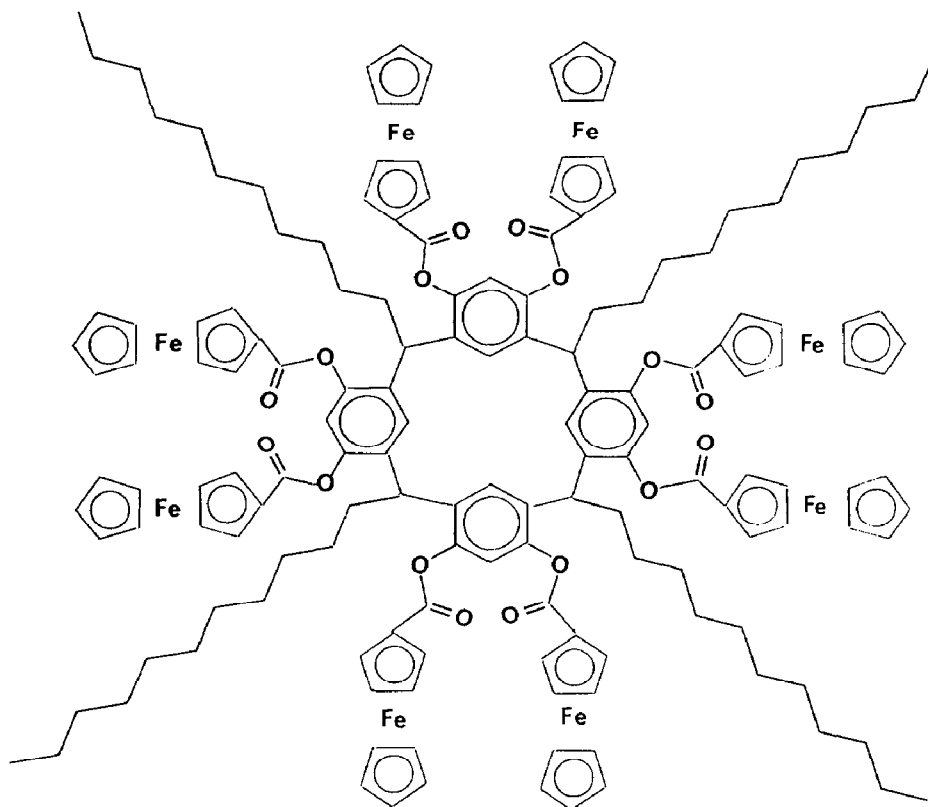
There is considerable current interest in the design and synthesis of receptor molecules containing a redox-active centre in close proximity to a crown ether [1–5] or cryptand [6,7] coordination site, but few examples of the incorporation of redox centres into hydrophobic macrocyclic host structural frameworks have been reported [8–10]. Interest in this latter class of molecule stems from the idea of investigating the potential catalytic interactions between the redox-active moiety and an included organic guest substrate. We describe here the synthesis and electrochemical properties of a new redox-active lipophilic host molecule (7) that contains eight ferrocenyl groups and a novel analogue (8) containing twelve ferrocenyl groups.

The acid catalysed reaction of 1,3-dihydroxybenzene (1) or 1,2,3-trihydroxybenzene (2) with dodecanal (3) in ethanol gave the tetrameric macrocycles (4) [11] and (5) respectively, in good yields. Subsequent reaction of an excess of ferrocene carbonylchloride (6) [12] with 4 and 5 in the presence of triethylamine gave, after column chromatography (alumina; CH₂Cl₂) respectively 7 (20% yield m.p. 161–163°C) and 8 (65% yield, m.p. 211–214°C) an orange powdery solids. These new air-stable compounds were characterised by elemental analyses, fast atom bombardment mass spectrometry (FABMS), and ¹H NMR spectroscopy.

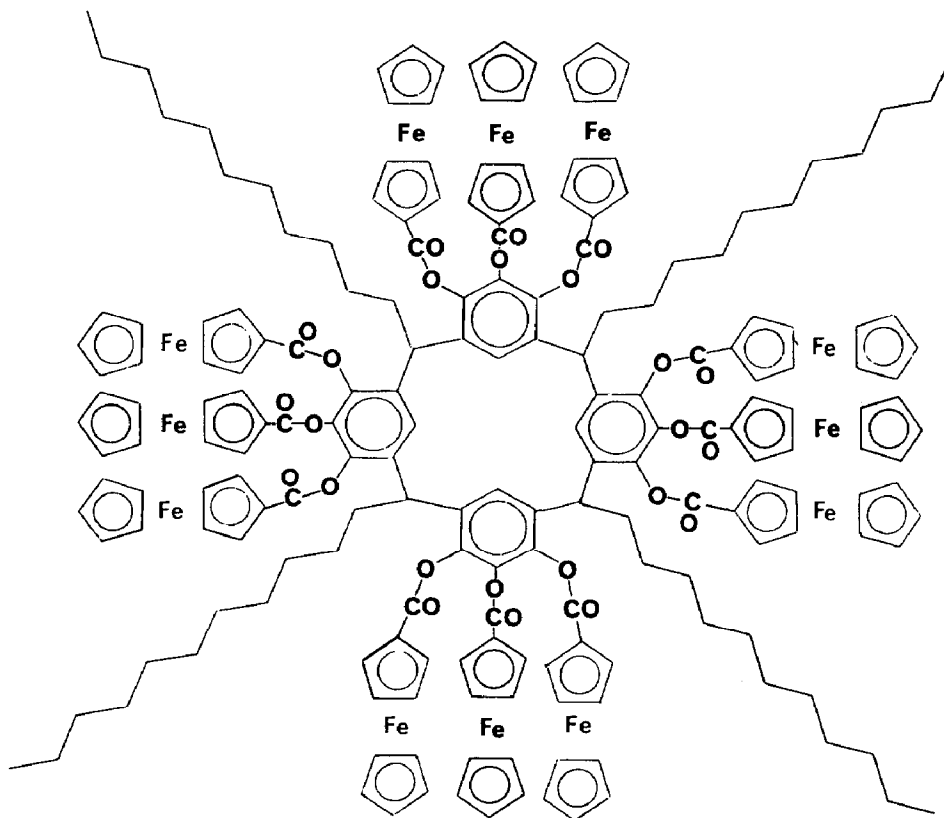
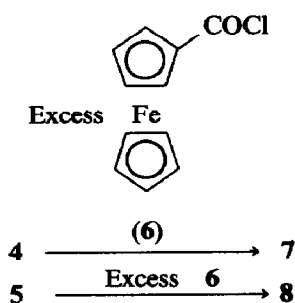




The respective reversible and quasi-reversible cyclic voltammograms of **7** and **8** in dichloromethane gave an oxidation wave at +0.89 V and a reduction wave at +0.79 V (versus standard calomel electrode, SCE) for **7** and an oxidation wave at +0.98 V, a reduction wave at +0.81 V (SCE) for **8**. Coulometric studies with **7** and **8** were thwarted by detrimental electrode deposition, however the cyclic voltammetric results suggest that all the respective ferrocene moieties present in the host compounds become oxidised in one step. Solution complexation experiments of **7** and **8** with polar organic guests in lipophilic solvent media and elucidation of their solid state liquid crystal properties [13] are currently under investigation.



(7)



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