Synthesis, electrochemistry and cyclodextrin binding of novel cobaltocenium-functionalized dendrimers

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A series of novel poly(propyleneimine) dendrimers functionalized with 4, 8, 16 and 32 peripheral cobaltocenium subunits were prepared and characterized with a special focus on their electrochemical properties and binding interactions with β-cyclodextrin.

The chemistry of dendrimers[1] continues its fast development as numerous research groups take advantage of dendrimer structural frameworks for a variety of applications.[2] Recently, we have reported[3] on the preparation and properties of dendrimers functionalized with multiple ferrocene sites on their surface and shown that they may act as multisite, redox active guests[3e] for inclusion complexation by cyclodextrins.[4] Here we report the preparation and characterization of four new dendrimers **1–4** having 4, 8, 16 and 32 peripheral cobaltocenium subunits. While these positively charged dendrimers are not complexed by β-cyclodextrin (β-CD) in aqueous media, their electrochemical reduction triggers the formation of high molecular weight, multisite inclusion complexes with this host.

The new dendritic macromolecules **1–4** were synthesized by condensation reactions of 1-chlorocarbonylcobaltocenium in MeCN with poly(propyleneimine) dendrimers bearing 4, 8, 16 and 32 NH_2 groups respectively, in the presence of Et_3N. After purification by repeated column chromatography (Sephadex LH-20 with MeCN as eluent) all four organometallic dendrimers were isolated as air-stable, yellow (**1** and **2**) or green solids (**3** and **4**). Compounds **1–4** are soluble in solvents such as MeCN and DMSO. The structures of the new dendrimers have been straightforwardly established on the basis of ^1H and ^{13}C NMR and IR spectroscopy, MS, and elemental microanalysis.

We have previously reported the voltammetric behavior of cobaltocenium and carboxycobaltocenium in aqueous media as well as their complexation by the host β-CD.[5] We found that the reduced form, cobaltocene, precipitates on the electrode surface giving rise to strong distortions from the wave shape expected for a reversible, one-electron reduction process. The electro-

Table 1 Half-wave potentials measured for the reduction of dendrimers **1–4** at 25 °C in several media

	E/V		
Dendrimer	0.1 M $TBA^+PF_6^-$/MeCN[a]	0.1 M NaCl[b]	0.1 M NaCl + excess β-CD[b]
1	−0.75	−0.81	−0.78
2	−0.74	−0.80	−0.77
3	−0.74	−0.78	−0.76
4	−0.73	insoluble	insoluble

[a] Measured by cyclic voltammetry *vs.* SCE. [b] Measured by normal pulse voltammetry against a Ag/AgCl electrode.

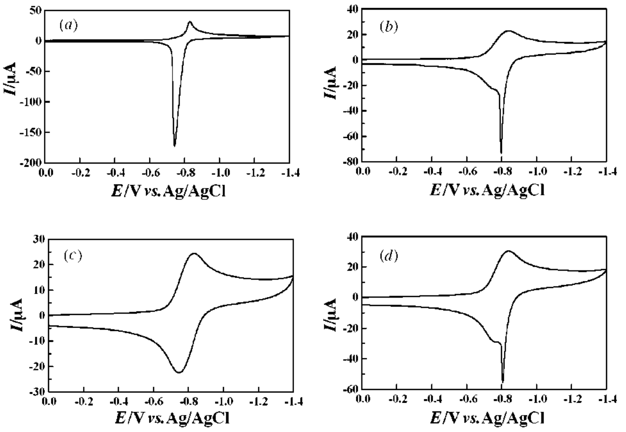
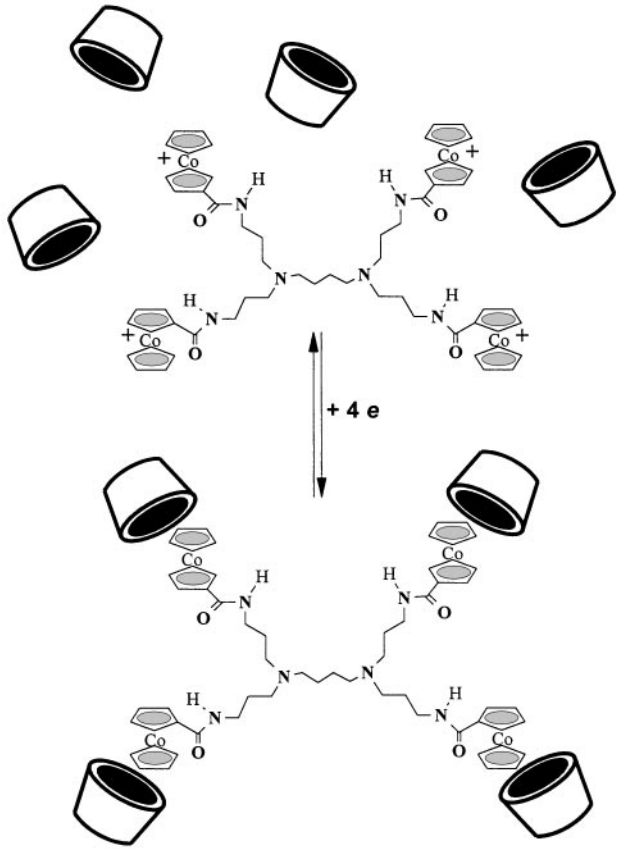
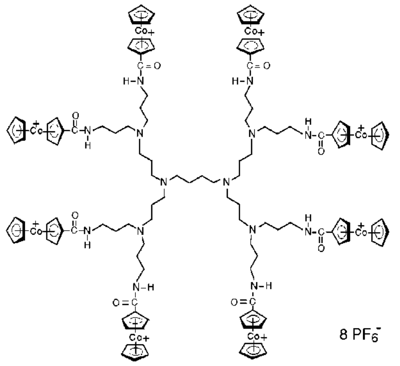


Fig. 1 Cyclic voltammetric behavior on glassy carbon (0.08 cm^2) of a solution containing 0.5 mM **1**, 0.1 M NaCl and (*a*) 0, (*b*) 5.0 and (*c*) 7.0 mM β-CD, and (*d*) 10 mM β-CD + 6.0 mM $Fc\text{-}N^+Me_3$. Scan rate: 0.100 V s^{-1}.



Scheme 1 Electrochemical activation of β-CD binding to dendrimer **1**.



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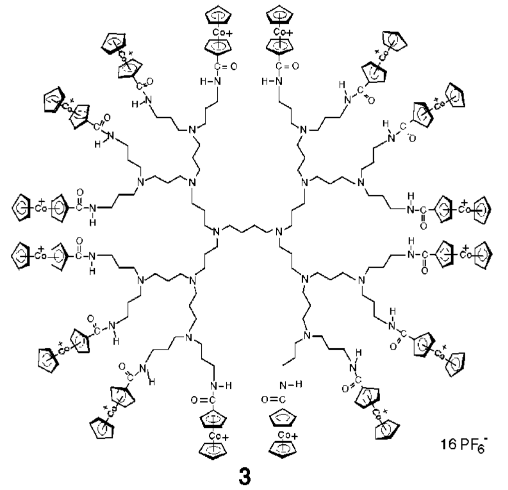

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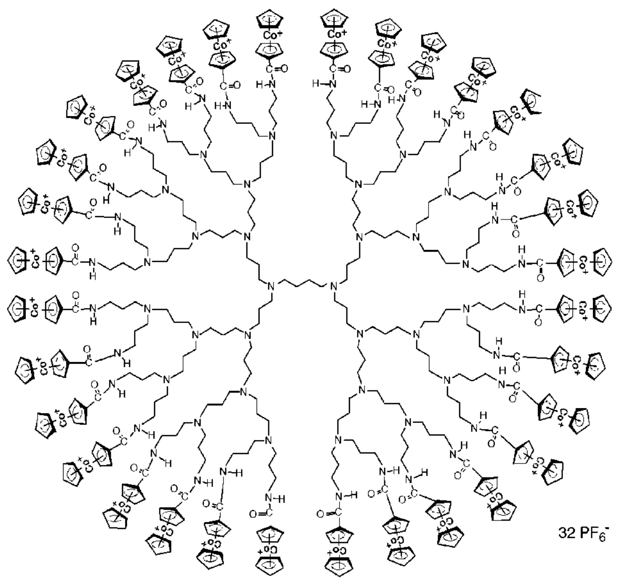

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chemical behavior of dendrimers **1**–**4** in 0.1 M NaCl is also characterized by the deposition on the electrode surface of their reduced forms, since electrochemical reduction of the peripheral cobaltocenium subunits transforms the highly charged dendrimer structures into very hydrophobic ones. For each dendrimer, all the cobaltocenium subunits are reduced around a single half-wave potential value (see Table 1). A typical cyclic voltammogram is shown in Fig. 1(*a*) (for **1**). Although the cathodic wave departs from the shape expected for a reversible reduction process, the sharp anodic wave clearly reveals the precipitation of the reduced form on the electrode surface. Addition of β-CD to this solution gradually eliminates the sharp anodic spike on the reverse scan [Fig. 1(*b*)]. In the presence of a four-fold excess of host (compared to the total concentration of cobaltocenium subunits in the solution), the cyclic voltammogram exhibits a shape consistent with a fully reversible process [Fig. 1(*c*)]. This finding clearly indicates the solubilization of the reduced form of the dendrimer by formation of inclusion complexes between the peripheral cobaltocene subunits and the freely diffusing β-CD hosts (see Scheme 1). In order to further prove this point, we performed additional experiments with a competing guest [(ferrocenylmethyl)trimethylammonium perchlorate, Fc-N$^+$Me$_3$·ClO$_4^-$]. This ferrocene derivative is an excellent guest for binding by β-CD[6] and competes with the dendrimer cobaltocene centers for the hosts present in the solution. This is confirmed by the voltammogram in Fig. 1(*d*), which shows that the addition of Fc-N$^+$Me$_3$ leads to the behavior (sharp anodic peak) associated with the precipitation of the reduced form of **1** on the electrode.

Although dendrimers **2** and **3** are less soluble than **1** in aqueous media (probably due to the hexafluorophosphate counterions) we performed voltammetric experiments with solutions containing 0.05 mM dendrimer and obtained comparable results. Dendrimers **1**–**3** in combination with β-CD constitute a novel type of host–guest system in which the formation of multisite β-CD–dendrimer complexes is driven by the reduction of the dendrimers. These systems afford an example of high molecular weight supramolecular assemblies which undergo association upon ‘electrochemical activation’ of the guest.

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