Organometallic ferrocenyl dendrimers: synthesis, characterization and redox properties

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A series of dendritic poly(aryl ether)s containing 3, 6, 12 and 24 ferrocene functionalities located exclusively at the peripheries of the dendritic structures have been synthesized using the stepwise convergent approach. The structures of these dendrimers have been characterized using $^1$H and $^{13}$C NMR spectroscopy. Cyclic and normal pulse voltammetric studies indicate that the ferrocenyl moieties located on the outer surfaces of these dendrimers are non-interacting redox centres, are electrochemically equivalent, and are oxidizable at the same potential. The results of controlled-potential coulometric oxidation show that nearly all the ferrocene residues in the dendrimers are accessible to electrode reactions.

Macromolecular materials with skeletons of transition-metal atoms in close proximity are attracting increasing attention because of their potentially interesting electrical, redox and optical characteristics. Among the organotransition-metal complexes, ferrocene has been shown to have excellent thermal and photochemical stability, and to undergo facile and reversible one-electron oxidation to ferrosoinum cation; the reaction leads to a marked change in electrical and spectroscopic properties and may be effected chemically, electrochemically or photochemically. Ferrocenyl-based polymers have been used in chemical modification of electrodes, in the construction of amperometric biosensors, and in the area of non-linear optical materials. Recently, dendritic macromolecules have received considerable attention because of their unique hyperbranched polymeric structure and well defined three-dimensional architectures. These dendritic macromolecules are characterized by a central polyfunctional core, from which arise successive layers of monomer units with branches occurring at each monomer unit. This results in a nearly entanglement-free hyperbranched structure that may adopt a spherical shape, the periphery of which consists of a large number of chain ends or surface functional groups. This unique macromolecular architecture allows precise control of molecule size, as well as of the disposition of the desired functionalities. The synthesis of well defined, highly branched macromolecules possessing functional components on their exterior surfaces, within their dendritic branches, and at their interior cores, giving rise to new materials with desirable properties has sparked much interest.

In this paper, we report full details on the synthesis, characterizations and redox behaviour of a family of dendritic poly(aryl ether) ethers that were synthesized using a stepwise convergent approach, and possess ferrocene functional groups located exclusively at the peripheries of their dendritic structures.

Experimental

Materials

Acetone was distilled from CaSO$_4$. Benzene was distilled from CaH$_2$. Tetrahydrofuran (THF) was distilled from Na/K alloy and benzophenone. n-Tetradecylammonium hexafluorophosphate (TBP$_{14}$Cl$_2$) was prepared as described previously and was purified by recrystallization three times from ethyl acetate and dried in vacuo at 60°C. 3-Ferrocenylpropanol$^{11}$ and 3,3-dihydroxybenzyl alcohol$^{12}$ were synthesized according to the reported procedures. Other commercially available chemicals were reagent grade and were used as purchased.

3-Bromopropylferrocene (Fc-G$_0$-Br)$^{13}$

To a solution of 3-ferrocenylpropionol (5.43 g, 22.3 mmol) and carbon tetrabromide (14.63 g, 46.6 mmol) in 10 ml of THF was added triphenylphosphate (11.53 g, 44 mmol). The reaction mixture was stirred at room temperature under nitrogen for 1 h. The resulting mixture was then poured into water and extracted with diethyl ether. The extract was dried over Na$_2$SO$_4$ and evaporated to dryness. The crude product was purified by column chromatography (SiO$_2$), eluting with 1:10 ethyl acetate-hexane, to give 4.67 g (69%) of Fc-G$_0$-Br as an orange oil.

$^1$H NMR (CDCl$_3$): 8 0.84 (s, CpCH$_3$), 3.42 (t, 2H, J = 6.3 Hz, CH$_2$), 4.07 (m, 4H, C$_3$H$_7$), 4.10 (s, 5H, C$_5$H$_5$), 5.38 (s, 15H, C$_6$H$_5$)$_3$. $^{13}$C NMR (CDCl$_3$): 8 27.91 (CH$_2$), 67.36, 68.14 (C$_3$H$_7$), 69.59 (C$_5$H$_5$), 87.28 (C$_6$H$_5$).

General procedure for the synthesis of Fc-G$_x$-OH ($x$ = 1, 2, 3)

A mixture of the appropriate Fc-G$_x$-Br ($x$ = 0, 1, 2) (2 equiv.), 3,3-dihydroxybenzyl alcohol (1 equiv.), potassium carbonate (3.5 equiv.) and 18-crown-6 (0.2 equiv.) in dry acetone was heated at reflux and stirred vigorously under nitrogen for 48 h. The mixture was allowed to cool, added to water and extracted with CH$_2$Cl$_2$ (3 ×). The combined extracts were dried over MgSO$_4$ and evaporated to dryness. The crude product was purified as outlined in the following text.

General procedure for the synthesis of Fc-G$_x$-Br ($x$ = 1, 2, 3)$^{13}$

To a solution of Fc-G$_x$-OH ($x$ = 1, 2, 3) (1 equiv.) in benzene was added dropwise PBr$_3$ (0.4 equiv.). The reaction mixture was stirred at room temperature under nitrogen for 4 h. For the latter generation ($x$ = 3), larger excesses of PBr$_3$ were required to force the reaction to completion. PBr$_3$ was added in 0.4 equiv. amounts at hourly intervals until TLC showed no starting material. The mixture was then added to water, neutralized with saturated aqueous NaHCO$_3$, and extracted with CH$_2$Cl$_2$ (3 ×). The combined extracts were dried over MgSO$_4$ and evaporated to dryness. The crude product was purified as outlined in the following text.

Fc-G$_x$-OH

This was prepared from Fc-G$_0$-Br and purified by column chromatography (SiO$_2$), eluting with 2:5 ethyl acetate-hexane.


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to give Fc-G1-OH (79%) as an orange solid. 1H NMR (DCDCl) δ 1.99 (m, 4H, CH2), 2.51 (t, 4H, J = 7.8 Hz, CH2), 3.96 (t, 4H, J = 6.5 Hz, CH2), 4.06 (m, 4H, CH2), 4.08 (m, 4H, CH2), 4.13 (t, 10H, CH2), 4.62 (t, 2H, J = 4.8 Hz, CH2OH), 5.76 (t, 1H, J = 2.0 Hz, ArH), 5.65 (d, 2H, J = 2.2 Hz, ArH). 13C NMR (DCDCl) δ 25.89 (CH2), 2.09 (s, 3H, CH3). This was prepared from Fc-G1-OH and purified by column chromatography (SiO2), eluting with 1.5-ethyl acetate-hexane to give Fc-G1-Br (85%) as an orange solid. 1H NMR (DCDCl) δ 1.98 (m, 4H, CH2), 2.51 (t, 4H, J = 7.8 Hz, CH2), 3.96 (t, 4H, J = 6.5 Hz, CH2), 4.06 (m, 4H, CH2), 4.08 (m, 4H, CH2), 4.11 (t, 10H, CH2), 4.42 (d, 2H, J = 4.8 Hz, CH2OH), 4.96 (s, 4H, ArCOCH2), 6.42 (2H, J = 2.0 Hz, ArH), 6.55 (d, 2H, J = 2.0 Hz, ArH), 6.57 (s, 1H, J = 1.0 Hz, J = 2.0 Hz, ArH), 6.57 (t, 1H, J = 2.0 Hz, ArH), 6.57 (s, 1H, J = 1.0 Hz, ArH). 13C NMR (DCDCl) δ 25.89 (CH2), 30.44 (CH2).

Dendrimer 1. This was prepared from Fc-G0-Br and purified by column chromatography (SiO2), eluting with 1:5 ethyl acetate-hexane to give dendrimer 1 (58%) as an orange solid. 1H NMR (DCDCl) δ 1.98 (m, 6H, CH2), 2.51 (t, 6H, J = 7.8 Hz, CH2), 3.95 (t, 12H, J = 6.3 Hz, CH2), 4.05 (m, 12H, CH2), 4.08 (m, 12H, CH2), 4.42 (t, 2H, J = 2.2 Hz, ArH), 4.96 (s, 4H, ArCOCH2), 6.42 (2H, J = 2.0 Hz, ArH), 6.67 (d, 4H, J = 2.8 Hz, ArH). This was prepared from Fc-G2-OH and purified by column chromatography (SiO2), eluting with 1:5:1 ethyl acetate-hexane to give dendrimer 1 (58%) as an orange solid. 1H NMR (DCDCl) δ 1.98 (m, 12H, CH2), 2.51 (t, 12H, J = 7.8 Hz, CH2), 3.95 (t, 12H, J = 6.3 Hz, CH2), 4.05 (m, 12H, CH2), 4.08 (m, 12H, CH2), 4.42 (t, 2H, J = 2.2 Hz, ArH), 4.96 (s, 4H, ArCOCH2), 6.42 (2H, J = 2.0 Hz, ArH), 6.67 (d, 4H, J = 2.8 Hz, ArH). This was prepared from Fc-G3-Br and purified by column chromatography (SiO2), eluting with 1:2 chloroform-hexane to give dendrimer 3 (41%) as an orange solid. 1H NMR (DCDCl) δ 1.97 (m, 24H, CH2), 2.51 (t, 24H, J = 7.8 Hz, CH2), 3.95 (t, 24H, J = 6.3 Hz, CH2), 4.05 (m, 24H, CH2), 4.08 (m, 24H, CH2), 4.42 (t, 24H, J = 2.2 Hz, ArH). This was prepared from Fc-G4-Br and purified by column chromatography (SiO2), eluting with 1:1 chloroform-hexane to give dendrimer 4 (33%) as an orange solid.

Dendrimer 2. This was prepared from Fc-G1-Br and purified by column chromatography (SiO2) to give Fc-G1-OH (79%) as an orange solid. 1H NMR (DCDCl) δ 1.99 (m, 4H, CH2), 2.51 (t, 4H, J = 7.8 Hz, CH2), 3.96 (t, 4H, J = 6.5 Hz, CH2), 4.06 (m, 4H, CH2), 4.08 (m, 4H, CH2), 4.11 (t, 10H, CH2), 4.42 (d, 2H, J = 4.8 Hz, CH2OH). This was prepared from Fc-G1-OH and purified by column chromatography (SiO2), eluting with 1:5:1 ethyl acetate-hexane to give dendrimer 2 (57%) as an orange solid. 1H NMR (DCDCl) δ 1.98 (m, 12H, CH2), 2.51 (t, 12H, J = 7.8 Hz, CH2), 3.95 (t, 12H, J = 6.3 Hz, CH2), 4.05 (m, 12H, CH2), 4.08 (m, 12H, CH2), 4.42 (t, 2H, J = 2.2 Hz, ArH), 4.96 (s, 4H, ArCOCH2), 6.42 (2H, J = 2.0 Hz, ArH), 6.67 (d, 4H, J = 2.8 Hz, ArH). This was prepared from Fc-G2-Br and purified by column chromatography (SiO2) to give Fc-G2-OH (79%) as an orange solid. 1H NMR (DCDCl) δ 1.99 (m, 4H, CH2), 2.51 (t, 4H, J = 7.8 Hz, CH2), 3.96 (t, 4H, J = 6.5 Hz, CH2), 4.06 (m, 4H, CH2), 4.08 (m, 4H, CH2), 4.11 (t, 10H, CH2), 4.42 (d, 2H, J = 4.8 Hz, CH2OH), 4.96 (s, 4H, ArCOCH2), 6.42 (2H, J = 2.0 Hz, ArH), 6.67 (d, 4H, J = 2.8 Hz, ArH). This was prepared from Fc-G3-Br and purified by column chromatography (SiO2) to give Fc-G3-OH (79%) as an orange solid. 1H NMR (DCDCl) δ 1.99 (m, 12H, CH2), 2.51 (t, 12H, J = 7.8 Hz, CH2), 3.95 (t, 12H, J = 6.3 Hz, CH2), 4.05 (m, 12H, CH2), 4.08 (m, 12H, CH2), 4.42 (t, 12H, J = 2.2 Hz, ArH), 4.96 (s, 12H, ArCOCH2), 6.42 (2H, J = 2.0 Hz, ArH), 6.67 (d, 12H, J = 2.8 Hz, ArH). This was prepared from Fc-G4-Br and purified by column chromatography (SiO2) to give Fc-G4-OH (79%) as an orange solid. 1H NMR (DCDCl) δ 1.97 (m, 24H, CH2), 2.51 (t, 24H, J = 7.8 Hz, CH2), 3.95 (t, 24H, J = 6.3 Hz, CH2), 4.08 (m, 24H, CH2), 4.08 (m, 24H, CH2), 4.42 (t, 24H, J = 2.2 Hz, ArH), 4.96 (s, 24H, ArCOCH2), 6.42 (2H, J = 2.0 Hz, ArH), 6.67 (d, 24H, J = 2.8 Hz, ArH). This was prepared from Fc-G5-Br and purified by column chromatography (SiO2) to give Fc-G5-OH (79%) as an orange solid. 1H NMR (DCDCl) δ 1.97 (m, 36H, CH2), 2.51 (t, 36H, J = 7.8 Hz, CH2), 3.95 (t, 36H, J = 6.3 Hz, CH2), 4.08 (m, 36H, CH2), 4.08 (m, 36H, CH2), 4.42 (t, 36H, J = 2.2 Hz, ArH), 4.96 (s, 36H, ArCOCH2), 6.42 (2H, J = 2.0 Hz, ArH), 6.67 (d, 36H, J = 2.8 Hz, ArH).
Scheme 1. This was made on the base of the Williamson ether spectroscopy is particularly crucial in confirming the structures of the dendritic macromolecules. The ferrocene-terminated dendritic wedges are illustrated in Scheme 1. This was made on the base of the Williamson ether synthesis for the formation of aryl ether from phenol and benzyl chloride (or alkyl bromide). We used 3,5-dihydroxybenzyl alcohol as the monomer unit. The ferrocene groups were introduced to the peripheries of the growing dendrimers by coupling two molecules of 3-bromopropyl ferrocene Fc-G0-Br to the phenolic groups of the monomer unit in the presence of potassium carbonate and 18-crown-6 in refluxing acetone, thereby obtaining the first generation alcohol Fc-G1-OH. We selected γ-propyldieneprocarne as the terminal group because bromomethylferrocene, which is an α-functional ferrocene derivative, is hydrolytically unstable and readily converted to ferrocenemethanol, and 2-bromomethylferrocene undergoes elimination during the alkylation reaction, producing vinylferrocene. The bromide Fc-G0-Br was obtained by bromination of 3-ferrocenylpropanol, which was prepared according to the literature procedures. Bromination of Fc-G1-OH with PBr3 restored the reactive bromomethyl functionality at the focal point of the dendritic wedge to give the corresponding bromide Fc-G1-Br. Reaction of Fc-G1-Br with 3,5-dihydroxybenzyl alcohol resulted in the formation of the next-generation bromide Fc-G2-Br, and subsequent bromination of Fc-G2-Br with PBr3 gave the second generation bromide Fc-G2-Br2. Repeated alkylation and bromination led to the third generation alcohol Fc-G3-OH and the bromide Fc-G3-Br. In the convergent approach, the dendritic wedges obtained are attached to a polyfunctional core. The polyfunctional core we chose was 1,1,1-tris(4-hydroxyphenyl)ethane. Coupling reactions of the phenolic groups of the core molecule with each bromide generation, from Fc-G0-Br to Fc-G3-Br, as shown in Scheme 2, were carried out. Thus, a family of dendritic poly(aryl ether)s, dendrimers 1, 2, 3 and 4, containing 3, 6, 12 and 24 ferrocene functionalities, respectively, at their peripheries were obtained. The products were purified by column chromatography, and their purities were evaluated by 1H and 13C NMR spectroscopy. No signal of the starting materials was detected in the NMR experiments.

Results and Discussion

Synthesis of dendritic macromolecules

A series of poly(aryl ether) dendrimers containing ferrocene functional groups located at the peripheries of their dendritic structures were prepared using the convergent approach developed by Haver and Fichten. The synthetic route to the ferrocene-terminated dendritic wedges is illustrated in Scheme 1. This was made on the base of the Williamson ether synthesis for the formation of aryl ether from phenol and benzyl chloride (or alkyl bromide). We used 3,5-dihydroxybenzyl alcohol as the monomer unit. The ferrocene groups were introduced to the peripheries of the growing dendrimers by coupling two molecules of 3-bromopropyl ferrocene Fc-G0-Br to the phenolic groups of the monomer unit in the presence of potassium carbonate and 18-crown-6 in refluxing acetone, thereby obtaining the first generation alcohol Fc-G1-OH. We selected γ-propyldieneprocarne as the terminal group because bromomethylferrocene, which is an α-functional ferrocene derivative, is hydrolytically unstable and readily converted to ferrocenemethanol, and 2-bromomethylferrocene undergoes elimination during the alkylation reaction, producing vinylferrocene. The bromide Fc-G0-Br was obtained by bromination of 3-ferrocenylpropanol, which was prepared according to the literature procedures. Bromination of Fc-G1-OH with PBr3 restored the reactive bromomethyl functionality at the focal point of the dendritic wedge to give the corresponding bromide Fc-G1-Br. Reaction of Fc-G1-Br with 3,5-dihydroxybenzyl alcohol resulted in the formation of the next-generation bromide Fc-G2-Br, and subsequent bromination of Fc-G2-Br with PBr3 gave the second generation bromide Fc-G2-Br2. Repeated alkylation and bromination led to the third generation alcohol Fc-G3-OH and the bromide Fc-G3-Br. In the convergent approach, the dendritic wedges obtained are attached to a polyfunctional core. The polyfunctional core we chose was 1,1,1-tris(4-hydroxyphenyl)ethane. Coupling reactions of the phenolic groups of the core molecule with each bromide generation, from Fc-G0-Br to Fc-G3-Br, as shown in Scheme 2, were carried out. Thus, a family of dendritic poly(aryl ether)s, dendrimers 1, 2, 3 and 4, containing 3, 6, 12 and 24 ferrocene functionalities, respectively, at their peripheries were obtained. The products were purified by column chromatography, and their purities were evaluated by 1H and 13C NMR spectroscopy. No signal of the starting materials was detected in the NMR experiments.

Characterization

The ferrocene-terminated dendrimers were characterized structurally using 1H and 13C NMR spectroscopy. 1H NMR spectroscopy is particularly crucial in confirming the structures produced by our synthetic strategy. 1H NMR spectra showed the exterior functional group gave five sets of resonances at δ 4.10 (3H, t, J = 8.7 Hz, CH2(Cp)), 4.08, 4.05 (4H, t, J = 8.7 Hz, core ArH), 3.95 (1H, t, J = 8.7 Hz, core ArH). 13C NMR (CDCl3) δ 25.89 (CH2), 30.47 (CpCH3), 67.21 (C(CH3)), 67.33 (CH2O), 67.71 (CH2O), 100.89, 105.79, 115.52, 138.94, 160.10, 160.36, 160.48 (Ar and ArC).
Dendritic wedges were attached to the core molecule 1,1,1-tris(4-hydroxyphenyl)ethane, two doublets of the aromatic rings of the core moiety were observed at δ 6.87 and 7.02, and were not obscured by the aromatic resonances of the dendritic wedges; the methyl group of the core resonated at δ 2.11. Integration data for the exterior ferrocene groups, the internal aromatic groups, and the aromatic rings of the core moiety confirmed the structures and the generation numbers of the dendrimers. The $^{13}$C NMR spectra provided further support for the structural assignments. Each of the different carbon resonances was found to agree with the observed spectral resonances.

**Electrochemistry**

Electrochemistry studies of the ferrocene dendrimers in CH$_2$Cl$_2$ solutions containing 0.1 mol dm$^{-3}$ TBAPF$_6$ as the supporting electrolyte were performed. Cyclic voltammograms of 1 and 2 show the characteristics of a reversible one-electron oxidation, with production of soluble, stable cations. However, with 3 and 4 a stripping peak appeared on scan reversal. The shape of the reduction peak indicated that the oxidized products were insoluble and accumulated on the electrode’s surface. The precipitation problems led us to use the normal pulse voltammetry (NPV) technique, which is less susceptible to problems of adsorption and precipitation as a means of determining the wave parameters.
of the oxidized product. The effects of absorbed reactants and products on the plateau currents and half-wave potentials in normal pulse voltammograms have been reported by Anson et al.\textsuperscript{13} In the absence of an independent determination, it is difficult to deduce the presence of product adsorption from normal pulse voltammograms. However, the appearance of a peak current in the voltammogram recorded in the reverse-scan direction verifies the occurrence of adsorption. Indeed, for dendrimer 3 there is a peak current recorded in the reverse-scan voltammogram, as shown in Fig. 1B.

In order to reduce perturbations in the shape of normal pulse voltammograms induced by adsorption, we used a mixed solvent, 3:5 CH\(_3\)CN–CH\(_2\)Cl\(_2\) in the electrochemical studies, where the adsorption of the dendrimers and their oxidized products was minimized. Fig. 2 shows the cyclic voltammogram of the ferrocene-terminated dendrimers in the mixed solvent containing 0.1 mol dm\(^{-3}\) TBAPF\(_6\) as the supporting electrolyte. The cyclic voltammogram of each dendrimer exhibits a single reversible oxidation wave corresponding to oxidisation of the exterior ferrocene groups. The peak current is linearly proportional to the square root of the scan rate; the peak shape is symmetrical, with \(i_{\text{pa}}/i_{\text{pc}} \approx 1\), and \(E_{\text{pa}}\) is independent of the scan rate. The peak potential separation \(\Delta E_p\) is ca. 59 mV for dendrimers 1 and 2, 52 mV for 3 and 50 mV for 4. The smaller \(\Delta E_p\) values for dendrimers 3 and 4 may be attributable to minor adsorption of the dendrimers (or oxidation products) on the electrode surface. The half-wave potentials \(E_{1/2}\) and \(\Delta E_p\) obtained from the cyclic voltammograms are given in Table 1. Note that the sharp anodic or cathodic peak current due to the adsorption of reactant or product is not observed in the mixed solvent system. The electrochemical properties of the dendrimers were also studied using the NPV technique. Normal pulse voltammograms of the dendrimers are displayed in Fig. 3. The half-wave potentials, limiting diffusion currents \(i_{\text{lim}}\), and slopes of \(E_{\text{pa}}\) vs. \(\log(i_{\text{lim}})\) plots, obtained from the normal pulse voltammograms are given in Table 1. The \(E_{1/2}\) values, as determined by NPV, are similar to those determined by cyclic voltammetry. Interestingly, the \(E_{1/2}\) values for the ferrocene redox couples remain essentially constant upon successive generation build up. This can be explained by noting that the ferrocene functional groups are located on the outer surfaces of the dendrimers and their microenvironments are independent of dendrimer generation. This result is in contrast to the recent observation by Diederich et al.\textsuperscript{14} that for zinc porphyrin dendrimers the redox potential shifts as generations build up. Because the redox group is located in the interior of the porphyrin macrocycle, the electrophore environment, as well as the redox potential of the zinc porphyrin, changes markedly with increasing generation number. (The effects of absorbed reactants and products on the plateau currents and half-wave potentials in normal pulse voltammograms have been reported by Anson et al.\textsuperscript{13})

Fig. 2 Cyclic voltammograms for A, 200 \(\mu\)mol dm\(^{-3}\) of 1; B, 100 \(\mu\)mol dm\(^{-3}\) of 2; C, 50 \(\mu\)mol dm\(^{-3}\) of 3; and D, 25 \(\mu\)mol dm\(^{-3}\) of 4 in 0.1 mol dm\(^{-3}\) TBAPF\(_6\)–3:5 CH\(_3\)CN–CH\(_2\)Cl\(_2\). Scan rate 60 mV s\(^{-1}\).

Fig. 3 Normal pulse voltammograms for the oxidation of A, 200 \(\mu\)mol dm\(^{-3}\) of 1; B, 100 \(\mu\)mol dm\(^{-3}\) of 2; C, 50 \(\mu\)mol dm\(^{-3}\) of 3; and D, 25 \(\mu\)mol dm\(^{-3}\) of 4 in 0.1 mol dm\(^{-3}\) TBAPF\(_6\)–3:5 CH\(_3\)CN–CH\(_2\)Cl\(_2\). Scan rate 20 mV s\(^{-1}\), sample width 17 ms; pulse width 50 ms.

Table 1 Results of cyclic voltammetry, normal pulse voltammetry and controlled-potential electrolysis for the oxidation of ferrocene-terminated dendrimers 1–4\textsuperscript{a, b, c}

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<th>(E_{\text{pc}}) (mV)</th>
<th>(\Delta E_p) (mV)</th>
<th>slope (mV)</th>
<th>(i_{\text{lim}}) ((\mu)A)</th>
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\textsuperscript{a}Experimental conditions are given in the captions to Fig. 2 and 3. \textsuperscript{b}By cyclic voltammetry. \textsuperscript{c}By normal pulse voltammetry. \textsuperscript{d}Slope of plot of \(E_{\text{pa}}\) vs. \(\log(i_{\text{lim}})\). \textsuperscript{e}The electrolysis solutions were 5 mL, and the concentration of each solution was as indicated in the captions to Fig. 2 and 3. Values are an average of three independent determinations, and standard deviations are listed in parentheses. \textsuperscript{f}Number of ferrocenes per molecule oxidized.
these dendrimers are equivalent, non-interacting and exchange electrons with the electrode in waves characteristic of one-electron transfer processes.

To evaluate the number of electrons transferred during oxidation without knowing the relative diffusion coefficients, controlled-potential electrolyses were carried out. Coulometric oxidation of the dendrimers was performed at a large-area platinum gauze electrode in a CH₂Cl₂-CH₂CN mixture at $E_{app}$ 150 mV more positive than the respective anodic potential. The results are given in Table 1. It is shown that values of $n_p$, the number of electrons per molecule consumed in the oxidation, calculated from the total number of coulombs, come close to matching the number of ferrocenyld groups anticipated in the synthetic strategy bound to the chain-ends of these dendrimers. Note that the values of $n_p$ obtained for 3 and 4 are somewhat smaller than the number of ferrocenyld groups attached to these dendrimers. This may have been because the rate of electron transfer of dendrimers 3 and 4 slowed drastically near the end of coulometric oxidation, and at the time the controlled-potential electrolysis was stopped, the ferrocene redox groups that were bound to the dendrimers in the solution were not totally oxidized.

**Conclusion**

Using the stepwise convergent approach we have synthesized a series of dendritic poly(aryl ether) mers that contain 3, 6, 12 and 24 ferrocene functionalities located exclusively at the peripheries of their dendritic structures. The structures of these dendrimers were characterized using $^{1}H$ and $^{13}C$ NMR spectroscopy. The results of electrochemical studies show that electron transfers from the dendritic macromolecules yielded voltammetric waves with shapes matching those of corresponding molecules with electroactive centres, but with magnitudes determined by the total number of redox centres present. On the basis of this observation, we conclude that the ferrocenyl moieties located on the outer surfaces of these dendrimers are non-interacting redox centres and are electrochemically equivalent and oxidizable at the same potential. This fully reversible multi-electron redox system may be useful for multi-electron redox catalysis.

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**References**


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