Synthesis and Electrochemistry of Octamethylferrocenyl-Functionalized Dendrimers

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New octamethylferrocenyl dendritic macromolecules are reported. The condensation reaction of octamethylferrocenyl aldehyde (**1**) with dendritic polyamines DAB-*dend*-$(NH_2)_x$ ($x = 4, 8, 16, 32$) affords up to the fourth generation of the octamethylferrocenylimine dendrimers DAB-*dend*-$(N{=}CHFc^{\#})_x$ ($x = 4, 8, 16, 32$) (**2**−**5**). Reduction of the imine groups leads to the corresponding octamethylferrocenylmethylamine dendrimers DAB-*dend*-$(NHCH_2Fc^{\#})_x$ (**6**−**9**) with 4, 8, 16, and 32 octamethylferrocenyl units per molecule, respectively. Characterization of the synthesized dendrimers by ^1H and $^{13}C\{^1H\}$ NMR and IR spectroscopy, mass spectrometry, and elemental analysis supports their assigned structures. The redox activity of the octamethylferrocenyl centers in **6**−**9** has been characterized by cyclic voltammetry. Solution electrochemical studies showed that all the octamethylferrocenyl redox centers attached to the dendritic surface are electrochemically independent and that, in CH_2Cl_2 as solvent, the neutral dendrimers undergo oxidative precipitation onto the electrode surfaces.

Introduction

Metal-containing dendrimers are an evolving class of macromolecules.[1] The interest in developing these materials resulted from the fact that the introduction of metals into dendritic structures allows access to highly ordered materials with attractive magnetic, electronic, and photo-optical properties. In particular, the incorporation of organometallic entities on the surface or within the dendritic structures represents a stimulating, challenging target in both organometallics and dendrimers research because it provides a unique opportunity for tailoring organometallic dendrimers to achieve desirable properties for well-defined applications (for example, as dendritic catalysts, in multielectron redox and photocatalytic processes, as molecular sensors, and others).[2]

Ferrocene and its various derivatives have found application in many fields such as synthetic organic chemistry, materials science, and catalysis,[3] and more recently it has emerged that ferrocenyl groups may be also advantageously used as redox centers in multiresponsive electrochemically active dendrimers.[4]

In the last few years we have prepared ferrocene-functionalized dendrimers by surface functionalization of silicon- and amine-based dendritic structures.[5] Some of these dendritic molecules have been used successfully in the modification of electrode surfaces,[6] as electron-transfer mediators in amperometric biosensors,[7] as exo-receptors for sensing anions,[8] and also, as effective guests for the formation of supramolecular complexes with β-cyclodextrin.[9]

While dendrimers containing ferrocenyl moieties are numerous, dendrimers decorated with permethylferrocenyl units have

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been relatively less explored.[10] The main reason for this underdeveloped chemistry is the synthetic difficulties that one encounters when trying to adapt from ferrocene chemistry well-established synthetic transformations. However, organometallic compounds containing polymethylcyclopentadienyl ligands are interesting since they often exhibit significantly different properties than their nonmethylated analogues.[11] As a result of the enhanced donor properties of the polymethylated cyclopentadienyl rings, polymethylferrocenyl derivatives exhibit lower redox potentials, and for this reason electrode surfaces functionalized with these materials have shown to be of importance in electrocatalysis; for instance, electrode surfaces modified with polymethyl ferrocene derivatives can be used as sensors for cytochrome c[12] and in the amperometric determination of hydrogen peroxide.[13]

The desire for ferrocene-based dendrimers having a redox potential more negative than that of ferrocene ones has prompted us to synthesize a series of octamethylferrocene dendrimers.

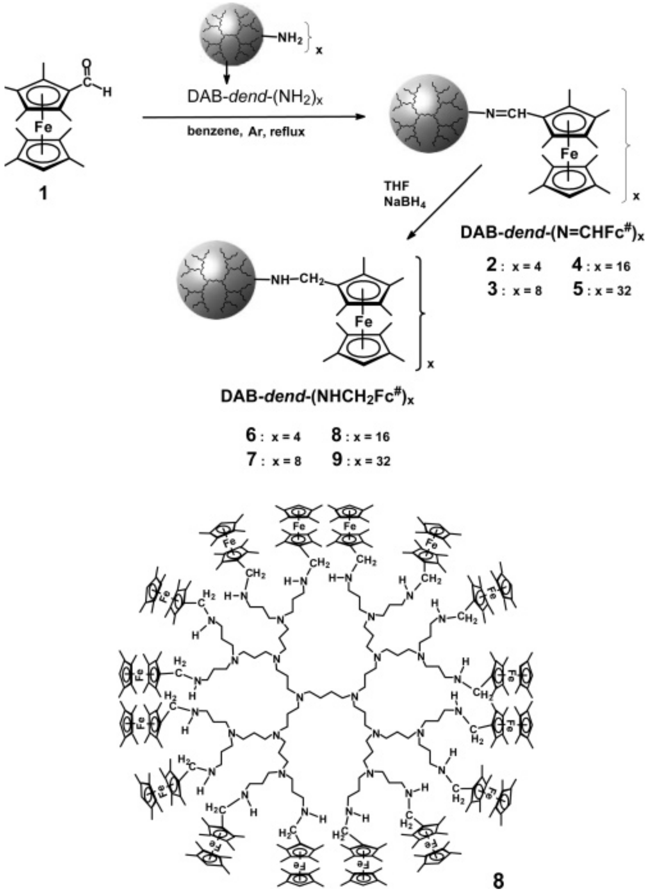
Here we report on the synthesis and redox properties of novel metallodendrimers containing octamethylferrocenyl units, which to our knowledge, constitute the ferrocenyl dendrimer family exhibiting the lowest redox potential to date.

Results and Discussion

Synthesis and Characterization of Dendrimers. Our first approach to incorporate octamethylferrocenyl-containing organometallic units into amine dendrimeric polyfunctional cores is shown in Scheme 1. In a first step, dendritic polyamines DAB-*dend*-$(NH_2)_x$ ($x = 4, 8, 16, 32$) in benzene were each added dropwise to a stirred benzene solution of the corresponding equivalents of octamethylferrocenyl aldehyde **1**,[12a] under argon at room temperature, and then refluxed (Scheme 1).

The condensation reactions were completed within 6 h for the first generation, whereas approximately 24 h was needed using the fourth generation, as indicated by the solution IR spectrum of the reaction mixture, which showed the disappearance of the band at 1670 cm^{-1} due to the starting (CO) group and the appearance of a new absorbance near 1640 cm^{-1} corresponding to the formation of the imine group (C═N). After appropriate workup, the products were purified by precipitation in cold hexane to afford DAB-*dend*-$(N{=}CHFc^{\#})_x$[14] ($x = 4$, 8, 16, 32) (**2**−**5**), which were isolated in high yields (80−85%) as reddish-orange, tacky oils.

Scheme 1. Synthesis of Octamethylferrocenyl Dendrimers



The structural identities of the octamethylferrocenylimine dendrimers were confirmed by ^1H NMR spectroscopy. The ^1H NMR spectra of **2**−**5** show the signals of the poly(propylene imine) dendritic framework and the key signals arising from the octamethylferrocenyl fragments, which are observed in the range δ 2.11−1.68 ppm. The completion of the condensation reaction was indicated by the total absence, in the ^1H NMR spectra, of the NH_2 signals of the starting dendritic polyamines around δ 1.3 ppm, as well as by the appearance of a new signal at low field in the range δ 8.36−8.41 ppm due to the methylidene group. In addition, estimations based on the signal intensities also confirm the complete functionalization of the NH_2 end groups of the starting dendritic polyamines.

The instability of the resulting imines toward hydrolysis is a problem when using them in electrochemical studies in solution. In order to avoid it, one can hydrogenate imines to yield the parent amines, which would be much more stable.

The hydrogenation of **2**−**5** with $NaBH_4$ in freshly distilled THF (see Scheme 1) yields the corresponding octamethylferrocenylmethylamine dendrimers DAB-*dend*-$(NHCH_2Fc^{\#})_4$ (**6**), DAB-*dend*-$(NHCH_2Fc^{\#})_8$ (**7**), DAB-*dend*-$(NHCH_2Fc^{\#})_{16}$ (**8**), and DAB-*dend*-$(NHCH_2Fc^{\#})_{32}$ (**9**) as yellow solids or orange-yellow, shiny solids. Longer reaction times are required in the imine group reduction reaction as the dendrimer generation increases and it goes from 6 to 12 h. This approach paralleled closely the

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(14) The nomenclature of these octamethylferrocenyl poly(propylene imine) dendrimers is DAB-*dend*-$(N{=}CHFc^{\#})_x$, where DAB = (diaminobutane) is the dendritic core and $Fc^{\#} = \{\eta^5\text{-}C_5(CH_3)_4H\}Fe\{\eta^5\text{-}C_5(CH_3)_4\}$ are the terminal groups.

synthetic procedure reported by Jutzi et al. for nonmethylated ferrocenyl imine dendrimers.[15]

We have also attempted an alternative synthetic route, which involves a nucleophilic attack on the octamethylferrocenylmethyl carbocation ($Fc^{\#}CH_2^+$).[12a] The facile reaction of this carbocation with various nucleophiles would provide an interesting method for peripheral modification of polyamine dendrimer backbones with octamethylferrocene derivatives. Nevertheless, attempts to prepare dendrimers **6**−**9** were unsuccessful. When solutions of poly(propylene imine) dendrimers in dry Et_2O were added dropwise to a suspension of the red octamethylferrocenylmethyl carbocation, a green solution was formed, probably due to the dimerization of the carbocation to a green paramagnetic species (1,2-bis(octamethylferroceniumyl)ethane).[12a]

The structures of the novel metallodendritic complexes **6**−**9** were straightforwardly determined on the basis of ^1H and $^{13}C\{^1H\}$ NMR spectroscopy, matrix-assisted laser desorption ionization time-of-flight mass spectrometry (MALDI-TOF), and elemental analysis. In the ^1H NMR spectra, the methylidene signal disappears when **2**−**5** are hydrogenated, and the corresponding methylene signal appears at high field in the 3.5−3.7 ppm range. Two peaks representative of the dendrimer methylene protons occur between 2.44 and 2.75 ppm, whereas the other methylene peaks are eclipsed by the methyl peaks in the range 1.9−1.6 ppm. In the spectra of the larger compounds the different signals of the dendritic methylene groups are no longer distinguishable. Only the signals of the respective octamethylferrocenyl units and of their α methylene groups could be separated and appear in the expected region.

The structures of the first- and second-generation dendrimers **6** and **7** were corroborated by matrix-assisted laser desorption and ionization time-of-flight mass spectrometry. The main peaks of the spectra are singly charged molecular ions at *m*/*z* 1557.0 (Figure 1A) and 3255.5 (Figure 1B), respectively, which correspond to the correct molecular mass. In addition, peaks arising from the loss of $C_5(CH_3)_4H$ (*m*/*z* 121.2) and $CH_2Fc^{\#}$ (*m*/*z* 311.2) units are observed. There are no peaks present that could be attributed to partially octamethylferrocenyl-functionalized compounds.

MALDI-TOF-MS studies performed for the third- and fourth-generation dendrimers were less conclusive, as no molecular ions for this type of generations could be generated and analysis of dendrimers **8** and **9** proved unsuccessful under the conditions used. However, this is not due to an ill-defined structure, as can be derived from the other characterization techniques. Most likely, this was due to a fast in situ loss of the $[\{C_5(CH_3)_4H\}Fe\{C_5(CH_3)_4\}CH_2]^+$ fragment under the experimental conditions, since the spectra of **8** and **9** displayed the most intensive peaks at *m*/*z* 311.2, which was attributed to this fragment. Modification of the laser fluence does not change this behavior. We assume that this fragmentation occurs under the ionizing conditions of the MALDI-TOF analysis.[16] Attempts to generate molecular ion data by electrospray ionization spectrometry (ESI-MS) were unsuccessful for all the octamethylferrocenyl dendrimers.

Electrochemical Behavior. The electrochemical behavior of the synthesized octamethylferrocenylmethylamine dendrimers **6**−**9** has been investigated by cyclic voltammetry (CV) and differential pulse voltammetry (DPV) of the materials in homogeneous solution, as well as confined to electrode surfaces (i.e., where the dendrimers serve as electrode modifiers). For all generations of this dendritic family a single redox process is observed in CH_2Cl_2 (Figure 2) or tetrahydrofuran with a formal potential of about 0.04 V vs SCE. This potential is considerably more negative (about 0.45 V) than those exhibited by analogous nonmethylated ferrocenyl dendrimers in the same medium[15] (0.02−0.05 V vs Fc/Fc$^+$ equals 0.48−0.51 V vs SCE). This fact is the result of the electron-donating effect of the eight methyl groups of the ferrocene rings.

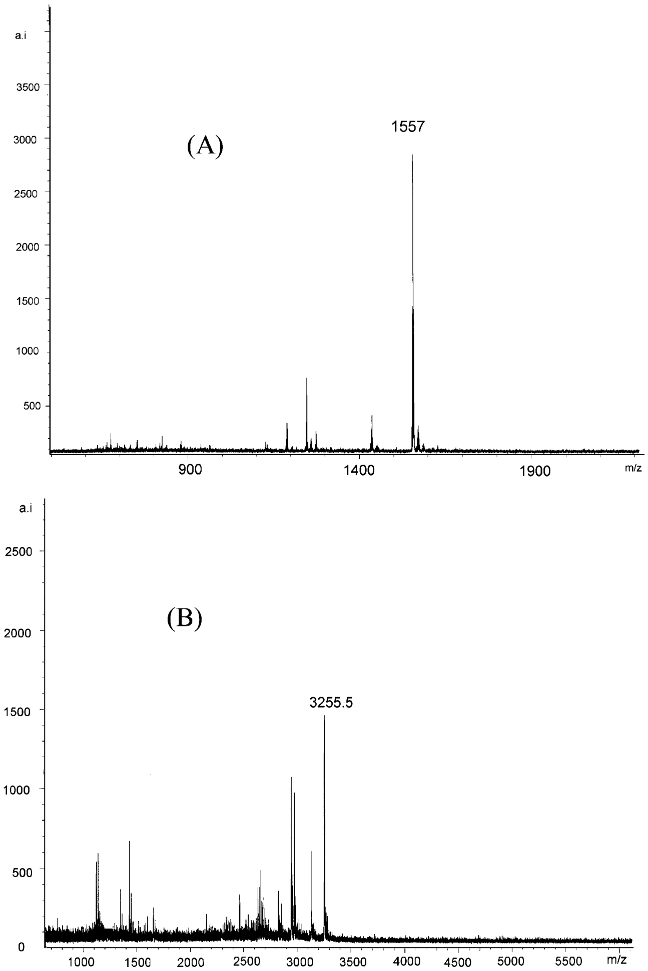

Figure 1. MALDI-TOF-MS of the octamethylferrocenylmethylamine dendrimers **6** (A) and **7** (B).

Differential pulse voltammograms (Figure 3) of the four dendrimers show a single wave at about 0.03 V vs SCE. These peak potential values are in accordance with the $E_{1/2}$ values obtained from cyclic voltammetry, taking into account that $E_{1/2} = E_{pk} + E_{pulse}/2$ (E_{pulse}, pulse height).

The fact that only a single redox process is observed implies simultaneous multielectron transfers at the same potential of the 4, 8, 16, and 32 octamethylferrocenyl units in **6**, **7**, **8**, and **9**, respectively, and indicates that the iron centers are essentially noninteracting in these dendrimers.[17]

A valuable feature of these organometallic dendrimers is their ability to modify electrodes, resulting in electroactive material that remains persistently attached to the electrode surface. The deposition of the dendrimers can be carried out onto Pt or GC electrodes, and presumably other materials, either by controlled potential electrolysis at 0.25 V or by repeated cycling between

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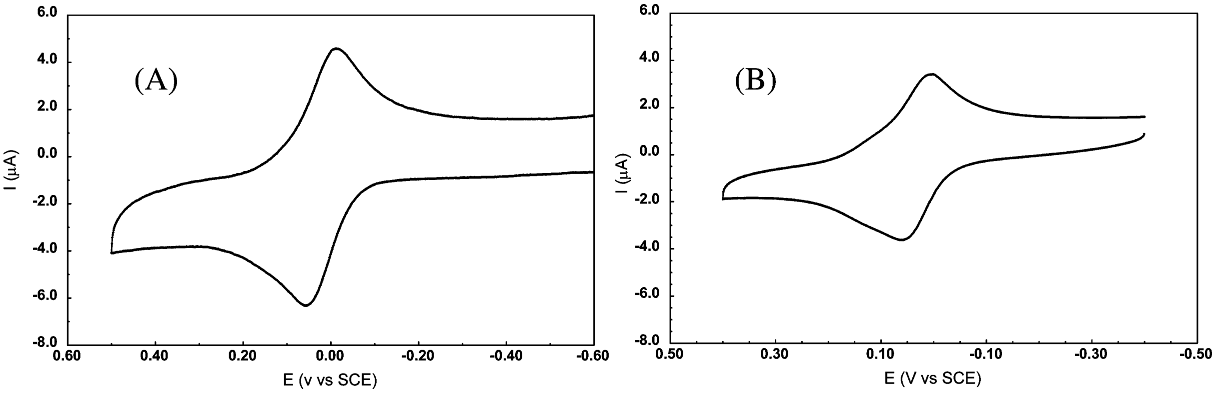

Figure 2. Cyclic voltammograms of the octamethylferrocenylmethylamino dendrimers **6** (A) and **9** (B) in CH_2Cl_2/TBAH at 100 mV s^{-1}.

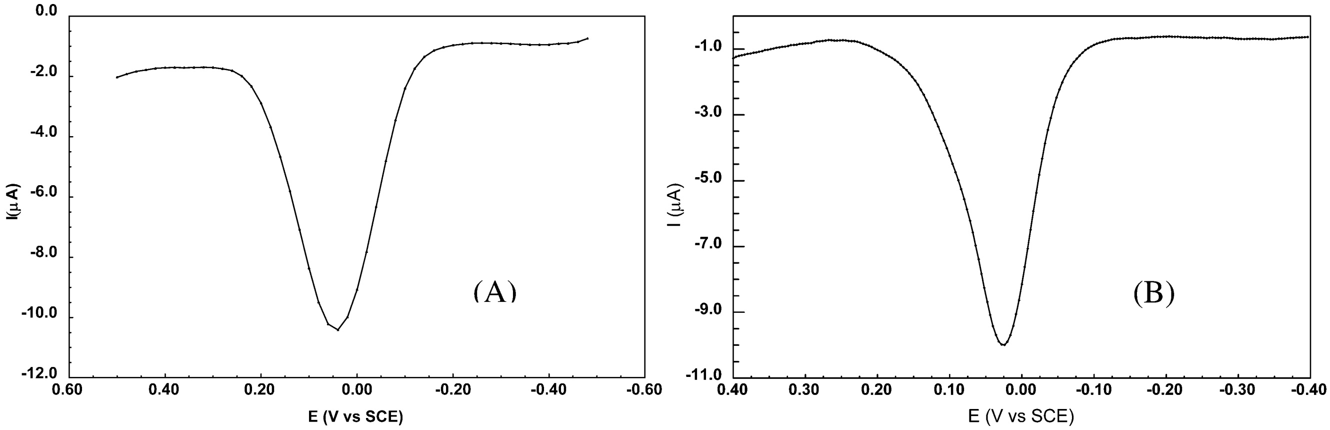

Figure 3. Differential pulse voltammograms of **6** (A) and **9** (B) recorded in CH_2Cl_2/TBAH using a glassy-carbon working electrode, GC.

−0.4 and 0.4 V versus SCE in degassed solutions of the dendrimer in CH_2Cl_2. Thus, the amount of electrodeposited material can be controlled through the time interval during which the potential was held fixed or the number of scans.

The redox behavior of films of the dendrimers electrodeposited onto electrode surfaces was studied by CV in fresh CH_2Cl_2, CH_3CN, and H_2O solutions containing only the supporting electrolyte. In all cases a well-defined symmetrical oxidation−reduction wave corresponding to the octamethylferrocene/octamethylferricinium couple is observed, with a formal potential value $E_{1/2}$ of about 0.10 V. The wave shape is typical of a surface-confined reversible couple with the expected linear relationship of peak current to potential sweep rate, v, for values up to 500 mV s^{-1}.[18] The voltammetric response of a film of dendrimer **7** is shown in Figure 4 as a representative example. The peak to peak separation values (ΔE_{pk}) are 40 mV at 50 mV s^{-1} and 60 mV at a scan rate of 200 mV s^{-1}. ΔE_{pk} increases with film thickness; however, at low coverages it remains equal to 60 mV over the sweep rate range 200−500 mV s^{-1}.

It should be noted that stable films of octamethylferrocenylmethylamine dendrimers can also be formed on electrode surfaces by a simple soaking procedure. If, after coming into contact with the dendrimer solution (i.e., no applied potential) during a short time, the electrode is transferred to a fresh electrolyte/CH_2Cl_2 solution containing no dendrimer, both peaks (anodic and cathodic) corresponding to the oxidation−reduction of the ferrocene centers of the immobilized dendrimers were observed on the potential scan. This indicates that the dendrimers in solution adsorb on Pt or GC electrodes in a manner analogous to DAB-*dend*-Fc_x[19] and polyamidoamine dendrimers surface-funcionalized with polypyridyl metal complexes.[20] The rate of these adsorption processes increases in the order **6** < **7** < **8** < **9** for dendrimer concentrations in the same range. Thus it is not possible to obtain cyclic voltammograms of **9** at bare electrodes, because the modification of the surface electrode in this case takes place in the voltammetry time scale. The cyclic voltammograms of dendrimers **8** and **9** in solution display a small pair of anodic and cathodic peaks (see for example Figure 2B), whose potential peaks are coincident with those of the surface-deposited dendrimer.

One of the most remarkable features of electrodes modified with films of these octamethylated dendrimers is that they are extremely durable and reproducible. In fact, the shape of the features in the cyclic voltammograms is independent of the scan rate from 5 to 1000 mV s^{-1}, and repeated scanning in CH_2Cl_2 electrolyte solutions does not change the voltammograms, demonstrating that films of different generations are stable to electrochemical cycling. Likewise, after standing in air for several weeks, the redox response was practically unchanged with no loss of electroactivity. The high stability of these surface-confined poly(octamethylferrocenyl) dendrimer films is an important observation since the applications of modified electrodes require extensive redox cycling.

The microstructure of a film of dendrimer **7** electrochemically deposited on a Pt wire by cyclic voltammetry was examined

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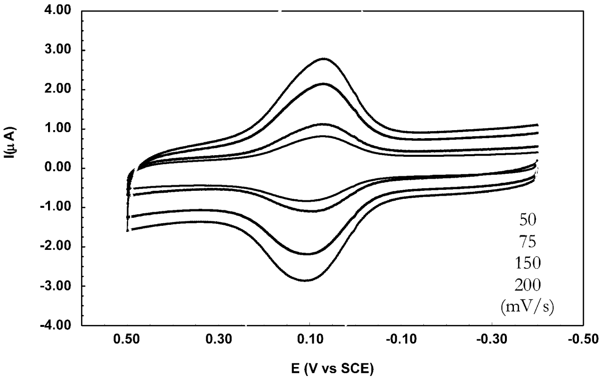

Figure 4. Voltammetric response of a GC-disk electrode modified with a film of dendrimer **7**, measured in CH_2Cl_2/TBAH.

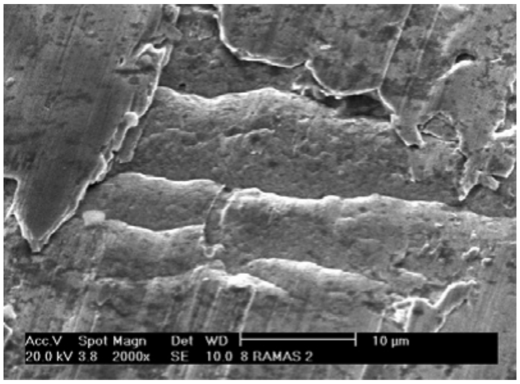

Figure 5. Scanning electron micrograph of a film of dendrimer **7** on a Pt wire electrode (0.25 mm of diameter).

by scanning electron microscopy. The SEM micrograph in Figure 5 shows a sheetlike compact morphology and exhibits small agglutinations and some porosity.

Some of these dendritic molecules have been used successfully as electron-transfer mediators in amperometric biosensors.[13] Electrodes modified with polymethylferrocenyl dendrimers have been shown to promote the redox reactions of hydrogen peroxide. As expected, the polymethylated ferrocene dendrimeric mediators allow using lower working potentials than those employed with nonmethylated ferrocene compounds.

Preliminary data show that electrodes modified with octamethylferrocenylmethylamine dendrimers appear to be sensitive to the presence of dihydrogenphosphate anion since a shift of the anodic peak to less positive potentials is observed (ca. 195 mV for the fourth generation in the presence of 2×10^{-5} M $[n\text{-}Bu_4N][H_2PO_4]$), which suggests that these modified electrodes could potentially be used as redox-responsive receptor systems for anion recognition.[21] Work in this direction in now underway and will be reported in future publications.

Conclusions

A novel evaluation of the reactivity of the surface functionalities of the NH_2-terminated dendrimers toward organometallic entities has been effected, affording a new family of octamethylferrocenyl-containing dendritic macromolecules. The new dendrimers were fully characterized. Solution voltammetric studies are characteristic of reversible oxidation processes with formal potentials considerably more negative than those corresponding to nonmethylated analogues as the result of the strong electron-donating effect of the eight methyl groups on the ferrocene rings. The dendrimers exhibit a tendency to adsorb on electrode surfaces, which is more pronounced for the higher generations. Pt or GC electrodes could be modified with films derived from **6**−**9** exhibiting a well-defined and persistent electrochemical response. Preliminary studies have shown that electrodes modified with these dendritic molecules containing redox-active octamethylferrocenyl moieties and amine $NH-CH_2$ hydrogen-bonding functionalities act as a new type of receptor system capable of electrochemically recognizing anionic guest species. Further work is now focused on exploring this area.

Experimental Section

Materials and Equipment. All reactions were performed under an inert atmosphere (prepurified N_2 or Ar) using standard Schlenk techniques. Solvents were dried by standard procedures over the appropriate drying agents and distilled immediately prior to use. Triethylamine (Merck) was distilled over KOH under N_2. 1,2,3,4-Tetramethylcyclopenta-1,3-diene,[22] octamethylferrocene,[23] and octamethylferrocenyl aldehyde[12a] were prepared according to published procedures. The following products were purchased from Aldrich: 2-butanone, toluene-4-sulfonic acid monohydrate, iron(II) chloride anhydrous beads-10 mesh $FeCl_2$, acetaldehyde, butyllithium 2.5 M in hexane, *tert*-butyllithium 1.7 M solution in pentane, sodium borohydride $NaBH_4$, and silanized silica. NMR spectra were recorded on Bruker AMX-300 and Bruker DRX-500 spectrometers. Chemical shifts are reported in parts per million (δ) with reference to residual solvent resonances for ^1H and ^{13}C NMR (C_6D_6: ^1H, δ 7.15 ppm; ^{13}C, δ 128.6 ppm). The MALDI-TOF mass spectra were obtained using a Reflex III (Bruker) mass spectrometer equipped with a nitrogen laser emitting at 337 nm. The matrix was ditranol. Elemental analyses were performed by the Microanalytical Laboratory, Universidad Autónoma de Madrid, Madrid, Spain.

Electrochemical Measurements. Cyclic voltammetric experiments were performed on a BAS CV-50W potentiostat. CH_3CN and CH_2Cl_2 (spectrograde) for electrochemical measurements were freshly distilled from calcium hydride under nitrogen. The supporting electrolyte was in all cases TBAH (tetra-*n*-butylammonium hexafluorophosphate) that was purchased from Fluka and was purified by recrystallization from ethanol and dried under vacuum at 60 °C. The supporting electrolyte concentration was typically 0.1 M. A conventional sample cell operating under an atmosphere of prepurified nitrogen was used for cyclic voltammetry. All cyclic voltammetric experiments were performed using either a platinum-disk working electrode ($A = 0.020$ cm^2) or a glassy carbon-disk working electrode ($A = 0.070$ cm^2), each of which was polished prior to use with either 0.05 μm alumina/water slurry or 1 μm diamond paste (Buehler) and rinsed thoroughly with purified water and acetone. All potentials are referenced to the saturated calomel electrode (SCE). A coiled platinum wire was used as a counter electrode. Solutions for cyclic voltammetry were typically 1.0 mM in the redox-active species and were deoxygenated by purging with prepurified nitrogen. No *iR* compensation was used. DPV was done with a scan rate of 20 mV s^{-1}, a pulse height of 50 mV, duration of 50 ms, and pulse intervals of 2 s.

Synthesis of Dendrimers. Synthesis of DAB-*dend*-(NH-$CH_2Fc^{\#})_4$ (6). A solution of the dendritic polyamine DAB-*dend*-$(NH_2)_4$ (0.15 g, 0.47 mmol) in 30 mL of benzene was added

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[21] Ferrocenyl dendrimers have been successfully used as receptor systems for anion recognition; see ref 8 and: (a) Ruiz, J.; Daniel M.-C.; Astruc, D. *Chem. Commun.* **2004**, 2637. (b) Daniel, M.-C.; Ruiz, J.; Nlate, S.; Astruc, D. *J. Inorg. Organomet. Polym. Mater.* **2005**, *15*, 107, and references therein.

[22] (a) Kohl, F. X.; Jutzi, P. *Organomet. Synth.* **1985**, *3*, 489. (b) Kohler, F. *Z. Naturforsch.* **1982**, *37b*, 144. (c) Fendrick, C. M.; Schertz, L. D.; Day, V. W.; Marks, T. J. *Organometallics* **1988**, *7*, 1828. (c) Kohl, F. X.; Jutzi, P. *J. Organomet. Chem.* **1983**, *243*, 119.

[23] Schimitt, V. G.; Ozman, S. *Chem. Ztg.* **1976**, *100*, 143.

dropwise to a stirred benzene solution of octamethylferrocenyl aldehyde (0.61 g, 1.89 mmol) under argon at room temperature. The solution was refluxed for 6 h. The red solution was then evaporated to dryness under reduced pressure, and the resulting oil was dissolved in hexane and cooled to −30 °C in order to precipitate the product. After drying under vacuum, product DAB-*dend*-($N = CHFc^{\#}$)$_4$ (**2**) was obtained as a reddish-orange, tacky oil. **2** was dissolved in 50 mL of THF, and to this solution was added slowly $NaBH_4$ (0.13 g, 3.50 mmol). After the addition, the mixture was refluxed for 2 h, cooled to 0 °C, and then hydrolyzed with water. The mixture was treated with diethyl ether, and the organic layer was washed with water and dried over Na_2SO_4. After the removal of the solvent the resulting residue was subjected to column chromatography on silanized silica using hexane/methanol (20:1) as eluents and triethylamine 1−2%. **6** was obtained as a yellow solid. Yield: 0.35 g (60%). Anal. Calcd (found) for $C_{92}H_{144}N_6Fe_4$: C, 70.94 (70.51); H, 9.32 (9.20); N, 5.39 (5.02). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.64, 1.72, 1.73, 1.88 (s, 96H, $C_5(CH_3)_4$), 2.44 (m, 12H, CH_2NCH_2), 2.72 (t, 8H, $CH_2CH_2CH_2NH$), 3.22 (s, 4H, $C_5(CH_3)_4H$), 3.63 (s, 8H, $NHCH_2C_5(CH_3)_4$). $^{13}C\{^1H\}$ NMR (C_6D_6, 75.43 MHz): δ 9.76, 10.16, 10.30, 11.71 $C_5(CH_3)_4$, 25.76, 28.74 ($CH_2CH_2CH_2$), 46.28, 48.53 (CH_2NHCH_2), 52.88, 54.77 (CH_2NCH_2), 71.04 ($C_5(CH_3)_4H$), 79.46, 79.74, 79.85, 80.04, 81.55 ($C_5(CH_3)_4$). MS (MALDI-TOF, *m/z*): 1556.9 (M^+).

Synthesis of DAB-*dend*-(NH-$CH_2Fc^{\#}$)$_8$ (7). The dendrimer of second generation was prepared in a manner similar to that for **6** starting from 0.5 g (1.55 mmol) of octamethylferrocenyl aldehyde and 0.15 g (0.19 mmol) of DAB-*dend*-(NH_2)$_8$. In this case the solution was refluxed during 12 h. Once the DAB-*dend*-($N{=}CHFc^{\#}$)$_8$ (**3**) had been isolated, the product was dissolved in 50 mL of THF, and to this solution was added slowly $NaBH_4$ (0.11 g, 3.10 mmol). The mixture was refluxed for 5 h. After the appropriate workup the resulting yellow residue was dissolved in ethanol and precipitated with CH_3CN at low temperature several times. After drying under vacuum dendrimer **7** was isolated as a yellow solid. Yield: 0.25 g (45%). Anal. Calcd (found) for $C_{192}H_{304}N_{14}Fe_8$: C, 70.84 (70.52); H, 9.41 (9.41); N, 6.02 (6.14). ^{1}H NMR (C_6D_6, 300 MHz): δ 1.68, 1.75, 1.77, 1.89 (s, 192H, $C_5(CH_3)_4$), 2.55 (m, 36H, CH_2NCH_2), 2.75 (m, 16H, $CH_2CH_2CH_2$-NH), 3.25 (s, 8H, $C_5(CH_3)_4H$), 3.60 (s, 16H, $NHCH_2C_5(CH_3)_4$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz): δ 9.40, 9.80, 9.96, 11.34 $C_5(CH_3)_4$, 25.50, 28.23 ($CH_2CH_2CH_2$), 45.84, 48.11 (CH_2NHCH_2), 52.57, (CH_2NCH_2), 70.66 ($C_5(CH_3)_4H$), 79.07, 79.36, 79.47, 79.97, 80.21 ($C_5(CH_3)_4$). MS (MALDI-TOF): *m/z* 3255.5 (M^+).

Synthesis of DAB-*dend*-(NH-$CH_2Fc^{\#}$)$_{16}$ (8). Using the same method as detailed for the preparation of dendrimer **6**, dendrimer **8** was synthesized starting from octamethylferrocenyl aldehyde (0.46 g, 1.42 mmol) and DAB-3-(NH_2)$_{16}$ (0.15 g, 0.09 mmol). The solution was refluxed during 20 h to achieve complete functionalization of the $-NH_2$ end groups. The subsequent reduction of **4** with $NaBH_4$ (0.04 g, 1.04 mmol) was produced in the same way, but in this case, the reaction mixture was heated during 8 h. After the appropriate workup the resulting yellow residue was dissolved in ethanol and precipitated with CH_3CN at low temperature several times. After drying under vacuum **8** was isolated as a orange-yellow, shiny solid. Yield: 0.21 g (35%). ^{1}H NMR (C_6D_6, 500 MHz): δ 1.7 1, 1.79, 1.80, 1.93 (s, 384H, $C_5(CH_3)_4$), 2.65 (br, 84H, $CH_2CH_2CH_2NH$ and CH_2NCH_2), 3.27 (s, 16H, $C_5(CH_3)_4H$), 3.62 (s, 32H, $NCH_2Fc^{\#}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz): δ 9.43, 9.85, 10.03, 11.38 (CH_3), 25.00, 28.83 ($CH_2CH_2CH_2$), 45.84, 48.12 (CH_2NHCH_2), 52.61 (CH_2NCH_2), 70.70 ($C_5(CH_3)_4H$), 79.11, 79.40, 79.51, 79.70, 79.96 ($C_5(CH_3)_4$).

Synthesis of DAB-*dend*-(NH-$CH_2Fc^{\#}$)$_{32}$ (9). This poly(octamethylferrocenyl) dendrimer was prepared by the procedure described for **6**, starting from octamethylferrocenyl aldehyde (0.44 g, 1.36 mmol) and DAB-*dend*-(NH_2)$_{32}$ (0.15 g, 0.04 mmol). The solution was refluxed during 24 h to obtain **5**. Reduction of **5** with $NaBH_4$ (0.07 g, 1.93 mmol) was produced in the same way, but in this case, the reaction mixture was heated during 10 h. The resulting yellow residue was dissolved in ethanol and precipitated with CH_3CN at low temperature several times, yielding **9** as an orange-yellow, shiny solid. Yield: (30%). ^{1}H NMR (C_6D_6, 300 MHz): δ, 1.75, 1.81, 1.95 (br, 768H, $C_5(CH_3)_4$), 2.61 (br, 180H, $CH_2CH_2CH_2NH$ and CH_2NCH_2), 3.31 (s, 32H, $C_5(CH_3)_4H$), 3.64 (s, 64H, $NCH_2Fc^{\#}$). $^{13}C\{^1H\}$ NMR (C_6D_6, 125.77 MHz): δ 9.46, 9.88, 10.08, 11.42 (CH3), 25.00, 28.83 ($CH_2CH_2CH_2$), 45.84, 48.12 (CH_2NHCH_2), 52.61 (CH_2NCH_2), 70.73 ($C_5(CH_3)_4H$), 79.14, 79.53, 79.73, 80.02, 80.98 ($C_5(CH_3)_4$).

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