Aza-Crown Ethers Attached to Dendrimers through Amidoferrocenyl Units

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*Summary: A novel family of diaminobutane-based poly(propy-leneamine) ferrocenyl dendrimers with aza-crown ethers, DAB-dend-(Fc-A18C6)$_x$ (**2**−**5**: x = 2, 4, 8, 16; Fc-A18C6 = {[η^5-C$_5$H$_4$CONH]Fe[η^5-C$_5$H$_4$CONCH$_2$CH$_2$(OCH$_2$CH$_2$)$_5$]}), has been prepared by reaction of the novel functionalized ferrocenyl derivative {[η^5-C$_5$H$_4$COCl]Fe[η^5-C$_5$H$_4$CONCH$_2$CH$_2$(OCH$_2$-CH$_2$)$_5$]} (**1**).*

The tailored design and synthesis of dendritic macromolecules with multiple organometallic units with specific applications has become a high-priority objective in a wide variety of areas.[1] Furthermore, the development of new electrochemical sensors for the molecular recognition of anions and cations, as well as neutral molecules, constitutes a very active field of research in continuous growth.[2] In this respect, ferrocenyl dendrimers have already been successfully used as receptor systems for anion recognition.[3] Nevertheless, despite the fact that considerable interest is currently being shown in the design and synthesis of heteroditopic receptors capable of simultaneous binding of

cationic and anionic guests by multisite receptors,[4] to the best of our knowledge no examples of organometallic heteroditopic dendrimers have been reported to date.

With this in mind and as a continuation of our studies on the design and synthesis of organometallic dendrimers displaying electrochemical sensing behavior,[5] herein we present a synthetic strategy aimed at obtaining dendritic macromolecules containing redox centers in close proximity to two different host binding sites for the simultaneous complexation of cationic and anionic guest species.

The key starting step in the preparation of the new family of dendrimers is the previous synthesis and purification of the highly reactive organometallic derivative {[η^5-C$_5$H$_4$COCl]Fe-[η^5-C$_5$H$_4$CONCH$_2$CH$_2$(OCH$_2$CH$_2$)$_5$]} (**1**).[6] The reaction of equimolar amounts of 1,1′-ferrocenedicarbonyl chloride[7] and 1-aza-18-crown-6 in dichloromethane in the presence of triethylamine at room temperature and under an argon atmosphere affords, after workup, the functionalized monomer **1** (Scheme 1), as a red solid which has to be handled under extremely dry conditions and used immediately after isolation.

Condensation reactions of **1** with 1,4-diaminobutane- and diaminobutane-based poly(propyleneamine) dendrimers functionalized with terminal −NH$_2$ groups, DAB-dend-(NH$_2$)$_x$ (x = 4, 8, 16), in dichloromethane, followed by the appropriate workup, afforded compound **2** (Scheme 2) and dendrimers **3**−**5**,

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(6) *Synthesis of **1***: under an inert atmosphere of Ar a solution of 1-aza-18-crown-6 (0.43 g, 1.63 mmol) and triethylamine (2 mL, excess) in dry CH$_2$Cl$_2$ (200 mL) was added dropwise (over a 4 h period of time) to a rapidly stirred solution of 1,1′-ferrocenedicarbonyl chloride[7] (0.51 g, 1.64 mmol) in dry CH$_2$Cl$_2$ (500 mL). The reaction mixture was stirred at room temperature for 15 min, and then the solvent was removed under vacuum. The resulting residue was extracted repeatedly with dry hexane. Solvent removal from the filtrate afforded **1** as a red solid (0.54 g, 61% yield) that was kept under Ar. ^{1}H NMR (300 MHz, CDCl$_3$): δ 4.95 (t, 2H, C$_5$H$_4$), 4.79 (t, 2H, C$_5$H$_4$), 4.72 (t, 2H, C$_5$H$_4$), 4.45 (t, 2H, C$_5$H$_4$), 3.72, 3.67, 3.65 (m, 24H, NCH$_2$, OCH$_2$).

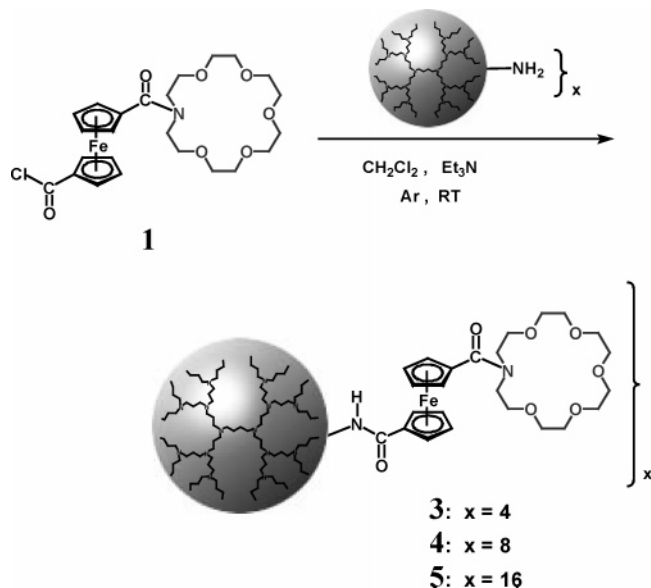(7) Knobloch, F. W.; Rauscher, W. H. *J. Polym. Sci.* **1961**, *54*, 651.

Scheme 1. Synthesis of Complex 1
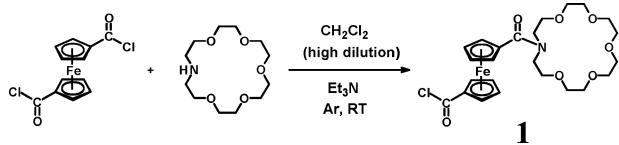
Scheme 2. Synthesis of Compound 2
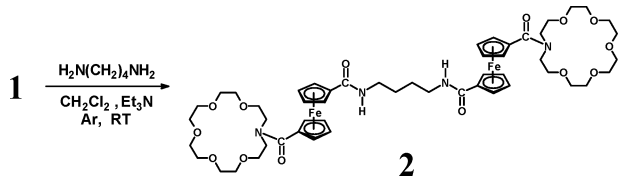
Scheme 3. Synthesis of Dendrimers 3−5

3: x = 4
4: x = 8
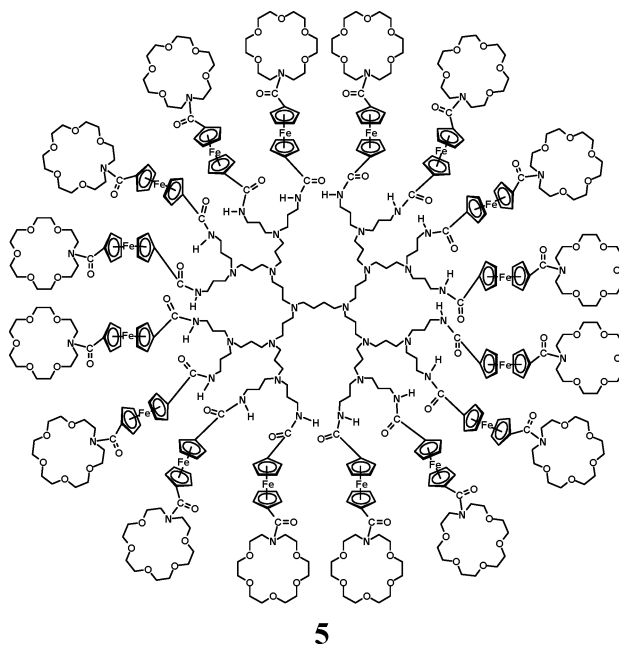5: x = 16

Chart 1

5

respectively (Scheme 3 and Chart 1), as air-stable orange to brown thick sticky oils, in yields that go from 70% for **2** to 39% for **5**.[8] The diferrocenyl complex **2**, which could be considered as the generation zero of this family of dendrimers, has been a valuable model not only for the characterization but also for preliminary complexation studies of the aza-crown ether dendrimers of higher nuclearity.

The structures of the ferrocenyl dendrimers **2**−**5** have been established on the basis of ^{1}H and ^{13}C NMR and were corroborated by matrix-assisted laser desorption/ionization time-of-flight (MALDI-TOF) and electrospray ionization time-of-flight (ESI-TOF) mass spectrometry.[9] In the ^{1}H NMR spectra (300 MHz, CDCl$_3$) key signals arising from the peripheral organometallic moieties are observed in the range 4.7−4.3 ppm, those corresponding to the methylene groups in the aza-crown ether appear as two or three broad signals within the range 3.7−3.6 ppm, and the signals of the poly(propyleneamine) dendritic

framework appear around 3.4, 2.5, 2.4, 1.7, and 1.5 ppm. The complete amidation of the peripheral amine groups was supported by the total absence, in the ^{1}H NMR spectra, of the −NH$_2$ signals of the starting dendritic polyamines around 1.3 ppm and the appearance of a new signal in the 8.5−8.4 ppm range due to the amide group, as well as by the integration ratios of the different protons, which are in agreement with the expected structures. The ^{13}C NMR resonances for **2** were assigned using one- and two-dimensional experiments, DEPT and HMQC (see the Supporting Information).

To obtain insight into the binding mode of these new aza-crown ferrocenyl amido dendrimers, NMR studies were carried out with complex **2** in acetone-d_6 (8.5 mM). The ^{1}H NMR

(8) *Synthesis of compounds 2-5*: compound **2** and dendrimers **3**−**5** have been prepared by following the same procedure. The synthesis of **4** is described as a representative example. To a solution of **1** (0.27 g, 0.50 mmol) in 15 mL of dry CH$_2$Cl$_2$ was added dropwise a solution of DAB-dend-(NH$_2$)$_8$ (0.04 g, 0.05 mmol) and 1 mL of triethylamine in 25 mL of dry CH$_2$Cl$_2$ under an inert atmosphere of Ar. The reaction mixture was stirred for 2 h under Ar at room temperature and filtered off and the solvent removed. The residue was redissolved in CH$_2$Cl$_2$ and washed with water. The solvent of the organic phase was removed under vacuum and, as column chromatographic purification under different conditions failed, the resulting oil was treated by successive reprecipitations from dichloromethane into hexane to afford **4** as a brown sticky solid (0.11 g, 43%).

(9) Selected characterization data for **2** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.52 (t, 2H, CON*H*), 4.58 (t, 4H, C$_5$*H*$_4$), 4.45 (t, 4H, C$_5$*H*$_4$), 4.32 (t, 4H, C$_5$*H*$_4$), 4.30 (t, 4H, C$_5$*H*$_4$), 3.72, 3.65 (m, 48H, NC*H*$_2$, OC*H*$_2$), 3.42 (br, 4H, C*H*$_2$NH), 1.75 (br, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): δ 170.7, 170.1 (*C*ON, *C*ONH), 80.6, 79.4, 72.0, 71.3 (*C*$_5$H$_4$), 70.4, 70.3, 70.2 (O*C*H$_2$), 70.1, 69.5 (*C*$_5$H$_4$), 69.4, 69.2, 49.6, 46.9 (O*C*H$_2$ and N*C*H$_2$), 39.2 (*C*H$_2$NH), 27.0 (CH$_2$*C*H$_2$*C*H$_2$CH$_2$). MS (MALDI-TOF): (ditranol) m/z 1091.4 [M + H$^+$]$^+$; (ditranol + NaI) m/z 1113.4 [M + Na$^+$]$^+$; M = C$_{52}$H$_{74}$O$_{14}$N$_4$Fe$_2$. Selected characterization data for **3** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.43 (t, 4H, CON*H*), 4.65 (t, 8H, C$_5$*H*$_4$), 4.51 (t, 8H, C$_5$*H*$_4$), 4.32 (m, 16H, C$_5$*H*$_4$), 3.72, 3.66, 3.64 (m, 96H, NC*H*$_2$, OC*H*$_2$), 3.41 (pseudoquartet, 8H, C*H*$_2$NH), 2.54 (t, 8H, NC*H*$_2$CH$_2$CH$_2$NH), 2.44 (br, 4H, NCH$_2$CH$_2$CH$_2$C*H*$_2$N), 1.73 (br, 8H, NCH$_2$C*H*$_2$CH$_2$N), 1.45 (br, 4H, CH$_2$C*H*$_2$C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): δ 6, 170.0, 80.3, 79.0, 72.0, 71.0, 70.7, 70.5, 70.4, 70.3, 70.0, 69.5, 69.3, 53.9, 51.6, 49.6, 47.0, 38.0, 26.9, 24.7. MS (MALDI-TOF): (ditranol) m/z 2323.1 [M + H$^+$]$^+$; (ditranol + NaI) m/z 2345.0 [M + Na$^+$]$^+$; M = C$_{112}$H$_{164}$O$_{28}$N$_{10}$Fe$_4$. Selected characterization data for **4** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.40 (br, 8H, CON*H*), 4.68 (br, 16H, C$_5$*H*$_4$), 4.52 (br, 16H, C$_5$*H*$_4$), 4.32 (br, 32H, C$_5$*H*$_4$), 3.71, 3.65 (m, 192H, NC*H*$_2$, OC*H*$_2$), 3.41 (br, 16H, C*H*$_2$NH), 2.53, 2.40 (m, 36H, C*H*$_2$-NC*H*$_2$), 1.76, 1.56 (m, 28H, NCH$_2$C*H*$_2$CH$_2$N, CH$_2$C*H*$_2$C*H*$_2$CH$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): δ 170.6, 170.0, 80.3, 79.1, 72.1, 71.0, 70.7, 70.6, 70.4, 69.7, 69.4, 52.4, 52.1, 51.7, 49.8, 47.3, 38.1, 27.2, 24.5. MS (MALDI-TOF): (ditranol) m/z 4785.3 [M + H$^+$]$^+$; (ditranol + NaI) m/z 4807.4 [M + Na$^+$]$^+$; M = C$_{232}$H$_{344}$O$_{56}$N$_{22}$Fe$_8$. Selected characterization data for **5** are as follows. ^{1}H NMR (300 MHz, CDCl$_3$): δ 8.38 (br, 16H, CON*H*), 4.72 (br, 32H, C$_5$*H*$_4$), 4.53 (br, 32H, C$_5$*H*$_4$), 4.31 (br, 64H, C$_5$*H*$_4$), 3.71, 3.65, 3.63 (m, 384H, NC*H*$_2$, OC*H*$_2$), 3.41 (br, 32H, C*H*$_2$NH), 2.52, 2.41 (m, 84H, C*H*$_2$NC*H*$_2$), 1.77, 1.57 (m, 60H, NCH$_2$C*H*$_2$CH$_2$N, CH$_2$C*H*$_2$C*H*$_2$-CH$_2$). ^{13}C{^{1}H} NMR (125.77 MHz, CDCl$_3$): δ 170.5, 169.9, 80.1, 78.8, 72.0, 71.1, 70.8, 70.6, 70.5, 70.3, 69.6, 69.3, 52.3, 51.9, 51.5, 49.7, 47.2, 38.0, 27.1, 24.1. MS (MALDI-TOF): (ditranol + NaI) m/z 9732.3 [M + Na$^+$]$^+$; M = C$_{472}$H$_{704}$O$_{112}$N$_{46}$Fe$_{16}$.
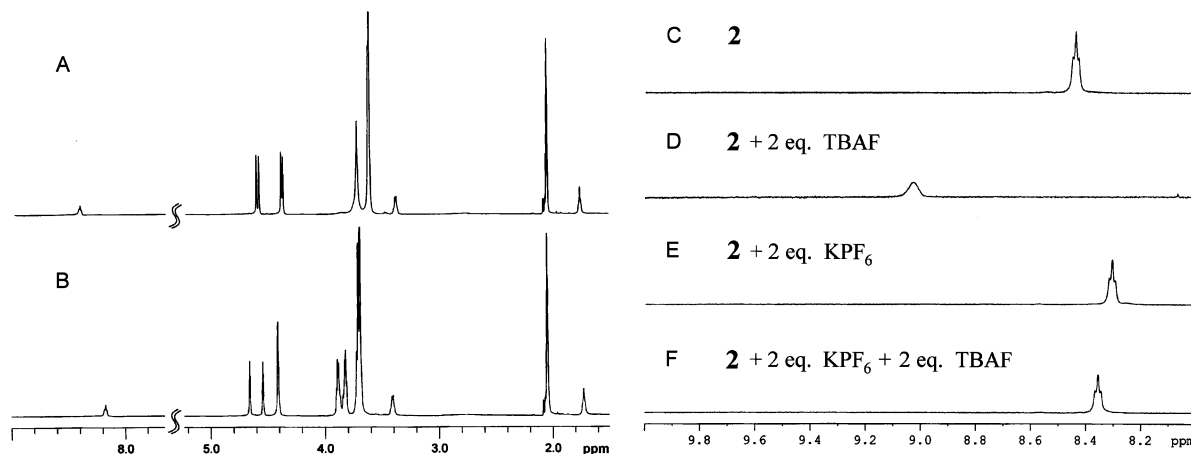
Figure 1. ^{1}H NMR spectra (500 MHz, acetone-d_6) of **2** (8.5 mM) (A) and of the sample in (A) upon addition of 20 equiv (10 equiv per aza-crown ether) of KPF_6 (B) and changes in the chemical shifts of the amide protons of compound **2** (C), **2** in the presence of 2 equiv (1 equiv per aza-crown ether) of TBAF (D), **2** in the presence of 2 equiv of KPF_6 (E), and **2** in the presence of 2 equiv of KPF_6 and 2 equiv of TBAF (F).

spectrum (500 MHz, acetone-d_6) of this compound shows the signal for the amide proton at 8.43 ppm and two resonances centered at 3.73 and 3.62 ppm corresponding to the methylenes in the aza-crown units (Figure 1A,C). When K^+ (20 molar equiv) was added to the solution of **2**, the aza-crown methylene proton signals split and shifted downfield (to 3.89, 3.82, 3.71, and 3.69 ppm), due to cation complexation by the aza-crown unit, which also causes significant perturbations in the resonances of the cyclopentadienyl protons (Figure 1B). These changes were accompanied by the signals for the amide NH proton moving upfield to 8.18 ppm because cation complexation prevents hydrogen bonding between the amide proton and the oxygen atoms of the aza-crown ether. Interestingly, upon addition of 5 molar equiv of F^- to the solution containing complex **2** and 20 molar equiv of K^+, the amide proton signal shifted downfield slightly to 8.23 ppm, which indicated a weak hydrogen-bonding interaction with F^-, while the aza-crown signals remained unchanged.

To further investigate the fluoride anion binding properties of **2** in solution, ^{1}H NMR titration with TBAF was carried out. The resulting titration curve generated from the change in chemical shift of the NH proton upon addition of the anion (see the Supporting Information) suggests a receptor–anion stoichiometry of 1:1. The computer program EQNMR[10] was used to estimate the binding constant, resulting in a value of 52 M^{-1} (error <19%). In the presence of 2 molar equiv of fluoride anion a significant downfield shift ($\Delta\delta = 0.59$) was observed for the amide NH protons of **2** (Figure 1D), which is consistent with the hydrogen-bonding interaction between the fluoride anion and the amide group. Figure 1E shows the slight upfield shift of the NH resonance of **2** in the presence of 2 equiv of KPF_6 (to 8.31 ppm), and upon addition of 2 equiv of TBAF to this solution, the NH resonance is very slightly downfield shifted again to 8.36 ppm (Figure 1F). From these results we can conclude that the presence of K^+ weakens the hydrogen bonding between the fluoride anion and the amide groups in **2**, probably due to the ion-pairing interaction K^+–F^-.

MALDI-TOF mass spectra showed peaks at m/z 1091.4 for **2**, m/z 2323.1 for **3**, and m/z 4785.3 for **4**, with isotopic patterns matching exactly the calculated values for the protonated dendrimers. The observation of some lower mass peaks

(for **3** and **4**) indicates the occasional presence of defective species having a cycled terminal chain as well as the possibility of fragmentation in the MS experiment;[11] however, in all cases the fully substituted species exhibit by far the highest abundance. When the MALDI-TOF mass spectra of compounds **2**−**4** were registered on doping the matrix with NaI, the spectra showed $[M + Na^+]^+$ as the most intense peak, with a higher ionization efficiency compared to those of the rest of the peaks in the same spectrum and also compared to those of the respective spectra without NaI. In this sense, the spectrum of **5** registered using only ditranol as matrix showed no significant results but, after addition of NaI as cationization compound, a peak centered at m/z 9732 was observed which matches the calculated value for $[M + Na^+]^+$.

Electrospray ionization mass spectrometry was used to analyze mixtures containing **2** and a 4-fold excess of KSCN in methanol and **3** and an 8-fold excess of KPF_6 in acetone. Singly, doubly, and triply charged complexes of the different dendritic aggregates were observed according to the peak spacing of their isotope patterns: $\Delta m/z = 1, 0.5, 0.33$, respectively. The ESI-TOF mass spectrum of **3** (8.6×10^{-5} M) in the presence of KPF_6 (8 equiv) in acetone (Figure 2) exhibits two series of equidistant signals with $\Delta_1 m/z = 61.3$ and $\Delta_2 m/z = 92$. Since the corresponding cations are triply and doubly charged, the apparent distance translates into a mass difference of 184 Da, which is in agreement with a successive association of KPF_6 molecules.

The electrochemistry of the new ferrocenyl aza-crown ether terminated dendrimers has been examined by cyclic voltammetry in dichloromethane solution with tetrabutylammonium hexafluorophophate (TBAH) as the supporting electrolyte. A representative voltammogram is shown in Figure 3. For each dendrimer, the cyclic voltammograms (CVs) show a single reversible oxidation wave. This finding reveals that there is no electronic communication between the multiple ferrocenyl centers in one dendrimer. The observed half-wave potentials ($E_{1/2}$) are all in the range +0.72 to +0.78 V vs SCE, and they tend to increase with dendrimer generation, a reflection of the enhanced steric congestion on the surface of the larger dendrimers. The diffusion coefficients, D_o, upon oxidation for the four ferrocenyl

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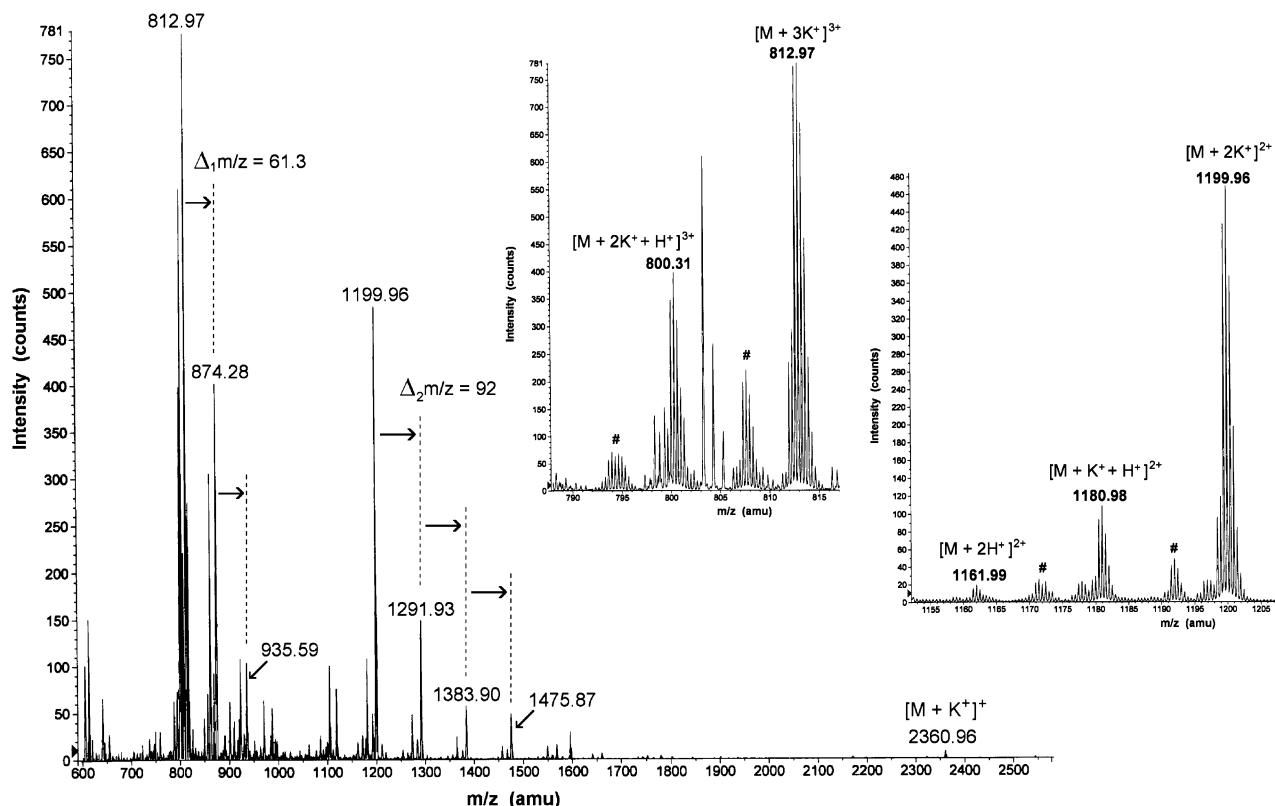
Figure 2. ESI-TOF mass spectrum of **3** in the presence of KPF_6 (8 equiv). Additional peaks corresponding to Na^+ aggregates are observed (denoted with #) and are due to the presence of an Na^+ trace impurity which is common in the instrument line and glassware.
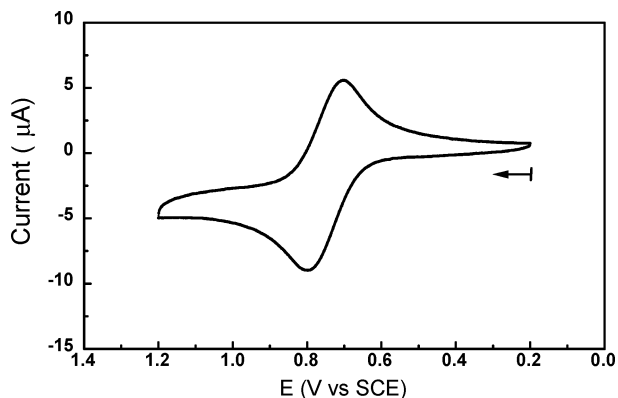

Figure 3. Representative cyclic voltammogram obtained with a GC working electrode (0.07 cm^2) in solution containing dendrimer **4** (1 mM in ferrocene centers) and TBAH (0.1 M) in CH_2Cl_2. Scan rate: 0.10 V s^{-1}.

dendrimers in CH_2Cl_2 have been calculated from CV,[12] resulting in values of $D_o = 4.9 \times 10^{-6}$, 2.8×10^{-6}, 2.6×10^{-7}, and 1.3×10^{-7} cm^2 s^{-1} for **2**−**5**, respectively. As expected, values of the apparent diffusion coefficients decrease with increasing molecular mass and are comparable to those for rather similar dendrimers containing cobaltocenium[13] as well as for dendrimers containing $[Ru(tpy)_2]^{2+}$ centers (tpy = terpyridine), in which case authors have also measured the diffusion coefficients using pulse field gradient spin−echo NMR spectroscopy.[14]

Modification of Pt and glassy-carbon electrodes with these organometallic dendrimers is possible. The deposition of the dendrimers has been carried out either by controlled-potential electrolysis at +1.10 V or by repeated cycling between 0 and +1.30 V vs SCE, in degassed dendrimer-containing CH_2Cl_2 solutions. Unfortunately, the electrodeposited films of these dendrimers are unstable to extended electrochemical cycling in CH_2Cl_2 or aqueous solution.

In conclusion, we have developed a synthetic approach to ferrocenyl dendrimers decorated with aza-crown ethers which, to the best of our knowledge, illustrate the first examples of redox-active organometallic heteroditopic dendrimers. Preliminary NMR studies confirmed that the dendrimers are capable of simultaneous coordination to cations and anions, thanks to the presence of aza-crown ether and amide binding sites. NMR and electrochemical studies on the binding and sensing of different guests by these dendrimers are currently in progress.

Supporting Information Available: Text and figures giving experimental details, NMR spectra of compounds **1** and **2**, TBAF titration data, and CVs of **2**−**5**. This material is available free of charge via the Internet at http://pubs.acs.org.

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