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Ferrocenyl Dendrimers with Ionic Tethers and Dendrons

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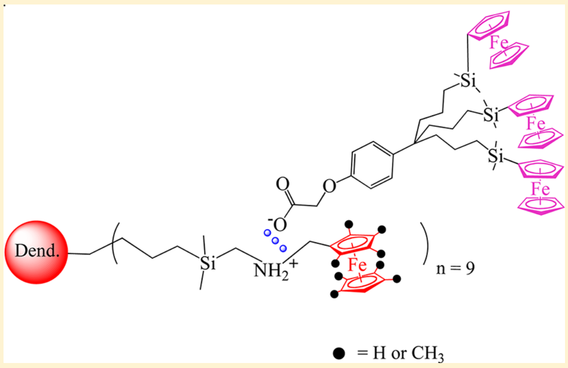
S *Supporting Information*



ABSTRACT: Whereas covalently constructed dendrimers are very numerous, there are only a few examples of dendrimers based on ionic bonds with tethers or dendrons. Here such constructions were designed in order to examine their physicochemical consequences: in particular, the electrochemical and redox properties. Two series of *secondary* polyamine dendrimers containing ferrocenyl and octamethylferrocenyl were synthesized by condensation of polyamine dendrimers, obtained by reduction of the polyazide dendrimers by $LiAlH_4$ or $NaBH_4$ with ferrocenyl aldehyde or octamethylferrocenyl aldehyde, followed by reduction of the resulting polyimine dendrimers. Primary and secondary ferrocenyl polyammonium dendrimer salts have been synthesized by quaternization of the dendritic amines including ferrocenyl secondary polyamines by reaction with a triferrocenyl dendron containing a carboxylic acid as the focal point. Cyclic voltammetry data show the electrostatic effect of the intradendritic secondary ammonium groups and the distinction between intradendritic and peripheral ferrocenyl groups.

INTRODUCTION

Dendrimers now constitute a well-developed field[1] that has applications in biomedicine,[2] materials science,[3] and catalysis.[4] Most dendrimers are constructed covalently, but ionic bonding has recently attracted attention for enhanced drug encapsulation and specific physicochemical properties, including mesogens and energy-related aspects.[5,6] Here we report arene-centered polyamine dendrimers with ferrocenyl termini and a triferrocenyl dendron with a carboxylic group at the focal point and their ionic assemblies, i.e. dendrimers containing ammonium carboxylate linkers, some of which contain two kinds of functional ferrocenyl termini. The goal was to investigate the possibility of ionic linkages as a viable method for the design of redox sensors and energy-related materials. Among redox-active dendrimers, ferrocenyl derivatives[7] are the most practical ones, given the richness and applications of ferrocene chemistry[8] that is well illustrated inter alia in this issue and the robustness of the ferrocenyl derivatives.

RESULTS AND DISCUSSION

Synthesis of New Ferrocenyl Dendrimers Containing Secondary Amine Groups. We begin with the synthesis of arene-centered dendrimers according to our classic $CpFe^+$-induced nonaallylation of mesitylene in $[FeCp(\eta^6\text{-}1,3,5\text{-}C_6H_3(CH_3)_3)][PF_6]$[9] according to a 1→3 connectivity[10] providing the nonaallyl core[11] followed by hydrosilylation with chloromethyldimethylsilane, substitution of the terminal chloro group in **1** by reaction with sodium azide to give the nonaazide **2**,[11] and reduction of the azido groups in **2** to primary amine termini.[12] This sequence of reactions provides the dendritic zeroth-generation nonaamine core **3** that is protonated using aqueous HPF_6 to give the nonaammonium salt **4** (Scheme 1). The following generation is obtained upon Williamson reaction of the nonachloro core **1** with the phenol triallyl dendron **9** according to a known procedure followed by substitution of the terminal chloride by the azido group[11] that is subsequently reduced to the primary amine.[12] This gives the first-generation dendrimer **5** containing 27 NH_2 termini, and the 27-ammonium species **8** is obtained upon protonation of **5** with aqueous HPF_6 or aqueous HCl[12] (Scheme 2). These 9-NH_2- and 27-NH_2-terminated dendrimers are used to introduce the ferrocenyl groups upon reaction with either ferrocenyl aldehyde or octamethylferrocenyl aldehyde, although **5** slowly polymerizes in the condensed phase and should be used as freshly prepared. Both ferrocenyl[13] and octamethylferrocenyl[14] derivatives have already been condensed with polyimine DAB dendrimers by the groups of Jutzi and Casado, respectively, and have also been successfully used here to synthesize new ferrocenyl-terminated dendrimers. The iminoferrocenyl dendrimers obtained using these reactions are reduced to the secondary aminomethylferrocenyl dendrimers **6** and **7** (Scheme 1). The new ferrocenyl-functionalized secondary polyamine dendrimer **6** (Scheme 1) is soluble in toluene, diethyl ether, dichloromethane, and tetrahydrofuran. This amino metallocene was insoluble in acetonitrile, but the ferrocenyl alcohol derived from the reduction of the excess of

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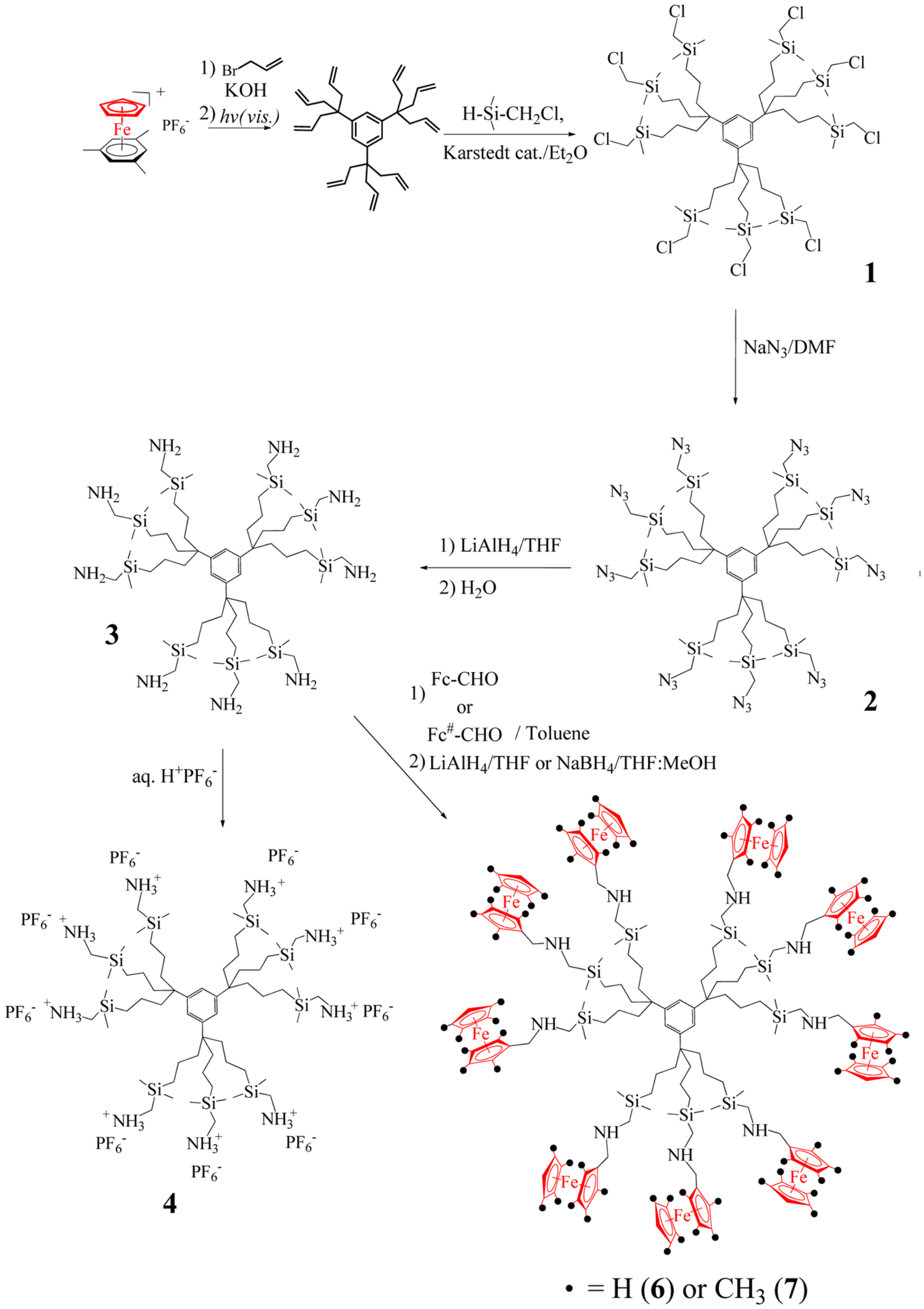
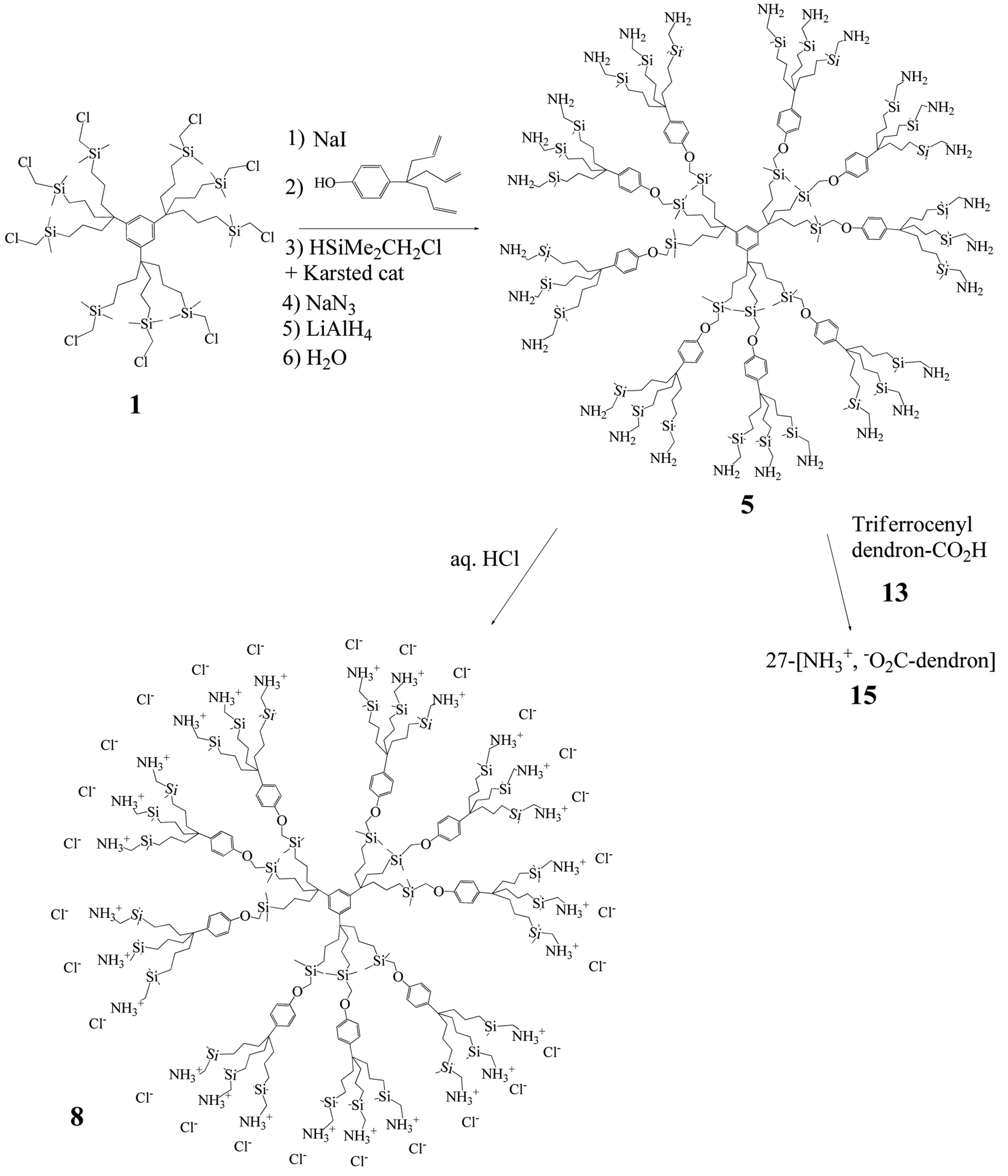
Scheme 1



ferrocenyl aldehyde in the reaction solution is soluble in acetonitrile. We acted on this solubility difference to purify the products by precipitation of the crude reaction from acetonitrile with a small amount of dichloromethane. For the synthesis of the octamethylferrocenyl-functionalized dendrimer 7, instead of ferrocenyl aldehyde, octamethylferrocenyl aldehyde[15] was used with the same route as the synthesis of the dendrimer ferrocenyl moieties, except for the process of reduction from imine to amine, which was achieved in this case by using $NaBH_4$ in a MeOH/THF mixture as solvent. The functionalized secondary polyamine dendrimer 7 with attached octamethylferrocenyl termini is soluble in toluene, diethyl ether, dichloromethane, and tetrahydrofuran. The polyamine ferrocenyl dendrimer is more aerobically stable than those containing octamethylferrocenyl termini in solution, because the eight methyl ferrocene substituents facilitate oxidation to ferrocenium derivatives by oxygen. These two secondary polyamine dendrimers **6** and **7** were characterized by ^1H NMR and ^{13}C NMR, IR, DOSY NMR, cyclic voltammetry, and elemental analyses.

Synthesis of the New Triferrocenyl Dendrons. A triferrocenyl dendron containing a carboxylic acid group at the focal point, **13**, used for the quaternization reaction, was synthesized according to Scheme 3. The synthesis of this dendron starts by the known $CpFe^+$-induced triallylation and exocyclic C−O cleavage in *p*-methylethoxytoluene obtained by

Scheme 2



reaction of ethanol and sodium carbonate with [FeCp(η^6-*p*-$CH_3C_6H_4Cl$)][PF_6]. The phenol triallyl dendron **9** obtained in this way was hydrosilylated with dimethylsilylferrocene to give the known complex **10**.[9c] Then an S_N2 reaction of $BrCH_2COOMe$ with the phenol derivative **10** in the presence of K_2CO_3 provided the new ester **11**. Saponification[15] of the ester group was conducted with NaOH in H_2O/dioxane. The sodium carboxylate dendron product was obtained as a red oil in 90% yield, and acidification was carried out upon addition of aqueous HCl to give the ether-soluble carboxylic acid dendron **13** (Scheme 3). These new triferrocenyl dendrons were characterized by ^1H NMR and ^{13}C NMR, IR, mass spectrometry, cyclic voltammetry, and elemental analyses.

Synthesis of the Primary Polyammonium Dendrimers. The nonaammonium hexafluorophosphate dendrimer **4** was synthesized from the primary polyamine nona dendrimer **3** in dichloromethane by dropwise addition of aqueous HPF_6. The turbid solution was stirred for an additional 30 min. The same procedure was used for the synthesis of the ionic dendrimer **8** from the polyamine precursor **5** with aqueous HCl. These dendrimers were soluble only in very polar solvents such as water, DMF, and DMSO. In ^1H NMR and ^{13}C

Scheme 3

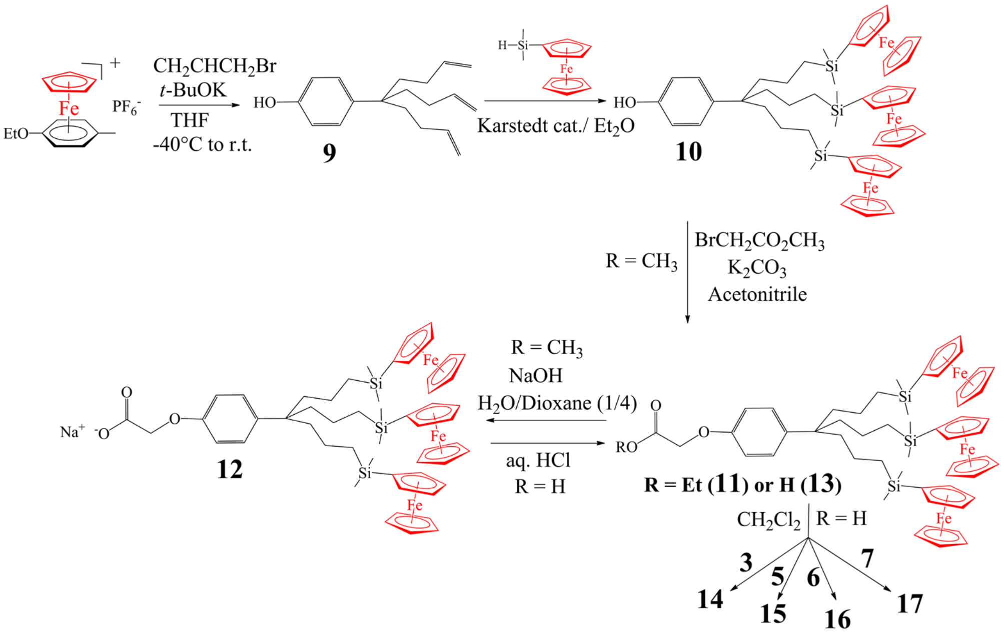


Chart 1

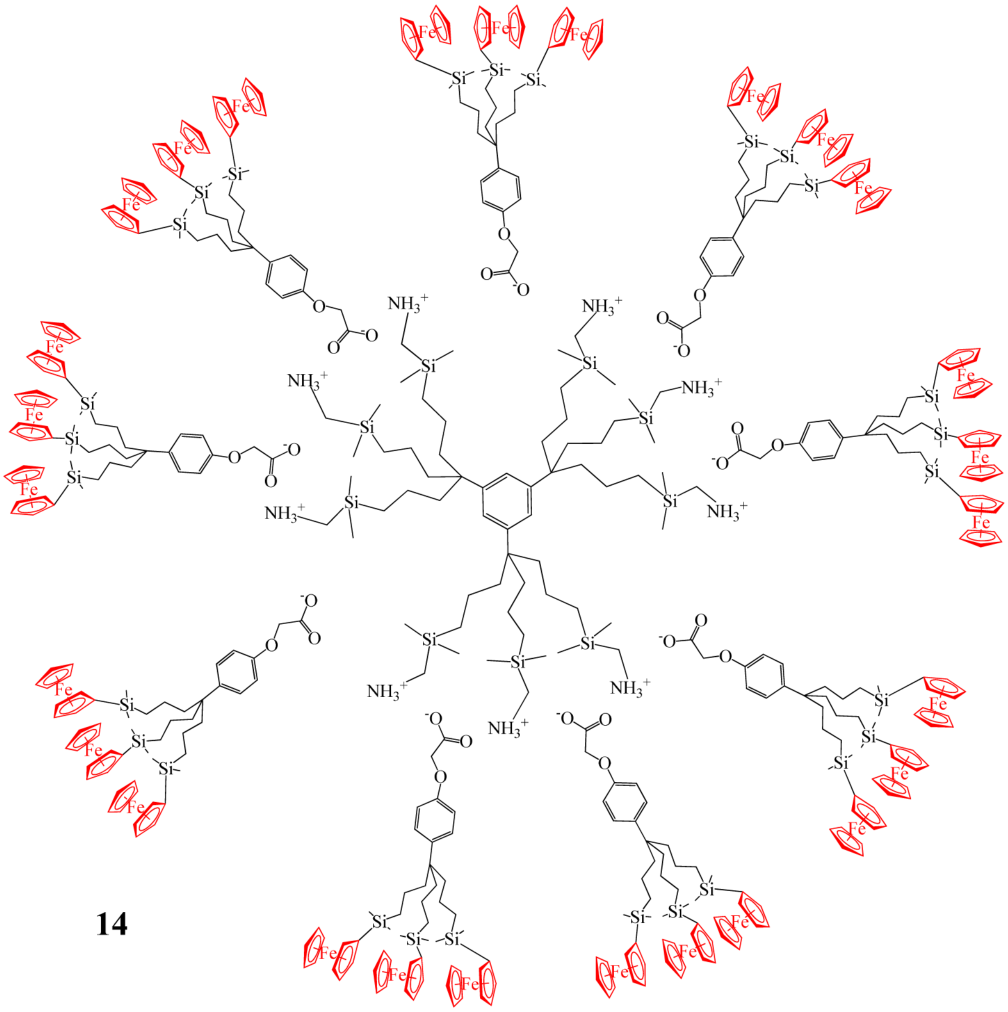
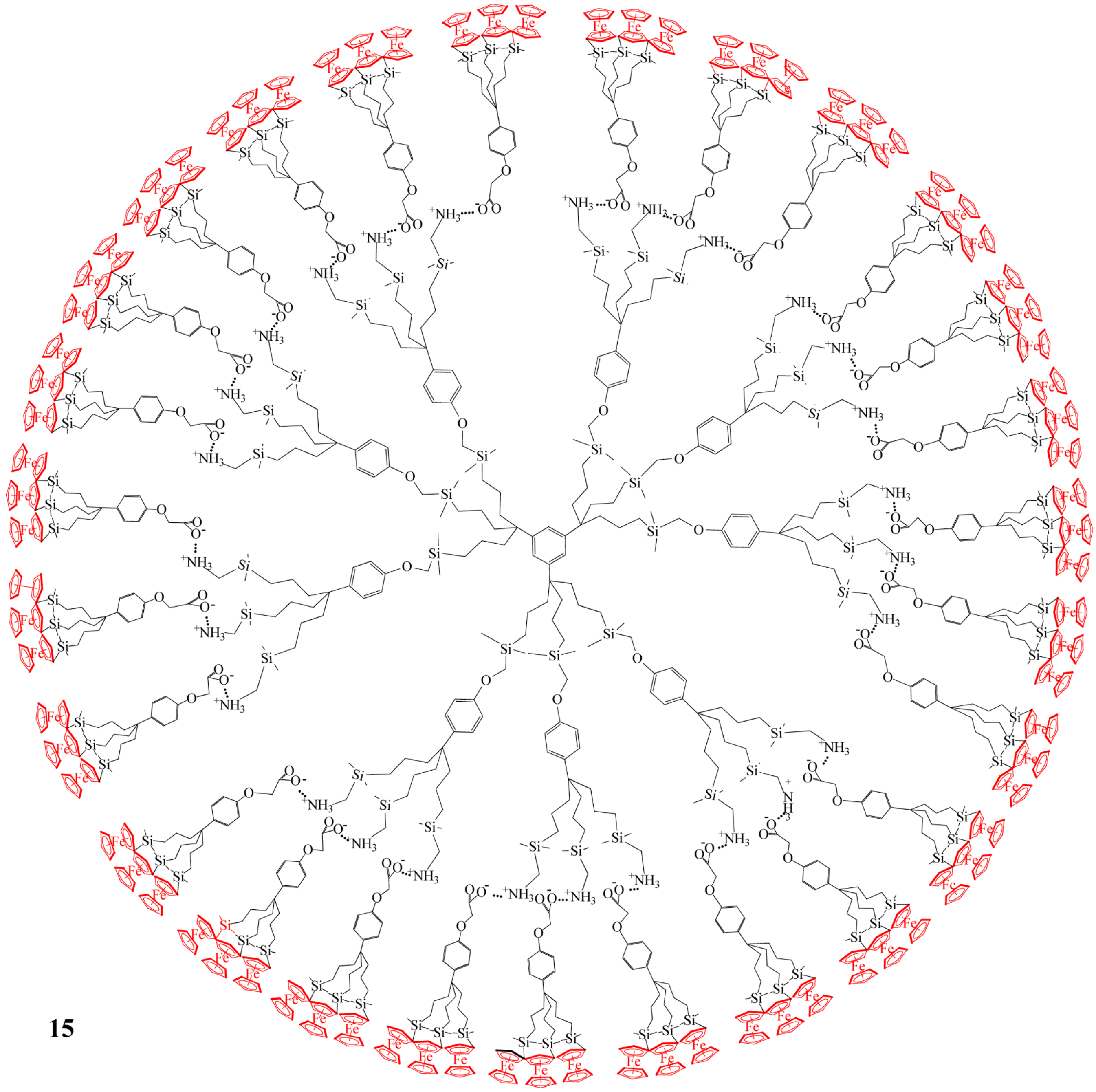


Chart 2



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NMR in D_2O, all of the characteristic peaks of the dendrimers are observed. Products **4** and **8** were also analyzed by IR and elemental analysis.

Synthesis of the Supramolecular Ionic Ferrocenyl Dendrimers. The construction of higher generations of ferrocenyl dendrimers, generations 1 (products **14**, **16**, and **17**) and 2 (product **15**), were achieved in a facile and clean acid–base reaction (Charts 1–3). One equivalent of the primary and secondary polyamine dendrimer precursors, generations 0 and 1, were mixed with 9 and 27 equiv of the dendron **13** in dichloromethane at room temperature, yielding orange sticky oils. The solubility of the final supramolecular products is influenced as expected by the periphery of the dendrimers that contains 27 (products **14**, **16**, and **17**) and 81 (product **15**) ferrocenyl moieties, and these final dendrimers were soluble in dichloromethane, toluene, and THF. The dendron **13** with carboxylic acid at the focal point was ether soluble, as well as the secondary polyamine ferrocenyl and octamethylferrocenyl dendrimers **6** and **7**. On the other hand, the sodium carboxylate dendron **12** was insoluble in ether. The same phenomenon is noticed in the polyammonium carboxylate dendrimers that are not ether soluble. Finally, as the ammonium carboxylate functions are located at the interior of the dendrimers, the ionic groups are shielded, and they cause these ionic dendrimers to be insoluble in polar solvents such as water, acetone, and acetonitrile. Products **14–17** were characterized by ^1H NMR and ^{13}C NMR, IR, DOSY NMR, cyclic voltammetry, and elemental analyses.

NMR Spectroscopy. NMR spectroscopy proved to be a key tool for this study, confirming the proposed structures.

Chart 3

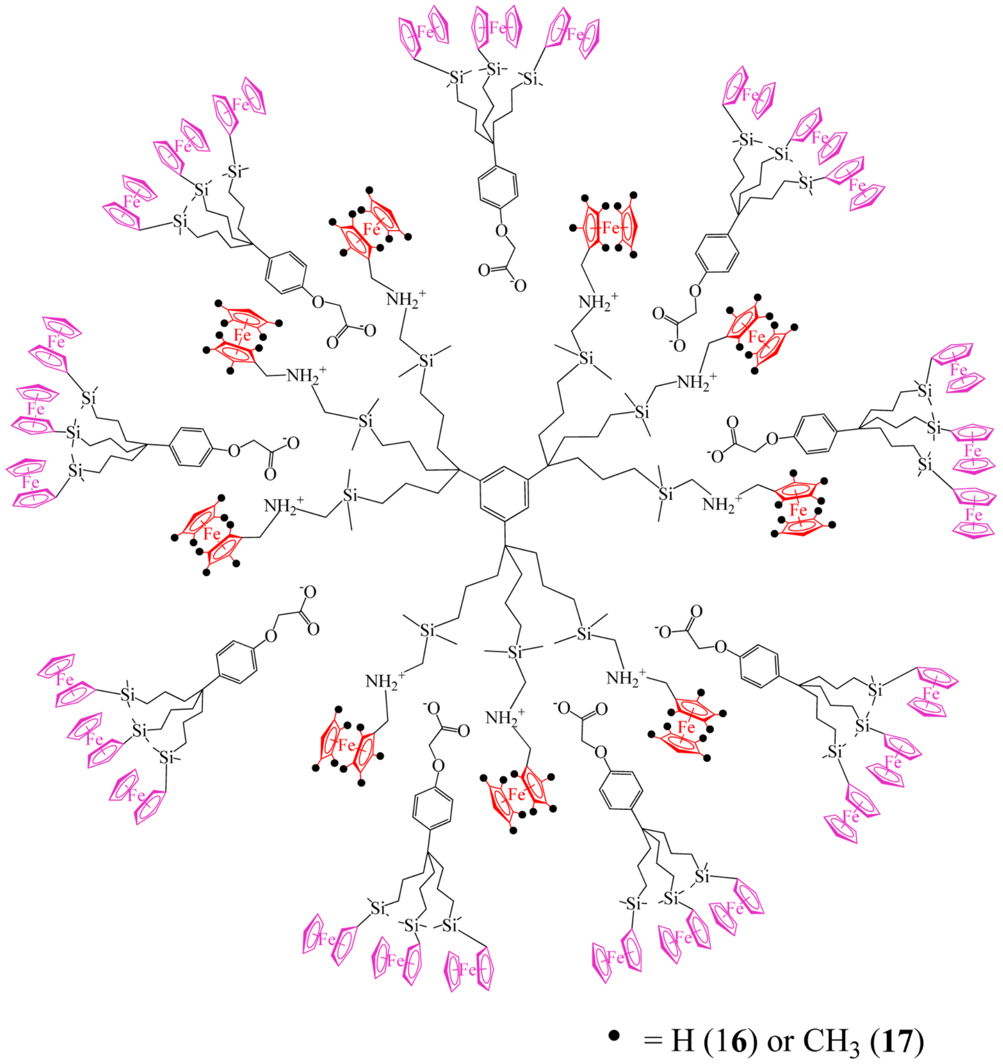

Table 1. ^{1}H NMR, ^{13}C NMR, and IR Data of Dendrons 11−13 and Dendrimers 3−8 and 14−17

compd	CH_2COOR ^{1}H/^{13}C (ppm)	SiCH_2NH$_x$ ^{1}H/^{13}C (ppm)	H$_x$NCH_2Cp ^{1}H/^{13}C (ppm)	IR KBr (cm^{-1})
dend-COOMe **11**[a]	4.66/65.10			1765; 1607
dend-COONa **12**[a]	4.29/64.00			1633
dend-COOH **13**[a]	4.56/66.29			1722; 1607
G0-NH$_2$ **3**[a]		2.04/29.90		3365; 1570
G1-NH$_2$ **5**[a]		2.06/30.00		3350; 1581
G0-NH$_3$PF$_6$ **4**[b]		2.34/27.76		3431; 830
G1-NH$_3$Cl **8**[b]		2.43/27.86		3425
G1-NH$_3$-Fc$_{27}$ **14**[a]	4.38/67.98	2.27/25.58		3445; 1636
G2-NH$_3$-Fc$_{81}$ **15**[a]	4.41/66.51	2.30/27.96		3452; 1643
G0-NH-Fc **6**[a]		2.10/29.70	3.54/53.15	3448; 1592
G0-NH-Fc$^{\#}$ **7**[a]		2.04/29.72	3.48/50.20	3456; 1593
G1-NH$_2$-Fc$_{36}$ **16**[a]	4.42/65.99	2.20/30.00	3.89/50.38	3452; 1641
G1-NH$_2$-Fc$^{\#}_9$Fc$_{27}$ **17**[a]	4.42/67.85	2.22/29.70	3.97/51.19	3461; 1630

[a] NMR in CDCl$_3$ at 25 °C. [b] NMR in D$_2$O at 25 °C.

Table 1 shows the comparative NMR (and IR) data for the dendronic carboxylic acid **13**, the corresponding carboxylate sodium salt **12**, the dendritic primary and secondary polyamines (**3** and **5**−**7**), and the dendritic primary and secondary polyammonium carboxylates (**4**, **8**, and **14**−**17**). For the dendron **11**, the ^{1}H NMR signals at 4.66 ppm of the CH_2COOMe group and the methyl group at 3.86 ppm appeared, integrating for two and three protons, respectively. After the saponification reaction, the dendron **12** showed the CH_2COONa signal at lower field as expected around 4.29 ppm, whereas the signal of the methyl group disappeared. The acidification reaction that turned the focal point into a carboxylic acid group was checked by the downfield shift of the CH_2COOH signal at 4.56 ppm. ^{13}C NMR spectroscopy also confirms the above structures (see the Supporting Information). The syntheses of the dendrimers **6** and **7** were also monitored by ^{1}H NMR. The resulting imine dendrimers resulting from the condensation reactions between **3** and the ferrocenyl and octamethylferrocenyl aldehydes showed the appearance of the $-N{=}CH-$ signal at 8.1–8.2 ppm. After reduction to the corresponding secondary amines, this signal completely disappeared, and the $-NHCH_2-$Cp signal appeared at 3.54 and 3.48 ppm, respectively. The corresponding signals of the ferrocene and octamethylferrocene moieties also confirmed the structures of the dendrimers **6** and **7**. The ionic dendrimers **4** and **8** were dissolved in D_2O, but their solubility in $CDCl_3$ (for the sake of comparison) was not determined. Nevertheless, the $-CH_2NH_3^+$ signals showed an important downfield shift. In the case of the primary polyammonium ferrocenyl dendrimers **14** and **15**, by comparison with the primary polyamine precursors **3** and **5** and dendron **13**, the $-CH_2NH_3^+$ proton signal was deshielded by about 0.25 ppm due to the presence of a nearby positive charge, and the signal of the $-CH_2COO^-$ protons was found to be shielded by about 0.17 ppm due to the presence of a nearby negative charge. These shifts in comparison to the neutral termini are in agreement with the formation of the ionic ammonium carboxylate linker. In the case of the secondary polyammonium dendrimers **16** and **17**, in comparison to the precursors **6** and **7** and dendron **13**, the differences are slightly smaller, as $-CH_2NH_2^+$ protons are deshielded by about 0.10 and 0.18 ppm, respectively and the $-CH_2COO^-$ protons are shielded by 0.14 ppm. This decrease of the charge effect is taken into account by the fact that the secondary ammonium groups are larger than the primary groups, resulting in a dilution of the positive charge and weaker (longer) ionic bond with the carboxylate. On the other hand, the $-NH_2^+CH_2-$Cp signal of the secondary polyammonium dendrimers **16** and **17** are much more shifted (0.3 and 0.5 ppm) toward lower field than the signals of the other protons. Interestingly, the ^{13}C NMR spectra show the opposite effect for the $-CH_2NH_3^+$ (shielded compared to $-CH_2NH_2$) and $-CH_2COO^-$ carbons (deshielded in comparison to $-CH_2COOH$) in comparison to proton signals in dendrimers **14** and **15** (see Table 1). Finally, for the ionic dendrimers, the corresponding proton signals of the carboxylates are found at an intermediate region between those of the dendronic acid **13** and those of the dendronic sodium carboxylate salt **12**, probably because of the hydrogen bonding between the primary or secondary ammonium group with the carboxylate group.

Infrared Spectroscopy. The infrared spectra also provided valuable information on the new series of dendrons and dendrimers. Dendron **11** has the characteristic absorption of the ester group at 1765 cm^{-1}, and in dendron **13** the presence of a focal point consisting of the carboxylic acid was checked by the frequencies related to the carbonyl group at 1722 and 1607 cm^{-1} (and a broad band due to the O–H stretching at 3400 cm^{-1}). For the dendron **12** the single carbonyl band was shifted to the region between the two, at 1633 cm^{-1} due to the carboxylate absorption (both resonance forms equally contribute to the ground state of the molecule). Similarly, for the dendritic polyammonium carboxylates **14–17**, a strong band due to $-COO^-$ stretching was found in the region 1630–1643 cm^{-1}.

For the primary polyamines **3** and **5** two broad bands were observed in the region 3400–3300 cm^{-1} ($-NH_2$ stretching), whereas for the secondary polyamines **6** and **7** one broad band was observed in this region ($-NH-$ stretching). For the primary and secondary polyammonium dendrimers (products **5**, **8**, and **14–17**), one broad absorption was observed in the region 3420–3460 cm^{-1} due to $-NH_3^+$ or $-NH_2^+-$ stretching (see Table 1).

DOSY NMR. DOSY (diffusion-ordered spectroscopy) experiments were conducted for the dendrimers **6**, **7**, **14**, **16**, and **17**. The main goal of these experiments was to measure the diffusion coefficient D and determine the size of the dendrimer in solution. The latter also reflects the purity of the products. The D value allows calculation of the hydrodynamic diameter of a molecule. Dendrimers are regarded as spherical molecular objects and characterized by an apparent diffusion coefficient. The Stokes–Einstein law, $D = k_BT/6\pi\eta r_H$, gives an estimate for the diameter of the molecule, where D is the diffusion coefficient, k_B the Boltzmann constant, T the absolute temperature, η the solvent viscosity, and r_H the hydrodynamic radius of the species (Table 2). The diameter values that are obtained include peripheral solvation of the products by solvent molecules in solution. This method was very useful for a clear comparison between the generations of the dendrimers and provided evidence for the formation of distinct ionic assemblies. For the nonionic dendrimers **6** and **7** (generation 0), the calculated r_H values are 2.08 and 2.29 nm, respectively, which shows the effect of the presence of methyl groups in **7** and provides a hydrodynamic radius that is 0.21 nm larger herewith. When the latter products were allowed to react with the dendron **13**, giving the next generation (generation 1) dendrimers **16** and **17**, it was found that the sizes of the obtained dendritic ionic assemblies represented by r_H are 3.21 and 3.33 nm, respectively. This finding that **17** has a larger r_H value than **16** is in agreement with the relative sizes of their precursors, respectively **6** and **7**. Finally, DOSY NMR, apart from providing valuable data such as the diffusion coefficients of the new dendrimers, also gives clear evidence of the size progression upon an increase of the dendrimer generation. It also allows comparing the sizes of the dendrimers (ionic and nonionic) that contain different metallocenes and distinguishing between the assemblies of primary and secondary polyammonium dendrimers of the same generation.

Table 2. Calculated Diffusion Coefficients and Hydrodynamic Radii Obtained by DOSY NMR

compd	D^a (±0.1), 10^{-10} m^2/s	$r_H{}^b$ (±0.1), nm
G0-NH-Fc **6**	1.947	2.08
G0-NH-Fc$^\#$ **7**	1.768	2.29
G1-NH_3-Fc_{27} **14**	1.044	3.87
G1-NH_2-Fc_{36} **16**	1.261	3.21
G1-NH_2-$Fc^\#_9Fc_{27}$ **17**	1.216	3.33

[a] D is the diffusion coefficient, measured in $CDCl_3$ at 25 °C, [b] r_H is the hydrodynamic radius, calculated using the Stokes–Einstein equation.

Cyclic Voltammetry.[16] The new dendron **13** and the series of polyamine and polyammonium ferrocenyl dendrimers were studied by cyclic voltammetry using decamethylferrocene ($FeCp^*_2$) as the internal reference,[17] although ferrocene was used in the cases of the octamethylferrocenyl dendrimers **7** and **17**. The cyclic voltammograms were recorded in dichloromethane, and the $E_{1/2}$ data (measured vs $FeCp^*_2$) are gathered

Table 3. Redox Potentials and Chemical (i_a/i_c) and Electrochemical ($E_{pa} - E_{pc} = \Delta E$) Reversibilities for Compounds 6, 7, and 13−17[α]

	$Fe^{III/II}$ dendron			$Fe^{III/II}$ dendrimer			$Fe^{\#III/II}$ dendrimer		
compd	$E_{1/2}$, V	ΔE, V	i_a/i_c	$E_{1/2}$, V	ΔE, V	i_a/i_c	$E_{1/2}$, V	ΔE, V	i_a/i_c
13	0.54	0.068	0.76						
6				0.55	0.065	1			
7							0.10	0.040	1
14	0.52	0.015	0.57						
15	0.53	0.012	0.42						
16	0.54	0.065	1	0.62	0.060	1			
17	0.52	0.025	1				0.27	0.030	0.9

[α] Conditions: supporting electrolyte, $[n\text{-}Bu_4N][PF_6]$ 0.1 M; solvent, CH_2Cl_2; reference electrode, Ag; working and counter electrodes, Pt; scan rate, 0.2 V/s; internal reference, $FeCp^*_2$.

in Table 3. For all of the dendrons and dendrimers, a single oxidation wave is observed for all the ferrocenyl groups, which appear seemingly equivalent, due to the weakness of the electrostatic factor between the redox sites of the dendron and metallodendrimers, as their redox sites are far away from one another, being separated by several bonds.[18] This single wave for all these three products is chemically and electrochemically reversible, although this reversibility is sometimes more or less perturbed by adsorption of these macromolecules onto the electrode. The electrochemical reversibility involving all the redox groups and signifying fast heterogeneous electron transfer is due to two factors that probably simultaneously occur: (i) fast rotation of the metallodendrimer within the electrochemical time scale, whereby all redox groups come in turn close to the electrode,[19] and (ii) electron hopping among the redox sites borne by flexible tethers, allowing hopping at an optimal distance and mutual orientation.[20] For dendron **13** and dendrimer **6**, the $Fe^{III/II}$ oxidation potentials of the ferrocenyl redox centers are about 0.54 V, whereas for dendrimer **7** this potential is 0.1 V. This cathodic shift is accounted for by both the electron-releasing property of the eight methyl substituents of the ferrocenyl groups that facilitate oxidation to ferrocenium. For primary polyammonium dendrimers **14** and **15**, the oxidation potentials are about the same as that of the dendron (only 20 mV less positive). The ferrocenyl centers at the periphery of the dendrimers are not influenced by the ammonium carboxylate linkages that are located in the dendritic interior. In the case of secondary polyammonium dendrimers with two kinds of ferrocenyl centers (product **16**) and the mixed ferrocenyl−octamethylferrocenyl dendrimer **17**, two waves are observed corresponding to each type of ferrocenyl redox center. For products **16** and **17**, oxidation of the peripheral ferrocenes also is recorded at 0.54 V, because they are not influenced by the remote interior ammonium carboxylate linkages. Oxidation of the interior ferrocenyl groups that are close to the ammonium groups now takes place at much more positive potentials, which is due to the interaction with and proximity of the ammonium cation. This trend is more marked for **17**, because the ammonium cation stabilizes the electron-rich octamethylferrocenyl group, which is oxidized at a potential 170 mV more positive (Figure 1).

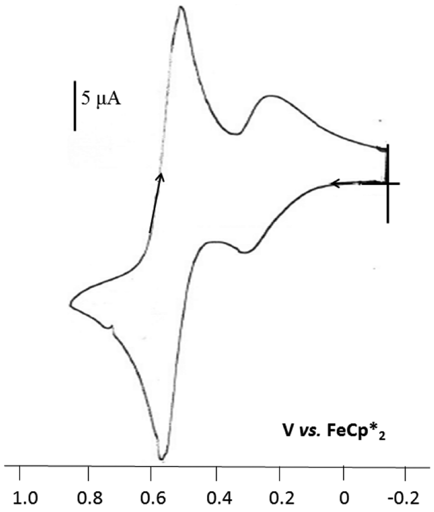

Figure 1. CV of **17** in CH_2Cl_2 solution. Conditions: reference electrode, Ag; working and counter electrodes, Pt; scan rate, 0.2 V/s; supporting electrolyte, $[n\text{-}Bu_4N][PF_6]$.

The adsorption phenomenon during cyclic voltammetry of cationic dendrimers is much more marked for ionic dendritic assemblies than for neutral species. Indeed, for the dendron **13** and the generation-0 dendrimers **6** and **7**, adsorption is not observed, but in the case of the ionic compounds **14**−**17** adsorption is strong. Especially for compounds **14** and **15** adsorption onto the electrode is observed by scanning around the oxidation potentials of the peripheral ferrocenyl groups, which confirms the formation of ionic generation-1 and -2 dendrimers and the existence of electrostatic forces. For the ionic compounds **16** and **17** adsorption is also highly marked. On the other hand, the dendron **13** and dendrimers **6** and **7** do not adsorb and cannot modify the Pt electrodes. This is not the case for dendrimers **14** and **16**, which deposit onto the electrode surfaces upon scanning toward potentials that are positive to ferrocenyl oxidation. Modification of electrodes with films of dendrimers containing reversible redox systems has been successful, resulting in detectable electroactive material. This electrochemical behavior of modified electrodes was studied in dichloromethane containing only the supporting electrolyte (Figures 2 and 3). A well-defined, symmetrical redox wave is observed, which is characteristic of a surface-confined redox couple, with the expected linear relationship of peak current with potential sweep rate v.[21] Repeated scanning does not change the voltammograms, demonstrating that the modified electrodes are stable to electrochemical recycling. However, splitting between oxidation and reduction peaks is observed (ΔE = 40 mV), which suggests that a structural reorganization takes place within the electrochemical redox process within these ionic dendritic assemblies. Values of the full width at half-maximum for compounds **14** and **16** were measured at a scan rate of 100 mV/s and found to be ΔE_{fwhm} = 150 and 140 mV, respectively, suggesting the existence of

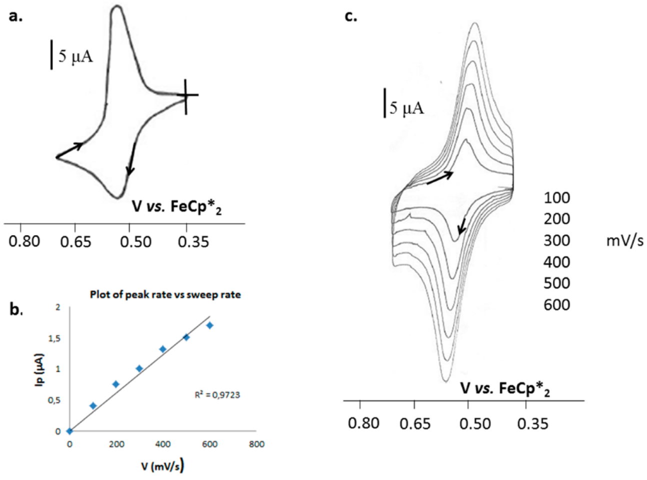

Figure 2. Cyclic voltammograms of **14** in CH_2Cl_2 solution containing 0.1 M [*n*-Bu$_4$N][PF$_6$]: (a) in solution; (b) intensity as a function of scan rate (linearity shows the expected behavior of an absorbed dendrimer); (c) modified Pt electrode at various scan rates in a CH_2Cl_2 solution (containing only the supporting electrolyte).

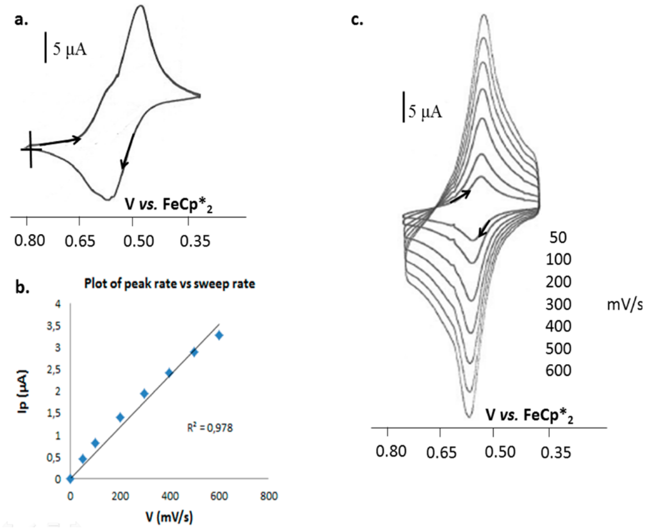

Figure 3. Cyclic voltammograms of **16** in CH_2Cl_2 solution containing 0.1 M [*n*-Bu$_4$N][PF$_6$]: (a) in solution; (b) intensity as a function of scan rate (linearity shows the expected behavior of an absorbed dendrimer); (c) modified Pt electrode at various scan rates in CH_2Cl_2 (solution containing only the supporting electrolyte).

repulsive forces between the ferrocenyl sites attached onto the electrode surface.[22] These Pt electrodes that are modified with dendrimers **14** and **16** are durable and reproducible, as no loss of electroactivity is observed after scanning several times or after standing in air for several days. The surface coverages of the electroactive ferrocenyl sites of the modified electrodes of metallodendrimers **14** and **16** are $\Gamma = 1 \times 10^{-11}$ and 1.7×10^{-11} mol cm^{-2}, respectively.

Concluding Remarks. The assembly of ionic dendrons and dendrimers represents a convenient way to synthesize large dendrimers with defect-free periphery insofar as the dendrimer purity solely depends on the purities of the dendrons and dendritic cores. The ionic linkers at the dendritic interiors are shielded so that the properties of these dendrimers essentially depend on the periphery. Of specific interest are ionic ferrocenyl dendrimers containing both intradendritic and peripheral ferrocenyl layers such as those synthesized here. The effect of the intradendritic positive charges of the ammonium groups clearly appears on the NMR chemical shifts and electrochemical potentials ($E_{1/2}$ values) of the inner ferrocenylmethyl groups. Interestingly, this electrostatic effect is more pronounced on the octamethylferrocenyl layer than on the parent ferrocenyl layer, probably because of the electron-rich methyl substituents in comparison to parent ferrocenyl sites. The $E_{1/2}$ value of the inner ferrocenyl layer is sufficiently shifted anodically to show a CV wave (shoulder) that is slightly distinct from that of the outer ferrocenyl layer. When the ferrocenyl substituents are different (H vs CH_3), the two separate CV waves clearly appear with relative intensities corresponding to their ratio (3/1). Finally, a characteristic of all the ionic ferrocenyl dendrimers is their strong ability to adsorb on electrodes and form derivatized electrodes that is considerably more marked than that of their neutral constituents. Potential applications are, for instance, the dendritic encapsulation of ionic or polar biomedical molecules in hydrophobic media and recyclable redox sensors.

■ EXPERIMENTAL SECTION

General Data. For general data including solvents, apparatuses, compounds, reactions, spectroscopy, and CV, see the Supporting Information . G$_n$ indicates the generation number *n*.

G$_0$-9-dend-NHCH$_2$-Fc (6). To a solution of ferrocenyl aldehyde (0.077 g, 0.358 mmol, 1.02 equiv/branch) in 30 mL of dry toluene was added dropwise at 70 °C a solution of polyamine dendrimer **3** (0.050 g, 0.033 mmol) in 20 mL of dry toluene under nitrogen. The reaction mixture was heated at 75 °C for 12 h. The red solution was then evaporated to dryness under reduced pressure, the resulting reddish solid containing G$_n$-3*n*+2-dend-N═CH-Fc was dissolved in 20 mL of THF, and a suspension of LiAlH$_4$ (2 equiv/branch) in 20 mL of THF was added slowly at 0 °C. After the addition, the mixture was stirred for 16 h at 50 °C under nitrogen. To the reaction solution at 0 °C was added dropwise H_2O (6 equiv/branch), and the mixture was stirred for 20 min. After drying under vacuum, the crude product was washed with acetonitrile in order to remove the excess of ferrocene aldehyde/methanol. Further purification was achieved from precipitation in acetonitrile, and the product was obtained as an orange sticky oil. Yield: 70%.

^{1}H NMR (CDCl$_3$, 300 MHz): δ (ppm) 7.01 (3H, C*H* core), 4.22 (18H, Cp sub), 4.15 (45H, Cp free), 4.15 (18H, Cp sub), 3.54 (18H, CpC*H*$_2$NH), 2.10 (18H, SiC*H*$_2$NH), 1.63 (18H, C$_q$C*H*$_2$CH$_2$CH$_2$Si), 1.11 (18H, C$_q$CH$_2$C*H*$_2$CH$_2$Si) 0.54 (18H, C$_q$C*H*$_2$CH$_2$C*H*$_2$Si), 0.03 (s, 54H, Si(C*H*$_3$)$_2$). ^{13}C NMR (CDCl$_3$, 75 MHz): δ (ppm) 145.7 (C$_q$ of arom core), 128.7 (CH of arom core), 86.3, 68.6, 68.4, 67.7 (Cp-C), 53.2 (CH$_2$-Cp), 43.1 (C$_q$CH$_2$CH$_2$CH$_2$Si), 42.1 (C$_q$H$_2$CH$_2$CH$_2$Si), 29.7 (Si(CH$_3$)$_2$CH$_2$NH), 17.7 (C$_q$CH$_2$CH$_2$CH$_2$Si), 15.1 (C$_q$CH$_2$CH$_2$CH$_2$Si), −3.8 (Si(CH$_3$)$_2$). Anal. Calcd for $C_{162}H_{237}Si_9N_9Fe_9$: C, 63.46; H, 7.79.. Found: C, 63.33; H, 7.80.

G$_0$-9-dend-NHCH$_2$-Fc# (7). To a solution of octamethylferrocene (54.8 mg, 0.16 mmol, 1.2 equiv/branch) in 30 mL of dry toluene was added dropwise at 70 °C a solution of nonaamine dendrimer (19.2 mg, 0.015 mmol) in 20 mL of dry toluene under nitrogen. The reaction mixture was heated to 75 °C for 16 h. The red solution was then evaporated to dryness under reduced pressure, and the resulting reddish solid containing G$_0$-dend-N═CH-Fc$^\#$ was washed with 20 mL of CH_3CN three times to remove the excess octamethylferrocene aldehyde/methanol. The resulting reddish solid was dried under reduced pressure and dissolved in a mixture of THF (10 mL) and CH_3OH (10 mL), and then NaBH$_4$ (3 equiv/branch) was slowly added at 0 °C. After the addition, the mixture was stirred for 30 min at 0 °C under nitrogen. The solvent was removed under reduced pressure. To the remaining solid was added dropwise H_2O (30 mL), and the compound was extracted three times with distilled diethyl ether. The combined organic phase was dried under anhydrous

Na_2SO_4. After evaporation, the compound was obtained as a yellow solid without further purification. Yield: 77%.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 6.92 (3H, $C\mathit{H}$ core), 3.48 (18H, $NHC\mathit{H_2}C_5(CH_3)_4$), 3.28 (9H, $C_5(CH_3)_4\mathit{H}$), 2.04 (18H, $SiC\mathit{H_2}NH$), 1.83, 1.79, 1.77, 1.71 (216H, $C_5(C\mathit{H_3})_4$), 1.58 (18H, $C_qC\mathit{H_2}CH_2CH_2Si$), 1.04 (18H, $C_qCH_2C\mathit{H_2}CH_2Si$), 0.47 (18H, $C_qC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.05 (54H, $Si(C\mathit{H_3})_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 145.7 (C_q of arom core), 128.7 (CH of arom core), 80.5, 80.0, 79.8, 79.7, 79.4, and 70.5 (Cp-C), 50.2 (Cp-CH_2NH), 43.8 ($C_qCH_2CH_2CH_2Si$), 42.0 ($C_qCH_2CH_2CH_2Si$), 29.7 (Si-$(CH_3)_2CH_2NH$), 17.8 ($C_qCH_2CH_2CH_2Si$), 15.1 ($C_qCH_2CH_2CH_2Si$), 11.0, 10.0, 9.9, 9.4 ($C_5(CH_3)_4$), −4.0 ($Si(CH_3)$=). Anal. Calcd for $C_{234}H_{381}Si_9Fe_9N_9$: C, 68.95; H, 9.43. Found: C, 68.71; H, 9.14.

G0-$NH_3^+PF_6^-$ (4). To a stirred solution of **3** (100 mg, 0.078 mmol) in 20 mL of distilled dichloromethane was added dropwise aqueous HPF_6 (1.1 equiv/branch) diluted in 3 mL of dichloromethane. Then a white precipitate started to form, but the product was stirred for an additional 30 min. The solution was evaporated, and the white solid was washed with acetone. The water-soluble white product **4** was obtained quantitatively.

^{1}H NMR (D_2O, 300 MHz): δ (ppm) 6.92 (3H, $C\mathit{H}$ core), 2.26 (18H, $SiC\mathit{H_2}NH_3^+$), 1.55 (18H, $C_qC\mathit{H_2}CH_2CH_2Si$), 0.99 (18H, $C_qCH_2C\mathit{H_2}CH_2Si$) 0.50 (18H, $C_qC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.03 (s, 54H, $Si(C\mathit{H_3})_2$). ^{13}C NMR (D_2O, 75 MHz): δ (ppm) 145.72 (C_q arom), 121.65 (CH arom), 43.66 ($C_qCH_2CH_2CH_2Si$), 41.11 ($C_qCH_2CH_2CH_2Si$), 27.76 ($Si(CH_3)_2CH_2NH_2^+$), 17.41 ($C_qCH_2CH_2CH_2Si$), 13.60 ($C_qCH_2CH_2CH_2Si$), −4.95 ($Si(CH_3)$). Anal. Calcd for $C_{63}H_{156}Si_9N_9P_9F_{54}\cdot 2H_2O$: C, 28.73; H, 6.13. Found: C, 28.82; H, 6.17.

G1-$NH_3^+Cl^-$ (8). To a stirred solution of **5** (50 mg, 0.009 mmol) in 20 mL of distilled dichloromethane was added dropwise aqueous HCl (1.2 equiv/branch) diluted in 5 mL of dichloromethane. Then a white precipitate started to form, but the product was stirred for an additional 30 min. The solution was evaporated, and the white solid was washed with acetone. The water-soluble white waxy product **8** was obtained quantitatively.

^{1}H NMR (D_2O, 300 MHz): δ (ppm) 7.15, 6.72 (39H, $C\mathit{H}$ core), 3.73 (18H, $C\mathit{H_2}OAr$), 2.43 (54H, $SiC\mathit{H_2}NH_3^+$), 1.88 (72H, $C_qC\mathit{H_2}CH_2CH_2Si$), 1.16 (72H, $C_qCH_2C\mathit{H_2}CH_2Si$), 0.63 (72H, $C_qC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.13 (216H, $Si(C\mathit{H_3})_2$). ^{13}C NMR (D_2O, 75 MHz): δ (ppm) 158.72 (OC_q arom of dendron), 139.56 (C_q arom), 127.23, 113.77 (CH arom), 43.16 ($C_qCH_2CH_2CH_2Si$), 41.69 ($C_qCH_2CH_2CH_2Si$), 27.86 ($Si(CH_3)_2CH_2NH_3^+$), 17.60 ($C_qCH_2CH_2CH_2Si$), 14.56 ($C_qCH_2CH_2CH_2Si$), −4.19 ($Si(CH_3)_2$). Anal. Calcd for $C_{288}H_{624}Si_{36}N_{27}O_9Cl_{27}\cdot 5H_2O$: C, 51.88; H, 9.59. Found: C, 51.60; H, 9.57.

Triferrocenyl Carboxylic Acid (13). To a solution of **10** (0.351 g, 0.365 mmol) in 40 mL of acetonitrile were added K_2CO_3 (0.101 g, 0.731 mmol) and methyl bromoethanoate (0.084 g, 0.548 mmol), and the resulting solution was heated at 90 °C for 16 h under a nitrogen atmosphere. After the solvent and excess methyl bromethanoate were removed, the crude product was dissolved in 100 mL of dichloromethane and the solution filtered through Celite. The solvent was removed under vacuum, and the product was obtained as an orange oil. Then product **11** (0.360 g, 0.35 mmol) was dissolved in 18 mL of dioxane, and a solution of NaOH (56 mg, 1.39 mmol) in 5 mL of H_2O was added dropwise. The solution was stirred for 16h at room temperature. Then, the solution was evaporated, and the product was washed in water and extracted from dichloromethane. Acidification of **12** in dichloromethane/water with aqueous HCl gave product **13** as an orange shiny oil. Yield: 90%.

Dendron 11. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.20, 6.90 (4H, arom), 4.66 (2H, $C\mathit{H_2}COOMe$), 4.35 (6H, Cp sub) 4.13 (15H, Cp free), 4.06 (6H, Cp sub), 3.86 (3H, $CH_2COO^-C\mathit{H_3}$), 1.65 (6H, $C_qC\mathit{H_2}CH_2CH_2Si$), 1.15 (6H, $C_qCH_2C\mathit{H_2}CH_2Si$), 0.65 (6H, $C_qC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.21 (18H, $Si(C\mathit{H_3})_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 168.48 (COOMe), 155.08 (OC_q arom), 141.20 (C_q arom), 127.32, 113.91 (CH arom), 72.75, 70.36 (CH of Cp sub), 71.16 (Cq of Cp sub), 67.81 (Cp free), 65.10 (CH_2COOMe), 52.17 ($COOCH_3$), 43.24 ($C_qCH_2CH_2CH_2Si$), 41.80 ($C_qCH_2CH_2CH_2Si$), 17.87 ($C_qCH_2CH_2CH_2Si$), 17.39 ($C_qCH_2CH_2CH_2Si$), −2.08 (Si-(CH_3)). MS (*m*/*z*): calcd for $C_{55}H_{72}O_3Si_3Fe_3$ 1032.2832, found 1032.7785.

Dendron 12. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.15, 6.81 (4H, arom), 4.34 (6H, Cp sub), 4.29 (2H, $C\mathit{H_2}COONa$), 4.12 (15H, Cp free), 4.08 (6H, Cp sub), 3.86 (3H, $CH_2COO^-C\mathit{H_3}$), 1.62 (6H, $C_qC\mathit{H_2}CH_2CH_2Si$), 1.12 (6H, $C_qCH_2C\mathit{H_2}CH_2Si$), 0.64 (6H, $C_qC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.19 (18H, $Si(C\mathit{H_3})_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 167.16 (COONa), 154.07 (OC_q arom), 140.17 (C_q arom), 127.61, 113.71 (CH arom), 73.00, 70.72 (CH of Cp sub), 70.98 (Cq of Cp sub), 68.17 (Cp free), 64.00 (CH_2COONa), 42.89 ($C_qCH_2CH_2CH_2Si$), 41.82 ($C_qCH_2CH_2CH_2Si$), 17.76 ($C_qCH_2CH_2CH_2Si$), 17.23 ($C_qCH_2CH_2CH_2Si$), −1.79 ($Si(CH_3)$).

Dendron 13. ^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.22, 6.90 (4H, arom), 4.56 (2H, $C\mathit{H_2}COOH$), 4.35 (6H, Cp sub), 4.13 (15H, Cp free), 4.06 (6H, Cp sub), 1.65 (6H, $C_qC\mathit{H_2}CH_2CH_2Si$), 1.17 (6H, $C_qCH_2C\mathit{H_2}CH_2Si$), 0.65 (6H, $C_qC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.21 (18H, Si-$(C\mathit{H_3})_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 174.41 (COOH), 155.11 (OC_q arom), 141.32 (C_q arom), 127.63, 114.42 (CH arom), 73.19, 70.90 (CH of Cp sub), 71.51 (Cq of Cp sub), 68.43 (Cp free), 66.29 (CH_2COOH), 43.33 ($C_qCH_2CH_2CH_2Si$), 42.04 ($C_qCH_2CH_2CH_2Si$), 18.26 ($C_qCH_2CH_2CH_2Si$), 17.74 ($C_qCH_2CH_2CH_2Si$), −1.87 ($Si(C\mathit{H_3})_2$). MS (*m*/*z*): calcd for $C_{54}H_{70}O_3Si_3Fe_3$ 1018.2681, found 1018.2715. Anal. Calcd for $C_{54}H_{70}O_3Si_3Fe_3$: C, 63.65; H, 6.92. Found: C, 63.32; H, 7.07.

General Synthesis of Ionic Polyammonium Carboxylate Dendrimers. To a stirred solution of secondary or primary polyamine dendrimer in 10 mL of distilled dichloromethane was added dropwise a solution of triferrocenyl carboxylic acid (1 equiv/branch) in 10 mL of dichloromethane, and the mixture was stirred for 20 min. The solvent was removed under vacuum, and the compound was obtained as an orange-yellow sticky oil in quantitative yield.

Dendrimer 14. The ionic dendrimer **14** was synthesized from **3** (10 mg, 0.008 mmol, 1 equiv) and **13** (71.5 mg, 0.070 mmol, 9 equiv) using the general synthesis of ionic polyammonium carboxylate dendrimers.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.17 (18H, arom), 7.02 (3H, arom core), 6.86 (18H, arom), 4.38 (18H, $C\mathit{H_2}COO^-$), 4.33 (54H, Cp sub), 4.12 (135H, Cp free), 4.05 (54H, Cp sub), 2.27 (18H, $SiC\mathit{H_2}NH_3^+$), 1.63 (72H, $C_qC\mathit{H_2}CH_2CH_2Si$), 1.15 (72H, $C_qCH_2C\mathit{H_2}CH_2Si$), 0.64 (72H, $C_qC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.20, 0.10 (216H, $Si(C\mathit{H_3})_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 174.88 (COO^-), 155.62 (OC_q arom of dendron), 140.46 (C_q arom), 127.48, 114.35 (CH arom), 72.91, 71.29, 70.75, 68.25 (Cp−C), 67.98 (CH_2COO^-), 43.24 ($C_qCH_2CH_2CH_2Si$), 42.19 ($C_qCH_2CH_2CH_2Si$), 25.58 ($Si(CH_3)_2CH_2NH_3^+$), 18.14 ($C_qCH_2CH_2CH_2Si$), 17.66 ($C_qCH_2CH_2CH_2Si$), −1.85, −3.99 ($Si(CH_3)_2$). Anal. Calcd for $C_{540}H_{777}Si_{36}Fe_{27}N_9O_{27}$: C, 62.69; H, 7.58. Found: C, 63.02; H, 7.73.

Dendrimer 15. The ionic dendrimer **15** was synthesized from **5** (10 mg, 0.002 mmol, 1 equiv) and **13** (49.5 mg, 0.049 mmol, 27 equiv) using the general synthesis of ionic polyammonium carboxylate dendrimers.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.17 (72H, arom), 6.95 (3H, arom core), 6.85 (72H, arom), 4.41 (54H, $C\mathit{H_2}COO^-$), 4.33 (162H, Cp sub), 4.12 (405H, Cp free), 4.05 (162H, Cp sub), 3.55 ($C\mathit{H_2}OAr$), 2.30 (54H, $SiC\mathit{H_2}NH_3^+$), 1.64 (234H, $C_qC\mathit{H_2}CH_2CH_2Si$), 1.13 (234H, $C_qCH_2C\mathit{H_2}CH_2Si$), 0.65 (72H, $C_qC\mathit{H_2}CH_2C\mathit{H_2}Si$), 0.21, 0.05 (216H, $Si(C\mathit{H_3})_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 174.10 (COO^-), 154.87 (OC_q arom of dendron), 141.22 (C_q arom), 127.54, 114.34 (CH arom), 72.92, 71.28, 70.62, 68.09 (Cp-C), 66.51 (CH_2COO^-), 43.27 ($C_qCH_2CH_2CH_2Si$), 42.09 ($C_qCH_2CH_2CH_2Si$), 27.96 ($Si(CH_3)_2CH_2NH_3^+$), 18.07 ($C_qCH_2CH_2CH_2Si$), 17.60 ($C_qCH_2CH_2CH_2Si$), −1.91, −3.40 ($Si(CH_3)_2$). Anal. Calcd for $C_{1719}H_{2487}Si_{117}Fe_{81}N_{27}O_{90}\cdot 2CH_2Cl_2$: C, 62.74; H, 7.63. Found: C, 62.64; H, 7.89.

Dendrimer 16. The ionic dendrimer **16** was synthesized from **6** (10 mg, 0.003 mmol, 1 equiv) and **13** (29.9 mg, 0.029 mmol, 9 equiv) using the general synthesis of ionic polyammonium carboxylate dendrimers.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.21, 6.89 (39H, arom), 4.41 (18H, CH_2COO^-), 4.35, 4.14, 4.07 (324H, Cp), 3.89 (18H, $^+NH_2CH_2Cp$), 2.20 (18H, $SiCH_2NH_2^+$), 1.65 (72H, $C_qCH_2CH_2CH_2Si$), 1.17 (72H, $C_qCH_2CH_2CH_2Si$) 0.66 (72H, $C_qCH_2CH_2CH_2Si$), 0.22, 0.07 (216H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 174.18 (COO^-), 155.70 (OC_q arom of dendron), 140.79 (C_q arom), 127.67, 114.56 (CH arom), 73.10, 71.50, 71.19, 70.81, 69.31, 68.99, 68.28 (Cp-C), 65.99 ($CH_2NH_2^+CH_2Cp$), 50.38 ($CH_2NH_2^+CH_2Cp$), 43.42 ($C_qCH_2CH_2CH_2Si$), 42.32 ($C_qCH_2CH_2CH_2Si$), 30.00 ($Si(CH_3)_2CH_2NH_2^+$), 18.26 ($C_qCH_2CH_2CH_2Si$), 17.76 ($C_qCH_2CH_2CH_2Si$), −1.73, −3.40 (Si-(CH_3)). Anal. Calcd for $C_{639}H_{867}Si_{36}Fe_{36}N_9O_{27}$: C, 63.28; H, 7.21. Found: C, 62.95; H, 7.12.

*Dendrimer **17**.* The ionic dendrimer **17** was synthesized from **7** (10 mg, 0.002 mmol, 1 equiv) and **13** (22.5 mg, 0.022 mmol, 9 equiv) using the general synthesis of ionic polyammonium carboxylate dendrimers.

^{1}H NMR ($CDCl_3$, 300 MHz): δ (ppm) 7.16, 6.95, 6.82 (39H, arom), 4.42 (18H, CH_2COO^-), 4.34, 4.13, 4.06 (324H, Cp of Fc), 3.93 (18H, $^+NH_2CH_2Cp$ of Fc$^\#$), 3.28 (9H, $C_5(CH_3)_4H$ of Fc$^\#$), 2.23 (18H, $SiCH_2NH_2^+$), 1.83−1.68 (216H, $C_5(CH_3)_4$), 1.66 (72H, $C_qCH_2CH_2CH_2Si$), 1.22 (72H, $C_qCH_2CH_2CH_2Si$), 0.65 (72H, $C_qCH_2CH_2CH_2Si$), 0.21, 0.07 (216H, $Si(CH_3)_2$). ^{13}C NMR ($CDCl_3$, 75 MHz): δ (ppm) 174.18 (COO^-), 155.70 (OC_q arom of dendron), 140.79 (C_q arom), 127.55, 114.53 (CH arom), 86.31, 83.14, 81.88, 72.94, 71.19, 70.63, 68.11 (Cp-C), 67.85 (CH_2COO^-), 51.19 ($CH_2NH_2^+CH_2Cp$), 43.27 ($C_qCH_2CH_2CH_2Si$), 42.15 ($C_qCH_2CH_2CH_2Si$), 29.70 ($Si(CH_3)_2CH_2NH_2^+$), 18.09 ($C_qCH_2CH_2CH_2Si$), 17.76 ($C_qCH_2CH_2CH_2Si$), −1.02, −3.20 (Si-($CH_3)_2$). Anal. Calcd for $C_{711}H_{1002}Si_{36}Fe_{36}N_9O_{27}\cdot 2CH_2Cl_2$: C, 64.39; H, 7.63. Found: C, 64.22; H, 7.85.

■ ASSOCIATED CONTENT

Ⓢ Supporting Information

Text and figures giving general data, spectroscopic data for compounds, NMR and mass spectra, IR and DOSY NMR spectra, and cyclic voltammograms. This material is available free of charge via the Internet at http://pubs.acs.org.

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Notes

The authors declare no competing financial interest.

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