# Molecular Batteries: Ferrocenylsilylation of Dendrons, Dendritic Cores, and Dendrimers: New Convergent and Divergent Routes to Ferrocenyl Dendrimers with Stable Redox Activity

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**Abstract:** The ferrocenylsilylation of the phenol triallyl dendron **2**, of the phenol nonaallyl dendron **4**, and of the 9-, 27-, 81-, and 243-allyl dendrimers **7**–**10** (monitored by the disappearance of the signals of the olefinic protons in $^1$H NMR spectra) has been achieved using ferrocenyldimethylsilane **1** and Karstedt's catalyst in diethyl ether at 40 °C, yielding the corresponding ferrocenyl dendrons and dendrimers. An alternative convergent synthesis of the nonaferrocenyl dendron **5** was carried out by reaction of the triferrocenyl dendron **2** with a protected triododendron followed by deprotection. Reaction of the nonaferrocenyl dendron **5** with hexakis(bromomethyl)benzene gave the 54-ferrocenyl dendron **6**. All the ferrocenyl dendron and dendrimers produce a chemically and electrochemically reversible ferrocenyl oxidation wave at seemingly the same potential. Stable platinum electrodes modified with the high ferrocenyl dendrimers were fabricated. The soluble orange-red ferrocenyl dendrimers can also be oxidized in $CH_2Cl_2$ by [NO][$PF_6$] to the insoluble deep blue polyferrocenium dendrimers. For instance, the 243-ferrocenium dendrimer has been characterized by its Mössbauer spectrum, which is of the same type as that of ferrocenium itself. The ferrocenium dendrimers can be reduced without any decomposition back to the ferrocenyl dendrimer, indicating that these multielectronic redox-stable dendrimers behave as molecular batteries.

**Keywords:** dendrimers · electrochemistry · electron transfer · hydrosilylations · metallocenes

## Introduction

The stable redox activity of nanoscopic materials is a desirable property in the design of electronic molecular-switch devices.[1] Dendrimers are a well-known source of nanoscopic materials for which the topology, dispersity, and introduction of redox active metal centers can be carefully controlled.[2–4] Recent reviews have indeed focused on metallodendrimers with promising functions and potential.[5–7] In particular, redox-active metallodendrimers such as polypyridine dendrimers prepared by the groups of Balzani,[8] Puddephat[9] and Constable,[10] ferrocenyl dendrimers prepared by Cuadrado et al.[11, 12] and tetrathiafulvalene dendrimers prepared by the groups of Bryce and Becher[13, 14] illustrate the potential access to precise redox-active nanoscopic molecules with original functions. Several other groups have also reported ferrocenyl dendrimers in which the ferrocenyl group is located at the center[15] or at the periphery[16–22] of the dendrimer. In the first case, the dendritic effect on the redox potential and reversibility have been disclosed whereas, in the latter case, the ferrocenyl groups appear independent, seemingly at the same redox potential. Although the synthesis of large ferrocenyl dendrimers has been achieved by Cuadrado's group (up to 64 branches),[16] the polyamidoferrocenyl dendrimers[16d, e] have not been chemically oxidized to stable ferrocenium dendrimers probably because the electron-withdrawing property of the amido group destabilizes the ferrocenium form. Although electrode surfaces coated with amidoferrocenyl derivatives have been successfully used in molecular recognition[22c] and biosensing[16f], this limitation may be somewhat damaging. We report here the ferrocenylsilylation of dendrons, dendritic cores, and dendrimers and valuable convergent and divergent routes[2–7] to redox-stable dendrons and dendrimers. Ferrocenyldimethylsilane (**1**),[24] has already been successfully used by Jutzi for the ferrocenylsilylation of

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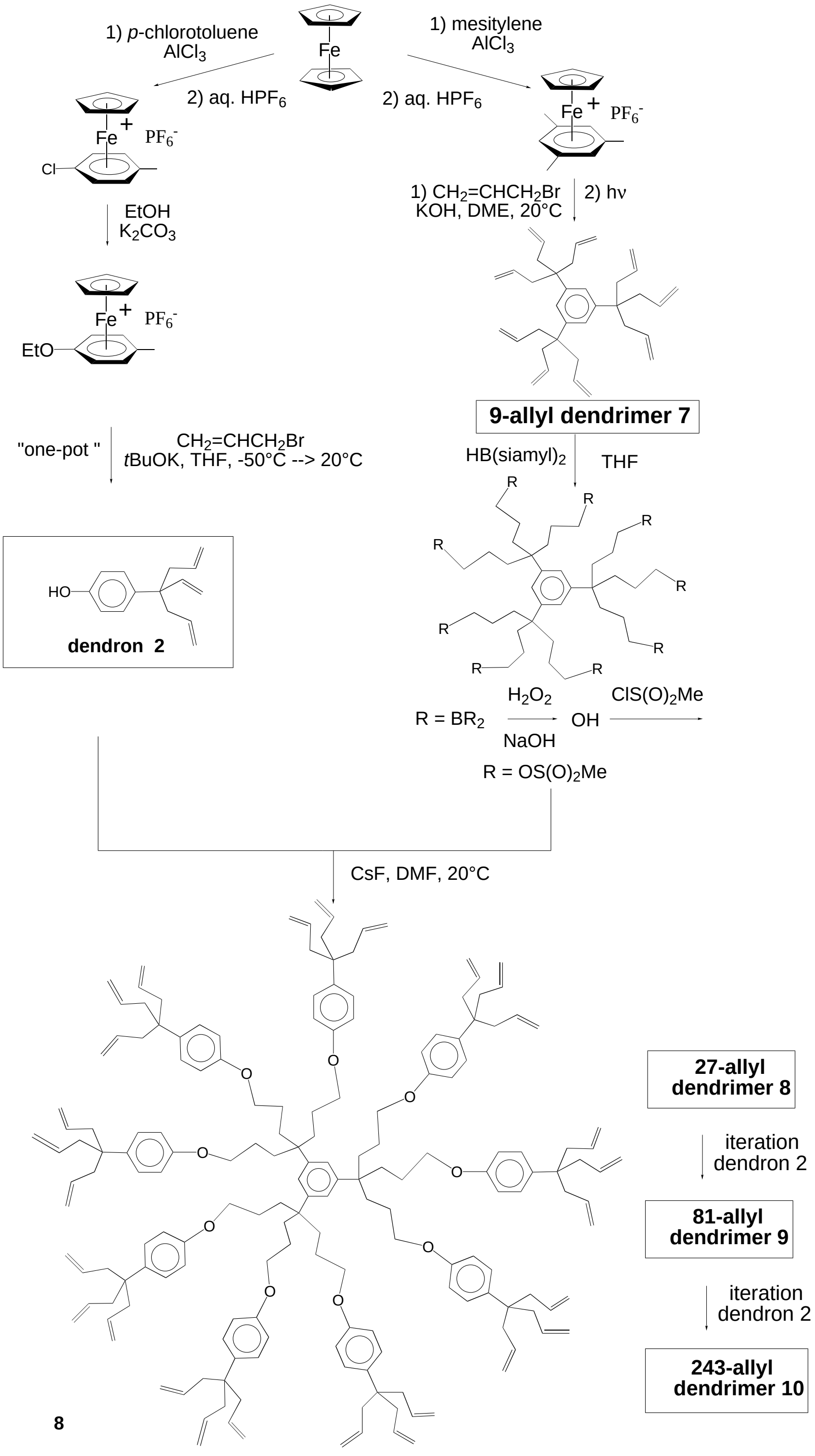
decaallylferrocenyl in the presence of air.[17] The ferrocenylsilylation of the olefin termini in dendrimers in its regiospecific version using **1** is represented in Equation (1).

$$\text{dendri-CH=CH}_2 + \text{FcSi(Me)}_2\text{H} \xrightarrow[\text{Fc=ferrocenyl}]{\text{Karstedt cat.}} \text{dendri-CH}_2\text{CH}_2\text{Si(Me)}_2\text{Fc} \quad (1)$$

Hydrosilylation of polyolefin dendritic cores using other silanes has also been utilized, in particular by Seyferth et al., for the synthesis of large organosilicon dendrimers and metallodendrimers.[25] Cuadrado's group has reported the synthesis of a number of ferrocenyl dendrimers with up to 16 ferrocenyl groups which have polysilane cores. Typically, these ferrocenyl dendrimers were synthesized by hydrosilylation of vinylferrocenyl using hydrogenosilane dendrimers.[11, 16] We have recently reported the organoiron-mediated syntheses of polyallyl dendrons, dendritic cores, and dendrimers,[22d] which are potentially an excellent source of metallodendrimers using hydroelementation reactions.[22e] The synthesis of these polyallyl dendrons, dendritic cores, and dendrimers, which we will use in the present report is represented in Scheme 1 and by compounds **9** and **10**.

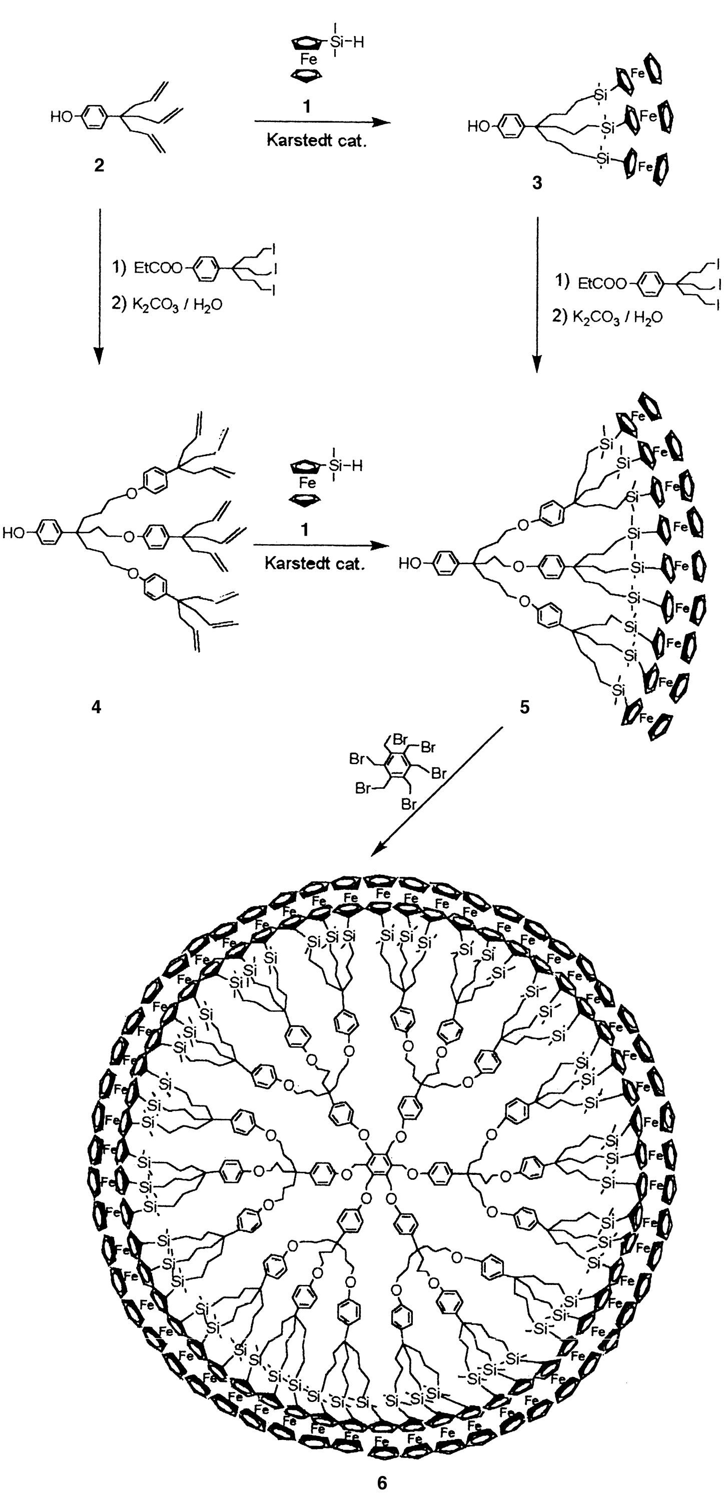
**Abstract in French:** *La ferrocénylsilylation du dendron phénol triallyl **2**, du dendron phénol nonaallyl **4**, et des dendrimères 9-, 27, 81 et 243-allyl **7**–**10** (suivie par la disparition des signaux des protons oléfiniques en RMN ¹H) a été réalisée de façon complète par action du ferrocényldiméthylsilane **1** et du catalyseur de Karstedt dans l'éther à 40°C, conduisant aux dendrons et aux dendrimères ferrocéniques correspondants. Alternativement, une synthèse convergente du dendron nonaferrocénylé **5** a été réalisée par réaction du dendron triferrocénylé **2** à l'aide d'un dendron triiodé, suivie de déprotection. La réaction du dendron nonaferrocénylé **5** avec l'hexakis (bromométhyl) benzène a conduit au dendron 54-ferrocénylé **6**. Tous les dendrons et les dendrimères ferrocénylés présentent une vague d'oxydation, chimiquement et electrochimiquement réversible, apparemment au même potentiel. Des électrodes de platine modifiées stables ont été fabriquées avec les dendrimères contenant un grand nombre de groupements ferrocényles, et ceci d'autant plus facilement que les dendrimères ferrocénylés sont plus grands. Ces dendrimères ferrocénylés orangé–rouges ont également été oxydés dans $CH_2Cl_2$ par $[NO][PF_6]$ en dendrimères polyferricinium bleu-foncés. Par exemple, le dendrimère 243-ferricinium a été caractérisé par son spectre Mössbauer analogue à celui du ferricinium luimême. Les dendrimères poly-ferricinium peuvent être réduits en dendrimères ferrocénylés par le décaméthylferrocéne, ce qui indique que ces dendrimères ferrocénylés ont une activité redox stable et se comportent comme des batteries moléculaires.*



Scheme 1. Divergent synthesis of the polyallyl dendrimers starting from ferrocene.

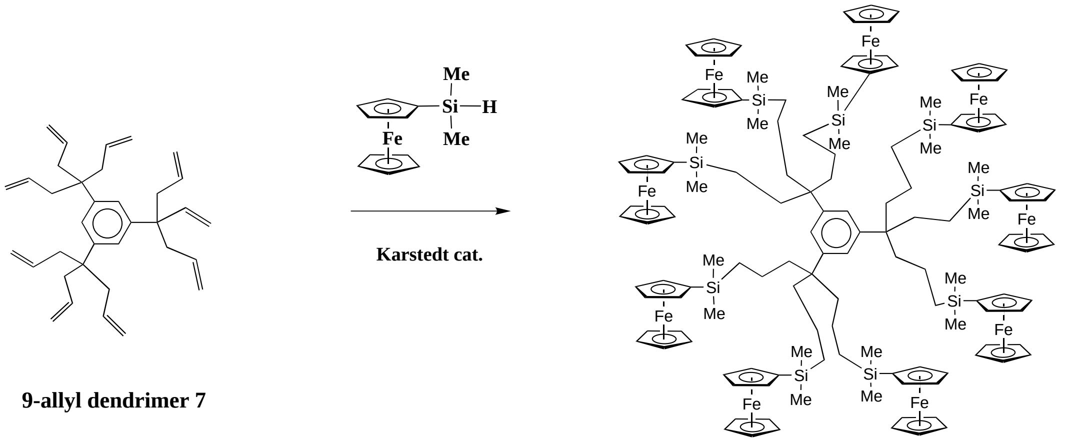
## Results

**Syntheses and spectroscopic characterization of the ferrocenyl dendrimers**: The ferrocenylsilylation of the phenoltriallyl dendron **2**[22d] using **1** is achieved with Karstedt's catalyst[27] in Et$_2$O in the absence of air without protection of the phenol function (Scheme 2). After chromatographic separation, the triferrocenylsilane dendron **3** is obtained in 90% yield. Contrary to Jutzi's reaction, the $^1$H and $^{13}$C NMR spectra indicate the absence of regioisomers, the analytical data are in agreement with the structure, and the matrix-assisted laser desorption ionization time-of-flight (MALDI TOF) mass spectrum show the molecular peak at $m/z$ 960.41 (calcd: 960.91) with a trace amount of impurities. Both the divergent and convergent routes were developed for the synthesis of the nonaferrocenyl dendron. Ferrocenylsilylation using **1** was also carried out on the nonaallylphenol dendron **4** giving the nonaferrocenyl dendron **5** in 90% yield after chromatography. The molecular peak is the major one in the MALDI TOF mass spectrum of **5**. Alternatively, the protected dendron $p$-Et-$CO_2C_6H_4C(CH_2CH_2CH_2I)_3$[26] reacts with **3** in DMF in the presence of $K_2CO_3$ to give **5** in 60% yield after deprotection and chromatography. The MALDI TOF mass spectrum of **5** shows that the molecular peak is also the dominant one (see Supporting Information). Reaction of dendron **5** with the core hexa(bromomethyl)benzene in DMF in the presence of $K_2CO_3$ at 80°C for two weeks gives the 54-ferrocenyl dendrimer **6** (Scheme 2). Ferrocenylsilylation of the 9-allyl dendritic core **7** [Eq. (2)] and of the 27-, 81- and 243-allyl dendrimers[26] **8**, **9**, and **10**, respectively, was also achieved in a similar manner, yielding the 9-, 27-, 81-, and 243-ferrocenyl dendrimers **11**, **12**, **13** and **14**, respectively ([Eq. (3)] and Scheme 3). The nonaferrocenyl dendrimer **11** also gives a good MALDI TOF mass spectrum with a molecular peak at $m/z$ 3110.44 (calcd: 3111.09) and only minor side peaks as shown in Figure 1. The spectra of the dendrimers **12** and **13** did not show the molecular peaks like those of their olefinic precursors, and instead a Gaussian distribution of peaks was observed, corresponding to the loss of ferrocenyldimethylsilane units. The ferrocenylsilylation of the 27- and 81-ferrocenyl dendrimers **8** and **9** was monitored by using $^1$H NMR spectroscopy by observing the disappearance of the olefinic protons. The $^1$H and $^{13}$C NMR spectra of **12** and **13** are clear and show sharp lines. It is therefore concluded that loss of the ferrocenyldimethylsilane units observed by mass spectrometry is most probably due to fragmentation in the mass spectrometer. The $^1$H NMR spectrum of the 243-ferrocenyl dendrimer **14** shows broader peaks and a complex pattern for the methyl protons. We believe these features are attributable to severe steric congestion, since the ferrocenylsilylation reaction of the 243-allyl dendrimer **10** was unique in requiring a longer reaction time of one week in order to reach completion (see Discussion).



Scheme 2. Convergent and divergent syntheses of the 9-ferrocenyl dendrimer **5** and of the 54-ferrocenyl dendrimer **6**.

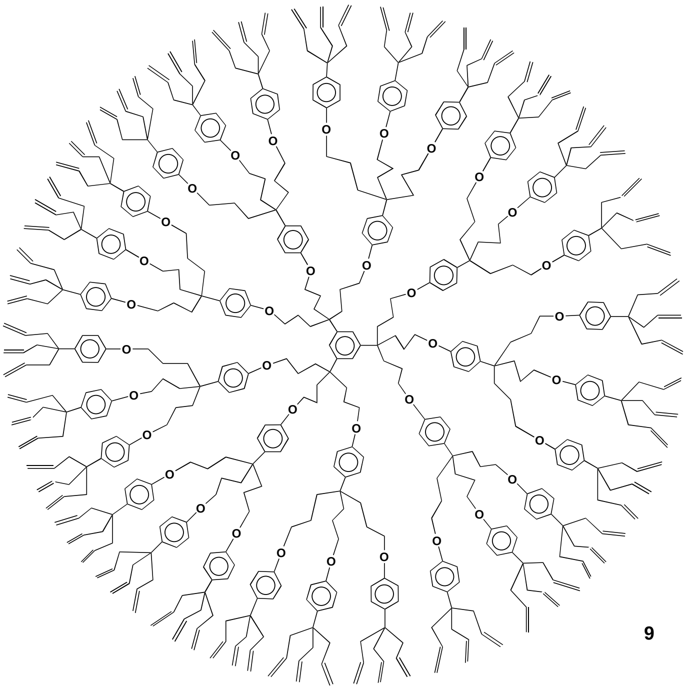
**Cyclic voltammetry and redox chemistry of the ferrocenyl dendrimers**: Cyclic voltammograms (CVs) of the ferrocenyl dendrons **3** and **5** and the ferrocenyl dendrimers **11**–**14** were recorded on a Pt anode in dichloromethane and in dimethyl form-



**9-allyl dendrimer 7**

**9-ferrocene dendrimer 11**

(2)



**9**

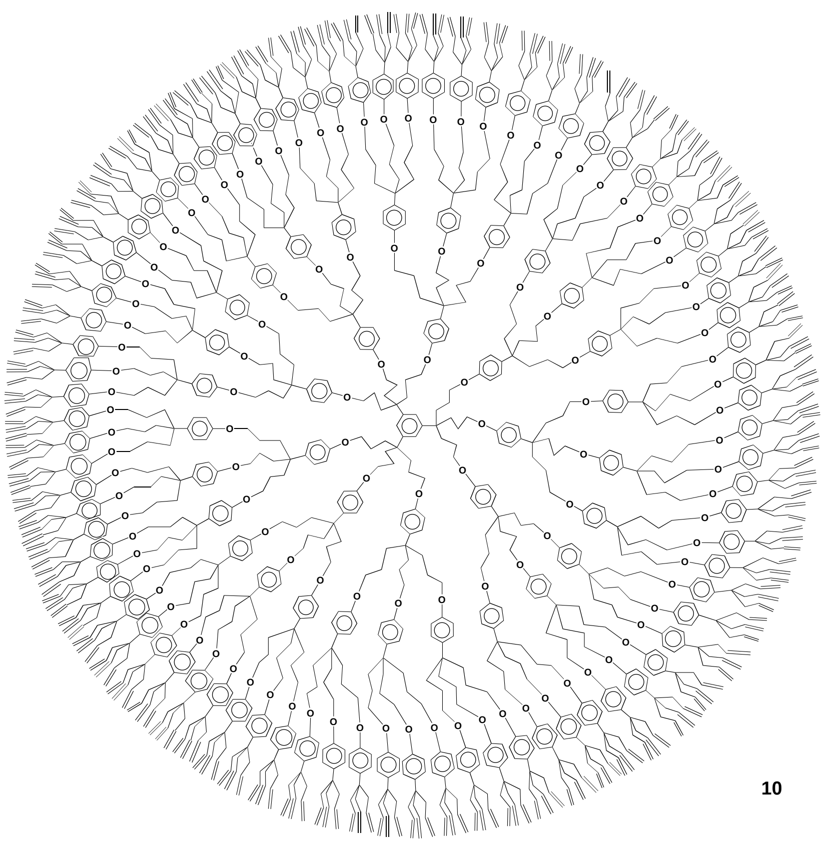
amide (DMF). In dichloromethane, dendrons **3** and **5** and dendrimer **11** show a reversible diffusion oxidation wave without adsorption. The number, $n_{\mathrm{d}}$, of electrons involved in this ferrocenyl dendrimer oxidation wave was determined by using Bard's equation [Eq. (4)] since this equation may be

$$n_{\mathrm{d}} = (I_{\mathrm{d}}/I_{\mathrm{m}})(c_{\mathrm{d}}/\,\mathrm{cm})(M_{\mathrm{d}}/M_{\mathrm{m}})^{0.275} \quad (4)$$

used for polymers containing identical redox centers.[29a,b] $I$, $c$ and $M$ are the intensities, concentrations and molecular masses of the dendrimer ($_{\mathrm{d}}$) and the monomeric decamethylferrocenyl reference ($_{\mathrm{m}}$) respectively.

The internal reference decamethylferrocene facilitated the accurate determination of the redox potential.[29c] The experimental number of electrons agreed with the actual number of dendritic branches within 5%. The cyclic voltammogram of the 27-ferrocenyl dendrimer **8** shows some adsorption in dichloromethane. This can be characterized by the low $\Delta E_{\mathrm{p}}$ value (40 mV) indicating a mixture of diffusion and adsorption phenomena. In the cases of **6**, **13** and **14**, $\Delta E_{\mathrm{p}}$ becomes even lower (30 mV). Modified electrodes[30] with the 27-, 54-, 81-, and 243-ferrocenyl dendrimers **6**–**10** could indeed be prepared by cyclic scanning between the ferrocenyl and ferrocenium regions of potentials on the Pt electrode in dichloromethane solution, washing with dichloromethane and drying in air. In the case of **11**, continuous cyclic scanning, repeated approximately twenty times is required before a constant voltammogram is obtained. However, for the modified electrode, the intensity of the current is very weak. With the large ferrocenyl dendrimers **6**, and **12**–**14**, shorter cyclic scanning of approximately ten repetitions is required in order to produce a constant curve, and the current of the modified electrode is much more intense. When such electrode derivatives are used in a new dendrimer-free solution containing only the electrolyte, the cyclic voltammogram of the adsorbed dendrimers is obtained with $\Delta E_{\mathrm{p}} = 0$ and there is a linear relationship between the scan rate and the intensity—both features being characteristic of derivatized electrodes with ferrocenyl polymers[30] and dendrimers[11, 16f] (see Figure 2). The electrode derivatives prepared by using this method with the various ferrocenyl dendrimers are stable for more than twenty cycles. No sign of diminished intensity was observed. The cyclic voltammograms of the 27-, 54-, and 81-ferrocenyl dendrimers **8**, **12**, and **13** in DMF showed no adsorption, with $E_{\mathrm{p}}$ values of 60 mV at 20 °C. Bard's equation provides a number of redox centers equal to $27 \pm 2$, $54 \pm 3$, and $75 \pm 6$ for **12**, **6**, and **13**, respectively. In the case of the 243-dendrimer **14**, the cyclic voltammogram shows some adsorption as indicated by the value $\Delta E_{\mathrm{p}} = 45$ mV in acetonitrile, and the number of electrons was estimated to be $250 \pm 30$. The use of Bard's equation in this case gives rise to a larger uncertainty as a result of the adsorption enhancing the wave intensity.

The orange-red ferrocenyl dendrimers can be oxidized quantitatively by $[\mathrm{NO}][\mathrm{PF}_6]$ in dichloromethane giving the dark blue polyferrocenium dendrimers, which immediately



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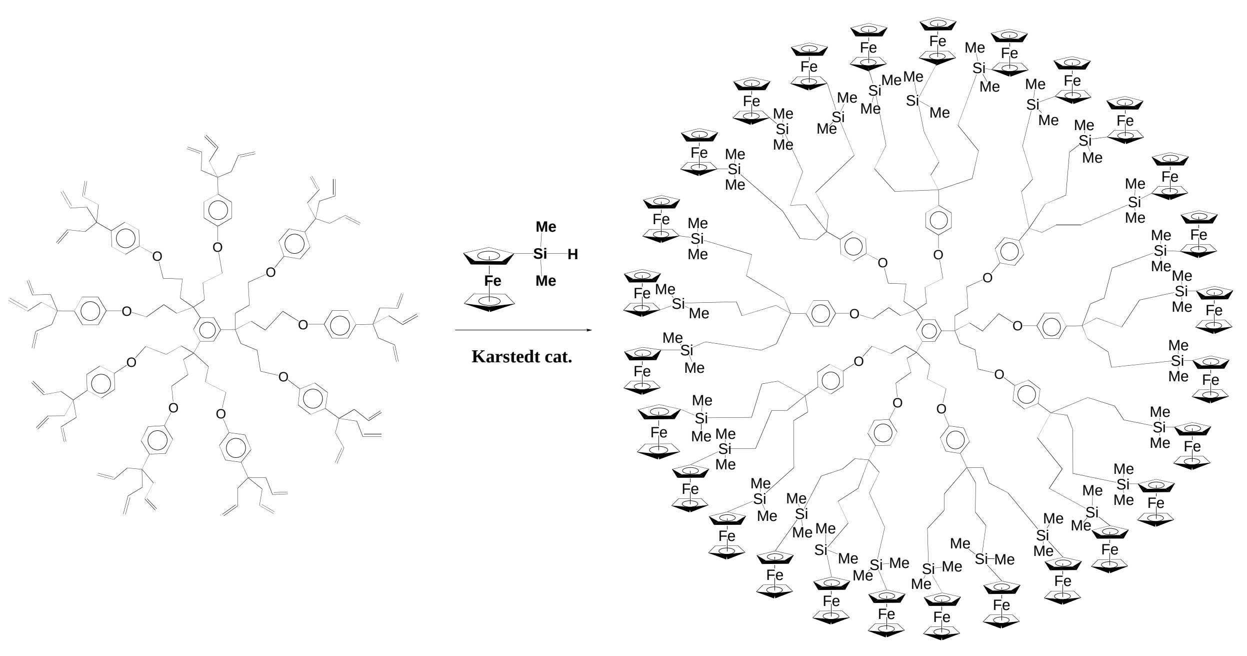
precipitate. These polyferrocenium dendrimers can be reduced back to the ferrocenyl dendrimers using the monoelectronic reductant decamethylferrocene without decomposition as indicated a comparison of the $^1$H NMR spectra recorded before and after these redox reactions. The zero-field Mössbauer spectra of the $PF_6^-$ salt of the 243-ferrocenium dendrimer **10**$^{243+}$ have been recorded at 293, 80, and 4 K. All show a single line with a nearly constant isomer shift and quadrupole splitting. The spectrum recorded at 4 K is shown on Figure 3. These spectra closely resemble those of ferrocenium and other known ferrocenium derivatives with the classical almost zero value of the quadrupole splitting.[31]

A comparison of the physical properties of the ferrocenyl dendrimers, obtained by thin-layer and column chromatography on silica and by cyclic voltammetry as a function of their size, is given in Table 1.

## Discussion

The ferrocenylsilylation of the terminal double bonds of polyolefin dendrons and dendrimers is a remarkably straightforward route to ferrocenyl dendrimers. In particular, we have observed that this reaction proceeds regioselectively with our dendrimers. It is of interest to compare the convergent and divergent routes since both procedures lead to the nonaallyl dendron **5**. The mass spectra show that **5** may be obtained by either the convergent or divergent pathway (the direct ferrocenylsilylation of the nonaallyldendron **4** gives a nonaferrocenyl dendrimer which has a good purity). The two routes may be compared in Scheme 2. This is a rare example in dendritic chemistry for which both the convergent and



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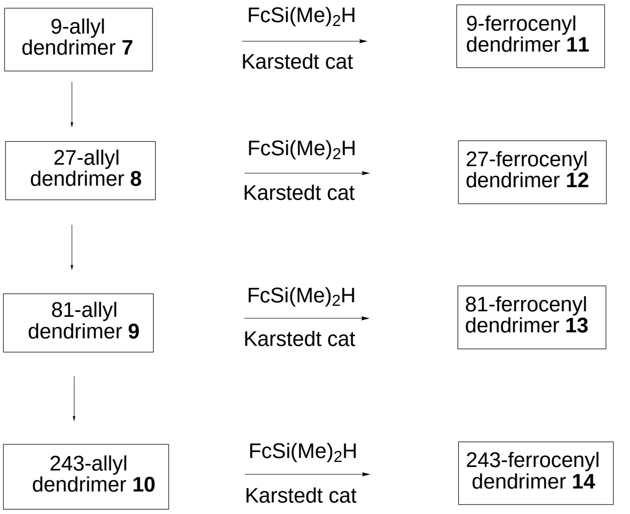

Scheme 3. Syntheses of the polyallyl dendrimers (according to Scheme 1) and of the polyferrocenyl dendrimers.

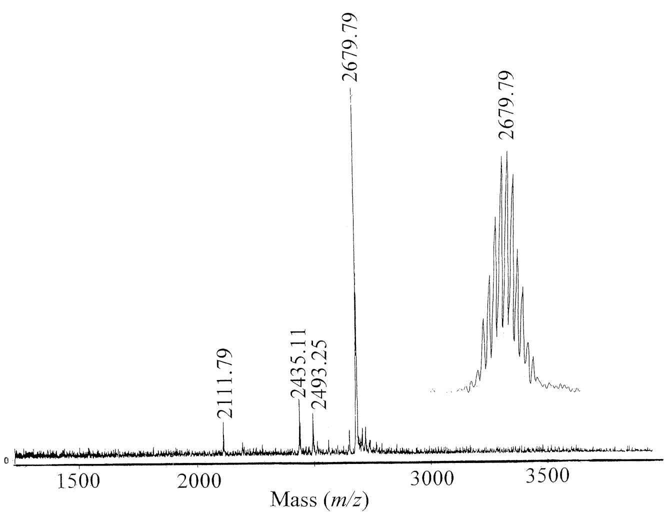

Figure 1. MALDI TOF mass spectrum of the 9-ferrocenyl dendrimer **10** showing the molecular peak and its isotopic distribution (right). The small peak at $m/z$ 2493.25 ($M = 186$) corresponds to the loss of a ferrocene unit and the small peak at $m/z$ 2435.11 ($M = 244$) corresponds to the loss of a ferrocenyl dimethyl silyl unit.

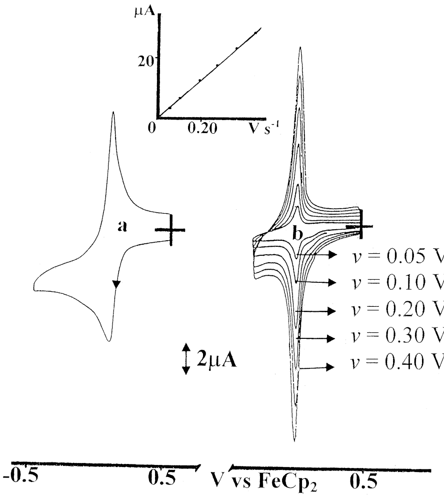

Figure 2. Cyclic voltammogram of the 243-ferrocenyl dendrimer **14** in $CH_2Cl_2$ solution containing 0.1 M [$n$Bu$_4$N][PF$_6$]: a) in solution ($10^{-4}$ M) at 100 mV s$^{-1}$; b) Pt anode modified with **14** at various scan rates (inset: intensity as a function of scan rate).

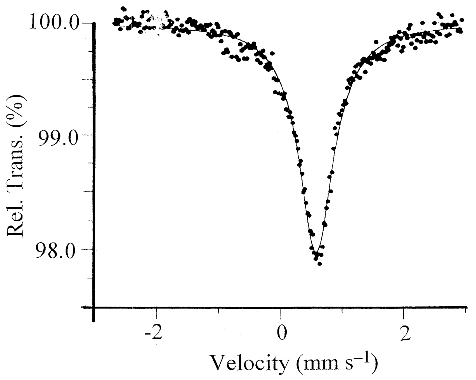

Figure 3. Zero-field Mössbauer spectrum of the 243-ferrocenium dendrimer **14** at 4 K showing the single line which corresponds to a almost zero quadrupole splitting. Isomer shift, $IS = 0.57(1)$ mm s$^{-1}$ versus Fe, $\Gamma = 100(4)$.

divergent syntheses were successful in producing the same dendrimer.

Finally, we have found that the presence of air, which was required in Jutzi's syntheses, is not necessary for the

Table 1. Physical properties of the ferrocenyl dendrons and dendrimers: solubilities, migration on thin-layer chromatography (tlc) plates, elution on silica-gel columns, $E_{1/2}$ values [mV] versus the ferrocene/ferrocenium redox couple determined by the average between the anodic and cathodic peak potentials in cyclic voltammetry (considered as equal to the standard redox potential $E°$, see also the general data of the experimental section) and adsorption characterized by the separation $\Delta E_p$ [mV] between the anodic and cathodic peaks of the ferrocenyl/ferrocenium redox system of the dendrons and dendrimers (see also Figure 2). Fc: ferrocenyl, p: pentane, e: diethyl ether

| polyferrocenyl (Fc) dendrimer | 3(3-Fc) | 5(9-Fc) | 11(9-Fc) | 12(27-Fc) | 6(54-Fc) | 13(81-Fc) | 14(243-Fc) |
|---|---|---|---|---|---|---|---|
| solubility | | | | | | | |
| pentane | good | good | good | low | low | nil | nil |
| ether | good | good | good | good | good | good | good |
| tlc $SiO_2$ | p + 20 % e | p + 20 % e | p + 2 % e | p + 3 % e | p + 20 % e | p/e:1/1 | no migr. |
| retention indices | 0.5 | 0.3 | 0.5 | 0.5 | 0.8 | 0.4 | |
| column $SiO_2$ | p + 10 % e | p + 10 % e | p + 2 % e | e/p:1/1 | p + 5 % e | pure e | no migr. |
| $E_{1/2}$ ([mV] $CH_2Cl_2$) | −5 | −10 | −5 | −10 | −10 | −15 | −15 |
| adsorption/Pt | | | | | | | |
| $CH_2Cl_2$, $\Delta E$ [mV] | nil (60) | nil (60) | nil (60) | weak (40) | good (30) | good (30) | good (30) |
| DMF, $\Delta E$ [mV] | nil (60) | nil (60) | nil (60) | nil (60) | nil (60) | nil (60) | some (45) |

ferrocenylsilylation. Dendron **3** was synthesized in either the presence or absence of air, and further reactions were achieved in the absence of air. We have noticed a modification of the appearance of the catalyst in the presence of air. This may explain the change of structure of the catalyst, provoking the presence of 10% of the less favored regioisomer mentioned by Jutzi. This has not been investigated any further since our procedure in the absence of air turned out to be satisfactory.

The convergent route cannot be continued beyond the synthesis of **5** because of steric effects. Indeed, a former attempt to synthesize a 27-allyl dendron from the nonaallyl dendron **6** and the protected dendron **4** specifically led to a 19-allyl dendron in which two iodo branches had correctly reacted, whereas the third one had undergone dehydroiodation because of the steric effect.[26f] Thus, the divergent route was the only possible pathway to the 27-ferrocenyl and higher ferrocenyl dendrimers. These syntheses proceeded smoothly in diethyl ether at reflux for two days, and the course of the reactions was easily monitored in $^1$H NMR spectroscopy by the disappearance of the low-field signals of the olefinic protons. Since the molecular peak was dominant in the MALDI TOF mass spectra of the precursor polyolefin dendrimers (except **10**)[26f], and since the product of divergent ferrocenylsilylation of the nonabranched dendron **4** and dendritic core **7** also gave dominant molecular peaks in the mass spectra, it is probable that the degree of purity of these large ferrocenyl dendrimers is reasonable. The integrations of the ferrocenyl signals compared to the core signals were in agreement with the structure within 5 to 10% accuracy of the $^1$H NMR integration. The effect of steric congestion was only observed during the synthesis of the 243-ferrocenyl dendrimer **14**. In this latter case, a longer reaction time was required in order to reach completion of the reaction—completion being indicated by the disappearance of the olefin protons in the $^1$H NMR spectra. For the polyolefin precursor, clear $^1$H and $^{13}$C NMR spectra had previously been obtained, but the MALDI TOF mass spectrum could not be recorded. The $^1$H NMR spectrum and the electrochemical data of **14** are in agreement with the 243-ferrocenyl dendrimer structure, but these data are not precise and cannot provide accuracy superior to 10%. Thus, in the worse case, the number of ferrocenyl branches in **14** could be a statistical distribution between 220 and 243 branches, and only a very small quantity of the 243-ferrocenyl dendrimer would be present.

The cyclic voltammetry of the ferrocenyl dendrimers shows only one wave for all the equivalent redox centers. This feature has already been reported with other dendrimers containing redox centers at the periphery. It has been observed in particular by Cuadrado's group[11, 16] for ferrocenyl dendrimers and by Bryce's group with TTF dendrimers.[13, 14a] Thus, it seems that all the redox centers have the same redox potential. However, this is not strictly true because it is more difficult to oxidize a monocation such as **14**$^+$ than the neutral compounds **14**, and so on, because of the electrostatic factor. There is in fact a distribution of redox potentials around a mean value, as indicated by Bard and Anson.[29] However, the redox centers are so far from one another in the dendritic molecules that the electrostatic effect is very weak and not even measurable. The $\Delta E_p$ values are 60 mV for all the ferrocenyl dendrimers in the situation of pure diffusion at 20°C just as for the monoelectronic wave of the internal decamethylferrocenyl reference.

It is possible to eliminate the adsorption up to a certain dendritic size and to determine the number of monoelectronic redox centers of the dendrimer with a reasonable accuracy in these cases. When the ferrocenyl dendrimer becomes too large, it is no longer possible to observe a pure diffusion current and the determination of the number of redox centers using Bard's formula becomes much less accurate, and leads to numbers of electrons in excess. On the other hand, the preparation of dendrimer-modified electrodes becomes easier as the size of the ferrocenyl dendrimer increases. Stable modified electrodes were prepared in this ferrocenyl-dendrimer chemistry on Pt anodes with the 54-, 81-, and 243-ferrocenyl dendrimers **6**, **13**, and **14**.

It is also of interest to note the full chemical and electrochemical reversibility of the cyclic voltammograms of the monoelectronic ferrocenyl oxidation wave obtained in the diffusion regime as well as in modified electrodes. The electrochemical reversibility means that the heterogeneous electron transfer between the electrode and the redox centers of the dendrimer in solution in the diffusion regime is fast. This sharply contrasts with the electrochemical irreversibility observed for metal-centered dendrimers in which the redox-active metal is buried inside the dendrimer. This latter trend has been reported by a number of research groups.[28] The distance between the electrode surface of the remote ferrocenyl centers of the large ferrocenyl dendrimers **6**, **13** and **14** is much larger than between the electrode and the buried redox centers in the reported metal-centered dendrimers of moderate size. However, the metallodendrimer rapidly rotates, bringing all the redox centers close to the electrode within the electrochemical time scale.[33] In addition, there is a possibility of a relay mechanism operating among the surface ferrocenyl dendrimers **6**, **13**, and **14** whose shape is close to globular. This relay mechanism would allow electrons from remote ferrocenyl units to be transferred to the electrode surface via the other ferrocenyl units located along the globular dendritic surface, in particular those located between the remote ferrocenyl units and the proximity of the electrode surface. Various mechanisms can be envisaged: electron hopping from one ferrocenyl unit to the next; relay from one ferrocenyl center to the next via the shortest σ-bond pathway (ten bonds); some sort of π stacking between two neighboring ferrocenyl units.

Finally, the ferrocenyl dendrimers can be oxidized to ferrocenium dendrimers using a chemical oxidant at room temperature. These deep-blue ferrocenium dendrimers have a huge amount of positive charges and spins and can be characterized and reduced back to the initial ferrocenyl dendrimer without any decomposition. Thus, it appears that these ferrocenyl dendrimers, which have a stable redox activity at about the same standard potential for all the branches, are molecular batteries which might find applications in molecular-electronic devices.

## Conclusions

1) The regiospecific ferrocenylsilylation of polyallyl dendrons, dendritic cores and dendrimers facilitates the synthesis of ferrocenyl dendrons and dendrimers of various sizes up to a theoretical number of 243 ferrocenyl termini.
2) Both convergent and divergent routes to a nonaferrocenyl phenol dendron are excellent and are comparative in that both lead to a compound which shows the dominant molecular peak in the MALDI TOF mass spectrum.
3) The cyclic voltammograms show chemical and electrochemical reversibility for all the ferrocenyl dendrons and dendrimers. In DMF, the current is due to the diffusion up to the 81-ferrocenyl dendrimer, which allows the determination of the number of monoelectronic redox centers of the ferrocenyl dendron or dendrimer with a relatively good accuracy (5 to 8%).
4) In $CH_2Cl_2$, only the cyclic voltammograms of the small ferrocenyl dendrons and dendrimers (up to nine branches) on a Pt anode disclose a pure diffusional current, and a mixture of currents due to diffusion and adsorption is observed for the higher ferrocenyl dendrimers in this solvent. This allows the fabrication of derivatized Pt electrodes with the ferrocenyl dendrimers, which is facilitated as the ferrocenyl dendrimer size increases.
5) The full electrochemical reversibility of the cyclic voltammetric waves means that the fast electron transfer between the electrode surface and all the ferrocenyl units is due to the fast rotation of the metallodendrimer. The rapid rotation results in all the redox centers of the metallodendrimer approaching the proximity of the electrode within the electrochemical time scale, and possibly gives rise to a relay-mechanism operating in these quasi-globular dendrimers that facilitates the transfer of electrons from the electrode surface to the most remote ferrocenyl groups. This situation contrasts with (and complements) the electrochemical irreversibility reported by several research groups when the redox centers is buried at the center of the dendrimer.
6) The orange ferrocenyl dendrimers can be oxidized by $[NO][PF_6]$ to stable deep-blue ferrocenium dendrimers. The 243-ferrocenium dendrimer has been characterized by Mössbauer spectroscopy, and the ferrocenium dendrimers can be reduced back to the ferrocenyl dendrimers without any decomposition along the redox cycle. Thus, these ferrocenyl dendrimers are molecular batteries and should find applications in molecular-electronic devices. Further synthetic developments and physical studies are underway in our laboratories.

## Experimental Section

**General data**: Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were predried over Na foil and distilled from sodium-benzophenone anion under argon immediately prior to use. Acetonitrile ($CH_3CN$) was stirred under argon overnight over phosphorus pentoxide, distilled from sodium carbonate, and stored under argon. Methylene chloride ($CH_2Cl_2$) was distilled from calcium hydride just before use. All other chemicals were used as received. The complex **1** was synthesized according to ref. [23]. The dendrons $p$-$OHC_6H_4C(CH_2CH{=}CH_2)_3$ (**2**) and $p$-$EtCO_2C_6H_4C(CH_2CH_2CH_2I)_3$ and the polyallyl dendrimers **7**–**10** were synthesized according to ref. [26]. The Karstedt catalyst was provided by ABCR GmbH (Karlsruhe), stored under nitrogen, and used as received. All manipulations were carried out using Schlenk techniques or in a nitrogen-filled Vacuum Atmospheres drylab. Infrared spectra were recorded with a Perkin–Elmer 1420 infrared spectrophotometer that was calibrated with polystyrene. Samples were examined in solution (0.1 mm cells with NaCl windows), between NaCl disks in Nujol, or in KBr pellets. $^1$H NMR spectra were recorded at 25 °C with a Brucker AC 250 (250 MHz) spectrometer. $^{13}$C NMR spectra were obtained in the pulsed FT mode at 62.91 MHz with a Brucker AC 250 spectrometer. All chemical shifts are reported with reference to $Me_4Si$ (TMS). Electronic spectra (UV and visible) were recorded at 20 °C with a Cary 219 spectrophotometer with 10 or 1 mm quartz cells. Cyclic voltammetry data were recorded with a PAR 273 potentiostat galvanostat. Care was taken in the CV experiments to minimize the effects of solution resistance on the measurements of peak potentials (the use of positive feedback *iR* compensation and dilute solution ($10^{-3}$ mol L$^{-1}$) maintained currents between 1 and 10 mA). When possible, the additional redox couple $[FeCp_2]/[FeCp_2]^+$ was used as a control for *iR* compensation. Thermodynamic potentials were recorded with reference to an aqueous SCE in THF (0.1 M $n$Bu$_4$NBF$_4$). The value of the $[FeCp_2]/[FeCp_2]^+$ redox couple was $E^{\circ\prime} = 0.470$ V versus SCE on Pt in DMF and 0.475 V versus SCE on Pt in $CH_2Cl_2$. The QRE potential was calibrated by adding the reference couple $[FeCp_2]/[FeCp_2]^+$. The counter electrode was platinum. Mössbauer spectra were recorded with a 25 mCi $^{57}$Co source on Rh, using a symmetric triangular sweep mode by Professor François Varret at the University of Versailles. Elemental analyses were performed by the Centre of Microanalyses of the CNRS at Lyon-Villeurbanne, France. Elemental analyses of the high dendrimer (from 27- to 243-ferrocenyl dendrimers) systematically showed low C content, which was a result of inclusion phenomena well-known in dendrimer chemistry.[32]

**Triferrocenyl dendron 3**: Karstedt catalyst (250 µL of a solution containing 2.2% Pt in xylene) was added to a solution containing the triallylphenol **2** (0.228 g, 1 mmol) and ferrocenyldimethylsilane (**1**) (1.1 g, 4.5 mmol) in toluene (20 mL) under an inert atmosphere (an alternative procedure using a stream of air gave analogous results). The closed reaction medium was heated to 45 °C for one day. Toluene was removed under vacuum, the reaction product extracted with pentane, and the resulting solution was concentrated and chromatographed on a silica column using a 9:1 pentane:diethyl ether mixture providing **3** as a red-orange oil (0.864 g, 0.900 mmol 90% yield). Analytical data for $C_{52}H_{68}OSi_3Fe_3$: calcd: H 7.14, C 64.98; found: H 7.21, C 64.75. MALDI TOF mass spectrum: major peak $m/z$: 960.26 (calcd for $m/z$: 960.41); $^1$H NMR ($CDCl_3$, 250 MHz): $\delta = 7.12$ (d, 2H; $C_6H_4$), 6.75 (d, 2H; $C_6H_4$), 4.20 (t, 6H; $C_5H_4$), 4.09 (s, 15H; $C_5H_5$), 4.01 (t, 6H; $C_5H_4$), 1.59 (s, br, 6H; $CH_2Ar$), 1.12 (s, br, 6H; $CH_2CH_2Ar$), 0.61 (s, br, 6H; $CH_2Si$), 0.17 (s, 18H; SiMe); $^{13}$C NMR ($CDCl_3$, 62.9 MHz): $\delta = 156.55$ ($C_q$, ArO), 139.88 ($C_q$, Ar), 127.66 (CH, Ar), 114.67 (CH, Ar), 72.95 ($C_5H_4$), 71.58 ($C_q$, $C_5H_4$), 70.52 ($C_5H_4$), 68.12 ($C_5H_5$), 43.12 ($C_q$-$CH_2$), 42.16 ($CH_2$), 18.08 ($CH_2CH_2Si$), 17.56 ($CH_2Si$), −1.93 (SiMe).

**9-Ferrocenyl dendron 5, convergent path**: Compound **3** (0.600g, 0.625 mmol) in freshly distilled DMF (10 mL) and $K_2CO_3$ (0.088g, 0.625 mmol) were introduced into a flamed and deaerated Schlenk flask. The reaction mixture was stirred for 30 min, then $p$-$EtCO_2C_6H_4C(CH_2CH_2CH_2I)_3$ (0.093g, 0.14 mmol), dissolved in DMF (10 mL) was added, and stirring was continued for two days at room temperature. $K_2CO_3$ (0.100 g) and water (0.150 mL) were added and the mixture was heated at 45 °C for two days. DMF was removed under vacuum and the reaction product was extracted with pentane/$Et_2O$ (50/50) and chromatographed on a silica column; **3** eluted first, then **5** eluted using a 80:20 pentane:$Et_2O$ mixture, and was obtained as red-orange oil (0.262 g, 0.084 mmol, 60% yield). Analytical data for $C_{17}H_{22}O_4Si_9Fe$: calcd: H 7.26, C 66.39; found: H 7.50, C 66.12. MALDI TOF mass spectrum, major peak: $m/z$: 3110.44 $[M+H^+]$ (calcd 3108.94); $^1$H NMR ($CDCl_3$, 250 MHz): $\delta = 7.18$ (m, 8H; $C_6H_4$), 7.04 (m, 8H; $C_6H_4$), 4.23 (m, br, 18H; $C_5H_4$), 4.02 (s, 45H; $C_5H_5$), 3.94 (m, br, 6H; $C_5H_4$), 3.89 (s, br, 6H; $CH_2O$), 1.54 (s, br, 24H; $CH_2CH_2Ar$), 1.18 (s, br, 24H; $CH_2CH_2Ar$); 0.56 (s, br, 18H; $CH_2Si$), 0.16 (s, 45H; SiMe); $^{13}$C NMR ($CDCl_3$, 62.9 MHz,): $\delta = 156.11$ (Cq, ArO), 152.39 ($C_q$, ArOH), 140.02 ($C_q$, Ar), 127.63 (CH, Ar), 127.60 (CH, Ar), 114.64 (CH, Ar), 113.69

(CH, Ar), 73.21 ($C_5H_4$), 71.83 ($C_q$, $C_5H_4$), 70.88 ($C_5H_4$), 68.38 ($C_5H_5$), 43.20 (Cq-$CH_2$), 42.16 ($CH_2$), 29.50 ($CH_2CH_2Ar$), 18.07 ($CH_2CH_2Si$), 17.56 ($CH_2Si$), −1.95 (SiMe).

**9-Ferrocenyl dendron 5, divergent path**: Karstedt catalyst (250 µL of a solution containing 2.2 % Pt in xylene) was added to a solution containing **4** (0.230 g, 0.25 mmol) and ferrocenyldimethylsilane (**1**) (0.732 g, 3.0 mmol) in toluene (20 mL). The system was closed and heated to 40 °C for one day, toluene was removed under vacuum, and the product was extracted with pentane, chromatographed on a silica column using a pentane:diethyl ether 9:1 mixture as the eluent. The compound **5** was obtained as an orange oil (0.505 g, 0.162 mmol, 65 % yield). MALDI TOF mass spectrum, dominant molecular peak: $m/z$: 3111.65 $[M+H^+]$ (calcd 3108.94 $[M]$).

**54-Ferrocenyl dendrimer 6**: Complex **5** (0.153 g, 0.049 mmol) in ethanol (5 mL) and $K_2CO_3$ (0.007 g, 0.051 mmol) were introduced into a flamed and deaerated Schlenk flask, the reaction mixture was stirred for one hour at room temperature, $C_6(CH_2Br)_6$ (0.004 g, 0.006 mmol) was added, and the reaction mixture was refluxed for 14 days. The solvent was removed under vacuum, and the product was extracted with diethyl ether and chromatographed on a silica column. Compound **6** was eluted with a 9:1 petroleum ether:ether mixture (thin layer chromatography: frontal retention indices: 0.8 using a 8:2 petroleum ether:diethyl ether mixture as the eluent), and was obtained as an orange solid (0.023 g, 0.0012 mmol, 20 % yield). The compound **5** was then eluted and recovered. **6**: $^1H$ NMR ($CDCl_3$, 250 MHz): $\delta = 7.12$ (m, 60 H; $C_6H_4$), 6.77 (m, 60 H; $C_6H_4$), 5.21 (s, br, 18 H; $PhCH_2O$), 4.29 (m, br, 108 H; $C_5H_4$), 4.09 (s, 270 H; $C_5H_5$), 4.01 (m, br, 108 H; $C_5H_4$), 3.86 (s, br, 36 H; $CH_2O$), 1.54 (s, br, 108 H; $CH_2CH_2Ar$), 1.12 (s, br, 108 H; $CH_2CH_2Ar$), 0.60 (s, br, 108 H; $CH_2Si$), 0.16 (s, 324 H; SiMe); $^{13}C$ NMR ($CDCl_3$, 62.9 MHz): $\delta = 156.11$ ($C_q$, ArO), 139.56 ($C_q$, Ar), 127.60 (CH, Ar), 127.3 (CH, Ar), 114.68 (CH, Ar), 113.72 (CH, Ar), 72.92 ($C_5H_4$), 70.62 ($C_q$, $C_5H_4$), 70.58 ($C_5H_4$), 68.08 ($C_5H_5$), 66.00 ($CH_2CH_2O$), 43.99 ($C_q$-$CH_2$), 41.36 ($CH_2$), 29.73 ($CH_2CH_2Ar$), 18.08 ($CH_2CH_2Si$), 17.67 ($CH_2Si$), −1.87 (SiMe); analytical data for $C_{1044}H_{1350}O_{24}Si_{54}Fe_{54}$, **6**: calcd: C 66.63, H 7.24; found: C 66.93, H 8.06.

**9-Ferrocenyl dendrimer 11**: Karstedt catalyst (250 µL of a solution containing 2.2 % Pt in xylene) and dimethylferrocenylsilane **1** (2 g, 8.20 mmol) in diethyl ether (10 mL) were added dropwise to a solution of **7** (0.30 g, 0.62 mmol) in diethyl ether (20 mL). The mixture was stirred overnight at 40 °C, and the solvent removed under high vacuum. The residue was purified by flash chromatography (silica gel column) with petroleum ether:diethyl ether (98:2). Unreacted ferrocenyldimethylsilane was eluted first (0.23 g), then **11** was obtained as a dark-orange waxy solid (1.05 g, 63 % yield). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 7.10$ (s, 3 H), 4.56 (m, 18 H), 4.36 (s, 45 H), 4.31 (m, 18 H), 1.89 (m, 18 H), 1.41 (m, 18 H), 0.90 (m, 18 H), 0.45 (s, 54 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta = 145.92$ ($C_q$, Ar), 121.81 (CH, Ar), 77.83, 76.83 ($C_5H_4$), 77.59 ($C_q$, $C_5H_4$), 71.58 ($C_5H_5$), 44.10 ($CH_2$), 42.39 ($C_q$), 18.52 ($CH_2$), 17.19 ($CH_2$), −1.63 ($CH_3$); analytical data for $C_{144}H_{192}Fe_9Si_9$: calcd: C 64.57, H 7.23; found: C 64.70, H 7.31. MALDI TOF: $m/z$: 2679.79 $[M^+ + H]$. $E_{1/2}$ (vs. $FeCp_2$, Pt, $CH_2Cl_2$) = −0.005 V.

**27-Ferrocenyl dendrimer 12**: Karstedt catalyst (250 µL of a solution containing 2.2 % Pt in xylene) and ferrocenyldimethylsilane (**1**) (0.117 g, 0.48 mmol) in diethyl ether (20 mL) were added dropwise to a solution of **8** (0.05 g, 0.012 mmol) in diethyl ether (20 mL). The mixture was stirred for two days at 45 °C, the solvent was removed under vacuum, and the residue was purified by flash chromatography (silica gel column) with petroleum ether:diethyl ether (50:50) as eluent. Unreacted ferrocenyldimethylsilane (0.018 g) was eluted first, then **12** was obtained as a dark-orange waxy solid (0.031 g, 28 % yield). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 7.12$ (d, 18 H), 6.72 (d, 18 H), 4.20 (m, 54 H), 4.03 (s, 135 H), 3.96 (m, 54 H), 3.89 (m, 18 H), 1.70–1.40 (m, 72 H), 1.01 (m, 72 H), 0.60 (m, 54 H), 0.15 (s, 162 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$): 130.42 (CH, Ar), 128.29 (CH, Ar), 126.93 (CH, Ar), 113.41 (CH, Ar), 75.93, 73.28 ($C_5H_4$), 71.03 ($C_5H_5$), 67.73 ($CH_2$), 22.53 ($CH_2$), 17.71 ($CH_2$), 13.63 ($CH_2$), 10.54 ($CH_2$), −2.41 ($CH_3$); analytical data for $C_{504}H_{660}Fe_{27}O_9Si_{27}$: calcd: C 66.31, H 7.29; found: C 63.37, H 7.66; $E_{1/2}$ (vs. $FeCp_2$, Pt, $CH_2Cl_2$) = −0.010 V.

**81-Ferrocenyl dendrimer 13**: Karstedt catalyst (250 µL of a solution containing 2.2 % Pt in xylene) was added to a solution of **9** (0.03 g, $3.33 \times 10^{-3}$ mmol) in toluene (10 mL). ferrocenyldimethylsilane (**1**) (0.100 g, 0.40 mmol) in toluene (20 mL) was added dropwise. The mixture was stirred for three days at 45 °C, and the solvent was removed under vacuum. The residue was purified by flash chromatography (silica-gel column) using petroleum ether:diethyl ether (98:2) as the eluent. Unreacted ferrocenyldimethylsilane (0.017 g) was eluted first. The compound **13** was eluted with diethyl ether and was obtained as a dark orange waxy solid (0.035 g, 37 % yield). $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 7.18$ (m, 72 H), 6.83 (m, 72 H), 4.20, 4.01 (br, m, 729 H), 3.81 (m, 72 H), 2.02 (br, m, 234 H), 1.29 (br, m, 234 H), 0.23 (br, m, 162 H), −0.25 (br, s, 486 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta = 156.81$ ($C_q$, Ar), 138.92 ($C_q$, Ar), 127.52 (CH, Ar), 114.81 (CH Ar), 74.21, 72.17 ($C_5H_4$), 69.15 ($C_5H_5$), 68.83 ($CH_2$), 42.31 ($C_q$), 41.90 ($CH_2$), 30.29 ($CH_2$), 19.27, 18.52, 15.21 ($CH_2$), −0.93 ($CH_3$); $^{29}Si$ NMR: $\delta = -2.39$; analytical data for $C_{1584}H_{2064}Fe_{81}O_{36}Si_{81}$: calcd: C 66.80, H 7.30; found: C 61.91, H 7.17; $E_{1/2}$ (vs $FeCp_2$, Pt, $CH_2Cl_2$) = −0.015 V.

**243-Ferrocenyl dendrimer 14**: Karstedt catalyst (250 µL of a solution containing 2.2 % Pt in xylene) was added to a solution of **10** (0.020 g, $1.103 \times 10^{-3}$ mmol) in toluene (10 mL). Ferrocenyldimethylsilane (**1**) (0.100 g, 0.40 mmol) in toluene (20 mL) was added dropwise. The mixture was heated to 45 °C for three days, then a 2 % solution of the Karstedt catalyst in xylene (250 L) was added, and the mixture was maintained at 50 °C for a further four days. The solvent was removed under vacuum, the residue washed with diethyl ether (3 × 20 mL), and **14** was obtained as an orange waxy solid (0.021 g, 22 % yield) that was found to be insoluble in both pentane and diethyl ether. $^1H$ NMR (250 MHz, $CDCl_3$): $\delta = 7.26$ (m, 234 H), 6.85 (m, 234 H), 4.33 (m, 486 H), 4.16–4.12 (br, m, 1701 H), 1.90 (br, m 720 H), 1.20, 0.60 (br, m 1206 H), 0.16 (br, m, 1458 H); $^{13}C$ NMR (62.9 MHz, $CDCl_3$): $\delta = 130.00$ (CH, Ar), 115.00 (CH, Ar), 72.97, 70.61 ($C_5H_4$), 68.14 ($C_5H_5$), 29.73 ($CH_2$), 18.91, 16.25 ($CH_2$), 0.1–0.2($CH_3$); $E_{1/2}$ (vs $FeCp_2$, Pt, $CH_2Cl_2$) = −0.015 V.

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