

{FeCp}⁺-Induced Hexafunctionalization of Hexamethylbenzene with Dendrons for the Direct Synthesis of Redox-Active Iron-Centered Metallodendrimers

Sylvain Nlate,^{*,[a]} Yolanda Nieto,^[a] Jean-Claude Blais,^[b] Jaime Ruiz,^[a] and Didier Astruc^{*,[a]}

Abstract: Phenol tri- and nonaallyl dendrons (**3** and **7**, respectively) were functionalized at the focal position to give the new triallyl dendrons **4** and **6** and the nonaallyl dendrons **11** and **13** that contain a iodoalkyl or a bromobenzyl termini. All these dendrons were used for the {FeCp}⁺-induced hexafunctionalization of hexamethylbenzene in [FeCp(η^6 -C₆Me₆)](PF₆) (**1**) under mild conditions in the presence of KOH. These reactions directly yielded the 18-allyl and 54-allyl dendrimers **9**, **10**, and **14** with a [FeCp(η^6 -arene)]⁺ unit located at the dendrimer core. Cyclic voltammetry

studies were recorded in THF and DMF with these metallodendrimers and compared with those of analogous dendrimers or complexes of smaller size that contain a [FeCp(η^6 -arene)]⁺ unit at the core. The decreased rate of heterogeneous electron transfer when the dendritic size increases first disclosed by Diederich and Gross is confirmed. The variation of the redox potential of

the Fe^{III/I} redox system with increasing dendritic size is negligible even in a solvent of high dielectric constant such as DMF. This trend is attributed to fact that the involved "redox" orbital is buried on the metal center, well protected by the shell of alkyl chains (electron-reservoir nature), unlike in ferrocene. The chemical irreversibility increases in THF as the dendrimer size increases, due to more facile ligand substitution with THF at the 19-electron level when the chain bulk increases.

Keywords: arene activation • dendrimers • electrochemistry • electron transfer • metallocenes

Introduction

Whereas catalysis is an ideal mode of activation of organic substrates by transition metals,^[1] stoichiometric processes can in some instances provide sophisticated types of activation/functionalization.^[2] This is especially the case when multiple iterative stoichiometric transformations are carried out at a single metal center without decoordination, a situation intermediate between those encountered in stoichiometric and catalytic reactions. The {FeCp}⁺-induced peralkylation and perfunctionalization of polymethylaromatics are striking examples of this principle, since up to twelve C–C bonds can be formed at a single ligand subsequent to twelve deprotonation–alkylation sequences in one pot,^[3] a process reminiscent of dendritic synthesis.^[4] This reaction has so far produced

a variety of hexafunctional arenes^[3,5] as well as larger architectures including hexabranched stars based on further stepwise divergent constructions.^[3]

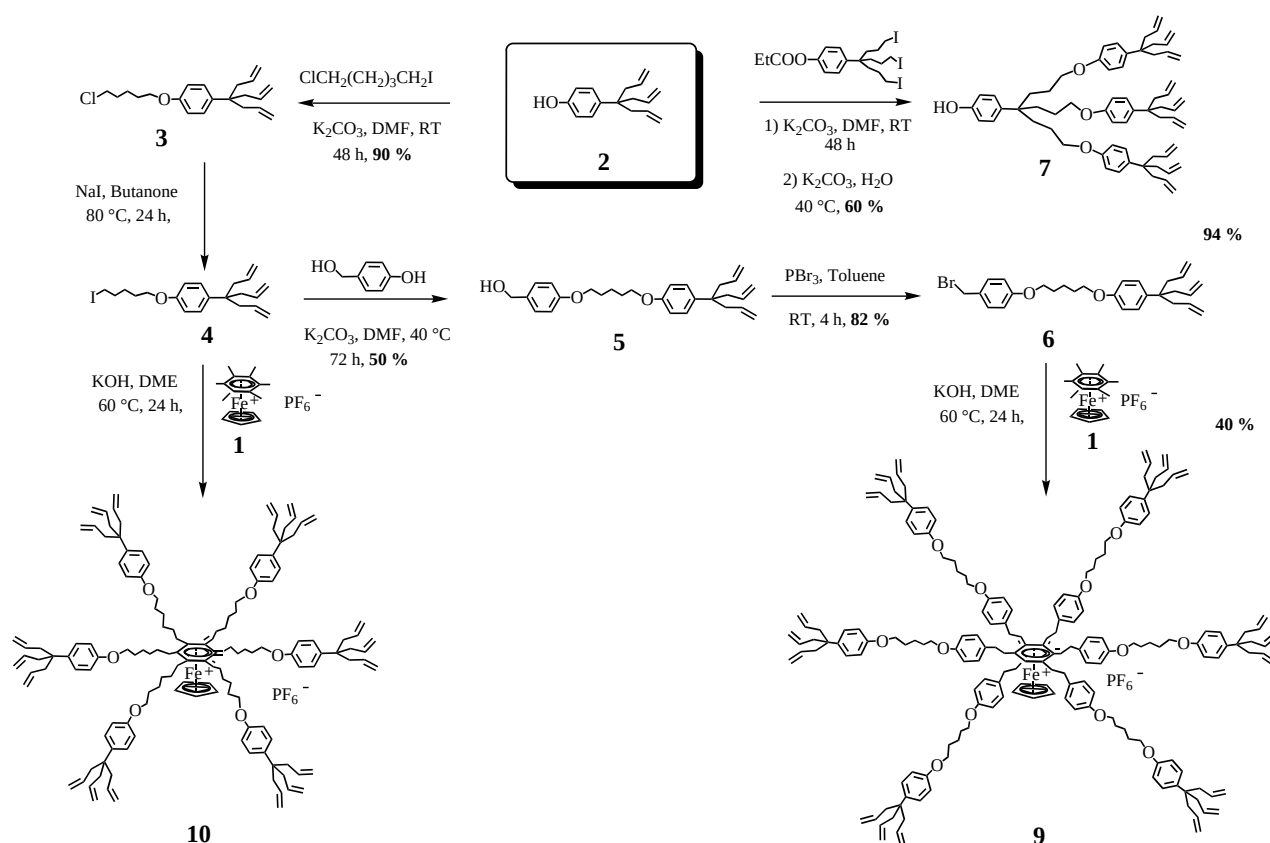
We now wish to report the direct synthesis of iron-sandwich-centered dendrimers using this {FeCp}⁺-induced hexafunctionalization of hexamethylbenzene in [FeCp(η^6 -C₆Me₆)](PF₆),^[6] **1**, with tri- and nonabranched dendrons. An advantage of this strategy is that it leaves a redox-active iron atom at the center of the dendritic framework and provides in this way the possibility to examine its electrochemistry. Redox-active, metal-centered dendrimers have recently attracted attention because of their analogies with redox proteins. Indeed, it has been possible to study electron-transfer processes between the buried metal center and electrodes,^[7–13] an area pioneered by Diederich and Gross with metalloporphyrin-centered dendrimers.^[7]

Results and Discussion

Two successful synthetic strategies for the synthesis of 18-allyl dendrimers are shown in Scheme 1. They start from the phenol triallyl dendron, **2**, a molecular brick which has already proved useful for rapid divergent dendritic construction.^[14] The dendron **2** was synthesized in 60 % yield by the known

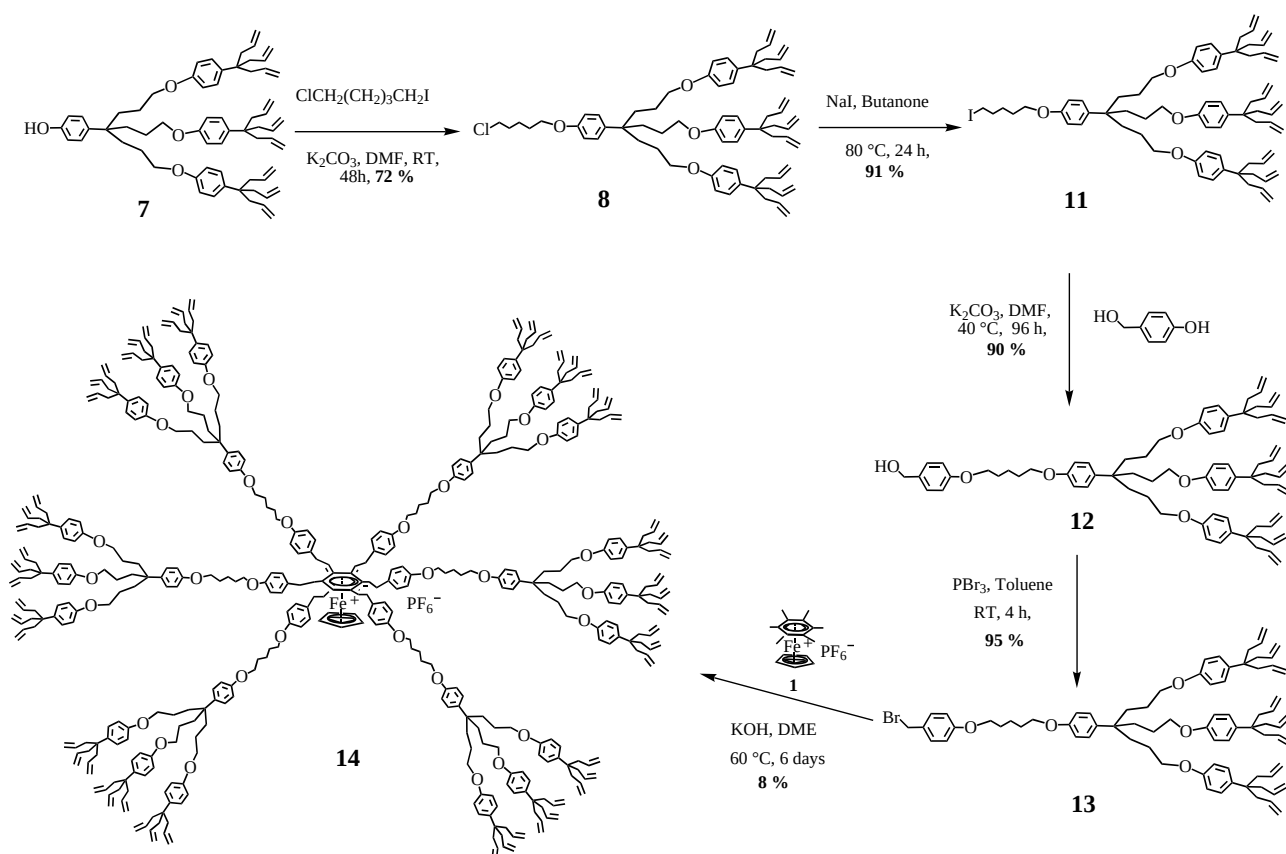
[a] Dr. S. Nlate, Prof. Dr. D. Astruc, Y. Nieto, Dr. J. Ruiz
Laboratoire de Chimie Organique et Organométallique
UMR CNRS 5802, Université Bordeaux I
33405 Talence Cedex (France)
E-mail: s.nlate@lcoo.u-bordeaux.fr, d.astruc@lcoo.u-bordeaux.fr

[b] Dr. J.-C. Blais
Laboratoire de Chimie Structurale Organique et Biologique
EP CNRS N° 103, Université Paris VI, 4 Place Jussieu
75252 Paris (France)
E-mail: blaisjc@moka.ccr.jussieu.fr

Scheme 1. Syntheses of the two 18-allyl dendrimers **9** and **10**.

Abstract in French: Les dendrons phenoltriallyle et nonaallyle (resp. **3** et **7**) ont été fonctionnalisés sur la position focale pour donner les nouveaux dendrons triallyle **4** et les dendrons nonaallyle **11** et **13** contenant une chaîne iodoalkyle ou bromobenzyle. Tous ces dendrons ont été utilisés pour l'hexafunctionalisation de l'hexaméthylbenzène induite par le groupement $[\text{FeCp}]^+$ dans $[\text{FeCp}(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$, **1** dans des conditions douces en présence de KOH. Ces réactions conduisent directement aux dendrimères 18-allyl ou 54-allyl **9**, **10** et **14** comportant un groupement $[\text{FeCp}(\eta^6\text{-arene})]^+$ situé au cœur du dendrimère. Des études de cyclovoltammétrie ont été réalisées dans le THF et le DMF avec ces metallodendrimères et comparées à celles réalisées avec des dendrimères ou complexes $[\text{FeCp}(\eta^6\text{-arene})]^+$ plus petits. La décroissance de la vitesse de transfert d'électron hétérogène au fur et à mesure que le metallodendrimère devient plus gros, reportée pour la première fois par les équipes de Diederich et Gross, est confirmée. La variation du potentiel redox du couple Fe^{III} , quand la taille du metallodendrimère croît, est négligeable, même dans un solvant de forte constante diélectrique tel que le DMF. Ceci est attribuable au fait que l'orbitale redox en jeu est enfouie sur le métal protégé par la coquille formée par les chaînes alkyles (réservoir d'électron), contrairement à la situation du ferrocène. L'irréversibilité chimique augmente dans le THF, lorsque la taille du metallodendrimère croît, en raison de l'échange de ligands avec le THF beaucoup plus facile lorsque les chaînes deviennent plus encombrantes.

eight-step one-pot FeCp^+ activation of *p*-ethoxytoluene.^[14a] On one hand, alkylation of **2** with $\text{Cl}(\text{CH}_2)_5\text{I}$ followed by Cl/I exchange by reaction with NaI gives a iodoalkyl derivative **4**, to which the $[\text{FeCp}]^+$ -induced hexaalkylation can be applied with **1** to give the 18-allyl iron-centered metallodendrimer **10**.^[15, 16] On the other hand, further convergent dendron synthesis gave the useful nonaallyl dendron **7**.^[14a] From the dendron **4**, the $[\text{FeCp}]^+$ -induced hexaalkylation of hexamethylbenzene in $[\text{FeCp}(\eta^6\text{-C}_6\text{Me}_6)][\text{PF}_6]$ ^[6] gives some dehydrohalogenation, a side reaction that partly consumes **4** and only allows the synthesis of **10**, if it is not marred by any steric constraint. The MALDI TOF mass spectrum of **10** contains an important molecular peak at m/z : 2061.64 $[M - \text{PF}_6]^+$, but a major peak is also found at m/z : 1765.38, which corresponds to the same dendrimer that lacks one phenol triallyl unit and thus only contains 15 allyl groups. In order to improve the purity of the 18-allyl dendrimer and with a view to the synthesis of a 54-allyl dendrimer by a convergent method, **4** was functionalized by reaction with $\text{HOCH}_2\text{-C}_6\text{H}_4\text{OH}$ and K_2CO_3 followed by PBr_3 . The *para*-substituted benzylbromide dendron **6** obtained cannot undergo β -dehydrohalogenation under the action of bases, and its reaction with **1** proceeds to give the metallodendrimer **9** in 50% yield and good purity as indicated by the prominent peak in its MALDI TOF mass spectrum (m/z : 2698.54 $[M - \text{PF}_6]^+$). In view of the construction of the 54-allyl dendrimer, we synthesized, from **7**, both the iodoalkyl dendron **11** and the bromobenzyl dendron **13** (Scheme 2). The reaction of **1** with **11** mostly gave a 45-allyl



Scheme 2.

iron-centered dendrimer in which one equivalent nonaallyl dendron is missing as shown by the MALDI TOF mass spectrum. This confirms that, in the presence of a significant bulk problem posed at a certain generation of the convergent construction, the dendritic synthesis cannot be completed because of the competition with the deshydroiodation. On the other hand, in the same reaction with the dendron **13**, derived from benzyl bromide, the convergent synthesis provides the 54-allyl dendrimer **14**, whose molecular peak is observed in the MALDI TOF mass spectrum (m/z : 6876.70 [$M - \text{PF}_6$] $^+$). The new metallodendrimers **9**, **10**, and **14** are yellow oils that were purified by column chromatography over silica gel.^[15, 16]

To study the influence of the dendrimer bulk around the central metal on the heterogeneous electron transfer, we recorded and compared the cyclic voltammograms (CVs) of the metal-centered dendrimers **9** and **10** as well as those of metallostars with identical cores and shorter arms. The CVs of seven iron-centered stars and dendrimers with identical cores were recorded with a solvent of low dielectric constant, THF ($\epsilon = 7.6$) and one of large dielectric constant, dimethylformamide

(DMF, $\epsilon = 36.7$). The data are gathered in Table 1. The most dramatic feature is the increased electrochemical irreversibility signifying a decreased heterogeneous electron-transfer rate between the buried metal center and the electrode as the star- or dendritic bulk increases around the iron center. This trend has already been clearly shown by the groups of Diederich,^[7] Gorman^[11] and Newkome^[12] with various metal-centered dendrimers. We also find that this decrease of electron-transfer rate upon increasing bulk is more marked in THF than in DMF, since the CVs of **9** and **10** are those of electrochemically irreversible systems in THF, but less so in

Table 1. $E_{1/2}$ (ΔE_p) values recorded by cyclic voltammetry on a PAR273 potentiostat (ohmic drop compensation) for the star and dendritic cationic iron complexes $[\text{FeCp}(\eta^6\text{-C}_6\text{R}_6)][\text{PF}_6]$ involving the monoelectronic reduction of Fe^{II} to Fe^{I} , with ferrocene as an *internal* reference for all the measurements.

R	$E_{1/2}$ [V] (ΔE_p [V]) in THF ^[b]		$E_{1/2}$ [V] (ΔE_p [V]) in DMF	
	20 °C	– 30 °C	20 °C	– 30 °C
<i>n</i> -propyl	– 1.935 (70)	– 1.945 (90)	– 1.935 (75)	– 1.955 (90)
<i>n</i> -butyl	– 1.940 (100)	– 1.960 (140)	– 1.935 (100)	– 1.960 (140)
<i>n</i> -heptyl	– 1.945 (150)	– 1.975 (170)	– 1.945 (100)	– 1.975 (140)
dendritic branch in 10	– 1.980 (250)	– 1.980 (100)	– 1.985 (140)	
<i>p</i> -CH ₂ CH ₂ C ₆ H ₄ OMe	– 1.765 (90)	– 1.800 (130)	– 1.835 (90)	– 1.875 (110)
<i>p</i> -CH ₂ CH ₂ C ₆ H ₄ O- <i>n</i> -C ₆ H ₁₃	– 1.800 (250)	– 1.835 (85)	– 1.875 (150)	
dendritic branch in 9	– 1.820 (irr.)	– 1.855 (140)	– 1.895 (230)	

[a] The ΔE_p values for the internal ferrocene ($\text{Fe}^{\text{II}} \rightarrow \text{Fe}^{\text{III}}$) reference were always 45 to 50 mV at – 30 °C and 55 to 60 mV at 20 °C. The working electrode was Pt, the supporting electrolyte was $[\text{n-Bu}_4\text{N}][\text{PF}_6]$ (0.1M), the concentration of complex was 5×10^{-3} M, and the scan rate was 0.5 V s $^{-1}$. In THF, the largest compounds gave rather flat waves from which values of peak potentials (not indicated in the table) could not be extracted with a meaningful accuracy. The complex **14** gave no visible CV wave. The uncertainty on $E_{1/2}$ is all the larger as ΔE_p is larger (10 mV for $\Delta E_p = 60$ mV to 30 mV when ΔE_p reaches 250 V). Large ΔE_p values correspond to slow electron transfer.^[12, 14a, 17a] [b] Versus $[\text{FeCp}_2]^{\text{0/+}}$.

DMF (Figure 1 and Table 1). This is logical insofar as the charges are more easily carried in a solvent of high dielectric constant than in a solvent of low dielectric constant. The other interesting feature is the variation of thermodynamic potential E° , a good estimation of which is provided by the half-wave potential $E_{1/2}$ when the redox systems are chemically

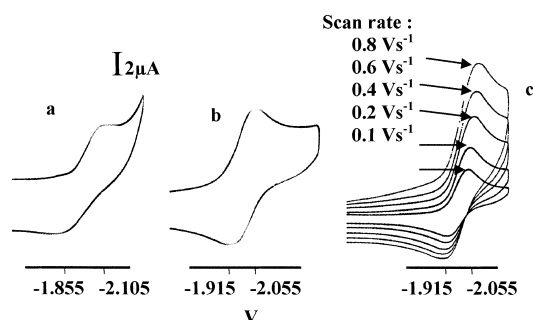


Figure 1. CVs of the 18-allyl dendrimer **10**, -30°C a) at 0.5 V s^{-1} in THF, b) at 0.5 V s^{-1} in DMF, c) at various scan rates in DMF (variation of the peak potential with scan rates and ΔE_p larger than 50 mV signify relatively slow heterogeneous electron transfer^[12, 14a, 17a]). The ΔE_p values as a function of scan rate above (DMF, c) are 105 mV at 100 mV s^{-1} , 125 mV at 200 mV s^{-1} , 140 mV at 400 mV s^{-1} , 160 mV at 600 mV s^{-1} and 180 mV at 800 mV s^{-1} . See the other conditions in the caption of Table 1.

reversible, which is the case here in most experiments. The $E_{1/2}$ values shift toward more negative values upon increasing the bulk around the metal center. The apparently surprising aspect, however, is that this shift is very small (near the limit of experimental errors) in DMF as well as in THF for the seven compounds whose CVs were recorded. The seminal studies by Diederich's group had shown that the shift was negligible in CH_2Cl_2 , but dramatically large (towards positive values) in water.^[7] We believe the difference of results concerning solvents of high dielectric constants can be taken into account by the nature of the orbitals involved in the redox changes. In porphyrin chemistry, redox changes often involve orbitals of high ligand character that are exposed to the surrounding solvent.^[17a] On the other hand, in the present case, the e_1^* orbital involved with the $18e/19e$ ($\text{Fe}^{\text{II}} \rightarrow \text{Fe}^{\text{I}}$) redox process has a high metal character (about 80% $d_{xz,yz}$), and is protected by the sandwich shell.^[17a] It is for this reason that the parent permethylated analogues of these systems have been named electron-reservoirs^[3, 17] and have been shown to serve as much better medium-independent references than ferrocene (to which their potential is related) for the determination of redox potential by means of cyclic voltammetry.^[17b,d]

Finally, the chemical reversibility is partly or completely lost for the bulky metallodendrimers **9** and **10** in THF, whereas this is not the case for the smaller ones in both solvents, or even for **9** and **10** in DMF. This shows that, in the presence of the potential ligand THF, the 19-electron Fe^{I} species is not stable at the center of bulky dendrimers, because the relatively facile ligand substitution at the 19-electron level is still accelerated by the presence of bulky chains. This is taken into account by the movement of the chains that favor the distortion of the arene ligand, that is, its hapticity change ($\eta^6 \rightarrow \eta^4$) is responsible for the first step of the ligand substitution.^[17a,c]

Conclusion

In conclusion, we have shown the first application of $\{\text{FeCp}\}^+$ -induced functionalization of hexamethylbenzene to one-step metallodendrimer synthesis up to 54 allyl branches, with the $[\text{FeCp}(\eta^6\text{-arene})]^+$ sandwich for the first time located at the core of dendrimers. This allowed us to study the heterogeneous electron transfer between this metal center of the dendrimers and the electrode by CV. Its main features are 1) the confirmation of the decreased rate of electron transfer as the dendritic bulk increases, 2) the negligible variation of the $E_{1/2}$ values even in a solvent of high dielectric constant (DMF) when the dendritic bulk increases, due to the buried redox orbital, and 3) the chemical irreversibility observed in THF for the largest complexes attributed to enhanced ligand substitution at the 19-electron level when the chain bulk increases. These results have applications for the fabrication of catalytically active and magnetic, dendrimer-encapsulated iron particles.^[18]

Experimental Section

General data: Reagent-grade tetrahydrofuran (THF), diethyl ether, and pentane were predried over Na foil and distilled from sodium/benzophenone 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]. All manipulations were carried out by using Schlenk techniques or in a nitrogen-filled Vacuum Atmosphere drylab. Samples were examined in solution (0.1 mm cells with NaCl windows), between NaCl disks in Nujol, or in KBr pellets. ^1H NMR spectra were recorded at 25°C with a Bruker AC250 (250 MHz) spectrometer. ^{13}C NMR spectra were obtained in the pulsed FT mode at 62.91 MHz with a Bruker AC250 spectrometer. All chemical shifts are reported in parts per million (δ , ppm) with reference to Me_4Si (TMS). Electronic spectra (UV and visible) were recorded at 20°C with a Cary219 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 ($\sim 10^{-3}\text{ mol L}^{-1}$) maintained currents between 1 and 10 mA). The additional redox couple $[\text{FeCp}_2]/[\text{FeCp}_2]^+$ was used when possible as a control for iR compensation. Thermodynamic potentials were recorded with reference to an aqueous SCE in THF ($0.1\text{ M } n\text{-Bu}_4\text{NBF}_4$). The value of the $[\text{FeCp}_2]/[\text{FeCp}_2]^+$ redox couple was $E^\circ = 0.470\text{ V}$ 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 $[\text{FeCp}_2]/[\text{FeCp}_2]^+$. The counter electrode was platinum. Elemental analyses were performed by the Center of Microanalyses of the CNRS at Lyon-Villeurbanne (France).

Chloroalkyl 3-allyl dendron 3: A mixture of **2** (1 g, 4.384 mmol), KOH (0.660 g, 4.714 mmol), and 1-chloro-5-iodopentane (1.6 g, 0.688 mmol) in DMF (20 mL) was stirred for 48 h at room temperature. The reaction mixture was then extracted with Et_2O ($3 \times 20\text{ mL}$), and the resulting solution was washed with water and dried over sodium sulfate. The solvent was removed under vacuum and the product was purified by chromatography on a silica-gel column with pentane, followed by a pentane/diethyl ether 99:1 mixture to provide **3** as a colorless oil (1.314 g, 3.96 mmol, 90%). ^1H NMR (CDCl_3 , 200 MHz): $\delta = 7.22$ (d, $^3J(\text{H,H}) = 8.8\text{ Hz}$, 2H; Ar), 6.87 (d, $^3J(\text{H,H}) = 8.8\text{ Hz}$, 2H; Ar), 5.58 (m, 3H; $\text{CH}_2=\text{CH}$), 5.06 (m, 6H; $\text{CH}_2=\text{CH}$), 3.95 (t, $^3J(\text{H,H}) = 6.2\text{ Hz}$, 2H; CH_2O), 3.57 (t, $^3J(\text{H,H}) = 6.6\text{ Hz}$, 2H; CH_2Cl), 2.42 (d, $^3J(\text{H,H}) = 7.2\text{ Hz}$, 6H; $\text{CH}_2=\text{CH}-\text{CH}_2$), 1.65 (m, 6H; $\text{CH}_2-\text{CH}_2-\text{CH}_2$); ^{13}C NMR (CDCl_3 , 50.33 MHz): $\delta = 156.70$ (C_q, ArO), 137.54 (C_q, Ar), 134.56 ($\text{CH}_2=\text{CH}$), 127.53 (CH, Ar), 117.41 ($\text{CH}=\text{CH}_2$),

113.69 (CH, Ar), 67.28 (CH₂O), 44.84 (ClCH₂), 42.55 (C_qCH₂), 41.83 (CH₂), 32.25 (CH₂), 28.55 (CH₂), 23.51 (CH₂); elemental analysis calcd (%) for C₂₁H₂₉OCl (332.91): C 75.76, H 8.78; found: C 75.14, H 8.50.

Chloroalkyl 9-allyl dendron 8: This compound was synthesized according to the same procedure described above for **3**, by using **7** (72 h). Dendron **8** was obtained in 72 % yield after chromatography. ¹H NMR (CDCl₃, 200 MHz): δ = 7.22 (d, ³J(H,H) = 8.8 Hz, 8H; Ar), 6.89 (d, ³J(H,H) = 8.8 Hz, 8H; Ar), 5.58 (m, 9H; CH₂=CH), 5.05 (m, 18H; CH₂=CH), 3.97 (t, ³J(H,H) = 7.0 Hz, 2H; CH₂O), 3.89 (t, ³J(H,H) = 8.0 Hz, 8H; CH₂O), 3.57 (t, ³J(H,H) = 8.0 Hz, 2H; CH₂Cl), 2.41 (d, ³J(H,H) = 7.2 Hz, 6H; CH₂=CH-CH₂), 1.83 (m, 8H; CH₂), 1.62 (m, 10H; CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 156.87 (C_q, ArO), 138.30 (C_q, Ar), 137.56 (C_q, Ar), 134.70 (CH₂CH), 127.62 (CH, Ar), 117.50 (CHCH₂), 113.84 (CH, Ar), 68.22 (CH₂O), 67.90 (CH₂O), 44.95 (ClCH₂), 42.68 (C_qCH₂), 41.97 (CH₂), 33.79 (CH₂), 32.39 (CH₂), 28.69 (CH₂), 23.78 (CH₂), 23.64 (CH₂); MALDI TOF mass spectrum: *m/z*: 1040.73 [M+Na]⁺ (calcd 1040.92); elemental analysis calcd (%) for C₆₉H₈₉O₄Cl (1017.92): C 81.42, H 8.81; found: C 80.52, H 8.65.

Iodoalkyl 3-allyl dendron 4: A mixture of **3** (1.314 g, 3.958 mmol) and NaI (2.968 g, 19.787 mmol) in butanone (30 mL) was stirred for 24 h at 80 °C. After removal of the solvent under vacuum, the residue was extracted with Et₂O (3 × 20 mL). The resulting solution washed with and an aqueous solution saturated with Na₂S₂O₃, dried over sodium sulfate and then filtered. The solvent was removed under vacuum to provide **4** as a colorless oil (1.580 g, 94 %). ¹H NMR (CDCl₃, 200 MHz): δ = 7.26 (d, ³J(H,H) = 8.8 Hz, 2H; Ar), 6.85 (d, ³J(H,H) = 8.8 Hz, 2H; Ar), 5.56 (m, 3H; CH₂=CH), 5.03 (m, 6H; CH₂=CH), 3.96 (t, ³J(H,H) = 6.2 Hz, 2H; CH₂O), 3.21 (t, ³J(H,H) = 7.0 Hz, 2H; CH₂I), 2.42 (d, ³J(H,H) = 7.2 Hz, 6H; CH₂=CH-CH₂), 1.85 (m, 4H; CH₂-CH₂), 1.57 (m, 2H; CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 156.67 (C_q, ArO), 137.54 (C_q, Ar), 134.55 (C_q, Ar), 127.53 (C_q, Ar), 117.44 (CH, Ar), 113.69 (CH, Ar), 67.24 (CH₂O), 42.55 (C_qCH₂), 41.83 (CH₂), 33.13 (CH₂), 28.20 (CH₂), 27.12 (CH₂), 6.73 (ICH₂); elemental analysis calcd (%) for C₂₁H₂₉OI (424.36): C 59.44, H 6.89; found: C 59.47, H 6.8.

Iodoalkyl 9-allyl dendron 11: Compound **11** was synthesized according to the same procedure described above for **4**, but with **8** instead of **3**. Yellow oil, 91 % yield. ¹H NMR (CDCl₃, 200 MHz): δ = 7.20 (d, ³J(H,H) = 8.8 Hz, 8H; Ar), 6.81 (d, ³J(H,H) = 8.8 Hz, 8H; Ar), 5.53 (m, 9H; CH₂=CH), 5.00 (m, 18H; CH₂=CH), 3.96 (t, ³J(H,H) = 8.0 Hz, 2H; CH₂O), 3.90 (t, ³J(H,H) = 8.0 Hz, 6H; CH₂O), 3.24 (t, ³J(H,H) = 8.0 Hz, 2H; CH₂Cl), 2.41 (d, ³J(H,H) = 7.0 Hz, 6H; CH₂=CH-CH₂), 1.83 (m, 8H; CH₂), 1.60 (m, 10H; CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 156.71 (C_q, ArO), 138.30 (C_q, Ar), 137.42 (C_q, Ar), 134.57 (CH₂=CH), 127.45 (CH, Ar), 117.39 (CH=CH₂), 113.88 (CH, Ar), 113.68 (CH, Ar), 68.06 (CH₂O), 67.28 (CH₂O), 42.54 (C_qCH₂), 41.95 (CH₂), 33.64 (CH₂), 32.13 (CH₂), 28.20 (CH₂), 27.12 (CH₂), 23.62 (CH₂), 6.71 (ICH₂); MALDI TOF mass spectrum: *m/z*: 1132.43 [M+Na]⁺ (calcd 1132.35); elemental analysis calcd (%) for C₆₉H₈₉O₄I (1109.38): C 74.71, H 8.09; found: C 74.91, H 8.04.

Benzylalcohol 3-allyl dendron 5: A mixture of HOCH₂-*p*-C₆H₄OH (0.146 g, 1.176 mmol) and K₂CO₃ (0.163 g, 1.18 mmol) in DMF (5 mL) was stirred for 30 min at room temperature. Dendron **4** (0.500 g, 1.18 mmol) was then added to the reaction mixture, and the resulting solution stirred at 40 °C for 72 h. The mixture was extracted with CH₂Cl₂ (3 × 20 mL), and the resulting solution washed with water and dried over sodium sulfate. After removal of the solvent under vacuum, the product was purified by chromatography on a silica-gel column with a 7:3 pentane/diethyl ether mixture to provide **5** as a yellow oil (0.248 g, 0.590 mmol, 50 %). ¹H NMR (CDCl₃, 200 MHz): δ = 7.24 (d, ³J(H,H) = 8.0 Hz, 4H; Ar), 6.85 (d, ³J(H,H) = 8.0 Hz, 4H; Ar), 5.50 (m, 3H; CH₂=CH), 5.03 (m, 6H; CH₂=CH), 4.62 (brs, 2H; HOCH₂), 3.98 (t, ³J(H,H) = 6.2 Hz, 2H; CH₂O), 3.97 (t, ³J(H,H) = 6.4 Hz, 2H; CH₂O), 2.44 (d, ³J(H,H) = 7.2 Hz, 6H; CH₂=CH-CH₂), 1.86 (m, 4H; CH₂-CH₂), 1.62 (m, 2H; CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 158.90 (C_q, ArO), 156.83 (C_q, ArO), 137.83 (C_q, Ar), 134.68 (CHCH₂), 132.96 (C_q, Ar), 128.92 (CH, Ar), 127.69 (CH, Ar), 117.53 (CHCH₂), 114.77 (CH, Ar), 114.00 (CH, Ar), 67.92 (CH₂O), 67.67 (CH₂O), 65.15 (CH₂OH), 42.76 (C_qCH₂), 40.00 (CH₂), 29.13 (CH₂), 29.07 (CH₂), 22.86 (CH₂); elemental analysis calcd (%) for C₂₈H₃₆O₃ (420.58): C 79.96, H 8.62; found: C 79.95, H 8.67.

Benzyl alcohol 9-allyl dendron 12: Dendron **12** was synthesized according to the same procedure as described above for **5**, but with **11** instead of **4** (96 h) giving a 90 % yield after chromatography. ¹H NMR (CDCl₃,

200 MHz): δ = 7.20 (d, ³J(H,H) = 8.0 Hz, 10H; Ar), 6.82 (d, ³J(H,H) = 8.0 Hz, 10H; Ar), 5.54 (m, 9H; CH₂=CH), 5.00 (m, 18H; CH₂=CH), 4.61 (s, 2H; HOCH₂), 3.98 (t, ³J(H,H) = 6.4 Hz, 4H; CH₂O), 3.87 (t, ³J(H,H) = 6.4 Hz, 6H; CH₂O), 2.41 (d, ³J(H,H) = 7.2 Hz, 18H; CH₂=CH-CH₂), 1.85 (m, 10H; CH₂), 1.60 (m, 8H; CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 158.90 (C_q, ArO), 156.81 (C_q, ArO), 156.72 (C_q, ArO), 138.24 (C_q, Ar), 137.42 (C_q, Ar), 134.57 (CH₂CH), 128.55 (CH, Ar), 127.49 (CH, Ar), 127.38 (CH, Ar), 117.37 (CHCH₂), 114.45 (CH, Ar), 113.91 (CH, Ar), 113.70 (CH, Ar), 68.09 (CH₂O), 67.72 (CH₂O), 67.50 (CH₂O), 65.00 (HOCH₂), 42.54 (C_qCH₂), 41.95 (CH₂), 33.65 (CH₂), 29.02 (CH₂), 28.93 (CH₂), 23.64 (CH₂), 22.67 (CH₂); MALDI TOF mass spectrum: *m/z*: 1127.55 [M+Na]⁺ (calcd 1128.58); elemental analysis calcd (%) for C₇₆H₉₆O₆ (1105.57): C 82.56, H 8.75; found: C 82.82, H 8.75.

Bromobenzyl 3-allyl dendron 6: PBr₃ (0.086 g, 0.317 mmol) was added to a cooled mixture (0 °C) of dendron **5** (0.400 g, 0.951 mmol) in toluene (10 mL). The resulting solution was stirred at room temperature for 4 h. After removal of the solvent, the residue was extracted with Et₂O, washed with water, and dried over sodium sulfate. The solvent was removed under vacuum providing **6** as a yellow oil (0.377 g, 0.779 mmol, 82 %). ¹H NMR (CDCl₃, 200 MHz): δ = 7.24 (d, ³J(H,H) = 8.0 Hz, 4H; Ar), 6.85 (d, ³J(H,H) = 8.0 Hz, 4H; Ar), 5.50 (m, 3H; CH₂=CH), 5.03 (m, 6H; CH₂=CH), 4.50 (s, 2H; BrCH₂), 3.98 (t, ³J(H,H) = 6.2 Hz, 2H; CH₂O), 3.97 (t, ³J(H,H) = 6.2 Hz, 2H; CH₂O), 2.43 (d, ³J(H,H) = 7.2 Hz, 6H; CH₂=CH-CH₂), 1.86 (m, 4H; CH₂-CH₂), 1.66 (m, 2H; CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 159.20 (C_q, ArO), 156.83 (C_q, ArO), 137.83 (C_q, Ar), 134.57 (CHCH₂), 130.33 (C_q, Ar), 127.53 (CH, Ar), 117.40 (CH, Ar), 114.62 (CH, Ar), 113.72 (CH, Ar), 67.72 (CH₂O), 67.43 (CH₂O), 42.76 (C_qCH₂), 41.84 (CH₂), 34.00 (BrCH₂), 29.01 (CH₂), 22.67 (CH₂); elemental analysis calcd (%) for C₂₈H₃₅O₂Br (483.48): C 69.55, H 7.29; found: C 69.58, H 7.61.

Bromobenzyl 9-allyl dendron 13: This compound was prepared according to the same procedure as described above for **6**, but with **12** instead of **5**; this gave a 95 % yield after chromatography. ¹H NMR (CDCl₃, 200 MHz): δ = 7.22 (m, 10H; Ar), 6.82 (m, 10H; Ar), 5.53 (m, 9H; CH₂=CH), 5.01 (m, 18H; CH₂=CH), 4.50 (s, 2H; BrCH₂), 4.00 (t, ³J(H,H) = 6.4 Hz, 4H; CH₂O), 3.89 (t, ³J(H,H) = 6.4 Hz, 6H; CH₂O), 2.42 (d, ³J(H,H) = 7.2 Hz, 18H; CH₂=CH-CH₂), 1.86 (m, 10H; CH₂), 1.63 (m, 8H; CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 157.31 (C_q, ArO), 157.23 (C_q, ArO), 138.74 (C_q, Ar), 137.93 (C_q, Ar), 135.06 (CH₂CH), 130.81 (CH, Ar), 130.16 (CH, Ar), 127.98 (CH, Ar), 127.87 (CH, Ar), 117.87 (CHCH₂), 115.13 (CH, Ar), 114.41 (CH, Ar), 114.20 (CH, Ar), 68.59 (CH₂O), 60.23 (CH₂O), 67.96 (CH₂O), 43.04 (C_q-CH₂), 42.45 (CH₂), 34.47 (CH₂), 34.15 (BrCH₂), 30.09 (CH₂), 29.50 (CH₂), 29.38 (CH₂), 24.14 (CH₂), 23.16 (CH₂); MALDI TOF mass spectrum: *m/z*: 1191.62 [M+Na]⁺ (calcd 1191.48); elemental analysis calcd (%) for C₇₆H₉₅O₅Br (1168.49): C 78.12, H 8.19; found: C 77.29, H 8.36.

18-Allyl dendrimer 10: A mixture of **1** (0.025 g, 0.058 mmol), KOH (0.059 g, 1.050 mmol), and **4** (0.370 g, 0.872 mmol) in dimethoxyethane (10 mL) was stirred for 24 h at 60 °C. After removal of the solvent under vacuum, the residue was extracted with pentane (3 × 10 mL), and the resulting solution was concentrated and purified by chromatography on a silica-gel column with a 4:1 pentane/diethyl ether mixture providing **10** as a yellow-orange oil (0.052 g, 0.0235 mmol, 40 %). ¹H NMR (CDCl₃, 200 MHz): δ = 7.22 (d, ³J(H,H) = 8.0 Hz, 12H; Ar), 6.85 (d, ³J(H,H) = 8.0 Hz, 12H; Ar), 5.54 (m, 18H; CH₂=CH), 5.03 (m, 36H; CH₂=CH), 4.62 (s, 5H; C₅H₅), 3.96 (m, 12H; CH₂O), 2.85 (br, 12H; CH₂Ar), 2.4 (d, ³J(H,H) = 7.0 Hz, 36H; CH₂=CH-CH₂), 1.85 (m, 4H; CH₂), 1.66 (m, CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 156.91 (C_q, ArO), 137.54 (C_q, Ar), 134.66 (CH₂=CH), 127.68 (CH_{Ar}), 117.51 (CH₂=CH), 113.87 (CH_{Ar}), 102.44 (C_q, Ar), 77.97 (C₅H₅), 67.59 (CH₂O), 42.69 (C_qCH₂), 41.98 (CH₂), 31.80 (CH₂), 29.36 (CH₂), 26.00 (CH₂); MALDI TOF mass spectrum: *m/z*: 2061.64 [M-PF₆]⁺ (calcd 2061.93); elemental analysis calcd (%) for C₁₄₃H₁₉₁O₆F₆PF₆ (2206.89): C 77.83, H 8.72; found: C 76.70, H 8.20.

18-Allyl dendrimer 9: Dendrimer **9** was synthesized according to the same procedure described above for **10**, but with **6** instead of **4** (60 °C, 24 h); this gave a 50 % yield after chromatography. ¹H NMR (CDCl₃, 200 MHz): δ = 7.26 (m, 24H; Ar), 6.89 (m, 24H; Ar), 5.56 (m, 18H; CH₂=CH), 5.03 (m, 36H; CH₂=CH), 4.87 (s, 5H; C₅H₅), 3.97 (m, 24H; CH₂O), 3.10 (br; CH₂Ar), 2.43 (d, ³J(H,H) = 7.0 Hz, 36H; CH₂=CH-CH₂), 1.87 (m, 4H; CH₂), 1.66 (m; CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ = 158.06 (C_q, ArO), 156.77 (C_q, ArO), 134.56 (CH₂=CH), 128.91 (C_q, Ar), 127.52 (CH_{Ar}), 117.39

(CH₂=CH), 114.95 (CH_{Ar}), 113.71 (CH_{Ar}), 77.91 (C₅H₅), 67.80 (CH₂O), 67.45 (CH₂O), 42.54 (C_qCH₂), 41.82 (CH₂), 29.06 (CH₂), 22.70 (CH₂), 22.52 (CH₂), 22.24 (CH₂); MALDI TOF mass spectrum: *m/z*: 2698.54 [*M* – PF₆]⁺ (calcd 2698.67); elemental analysis calcd (%) for C₁₈₅H₂₂₇O₁₂F₆PFe (2843.64): C 78.14, H 8.05; found: C 76.82, H 8.65.

54-Allyl dendrimer 14: Dendrimer **14** was synthesized according to the same procedure described above for **10**, with **13** (60 °C, 6 days); this gave an 8% yield after chromatography. ¹H NMR (CDCl₃, 200 MHz): δ = 7.22 (m, 60H; Ar), 6.84 (m, 60H; Ar), 5.55 (m, 54H; CH₂=CH), 5.01 (m, 108H; CH₂=CH), 4.00 (br, 60H; CH₂O), 3.00 (br, 24H; ArCH₂), 2.42 (d, ³J(H,H) = 7.0 Hz, 108H; CH₂=CH–CH₂), 1.86 (br, CH₂), 1.63 (br, CH₂); ¹³C NMR (CDCl₃, 50.33 MHz): δ ?? = 156.59 (C_q, ArO), 137.54 (C_q, Ar), 134.69 (CH₂=CH), 127.61 (CH_{Ar}), 117.47 (CH₂=CH), 113.90 (CH_{Ar}), 113.84 (CH_{Ar}), 67.92 (CH₂O), 67.44 (CH₂O), 42.68 (C_q–CH₂), 41.97 (CH₂), 33.78 (CH₂), 29.59 (CH₂), 23.87 (CH₂); MALDI TOF mass spectrum: *m/z*: 6876.70 [*M* – PF₆]⁺ (calcd 6880.75); elemental analysis calcd (%) for C₄₇₉H₅₈₇O₃₀F₆PFe (7025.72): C 81.89, H 8.42; found: C 83.00, H 8.09.

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