Synthesis of Five Generations of Redox-Stable Pentamethylamidoferrocenyl Dendrimers and Comparison of Amidoferrocenyl- and Pentamethylamidoferrocenyl Dendrimers as Electrochemical Exoreceptors for the Selective Recognition of $H_2PO_4^-$, HSO_4^-, and Adenosine 5′-Triphosphate (ATP) Anions: Stereoelectronic and Hydrophobic Roles of Cyclopentadienyl Permethylation

Marie-Christine Daniel,[a] Jaime Ruiz,[a] Jean-Claude Blais,[b] Nathalie Daro,[c] and Didier Astruc*[a]

Abstract: A family of five metallodendrimers with pentamethylamidoferrocenyl termini were synthesized from the DSM dendrimers G_n-DAB-dend-$(NH_2)_x$ ($x = 4, 8, 16, 32, 64$) and characterized by standard techniques, including prominent molecular peaks (broad for $x = 64$) in their MALDI-TOF mass spectra. Oxidation of G_4-DAB-dend-$(NHCOFc^*)_x$ ($Fc^* = C_5H_4FeCp^*$, $Cp^* = \eta^5$-C_5Me_5) with $SbCl_5$ in CH_2Cl_2 yields the stable 17-electron pentamethylferrocenium analogue, which can be characterized by ESR and Mössbauer spectroscopy and reduced back to the initial Fe^{II} dendrimer, the cycle being carried out without decomposition. The cyclic voltammograms (CVs) of all dendrimers, recorded in CH_2Cl_2 or DMF, show a fully reversible ferrocenyl wave without adsorption. They are much cleaner than those of the parent ferrocenyl analogues previously synthesized and studied by Cuadrado et al. These properties allow much easier recognition and titration of $H_2PO_4^-$ and ATP^{2-} by CV with the permethylated series than with the parent series. On the other hand, permethylation reduces the difference between the potentials recorded before and after titration. This is not crucial for $H_2PO_4^-$ and ATP^{2-}, but it is for HSO_4^-, because of the weak interaction in this case. Thus recognition and titration in CH_2Cl_2 proceeds best with the parent series, and a positive dendritic effect is revealed by the appearance of a new wave whose difference in potential relative to the initial wave increases with increasing generation number. In DMF, recognition and titration are only possible with the permethylated series and are subject to a dramatic dendritic effect. Indeed, the titration is followed by only a shift of the initial wave with G_1 and by the appearance of a new wave with G_2 and G_3. In conclusion, the permethylated dendrimers allow excellent recognition and titration of the oxoanions by CV due to the stereoelectronic stabilization of the 17-electron form and their hydrophobic effect. The magnitude of the recognition and positive dendritic effects is very sensitive to the dendrimer structure and to the nature of the solvent. The recognition is of the strong-interaction type (square scheme) between these dendrimers and ATP^{2-} with a stoichiometry of 0.5 equiv ATP^{2-} per ferrocenyl branch.

Keywords: cyclic voltammetry · dendrimers · metallocenes · molecular recognition · receptors

Introduction

Molecular recognition by means of weak supramolecular interactions is a key area,[1] because it opens a route to sensors that work in a reversible and thus practical way. Application of this principle to the recognition and sensing of anions is especially crucial in view of their role in biology. Beer et al. have developed electrochemical sensors with a rich variety of endoreceptors by modulation of the redox potential of ferrocenyl systems.[2] We are interested in dendritic and colloidal exoreceptors that, like viruses, recognize anions at their periphery.[3] In particular, the dendritic organization[4] involves channels and microcavities at the surface that

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[a] Prof. Dr. D. Astruc, M.-C. Daniel, Dr. J. Ruiz
Groupe Nanosciences Moléculaires et Catalyse
LCOO, UMR CNRS No. 5802
Université Bordeaux I, 33405 Talence Cedex (France)
Fax: (+33) 5-40-00-69-94
E-mail: d.astruc@lcoo.u-bordeaux1.fr

[b] Dr. J.-C. Blais
LCOSB, UMR CNRS No. 7613, Université Paris VI
75252 Paris (France)

[c] Dr. N. Daro
ICMCB, Université Bordeaux I
33608 Pessac Cedex (France)

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provide useful topological conditions for the function as an exoreceptor.

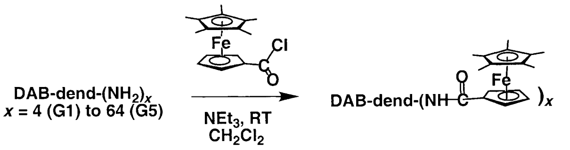
Amidoferrocenyl dendrimers were independently reported by Cuadrado et al.[5] and by us[3a] with two different families of cores. Cuadrado et al. reported amidoferrocenyl dendrimers based on the well-known commercial DSM polyamine dendrimers DAB-dend-$(NH_2)_x$ ($x = 4$, 8, 16, 32, 64),[6] and studied their electrochemistry in the context of deposition on metal surfaces.[5] For our dendrimers, made with different cores, we reported the recognition of $H_2PO_4^-$ and HSO_4^- anions by means of the dendritic effect, that is, the increase in perturbation of the ferrocenyl redox potential with increasing generation, using cyclic voltammetry.[3a]

There were two major drawbacks in using amidoferrocenyl dendrimers[7] for electrochemical recognition of anions: 1) the cyclic voltammetry wave of the amidoferrocenyl system was not reversible, due to decomposition of the amidoferrocenium species, and 2) the cyclic voltammetry waves were marred by considerable adsorption. Therefore, given the well-known stabilizing effect of Cp permethylation,[8] we synthesized pentamethylamidoferrocenyl dendrimers from the DSM family, starting from the previously disclosed complex $[Fe(\eta^5\text{-}C_5Me_5)(CO)_3](PF_6)$.[3c, 9] It was shown that the cyclic voltammetric recognition of $H_2PO_4^-$ was much easier with these compounds than with the ferrocenyl derivatives.[10]

Here we report 1) the full characterization of five generations of these metallodendrimers and spectroscopic data for their 17-electron pentamethylamidoferrocenium forms, 2) new recognition studies on the HSO_4^- anion that, surprisingly, are best performed with the parent amidoferrocenyl dendrimers, and 3) details and extension of the recognition of $H_2PO_4^-$ to the recognition of the biologically important adenosyltriphosphate dianion, including the selectivity of this recognition in the presence of other anions such as HSO_4^- and Cl^-.

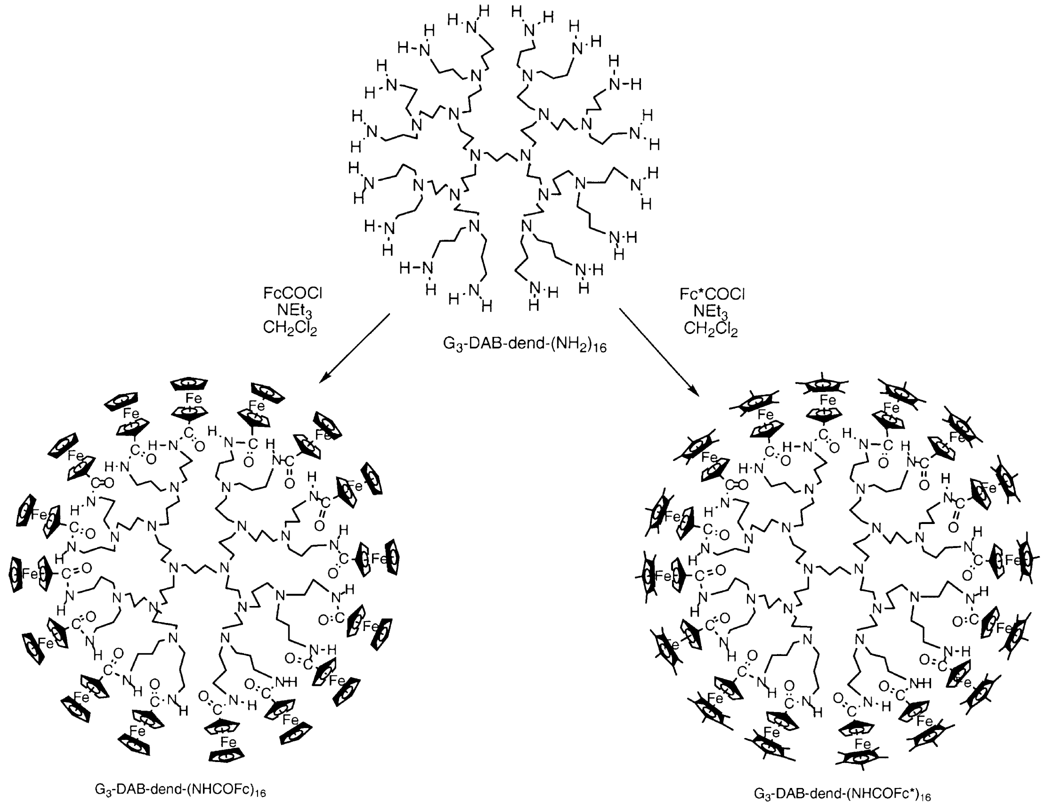
Results

Syntheses and oxidation of the pentamethylamidoferrocenyl-dendrimers: The five generations of metallodendrimers were synthesized by reactions of DSM's polyamine dendrimers DAB-dend-$(NH_2)_x$ ($x = 4$, 8, 16, 32, 64) with pentamethylferrocenoyl chloride in dichloromethane at room temperature overnight in the presence of triethylamine and obtained after purification as yellow-orange powders [Eq. (1) and Scheme 1].



(1)

All dendrimers were characterized by standard analytical and spectroscopic techniques, including MALDI-TOF mass spectrometry, which showed prominent and sharp molecular peaks except for G_5-DAB-dend-$\{[NHCOCpFeCp^*][PF_6]\}_{64}$, for which the molecular signal was broad, like that of the parent Cp compound.[5, 11] The dendrimer G_5-DAB-dend-$(NHCOCpFeCp^*)_{64}$ was oxidized by $SbCl_5$ in CH_2Cl_2 to the



Scheme 1. Synthesis of G_1-G_5 (Fc and Fc* series) from the DSM dendrimers G_n-DAB-dend-$(NH_2)_x$ (× = 4, 8, 16, 32, 64).

blue-green 17-electron complex G_5-DAB-dend-{[NHCOCp-FeCp*][SbCl$_6$]}$_{64}$. The Mössbauer and EPR spectra of the oxidized dendrimer are shown in Figure 1 and confirm that its electronic structure is identical to that of the ferrocenium cation[12] and that this 17-electron dendrimer is thermally stable. This stability is confirmed by the quantitative exergonic reduction back to the pentamethylamidoferrocene dendrimer with decamethylferrocene in CH_2Cl_2 [Eq. (2)].

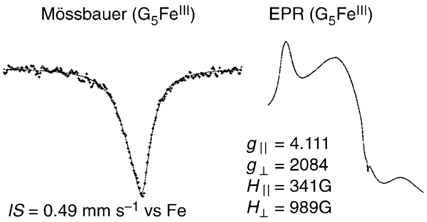


Figure 1. Mössbauer (left, $QS = 0$) and EPR (right) spectra of [G_5-64-Fc*][SbCl$_6$]$_{64}$ at 4 K for neat samples.

$$G_5\text{-64-NHCOFc*} \xrightleftharpoons[\text{[FeCp*}_2\text{], CH}_2\text{Cl}_2\text{, RT}]{\text{SbCl}_5\text{, CH}_2\text{Cl}_2\text{, RT}} G_5\text{-64-\{[NHCOFc*][SbCl}_6\text{]\}}$$

Cyclic voltammetry of the dendrimers G_n-DAB-dend-(NHCOCpFeCp*)$_x$: Cyclic voltammetry (Table 1) was performed for all dendrimers with a Pt anode in CH_2Cl_2 or DMF. The fact that only one CV wave is observed is attributable to the following factors: First, the electrostatic factor is very weak, since two ferrocenyl groups are separated by at least 11 atoms in the metallodendritic molecules. Then, the rotation of the dendrimers is much more rapid relative to the electrochemical timescale than for other ferrocenyl dendrimers.[13] The redox potentials of the different ferrocenyl centers do not have exactly the same value, but the differences, due to the electrostatic factor, must be on the order of a fraction of millivolt or a few millivolts. Therefore, they are negligible and, in any case, not observed. The $E_{1/2}$ values are 0.405 ± 0.05 V versus [FeCp$_2^*$], and thus do not significantly vary from G_1 to G_5. The value for the parent series is 0.690 ± 0.010 V versus [FeCp$_2^*$] under the present conditions (Table 1). The internal [FeCp$_2^*$] reference is much better than ferrocene, as we have already reported.[14] Indeed, ferrocenium is too sensitive to the medium. Possible small dendritic effects were investigated, and we conclude that they are absent here with [FeCp$_2^*$] as internal reference ($E_{1/2}$ vs $FeCp_2 = E_{1/2}$ vs $FeCp_2^* + 0.545$ V in CH_2Cl_2, or $+0.595$ V in DMF[14]).

The comparison of these CV data with those of the parent series shows that the permethylated dendrimers (Fc*) behave in a much better fashion than the parent series (Fc). One of the dramatic differences between the CV of the dendritic Cp* and parent Cp series is that the Cp* series shows no or almost no adsorption in CH_2Cl_2, the i_{pc}/i_{pa} values being 1.00 ± 0.03 for G_1, G_2, and G_3, 1.1 for G_4, and 1.2 for G_5. In contrast, the parent Cp series shows i_{pc}/i_{pa} values between 2 and 3.4 under the same conditions (0.2 V s^{-1}, 20 °C, Pt anode, CH_2Cl_2, 0.1 M nBu$_4$NPF$_6$), which are indictive of strong adsorption (Figure 2A). This difference of behavior toward adsorption is confirmed by $E_{pc} - E_{pa}$ values of 0.06 V for G_1, G_2, and G_3, 0.05 V for G_4, and 0.035 V for G_5 for the Cp* series, but only 0.03 V for G_1 to G_5 in the parent Cp series. In DMF, the i_{pc}/i_{pa} value is 1.05 ± 0.05 for the Cp* series, but it decreases from 0.9 for G_1 to 0.4 for G_2, G_3, and G_4 in the parent Cp series under these conditions. This indicates chemical irreversibility in the Cp series, that is, decomposition of the parent ferrocenium dendrimers becomes faster in this solvent with increasing generation number, even on the short CV timescale (Figure 2B).

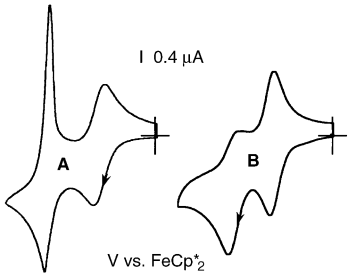


Figure 2. Cyclic voltammograms of a mixture of G_3-16Fc and G_3-16Fc* (10^{-4} M, Pt anode; 0.1 M [nBu$_4$N][PF$_6$], 20 °C). A) In CH_2Cl_2 showing the extensive adsorption only for G_3-16Fc. B) In DMF showing the chemical irreversibility for G_3-16Fc which perturbs access to $E_{1/2}$ and K.

The number n of electrons involved in the CV waves for ferrocenyl dendrimers is usually determined by using the Bard–Anson formula, which gives fairly correct results.[15–17] For the dendritic Cp* series it gave values of n that correspond to the theoretical numbers to within 5 % in CH_2Cl_2 or DMF for generations G_1 to G_4, but significantly lower for G_5 (Table 1).[11]

Electrochemical recognition and titration of the oxoanions $H_2PO_4^-$, HSO_4^-, and ATP^{2-}

$H_2PO_4^-$: Numerous studies by Beer et al. with endoreceptors to which one or more ferrocenyl groups are attached have paved the way for the recognition of oxoanions. Addition of [nBu$_4$N][H$_2$PO$_4$] to an electrochemical cell containing a solution of amidoferrocenyl or pentamethylamidoferrocenyl dendrimer in CH_2Cl_2 leads to the appearence of a new wave at a potential less positive than the initial wave, the intensity of which decreases while that of the new wave increases. The equivalence point is reached when the initial wave is completely replaced by the new wave, as is already known for endoreceptors and another ferrocenyldendrimer structures.[2, 3] This was rationalized by Echegoyen and Kaifer using the square scheme in a seminal article.[18] We used this analysis to determine the ratio of apparent equilibrium constants $K_{(+)}$ and K_0 related to the strong interaction of the anion with the cationic ferrocenium form of the redox system, but also with the neutral ferrocenyl form ($K \gg 1$).

There are large differences in behavior between the amidoferrocenyl dendrimers and the pentamethylamidoferrocenyl series. In the case of the parent Cp dendrimer series, the cyclic voltammograms are marred by both chemical and,

Table 1. Cyclic voltammetry data for G_1-G_5 (both Fc and Fc* series) before and after titration of $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$, $[n\mathrm{Bu_4N}]_2[\mathrm{ATP}]$, and $[n\mathrm{Bu_4N}][\mathrm{HSO_4}]$.

	$E_{1/2}$[a] $(E_{pa}-E_{pc})$ [V]		i_{pc}/i_{pa}		n[b]		$\Delta E_{1/2}(H_2PO_4^-)$[a] $(E_{pa}-E_{pc})$ [V]		$K_{(+)}/K_{(o)}$[c]	$H_2PO_4^-$ $K_{(+)}/K_{(o)}$[c]	$K_{(+)}$[d]
	CH_2Cl_2	DMF	CH_2Cl_2	DMF	CH_2Cl_2	DMF	CH_2Cl_2	DMF	CH_2Cl_2	DMF	DMF
G_0-1Fc	0.700 (0.06)	0.615 (0.06)	1.1	0.92	1.1	1.1	0.155 (0.15)	0.065 (0.09)	470	13	
G_1-4Fc	0.695 (0.03)	0.645 (0.07)	3.2	0.75	3.5		0.310 (0.09)	0.150 (0.16)	2.2×10^5	386	
G_2-8Fc	0.675 (0.03)	0.650 (0.08)	2.2	0.46	7.2		0.250 (0.11)	–[e]	2.0×10^4		
G_3-16Fc	0.690 (0.03)	0.650 (0.08)	3.5	0.42	16.0		0.170 (0.15)	–[e]	850		
G_4-32Fc	0.690 (0.04)	0.650 (0.08)	1.9	0.40	32	31.5	–[e]	–[e]			
G_5-64Fc	0.680 (0.03)	0.670 (0.10)	3.4	0.62		53	–[e]	–[e]			
G_1-4Fc*	0.406 (0.06)	0.360 (0.07)	1.05	1.07	3.8	4.2	0.155 (0.16)	0.115 (0.06)	470		9.6×10^3
G_2-8Fc*	0.395 (0.06)	0.370 (0.08)	1.02	1.1	7.9	8.0	0.160 (0.11)	0.125 (0.07)	570		14×10^3
G_3-16Fc*	0.410 (0.06)	0.370 (0.07)	1.01	1.12	15.1		0.130 (0.13)	0.145 (0.08)	170		32×10^3
G_4-32Fc*	0.400 (0.05)	0.390 (0.07)	1.1	1.05	32		0.140 (0.17)	0.165 (0.06)	260		70×10^3
G_5-64Fc*	0.410 (0.035)	0.375 (0.03)	1.2	1.06	55		0.160 (0.17)	0.140 (0.03)	570		26×10^3

[a] $E_{1/2}=(E_{pa}+E_{pc})/2$ vs $FeCp_2^*$ (in V). Electrolyte: $[n\mathrm{Bu_4N}][\mathrm{PF_6}]$ 0.1M; working and counterelectrodes: Pt; reference electrode: Ag; internal reference: $FeCp_2^*$; scan rate: 0.200 $\mathrm{V\,s^{-1}}$; 20 °C. [b] Values of the number of electrons involved calculated from the Anson–Bard equation[9] using anodic intensities. [c] Error = 10%; $\Delta E_{1/2}=0.058\log(K_{(+)}/K_{(o)})$[11] at 20 °C. [d] Error = 10%; progressive shift of the wave: $K_{(o)}\ll 1$, $\Delta E_{1/2}=0.058\log(cK_{(+)})$. [e] No cathodic wave (no accessible $\Delta E_{1/2}$ value).

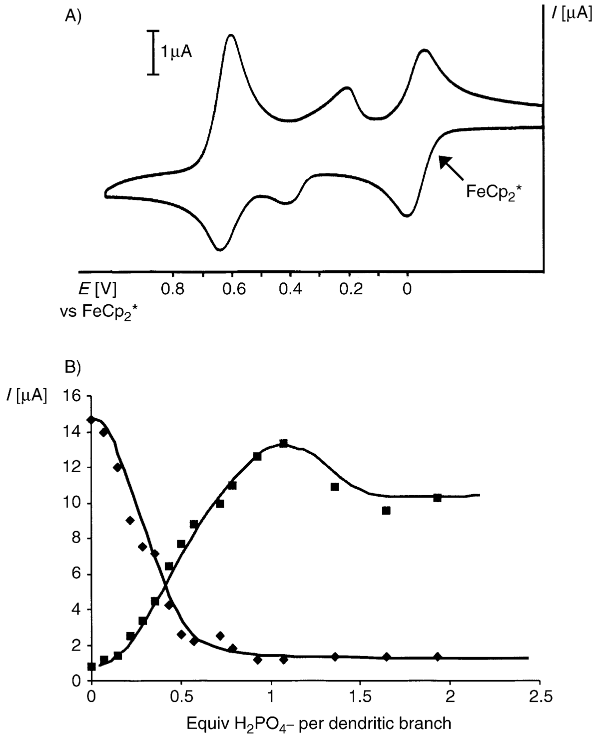


Figure 3. Titration of a 9.7×10^{-4}M solution of G_1-4Fc with a 10^{-3}M solution of $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$ in CH_2Cl_2 in the presence of 0.1M $[n\mathrm{Bu_4N}][\mathrm{PF_6}]$, Pt anode, 20 °C. A) Cyclic voltammogram obtained after addition of 0.5 equiv $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$ per dendritic branch. B) Variation of the intensities of the initial (●) and new (◆) waves during the titration.

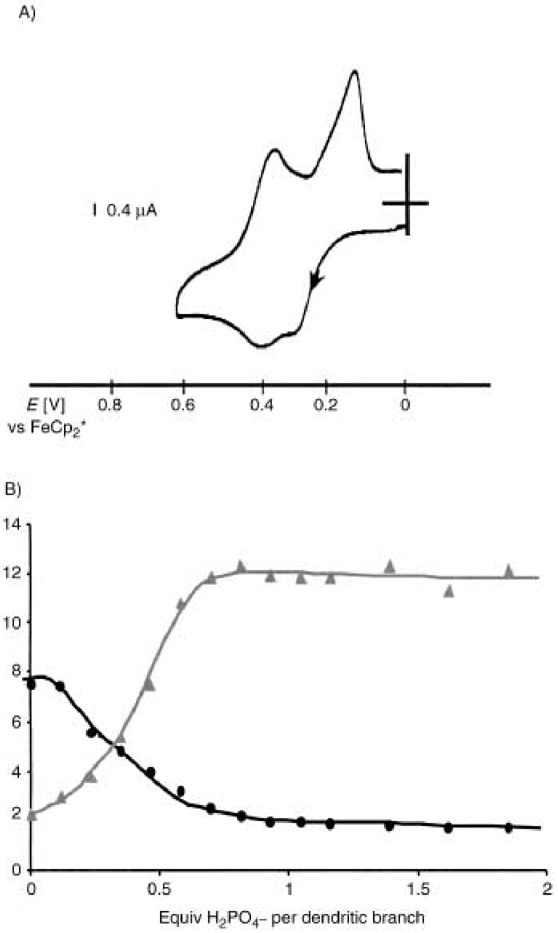


Figure 4. Titration of a 2.7×10^{-4}M solution of G_3-16Fc* by a 10^{-3}M solution of $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$ in CH_2Cl_2 in the presence of 0.1M $[n\mathrm{Bu_4N}][\mathrm{PF_6}]$, Pt anode, 20 °C. A) Cyclic voltammogram obtained after addition of 0.5 equiv $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$ per dendritic branch. B) Variation of the intensities of the initial (●) and new (▲) waves along the titration.

electrochemical irreversibility[11b, 14] of the new wave (Figure 3 and Figure S5 in the Supporting Information). Gratifyingly the chemical irreversibility is not found with the new Cp* dendrimer series, and this allows a much easier analysis of this electrochemical recognition phenomenon (Figure 4 and Figure S6 in the Supporting Information). The electrochemical irreversibility is characterized by $E_{pc}-E_{pa}$ values[14] of 0.150 ± 0.010 V without significant dendritic effect, and adsorption by i_{pc}/i_{pa} values of 4 ± 1, also without significant dendritic effect. The difference in $E_{1/2}$ values between the initial and the new wave (determined after addition of 0.5 equiv $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$, in order to observe both waves at the same time) is 0.150 ± 0.010 V without significant dendritic effect. This corresponds to a ratio of apparent association constants $K_{(+)}/K_{(0)}$ of 400 ± 100 (resp. 170 ± 40) according to the Echegoyen–Kaifer model.[18]

Interestingly, a different phenomenon is found in DMF as solvent. Again, use of the parent Cp dendrimer series is difficult in this solvent because of the complete chemical irreversibility, except for the first generation. In contrast, the whole Cp* dendrimer series shows a CV wave that is fully chemically reversible and progressively shifted upon addition of $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$, with an adsorption characterized by an i_{pc}/i_{pa} ratio of 3 ± 1 without significant dendritic effect. This shift in $E_{1/2}$ values is subject to a small dendritic effect, for instance, with $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$: 115 mV ($G_1$), 125 mV ($G_2$), 145 mV ($G_3$), 165 mV ($G_4$) (all values ± 0.010 V), 140 mV (G_5, with more adsorption; see Figure S1 in the Supporting Information). The largest shift is that observed in the parent Cp series between FcCONHPr (65 mV) and G_1 (150 mV). These shifts provide direct access to the apparent association constants $K_{(+)}$ in DMF (± 20 %) only for the whole Cp* series: 9600 (G_1), 14000 (G_2), 32000 (G_3), 70000 (G_4) according to the Echegoyen–Kaifer model.[15]

ATP^{2-}: Electrochemical recognition was first studied in CH_2Cl_2. In this solvent, the trends found for ATP^{2-}[19, 20] closely follow those found for $H_2PO_4^-$ (Table 2). The addition of $[n\mathrm{Bu_4N}]_2[\mathrm{ATP}]$ to the electrochemical cell containing the amidoferrocenyl- or pentamethylamidoferrocenyl dendrimer causes, as with $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$, the appearance of a new wave at a potential less positive than the initial one, whose intensity decreases while that of the new wave increases (Figure 5 A and Figure S2A in the Supporting Information). Thus, this is a case of strong-type interaction and can be treated by using the square scheme, as with $[n\mathrm{Bu_4N}]_2[\mathrm{H_2PO_4}]$. As for $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$, the pentamethylamidoferrocenyl dendrimers were greatly superior to the parent dendrimers with regard to the quality of the CVs, and consequently the study was carried out with this permethylated series (see Table 2). The difference in ferrocenyl redox potential between the initial wave and the new wave is of the same order of magnitude as with $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$, but slightly lower than for the latter (0.130 mV for $[n\mathrm{Bu_4N}]_2[\mathrm{ATP}]$, i.e., 20 mV less than with $[n\mathrm{Bu_4N}][\mathrm{H_2PO_4}]$; see Table 2). The corresponding ratio of apparent association constants is $K_{(+)}/K_{(0)} = 170 \pm 40$. The equivalence point is reached when 0.5 equiv $[n\mathrm{Bu_4N}]_2$-[ATP] has been added, which is in accordance with the double negative charge of this anion (Figure 5B and Figure S5B in the Supporting Information). Other large stoichiometries have been found for ATP^{2-} with receptors based on other functional groups such as amines.[19]

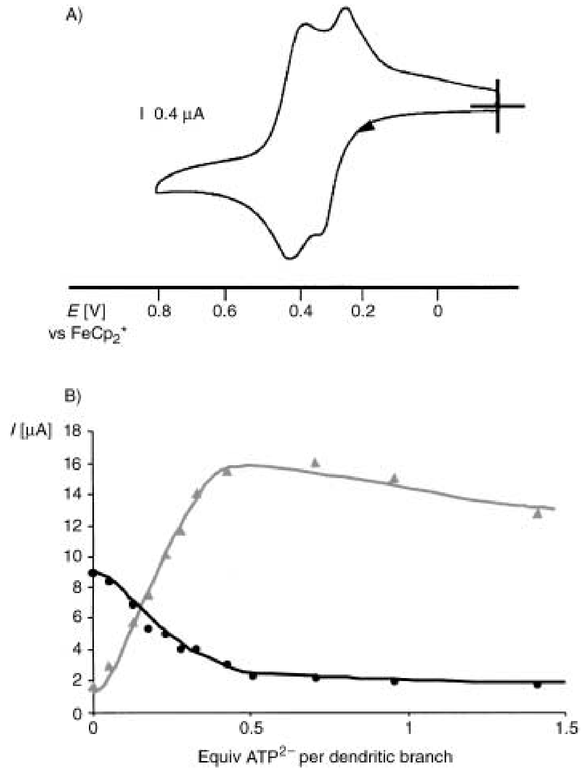


Figure 5. Titration of a 1.25×10^{-4} M solution of G_2-32Fc* with a 10^{-3} M solution of $[n\mathrm{Bu_4N}]_2[\mathrm{ATP}]$ in CH_2Cl_2 in the presence of 0.1 M $[n\mathrm{Bu_4N}][\mathrm{PF_6}]$, Pt anode, 20 °C. A) Cyclovoltammogram obtained after addition of 0.25 equiv $[n\mathrm{Bu_4N}]_2[\mathrm{ATP}]$ per dendritic branch; B) Variation of the intensities of the initial (●) and new (▲) waves during the titration.

A study in DMF revealed remarkable dendritic effects. With the first generation (G_1-4Fc*), the addition of $[n\mathrm{Bu_4N}]_2$-[ATP] does not lead to the appearance of a new CV wave, but only a progressive shift of the wave (see Figure 6). The overall shift up to the equivalence point is $\Delta E_{1/2} = 145$ mV. Although the initial CV wave does not show adsorption, an adsorption phenomenon appears with increasing intensity along the titration. For the 2nd and 3rd generations G_2-8Fc* and G_3-16Fc, addition of $[n\mathrm{Bu_4N}]_2[\mathrm{ATP}]$ to the electrochem-

Table 2. Cyclic voltammetry data for G_1–G_4 (both Fc and Fc* series) after titration of ATP^{2-} and HSO_4^-.

	$\Delta E_{1/2}(\mathrm{ATP}^{2-})$[a] $(E_{pa}-E_{pc})$ [V]		ATP^{2-}			$\Delta E_{1/2}(\mathrm{HSO_4^-})$[a] $(E_{pa}-E_{pc})$ [V]		HSO_4^-	
		$K_{(+)}/K_{(o)}$[b]		$K_{(+)}/K_{(o)}$[b]		$K_{(+)}$[c]		$K_{(+)}/K_{(o)}$[b]	$K_{(+)}$[c]
	CH_2Cl_2	DMF	CH_2Cl_2	DMF	DMF	CH_2Cl_2	DMF	CH_2Cl_2	DMF
G_1-4Fc	–[d]					0.120 (0.06)		140	
G_2-8Fc									
G_3-16Fc	–[d]					0.165 (0.10)		700	
G_4-32Fc						0.110 (0.14)		80	
G_1-4Fc*	0.130 (0.09)	0.145 (0.06)	170		24.10^4	0.080 (0.06)		24	
G_2-8Fc*	0.130 (0.10)	0.065 (0.10)	170	13		0.105 (0.07)	0.05 (0.06)	65	2.8×10^3
G_3-16Fc*	0.130 (0.09)	0.065 (0.07)	170	13		0.100 (0.06)		53	
G_4-32Fc*	0.110 (0.10)		80			0.095 (0.06)		44	

[a] $E_{1/2} = (E_{pa} + E_{pc})/2$ vs $FeCp_2$*(in V). Electrolyte: $[n\mathrm{Bu_4N}][\mathrm{PF_6}]$ 0.1 M; working and counterelectrodes: Pt; reference electrode: Ag; internal reference: $FeCp_2^*$; scan rate: 0.200 V s^{-1}; 20 °C. [b] Error = 10 %; $\Delta E_{1/2} = 0.058\lg(K_{(+)}/K_{(o)})$[11] at 20 °C. [c] Error = 10 %; progressive shift of the wave: $K_{(o)} \ll 1$, $\Delta E_{1/2} = 0.058\lg(cK_{(+)})$. [d] No cathodic wave (no accessible $\Delta E_{1/2}$ value).

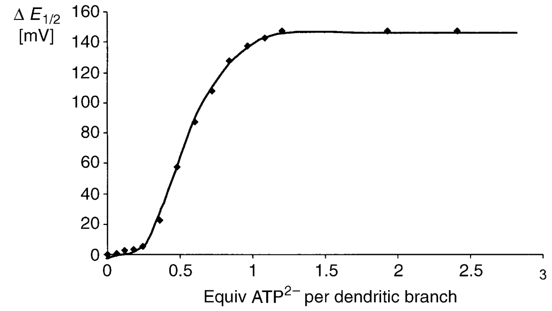


Figure 6. Titration of a 4.1×10^{-4} M solution of G_1-4Fc* with a 10^{-3} M solution of [nBu$_4$N]$_2$[ATP] in DMF in the presence of 0.1 M [nBu$_4$N][PF$_6$], Pt anode, 20 °C: shift of $E_{1/2}$ toward positive potentials recorded by CV as a function of the number of equivalents of [nBu$_4$N]$_2$[ATP] added per dendritic branch.

ical cell leads to the appearance of a new wave at a potential 65 mV less positive than that of the initial wave. This new wave is also accompanied by some adsorption. Thus, this change in behavior from G_1 to G_2 and G_3 means that the interaction between the neutral ferrocenyl form of the dendrimer and [nBu$_4$N]$_2$[ATP] progresses from weak for G_1 ($K_{(0)} \ll 1$) to relatively strong for G_2 and G_3 ($K_{(0)} \gg 1$).

HSO_4^-: This is the only anion for which the electrochemical recognition is sometimes easier with the amidoferrocenyl dendrimers than with the permethylated dendrimers. Indeed, the addition of [nBu$_4$N][HSO$_4$] to G_1–G_4 amidoferrocenyl dendrimers in CH_2Cl_2 solution leads to the appearance of a new wave, contrary to what is observed with other amidoferrocenyl dendrimers, for which only a shift of the wave was observed. The difference in potential between the new and initial waves increases from the first to the third generation, that is, this recognition is subject to a positive dendritic effect. The maximum $\Delta E_{1/2}$ value (3rd generation, G_3-16Fc) is 165 mV. Figure 7 shows the titration of HSO_4^- with G_3-16Fc in CH_2Cl_2 (see also Figure S7 in the Supporting Information). As usual, adsorption is found on the new wave and on the initial wave, but recognition and titration are possible.

With the new permethylated metallodendrimer series, this adsorption is observed neither at the beginning of nor during the titration. A new wave is observed when [nBu$_4$N][HSO$_4$] is added to the electrochemical cell containing permethylated metallodendrmer in CH_2Cl_2, but the difference in potential between the new wave and the initial wave is only 105 mV (max.) for G_2-8Fc*. This $\Delta E_{1/2}$ value is relatively small, so that there is much overlap between the two waves. Figure S3 (Supporting Information) shows the cyclovoltammogram of G_4-32Fc* in the presence of HSO_4^- in CH_2Cl_2, and Figure S4 (Supporting Information) shows the variation of the intensities of the initial and new waves during the titration of HSO_4^- with G_3-16Fc* in CH_2Cl_2.

In DMF, the irreversibility of the redox process does not allow a correct CV analysis with the parent amidoferrocenyl dendrimer series. In this solvent, the CV of the pentamethylamidoferrocenyl dendrimers is not marred by adsorption either, but it is only shifted upon addition of [nBu$_4$N][HSO$_4$], and this shift is rather modest ($\Delta E_{1/2} = 50$ mV). Nevertheless, it allows a titration to be performed by plotting this potential shift as a function of the amount of [nBu$_4$N][HSO$_4$] added, especially because the shape of the CV wave is not perturbed from the beginning to the very end of the titration.

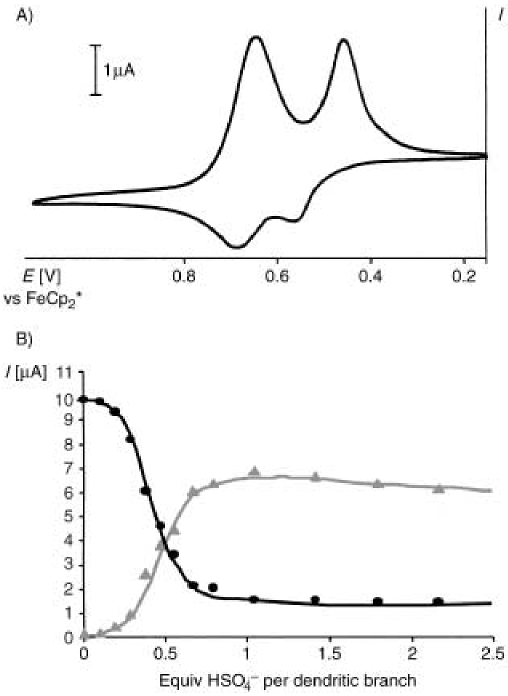


Figure 7. Titration of a 3.3×10^{-4} M solution of G_3-16Fc with a 10^{-3} M solution of [nBu$_4$N][HSO$_4$] in CH_2Cl_2 in the presence of 0.1 M [nBu$_4$N][PF$_6$], Pt anode, 20 °C. A) Cyclic voltammogram obtained after addition of 0.5 equiv [nBu$_4$N][HSO$_4$] per dendritic branch. B) Variation of the intensities of the initial (●) and new (▲) waves during the titration.

Selective recognition and titration of $H_2PO_4^-$ and ATP^{2-} in the presence of [nBu$_4$N][HSO$_4$] and [nBu$_4$N][Cl]: Since addition of nBu$_4$N$^+$ salts of Cl$^-$ or HSO_4^- only has a slight influence, provoking a weak shift in the Fe^{II}/Fe^{III} wave of the pentamethylamidoferrocenyl dendrimers by 40 mV for Cl$^-$ and 50 mV for HSO_4^-, selective recognition and titration were investigated after addition of 1 equiv of each anion to G_2-8Fc*. Indeed, the recognition of $H_2PO_4^-$ or ATP^{2-} can be carried out in the presence of these anions. Instead of leading to the appearance of a new Fe^{II}/Fe^{III} wave, as in the absence of Cl$^-$ and HSO_4^-, the addition of $H_2PO_4^-$ or ATP^{2-} when Cl$^-$ and HSO_4^- are both present induces a shift of this wave by $\Delta E_{1/2} = 180$ mV for $H_2PO_4^-$ and 160 mV for ATP^{2-}. Figure 8 shows that titration of ATP^{2-} proceeds smoothly in the presence of these anions.

Discussion

Several reports have already appeared on the recognition of various anions by metallodendrimers.[3a, 21, 22] In particular, the recognition of $H_2PO_4^-$ has been shown to result from a strong interaction with ferrocenyl derivatives. These first pentamethylferrocenyl dendrimers have two favorable properties derived from the presence of a permethylated cyclopentadienyl ligand that clearly distinguish them from ferrocenyl

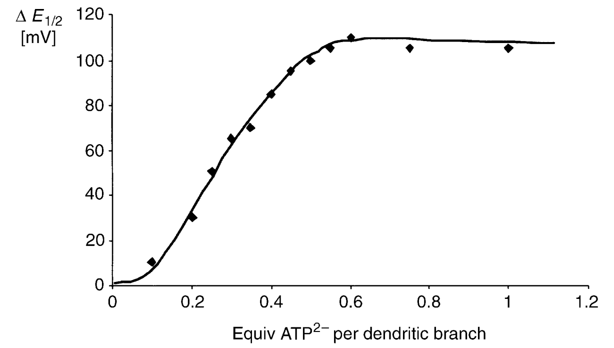


Figure 8. Titration of a 4×10^{-4} M solution of G_2-8Fc* with a 10^{-3} M solution of $[nBu_4N]_2[ATP]$ in CH_2Cl_2 in the presence of 0.1 M $[nBu_4N][PF_6]$, 2.10^{-4} M $[nBu_4N][Cl]$, and 2.10^{-4} M $[nBu_4N][HSO_4]$, Pt anode, 20°C. Shift of $E_{1/2}$ toward positive potentials, recorded by CV, as a function of the number of equivalents of $[nBu_4N]_2[ATP]$ added per dendritic branch.

dendrimers: stabilization of the oxidized 17-electron ferrocenium form and hydrophobicity bestowed on the periphery of the dendrimers by methyl substituents on the Cp rings. Both properties are essential in overcoming the problems encountered with amidoferrocenyl dendrimers: the instability of the oxidized ferrocenium form, largely due to the presence of the electron-withdrawing amido group, and adsorption due to the polarity of the amidoferrocenium groups. Indeed the comparison of the CV waves before and during the recognition and titration of the oxoanions clearly shows that the permethylated dendrimers are no longer marred by the problems encountered in the Cp series. The result is that the recognition and titration of $H_2PO_4^-$ and ATP^{2-} are clean with the permethylated series.

Another difference between permethylated Cp* and Cp is the increased donor strength due to the electron-releasing methyl groups. In recognition studies with thiolate–gold nanoparticles,[2a] it was shown that this factor weakens the key hydrogen bond between the amido group and $H_2PO_4^-$ and thus decreases the difference in potential $\Delta E_{1/2}$ between the initial ferrocenyl wave and the new wave. We have the same situation here, but this $\Delta E_{1/2}$ value is large anyway, so that these two waves are distinct. Thus, the recognition and titration of $H_2PO_4^-$ do not really suffer from this factor. In the case of HSO_4^- in DMF, however, for which the interaction of the amido group with the oxoanion is not as strong as with $H_2PO_4^-$, the difference in potential between the new wave and the initial wave is generally much smaller. Then, the decrease in this difference becomes a decisive factor that leads to a preference for the parent amidoferrocenyl dendrimers (early generation) over the permethylated dendrimers, because the small difference in potential in the latter series causes overlap of the two waves.

Various dendritic effects on $\Delta E_{1/2}$ are evident in the present study. A distinction can be made between the dendritic effect in comparing a monoamidoferrocenyl compound with G_1-4-NHCOFc, and the dendritic effects among dendrimers of different generations. Whereas the former is always significant, the latter varies from negligible to very significant. No dendritic effect of the second type is found for $H_2PO_4^-$ and ATP^{2-} in CH_2Cl_2, whereas a modest dendritic effect is observed in DMF. A significant dendritic effect is found for the recognition of HSO_4^- in CH_2Cl_2 by the amidoferrocenyl dendrimers. The most spectacular dendritic effect of the second type is found in the recognition of ATP^{2-} in DMF by pentamethylamidoferrocenyl dendrimers, since the recognition goes from the weak type for G_1-4-NHCOFc* (only shift of the wave) to the strong type with G_2-8-NHCOFc* and G_3-16-NHCOFc* (new wave). In these studies of dendritic effects, it is not possible to compare the amidoferrocenyl dendrimers with the pentamethylamidoferrocenyl dendrimers. Indeed, the former series does not present CVs that are clean enough for a family of several generations (the study of the first generation G_1-4-NHCOFc is most often possible, but usually not those of higher generations).

Finally, one can try to compare the amidoferrocenyl dendrimers to those previously reported with a different core, which showed strong dendritic effects. These dendritic effects are always positive in both families, although of different nature and magnitude. They are also very sensitive to many factors, especially to the solvent and the dendrimer structure. Thus, a comparison between two series of different structure is all the more delicate as the dendritic effects are very variable even within a single family, as shown in the present study. Thus, one can simply underline their great sensitivity to the structural variations from one dendrimer family to another, even with the same terminal amidoferrocenyl groups.

Conclusion

The synthesis of the first pentamethylamidoferrocenyl dendrimers has facilitated the clean recognition of oxoanions including ATP^{2-} due to stabilization of the 17-electron ferrocenium form and the hydrophobicity of the many methyl groups of the Cp* ligands around the dendrimers.

The relatively strong interaction between the hydrogenphosphate anions (including ATP^{2-}) and the amido group allows analysis according to the square scheme with very distinct initial and new ferrocenyl waves. The effect of ATP^{2-} is almost as strong as that of the $H_2PO_4^-$ anion itself, but the stoichiometry in the titration is halved.

With HSO_4^-, the donor strength of the methyl groups of the Cp* groups brings the two waves close to each other, so that the parent amidoferrocenyl dendrimers are more suitable than the permethylated dendrimers in CH_2Cl_2 (but not in DMF). With these dendrimers, recognition is also of the strong-interaction type in CH_2Cl_2.

In the permethylated series, recognition and titration are subject to a remarkable dendritic effect in DMF: from the weak-type with G_1, the interaction changes to the strong-interaction type with G_2 and G_3. The dendritic effects are strongly dependent on the structure and solvent and range from negligible to dramatic as a function of these factors.

Experimental Section

NEt_3 (2 mmol), CH_2Cl_2 (20 mL), and then $[FeCp^*(C_5H_4COCl)]$ (1.2 mmol), prepared according to ref. [3b], were added to the commercial

DSM polyamine dend-DAB(NH_2)$_x$ (1 mmol). After stirring overnight at room temperature, the solution was washed with a saturated aqueous solution of K_2CO_3 and then with distilled water, and dried over Na_2SO_4, filtered, and concentrated. Addition of diethyl ether led to precipitation of a yellow-orange powder of the metallodendrimer, which was further purified by dissolution in CH_2Cl_2 and reprecipitation by addition of diethyl ether.

G_1: ^1H NMR ($CDCl_3$): $\delta = 6.65$ (t, 4H, NH), 4.24 (br, 8H, C_5H_4), 3.88 (br, 8H, C_5H_4), 3.43 (br, 8H, $NHCH_2$), 2.47 (br, 12H, CH_2N), 1.85 (s, 60H, $C_5(CH_3)_5$), 1.51 (br, 8H, CH_2), 1.48 (br, 4H, CH_2); ^{13}C NMR ($CDCl_3$): $\delta =$ 169.28 (CO), 82.07 (Cq, C_5H_4), 81.06 (Cq, CCH_3), 76.05 and 70.21 (C_5H_4), 52.81 (CH_2), 38.92 (CH_2), 27.92 (CH_2), 10.67 (CH_3); IR (Nujol): $\tilde{\nu} = 1623$ (ν(CO)), 1539 cm^{-1} (ν(CN)); MS (MALDI-TOF): *m*/*z*: calcd for $C_{80}H_{112}N_6Fe_4O_4$: 1445.163; found: 1445.72; elemental analyis (%) calcd for $C_{80}H_{112}N_6Fe_4O_4$: C 66.48, H 7.81; found: C 66.05, H 7.36.

G_2: ^1H NMR ($CDCl_3$): $\delta = 6.90$ (br, 8H, NH), 4.31 (br, 16H, C_5H_4), 3.86 (br, 16H, C_5H_4), 3.43 (br, 16H, $NHCH_2$), 2.35 (br, 36H, CH_2N), 1.84(s, 120H, $C_5(CH_3)_5$), 1.68 (br, 28H, CH_2), 1.48 (br, 4H, CH_2); ^{13}C NMR ($CDCl_3$): $\delta =$ 170.28 (CO), 81.16 (Cq, CCH_3), 76.40 and 70.32 (C_5H_4), 53.21(CH_2), 39.12(CH_2), 28.45 (CH_2), 10.31 (CH_3); IR (Nujol): $\tilde{\nu} = 1620$ (ν(CO)), 1539 cm^{-1} (ν(CN)); MS (MALDI-TOF): *m*/*z*: calcd for $C_{168}H_{240}N_{14}Fe_8O_8$: 3028; found: 3029; elemental analyis (%) calcd for $C_{168}H_{240}N_{14}Fe_8O_8$: C 66.58, H 7.98; found: C 65.12, H 7.28.

G_3: ^1H NMR ($CDCl_3$): $\delta = 7.16$ (br, 16H, NH), 4.31 (br, 32H, C_5H_4), 3.86 (br, 32H, C_5H_4), 3.43 (br, 32H, $NHCH_2$), 2.35 (br, 84H, CH_2N), 1.84 (s, 240H, $C_5(CH_3)_5$), 1.68 (br, 56H, CH_2), 1.48 (br, 4H, CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.28$ (CO), 80.98 (Cq, CCH_3), 76.40, 70.45 (C_5H_4), 53.21 (CH_2), 39.08 (CH_2), 28.36 (CH_2), 10.52 (CH_3); IR (Nujol): $\tilde{\nu} = 1620$ (ν(CO)), 1540 cm^{-1} (ν(CN)); MS (MALDI-TOF): *m*/*z*: calcd for $C_{344}H_{496}N_{30}Fe_{16}O_{16}$: 6201.33; found: 6204.3; elemental analyis (%) calcd for $C_{344}H_{496}N_{30}Fe_{16}O_{16}$: C 66.62, H 8.06; found: C 65.32, H 7.28.

G_4: ^1H NMR ($CDCl_3$): $\delta = 7.21$ (br, 32H, NH), 4.31 (br, 64H, C_5H_4), 3.86 (br, 64H, C_5H_4), 3.43 (br, 64H, $NHCH_2$), 2.35 (br, 180H, CH_2N), 1.84 (s, 480H, $C_5(CH_3)_5$), 1.68 (br, 60H, CH_2), 1.48 (br, 4H, CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 169.87$ (CO), 80.97 (Cq, CCH_3), 76.40, 70.40 (C_5H_4), 53.21 (CH_2), 39.01(CH_2), 28.42 (CH_2), 10.31(CH_3); IR (Nujol): $\tilde{\nu} = 1622$ (ν(CO)), 1540 cm^{-1} (ν(CN)); MS (MALDI-TOF): *m*/*z*: calcd for $C_{696}H_{1008}N_{62}Fe_{32}O_{32}$: 12542.89; found: 12544.9; elemental analyis (%) calcd for $C_{696}H_{1008}N_{62}Fe_{32}O_{32}$: C 66.64, H 8.10; found: C 65.10, H 7.78.

G_5: ^1H NMR ($CDCl_3$): $\delta = 7.43$ (br, 64H, NH), 4.41 (br, 128H, C_5H_4), 3.82 (br, 128H, C_5H_4), 3.43 (br, 128H, $NHCH_2$), 2.37 (br, 372H, CH_2N), 1.84 (s, 960H, C_5CH_3), 1.51 (br, 252H, CH_2); ^{13}C NMR ($CDCl_3$): $\delta = 170.15$ (CO), 81.16 (Cq, CCH_3), 76.47 and 70.46 (C_5H_4), 53.21(CH_2), 39.23 (CH_2), 2838 (CH_2), 10.50 (CH_3); IR (Nujol): $\tilde{\nu} = 1622$ (ν(CO)), 1540 cm^{-1} (ν(CN)); MS (MALDI-TOF): *m*/*z*: calcd for $C_{1400}H_{2032}N_{126}Fe_{64}O_{64}$: 25226; found: ≈ 25000 (br).

Titrations by cyclic voltammetry: *Conditions*: Solvent: distilled dichloromethane or anhydrous DMF; 20 °C; supporting electrolyte: [nBu$_4$N][PF$_6$], 0.1 M; internal reference: $FeCp^*_2$; reference electrode: Ag; auxiliary and working electrodes: Pt; scan rate: 0.2 Vs^{-1}; [nBu$_4$N][H_2PO_4] or [nBu$_4$N]$_2$[ATP]: 5×10^{-3} M; nBu$_4$NCl and [nBu$_4$N][HSO_4]: 5×10^{-2} M.

General method for the titration of $H_2PO_4^-$, ATP^{2-}, or HSO_4^-: First, [nBu$_4$N][PF$_6$] was introduced into the electrochemical cell containing the working electrode, the reference electrode, and the counterelectrode and dissolved in dichloromethane or DMF. A blank voltammogram was recorded without dendrimer to check the working electrode. Then, the dendrimer was dissolved in a minimum amount of dichloromethane or DMF and added to the cell. About 1 mg decamethylferrocene (3×10^{-6} mol) was also added. The solution was degassed by flushing with dinitrogen, and the CV of the dendrimer alone was recorded. Then, the anion $H_2PO_4^-$, ATP^{2-},or HSO_4^- was added in small quantities with a microsyringe). After each addition, the solution was degassed, and a CV was recorded. The appearance and progressive increase of a new wave was observed, while the initial wave decreased and finally disappeared. When the initial wave had completely disappeared, addition of the salt of the anion was continued until twice the volume already introduced was reached. The titration of $H_2PO_4^-$ (or ATP^{2-}) in the presence of Cl^- and HSO_4^- was carried out similarly, the salts [nBu$_4$N][Cl] and [nBu$_4$N][HSO_4] being added before [nBu$_4$N][H_2PO_4] (or [nBu$_4$N]$_2$[ATP]).

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Helpful assistance of Professor François Varret (Université de Versailles, Mössbauer spectroscopy), contribution of Maria Jesus Ruiz Medel (Bordeaux group) to preliminary experiments, and financial support from the Institut Universitaire de France (IUF, DA), the Centre National de la Recherche Scientifique (CNRS), the Universities Bordeaux I and Paris VI, and the Ministère de la Recherche et de la Technologie (MRT, Ph.D. grant to M.-C.D.) are gratefully acknowledged.

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