Redox-active organotransition-metal dendrimers: The dendritic effect in supramolecular recognition

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Abstract: Metallocene dendrimers are used as sensors for the recognition of inorganic anions and a dramatic dendritic effect is found.

Dendrimers are monodisperse macromolecules that are promising in materials science (1-4) and biology (5), for instance as receptors (6-8). We have synthesized dendritic cores (9-39) including polynitriles reducible to polyamines (32-37) (Schemes 1 and 2).

1. SYNTHESIS OF POLYMETALLOCENE DENDRIMERS

A first nona-iron dendrimer was synthesized by reaction of a nonol with [FeCp(p-F-C_6H_4)][PF_6] (31) (Scheme 1). For this metallodendrimer, a single reversible wave was obtained in cyclic voltammetry at -30°C in DMF corresponding to the cathodic reduction of d^6 Fe(II) to d^7 Fe(I). From the intensity of the current (40,41), the number of electrons involved in the process was found to be 8±1 (30). However, this wave is not reversible at room temperature, and we have subsequently been seeking more robust redox systems for applications. The above polyamine were thus synthesized with the aim to obtain polyamidometallocene dendrimers by reactions with metallocenylcarbonylchlorides. The first obvious target was ferrocene units since the famous ferrocene/ferricinium redox couple had found considerable use as a redox sensor. Reactions between the polyamine and chlorocarbonylferrocene were performed at room temperature for 1-3 days in CH_2Cl_2 in the presence of NEt_3 (6-8):

Scheme 1

Scheme 2

Dendri-NH2 + FcCOCl + NEt₃ ------> Dendri-NHCOFc + FcCOCl + NEt₃H⁺Cl⁻
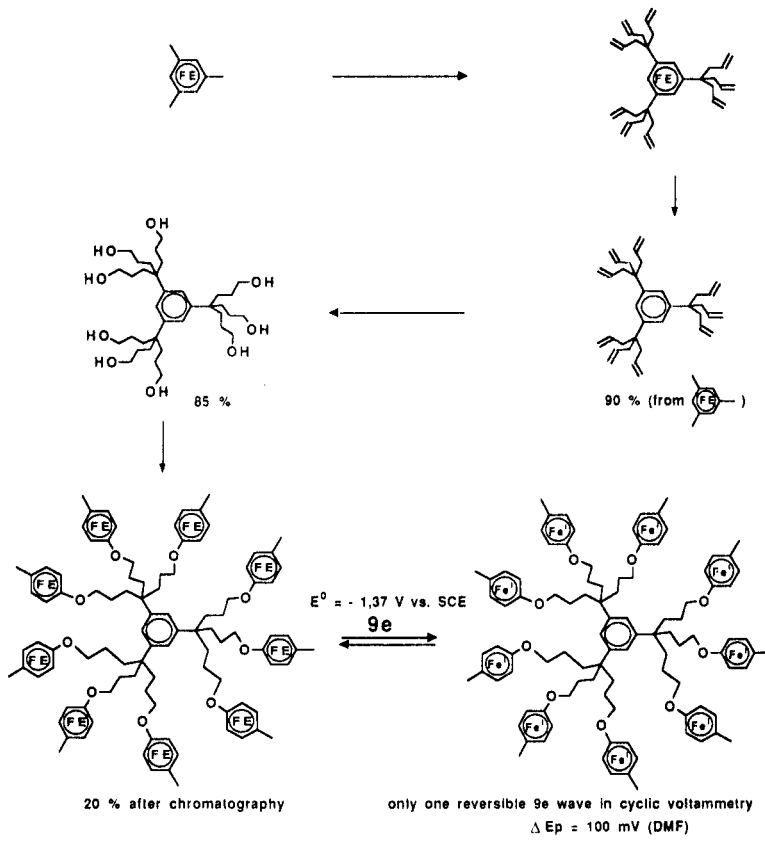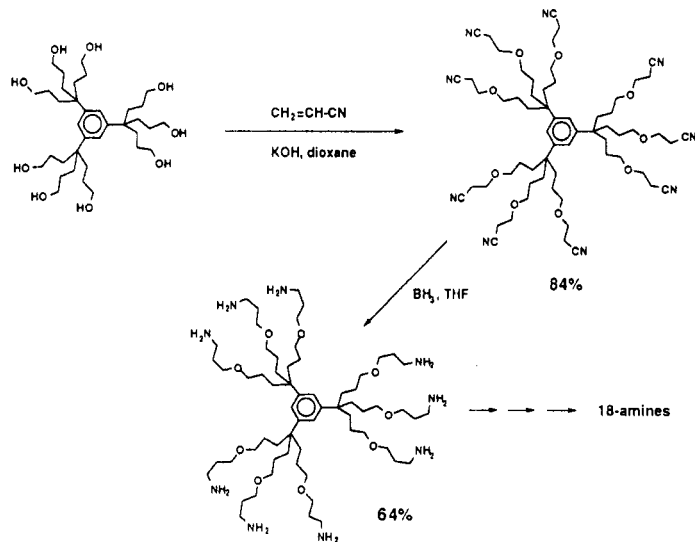
Only the 9- and 18-amine dendrimers gave soluble ferrocene dendrimers whereas the awaited 36 and 72-amido-ferrocene dendrmers were totally insoluble in all the solvents. The insolubility reached for the 36-Fc dendrimer is a sign of steric saturation at the surface which prevents the solvents from penetrating inside the dendrimer. This also means that, at or above the 36-Fc generation, the number of ferrocene units becomes lower than expected in a default-free dendrimer, which is confirmed by the elemental analyses and molecular modelization. On the other hand, the 9-Fc and 18-Fc dendrimers were characterized by ^1H and ^{13}C NMR and infrared spectra, correct elemental analyses and the molecular peaks in the MALDI-TOF mass spectra (MH^+: m/z = 3066 for 9-Fc and MNa^+: m/z = 6024 for 18-Fc) (6, 37). These condensation reactions of the polyamines were also carried out with cationic transition-metal-sandwich complexes, namely [Co(CpCOCl)Cp][PF6] or analogues (37,42,43) and [Fe(CpCOCl)(arene)][PF6] (43). The nona-metal dendrimers with these sandwichs could be synthesized and characterized by standart spectroscopic techniques and elemental analyses. Electrospray mass spectra, recorded by E. Leize and A. van Dorsseler from Strasbourg University, showed the molecular peaks for 9-Co and 9-Fe-toluene. Their solubilities are weaker than those of the ferrocene dendrimers, however, and decrease as the bulk of the sandwich moiety increases (i.e. when the number of methyl groups increases on the arene ligand of the iron complex).The 18-Co dendrimer could also be made, but its solubility in MeCN is very weak, which makes NMR characterization less unambiguous, and elemental analysis suggested the inclusion of water molecules. Thus its purity is highly uncertain. Very recently, the synthesis of ferrocenedendrimers of closely related structure has also been communicated by the group of Moran and Cuadrado (44). The area of metallodendrimers has recently been very prolific (for beautiful exemples, see references 45 to 54).

2. RECOGNITION OF INORGANIC ANIONS

The area of anion recognition , pionierred by Lehn (55-58), is of particular importance for its biological implications. Various types of sensors are known, including redox sensors with macrocycles and tripods (59-64). The anion receptors designed so far are endo-receptors (65-69). On the other hand, dendrimers with redox sensors at the extremities of the branches could function as exo-receptors, especially if the surface covered with redox sensors is not too far from steric

saturation. At this point, it could mimic the surface of micro-organisms such as viruses. The ferrocene unit has long been used as a redox sensor since both Fe(II) and Fe(III) forms are stable enough for electrochemical scanning without loss of reversibility. The principle is that the redox potentiel of the Fe(II/III) redox system of the ferrocene unit is not the same in the presence and absence of substrate whose recognition is looked for. In the meantime, the binding constant of the substrate with the host bearing the ferrocene unit close to the receptor is not the same in the neutral Fe(II) redox form of ferrocene and in its Fe(III) cationic form. These thermodynamic values are related by the following thermodynamic cycle (Scheme 3):

The amidoferrocene fragment also has the benefit of the acidic amide hydrogen atom which can form a hydrogen bond with an oxygen atom of oxo-anions. Amidoferrocenes have indeed been used as redox sensors in tripodal units (68,69). We have compared the 9-Fc and 18-Fc dendrimers with mono- and tripodal amidoferrocenes of closely related structure in order to investigate dendritic effects. Recognition studies have been carried out by cyclic voltammetry and by ^{1}H NMR. In each case, titrations of the ferrocene dendrimers were effected by n-Bu$_4$N$^+$ salts of H$_2$PO$_4^-$, HSO$_4^-$, Cl$^-$ and NO$_3^-$. By far, the most informative results were obtained by cyclic voltammetry by scanning the Fe(II/III) wave. Before any titration, the cyclic volammograms or the 9-Fc and 18-Fc dendrimers show a unique wave at 0.59 V vs SCE in CH$_2$Cl$_2$ corresponding to the oxidation of the 9 redox centers, which indicates that, as expected, the 9 or 18 redox centers are electrochemically equivalent, thus independant (when for instance two equivalent redox centers are not so far away from each other, two waves are observed at two distinct potentials, even if there is no electronic connection, because of the electrostatic effect). Upon addition of the anion, two situations can arise (70). In the case of H$_2$PO$_4$, a new wave starts appearing at less positive potentials and corelatively, the intensity of the initial wave starts decreasing. When one equivalent of anion per dendrimer branch has been added, the initial wave has disappeared and, upon addition of the anion, the intensity of the new wave does not increase any longer. In the case of the other anions, no new wave appears but the initial wave is progressively shifted to less positive potentials upon titration untill one equivalent of anion has been added per dendrimer branch. The shifts $\Delta E°$ of potentials observed after addition of one equiv. anion per dendrimer branch are given in table 1 for the four anions. It clearly appears that the $\Delta E°$ value considerably increases in the series: 1-Fc ---> 3-Fc ---> 9-Fc ---> 18 Fc, which shows a dramatic dendritic effect represented in Figure 1 for the titration with the HSO$_4^-$ anion. The magnitude of interaction with the anion increases as follows:
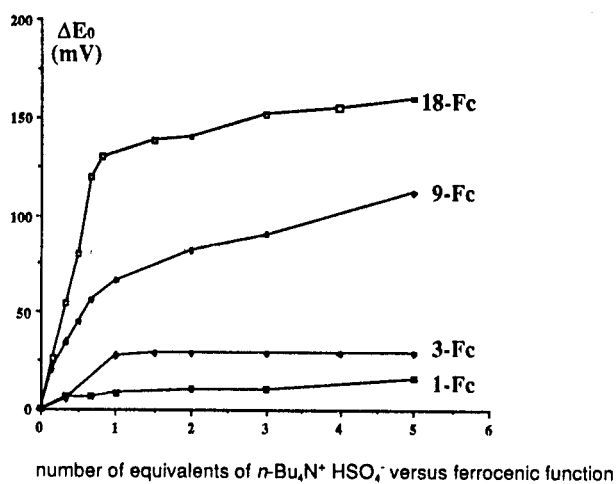
$$H_2PO_4^- > HSO_4^- > Cl^- > NO_3^-.$$
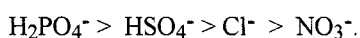
Figure 1: Titration of 1-Fc (1-Fc = [Fe(C$_5$H$_5$)(C$_5$H$_4$CONHCH$_2$CH$_2$OPh)], 3-Fc, 9-Fc and 18-Fc (see Chart 1) by n-Bu$_4$N$^+$ HSO$_4^-$ monitored by CV. Concentrations in FcDs were 0.001 M, CH$_2$Cl$_2$, n-Bu$_4$N$^+$BF$_4^-$ (0.1 M), 20 °C, reference electrode: SCE, auxiliary and working electrodes: Pt, scan rate: 100 mV.s^{-1}.

3-Fc

9-Fc

18-Fc

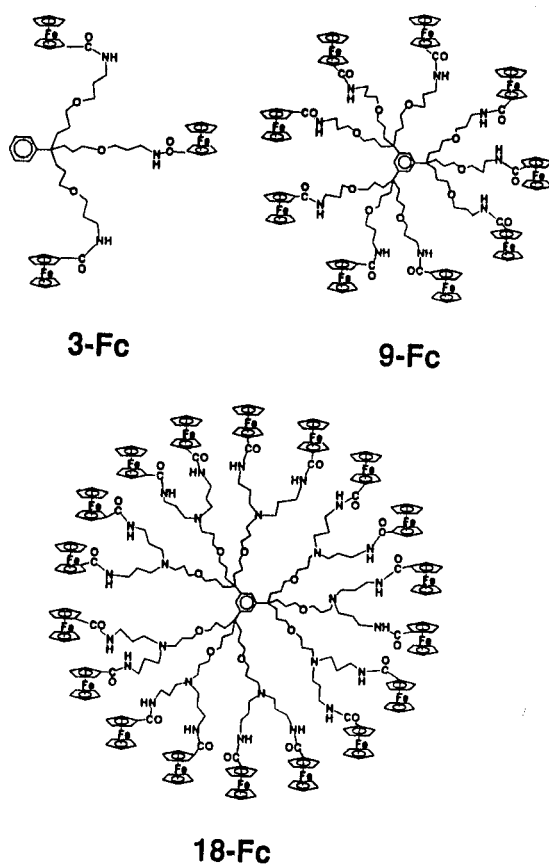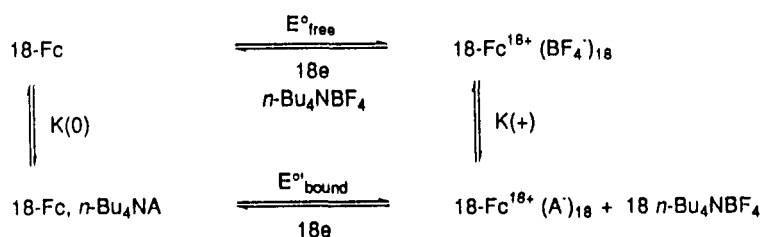Chart 1 (see figure 1)

18-Fc $\xrightleftharpoons[18e]{E^\circ_{free}}$ 18-Fc^{18+} (BF$_4^-$)$_{18}$

n-Bu$_4$NBF$_4$

K(0)   K(+)

18-Fc, n-Bu$_4$NA $\xrightleftharpoons[18e]{E^{\circ\prime}_{bound}}$ 18-Fc^{18+} (A$^-$)$_{18}$ + 18 n-Bu$_4$NBF$_4$

Scheme 3

Table 1: Titration of the FcDs by Various n-Bu$_4$N$^+$ Salts Monitored by the Variation ΔE° (mV for 1 Equivalent of Anion per Branch) of the Standard Redox Potential E° of the Redox Couple in Cyclic Voltammetry[a]

	1- Fc	3-Fc	9-Fc	18-Fc
H$_2$PO$_4^-$	45	110	220	315
HSO$_4^-$	ε	30	65	130
Cl$^-$	ε	ε	20	45
NO$_3^-$	ε	ε	ε	30

[a] In the case of HSO$_4^-$, the variation ΔE° along the titration is represented in Figure 1 for the various dendrimers. The uncertainties of the ΔE° values are estimated to be 20 mV. Thus, lower shifts are indicated by ε.

Table 2: Apparent Association Constants $K(+)$ Determined in CH$_2$Cl$_2$ by CV for the FcD Series from the Shift of the CV Wave using Eqs 1 and 2.

	1-Fc	9-Fc	18-Fc
H2PO4$^-$	9390	216900[a]	[b]
HSO4$^-$	544	8530	61400
Cl$^-$	[c]	917	2120
NO3$^-$	[c]	[c]	403

[a] $K(+)$ determined for the 9-Fc dendrimer from the combination of $K(0)$ determined by ^{1}H NMR in CD$_2$Cl$_2$ and the $K(+)/K(0)$ ratio determined by CV in CH$_2$Cl$_2$ using eq 1. [b] For 18-Fc, the $K(+)/K(0)$ ratio was found to be 219000. The uncertainties on K values are estimated to 10%. [c] Since the ΔE° values are much smaller than the uncertainties (Table 1), calculation of the small K values would be meaningless.

Both situations upon titration - appearance of a new wave and shift of the initial wave - have already been analyzed from the thermodynamic standpoint (70).

In the first situation in which $H_2PO_4^-$ is concerned, equation (1) applies:

$$\Delta E°(V) = 0.059 \log [K(+)/ K(0)] \qquad \text{at } 25°C \qquad (1)$$

Measurement of $\Delta E°$ leads to $K(+)/ K(0)$. The determination of $K(+)$ requires the determination of $K(0)$, the binding constant between the neutral ferrocene form of the dendrimer and $H_2PO_4^-$, in the present case by ^{1}H NMR using Hynes' EQ NMR program (71). Indeed the shift of the amide proton also shows that the equivalence point is reached after addition of one equiv. $H_2PO_4^-$ per dendrimer branch (from δ = 6.82 ppm before titration to 6.65 ppm after this addition).

 In the second situation concerning the other anions, this binding constant $K(0)$ between the neutal ferrocene dendrimer and the anionic substrate is very small (>1) and does not intervene in the expression of $\Delta E°$ (equation (2)):

$$\Delta E°(V) = 0.059 \log [cK(+)] \qquad \text{at } 25°C \qquad (2)$$

were c is the concentration of added anion. Thus, $K(+)$ is directly accessible by measurement of $\Delta E°$ only. These apparent association constants $K(+)$ between the ferricinium form of the dendrimer and the anionic substrate are gathered in table 2.

The [1]NMR monitoring of the titrations is not as useful in the case of the other anions as in the case of $H_2PO_4^-$ because, as indicated above, the ineraction is weak. Indeed, equivalent points are very variable and very far from corresponding to one equiv. anion per branch, wheras they do so for the ferricinium form which more strongly binds the different anions.

In general, the ferricinium form of the tripod or dendrimer binds the anions relatively strongly because of the synergy of the electrostatic attraction with the intermolecular hydrogen bond formed between the acidic amide H atom and the anionic substrate throught an oxygen atom of an oxoanion or the halogen anion. Both factors are important and, if one of them is absent, the interaction becomes loose and cannot be used for sensing (except in the case of $H_2PO_4^-$ for the dendrimers). This effect has previously been recognized and used (68,69).

Of special interest here is the dramatic dendritic effect observed for all the anions. Even when the synergy between the electrostatic and H-bonding is fulfilled, the $\Delta E°$ value is unobservable or small when the amido-ferrocene used is monometallic (1-Fc) or trimetallic (3-Fc). The shape selectivity designed in the dendrimer is crucial and its effect is much more marked for 18-Fc than for 9-Fc as the ferrocene termini are closer to each other when the dendritic generation increases. This

dendritic effect is thus maximum for the generation (18-Fc) which precedes steric saturation by ferrocene groups on the dendrimer surface (36-Fc). It can be understood in the course of the dendritic synthesis as the insolubility of sterically saturated ferrocene dendrimers is complete in all the solvents. In the amido-ferrocene dendrimers, the amide H atom is located on the branch behind the ferrocene unit which provide the surface bulk. Thus the anion has to reach the inside of the microcavity formed by the amido-ferrocene units at the surface of the dendrimer. These conditions become optimal for redox sensing and recognition by the close ferrocene units at the 18-Fc generation, since the channels allowing the entry of the anions into the surface microcavity to reach the amide H atom are as narrow as possible.

In conclusion, after having synthesized organometallic dendrimers, we have now been able to demonstrate a dendritic effect in molecular recognition. Other effects are expected with polycationic organometallic dendrimers and molecular recognition studies are presently in progress in our laboratories along this line.

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