Inhibition of the electrochemistry of ferrocenes by polyamine dendrimers and the key role of hydrogen-bonding with hydroxy groups†

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Commercial DSM polyamine dendrimers inhibit the observation of the cyclic voltammetry (CV) of simple ferrocenes all the more as they are larger (marked dendritic effect); the CV is re-established, however, if a OH-containing group is present in the ferrocene derivative.

Dendrimers[1] might be essential parts of future bio-medical, electronic, optical and magnetic nano-devices (sensors, switches, memories, transistors).[2] Therefore, electrochemistry involving these nano-molecules is crucial to the analysis of electron-transfer properties.[3–5] Among the dendritic redox probes,[6] ferrocenes occupy a central place, because of the stability of both Fe^{II}/Fe^{III} states, the fast interstate electron transfer, and the mild, easily accessible oxidation potential.[7] Ferrocene itself serves as a IUPAC reference for the determination of redox potentials,[8] and ferrocenes are used as mediators between electrodes and buried metal centers of metallo-enzymes, a property that has been applied to glucose sensors.[9]

We now wish to report that the well-known commercial DSM polyamine – or so-called poly(propyleneimine) dendrimers[10] – inhibit the electrochemistry of simple ferrocene derivatives. We also show how this electrochemical activity is re-established using hydrogen bonding[11–13] between the primary amino groups of these dendrimers and metallocenyl alcohols and phenols.[12]

The electrochemistry of ferrocene,[7,8] **1** (Chart 1), and decamethylferrocene,[8b,14] [$FeCp^*_2$] **2**, is well known. Yet, Fig. 1 shows that the electrochemical activity of **2** in CH_2Cl_2 on a Pt electrode at a fixed return potential is all the more inhibited by the presence of a polyamine dendrimer as the dendrimer generation increases, *i.e.* this inhibition is subjected to a dramatic *dendritic* effect. Although the cyclic voltammogram (CV) is not perturbed in the presence of propylamine (Fig. 1(a)) or even dodecylamine (Fig. S2(a), ESI†) it completely vanishes in presence of G_5 dendr-$(NH_2)_{64}$ (Fig. 1(d)). The effect observed with the non-dendritic triethylenetetramine (Fig. S2(b), ESI†) is weak, even less marked than with G_1. The Pt electrode is passivated by the polyamine dendrimer that shields the redox-active species in solution.

The inhibition is all the more marked as the return potential is more positive. This results from modification of the electrode by scanning beyond the potential at which the dendritic polyamine is oxidized (Fig. S1, see ESI†). Thus, the large polyamine dendrimers adsorbed on the passivated Pt electrode are insulating barriers between the Pt electrode and [$FeCp_2$] **1** or [$FeCp^*_2$] **2**.

Fig. 2 compares the CVs of **2** together with those of various ferrocene derivatives in the presence of G_3 dendr-$(NH_2)_{16}$. showing rectification only with the dendrimers and the re-established reversibility when a hydroxymethyl or phenol group is present on the ferrocene substituent.

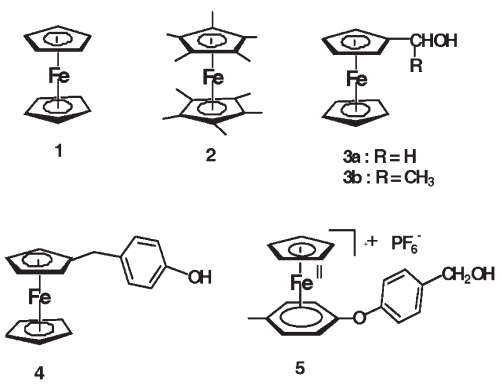

Chart 1

† Electronic supplementary information (ESI) available: Fig. S1: CV of G_5 dendr-$(NH_2)_{64}$ showing its oxidation. Fig. S2: CVs of non-dendritic amine **2** in the presence of dodecylamine and triethylenetetramine. Fig. S3: Scan rate variations on the CV of **2** + G_5. See http://www.rsc.org/suppdata/cc/b4/b418437h/

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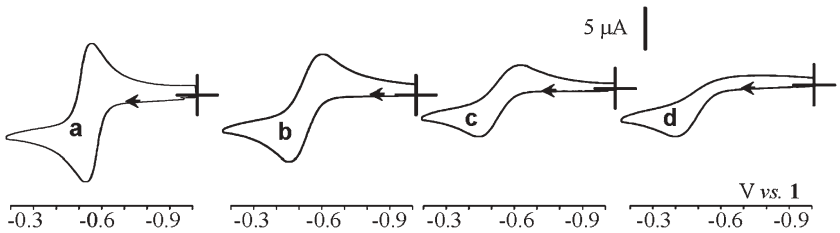

Fig. 1 CVs of $FeCp^*_2$ **2** (10^{-3} M), CH_2Cl_2; *n*-Bu_4NPF_6 (0.1 M); reference electrode: Ag/Ag^+; working and counter electrodes: Pt; scan rate: 0.2 V s^{-1}; scan rate variations do not cause significant changes, see ESI:† (a) **2** in the presence of 1 equiv. propylamine; (b) **2** in the presence of 1/4 equiv. G_1 dendr-$(NH_2)_4$; (c) **2** in the presence of 1/16 equiv. G_3 dendr-$(NH_2)_{16}$; (d) **2** in the presence of 1/64 equiv. G_5 dendr-$(NH_2)_{64}$.

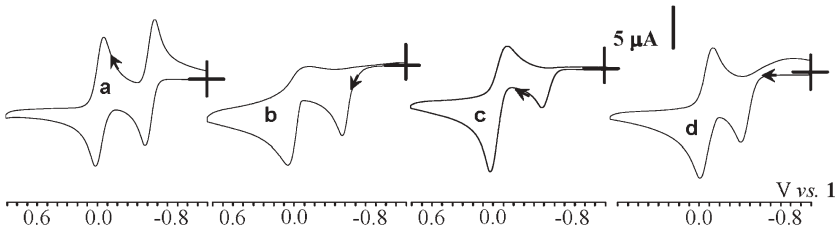

Fig. 2 CVs of **2** (10^{-3} M): CH_2Cl_2; *n*-Bu_4NPF_6 (0.1 M); ref. electrode: Ag/Ag^+; working and counter electrodes: Pt; scan rate: 0.2 V s^{-1}; (a) **1** + **2** + 1 equiv. propylamine; (b) **1** + **2** + 1/16 equiv. G_3 dendr-$(NH_2)_{16}$; (c) **2** + **3a** + 1/16 equiv. G_3 dendr-$(NH_2)_{16}$; (d) **2** + **4** + 1/16 equiv. G_3 dendr-$(NH_2)_{16}$.

The complex **3b** is less efficient than **3a** due to the steric effect of the methyl group. Fig. 2(d) shows that the effect is more marked with the more acidic phenol-group-containing ferrocene derivative [Fc–$CH_2C_6H_4OH$-*p*] **4**,[15] that forms stronger hydrogen bonds with amines than **3a**. Altogether, the magnitude of the inhibition follows the sequence:

$[FeCp^*_2] > [FeCp_2] >$ FcCH(Me)OH–Me $>$ [Fc–CH_2OH] $>$ [Fc–$CH_2C_6H_4OH$-*p*]

For instance, it is remarkable that the ferrocenyl estradiol derivative **6**[16] gives a reversible CV wave in the presence of G_3 dendr-$(NH_2)_{16}$ (Fig. 3), whereas the CVs of the standard references **1** and **2** themselves are inhibited or strongly rectified under the same conditions. Note, however, that the CV of **6** is slightly rectified by comparison to those of **4**. Indeed, the rigid steroidal frame keeps the redox center away from the phenol group unlike in **4**. This is also in accord with the selective OH···H_2N hydrogen bonding with the distal phenol rather than with the tertiary alcohol nearby the redox center of **6**. The recovery of the CV in hydroxy-containing redox-active compounds can tentatively be taken into account by the dendrimeric linkage between **6** and the Pt electrode

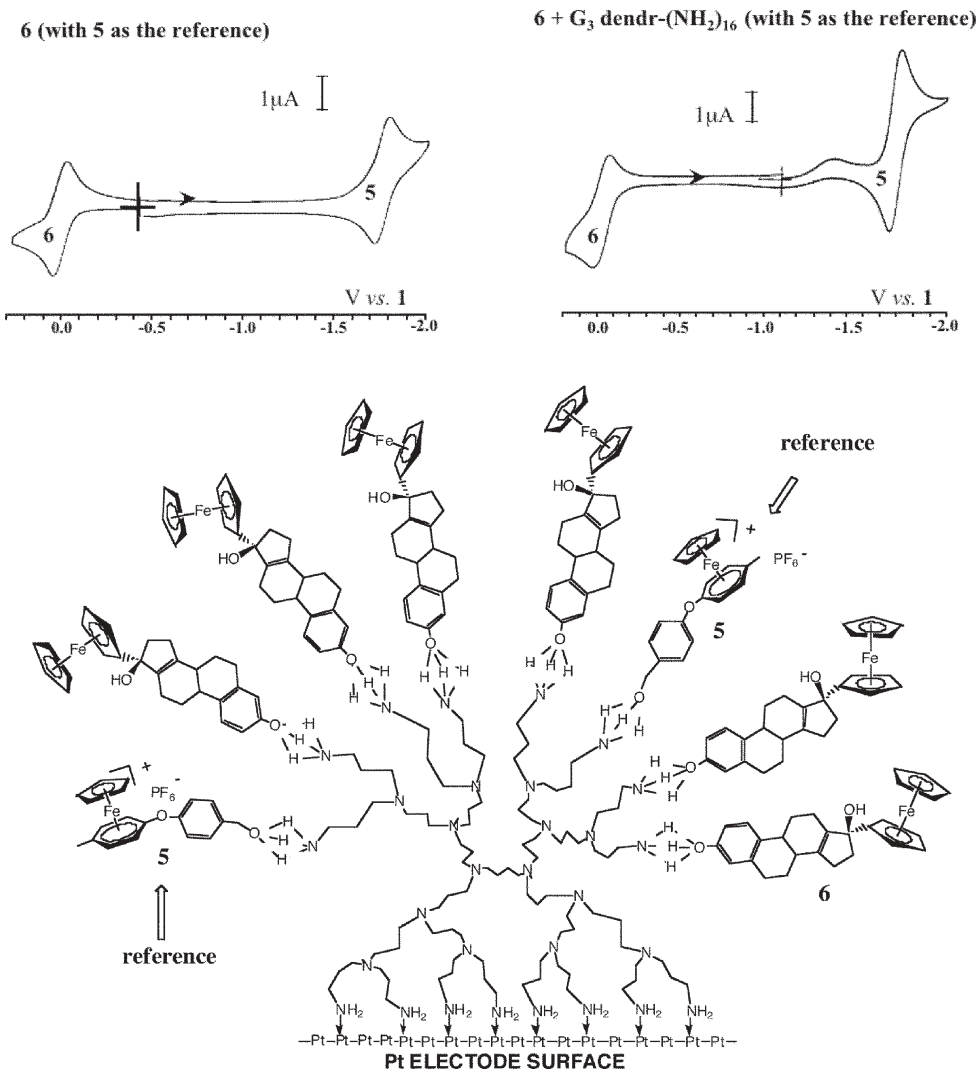

Fig. 3 CV of the steroid derivative **6** in the presence of the reference compound **5**, both containing hydroxy groups without (top left) and with (top right) G_3 dendr-$(NH_2)_{16}$; note the slight rectification for **6**; linkage of redox-active groups to the Pt electrode *via* G_3 dendr-$(NH_2)_{16}$ (bottom).

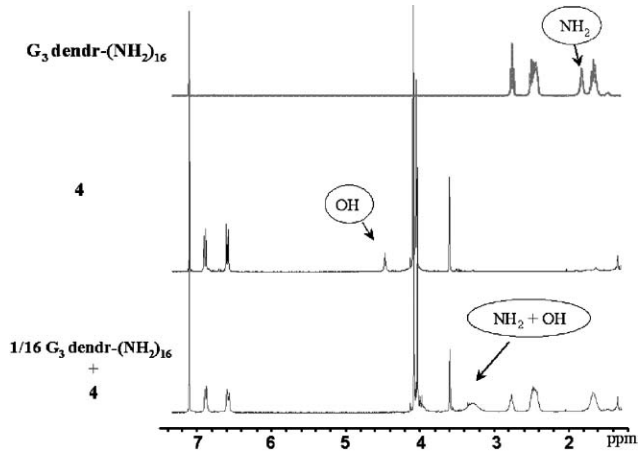

Fig. 4 300 MHz ^{1}H NMR spectra of G_3 dendr-$(NH_2)_{16}$ (top), **4** (middle) and their mixture (one equiv. **4** per amino group of the dendrimer; bottom) in $CDCl_3$.

via the amino termini of the polyamine dendrimer represented in Fig. 3.

This suggestion implies that the hydrogen bonding between the hydroxy groups and the dendrimer amino groups brings **3a**, **4** or **6** near the electrode, so that it be close enough to remain electro-active. Indeed, it is well known that dendrimers adsorb strongly[17] and flatten[18] on metal surfaces. It has also been shown that, in the dendrimers containing ferrocenyl termini, all the ferrocenyl centers are electro-active with fast electron transfer even in the solid state due to electron hopping.[4,6b,19] This is true even with ferrocenyl dendrimers containing several hundred ferrocenyl groups.[19] A similar situation is found here in supramolecular dendrimers.

This reversible hydrogen bonding between polyamine dendrimers and phenols is shown by the comparison of the ^{1}H NMR spectra of the phenol derivative **4** and G_3 dendr-$(NH_2)_{16}$ alone with that of a mixture of these compounds (equimolar mixture of hydroxy and amino groups (Fig. 4)).

Thus, in the ^{1}H NMR spectrum of the mixture, the signals of the OH and NH_2 groups of the isolated compounds have disappeared, and a new broad average signal common to the OH + NH_2 groups has appeared. In conclusion, the inhibition of ferrocene CVs is all the more important as the dendrimer generation increases, but hydrogen bonding with hydroxy groups re-establishes the reversibility.

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