

Supramolecular H-Bonded Assemblies of Redox-Active Metallodendrimers and Positive and Unusual Dendritic Effects on the Recognition of H_2PO_4^-

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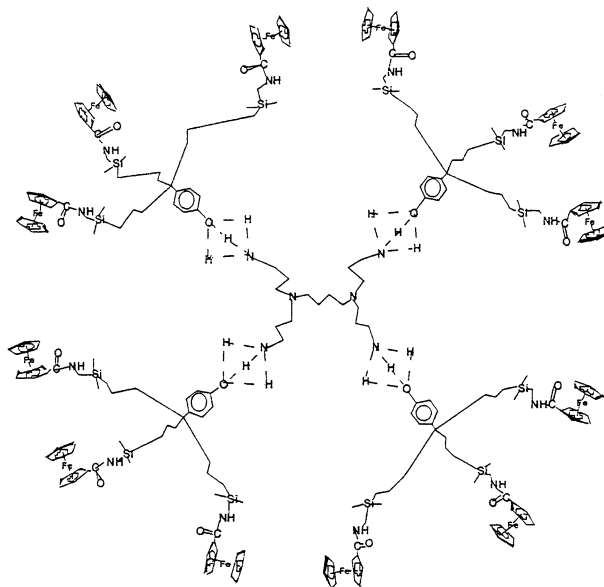
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The recognition of anions such as H_2PO_4^- is of interest in the biological and environmental contexts and has been investigated using a variety of *endoreceptors*.¹ We have recently addressed the recognition of small anions using metallodendrimers^{2a} and gold nanoparticles^{2b} as *exoreceptors*. Because topological effects were found to be essential factors in these studies, we envisaged assembling redox-active metallodendrimers by multiple H-bonding to possibly benefit from positive dendritic effects.^{2a} We now report our first findings along this line that involve the dramatic influence of these supramolecular assemblies on the recognition of H_2PO_4^- . Although dendrimers are a well-established field,^{2,3} there are still only very few examples of dendrimers assembled using H-bonding.^{4,5} Simple alcohols mixed with primary amines are known to form complementary O–H–N bonds with tetrahedral disposition of both O and N valences and 1:1 stoichiometry⁶ (e.g., minimal melting point for this stoichiometry^{6b}), a property that has been astutely used in crystal engineering^{6c} and chiral recognition.^{6d} We applied this principle to the association of the AB_3 phenol units *p*-OH– $\text{C}_6\text{H}_4\text{C}(\text{CH}_2\text{CH}=\text{CH}_2)_3$, **1**, and *p*-OH– $\text{C}_6\text{H}_4\text{C}\{(\text{CH}_2)_3\text{SiMe}_2\text{-CH}_2\text{NHCOFc}\}_3$, **2** (Fc = ferrocenyl), with the dendritic DAB polyamines of generations 1 to 4 (G_1 – G_4 , see G_1 in Chart 1).⁷ The ^1H NMR signals of the phenolic H in **1** and **2** at 5 ppm and of the NH_2 amine protons of DAB- G_1 to G_4 at 1.5 ppm are strongly shifted to a common signal between 2.4 and 4.1 ppm (broad, concentration-dependent, see the Supporting Information) for the H-bonded, assembled dendrimers.

The recognition of H_2PO_4^- by monomeric amidoferrocenes using cyclic voltammetry is weak, but it is enhanced when amidoferrocenes are attached to receptors.^{1,2} In the latter, a new amidoferrocenyl wave at less positive potential progressively replaces the initial one in the course of the addition of H_2PO_4^- , until the initial wave disappears when a 1:1 stoichiometry is reached.^{2a} For instance, the difference $\Delta E_{1/2}$ between the potential of the initial ferrocenyl wave⁸ and that of the new wave reached after addition of 1 equiv of H_2PO_4^- per amidoferrocenyl branch is 150 mV with FcCONHPr and is raised to 205 mV with **1** alone (apparition of a new wave along with the intensity decrease of the original wave in CH_2Cl_2 (Pt anode, $[n\text{-Bu}_4\text{N}][\text{PF}_6]$). The addition of propylamine to **2** does not change this $\Delta E_{1/2}$ value, but it is then necessary to add 2.5 equiv of H_2PO_4^- instead of 1 equiv per ferrocenyl branch, because the amine strongly competes with the amidoferrocenyl group in H_2PO_4^- binding. The addition of a stoichiometric amount of $[n\text{-Bu}_4\text{N}][\text{H}_2\text{PO}_4^-]$ to a DAB dendritic amine enhances the $\Delta E_{1/2}$ value from 205 mV for PrNH_2 to 250 mV for DAB- G_1 and 280 mV for DAB- G_2 . The larger DAB dendritic polyamines DAB- G_3 and - G_4 also give a value of 280 mV, indicating that saturation is obtained with DAB- G_2 . An increase of the $\Delta E_{1/2}$ values upon increasing the generation is the signature of a *positive dendritic effect*.^{2a} The number of equivalents of H_2PO_4^- per dendritic branch found at the equivalent point dramatically varies from *n*- PrNH_2 to

Chart 1. Supramolecular Assembly between the AB_3 Unit **2** and the G_1 DAB Dendrimer Characterized by the Concentration-Dependent Single Phenolic + Amine ^1H NMR Broad Signal between 2.4 and 4.1 ppm versus TMS in CDCl_3 (see Supporting Information)^a



^a The H-bonding representation is arbitrary.

the DAB series. It drops from 2.5 for PrNH_2 to 0.5 for DAB- G_1 , and then raises to 0.8 for DAB- G_2 and 2.0 for DAB- G_3 and DAB- G_4 . The considerable drop of this value from PrNH_2 to DAB- G_1 and - G_2 seemingly results from difficult access of the guest to the core amines and from the chelation of H_2PO_4^- to two amidoferrocenyl groups. The increase of the value from DAB- G_1 to - G_2 and - G_3 indicates progressive steric congestion and/or destabilization of the H-bonding as the dendritic size increases, which is consistent with the limit of the $\Delta E_{1/2}$ increase. The increased number of tertiary amines upon generation increase might also be responsible for the binding of more H_2PO_4^- . Thus, the most dramatic supramolecular dendritic effect combining both values of $\Delta E_{1/2}$ and of the variation of number of equivalents of H_2PO_4^- per amidoferrocenyl branch is found for G_1 and G_2 , for which 12 and 24 amidoferrocenyl groups, respectively, are present at the dendrimer periphery. For G_1 , the fact that the equivalent point is reached for 0.5 equiv of H_2PO_4^- shows that a single unit is interacting with two amidoferrocenyl arms (also by H-bonding), a unique situation. In addition, for G_1 and G_2 , a dramatic cooperative effect is found in the course of the titration: the replacement of the initial ferrocenyl wave by the incoming wave during the titration is very sudden. It occurs within the addition of about 0.1 equiv of H_2PO_4^- (Figure 1), whereas it is normally proportional to the quantity of added H_2PO_4^-

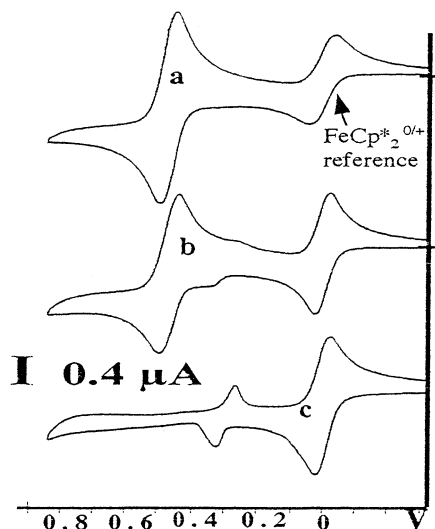
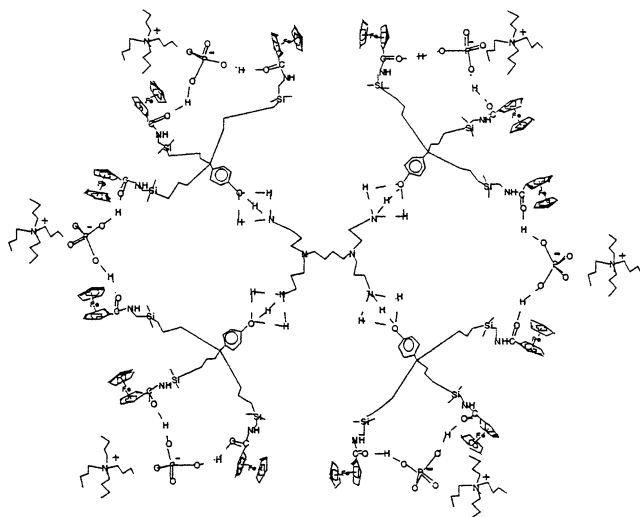


Figure 1. Titration of DAB-G₁ in CH₂Cl₂ (Pt, 0.1 M [nBu₄N][PF₆], 20 °C; reference: FeCp₂* = decamethylferrocene) by [nBu₄N][H₂PO₄]: (a) before addition, (b) 0.4 equiv, (c) 0.5 equiv.

Chart 2. Supramolecular Assembly between **2** + DAB-G₁ and 0.5 equiv of [n-Bu₄N][H₂PO₄] Characterized by Its Large Diffusion Coefficient (i.e., Reduced Intensity in the CV, See Figure 1c)



in the absence of DAB.^{2a} This means that, for **2** + DAB-G₁, the six H₂PO₄⁻ units probably cooperatively bind the 12 amidoferrocenyl groups of G₁ when the correct 1:2 stoichiometry is reached (Chart 2). About the same event is noted with **2** + DAB-G₂; that is, the 12 H₂PO₄⁻ units cooperatively bind 24 amidoferrocenyl groups of G₂, although the increase of the H₂PO₄⁻ stoichiometry from 0.5 to 0.8 for this generation indicates that competition among several phenomena is beginning. Finally, an exceptional drop from the intensity of the initial wave to that of the incoming wave (4 times weaker) is noted during the titration of H₂PO₄⁻ with **2** + DAB-G₁ or **2** + DAB-G₂. This shows a large difference in the diffusion coefficients, that is, in the size of the electroactive species before and after addition of H₂PO₄⁻. Thus, the electroactive assembly is considerably larger when H₂PO₄⁻ is present than when it is absent. Because H-bonding equilibria are much faster than the electrochemical time scale, the electroactive species involved before H₂PO₄⁻ titration is a mixture of free **2** and DAB-bonded **2**, and the electrochemical response is an average of these two situations. On the other hand, after titration, the fact that the new

wave intensity is so much smaller than before shows that each H₂PO₄⁻ unit links two amidoferrocenyl groups around the dendritic periphery to form a large dendritic assembly whose lifetime is larger than the electrochemical time scale. The absence of such a phenomenon during the titration of H₂PO₄⁻ with reported covalent amidoferrocenyl dendrimers^{2a} indicates that no interdendritic linking by H₂PO₄⁻ significantly occurs and that this linking of two amidoferrocenyl branches by each H₂PO₄⁻ unit is thus intradendritic as shown in Chart 2.

In summary, H₂PO₄⁻ titrations by **2** + DAB-G₁ and **2** + DAB-G₂ show new positive dendritic effects^{2a} characteristic of amidoferrocenyl dendrimers assembled by H-bonding. The completely unusual trends found during electrochemical monitoring of the titration (half-stoichiometry, sudden wave change, dramatic intensity decrease) are rationalized in terms of the formation of a dendritic assembly in which each H₂PO₄⁻ unit links two amidoferrocenyl groups at the dendrimer periphery. The characteristics found for the higher DAB generations (G₃ and G₄) show saturation, indicating that the above trend, pure only with DAB-G₁, is less efficient for these high generations because of steric congestion and/or competition of H₂PO₄⁻ binding between the amido and amino groups. Practically, the addition of DAB-G₁ to **2** for the titration of H₂PO₄⁻ has the best positive effects facilitating this titration (large ΔE_{1/2} and sudden potential change at the equivalent point).

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Supporting Information Available: Compared 400 MHz ¹H NMR spectra of **1**, **2**, G₃-DAB-16NH₂ and their dendritic H-bonded assemblies at different concentrations in CDCl₃ (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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