Electrodes Modified with Electroactive Films of Organometallic Dendrimers

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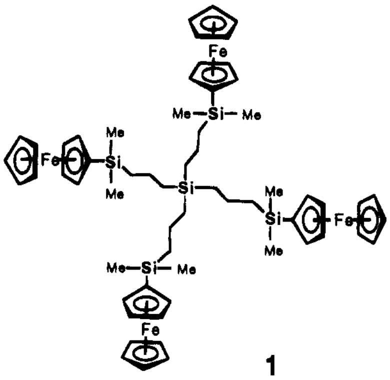
Over the past few years the development of a new class of well-defined macromolecules which possess highly branched molecular architectures, known as dendrimers, has become an area of growing interest.[1] Recently the emphasis has been focused in the modification of the properties of dendritic molecules by changing the functional groups on the outer dendrimer surfaces.[2] Until now few of these macromolecules containing organometallic centers have been reported.[3] One especially challenging target is the modification of electrode surfaces with dendritic macromolecules containing a controlled number of equivalent redox centers, which promise to be useful in multielectron redox catalysis. However, to our knowledge, no example of electrodes derivatized with dendrimers has been reported so far. As part of our research aimed to the construction of novel organometallic-containing silicon dendrimers, we recently synthesized the peripherally functionalized tetra- and octaferrocenyl dendritic systems **1** and **2** (Chart 1).[4] Preliminary results of the successful preparation of electrode surfaces modified with these well-defined redox-active macromolecules are reported herein. In addition, we have now isolated and characterized the oxidized forms of these polymetallic dendrimers.

Chart 1



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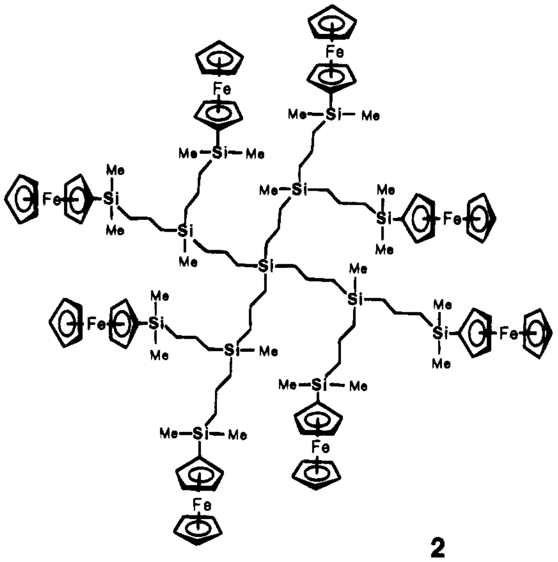

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The results of cyclic voltammetry, differential pulse voltammetry, and bulk coulometry[5] in CH$_2$Cl$_2$ with Bu$_4$NPF$_6$ as electrolyte, clearly show that in **1** and **2** the observed reversible oxidation waves ($E_{1/2}$ = + 0.41 for **1** and + 0.43 V vs SCE for **2**) represent a simultaneous multielectron transfer of four- and eight-electron respectively, as expected for independent reversible one-electron process, at the same potential, of the four (in **1**) or eight (in **2**) ferrocenyl moieties. The diffusion coefficients of both ferrocenyl-containing dendrimers were calculated using the Randles−Sevcik equation,[6] resulting $D_0 = 1.34 \times 10^{-6}$ cm^2 s^{-1} for **1**, and $D_0 = 8.58 \times 10^{-7}$ cm^2 s^{-1} for **2**. Chemical oxidation of the ferrocenyl units in both **1** and **2** has been achieved by reaction with NOPF$_6$, and affords the blue tetra- and octanuclear ferrocenium cations **[1^{4+}][PF$_6^-$]$_4$** and **[2^{8+}][PF$_6^-$]$_8$**.[7] UV−visible spectra of CH$_2$Cl$_2$ solutions of these cations show the presence of a new band at 625

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(1) (a) Newkome, G. R.; Moorefield, C. N. In *Advances in Dendritic Macromolecules*; Newkome, G. R., Ed.; JAI Press: Greenwich, Connecticut, CT, 1994; Vol. 1. (b) Tomalia, D. A.; Durst, H. D. *Topics in Current Chemistry*; Weber, E., Ed.; Springer-Verlag: Berlin, 1993; Vol. 165, pp 193−313. (c) Issberner, J.; Moors, R.; Vögtle, F. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2413. (d) Fréchet, J. M. *Science* **1994**, *263*, 1710. (e) Tomalia, D. A. *Adv. Mater.* **1994**, *6*, 529. (f) Newkome, G. R.; Moorefield, C. N.; Baker, G. R. *Aldrichim. Acta* **1992**, *25*, 2, 31.

(2) See, for example: (a) Newkome, G. R.; Cardullo, F.; Constable, E. C.; Moorefield, C. N.; Thompson, A. M. W. C. *J. Chem. Soc., Chem. Commun.* **1993**, 925. (b) Miller, L. L.; Hashimoto, T.; Tabakovic, I.; Swanson, D. R.; Tomalia, D. A. *Chem. Mater.* **1995**, *7*, 9. (c) Bryce, M. R.; Devonport, W.; Moore, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1716. (d) Miedaner, A.; Curtis, C. J.; Barkley, R. M.; Dubois, D. L. *Inorg. Chem.* **1994**, *33*, 5482. (e) Launay, N.; Caminade, A. M.; Lahana, R.; Majoral, J. P. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1598.

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(4) Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575.

(5) Bulk coulometry of **1** and **2** has been carried out using a Pt gauze as working electrode, in CH$_2$Cl$_2$ solutions, at E_{appl} 100 mV more positive than the anodic potentials, resulting in the removal of four and eight electrons per molecule, respectively. The initial orange solutions turned blue during the oxidation, and reelectrolysis quantitatively regenerated the starting neutral dendrimers.

(6) Bard, A. J., Faulkner, L. R. *Electrochemical Methods*; Wiley: New York, 1980.

(7) The blue dendritic cations **[1^{4+}][PF$_6^-$]$_4$** and **[2^{8+}][PF$_6^-$]$_8$** were prepared by rapid addition of the appropriate equivalents of NOPF$_6$ to a solution of the corresponding neutral dendrimers in CH$_2$Cl$_2$. **[1^{4+}][PF$_6^-$]$_4$**: Anal. Calcd for C$_{60}$H$_{84}$Fe$_4$Si$_5$P$_4$F$_{24}$: C, 41.19; H, 4.84. Found: C, 40.95; H, 4.98. **[2^{8+}][PF$_6^-$]$_8$**: Anal. Calcd for C$_{136}$H$_{204}$Fe$_8$Si$_{13}$P$_8$F$_{48}$: C, 42.85; H, 5.40. Found: C, 42.15; H, 5.79.

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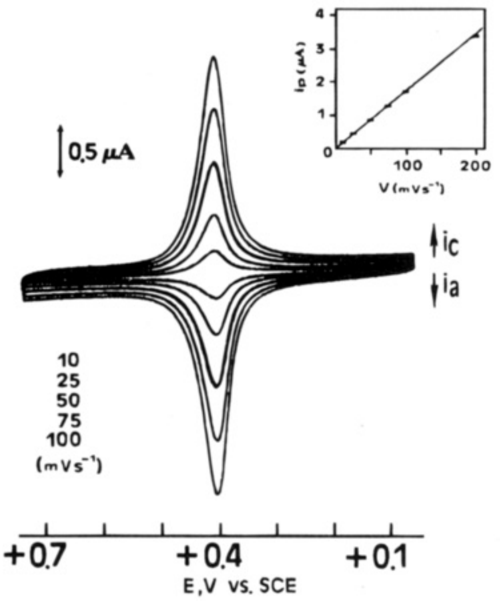

Figure 1. Cyclic voltammograms of a platinum disk electrode modified with a film of dendrimer **2**, measured in 0.1 M Bu_4NPF_6/CH_2Cl_2. Inset: plot of peak current vs sweep rate.

nm characteristic of ferrocenium cations,[8] which is absent in those of the neutral dendrimers (see Figure 3, inset). In addition, the EPR spectra of CH_2Cl_2 frozen solutions (liquid nitrogen) of the PF_6^- salts of the ferrocenium dendrimers **[1^{4+}]** and **[2^{8+}]** exhibit one isotropic broad signal ($\Delta H = 280$ G for **1** and $\Delta H = 340$ G for **2**) with g values of 2.03 and 2.02, respectively, which indicate that both polyferrocenium species have the unpaired electron essentially localized on the silicon-substituted cyclopentadienyl fragment.[8a,9]

It is worth noting that both multinuclear dendrimers **1** and **2** deposit onto electrode surfaces as they become oxidized. Thus modification of electrodes with films of dendrimers containing reversible four- and eight-electron redox systems has been successful, resulting in detectable electroactive material persistently attached to the electrode surfaces. The electrochemical behavior of films of the polyferrocenyl dendrimers was studied by cyclic voltammetry in fresh CH_2Cl_2 and CH_3CN solutions containing only supporting electrolyte. The voltammetric response of an electrodeposited film of **2** in CH_2Cl_2 with 0.1 M Bu_4NPF_6 is shown in Figure 1.[10] A well-defined, symmetrical oxidation–reduction wave is observed, which is characteristic of a surface-confined redox couple, with the expected linear relationship of peak current with potential sweep rate v.[11] The shape of the features in the cyclic voltammograms is independent of the scan rate from 5 to 1000 mV s^{-1}, and repeated scanning does not change the voltammograms demonstrating that films of **2** are stable to electrochemical cycling. A formal potential value of $E_{1/2} = +0.42$ V vs SCE was found for films of **2**, which is nearly identical to the formal potential of the octanuclear dendrimer in solution. For films examined at scan rates lower than 20 mV s^{-1}, no splitting between the oxidation and reduction peaks was observed, and ΔE_p increases only slightly with increasing sweep rate ($\Delta E_p = 10$ mV at 100 mV s^{-1}), suggesting that the rate of electron transfer is rapid on the experimental time scale. Likewise, a value of the full width at half-maximum, ΔE_{fwhm}, of 60 mV was measured at a scan rate of 10 mV s^{-1} which is slightly smaller than the ideal peak widths expected for surface-confined redox species, indicating attractive interactions between the electroactive ferro-

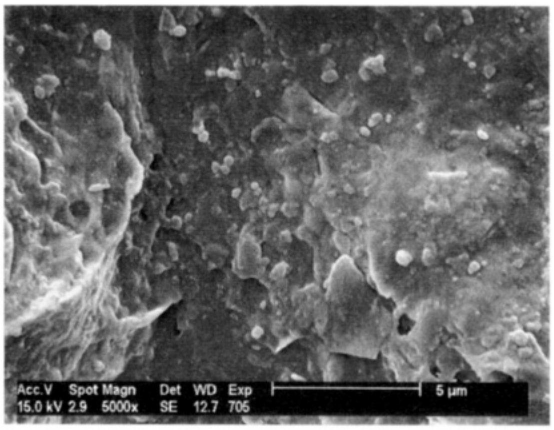

Figure 2. Scanning electron micrograph of a film of **2** electrochemically deposited on a platinum wire electrode.

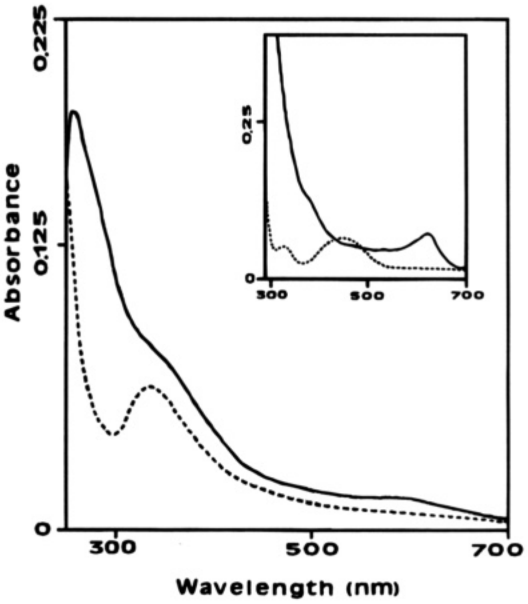

Figure 3. UV–visible spectra of a film of **2** electrodeposited on an ITO electrode, recorded after the film was oxidized at +0.70 V (—) and subsequently reduced at 0.0 V (– – –). Inset: UV–visible spectra in CH_2Cl_2 solution of the octanuclear dendrimers **[2^{8+}][PF_6^-]$_8$** (—) and **2** (– – –).

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(8) (a) Duggan, D. M.; Hendrickson, D. N. *Inorg. Chem.* **1975**, *14*, 955. (b) Cowan, D. O.; Candela, G. A.; Kaufman, F. *J. Am. Chem. Soc.* **1971**, *93*, 3889.

(9) Pannell, K. H.; Sharma, H. K. *J. Organomet. Chem.* **1993**, *450*, 193.

(10) The octanuclear dendrimer **2** was electrodeposited in its oxidized form onto platinum-disk electrodes ($A = 0.070$ cm^2) from a degassed CH_2Cl_2 solution of **2**, by maintaining the working electrode potential at +0.60 V, vs SCE. The amount of electroactive material deposited can be controlled with the electrolysis time (for example: 3 min, ca. $\Gamma = 1.03 \times 10^{-10}$ mol cm^{-2}; 10 min, ca. $\Gamma = 2.01 \times 10^{-10}$ mol cm^{-2}, 20 min, ca. $\Gamma = 2.67 \times 10^{-10}$ mol cm^{-2} (mol of ferrocenyl sites/cm^2)). The electrodes thus coated were rinsed with CH_2Cl_2 to remove any adhering solution and dried in air.

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(12) (a) Peerce, P. J.; Bard, A. J. *J. Electroanal. Chem.* **1980**, *114*, 89. (b) Lenhard, J. R.; Murray, R. W. *J. Am. Chem. Soc.* **1978**, 100, 7870. (c) Brown, A. P.; Anson, F. C. *Anal. Chem.* **1977**, *49*, 1589. (d) Laviron, E. *J. Electroanal. Chem.* **1981**, *122*, 37 and references therein.

cenyl sites attached to the electrode surface.[11,12] The waves retained this small ΔE_{fwhm} value over a scan rate range of 10−500 mV s^{-1}. The surface coverage of electroactive ferrocenyl sites in the film, Γ, was determined from the integrated charge of the cyclic voltammetric wave, and for the studied example shown in Figure 1 was found to be $\Gamma = 2.01 \times 10^{-10}$ mol cm^{-2}. The electrochemical response of the octanuclear dendrimer films is solvent dependent as a narrower surface redox wave is observed in CH_3CN solution ($\Delta E_{\mathrm{fwhm}} \approx$ 30 mV at 20 mV s^{-1}). One of the most noteworthy features of Pt electrodes modified with films of **2** is that they are extremely durable and reproducible. Cyclic voltammetric scans can be carried out in either organic or aqueous electrolyte solutions hundreds of times, with no loss of electroactivity. Likewise, after standing in air for several weeks, the redox response was practically unchanged without loss of electroactive material. In addition the wave shapes as well as the surface coverages are reproducible for a number of independent preparations. The above-described results are essentially the same for gold and glassy carbon-disk electrodes. Electrodeposited films of the tetraferrocenyl dendrimer **1**, obtained under the same conditions as for **2**, showed similar voltammetric responses and a comparable stability to the redox process.

The SEM micrograph of a film of the octanuclear dendrimer **2**, electrodeposited on a platinum wire (0.25 mm of diameter; coverage of electroactive material $\Gamma = 5.90 \times 10^{-9}$ mol cm^{-2}), Figure 2, shows a sheetlike compact morphology and exhibits small agglutinations and some porosity.

Ferrocenyl dendrimers **1** and **2** also afford electroactive films on ITO (indium tin oxide) electrodes in the same manner as described above. The UV−visible absorption spectrum of a film of **2** electrodeposited on a transparent ITO electrode, (measured after the film was oxidized at an E_{appl} of +0.7 V, Figure 3) shows a strong band at 260 nm and a weak absorption band centered at 600 nm which agree with those observed for the cationic dendrimer $[\mathbf{2}^{8+}][\mathbf{PF_6}^-]_8$ in solution.

In summary, we have demonstrated the feasibility of modifying electrode surfaces with organometallic dendrimers bearing a predetermined number of equivalent redox centers. Further studies directed to prove the efficiency of such dendritic macromolecules as mediating species in amperometric glucose biosensors are in progress.

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