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# Iron−Sulfur Core Dendrimers Display Dramatically Different Electrochemical Behavior in Films Compared to Solution

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We report the electrochemical behavior of films of redox-active core dendrimers. Two motivations prompted this study. First, electron hopping in polymer films has generated substantial interest for electrode design and molecular electronics applications. Systems previously studied include polymers containing pendent redox groups,[1] polyether melts,[2−4] and films of dendrimers terminated with electroactive groups.[5] From a molecular electronics perspective[6] it is of interest to question how a polymeric coating around a redox unit encapsulates this unit. Measurement of electron self-exchange rates during redox hopping through a polymer film potentially provides a probe by which to explore encapsulation.

Second, we have recognized that the iron−sulfur clusters employed as the core unit in these dendrimers display redox potentials that are very sensitive to environment. In ferredoxin proteins, [4Fe-4S] clusters can assume a wide variety of redox potentials depending on environmental factors such as protein structure and solvent accessibility to the cluster.[7] This fact suggests that these iron−sulfur clusters could be probes of microenvironment in macromolecules. The microenvironment within various dendrimers is largely uncharacterized.

Films of previously reported iron−sulfur cluster core dendrimers (Figure 1) were cast onto a platinum electrode surface in a fashion analogous to that reported by Murray et al.[3] (see Supporting Information for details). Cyclic voltammetry and chronoamperometry were employed to evaluate their electrochemical behaviors in propylene carbonate, a nonsolvent environment for the dendrimers (Figure 2A and Table 1).[3] These data are contrasted with cyclic voltammetric measurements on these dendrimers dissolved in dimethyl formamide solution (Figure 2B).

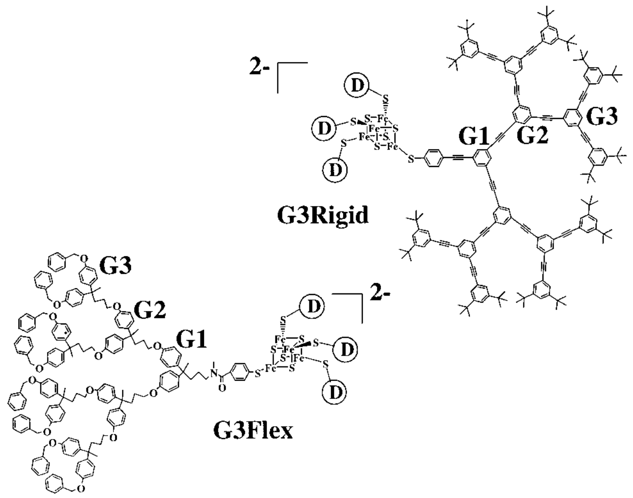

**Figure 1.** Structures of the dendrimers employed in this study. Third generation representations are shown. Second and fourth generation dendrimers have one fewer and greater hyperbranches, respectively. Circled-D represents additional arms identical to the one fully drawn out.

When cyclic voltammetry was performed on films of the iron−sulfur core dendrimers (Figure 2A), a large change in redox potential was observed with dendrimer generation. Specifically, in going from a film of a second generation dendrimer to a film of a fourth generation dendrimer, the redox potential shifted by ca. 500 mV. This behavior is in sharp contrast to that observed in solution (Figure 2B) where the redox potential does not change with generation within experimental error. Thus, the thermodynamic driving force for electron transfer in a film environment is dramatically influenced by the dendrimer generation and, in a film, dendrimer architecture can be used to influence redox potential in iron−sulfur core dendrimers. Specifically, a larger amount of essentially hydrophobic dendrimer dilutes the effective concentration of counterions in the film and shifts the redox potential of the iron−sulfur cluster to more negative potentials. This behavior is consistent with the observed redox potentials of iron−sulfur clusters in solvents of decreasing polarity.[8] The much smaller variation of redox potential with generation in solution electrochemistry (Figure 2B) may be because the iron−sulfur redox unit in each of these dendrimers was solvated similarly, and this solvent shell largely defined the microenvironment and thus the redox potential.

In contrast to the large variation in redox potential with generation observed, little change in the kinetics of charge transfer is observed with generation (Figure 2A). Assuming a diffusive hopping mechanism and accounting for the different dendrimer sizes and therefore effective concentrations (Table 1) these rates are quantitatively similar.[3] This behavior contrasts sharply with that observed in dendrimer solutions in which the rate of interfacial electron transfer changed by 2 orders of magnitude in going from a second generation to a fourth generation dendrimer.[6] This lack of variation in $k_{\mathrm{EX}}$ with generation can be rationalized by assuming that the redox units within the dendrimer are mobile, permitting close approach of redox units in neighboring dendrimers over the time scale of electron hopping through the film. Thus, the effective distance for electron hopping is not strongly influenced by dendrimer size. Similar observations and conclu-

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(1) (a) Pickup, P. G. *J. Mater. Chem.* **1999**, *9*, 1641−1653. (b) Sosnoff, C. S.; Sullivan, M.; Murray, R. W. *J. Phys. Chem.* **1994**, *98*, 13643-13650. (c) Surridge, N. A.; Sosnoff, C. S.; Schmehl, R.; Facci, J. S.; Murray, R. W. *J. Phys. Chem.* **1994**, *98*, 917−923. (d) Jernigan, J. C.; Murray, R. W. *J. Am. Chem. Soc.* **1987**, *109*, 1738−1745. (e) Pickup, P. G.; Kutner, W.; Leidner, C. R.; Murray, R. W. *J. Am. Chem. Soc.* **1984**, *106*, 1991−1998. (f) Pickup, P. G.; Murray, R. W. *J. Am. Chem. Soc.* **1983**, *105*, 4510−4514.

(2) (a) Poupart, M. W.; Velazquez, C. S.; Hassett, K.; Porat, Z.; Haas, O.; Terrill, R. H.; Murray, R. W. *J. Am. Chem.* **1994**, *116*, 1165−1166. (b) Velázquez, C. S.; Hutchison, J. E.; Murray, R. W. *J. Am. Chem. Soc.* **1993**, *115*, 7896−7897. (c) Dickinson, E.; Williams, M. E.; Hendrickson, S. M.; Masui, H.; Murray, R. W. *J. Am. Chem. Soc.* **1999**, *121*, 613−616.

(3) Long, J. W.; Kim, I. K.; Murray, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 11511−11515.

(4) Williams, M. E.; Masui, H.; Long, J. W.; Malik, J.; Murray, R. W. *J. Am. Chem. Soc.* **1997**, *119*, 1997−2005.

(5) (a) Takada, K.; Díaz, D. J.; Abruña, H. D.; Cuadrado, I.; Casado, C.; Alonso, B.; Morán, M.; Losada, J. *J. Am. Chem. Soc.* **1997**, *119*, 10763-10773. (b) Storrier, G. D.; Takada, K.; Abruña, H. *Langmuir* **1999**, *15*, 872−884. (c) Takada, K.; Storrier, G. D.; Moran, M.; Abruña, H. D. *Langmuir* **1999**, *15*, 7333−7339.

(6) Gorman, C. B.; Smith, J. C.; Hager, M. W.; Parkhurst, B. L.; Sierzputowska-Gracz, H.; Haney, C. A. *J. Am. Chem. Soc.* **1999**, *121*, 9958−9966.

(7) (a) Chen, K. S.; Tilley, G. J.; Sridhar, V.; Prasad, G. S.; Stout, C. D.; Armstrong, F. A.; Burgess, B. K. *J. Biol. Chem.* **1999**, *274*, 36479−36487. (b) Brereton, P. S.; Verhagen, M.; Zhou, Z. H.; Adams, M. W. W. *Biochemistry* **1998**, *37*, 7351−7362. (c) Ueno, T.; Inohara, M.; Ueyama, N.; Nakamura, A. *Bull. Chem. Soc. Jpn.* **1997**, *70*, 1077−1083.

(8) Que, L., Jr.; Anglin, J. R.; Bobrik, M. A.; Davison, A.; Holm, R. H. *J. Am. Chem. Soc.* **1974**, *96*, 6042−6048.

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**Table 1.** Dendrimer Size, Effective Concentration, Kinetic Parameters and Thermodynamic Redox Potential in Semisolid Films

| molecule | MW | $R_H$ (Å)[a,b] | $C_{eff}$ ($\mu$mol/cm$^3$)[c] | $10^{-10}D_{APP}$ (cm$^2$/s)[d,e] | $10^8k_{ex}$ (cm$^3$/mol·s)[d,e] | $E_{1/2}$ (mV) film[f] | $E_{1/2}$ (mV) DMF solution[g] |
|---|---|---|---|---|---|---|---|
| **G2Flex** | 5995 | 10.86 ± 1.94 | 162 | 1.0 ± 0.7 | 1.1 ± 0.7 | −1250 ± 13 | −1312 ± 10 |
| **G3Flex** | 11507 | 13.49 ± 4.02 | 84.6 | 0.7 ± 0.5 | 0.7 ± 0.5 | −1450 ± 14 | −1317 ± 19 |
| **G4Flex** | 22529 | 16.92 | 42.9 | 4 ± 3 | 5 ± 4 | −1744 ± 17 | *h* |
| **G2Rigid** | 5867 | 14.43 ± 3.50 | | | | −1885 ± 18 | −1275 ± 16 |

[a] $R_H$ was obtained using the Stokes−Einstein equation and self-diffusion coefficients obtained experimentally from chronoamperometry or molecular modeling for **G4Flex**.[6] [b] Error represents the magnitude of the 90% confidence intervals for at least three different experimental runs. [c] Values calculated by considering a cubic close packed model of spheres with radius $R_H$ in dendrimer film. [d] Obtained as described in the Supporting Information. [e] Error assumes a ±20% error in dendrimer radii. [f] Thermodynamic redox potential observed in dendrimer films (vs ferrocene/ferricinium). [g] Thermodynamic redox potential observed in DMF containing 100 mM tetraethylammonium tetrafluoroborate (vs ferrocene/ferricinium). [h] Irreversible couple.

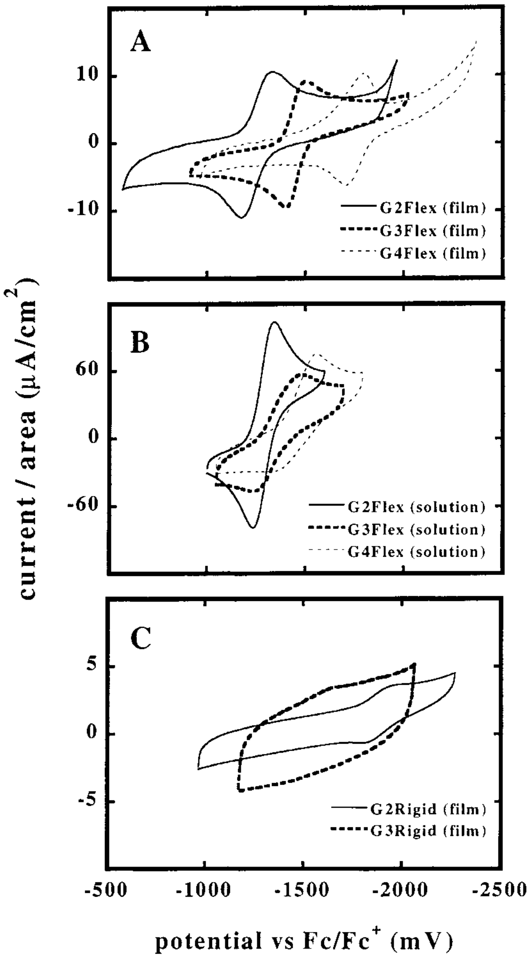

**Figure 2.** (A) Cyclic voltammograms of films of flexible dendrimers (scan rate = 20 mV/s, propylene carbonate/100 mM tetrabutylammonium hexafluorophosphate). (B) Cyclic voltammograms of 1 mM solutions of flexible dendrimers (scan rate = 100 mV/s, dimethyl formamide/100 mM tetraethylammonium tetrafluoroborate). (C) Cyclic voltammograms of films of rigid dendrimers (same conditions as in A).

sions were made by Murray et al. in their study of redox units solvated in films by covalently attached poly(ethylene glycol) chains.[3,4]

We speculate that the time scale of core motion relative to electron transfer is important in rationalizing the different trends obtained in film and solution environments. Although it is not possible to compare strictly the rate of electron hopping through a film with electron transfer across a metal−solution interface, film voltammetry requires slower scan rates to achieve the peak shapes observed in solution voltammetry. On the time scale of electron transfer in the film, iron−sulfur cores may be able to move rapidly enough that they do not bottleneck electron transfer. Alternatively, in solution, residence time at the electrode may be too short for the core to achieve an optimal position for electron transfer, giving rise to a dependence of rate on generation.

The importance of a mobile redox core is further supported by comparing the results of these voltammetry experiments with those obtained on rigid dendrimers (Figure 2C). In the data shown in Figure 2C, the charge transfer kinetics are too slow to reliably obtain $D_{APP}$ or $k_{EX}$. However, although the voltammogram of **G2Rigid** displays a shape attributable to quasireversible electron transfer, that of **G3Rigid** shows slow electron transfer (the film effectively acts as an insulator, not displaying diffusive behavior of carriers). Thus, both the kinetics and thermodynamics of electron transfer are influenced by generation in the rigid dendrimer films.[6]

These results are remarkable in that flexible iron−sulfur cluster core dendrimers represent a system where dendrimer architecture exerts a big influence on driving force but not on $k_{EX}$. Although in many systems driving force strongly influences electron-transfer rate,[9] here, rate is apparently driven by the preexponential term ($V_{DA}^2$) and not the thermodynamic driving force term ($\Delta G°$) of the Marcus equation.

$$k = \frac{2\pi V_{DA}^{2} \exp((-\Delta G^\circ + \lambda)^2/4\lambda k_B T)}{\hbar(4\pi\lambda k_B T)^{1/2}}$$

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**Supporting Information Available:** Experimental details (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(9) (a) Marcus, R. A. *Annu. Rev. Phys. Chem.* **1964**, *15*, 155−196. (b) Miller, J. R.; Beitz, J. V.; Huddleston, R. K. *J. Am. Chem. Soc.* **1984**, *106*, 5057−5068.