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Asymmetric Redox-Active Dendrimers Containing a Ferrocene Subunit. Preparation, Characterization, and Electrochemistry

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The chemistry of dendrimers has experienced an spectacular development in the past few years, and very recently, dendrimer functionalization has received substantial attention.[1] In this regard, several groups have reported the covalent incorporation of redox-active subunits in the interior[2] or at the surface[3] of dendrimer structures. While redox-active dendrimers may be of considerable interest in fundamental electron-transfer studies, the compounds reported so far have in common a rather symmetric structure. In this work, we describe the preparation and electrochemical behavior of a series of novel, asymmetric macromolecules containing a single ferrocene subunit appended to a dendrimer-type branch of variable size.

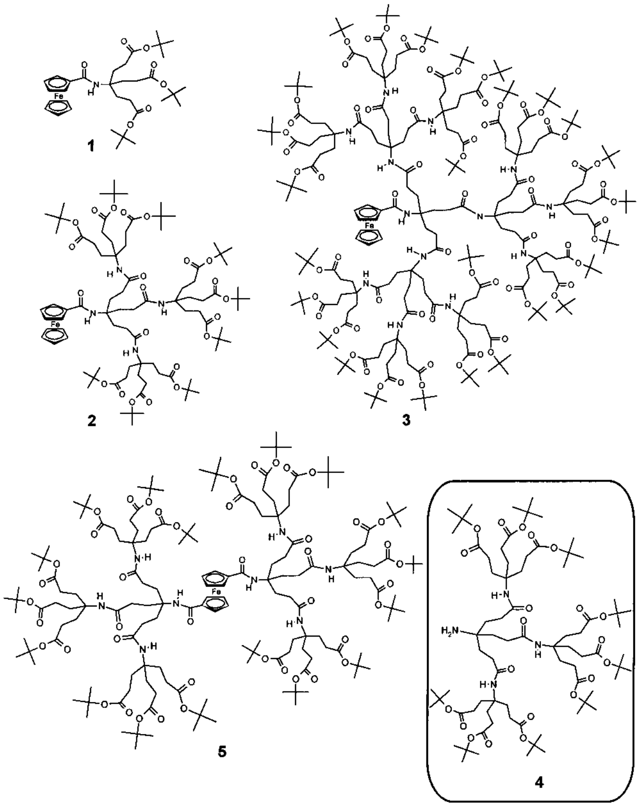
Macromolecules **1**−**3** (Chart 1) were prepared using the methodology developed by Newkome and co-workers.[4] Compound **1** was obtained by reaction of chlorocarbonylferrocene with Behera's amine.[4] Hydrolysis of the peripheral ester groups and reaction of the resulting triacid with Behera's amine produced the second-generation dendrimer **2**. This two-step process can be repeated to prepare **3**, but we found that the direct reaction of the triacid (obtained from the hydrolysis of **1**) with a second-generation analogue of Behera's amine (compound **4**)[5] yielded **3** more efficiently. By a combination of convergent and divergent synthetic approaches, amine **4** allows the one-step preparation of the ($n + 1$)th generation dendrimer from the ($n - 1$)th generation acid. All new dendrimers were characterized by ^{1}H and ^{13}C NMR, UV−vis, and IR spectroscopies and MALDI-TOF MS (see the Supporting Information).

Table 1. Structural and Electrochemical Parameters (0.2 M $TBA^+PF_6^-$ in CH_2Cl_2 at 25 °C) for the Ferrocene-Containing Dendrimers

	MW[a] (amu)	radius[b] (Å)	$E_{1/2}$ (V vs Ag/AgCl)	D_o[c] (10^6 cm^2 s^{-1})	α[c]	$k°$[c] (10^3 cm s^{-1})
1	627.6	3.5−8	0.63	9.5 ± 1.0	0.5	80 ± 20
2	1652.0	3.5−12	0.60	4.0 ± 0.5	0.5	17 ± 3
3	4725.0	3.5−18	0.54	2.3 ± 0.3	0.4	5 ± 1
5	3117.9	12	0.73	2.5 ± 0.3	0.3	9 ± 2

[a] The molecular weights listed were calculated and verified in MALDI TOF MS experiments. [b] Estimated from molecular modeling. [c] Determined using digital simulations of voltammetric data obtained with a glassy carbon electrode (0.0078 cm^2).

Chart 1



Relevant properties of the ferrocene-containing dendrimers are given in Table 1. Their electrochemical parameters were determined in 0.2 M $TBA^+PF_6^-/CH_2Cl_2$, a solvent system in which all of these compounds were soluble. Representative voltammograms are shown in Figure 1. As anticipated, the anodic electrochemistry is characterized by the one-electron oxidation of the ferrocene nucleus. This electrochemical process is fast in simple ferrocene derivatives.[6] In agreement with this, the first-generation dendrimer (compound **1**) exhibits a voltammetric behavior described by a reasonably fast heterogeneous electron-transfer rate constant (k^0). However, the $k°$ values[7] quickly decrease for the second- and third-generation dendrimers. This observation agrees with qualitative[7] observations previously

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(1) For a recent comprehensive monograph, see: Newkome, G. R.; Moorefield, C. N.; Vogtle, F. *Dendritic Molecules: Concepts, Synthesis, and Perspectives*; VCH: Weinheim, Germany, 1996.

(2) (a) Dandliker, P. J.; Diederich, F.; Gross, M.; Knobler, C. B.; Louati, A.; Sadford, E. M. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1739. (b) Newkome, G. R.; Guther, R.; Moorefield, C. N.; Cardullo, F.; Echegoyen, L.; Perez-Cordero, E.; Luftmann, H. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2023. (c) Dandliker, P. J.; Diederich, F.; Gisselbrecht, J.-P.; Louati, A.; Gross, M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 2725. (d) Chow, H.-F.; Chan, I. Y.-K.; Chan, D. T. W.; Kwok, R. W. M. *Chem. Eur. J.* **1996**, *2*, 1085. (e) Sadamoto, R.; Tomioka, N.; Aida, T. *J. Am. Chem. Soc.* **1996**, *118*, 3978. (f) Bhyrappa, P. Young, J. K.; Moore, J. S.; Suslick, K. S. *J. Am. Chem. Soc.* **1996**, *118*, 5708. (g) Gorman, C. B.; Parkhurst, B. L.; Su, W. Y.; Chen, K.-Y. *J. Am. Chem. Soc.* **1997**, *119*, 1141.

(3) (a) Moulines, F.; Djakovitch, L.; Boese, R.; Glaguen, B.; Thiel, W.; Fillaut, J.-L.; Delville, M.-H.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1993**, *32*, 1075. (b) Alonso, B.; Cuadrado, I.; Morán, M.; Losada, J. *J. Chem. Soc., Chem. Commun.* **1994**, 2575. (c) Bryce, M. R.; Devonport, W.; Moore, A. J. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 1761. (d) Fillaut, J.-L.; Linares, J.; Astruc, D. *Angew. Chem., Int. Ed. Engl.* **1994**, *33*, 2460. (e) Alonso, B.; Morán, M.; Casado, C. M.; Lobete, F.; Losada, J.: Cuadrado, I. *Chem. Mater.* **1995**, *7*, 1440. (f) Cuadrado, I.; Moran, M.; Casado, C. M.; Alonso, B.; Lobete, F.; García, B.; Ibisate, M.; Losada, J. *Organometallics* **1996**, *15*, 5278. (g) Lange, P.; Schier, A.; Schmidbaur, H. *Inorg. Chem.* **1996**, *35*, 637. (h) Haga, M.-A.; Ali, M.-M.; Arakawa, R. *Angew. Chem., Int., Ed. Engl.* **1996**, *35*, 76. (i) Valerio, C.; Fillaut, J.-L.; Ruiz, J.; Guittard, J.; Blais, J.-C.; Astruc, D. *J. Am. Chem. Soc.* **1997**, *119*, 2588. (j) Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J.; Belsky, V. *J. Am. Chem. Soc.* **1997**, *119*, 7613. (k) Bodige, S.; Torres, A. S.; Maloney, D. J.; Tate, D.; Kinsel, G. R.; Walker, A. K.; MacDonnell, F. M. *J. Am. Chem. Soc.* **1997**, *119*, 10364. (l) Takada, K.; Díaz, D. J.; Abruña, H. D.; Cuadrado, I.; Casado, C. M.; Alonso, B.; Morán, M.; Losada, J. *J. Am. Chem. Soc.* **1997**, *119*, 10763. (m) Serroni, S.; Juris, A.; Venturi, M.; Campagna, S.; Resino, R. I.; Denti, G.; Credi, A.; Balzani, V. *J. Mater. Chem.* **1997**, *7*, 1227. (n) Newkome, G. R.; He, E. *J. Mater. Chem.* **1997**, *7*, 1237. (o) Wang, C.; Bryce, A.; Batsanov, A. S.; Goldenberg, L. M.; Howard, J. A. K. *J. Mater. Chem.* **1997**, *7*, 11189.

(4) Newkome, G. R.; Behera, R. K.; Moorefield, C. N.; Baker, G. R. *J. Org. Chem.* **1991**, *56*, 7126.

(5) This compound was prepared by hydrolysis of the nitro triester precursor to Behera's amine, followed by treatment of the resulting nitro triacid with excess Behera's amine and reduction of the nitro group to amine (see details in the Supporting Information).

(6) Kaifer, A. E. In *Transition Metals in Supramolecular Chemistry*; NATO ASI Series; Fabbrizzi, L., Poggi, A., Eds.; Kluwer: Dordrecht, The Netherlands, 1994; p 227.

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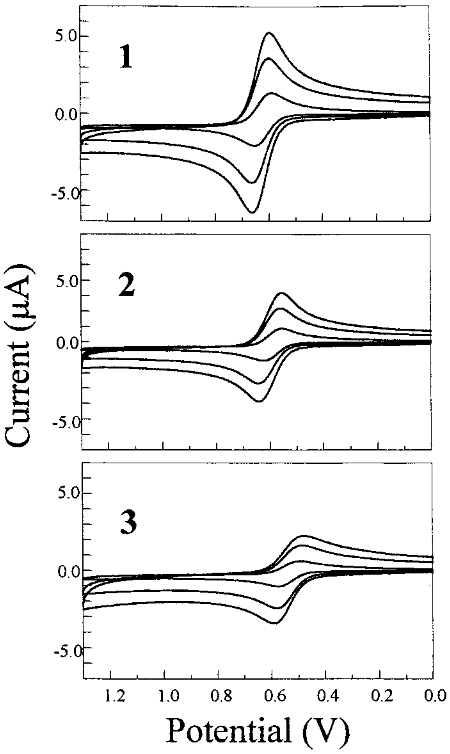

Figure 1. Representative cyclic voltammograms obtained with a glassy carbon working electrode (0.0078 cm^2) in solutions containing dendrimers **1**−**3** (1 mM) and $TBA^+PF_6^-$ (0.2 M) in CH_2Cl_2. Scan rates: 0.100, 0.500, and 1.00 V s^{-1}.

reported by several groups working with dendrimers containing other electroactive core subunits. Both the apparent diffusion coefficients (D_o) and the half-wave potentials ($E_{1/2}$) for ferrocene oxidation also decrease with increasing molecular mass. While the trend exhibited by the D_o values is easy to rationalize, the variation observed with the $E_{1/2}$ values is more surprising. Diederich and co-workers have reported a similar variation of the oxidation potentials of dendritic metal porphyrin cores.[2a] In our series of compounds, the observed $E_{1/2}$ values reflect the destabilization of the reduced ferrocene nucleus and/or the stabilization of the oxidized ferrocenium (1+) nucleus by the dendritic environment relative to the solvent medium. Rowe and Creager[8] have demonstrated that ferrocene oxidation becomes thermodynamically more difficult as the ferrocene subunits are buried inside the aliphatic region of alkanethiolate self-assembled monolayers. Their experiments clearly show that an increasing hydrophobic environment hinders ferrocene oxidation. Our half-wave potential data were obtained in dichloromethane solution and are not directly comparable to Creager's results. Nonetheless, our data indicate that the generation of positive charge in the ferrocene moiety is thermodynamically favored by the dendritic structure.

Due to the well-known problems associated with electrochemical kinetic measurements using conventional size electrodes,[9] we utilized platinum ultramicroelectrodes (4-μm radius) to determine $k°$ values for compounds **1** and **2**. The resulting current−potential graphs were analyzed by the method of Milkin and Bard,[10] yielding values of 0.20 ± 0.05 cm s^{-1} for **1** and 0.023 ± 0.007 cm s^{-1} for **2**. These $k°$ values are in reasonable agreement with those reported in Table 1. Unfortunately, we could not obtain a full set of electrochemical data with ultramicroelectrodes because compounds **3** and **5** exhibited highly irreproducible behavior in these experiments. Nonetheless, the analysis of the $k°$ values measured with conventional size electrodes (Table 1) in terms of the structural parameters characteristic of these dendrimers is of considerable fundamental interest. In this regard, we must note that the bisdendritic compound **5**, synthesized for comparison purposes, exhibits slower heterogeneous electron-transfer kinetics than its monodendritic analogue **2**. This finding reflects the marked asymmetric character of monodendrons **1**−**3**. These compounds may approach the electrode surface either with the dendritic side or with the ferrocene side facing the electrode. The first type of approach may lead to slow heterogeneous electron transfer, while the second should result in faster kinetics. By contrast, "bisdendron" **5** is more symmetric, and when approaching the electrode, its two dendritic regions set the minimum distance between the central ferrocene nucleus and the electrode surface, resulting in comparatively slower kinetics.

Compounds **1**−**3** constitute a novel series of redox-active dendrimers. The asymmetric and partially "buried" location of the redox center in these rather large molecules is very similar to that found in numerous redox proteins.[11] As such, compounds **1**−**3** may exhibit orientation-dependent rates of electron transfer, a possibility which is currently under investigation in our laboratory.

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Supporting Information Available: Experimental details (5 pages, print/PDF). See any current masthead page for ordering information and Web access instructions.

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[7] To our knowledge, this is the first report of standard rate constants for heterogeneous electron-transfer reactions involving dendrimer systems. Several groups have noted that in dendrimers containing one or several electroactive cores the voltammetric behavior becomes more irreversible with increasing dendrimer generation (see ref 2).

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[11] See, for instance: Guo, L.-H.; Hill, H. A. O. *Adv. Inorg. Chem.* **1991**, *36*, 341.