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Unusual Electrochemical Properties of Unsymmetric Viologen Dendrimers

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Redox-active dendrimers are one of the major classes of functionalized dendrimers[1] and have thus been the subject of considerable research work. Dendrimers functionalized with redox-active cores usually exhibit attenuation of their heterogeneous rates of electron transfer with increasing molecular weight.[2] A series of Fréchet-type dendrimers with 4,4′-bipyridinium (viologen) cores recently reported by our group[3] and Balzani's[4] constitutes the first exception to this general trend. In addition to this, we have also described a series of "unsymmetric" dendrimers containing a ferrocenyl residue at the focal point of Newkome-type dendrons.[5] In dichloromethane solution, the half-wave potential for oxidation of the ferrocene group shifts to less positive values with increasing dendrimer generation. In other words, dendrimer growth translates into a relative thermodynamic stabilization of the positively charged ferrocenium form. The fact that the literature contains only one other example of a dendrimer series exhibiting a similar potential trend has been recently highlighted by Smith et al.[6] Driven by these findings we decided to prepare a new series of redox-active dendrimers (**1**−**3**) (Figure 1) containing viologen residues covalently attached to the focal point of Newkome-type dendrons and whose structures are considerably different from those of other viologen-containing dendrimers previously reported by our group[3] and others.[4,7] Our electrochemical results confirm that viologen dendrimers maintain fast heterogeneous electron-transfer rates, even at third-generation sizes. Also, dendrimers **1**−**3** show the unusual potential variation already observed with our unsymmetric ferrocene dendrimers.[5]

The synthesis of dendrimers **1**−**3** began with the preparation of the viologen-containing acid **4** by the stepwise quaternization of 4,4′-bipyridine with bromoethane and 6-bromohexanoic acid. The amidic coupling of **4** with Newkome-type amine dendrons, available in our laboratory from previous work,[5b] was accomplished by using *n*-HATU/Proton Sponge in dry DMF at room temperature under N_2 for 12 h. After chromatography and counterion exchange with NH_4PF_6 in H_2O/acetone, dendrimers **1**−**3** were isolated in good yields (69−81%) as their hexafluorophosphate salts. These dendrimers were fully characterized by ^{1}H, ^{13}C, COSY, and HMQC NMR spectroscopies and FAB or MALDI-TOF mass spectrometry. Intense singly charged molecular ion peaks (M^+) were detected in the mass spectra of all three dendrimers, suggesting the easy one-electron reduction of the viologen subunit under MS conditions.[8]

Representative current−potential curves for compounds **1**−**3** in 0.2 M $TBAPF_6/CH_3CN$ are shown in Figure 2. Both one-electron reduction processes ($V^{2+} \rightarrow V^{+\bullet}$ and $V^{+\bullet} \rightarrow V$) are fully reversible in the surveyed range of scan rates (0.1 to 2.0 V/s), as evidenced by the invariance of the peak potentials with scan rate. The half-wave potentials for both processes shift to more negative values as the dendrimer generation increases. These findings confirm that dendrimers **1**−**3** maintain the fast heterogeneous electron-transfer kinetics detected in Fréchet-type viologen core dendrimers[3,4] and the same correlation between half-wave potentials and molecular weights as observed with our unsymmetric ferrocene dendrimers.[5]

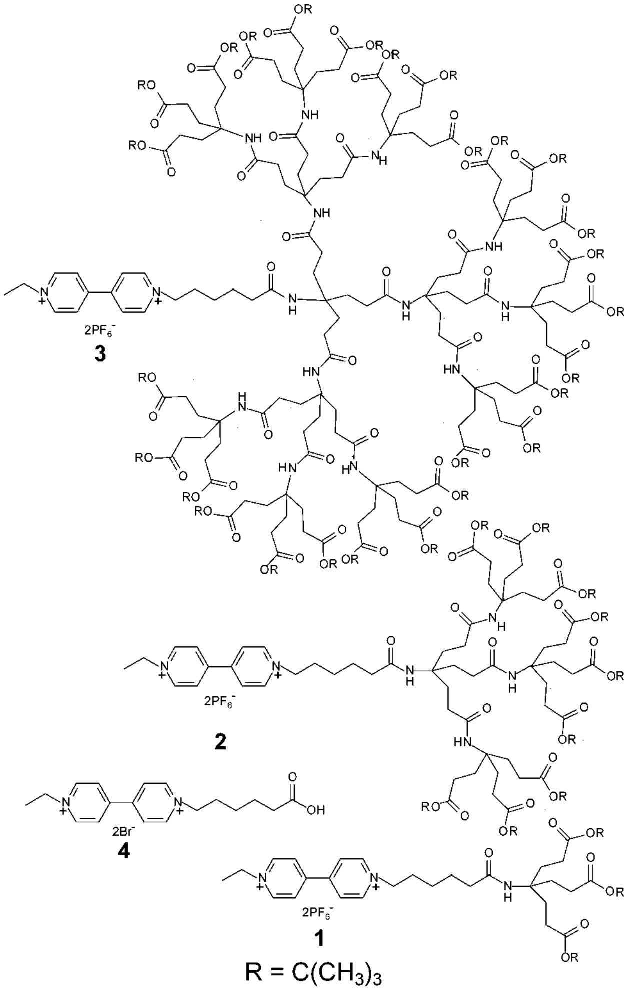

Figure 1. Structures of viologen dendrimers **1**−**3** and precursor **4**.

We took advantage of the solubility of **1**−**3** in a variety of organic solvents to perform cyclic voltammetric (CV) experiments in CH_2Cl_2, THF, and DMSO. The voltammetric waves in the less polar solvents CH_2Cl_2 and THF showed some quasi-reversible character (probably related to uncompensated resistance effects) at the faster scan rates surveyed (1 and 2 V/s), while reversibility was maintained in DMSO up to 2 V/s. We used the increasingly popular pulsed gradient spin−echo (PGSE) NMR technique[9] to determine the diffusion coefficients of the dendrimers in deuterated forms of these solvents. The results are summarized in Table 1.

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Table 1. Diffusion Coefficients[a] (D_o, in cm^2/s) and Half-Wave Potentials[b] ($E_{1/2}{}^1$ and $E_{1/2}{}^2$, in V vs Ag/AgCl) for Dendrimers **1**−**3** at 25 °C in Several Organic Solvents Also Containing 0.2 M TBAPF$_6$

	1	**2**	**3**		**1**	**2**	**3**
	medium: CH_2Cl_2				medium: CH_3CN		
D_o	8.5×10^{-6}	6.7×10^{-6}	4.9×10^{-6}	D_o	1.0×10^{-5}	7.9×10^{-6}	5.5×10^{-6}
$E_{1/2}{}^1$	−0.28	−0.34	−0.42	$E_{1/2}{}^1$	−0.390	−0.394	−0.421
$E_{1/2}{}^2$	−0.81	−0.84	−0.87	$E_{1/2}{}^2$	−0.817	−0.821	−0.838
	medium: THF				medium: DMSO		
D_o	6.6×10^{-6}	5.4×10^{-6}	3.9×10^{-6}	D_o	1.7×10^{-6}	1.2×10^{-6}	8.7×10^{-7}
$E_{1/2}{}^1$	−0.31	−0.32	−0.37	$E_{1/2}{}^1$	−0.390	−0.386	−0.375
$E_{1/2}{}^2$	−0.72	−0.73	−0.76	$E_{1/2}{}^2$	−0.754	−0.756	−0.752

[a] Error margin: ±10%. [b] Error margin: ±0.010 V in CH_2Cl_2 and THF; ±0.002 V in CH_3CN and DMSO.

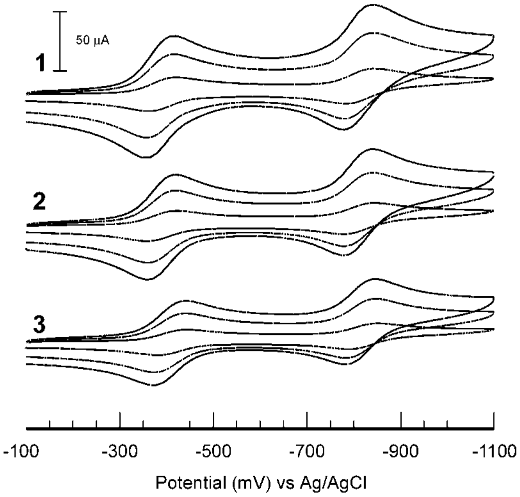

Figure 2. Cyclic voltammetric responses on a glassy carbon electrode (0.071 cm^2) of dendrimers **1**, **2** and **3** in 0.2 M TBAPF$_6$/CH_3CN. Scan rates: 0.1, 0.5 and 1.0 V/s.

The $E_{1/2}$ values for both reduction processes are clearly affected by dendrimer growth in all solvents, revealing that the five-methylene tether between the viologen group and the focal point of the dendron is not long enough to keep the redox-active residue away from the environment created by the dendrimer. Both half-wave potentials shift to more negative values with increasing molecular weight in CH_2Cl_2, THF, and CH_3CN. This trend is most pronounced in CH_2Cl_2 and least pronounced in CH_3CN. In contrast to this, half-wave potential shifts to less negative values with increasing dendrimer generation are observed in the most polar solvent surveyed (DMSO). Taken together, the observed $E_{1/2}$ values for the reduction of the viologen subunit strongly suggest that these Newkome-type dendrimers create a microenvironment around their focal points that presents an average polarity intermediate between those of CH_3CN and DMSO. The unusual degree of inner polarity in these dendrimers may result from their amide groups, which could be brought to the proximity of the viologen moiety by surface-crowding effects caused by the bulky *tert*-butyl groups.

The diffusion coefficients measured by PGSE NMR correlate extremely well with the electrochemical data. A plot of cathodic peak currents for the first viologen reduction process, obtained in the CV experiments, against the square root of the D_o values, obtained from NMR experiments, is linear (see Supporting Information), as expected from the Randles Sevcik equation.[10] Furthermore, for all three dendrimers, plots of D_o values versus reciprocal solvent viscosities are also linear, in agreement with the Stokes−Einstein equation, $D_o = kT(6\pi\eta r)^{-1}$, where η is the solvent viscosity and r is the hydrodynamic radius (see Supporting Information). This implies that the dendrimers maintain an approximately constant shape and size in the four solvents surveyed. The slopes of these linear plots allow the calculation of the hydrodynamic diameters for **1**, **2**, and **3** as 1.0, 1.3, and 1.8 nm, respectively, at 25 °C. Despite the approximations involved in these calculations, these values are perfectly within the dimensions expected for these dendrimers.

Perhaps the most remarkable result from all these experiments is that the electrochemical kinetics for each of the two one-electron reduction processes in these viologen-containing dendrimers remains fast—in acetonitrile and dimethyl sulfoxide—regardless of molecular size in the time scale of our voltammetric experiments. The fact that the peak-to-peak potential splittings (ΔE_p) did not go significantly above 60 mV, even at scan rates of 2.0 V/s, means that the standard rate constants (k^o) for both viologen-reduction processes remain larger than ~0.2 cm/s, as estimated using Nicholson's method.[11] To the best of our knowledge, these are the fastest k^o values observed with redox-active dendrimers in this size range,[12] reaffirming our previous findings with Fréchet-type, viologen core dendrimers.[3]

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Supporting Information Available: MALDI-TOF MS spectrum of dendrimer **3**, PGSE plots for dendrimers **1**−**3**, plot of voltammetric cathodic peak currents vs the square root of PGSE NMR diffusion coefficients for dendrimers **1**−**3**, and plots of diffusion coefficients against (solvent viscosity)$^{-1}$ for **1**−**3** (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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(11) Reference 10, p 242.

(12) The molecular weights of **1**, **2**, and **3** are 987.9, 2012, and 5085, respectively.

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