Preparation, Characterization, and Electrochemical Properties of a New Series of Hybrid Dendrimers Containing a Viologen Core and Fréchet and Newkome Dendrons

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Preparation, Characterization, and Electrochemical Properties of a New Series of Hybrid Dendrimers Containing a Viologen Core and Fréchet and Newkome Dendrons

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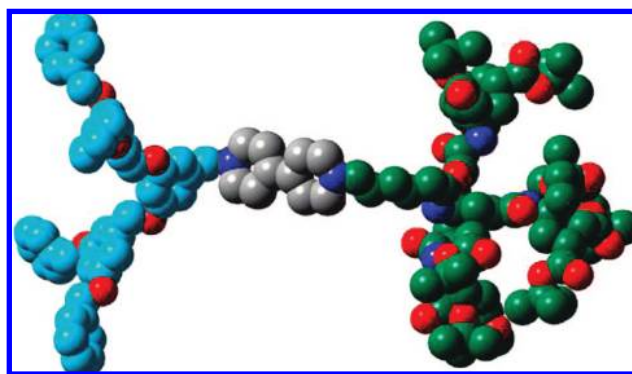
Five new 4,4′-bipyridinium (viologen) core dendrimers containing a Fréchet (**Fn**, $n = 1-3$, first to third generation) and a Newkome (**Nn**, $n = 1-3$) dendron linked to each of the termini of the viologen residue were prepared and characterized. These macromolecules (**FnNn**) were prepared according to synthetic methodology already developed by our group. The electrochemical behavior of these dendrimers is characterized by the stepwise reduction of the viologen nucleus (V^{2+}/V^+ and V^+/V). The recorded half-wave potentials are affected by dendron growth in the three surveyed solvent media (dichloromethane, tetrahydrofuran, and acetonitrile). The size of the Newkome dendron has a more pronounced effect on the half-wave potentials than the size of the Fréchet dendron. However, increasing the size of the Fréchet dendron diminishes the magnitude of the cathodic potential shifts resulting from Newkome dendron growth. The largest dendrimers investigated (**F1N3** and **F2N3**) exhibit quasi-reversible voltammetric behavior. The diffusion coefficients of these molecules were also determined using pulse gradient stimulated echo NMR techniques.

Introduction

The functionalization of dendrimers with redox groups has been an active topic of research during the last $10-15$ years.[1] Peripheral,[2] core,[3] or mixed[4] functionalization approaches have been used with a variety of redox-active residues. Within this extensive body of work, dendrimer functionalization with 4,4′-bipyridinium (viologen) groups has received considerable attention.[5] Our group[5m] and Balzani's[5n] independently reported several years ago the preparation and characterization of a series of symmetric dendrimers containing two identical Fréchet-type dendrons[6] covalently attached to the viologen core. Both groups reported that the cyclic voltammetric behavior for the reduction of the viologen core remains reversible even when the two dendritic substituents were relatively large, third-generation Fréchet dendrons. This was a surprising result because any other dendrimers with core redox groups show efficient attenuation of their electrochemical kinetics[1d] and, typically, the voltammetric behavior loses reversibility by (or even before) the third generation of dendrimer growth. Intrigued by these findings, our group prepared another series of dendrimers[5j] containing a single Newkome-type dendron[7] covalently linked to the viologen core. The second viologen substituent was a simple ethyl group

(1) (a) For reviews, see: Kaifer, A. E. *Eur. J. Inorg. Chem.* **2007**, 5015. (b) Abruña, H. D. *Anal. Chem.* **2004**, *76*, 310A. (c) Amatore, C.; Gruen, F.; Maisonhaute, E. *Angew. Chem., Int. Ed.* **2003**, *42*, 4944. (d) Cameron, C.; Gorman, C. B. *Adv. Funct. Mater.* **2002**, *12*, 17.

in this dendrimer series, which renders these dendrimers "unsymmetric" in terms of the substitution pattern around the viologen nucleus. Not surprisingly, the cyclic voltammetric behavior was again reversible up to the third generation of growth.[5j] A few years later, in joint work with Peinador and co-workers, we observed the same kind of persistently reversible electrochemical behavior with two series of unsymmetric viologen dendrimers containing a single Fréchet dendron.[5e]

While in all these macromolecules dendron growth (Fréchet or Newkome) to the third generation does not affect the reversible voltammetric behavior of the viologen core, the reduction half-wave potentials are clearly affected by the nature and size of the attached dendrons. At similar generational growth Newkome dendrons seem to fill space more effectively than their Fréchet counterparts.[5e] Additionally, the former dendrons have a more polar interior, as they contain numerous amide bonds, while the latter dendrons are characterized by the presence of aromatic ether moieties. In solvents of low to intermediate polarity (dichloromethane to acetonitrile), growth of the Newkome dendrons around the viologen residue tends to shift the reduction potentials to more negative values,[5j] while the Fréchet dendrons have a more modest, but opposite, effect.[5e,m] We have recently reported the combination of both dendron types in a new series of hybrid, triazine-based macromolecules that contain ferrocenyl redox-active residues.[3a]

Here, we report the preparation, characterization, and electrochemical properties of a new series of hybrid dendrimers (see Figure 1 for structures) containing a viologen nucleus and covalently attached Fréchet and Newkome dendrons.

Results and Discussion

Synthesis. The Fréchet dendrons were prepared as bromide building blocks following reported procedures.[6] The Newkome dendron amines were prepared according to previous reports.[7,8] The convergent preparation of dendrimers **FnNn** (the dendrimer shorthand system is briefly explained in the caption of Figure 1) draws heavily from prior synthetic procedures reported by our group.[5e] We first monoquaternized 4,4′-bipyridine with 6-bromohexanoic acid in refluxing acetonitrile to obtain acid **1** (Scheme 1). The Fréchet dendron was attached by quaternization with the corresponding dendron bromide of the free nitrogen in compound **1**.[5e] Finally, the Newkome amine building block was reacted with the free acid, using *n*-HATU as the coupling reagent, to yield dendrimers **FnNn** in 10−14% yields. The dendrimers were fully characterized by ^{1}H and ^{13}C NMR spectroscopies and FAB or MALDI-TOF mass spectrometry.

Notice that a total of nine compounds may result from all possible unsymmetric combinations of first- to third-generation Fréchet and Newkome dendrons around the viologen nucleus. While it should be entirely possible to prepare all nine compounds, we elected to synthesize only the five macromolecules shown in Figure 1 not only for reasons of economy but also because we were able to answer a good number of questions about the interplay between the two types of dendrons with a well selected set of **FnNn** dendrimers.

Electrochemistry. As anticipated, the voltammetric behavior of these dendrimers is characterized by the stepwise reduction of the viologen nucleus, which generally takes place as two consecutive one-electron reduction processes (V^{2+}/V^+ and V^+/V).[9] All dendrimers follow this reduction mechanism. Figure 2 shows cyclic voltammograms obtained with **F2N2**, as an illustrative example of the electrochemical behavior observed with these dendrimers. The half-wave potentials measured in dichloromethane (DCM), tetrahydrofuran (THF), and acetonitrile (ACN) for the two reduction processes in each dendrimer are given in Table 1.

The potential values are clearly affected by dendron growth. The first reduction half-wave potential ($E_{1/2}^1$) in DCM covers a range of ca. 110 mV, while the corresponding ranges in THF and ACN are narrower (40−50 mV). This is probably a reflection of the low polarity of DCM, which gives rise to the most pronounced polarity contrast, especially with the relatively polar inner phase of the Newkome dendrons. Since the dendron-induced potential differences are largest in DCM, it is instructive to analyze carefully the values recorded in this medium. First, we note that the $E_{1/2}^1$ value is invariant in going from **F1N1** to **F2N1**, which reflects the small effect that Fréchet dendron growth has on the reduction potential of the viologen nucleus. Conversely, from **F2N1** to **F2N2** there is a measurable $\Delta E_{1/2}^1$ of −37 mV. Clearly, the reduction half-wave potential is more

(2) Selected recent examples: (a) Ornelas, C.; Ruiz Aranzaes, J.; Salmon, L.; Astruc, D. *Chem. Eur. J.* **2008**, *14*, 50. (b) Zamora, M.; Alonso, B.; Pastor, C.; Cuadrado, I. *Organometallics* **2007**, *26*, 5153. (c) Zamora, M.; Herrero, S.; Losada, J.; Cuadrado, I.; Casado, C. M.; Alonso, B. *Organometallics* **2007**, *26*, 2688. (d) Krishanamoorthy, K.; Reddy Dasari, R.; Nantalaksakul, A.; Thayumanavan, S. *Chem. Commun.* **2007**, 739. (e) Nijhuis, C. A.; Dolatowska, K. A.; Ravoo, B. J.; Huskens, J.; Rienhoudt, D. N. *Chem. Eur. J.* **2007**, *13*, 69. (f) Ong, W.; McCarley, R. L. *Macromolecules* **2006**, *39*, 7295. (g) Li, Z.; Lam, J. W. Y.; Dong, Y.; Dong, Y.; Sung, H. H. Y.; Williams, I. D.; Tang, B. Z. *Macromolecules* **2006**, *39*, 6458. (h) Lear, B. J.; Kubiak, C. P. *Inorg. Chem.* **2006**, *45*, 7041. (i) Hogan, C. F.; Harris, A. R.; Bond, A. M.; Sly, J.; Crossley, M. J. *Phys. Chem. Chem. Phys.* **2006**, *8*, 2058. (j) Ruiz Aranzaes, J.; Belin, C.; Astruc, D. *Angew. Chem., Int. Ed.* **2006**, *45*, 132.

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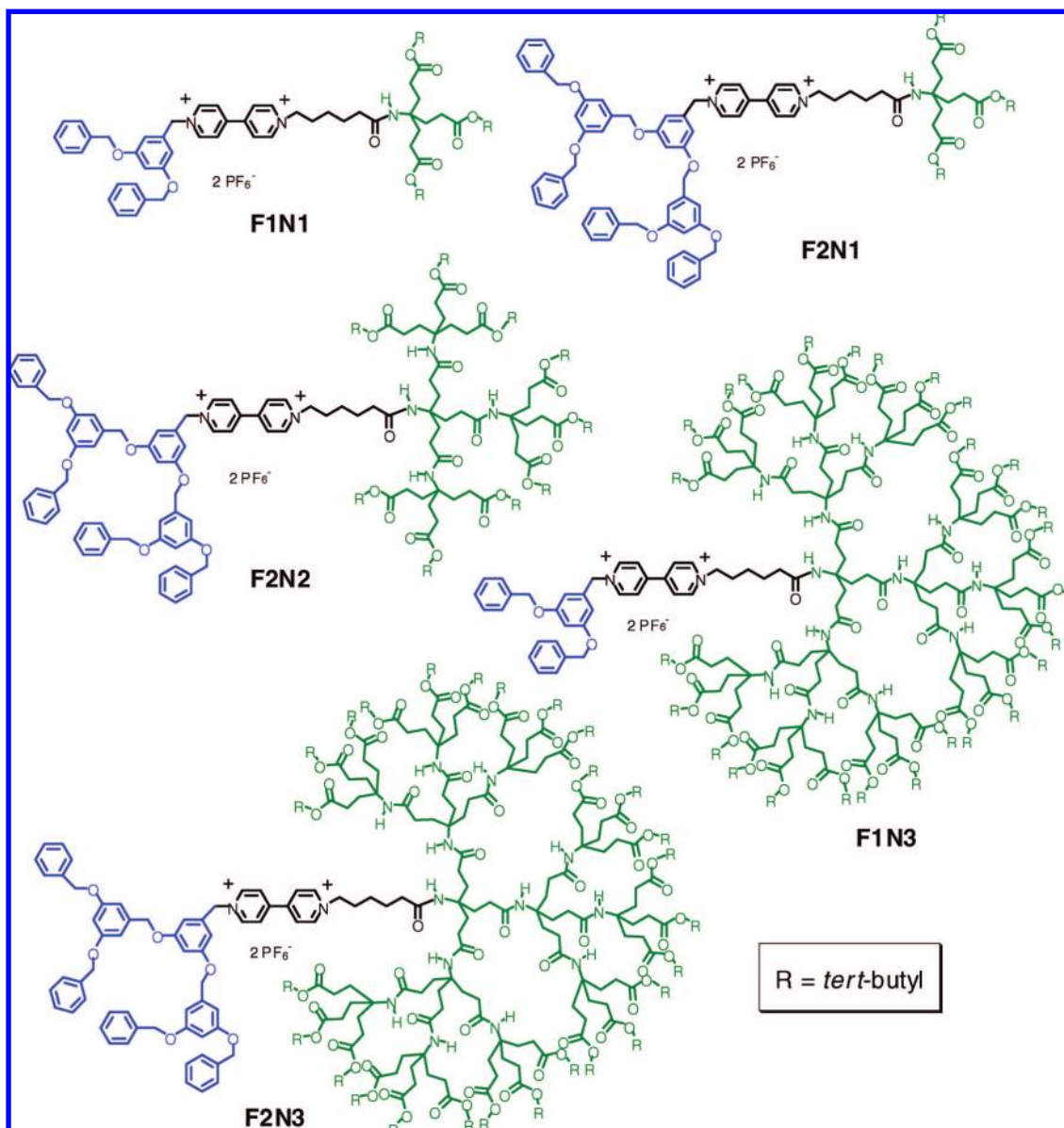
FIGURE 1. Structures of the hybrid dendrimers used in this work. All dendrimers are named (**FnNn**) according to the generational sizes of the two dendrons attached to the viologen nucleus.

sensitive to Newkome dendron growth than to Fréchet dendron growth. A more pronounced size differential in the Newkome dendron, such as that experienced from **F1N1** to **F1N3**, leads to a more prominent potential shift of −111 mV. It is very interesting to compare this $\Delta E_{1/2}^1$ value with that observed in going from **F2N1** to **F2N3** (−52 mV). In the latter two cases, the potential shift is the result of replacing the first-generation Newkome dendron (**N1**) by its third-generation analogue (**N3**) while maintaining the Fréchet dendron unchanged. However, the magnitude of the potential shift is diminished by the growth of the invariant Fréchet dendron. A comparison with our previously reported unsymmetric viologen derivatives[5e,j] (**EtN1**−**EtN3**) containing a single Newkome dendron and an ethyl group as the two substituents on the viologen residue is also illustrative. In this case, the $\Delta E_{1/2}^1$ value from **EtN1** to **EtN3** was measured as −140 mV in DCM solution. Our data reveal that the **N1**-to-**N3** dendron-induced potential shift is gradually tempered by the growth of the other viologen substituent (from **Et** to **F1** to **F2**). In spite of its five methylene

tether to the viologen residue, the Newkome dendron is quite efficient at modifying the core's microenvironment. In DCM solution, the inner phase of the Newkome dendron is more polar than the bulk solution, and thus, dendron growth stabilizes the oxidation states having the larger positive charge (+2 vs +1 in the first reduction process and +1 vs 0 in the second). The overall effect is a shift of the half-wave potential to more negative values. However, as the substituent on the other viologen end becomes bulkier, the magnitude of the potential shift decreases, probably as a result of partial steric hindrance, which modulates the relative degree of viologen encapsulation by the growing Newkome dendron.

The potential values recorded in THF and DCM follow similar trends, although the magnitude of the potential shifts is generally smaller. The half-wave potential values for the second reduction process ($E_{1/2}^2$) recorded in all three media can also be rationalized with similar arguments.

The electrochemical behavior of the two largest dendrimers **F1N3** and **F2N3** exhibits a peculiar anomaly in all the media

SCHEME 1. Synthesis of Dendrimers FnNn[a]
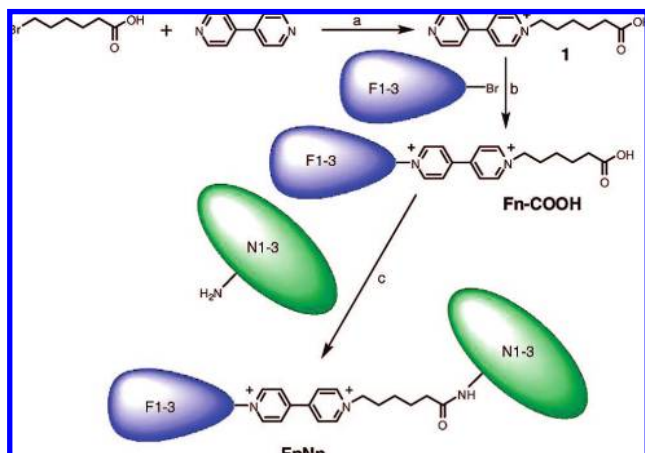
[a] Key: (a) reflux in CH_3CN for 48 h, followed by counterion exchange with NH_4PF_6; (b) reflux in CH_3CN at 70°C for 48 h, followed by counterion exchange with NH_4PF_6; (c) treatment with *n*-HATU and Proton Sponge in dry DMF.
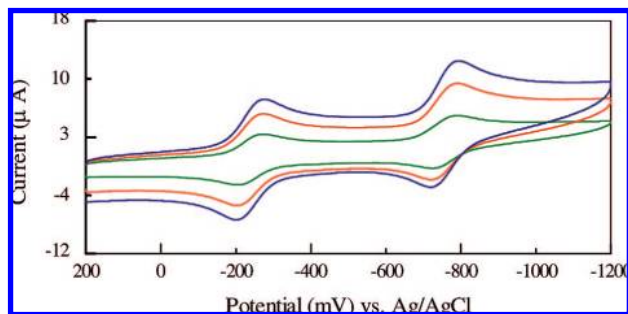
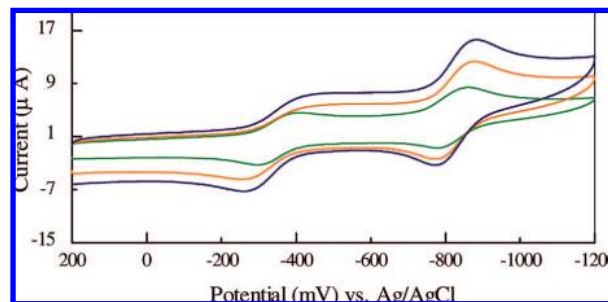**FIGURE 2.** Cyclic voltammetric response on glassy carbon (0.071 cm²) of a 0.5 mM solution of **F2N2** in dichloromethane also containing 0.1 M TBAPF₆. Scan rates: 0.1 (green), 0.3 (orange) and 0.5 (blue) V s⁻¹.

TABLE 1. Half-Wave Potentials[a] ($E_{1/2}^1$ and $E_{1/2}^2$ in V vs Ag/AgCl) for FnNn Dendrimers (0.5 mM) Obtained at 23 °C in Organic Solutions Containing 0.1 M TBAPF₆ as the Supporting Electrolyte

solvent		F1N1	F2N1	F2N2	F1N3	F2N3
DCM	$E_{1/2}^1$	−0.240	−0.240	−0.277	−0.351	−0.292
	$E_{1/2}^2$	−0.755	−0.764	−0.772	−0.821	−0.784
THF	$E_{1/2}^1$	−0.276	−0.271	−0.285	−0.320	−0.300
	$E_{1/2}^2$	−0.676	−0.676	−0.685	−0.706	−0.708
ACN	$E_{1/2}^1$	−0.325	−0.322	−0.345	−0.369	−0.358
	$E_{1/2}^2$	−0.754	−0.756	−0.770	−0.776	−0.772

[a] The error margin estimated for all reported potentials is ±0.005 V.

surveyed. Figure 3 shows the cyclic voltammetric behavior recorded in DCM with dendrimer **F1N3**. While the voltammogram at 100 mV s⁻¹ shows an essentially reversible set of waves for each of the one-electron reduction processes, at faster scan rates the first reduction peak in the forward scan loses definition and is replaced by a current plateau. This current−potential behavior is usually associated with a chemical equilibrium preceding the electron transfer (a CE mechanism in electrochemical parlance) in which the kinetics of the chemical reaction limits the amount of electroactive species available for reduction at the electrode surface.[10,11] In contrast to this, the second reduction appears as an uncomplicated quasi-reversible process,

FIGURE 3. Cyclic voltammetric response on glassy carbon (0.071 cm²) of a 0.5 mM solution of **F1N3** in dichloromethane also containing 0.1 M TBAPF₆. Scan rates: 0.1 (green), 0.3 (orange), and 0.5 (blue) V s⁻¹.

with well-developed cathodic and anodic waves. It must be noted here that the previously reported dendrimer **EtN3** exhibits two reversible sets of waves, without any of the complications apparent in the electrochemical behavior of **F1N3** (or the similarly behaved **F2N3**). Although the differences in molecular weights and sizes among all these dendrimers are relatively minor, the replacement of an ethyl group by a first (or second) generation Fréchet dendron on the viologen terminus across from the **N3** dendron has a considerable effect on the overall voltammetric response. In addition to the already described flattening of the first reduction wave, the second wave exhibits quasi-reversible behavior, in contrast to the perfectly reversible behavior observed with **EtN3** at these scan rates.

The shape of the first reduction peak on the forward scan for dendrimers **F1N3** and **F2N3** is not well understood at this time. The current plateau is only visible for reduction of the dicationic viologen residue, while the one-electron reduced, +1 species is not affected. This suggests that the +2 state, as a good electron acceptor, may be involved in the formation of a charge transfer complex with the π donor aromatic units present in the Fréchet dendrons.[5f] This interaction would be broken after one-electron reduction, since the +1 viologen oxidation state is a relatively poor electron acceptor. However, we could not detect the development of a charge transfer band in dendrimers **F1N3** and **F2N3**, and similar effects were not observed in the cyclic voltammetric behavior of dendrimers having smaller Newkome dendrons. The moderate attenuation of the electrochemical kinetics in going from our previously investigated **EtN3** dendrimer to **F1N3** and **F2N3** probably results from the increase in the overall dendrimer size and, perhaps, is also related to the modest contribution of the Fréchet dendrons toward the complete encapsulation of the viologen residue.

We also measured the diffusion coefficients (D_o) of these dendrimers using pulse gradient stimulated echo (PGSE) NMR techniques.[12] The values, measured in a 50:50 (v/v) mixture of deuterated DCM and ACN, are given in Table 2. In general terms, the D_o values decrease with increasing molecular weight, as expected. However, dendrimers **F1N3** and **F2N3** exhibit essentially identical D_o values, suggesting that their overall diffusivity is essentially controlled by the large Newkome dendron. It is important to point out that any attempt to estimate hydrodynamic radii using the Stokes−Einstein equation would be seriously flawed as these dendrimers have shapes that depart considerably from spherical or ellipsoidal.[13] We utilized the D_o

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TABLE 2. Molecular Weights, Diffusion Coefficients (D_o), Voltammetric Peak-to-Peak Splittings (ΔE_p^1 and ΔE_p^2), and Standard Rate Constants ($k^{\circ 1}$ and $k^{\circ 2}$) for the Two One-Electron Reductions of the Viologen Residue in FnNn Dendrimers at 25 °C

	F1N1	F2N1	F2N2	F1N3	F2N3
MW[a]	1262	1671	2711	5359	5784
D_o ($\times 10^6$ cm^2/s)[b]	7.78	6.84	6.02	4.16	4.19
ΔE_p^1 (mV)[c]	61	66	68	81	NA
ΔE_p^2 (mV)[c]	63	62	65	65	107
$k^{\circ 1}$ (cm/s)[d]	rev.	0.004	0.003	0.001	n.m.
$k^{\circ 2}$ (cm/s)[d]	rev.	rev.	rev.	0.004	0.0004

[a] As hexafluorophosphate salts. [b] In 50:50 (v/v) CD_2Cl_2–CD_3CN. Maximum standard deviation: 0.3×10^{-6} cm^2/s. [c] Measured at 0.1 V s^{-1} in 50:50 (v/v) CH_2Cl_2–CH_3CN also containing 0.1 M TBAPF$_6$. [d] In 50:50 (v/v) CH_2Cl_2–CH_3CN also containing 0.1 M TBAPF$_6$. Error margin: ±25%.

values measured in the PGSE NMR experiments, along with the peak-to-peak potential splittings (ΔE_p) measured in cyclic voltammetry to estimate the standard rate constants (k°) for heterogeneous electron transfer using the Nicholson method.[14] These data are also given in Table 2. The collected values show the expected tendency to attenuated rates of electron transfer as the dendrimer size increases. Not surprisingly, dendrimers **F1N1**, **F2N1** and **F2N2** exhibit essentially reversible behavior under the conditions of our experiments. These are relatively small dendrimers and viologen core macromolecules are known to maintain relatively fast electron transfer rates at molecular sizes larger than other core redox dendrimers.[5e] However, the voltammetric behavior of **F1N3** and **F2N3** exhibits measurably slower electrochemical kinetics. These are the largest molecular weight viologen dendrimers ever studied by our group, and thus, the loss of electrochemical reversibility is to be expected.

Conclusions

The structures of the **FnNn** dendrimers prepared and characterized in this work are modular in the sense that each dendrimer has three well-defined regions: (i) a Fréchet dendron, (ii) a redox-active viologen residue, and (iii) a Newkome dendron linked through a five-methylene tether. The half-wave potentials measured for each of the two consecutive one-electron reductions of the viologen core are sensitive to growth of the adjacent dendrons. Clearly, growth of the Newkome dendron leads to pronounced half-wave potential shifts to more negative values. In contrast, growth of the Fréchet dendron has a very minor direct influence on the viologen potential values, but it does temper the potential shifts originating from growth at the other molecular end (Newkome dendron). These results agree with data previously reported by our group on the rates of space filling and relative inner phase polarities of these two important dendron families.[3a,5e] Finally, compounds **F1N3** and **F2N3** are the two largest core viologen dendrimers ever reported by our group and show quasi-reversible voltammetric behavior under the same conditions in which all previously reported viologen core dendrimers are fully reversible.

Experimental Section

Materials. All chemicals and solvents were obtained from commercial sources and used without further purification.

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Synthesis. The Fréchet bromide[6] and Newkome amine[7] dendritic building blocks were prepared following literature procedures. The acid-functionalized viologen core (acid **1**) was synthesized as previously reported by our group.[5e] Quaternization of the free nitrogen of **1** with each of the Fréchet bromide dendrons also followed our previously reported procedures.[5e]

Synthesis of F1N1. The Fréchet-dendronized viologen acid F1 (400 mg, 0.463 mmol), Behera's amine N1 (213.6 mg, 0.514 mmol), O-(7-azabenzotriazol-1-yl)-N,N,N′,N′-tetramethyluronium hexafluorophosphate (n-HATU, 195.2 mg, 0.514 mmol), and 1,8-bis(dimethylamino)naphthalene (Proton Sponge, 110.2 mg, 0.514 mmol) were stirred in 3 mL of dry DMF for 12 h under N_2. The solution was concentrated under vacuum, diluted with 20 mL of EtOAc, and then extracted with 1 M NH_4Cl (2 × 10 mL) and brine (2 × 10 mL). The organic layer was concentrated and loaded into a chromatographic column (SiO_2) and first eluted with EtOAc followed by 60:40 (v/v) mixture of acetone and 7:2:1 MeOH/2 M NH_4Cl/CH_3NO_2. The organic solvents in the combined fractions were removed under vacuum. The oily residue was dissolved in a 1:1 H_2O/ethyl acetate mixture and extracted three times with ethyl acetate. The organic layers were combined and after evaporation of the solvent, the oily residue was first dissolved in acetone, followed by a saturated solution of NH_4PF_6 in 2:1 acetone/H_2O. The solution was stirred for 30 min before gentle removal of the acetone under vacuum. The remaining oily suspension was extracted with EtOAc (2 × 10 mL). The combined extracts were dried over anhydrous Na_2SO_4 and the organic solvent was evaporated. Residual solvent was washed with CH_2Cl_2 to afford the viologen dendrimer as pale yellow solid after evaporation. The final product was purified by washing with hexanes and dried under vacuum overnight to get ~80 mg of pure F1N1 (13.7% yield).

The same procedure was used for **F2N1**, **F2N2**, **F2N3**, and **F1N3** (using the appropriate Fréchet and Newkome dendrons). **F1N1** and **F2N1** were highly hygroscopic, **F2N2** was moderately hydroscopic, while **F1N3** and **F2N3** were slightly hydroscopic. The isolated yields for all these dendrimers were in the range 10−14%.

F1N1. ^{1}H NMR (400 MHz, CD_3CN): 1.38 (27H, s), 1.6 (2H, m), 1.85 (6H, t), 2.05 (4H,m), 2.1 (8H, t), 4.64 (2H, t), 5.09 (4H, s), 5.70 (2H, s), 5.91 (1H, s), 6.71 (3H, ds), 7.3−7.4 (10H, m), 8.4 (4H, d), 8.9 (4H, dd). ^{13}C NMR (100 MHz, CD_3CN): 25.4, 26.2, 28.7, 30.6, 30.7, 31.8, 37.0, 58.6, 61.4, 63.1, 66.0, 71.4, 81.3, 104.4, 109.8, 128.6, 128.7, 129.1, 130.0, 136.1, 138.1, 146.9, 162.1, 172.1, 173.5, 174.0. FAB-MS: m/z 972 [M − 2PF$_6$]$^+$.

F2N1. ^{1}H NMR (400 MHz, CD_2Cl_2): 1.39 (27H, s), 1.44 (2H, m), 1.59 (2H, m), 1.84 (6H, t), 2.05 (2H, m), 2.16 (8H, t), 4.37 (2H, t), 4.9−4.94 (12H, ds), 5.46 (2H, s), 5.88 (1H, s), 6.5 (2H, s), 6.59−6.63 (7H, ds), 7.22−7.36 (20H, m), 8.2 (4H, d), 8.8 (4H, dd). ^{13}C NMR (100 MHz, CD_2Cl_2): 28.4, 30.8, 31.1, 71.2, 81.7, 103.1, 107.5, 128.6, 128.8, 129.1, 129.2, 138.6, 147.2, 162.1, 162.5, 174.2. FAB-MS: m/z 1542 [M − PF$_6$]$^+$, 1396 [M − 2PF$_6$]$^+$ (reduced viologen).

F2N2. ^{1}H NMR (400 MHz, CD_3CN): 1.39 (81H, s), 1.6 (4H, m), 1.82 (28H, t), 2.1 (26H, t), 4.67 (2H, t), 5.04−5.09 (12H, ds), 5.71 (2H, s), 6.03 (4H, s), 6.57 (4H, s), 6.65 (3H, s), 6.68 (2H, s), 7.32−7.41 (20 H, m), 8.41 (4H, d), 8.99 (4H, dd). ^{13}C NMR (100 MHz, CD_3CN): 24.7, 25.7, 28.8, 30.8, 32.3, 32.4, 58.6, 59.1, 71.17, 71.22, 81.3, 102.9, 108.0, 109.9, 110.0, 128.7, 128.8, 129.1, 129.2, 129.4, 129.6, 129.96, 130.03, 136.1, 138.6, 161.5, 161.9, 173.6, 174.0. MALDI-TOF: m/z 2565 [M − PF$_6$]$^+$, 2420 [M − 2PF$_6$]$^+$ (reduced viologen).

F1N3. ^{1}H NMR (400 MHz, CD_2Cl_2): 1.41 (243H, s), 1.91 (84H, m), 2.14 (80H, t), 4.74 (2H, t), 5.05 (4H, s), 5.81 (2H, s), 6.68 (1H, s) 6.74 (2H, d), 7.39 (10H, m), 8.62 (4H, t), 9.07 (4H, t). ^{13}C NMR (100 MHz, CD_2Cl_2): 24.4, 28.4, 30.3, 30.4, 31.4, 31.6, 31.7, 58.3, 58.4, 68.5, 70.9, 81.4, 81.5, 108.9, 128.2, 128.7, 129.1, 129.3, 129.5, 137.0, 146.0, 146.1, 173.85, 173.93, 174.4, 174.6. MALDI-TOF: m/z 5071 [M − 2PF$_6$]$^+$ (reduced viologen).

F2N3. ^{1}H NMR (400 MHz, CD_2Cl_2): 1.41 (243H, s), 1.90 (84H, t), 2.14 (80H, t), 4.68 (2H, t), 5.00 (4H, s), 5.02 (8H, s), 5.78 (2H,

s), 6.55 (3H, t), 6.66 (6H, ds), 7.31−7.41 (20H, m), 8.50 (4H, m), 8.94−8.99 (4H, m). ^{13}C NMR (100 MHz, CD_2Cl_2): 23.6, 24.4, 28.4, 29.6, 30.4, 31.0, 32.6, 39.4, 58.5, 68.6, 70.7, 81.7, 102.1, 107.1, 128.2, 128.6, 128.8, 129.1, 129.4, 129.6, 131.5, 137.6, 139.6, 160.8, 161.5, 168.2, 174.2, 174.9, 175.1. MALDI-TOF: *m/z* 5498 [M − 2PF$_6$]$^+$ (reduced viologen).

Electrochemical Experiments. The voltammetric experiments were recorded using a single-compartment cell fitted with a glassy carbon working electrode (0.071 cm^2), a platinum auxiliary electrode, and a Ag/AgCl reference electrode. The working electrode was polished immediately before the experiments using a water−alumina (0.050 μm) slurry on a felt surface. The solution was thoroughly deoxygenated with high purity nitrogen, which was previously saturated with the solvent used in the electrochemical cell in order to avoid its evaporation while purging with nitrogen gas.

NMR Determination of Diffusion Coefficients. The diffusion coefficients of the dendrimers were obtained using PGSE NMR techniques.[12] The gradient strength was calibrated by using the residual HDO peak in D_2O samples. We recorded a minimum of seven data points per dendrimer with variable applied gradients, causing the monitored resonance to show between 10−90% of the intensity recorded in the absence of any applied gradient. The resulting data were reproducible from sample to sample. The standard deviation did not exceed 0.3×10^{-6} cm^2/s in any of our measurements.

Supporting Information Available: Spectroscopic characterization data for **FnNn** dendrimers. This material is available free of charge via the Internet at http://pubs.acs.org.

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