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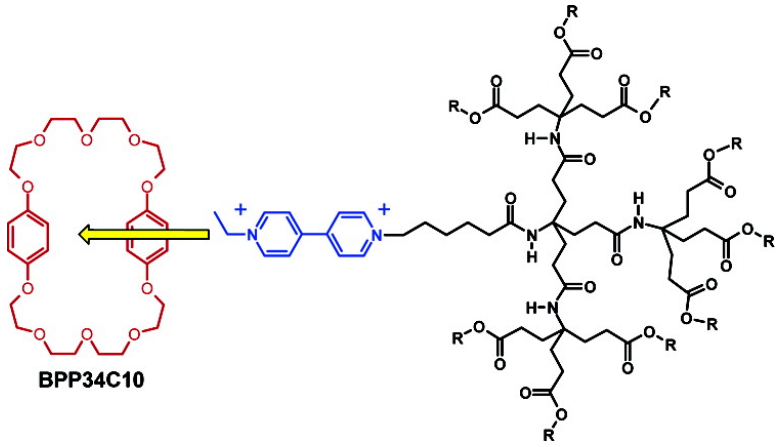

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Electrochemical and Guest Binding Properties of Fréchet- and Newkome-Type Dendrimers with a Single Viologen Unit Located at Their Apical Positions

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Abstract: Several new series of dendrimers containing a single redox-active 4,4′-bipyridinium (viologen) residue were synthesized and characterized. In these dendrimers, the viologen group is covalently attached to the apical position of a Newkome- or Fréchet-type dendron, ranging in size from first to third generation of growth. The half-wave potentials corresponding to the two consecutive one-electron reductions of the viologen residue are affected by the size of the dendritic component. The size effects are more pronounced in the Newkome-type dendrimers and seem to result from the polarity contrast between the microenvironments provided by the solution and the internal phase of the dendrimer. Unlike in many other dendrimers having a redox-active core, the voltammetric behavior remains fast (reversible) even in third generation dendrimers. Pulse gradient stimulated echo NMR diffusion coefficient measurements on the Newkome-type dendrimers reveal that their hydrodynamic radii are relatively invariant in solvents of widely different polarities (dichloromethane to dimethyl sulfoxide). The host−guest binding interactions between the viologen residue in these dendrimers and the crown ether host bis-*p*-phenylene-34-crown-8 were also investigated. While in Newkome-type dendrimers the growth of the dendron caused a substantial attenuation of the binding constant values, this size effect was not observed in the Fréchet-type dendrimers. These electrochemical and binding measurements underscore some of the structural differences between these two common types of dendritic architectures.

Introduction

Functionalization of dendrimers with redox-active groups has received considerable attention because the resulting macromolecules show interesting properties in electron-transfer reactions.[1,2] For instance, it is possible to position redox groups on the periphery of dendrimers, affording structures capable of multiple electron-transfer events.[3−14] More relevant to the work reported here, the placement of redox groups inside the dendrimer core gives rise to structures with partially or completely buried redox centers,[15−26] which may show orientation effects on their electron-transfer reactions,[1] in analogy to some redox proteins. In general terms, dendrimers with a redox-active core present decreasing rates of heterogeneous electron transfer with increasing dendrimer size.[27,28] The progressive

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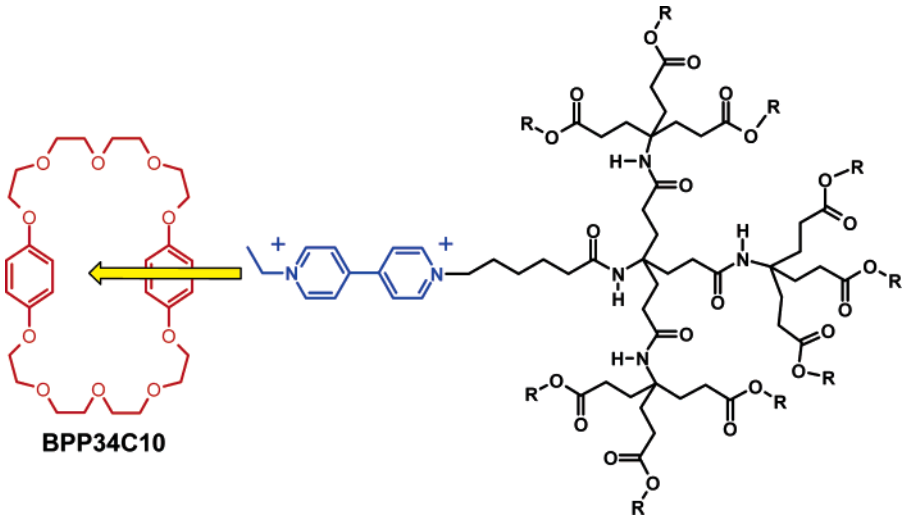
Scheme 1. Binding of a Newkome-Type Dendrimer Guest by the BPP34C10 Crown Host



encapsulation of the redox group by a growing dendritic framework tends to increase the average distance between the redox center and the electrode surface, leading to decreased electron-transfer rates. Recently, our group[29] and Balzani's[30] reported that Fréchet-type dendrimers with a single 4,4′-bipyridinium (viologen) unit at their cores exhibit fast (reversible) voltammetric behavior from the first to the third generation of growth. Our group has also reported preliminary results with a different series of dendrimers containing a single viologen unit covalently attached to a Newkome-type dendron.[24] Again, these dendrimers show reversible electrochemistry from the first to the third generation of growth.

Many of the dendrimers prepared in our group contain a redox or fluorescent group attached to the apical position of Newkome-type dendrons.[31,32] This general design allows the investigation of host−guest binding interactions between the guest residue attached to the apical position of the dendrimer and freely diffusing hosts.[33] The thermodynamic stability of the host−guest complexes formed in this way is affected by dendrimer growth. Here, we report on the preparation and characterization of several series of viologen-containing dendrimers, their electrochemical properties, and their binding interactions with the crown ether host bis-*p*-phenylene-34-crown-10 (BPP34C10, see Scheme 1 for structure). We have prepared and surveyed three series of dendrimers containing a viologen group attached to Newkome-type dendrons (dendrimers N1−N9 in Chart 1). The three dendrimer series differ on the terminal peripheral groups: *tert*-butyl esters (N1−N3), carboxylic acids (N4−N6), and methyl esters (N7−N9). We have also prepared two series of dendrimers having a viologen residue attached to Fréchet-type dendrons (dendrimers F1−F6 in Chart 2). These two dendrimer series differ on the structure of the terminal group attached to the other end of the viologen moiety. The comparison of the electrochemical and BPP34C10 binding data obtained with these dendrimers allows us to draw some conclusions on the encapsulating properties of both types of dendrons.

Results and Discussion

Synthesis. The synthesis of dendrimers N1−N3 has been described already.[24] Dendrimers N4−N6 were prepared by hydrolysis of the *tert*-butyl esters on the periphery of N1−N3. Hydrolysis with formic acid proceeded easily and led to N4−N6 in high yields (>90%). The methyl ester dendrimers N7−N9 were prepared by exhaustive esterification of N4−N6 with excess methanol. The synthesis of the Fréchet-type dendrimers F1−F6 first requires the monoquaternization of 4,4′-bipyridine with 4-bromomethylphenylacetic acid or 6-bromohexanoic acid in refluxing acetonitrile, followed by treatment of the monoquaternized acid with the known dendritic bromides (prepared according to the procedure of Fréchet and Hawker[34]). Dendrimers F1−F6 were finally isolated in good yields (50−90%) as their hexafluorophosphate salts, after counterion exchange with NH_4PF_6. All dendrimers were characterized using ^1H and ^{13}C NMR spectroscopy, as well as MALDI-TOF or FAB mass spectrometry.

Diffusion Coefficients. The technique of pulse gradient stimulated echo (PGSE) NMR[35,36] was extremely useful to determine the diffusion coefficients (D_o) of these dendrimers. The resulting values are listed in Table 1. When the solubility properties allow it, D_o values were measured in a range of solvents.

The D_o values listed in Table 1 are consistent with the relative dendrimer sizes. For instance, within each dendrimer series the diffusion coefficient decreases monotonically with increasing generation, since higher molecular mass dendrimers are expected to diffuse more slowly, as their hydrodynamic radius increases. Generation by generation, the diffusion coefficients for dendrimers N7−N9 tend to be slightly larger than the corresponding values in the same solvent for the series N1−N3, as anticipated from the higher molecular mass of the latter dendrimer series (*tert*-butyl vs methyl ester groups on their peripheries). Unfortunately, the same comparison with the carboxylic acid series

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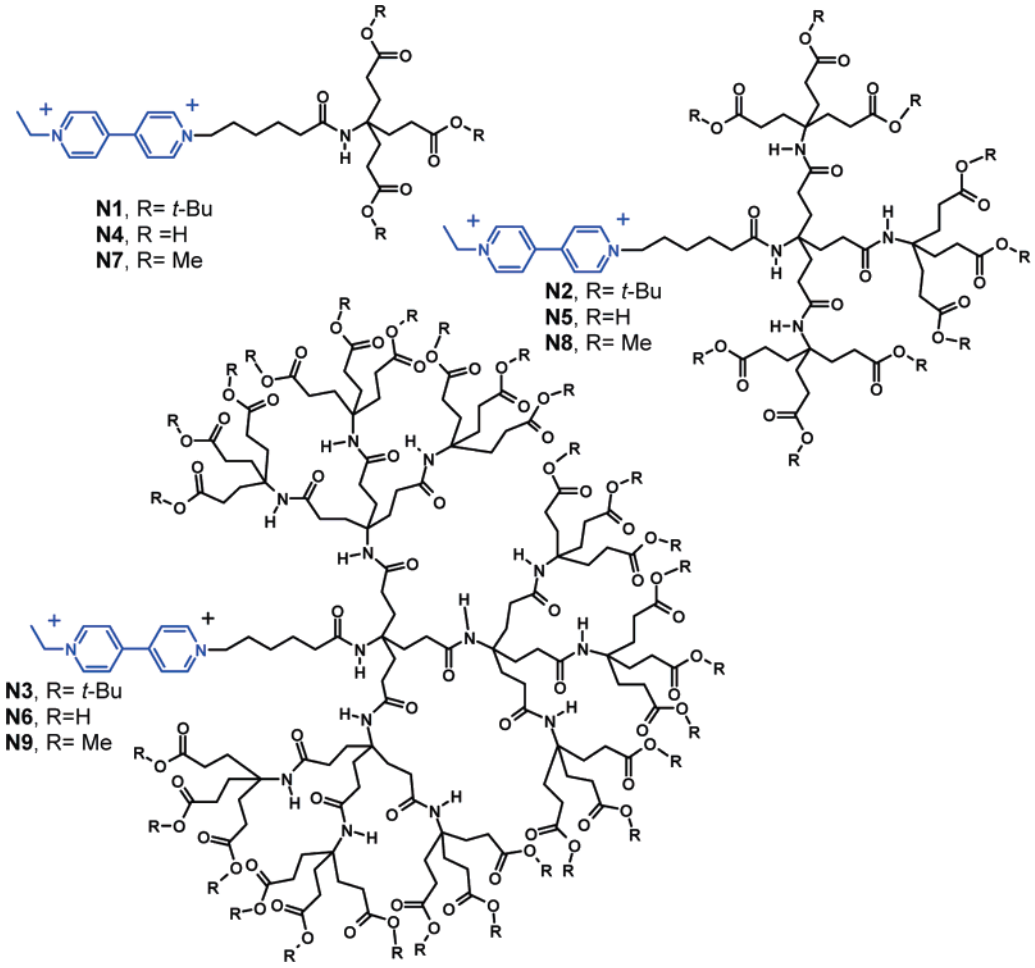
Chart 1. Structures of the Newkome-Type Dendrimers



N4−N6 is not possible since these dendrimers are soluble only in aqueous media. The two series of Fréchet-type dendrimers show identical D_o values within error margins, reflecting the similarity of their molecular masses and structures.

The series of dendrimers N1−N3 shows good solubility in a variety of solvents, which permitted us to correlate their diffusion coefficients with the viscosity of the solvent. According to the Stokes−Einstein equation, the D_o value is proportional to the reciprocal solvent viscosity (η^{-1}):

$$D_o = kT\eta^{-1}/(6\pi r) \qquad (1)$$

where r is the hydrodynamic radius of the diffusing species, k is Boltzmann's constant, and T is the absolute temperature. Figure 1 shows plots obtained using the experimental D_o values for N1−N3 in four solvents. The D_o vs η^{-1} plots are linear for N1, N2, and N3, revealing that each of these dendrimers maintains a reasonably constant hydrodynamic radius in all the solvents surveyed. From the slope of these plots we determined r values of 1.0, 1.3, and 1.8 nm for dendrimers N1, N2, and N3, respectively. This finding suggests that the dendrimers do not undergo extensive conformational changes from solvent to solvent. At least, the conformational changes are not significant enough to cause pronounced changes in the hydrodynamic radii. Similar results were obtained with dendrimers N6−N9, but the relevance of this particular data set was diminished by their limited solubility in CH_2Cl_2.

Electrochemistry. Viologen (V^{2+}) derivatives usually undergo two consecutive one-electron reductions, both chemically and electrochemically reversible.[37] The first reduction leads to the cation radical species (V^{+}), and the second reduction yields the fully neutral residue (V). Predictably, the cathodic voltammetric behavior of all dendrimers investigated in this work was dominated by the electrochemistry of the viologen residue, and two reversible voltammetric waves were recorded in each case. The corresponding half-wave potentials ($E_{1/2}$) are listed in Table 2.

The values of the half-wave potentials reflect the relative stabilities of the various oxidation states of the dendrimer viologen units. It is particularly interesting to monitor the variation of the half-wave potentials as a function of generation in each dendrimer series. For instance, in dichloromethane solution the series N1−N3 shows decreasing half-wave potentials (shifting to more negative values) with increasing dendrimer molecular mass. This potential trend can be rationalized as the result of increased thermodynamic hindrance for the reduction processes. In other words, as the dendrimer grows and starts to surround the viologen moiety, it creates a more polar microenvironment, which disfavors electrochemical reduction (loss of positive charge) on the redox-active center. The high density of amide groups inside the structure of Newkome-type den-

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Chart 2. Structures of the Fréchet-Type Dendrimers

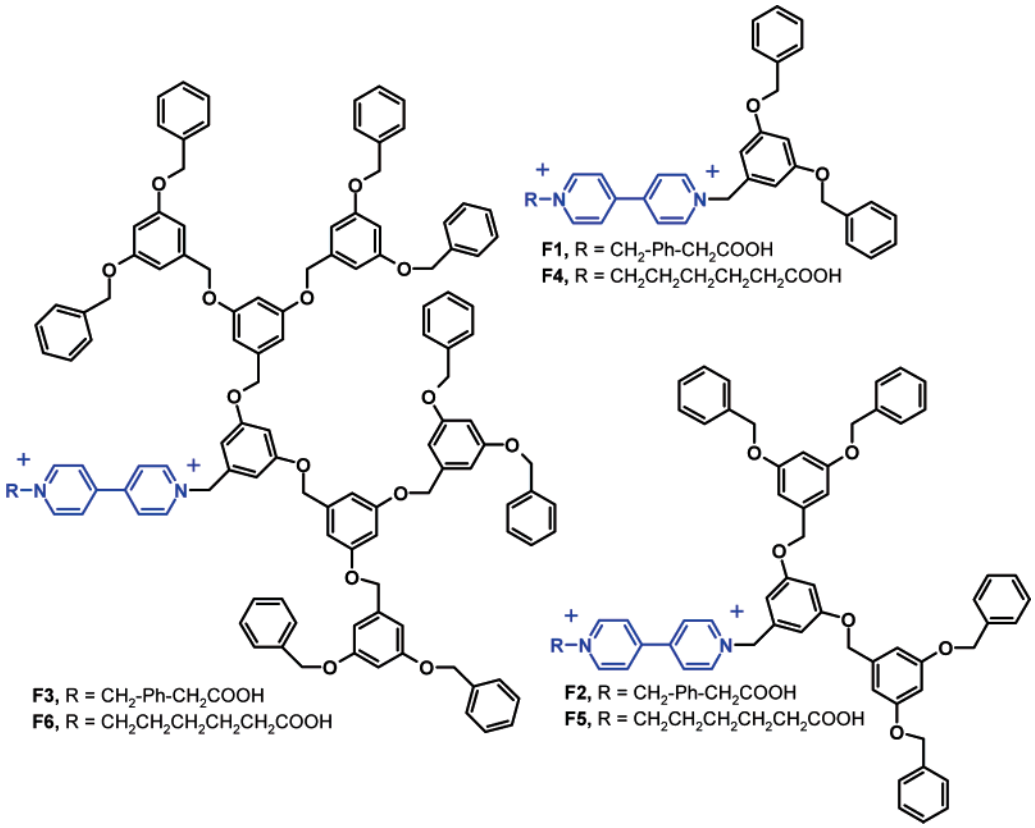

Table 1. Diffusion Coefficients (D_o, in cm^2/s) of Viologen-Containing Dendrimers As Measured with PGSE NMR at 25 °C

(A) Newkome Dendrimers[a]

solvent	N1 (988)	N2 (2012)	N3 (5085)	N7 (856)	N8 (1615)	N9 (3895)
CD_2Cl_2	8.5×10^{-6}	6.7×10^{-6}	4.9×10^{-6}	nm[b]	nm	nm
THF-d_8	6.6×10^{-6}	5.4×10^{-6}	3.9×10^{-6}	7.2×10^{-6}	4.8×10^{-6}	3.8×10^{-6}
CD_3CN	1.0×10^{-5}	7.9×10^{-6}	5.5×10^{-6}	12×10^{-6}	8.4×10^{-6}	5.8×10^{-6}
DMSO-d_6	1.7×10^{-6}	1.2×10^{-6}	0.87×10^{-6}	1.8×10^{-6}	1.3×10^{-6}	0.9×10^{-6}

solvent	N4 (820)	N5 (1507)	N6 (3570)
D_2O	4.0×10^{-6}	2.6×10^{-6}	1.9×10^{-6}

(B) Fréchet Dendrimers[a]

solvent	F1 (899)	F2 (1322)	F3 (2172)	F4 (865)	F5 (1289)	F6 (2138)
CD_3CN	11×10^{-6}	8.7×10^{-6}	7.0×10^{-6}	11×10^{-6}	8.7×10^{-6}	7.0×10^{-6}

[a] Molecular weights are given in parentheses. [b] Not measured due to poor solubility.

drimers is consistent with this finding, and it is reasonable to conclude that the environment created by the inner phase of these dendrimers is more polar than the environment afforded by the dichloromethane solution.

Both Newkome dendrimer series (N1−N3 and N7−N9) exhibit similar half-wave potential trends in THF and to a lesser extent in acetonitrile, suggesting that the amide-rich interior phase of the dendrimers is more polar than the environment offered by these solutions. However, this potential vs size trend is no longer detected in DMSO; in fact, series N1−N3 offers evidence for a reversal in the trend. Therefore, we conclude from our voltammetric measurements that the effective polarity of the inner phase of these Newkome-type dendrimers is intermediate between those of acetonitrile and DMSO solutions. Furthermore, the potential trends are similar in dendrimers N1−N3 and N7−N9, suggesting that peripheral crowding is not a major factor determining the potential values in these dendrimers.

Although they are not shown in Table 2, we also determined the half-wave potentials for the reduction of dendrimers N4−N6 in aqueous media (also containing 0.10 M NaCl and 0.050 M Tris, pH 7.2). The half-wave potentials for the first reduction process ($V^{2+} \rightarrow V^{+}$) were −0.660, −0.659, and −0.626 V vs Ag/AgCl, respectively. In this case, the $E_{1/2}$ values increase with dendrimer size, suggesting that the aqueous solution is more polar than the dendrimer interior phase. Thus, dendrimer growth favors thermodynamically the reduction process (loss of positive charge). This finding is in general agreement with the half-wave potential trends reported in Table 2. Similar trends were

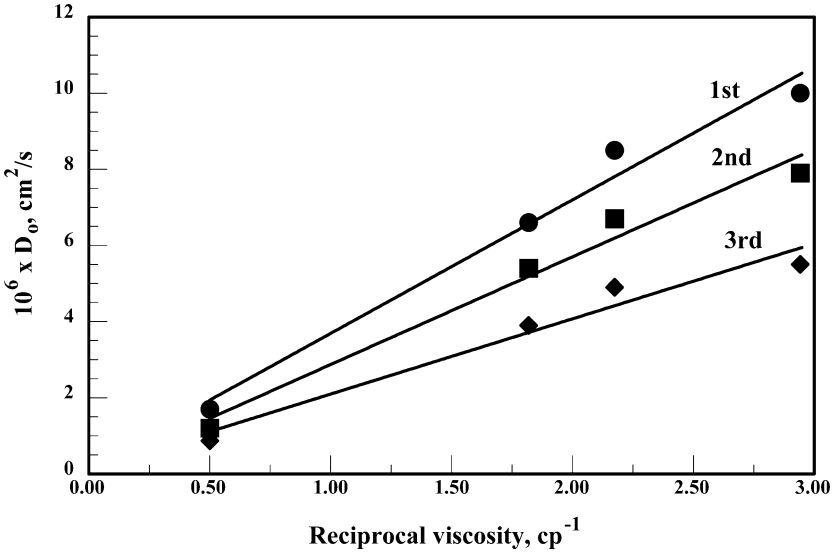

Figure 1. Diffusion coefficients of dendrimers N1−N3 as a function of the reciprocal viscosity of the solvent. The diffusion coefficients were measured by PGSE NMR techniques at 25 °C in CD_2Cl_2, CD_3CN, THF-d_8, and DMSO-d_6.

Table 2. Half-Wave Potentials ($E^1_{1/2}$ and $E^2_{1/2}$, in V vs Ag/AgCl) for Viologen-Containing Dendrimers at 25 °C in Several Organic Solvents Also Containing 0.2 M $TBAPF_6$ as the Supporting Electrolyte

(A) Newkome Dendrimers

solvent		N1	N2	N3	N7	N8	N9
CH_2Cl_2	$E^1_{1/2}$	−0.28	−0.34	−0.42	nm[a]	nm	nm
	$E^2_{1/2}$	−0.81	−0.84	−0.87	nm	nm	nm
THF	$E^1_{1/2}$	−0.31	−0.32	−0.37	−0.31	−0.33	−0.36
	$E^2_{1/2}$	−0.72	−0.73	−0.76	−0.72	−0.75	−0.75
CH_3CN	$E^1_{1/2}$	−0.390	−0.394	−0.421	−0.391	−0.394	−0.412
	$E^2_{1/2}$	−0.817	−0.821	−0.838	−0.817	−0.819	−0.823
DMSO	$E^1_{1/2}$	−0.390	−0.386	−0.375	−0.414	−0.408	−0.408
	$E^2_{1/2}$	−0.754	−0.756	−0.752	−0.780	−0.776	−0.778

(B) Fréchet Dendrimers

solvent		F1	F2	F3	F4	F5	F6
CH_3CN	$E^1_{1/2}$	−0.307	−0.297	−0.291	−0.343	−0.336	−0.330
	$E^2_{1/2}$	nm	nm	nm	−0.761	−0.768	−0.768

[a] Not measured due to solubility problems.

observed with the half-wave potentials corresponding to the second one-electron reduction of the viologen unit.

Finally, the more limited solubility of the Fréchet-type dendrimers did not allow us to determine their half-wave potentials in various solvents. However, their voltammetric behavior in acetonitrile clearly differs from that observed with the N1−N3 and N7−N9 series. Both dendrimer series F1−F3 and F4−F6 show small potential changes as a function of generation. However, both series show a slight but measurable trend to higher half-wave potentials (less negative values) with dendrimer growth, which is consistent with the interior phase of these dendrimers being less polar than the environment in acetonitrile solutions. This finding underscores the differences in the composition of the interior phases of the Newkome- and Fréchet-type dendrimers. The amide bonds within the former dendrimers are considerably more polar than the aromatic ether functional groups found in the latter.

The increasing popularity of PGSE NMR techniques to determine diffusion coefficients led us to ask how these D_o values would correlate with electrochemical current parameters which also depend on the diffusion coefficients of the electroactive species. Since cyclic voltammetric peak currents are directly proportional to the square root of the corresponding diffusion coefficients, we plotted voltammetric cathodic peak currents—measured for the first reduction of the viologen unit at constant scan rate—against $(D_o)^{1/2}$ values obtained from PGSE NMR for dendrimers N1−N3 in four different solvents (acetonitrile, dichloromethane, DMSO, and THF). The resulting plot (Supporting Information) is linear, with a correlation coefficient of 0.9860. We have constructed similar plots for other dendrimer series and obtained entirely similar results. These findings provide strong support to the idea that diffusional data obtained using these two techniques (PGSE NMR spectroscopy and voltammetry) show very good correlations despite the pronounced differences in the composition of the solutions used in both types of experiments; i.e., electrochemical experiments require a high concentration (∼0.1 M) of supporting electrolyte, while NMR experiments do not require and may not tolerate high concentrations of alkylammonium salts as supporting electrolytes. In contrast to our findings, Abruña and co-workers have found pronounced differences between D_o values measured by PGSE and voltammetric techniques on dendrimers containing multiple redox sites.[3]

A particularly important finding common to all the dendrimers surveyed in this work is that their voltammetric behavior remains reversible from first to third generation of growth at scan rates within the range 0.1−2 V/s. Figure 2 shows the cyclic voltammetric behavior of dendrimer F6 as an example, but similar results were obtained in all cases. Most dendrimers with electroactive cores show pronounced attenuation of their rates of heterogeneous electron transfer with dendrimer growth.[27,28] The dendrimers investigated here are a clear exception to this rule. We have previously reported similar findings with symmetric viologen core Fréchet dendrimers,[29] as well as with larger dendrimers having a tetrakis(viologen) cavitand core.[38] The

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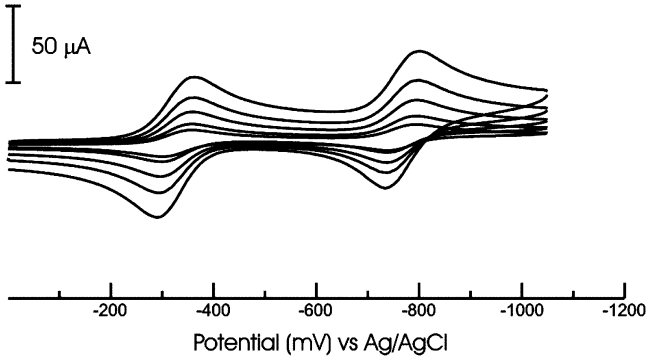

Figure 2. CV response on a glassy carbon electrode (0.071 cm^2) of a 1.0 mM solution of dendrimer F6 in acetonitrile also containing 0.2 M $TBAPF_6$. The current−potential curves shown were recorded at scan rates of 0.1, 0.2, 0.5, 1.0, and 2.0 V/s.

reasons for the reversible electrochemistry of viologen-containing dendrimers are still not completely clear. Although the electrochemical kinetics of viologens is known to be quite fast,[37] other redox subunits such as ferrocene and ruthenium complexes are also very fast, but their encapsulation within dendrimers readily leads to a pronounced decrease in their electrochemical kinetics. Why do viologen core dendrimers remain electrochemically reversible? A cogent rationalization may rely on interfacial orientation effects due to electrostatic interactions between the electrode surface and the viologen subunit. At the potentials required to electrochemically reduce these dendrimers, the electrode exhibits a negative charge density on its surface, which can then attract the positively charged viologen unit in the dendrimer, thus ensuring that the redox center will remain relatively close to the electrode surface, enhancing the rate of heterogeneous electron transfer and partially or completely attenuating the effect of dendrimer size.

Complex Formation with the Crown Ether Host BPP34C10. While the use of dendrimers as molecular hosts has attracted considerable attention, the literature contains a relatively reduced number of reports in which dendrimers act as guests in host−guest molecular recognition interactions.[33] To some extent this is a simple reflection of the large molecular weight of dendrimers and their ability to trap small molecules in their internal cavities. However, dendrimers containing binding sites accessible to freely diffusing hosts constitute interesting model systems for molecular recognition events at the surface of membranes or biological macromolecules. This biological connection has been a major motivation for our previous work on noncovalent binding interactions between β-cyclodextrin hosts and dendrimer guests containing a ferrocene[32] or dansyl[31] group as the single binding site. The interactions between the latter type of dendrimers and polyclonal anti-dansyl antibodies were also surveyed.[31] More recently, we have reported the binding interactions between the viologen residue of dendrimers N4−N6 and cucurbit[7]uril hosts.[39] In all these studies, the dendrimer guests were prepared by attachment of Newkome-type dendrons to a single ferrocene,[32] dansyl,[31] or viologen[39] group. Therefore, we decided to investigate the binding interactions between the crown ether host bis-*p*-phenylene-34-crown-10 (BPP34C10) and the viologen subunit of some of the Newkome- and Fréchet-type dendrimers reported here (see Scheme 1).

(39) Ong, W.; Kaifer, A. E. *Angew. Chem., Int. Ed.* **2003**, *42*, 2164.

Table 3. Equilibrium Association Constants[a] (L/mol) and Standard Free Energies (kcal/mol, in Parentheses) for Complex Formation between Host BPP34C10 and Viologen-Containing Guests at 25 °C

	medium	
dendrimer guest	acetone	acetonitrile
methyl viologen	560 (−3.8)	200 (−3.1)
N1	370 (−3.5)	93 (−2.7)
N2	210 (−3.2)	85 (−2.6)
N3	92 (−2.7)	NB[b]
F1	480 (−3.7)	100 (−2.7)
F2	630 (−3.8)	100 (−2.7)
F3	670 (−3.9)	85 (−2.6)
F4	420 (−3.6)	70 (−2.5)
F5	560 (−3.7)	100 (−2.7)
F6	740 (−3.9)	75 (−2.6)

[a] The error margin in the binding constants is no larger than ±12%. [b] No binding detected.

The formation of noncovalent complexes between these viologen-containing dendrimers and BPP34C10 can be easily monitored by the development of a characteristic charge-transfer absorption band in the visible region of the spectrum ($\lambda_{max} \approx$ 436 nm).[40] ^{1}H NMR spectroscopy with the N1−N3 dendrimer series reveals that the presence of the crown host leads to a pronounced upfield shift of the β aromatic protons of the viologen moiety (see Supporting Information). The fact that the largest complexation-induced NMR shifts correspond to the viologen protons clearly indicates that the viologen residue is the active binding site for complexation by the BPP34C10 crown host in all cases.

The equilibrium association constants for the formation of the noncovalent complexes between BPP34C10 and the viologen dendrimers were readily obtained by analysis of the electronic absorption data (see Supporting Information for some typical data sets). Table 3 gives the thermodynamic parameters determined for all the complexes in acetone and acetonitrile solution. Several trends are clearly evident in the data. First, all the complexes exhibit higher binding constants in acetone solution than in acetonitrile solution. This finding reflects the ion−dipole nature of the main intermolecular forces that hold the complex together. The more polar acetonitrile molecules interfere more effectively with the attractive forces between the oxygen atoms in the crown and the positive charges on the viologen unit. Second, the stability of the complexes between BPP34C10 and the Newkome-type dendrimers N1−N3 is very sensitive to dendrimer growth. In fact, the corresponding binding constants decrease as the size of the attached dendron grows. With the third generation dendrimer (N3) no binding was detected in acetonitrile, while a small binding constant of 92 L/mol was measured in acetone solution. A five-methylene tether connects the viologen group to the focal point of the Newkome dendrons in N1−N3. No such tether exists in the Fréchet-type dendrimers shown in Chart 2. Despite the closer proximity of the viologen group to the dendron, and in marked contrast to the behavior of the Newkome-type dendrimers, the equilibrium association constants determined with both series of Fréchet-type dendrimers, F1−F3 and F4−F6, *do not decrease at all with dendrimer size*. If anything, dendrimer growth results

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in small gains in complex stability with these two series of macromolecules. No significant differences in the binding constants are observed between the two series of Fréchet-type dendrimers, which differ in the structure of the substituents connected to the viologen moiety on the opposite side to the dendron. The lack of effect on the overall stability of the complex suggests that the terminal −COOH group does not influence the binding in a significant way. In fact, both series of Fréchet-type dendrimers were also found to have very similar diffusion coefficients and electrochemical properties, as discussed before.

The structure of the complex between BPP34C10 and methyl viologen is well known.[41,42] Briefly, the crown's oxygen atoms interact with the two positive charges on the viologen while the two π-donor hydroquinol units on the host develop charge-transfer interactions with the π-acceptor bipyridinium residue. Overall, the crown host encircles the viologen group and the stability of the resulting complex is relatively modest, which allows easy interference on complex formation by steric hindrance from the growing dendritic mass. Clearly, this seems to be the case with the Newkome-type dendrimers (N1−N3). However, growth of the Fréchet-type dendrons has no negative effects on complex stability. The more rigid character of the polyaryl ether (Fréchet) dendrons, built around the 1,3,5 substitution pattern on the phenyl ring,[43] leads to wedge-like dendritic shapes, which afford less effective encapsulation of the viologen sites than the more flexible Newkome-type dendrons. Although the series of dendrimers reported here show some significant structural differences (for instance, the viologen−dendron tether length), the specific trends observed in the association equilibrium constants measured with the host BPP34C10 still allow a very reasonable comparison of the encapsulating properties of both types of dendrons.

In conclusion, judging from the binding data in Table 3, at the same generation of growth, Newkome-type dendrons provide a larger, more flexible dendritic mass, which affords faster encapsulation effects on functional groups covalently attached to the apical position. The variation of the electrochemical reduction potentials with dendrimer size is more pronounced in the case of Newkome-type dendrimers, which exhibit a more polar interior phase owing to the presence of amide groups in their frameworks. The inner phase of Fréchet-type dendrimers appears to be less polar, as evidenced form the voltammetric data in acetonitrile solution. Overall, the electrochemical, PGSE NMR diffusional, and binding data reported in this work illustrate some of the differences between these two important classes of dendrimer architectures.

Experimental Section

Synthesis of Newkome-Type Dendrimers. All reagents were obtained from commercial suppliers and typically used without further purification. Deuterated solvents were purchased from Cambridge Isotope Laboratories (Andover, MA). ^{1}H and ^{13}C NMR spectra were obtained in a Bruker Avance 400 MHz spectrometer. FAB mass spectra were recorded in a VG Trio 2000 instrument, and MALDI-TOF mass spectra were obtained in a Bruker Biflex IV.

Synthesis of 6-(1′-Ethyl-[4,4′]bipyridinyl-1-yl)hexanoic Acid) (1). The monoquaternized precursor 1-ethyl-4-(4′-pyridyl)pyridinium[44] (600 mg, 2.26 mmol) and 6-bromohexanoic acid (2.3 g, 11.8 mmol) were refluxed in CH_3CN (50 mL) for 12 h. The yellow precipitate was filtered and washed with acetone (2 × 50 mL) to remove excess 6-bromohexanoic acid. The precipitate was further stirred in boiling $CHCl_3$ (3 × 100 mL) to remove residual monoquaternized product, washed with acetone (50 mL), and dried under vacuum to afford the viologen acid **1** as its dibromide salt. Yield: 738 mg (78%). ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.43 (d, 2H, d 2H), 8.82 (d, 4H), 4.74 (q, 4H), 4.71 (t, 4H), 2.24 (t, 2H), 1.98 (m, 2H), 1.61 (t, 3H), 1.58 (m, 2H), 1.34 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 36.4, 43.9, 45.0, 50.6, 53.4, 76.5, 80.6, 146.7, 165.7, 165.9, 168.5, 194.4. FAB-MS: *m/z* 316 (M − 2Br)$^{\bullet+}$.

Synthesis of Dendrimer N1. Viologen acid **1** (1.00 g, 2.17 mmol), Behera's amine[45] (1.00 g, 2.41 mmol), *n*-HATU (915 mg, 2.41 mmol), and 1,8-bis(dimethylamino)naphthalene, *N,N,N′,N′*-tetramethyl-1,8-naphthalenediamine (Proton Sponge, 980 mg, 4.57 mmol), were stirred in dry DMF (15 mL) for 12 h under N_2. The solution was concentrated under vacuum, diluted with 100 mL of EtOAc, and then extracted with 1 M NH_4Cl (2 × 50 mL) and brine (2 × 50 mL). The organic layer was concentrated and loaded into a chromatographic column (SiO_2, 60:40 acetone/(7:2:1 MeOH:2 M NH_4Cl:CH_3NO_2)). The organic solvents on the combined fractions were removed under vacuum, and the remaining aqueous solution was concentrated to about 3 mL before precipitating the viologen dendrimer with saturated aqueous NH_4PF_6. The precipitate was filtered, washed with cold H_2O (2 × 15 mL), and dried under vacuum to yield N1 as an off-white solid. Yield: 1.75 g (81%). ^{1}H NMR (400 MHz, acetonitrile-d_3): δ 8.92 (d, 2H, d, 2H), 8.38 (d, 4H), 5.86 (s, 1H), 4.66 (q, 4H), 4.64 (t, 4H), 2.14 (t, 2H), 2.12 (t, 6H), 2.03 (m, 2H), 1.86 (t, 6H), 1.66 (t, 3H), 1.62 (m, 2H), 1.40 (t, 2H, s, 27H). ^{13}C NMR (100 MHz, acetonitrile-d_3): δ 8.92 173.5, 172.9, 150.8, 146.6, 146.3, 128.1, 80.8, 62.6, 58.6, 58.1, 36.6, 31.4, 30.3, 30.2, 28.2, 25.8, 25.0, 16.5. FAB-MS: *m/z* 698 (M − 2PF_6)$^{\bullet+}$, 649 ((M − 2PF_6)$^{\bullet+}$)/2. UV−vis (CH_3CN): ϵ_{260nm} = 23 800 M^{-1} cm^{-1}.

Synthesis of Dendrimers N2 and N3. The same procedure was used as for N1 (with the appropriate building block second or third generation analogues of Behera's amine[32]), except the chromatographic column (SiO_2) was first eluted with EtOAc, followed by 60:40 acetone/(7:2:1 MeOH:2 M NH_4Cl:CH_3NO_2). After evaporation of the solvents, acetone was added to the oily residue, and then a saturated solution of NH_4PF_6 in 2:1 acetone:H_2O was added. The solution was stirred for 15 min further before acetone was gently removed under vacuo. The remaining oily suspension was extracted with EtOAc (2 × 10 mL), and the combined extracts were evaporated and chased with CH_2Cl_2 to afford viologen dendrimers N2 and N3. Yields: 69% N2 and 74% N3.

Dendrimer N2. ^{1}H NMR (400 MHz, acetonitrile-d_3): δ 9.03 (d, 2H), 8.95 (d, 2H), 8.48 (d, 4H), 6.54 (s, 1H), 6.01 (s, 3H), 4.70 (q, 2H, t, 2H), 2.16 (m, 2H), 2.12 (m, 24 H), 2.02 (m, 2H), 1.86 (m, 24H), 1.67 (t, 3H), 1.63, (m, 2H), 1.40 (s, 81 H, m, 2H). ^{13}C NMR (100 MHz, acetonitrile-d_3): δ 173.7, 173.3, 151.1, 150.8, 146.9, 146.5, 128.3, 81.0, 62.6, 58.8, 58.2, 36.5, 32.0, 31.3, 30.4, 28.4, 25.5, 24.5, 16.7. FAB-MS: *m/z* 1723 (M − 2PF_6)$^{\bullet+}$, 1667 (M − C$(CH_3)_3$ − 2PF_6)$^+$. UV−vis (CH_3CN): ϵ_{262nm} = 22 200 M^{-1} cm^{-1}.

Dendrimer N3. ^{1}H NMR (400 MHz, acetonitrile-d_3): δ 9.22 (d, 2H), 9.14 (d, 2H), 8.71 (d, 2H), 8.67 (d, 2H), 6.91 (s, 1H), 6.54 (s, 3H), 6.17 (s, 9H), 4.77 (q, 2H, t, 2H), 2.14 (m, 72 H), 2.05 (t, 6H), 2.0 (m, 2H), 1.87 (m, 78 H), 1.80 (m, 2H), 1.69 (t, 3H), 1.61 (m, 2H), 1.41 (s, 243 H, m, 2H). ^{13}C NMR (100 MHz, acetonitrile-d_3): δ 173.1, 172.9, 150.5, 149.9, 146.5, 145.9, 127.8, 80.3, 61.6, 58.2, 57.9, 57.6, 35.6, 31.3, 29.8, 27.9, 16.2. MALDI-TOF MS: *m/z* 4940 (M + PF_6)$^+$,

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4795 ($M - 2PF_6$)$^{\bullet+}$, 4738 ($M - C(CH_3)_3 - 2PF_6$)$^+$. UV−vis (CH_3CN): $\epsilon_{264nm} = 21\,300\ M^{-1}\ cm^{-1}$.

Synthesis of Newkome-Type Dendrimers N4, N5, and N6. The *tert*-butyl viologen dendrimer N1, N2, or N3 (200 mg) was dissolved in formic acid (10 mL), and the clear solution was stirred overnight at room temperature. Formic acid was removed under reduced pressure and chased with ethyl acetate (2 × 20 mL). The oily residue was stirred in AmberJet ion-exchange resin (Br^-) for 1 h. The resin was filtered, and the solution was freeze-dried to dryness. The resulting yellow solid was quickly washed and filtered using acetone, dried under vacuum, and stored under nitrogen (N4 was very hygroscopic, N5 was intermediately hygroscopic, and N6 was slightly hygroscopic). Yields were higher than 95%.

Dendrimer N4. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.43 (m, 4H), 8.81 (d, 4H), 7.19 (s, 1H), 4.73 (q, 2H), 4.70 (t, 2H), 2.10 (m, 8H), 1.98 (t, 2H), 1.80 (t, 6H), 1.60 (t, 3H), 1.51 (m, 2H), 1.28 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.3, 24.6, 24.9, 28.1, 29.0, 30.5, 35.4, 56.3, 56.5, 60.6, 126.6, 145.6, 145.8, 148.5, 171.8, 174.4. FAB-MS: *m/z* 530 ($M - 2Br$)$^{\bullet+}$. UV−vis (H_2O−HCOOH·NaOH buffer at pH 3.2): $\epsilon_{260nm} = 21\,100\ M^{-1}\ cm^{-1}$.

Dendrimer N5. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.41 (d, 2H), 9.37 (d, 2H), 8.79 (d, 4H), 7.24 (s, 1H), 7.22 (s, 3H), 4.71 (q, 2H), 4.68 (t, 2H), 2.11−1.95 (m, 28 H), 1.60 (m, 24 H), 1.55 (t, 3H), 1.52 (m, 2H), 1.30 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.3, 24.3, 24.7, 28.0, 29.0, 30.3, 30.7, 35.4, 56.3, 56.5, 56.9, 60.6, 126.6, 145.6, 145.7, 148.6, 171.5, 172.3, 174.4. MALDI-TOF MS: *m/z* 1217 ($M - 2Br$)$^{\bullet+}$. UV−vis (H_2O−HCOOH·NaOH buffer at pH 3.2): $\epsilon_{261nm} = 20\,900\ M^{-1}\ cm^{-1}$).

Dendrimer N6. ^{1}H NMR (400 MHz, DMSO-d_6): δ 9.36 (m, 4H), 8.77 (m, 4H), 7.39 (s, 1H), 7.22 (s, 9H), 7.18 (s, 3H), 4.72 (m, 4H), 2.10−1.61 (m, 163H), 1.51 (m, 2H). 1.22 (m, 2H). ^{13}C NMR (100 MHz, DMSO-d_6): δ 16.2, 23.9, 28.0, 29.0, 29.7, 30.3, 30.7, 30.8, 35.2, 56.4, 56.6, 56.8, 57.1, 126.6, 145.5, 145.7, 148.7, 148.8, 171.9, 172.3, 174.5. MALDI-TOF MS: *m/z* 3280 ($M - 2Br$)$^{\bullet+}$. UV−vis (H_2O−HCOOH·NaOH buffer at pH 3.2): $\epsilon_{261nm} = 20\,500\ M^{-1}\ cm^{-1}$.

Synthesis of Newkome-Type Dendrimers N7, N8, and N9. The COOH-terminated dendrimer N4, N5, or N6 and acetyl chloride (9.0, 27.0, and 81.0 equiv, respectively) were stirred in dry MeOH (7 mL) for 12 h under N_2. The solution was concentrated under vacuum. Acetone was added to the residue, and then a saturated solution of NH_4PF_6 in 2:1 acetone:H_2O was added. The solution was stirred for 15 min, and acetone was gently removed in vacuo. The remaining suspension was extracted with EtOAc (2 × 10 mL), and the combined extracts were evaporated to afford viologen dendrimers N7, N8, and N9.

Dendrimer N7. Yield: 68%. ^{1}H NMR (400 MHz, acetonitrile-d_3): δ 8.95 (d, 4H), 8.42 (d, 4H), 5.94 (s, 1H), 4.68 (m, 4H), 3.61 (s, 9H), 2.23 (t, 6H), 2.14 (t, 2H), 2.06 (m, 2H), 1.96 (m, 6H), 1.67 (t, 3H), 1.65 (m, 2H), 1.35 (m, 2H). ^{13}C NMR (100 MHz, acetonitrile-d_3): δ 175.0, 174.7, 173.5, 151.0, 146.5, 128.3, 62.8, 58.8, 58.2, 52.3, 36.7, 31.6, 30.2, 29.0, 26.0, 25.2, 16.7. FAB-MS: *m/z* 717 ($M - PF_6$)$^+$, 572 ($M - 2PF_6$)$^{\bullet+}$.

Dendrimer N8. Yield: 73%. ^{1}H NMR (400 MHz, acetonitrile-d_3): δ 9.05 (d, 2H), 9.00 (d, 2H), 8.51 (d, 4H), 6.70 (d, 1H), 6.28 (t, 3H), 4.72 (m, 4H), 3.62 (s, 27H), 2.26 (t, 24H), 2.18 (t, 2H), 2.08 (m, 2H), 1.98 (m, 24H), 1.69 (t, 3H), 1.68 (m, 2H), 1.40 (m, 2H). ^{13}C NMR (100 MHz, acetonitrile-d_3): δ 175.7, 174.9, 174.1, 150.9, 146.8, 128.3, 62.8, 58.9, 58.3, 52.4, 36.9, 31.9, 30.2, 29.0, 25.9, 25.3, 16.7. MALDI-TOF MS: *m/z* 1343 ($M - 2PF_6$)$^{\bullet+}$, 1086 ($M - 2PF_6$ − viologen).

Dendrimer N9. Yield: 96%. ^{1}H NMR (400 MHz, acetonitrile-d_3): δ 9.15 (d, 2H), 9.05 (d, 2H), 8.62 (d, 4H), 6.70 (s, 1H), 6.30 (t, 3H), 6.23 (t, 9H), 4.72 (m, 4H), 3.60 (s, 81H), 2.25 (m, 78H), 2.08 (m, 4H), 1.94 (m, 78H), 1.85 (m, 2H), 1.69 (t, 3H), 1.27 (m, 2H). ^{13}C NMR (100 MHz, acetonitrile-d_3): δ 176.5, 175.2, 151.2, 147.3, 146.8, 128.6, 63.3, 59.5, 59.0, 52.7, 50.3, 32.1, 30.5, 29.3, 17.0. MALDI-TOF MS: *m/z* 3801 ($M - PF_6$)$^+$, 3658 ($M - 2PF_6$)$^{\bullet+}$, 3400 ($M - 2PF_6$ − viologen).

Synthesis of Fréchet-Type Dendrimers. Solvents and chemicals for synthesis were commercially available or reagent grade quality and were used without any further purification. Acetonitrile was distilled over CaH_2 prior to use. ^{1}H and ^{13}C NMR spectra were obtained on a Bruker AC 200F (200 MHz) instrument at room temperature. Mass spectra were recorded on a VG QUATTRO spectrometer. Microanalyses for C, H, and N were performed by the elemental analyses general service of the University of La Coruña.

Synthesis of 1-(4-Carboxymethyl-benzyl)-[4,4′]bipyridinyl-1-ium Hexafluorophosphate (2). A solution 4-bromomethylphenylacetic acid (1.00 equiv) and 4,4′-bipyridine (8.00 equiv) was refluxed in dry CH_3CN for 48 h. After cooling, the solid formed was filtered off and washed with ether. This material was dissolved in MeOH/AcOEt (10:1). To this solution was added NH_4PF_6(satd) until further precipitate formation was not observed. The solvents were removed under reduced pressure, and the residue was triturated in water. Filtration gave the desired compound (57%). ^{1}H NMR (CD_3CN): δ 3.68 (s, 2H), 5.75 (s, 2H), 7.38−7.48 (m, 4H), 7.80 (d, 2H), 8.34 (d, 2H), 8.87 (m, 4H). ^{13}C NMR (CD_3CN): δ 40.6, 64.7, 122.9, 127.2, 130.0, 131.5, 132.4, 137.7, 142.4, 145.8, 151.6, 155.3, 172.9. FAB-MS: *m/z* 305 ($M - PF_6^-$)$^+$. Anal. Calcd for $C_{19}H_{17}N_2O_2PF_6$ (450.09): C, 50.68; H, 3.81; N, 6.22. Found: C, 50.31; H, 3.42; N, 6.32.

Synthesis of 1-(5-Carboxypentyl)-[4,4′]bipyridinyl-1-ium Hexafluorophosphate (3). A similar procedure was used starting from 6-bromohexanoic acid (1.00 equiv) to yield 79% of the desired product. ^{1}H NMR (CD_3CN): δ 1.42 (m, 2H), 1.66 (m, 2H), 2.04 (m, 2H), 2.33 (t, 2H), 4.58 (t, 2H), 7.87 (d, 2H), 8.33 (d, 2H), 8.85 (m, 4H). ^{13}C NMR (CD_3CN): δ 24.6, 25.7, 31.3, 33.6, 62.16, 123.2, 127.0, 143.2, 145.8, 151.1, 154.5, 175.0. FAB-MS: *m/z* 271 ($M - PF_6^-$)$^+$. Anal. Calcd for $C_{16}H_{19}N_2O_2PF_6$ (416.3): C, 46.16; H, 4.60; N, 6.73. Found: C, 46.61; H, 4.77; N, 6.75.

General Procedure for the Synthesis of Dendrimers F1−F3 and F4−F6. A solution of the corresponding Fréchet dendron[34] (1.1 equiv) and viologen precursor **2** or **3** (1.00 equiv) was stirred in dry CH_3CN at 70 °C for 48 h. For the latter generations (F3 and F6) longer reaction times were required. After cooling, the solvent was evaporated under reduced pressure and the residue triturated with ether. The solid was filtered off and dissolved in MeOH/acetone (1:1). A saturated solution of NH_4PF_6 was then added dropwise until precipitation was complete. The solvents were partially evaporated, and 10 mL of water was added. The solid was filtered off to give the dendrimer.

Dendrimer F1. Yield: 90%. ^{1}H NMR (CD_3CN): δ 3.68 (s, 2H), 5.11 (s, 4H), 5.70 (s, 2H), 5.80 (s, 2H), 6.67 (m, 3H), 7.36−7.46 (m, 14 H), 8.37 (m, 4H), 8.97 (m, 4H). ^{13}C NMR (CD_3CN): δ 40.6, 65.3, 65.4, 70.9, 103.9, 109.3, 128.3, 128.6, 128.9, 129.4, 130.2, 131.6, 132.1, 135.5, 137.6, 137.9, 146.4, 151.2, 161.5. FAB-MS: *m/z* 753 ($M - PF_6^-$)$^+$. Anal. Calcd for $C_{40}H_{36}N_2O_4P_2F_{12}$ (898.20): C, 53.46; H 4.04; N, 3.13. Found: C, 53.20; H, 3.62; N, 3.30.

Dendrimer F2. Yield: 70%. ^{1}H NMR (CD_3CN): δ 3.68 (s, 2H), 5.10 (s, 12H), 5.70 (s, 2H), 5.80 (s, 2H), 6.45−6.62 (m, 2H), 6.63−6.82 (m, 7H), 7.30−7.49 (m, 24 H), 8.22−8.24 (m, 4H), 8.81−8.90 (m, 4H). ^{13}C NMR (CD_3CN): δ 40.6, 65.3, 70.5, 70.6, 102.3, 104.2, 107.45, 109.4, 128.1, 128.3, 128.5, 128.8, 129.4, 130.2, 130.7, 131.6, 135.4, 138.0, 140.26, 146.3, 151.0, 160.9, 161.3. FAB-MS: *m/z* 1177 ($M - PF_6^-$)$^+$, 516 ($M - 2PF_6^-$)$^{2+}$. Anal. Calcd for $C_{68}H_{60}N_2O_8P_2F_{12}$ (1322.36): C, 61.73; H, 4.57; N, 2.12. Found: C, 61.33; H, 4.27; N, 2.30.

Dendrimer F3. Yield: 75%. ^{1}H NMR (CD_3CN): δ 3.67 (s, 2H), 4.90−5.00 (m, 28H), 5.59 (s, 2H), 5.74 (s, 2H), 6.48−6.63 (m, 21H), 7.31−7.41 (m, 44 H), 8.18−8.24 (m, 4H), 8.78−8.89 (m, 4H). ^{13}C NMR (CD_3CN): δ 40.6, 65.3, 70.3, 70.6, 102.2, 102.4, 104.1, 107.1, 109.5, 128.1, 128.2, 128.5, 128.7, 128.8, 129.4, 130.2, 131.6, 131.9, 135.3, 138.0, 140.2, 140.5, 146.2, 150.8, 160.77, 160.89, 161.3, 172.7

ppm. FAB-MS: *m*/*z* 2027 ($M - PF_6^-)^+$, 1882 ($M - 2PF_6^-)^+$, 941 ($M - 2PF_6^-)^{2+}$. Anal. Calcd for $C_{124}H_{108}N_2O_{16}P_2F_{12}$ (2172.12): C, 68.57; H, 5.01; N, 1.29. Found: C, 68.8; H, 4.70; N, 1.00.

Dendrimer F4. Yield: 58%. ^{1}H NMR (CD_3CN): δ 1.42 (m, 2H), 1.65 (m, 2H), 2.09 (m, 2H), 2.33 (t, 2H), 4.64 (t, 2H), 5.11 (s, 4H), 5.72 (s, 2H), 6.72 (m, 3H), 7.34−7.42 (m, 10H), 8.37 (m, 4H), 8.93 (m, 4H). ^{13}C NMR (CD_3CN): δ 24.5, 25.8, 31.4, 33.5, 62.7, 65.4, 70.9, 103.9, 109.3, 128.1, 128.2, 128.6, 128.9, 129.4, 130.2, 135.5, 137.6, 146.4, 150.6, 151.2, 161.5, 174.7. FAB-MS: *m*/*z* 719 ($M - PF_6^-)^+$, 574 ($M - 2PF_6^-)^+$. Anal. Calcd for $C_{37}H_{38}N_2O_4P_2F_{12}$ (864.64): C, 51.4; H, 4.43; N, 3.05. Found: C, 51.89; H, 4.15; N, 3.05.

Dendrimer F5. Yield: 88%. ^{1}H NMR (CD_3CN): δ 1.42 (m, 2H), 1.63 (m, 2H), 2.09 (m, 2H), 2.33 (t, 2H), 4.61 (t, 2H), 5.06 (s, 12H), 5.70 (s, 2H), 6.56−6.69 (m, 9H), 7.32−7.43 (m, 20H), 8.30 (m, 4H), 8.88 (m, 4H). ^{13}C NMR (CD_3CN): δ 24.6, 25.8, 31.4, 33.5, 62.7, 65.4, 70.5, 70.6, 102.3, 104.2, 107.4, 109.4, 128.0, 128.1, 128.5, 128.9, 129.4, 135.4, 138.0, 140.3, 146.4, 150.4, 151.1, 160.9, 161.3, 174.6. FAB-MS: *m*/*z* 1144 ($M - PF_6^-)^+$, 999 ($M - 2PF_6^-)^+$. Anal. Calcd for $C_{65}H_{62}N_2O_8P_2F_{12}$ (1289.12): C, 60.56; H, 4.85; N, 2.17. Found: C, 60.80; H, 4.40; N, 1.90.

Dendrimer F6. Yield: 68%. ^{1}H NMR (CD_3CN): δ 1.42 (m, 2H), 1.63 (m, 2H), 4.54 (t, 2H), 4.90−5.03 (m, 28H), 5.60 (s, 2H), 6.48−6.63 (m, 21H), 7.31−7.40 (m, 40H), 8.20 (m, 4H), 8.79 (m, 4H). ^{13}C NMR (CD_3CN): δ 24.5, 25.8, 31.4, 33.5, 62.7, 65.4, 70.6, 102.2, 102.4, 104.1, 107.4, 109.5, 127.92, 128.0, 128.5, 128.81, 129.4, 135.3, 138.0, 140.2, 140.5, 140.6, 146.3, 150.9, 160.7, 160.9, 161.3. FAB-MS: *m*/*z* 1993 ($M - PF_6^-)^+$, 1848 ($M - 2PF_6^-)^+$, 924 ($M - 2PF_6^-)^{2+}$. Anal. Calcd for $C_{121}H_{110}N_2O_{16}P_2F_{12}$ (2138.1): C, 67.97; H, 5.19; N, 1.31. Found: C, 68.10; H, 4.90; N, 1.01.

Electrochemical Experiments. Cyclic voltammetric experiments were done in a 5-mL single-compartment cell containing ∼1 mM solution of the viologen dendrimer in the solvent of choice. Tetrabutylammonium hexafluorophosphate (0.1−0.2 M) was utilized as the supporting electrolyte in nonaqueous solvents. Solutions were purged with purified nitrogen and kept under an inert atmosphere during the experiments. The cell was fitted with a glassy carbon working electrode (0.071 cm^2), a Pt counter electrode, and a Ag/AgCl reference electrode. The working electrode was polished with an aqueous alumina (0.05 μm) slurry on a felt surface before each experiment.

Diffusion Coefficient Measurements. These measurements were carried out using standard PGSE NMR experiments in a Bruker Avance 400 MHz spectrometer equipped with a gradient unit capable of producing magnetic pulsed field gradients in the *z*-direction of up to 0.5 T/m. We utilized 4-ms gradient pulses of variable gradient amplitude separated by delays of ∼200 ms.

Binding Constant Measurements. The association equilibrium constants between host BPP34C10 and dendrimers N1−N3 and F1−F6 were determined from electronic absorption spectroscopic measurements using a method previously reported by our group.[46]

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Supporting Information Available: Additional figures as mentioned in the text. This material is available free of charge via the Internet at http://pubs.acs.org.

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