Electrochemical and Spectroscopic Characterization of Viologen-Functionalized Poly(Amidoamine) Dendrimers†

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We report the preparation and characterization of viologen-functionalized generation 2, 4, and 6 poly(amidoamine) (PAMAM) dendrimers. An amidation reaction between the succinimide ester of 1-ethyl-1′-(3-propionic acid)-4,4′-bipyridylium dibromide and the dendrimer primary amines resulted in 13−34% end group functionalization. The water-soluble dendrimers were examined by ^{1}H NMR, MALDI-TOF MS, and UV−vis spectroscopy to determine the extent of functionalization. UV−vis spectra, obtained following chemical reduction of the viologenated dendrimers, indicated that the viologen radical cations were largely dimerized, which demonstrates the close proximity of the terminal viologens. Dynamic light scattering (DLS) measurements indicate that the oxidized viologenated-dendrimers are predominately unaggregated in aqueous electrolyte solutions. Diffusion coefficients determined by chronoamperometry for the three generations of viologenated PAMAM dendrimer are within 15% of values calculated using the Stokes−Einstein relationship for individual unaggregated dendrimers. Reversible voltammetry was obtained for all three generations of dendrimers for the first viologen reduction wave. The magnitude of the peak or steady-state currents indicated incomplete electrolysis of the dendrimer viologen moieties, whereas the presence of a single wave showed that all electrochemically addressable groups were equivalent. Cycling through the second reduction wave resulted in electrode passivation due to irreversible electroprecipitation. Adsorption of a stable film of oxidized viologenated-dendrimer on a Au electrode is also demonstrated by cyclic voltammetry.

Introduction

In this paper, we describe the preparation and characterization of poly(amidoamine) (PAMAM) dendrimers functionalized on their periphery with viologen groups (Scheme 1).[1−3] We undertook this study in an effort to develop a series of electrochemically active, water-soluble macromolecules having well-defined geometrical characteristics and discrete sizes in the range of 1−10 nm. This size range spans the gap between molecular chemistry and state-of-the-art lithography. In the future, we will report on electrode reactions in which the redox-active probe molecule and the electrode are on the same scale. The unique structural and chemical properties of the viologenated dendrimers make them promising candidates for understanding other fundamental electrochemical processes as well such as charge-trapping, cooperative electrocatalysis, and the dependence of heterogeneous electron-transfer kinetics on molecular geometry.

PAMAM dendrimers are synthesized by addition of branches to a molecular core (typically ammonia or ethylenediamine) by sequential Michael reaction with methyl methacrylate followed by amidation with ethylenediamine.[4] Dendrimers have been used to study light-harvesting phenomena and gene transfection, for chemical sensing applications, as templates for preparing dendrimer-stabilized nanoparticles, and as vehicles for drug delivery.[3,5,6] PAMAM dendrimers were chosen for the studies presented here because they have relatively well-defined sizes, are water-soluble, and because they can be functionalized using standard peptide coupling chemistry. Viologens are likewise water-soluble and they have well-behaved electrochemical properties. Applications for viologens range from electron-transfer mediation to electrochromic devices.[7,8]

There has been significant recent interest in the synthesis and characterization of electroactive dendrimers. These studies are motivated principally by the prospect of correlating electrochemical properties with the geometrically well-defined macromolecular structure of dendrimers. In an electroactive dendrimer the redox-active site may be: (1) incorporated as a single core unit,[9−16] (2) contained within the repeating branch units of the dendrimer,[17,18] (3) located on the dendrimer periphery,[19−34] or (4) positioned in more than one of these locations.[30,31,35−37] Electroactive dendrimers have been prepared that incorporate electroactive species such as ferrocene,[10,11,25−27,32,34] anthraquinone,[17,18,29] cobalt polypyridyl complexes,[21] pyrrole,[28] thiophene,[12,13] tetrathiafulvalene,[29−31,37], porphyrins,[9,15,16] and ruthenium complexes.[19,20] The preparation of an electroactive dendrimer based on a viologen skeleton has been reported by Walder et al.[35,36] These dendrimers, which were prepared by linking benzyl viologen branches to a phenyl or benzyl viologen core, were soluble in DMF and exhibited charge-trapping behavior. PAMAM dendrimers in particular have been functionalized with electroactive ruthenium complexes[19,20] and naphthalene diimide.[22−24] In the majority of these studies, a single reduction/oxidation process was observed, and it was reported that all electroactive groups appended to the dendrimer were electroactive regardless of generation. Adsorption and electroprecipitation of electroactive dendrimers is also common.[12,19−22,24,27−29,31,32,36,37]

The specific objective of the study reported here was to synthesize and characterize a series of viologen-functionalized

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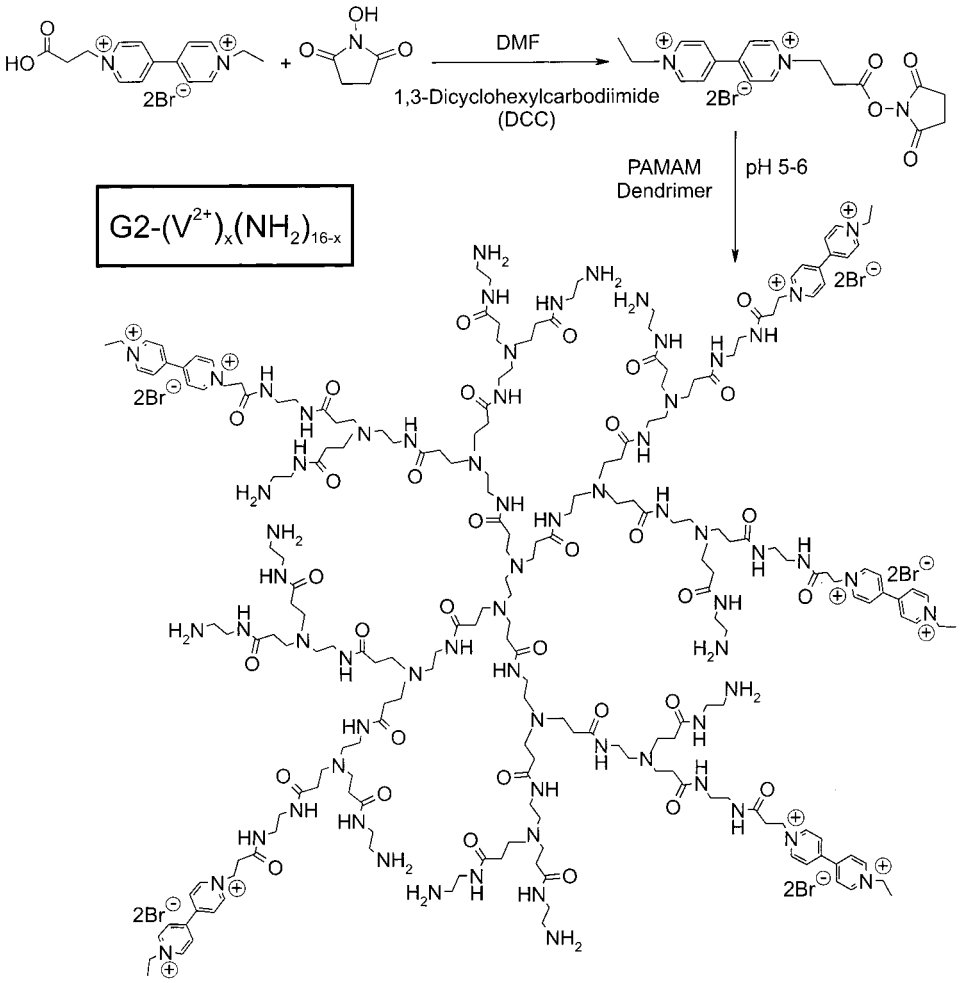
SCHEME 1



PAMAM dendrimers prepared using the simple synthetic strategy shown in Scheme 1. ^{1}H NMR, matrix-assisted laser desorption−ionization time-of-flight mass spectrometry (MALDI-TOF MS), and UV−vis spectroscopy verified the extent of functionalization of the peripheral groups. Dynamic light scattering (DLS) measurements showed that there is little interdendrimer aggregation in low ionic strength electrolytic solutions. Cyclic voltammetry at a glassy carbon macroelectrode indicated that the reversibility of the electrochemical response depends on the identity of the supporting electrolyte. In 0.1 M K_2SO_4, a thermodynamically reversible response was obtained for the first reduction wave of generations 2, 4, and 6 viologenated dendrimers (G2-$(V^{2+})_x(NH_2)_{16-x}$, G4-$(V^{2+})_x(NH_2)_{64-x}$, and G6-$(V^{2+})_x(NH_2)_{256-x}$, respectively), allowing diffusion coefficients to be determined. UV−vis spectra of the reduced viologenated-dendrimers indicate intramolecular dimerization, as has been previously observed upon reduction of dendrimers peripherally functionalized with naphthalene diimide.[22−24] Further reduction of the viologen to its direduced species resulted in reduced solubility and electroprecipitation.

Experimental Section

Chemicals. Generation 2, 4, and 6 amine-terminated PAMAM dendrimers (G2-NH_2, G4-NH_2, and G6-NH_2, respectively) were purchased from Dendritech, Inc. (Midland, MI). *N*-hydroxysuccinimide (97%), 1,3-dicyclohexylcarbodiimide (99%), bromoethane (98%), 3-bromopropionic acid (97%), 4,4′-dipyridyl (98%), $Na_2S_2O_4$ (85%), KF (99%), K_2SO_4 (99%), β-cyclodextrin hydrate, NaOD (98+%) and anhydrous dimethylformamide (99.8%) were purchased from the Aldrich Chemical Co. (Milwaukee, WI). KNO_3 (99%), HCl, CH_2Cl_2 (99.5%), acetonitrile (99.8%), and benzene (99%) were from EM Science. Toluene (Mallinckrodt), Na_2SO_4 (Mallinckrodt), TRIZMA Base (99.9%,Sigma), $Ru(NH_3)_6Cl_3$ (Strem, 99%), ethanol (Aaper, 100%), D_2O (99.9% Cambridge Isotopes Lab), and all other chemicals were used as received unless otherwise noted. Deionized water (Milli-Q, Millipore, 18 MΩ-cm) was used throughout.

Electrochemistry. Electrochemical experiments were performed in deoxygenated aqueous solutions (>15 min N_2 purge) in a sealed cell using a Pt-gauze counter electrode and a Ag/AgCl (3M NaCl) reference electrode (Bioanalytical Systems, Inc. (BAS), West Lafayette, IN). Microelectrode experiments were performed in a Faraday cage using a BAS model 100B electrochemical analyzer coupled to a PA-1 current preamplifier and i−E transducer (BAS). Prior to microelectrode experiments, the 5.2 μm-radius Pt electrode (BAS) was polished for 5 min on a polishing cloth (Microcloth, Buehler, Lake Bluff, IL) using an aqueous 1 μm γ-Al_2O_3 (Buehler) slurry, rinsed with deionized water, and polished again with 0.1 μm γ-Al_2O_3 (GAMAL, Fisher). Polishing was followed by 2 min of sonication in a water/ethanol mixture. Microelectrode chronoamperometry experiments were performed at least five times. Background voltammograms, obtained using 0.1 M K_2SO_4 electrolyte solutions adjusted to the pH of the viologenated dendrimer solutions (pH 6.0−6.3), were subtracted from the microelectrode

voltammograms. A similar background subtraction procedure was performed for all chronoamperometry experiments.

A Pine Instruments AFRDE4 bipotentiostat (Grove City, PA) and Kipp and Zonen XYY′ chart recorder (Bohemia, NY) were employed for all macroelectrode experiments. The Au (BAS) and glassy carbon (BAS) macroelectrodes were polished for 5 min on a polishing cloth in an aqueous 1 μm γ-Al_2O_3 slurry, cleaned gently with a Kimwipe, and sonicated for 2 min in a water/ethanol solution prior to each experiment.

The areas of the macroelectrodes were determined by obtaining cyclic voltammograms at different scan rates in 2.0 mM $Ru(NH_3)_6Cl_3$/0.1 M K_2SO_4 and fitting the data to the Randles−Sevcik equation.[38] The microelectrode radius was determined from the magnitude of the steady-state limiting current obtained at 2 mV/s in 5.0 mM $Ru(NH_3)_6Cl_3$/0.1 M K_2SO_4 using the equation for a disk electrode (See eq 5). For these calculations, the diffusion coefficient for $Ru(NH_3)_6Cl_3$ was taken as 5.5×10^{-6} cm^2/s.[39] The areas of the Au and glassy carbon macroelectrodes were 0.0220 and 0.0680 cm^2, respectively, and the microelectrode radius was 5.2 μm.

Microscopy. Optical microscopy was performed using a Nikon Optiphot microscope (Nikon Corporation, Tokyo, Japan).

Spectroscopy. UV−vis spectra were obtained using a Hewlett-Packard HP8453 spectrometer (Hewlett-Packard, Wilmington, DE). A capped quartz cuvette was used for all experiments. Spectra of the viologen radical cation were obtained after 20 min deoxygenation in flowing N_2, followed by addition of $Na_2S_2O_4$ in a N_2-purged glovebag. Less than a 2- to 3-fold excess of reducing agent was employed to minimize adsorption at 314 and 240 nm by $Na_2S_2O_4$. All spectra were obtained at 25 °C.

DLS experiments were performed at 25 °C using a PDDLS/Cool Batch dynamic light scattering instrument (Precision detectors, Franklin, MA). Diffusion coefficients were obtained by fitting the modified dendrimer autocorrelation functions with the manufacturer's proprietary PrecisionDeconvolve software. Hydrodynamic radii were calculated using the Stokes−Einstein equation.

NMR experiments were performed using a Varian VXR-300 spectrometer (Varian Associates, Palo Alto, CA). D_2O solutions were adjusted to pH 9 with NaOD to improve the spectral baseline and decrease peak broadening.

MALDI-TOF MS data were obtained using a Voyager Elite XL spectrometer (PerSeptive Biosystems, Farmingham, MA) and a 2′,4′,6′-trihydroxyacetophenone matrix.

Synthesis of 1-ethyl-1′-(3-propionic acid)-4,4′-bipyridylium Dibromide. The synthesis was derived from a procedure employed by Kaifer et al.[40] 15 g (0.1 mol) of 4,4′-dipyridyl was combined with 75 mL (1 mol) bromoethane and 150 mL of benzene. The reaction mixture, which formed a greenish-white precipitate during the first 2 h, was stirred under reflux (85−93 °C) overnight. The solution was then cooled and stirred with 500 mL of toluene for a minimum of 2 h. The product was isolated by vacuum filtration, washed with toluene, and recrystallized in approximately 50 mL of warm acetonitrile. This procedure resulted in a 60−75% yield of 1-ethyl-4,4′-dipyridyl, as verified by ^{1}H NMR. Next, the monoquaternized salt was combined with a 10-fold excess of 3-bromopropionic acid in 500 mL of acetonitrile and refluxed overnight at 93−103 °C. The mixture, which produced a white precipitate, was cooled and stirred with 300 mL toluene. The precipitate was collected, washed with toluene, and then stirred in 500 mL of toluene for 1 h. The product, a yellow powder, was collected, washed with CH_2Cl_2, recrystallized in 50 mL of warm acetonitrile, and dried.

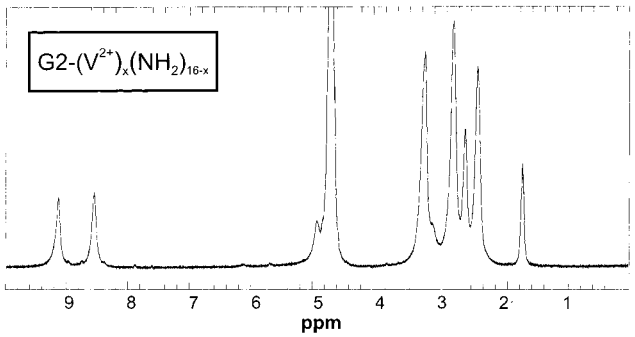


Figure 1. 300 MHz ^{1}H NMR spectra of G2-$(V^{2+})_x(NH_2)_{16-x}$ obtained in pH 9 D_2O.

The net yield of viologen acid for the two reactions was 30−40%. ^{1}H NMR (300 MHz, D_2O, δ) 9.23 (d, 2H), 9.16 (d, 2H), 8.58 (d, 4H), 5.03 (t, 2H), 4.79, 3.29 (t, 2H), 1.73 (t, 3H).

Synthesis of the Viologen-NHS Ester. An 8 mmol portion of 1-ethyl-1′-(3-propionic acid)-4,4′-bipyridylium dibromide was mixed with 8 mmol of *N*-hydroxysuccinimde (NHS) and 8 mmol 1,3- dicyclocarbodiimide (DCC) in 1 L of anhydrous DMF. The reaction mixture was stirred overnight, and the solvent was removed under vacuum leaving a yellow residue. The solid was washed with 300 mL of acetonitrile to remove unreacted NHS, and then filtered and dried under vacuum. Next, the solid was dissolved in 20 mL of water resulting in precipitation of dicyclohexylurea (DCU). The solution was filtered to remove DCU, immediately frozen to minimize ester hydrolysis, and then lypholized overnight. The product was a hygroscopic orange crystalline material which, according to ^{1}H NMR integrated intensities, consisted of a 1:1 ratio of viologen NHS ester-to-unreacted viologen acid. ^{1}H NMR (300 MHz, D_2O, δ) 9.20 (br, 4H), 8.59 (br, 4H), 5.04 (br, 2H), 4.79, 3.29 (br, 2H),2.80 (s, typically 2−3H), 1.73 (br, 3H).

Synthesis of Viologenated Dendrimers. Methanolic solutions of G2-NH_2, G4-NH_2, and G6-NH_2 PAMAM dendrimers were combined with the mixed viologen-NHS ester/viologen acid product in 10 mL of deionized water. A 1:1 ratio of viologen ester to dendrimer primary amine groups was maintained for all syntheses. The concentration of viologen-NHS ester ranged from 0.2 to 0.4 M for the series of reactions, and the pH was 5.7−6.0. The slightly acidic reaction conditions were chosen to prevent degradation of the viologen.[7,41]

The reaction mixtures were stirred overnight and dialyzed (sigma, cellulose, and benzoylated cellulose dialysis tubing) in deionized water to separate the viologenated-dendrimers from the other reactants. To remove the solvent, the dialyzed product was lypholized overnight. The product was a hygroscopic yellow fiber. ^{1}H NMR spectra are presented in Figure 1 and in the Supporting Material.

Results and Discussion

The synthetic procedure resulted in only partial viologen functionalization of the dendrimer periphery (Scheme 1). Incomplete end group functionalization was anticipated because of the ease of hydrolysis of the NHS ester in water and because a low ratio (1:1) of NHS ester to dendrimer terminal amines was employed. We anticipate that the mixed amine/viologen dendrimer periphery will provide future chemical versatility. Three independent methods were used to determine the extent of dendrimer functionalization: Table 1 summarizes the results from UV−vis spectroscopy, MALDI-TOF MS, and ^{1}H NMR spectroscopy. For the synthetic approach employed here, the degree of functionalization varied from 13 to 34%.

TABLE 1: Spectroscopic and Electrochemical Parameters for the Viologen Acid and Viologenated Dendrimers

	UV−vis[a]	MALDI[b]	NMR[c]	D_o (cm^2/s)[d,e] experimental	D_o (cm^2/s)[f] calculated	$E(1)_{1/2}$ (mV)[d,g,h]	ΔE_{p1} (mV)[d,g]	i_{pa1}/i_{pc1} (50 mV/s)[d,g,i]	i_{pa1}/i_{pc1} (200 mV/s)[d,g,i]
viologen acid	NA	NA	NA	$5.0 \pm 0.1 \times 10^{-6}$	5.5×10^{-6}	−663	70	1.1	1.2
G2-$(V^{2+})_x(NH_2)_{16-x}$	4−5 (28%)	5−6 (34%)	5−6 (34%)	$1.7 \pm 0.1 \times 10^{-6}$	1.5×10^{-6}	−560	50	1.1	1.2
G4-$(V^{2+})_x(NH_2)_{64-x}$	10−11 (16%)	8−9 (13%)	11−12 (18%)	$1.1 \pm 0.3 \times 10^{-6}$	9.5×10^{-7}	−557	58	1.1	1.2
G6-$(V^{2+})_x(NH_2)_{256-x}$	57 (22%)	NA	63 (25%)	$7.2 \pm 0.4 \times 10^{-7}$	6.3×10^{-7}	−541	58	1.1	1.1

[a] Viologens per dendrimer (percent end group functionalization) determined by UV−vis/gravimetric analysis. [b] Viologens per dendrimer (percent end group functionalization) determined by MALDI-TOF MS analysis. [c] Viologens per dendrimer (percent end group functionalization) determined by integrated ^1H NMR intensities. [d] Electrochemical experiments performed in 0.1 M K_2SO_4. [e] Diffusion coefficients (D_o) determined by chronoamperometry/cyclic voltammetry at a Pt microelectrode (See eq 7). [f] Stokes−Einstein calculated diffusion coefficients (See eq 4). [g] Electrochemical parameters determined in 1.0 mM total viologen concentration using a glassy carbon electrode. [h] Potentials are reported with respect to Ag/AgCl (3 M NaCl). [i] i_{pa1}/i_{pc1} values calculated using the first reduction wave and eq 8.

The viologenated dendrimer solid is a pale yellow fiber, whereas its aqueous solutions are transparent and colorless. The material is insoluble in many nonaqueous solvents, such as acetonitrile, methanol, ethanol, and only slightly soluble in DMF. The dried material remains water-soluble for a period of 3−5 days if stored in a closed container in air. Upon absorbing water from the atmosphere, the viologenated dendrimer is transformed into a black syrup and becomes insoluble in water. The chemistry underlying this transformation is unknown.

Figure 1 is a ^1H NMR spectrum of the viologenated-G2 (G2-$(V^{2+})_x(NH_2)_{16-x}$) dendrimer. The spectrum of the G2-$(V^{2+})_x$-$(NH_2)_{16-x}$ dendrimer exhibits significant peak broadening, a phenomenon commonly observed in NMR spectra of dendrimers and related macromolecules. Peak broadening is more pronounced in the spectra of the G4-$(V^{2+})_x(NH_2)_{64-x}$ and G6-$(V^{2+})_x(NH_2)_{256-x}$ samples (see Supporting Material).[19,42] Four peaks representative of the dendrimer methylene protons occur between 2.20 and 3.60 ppm, whereas the viologen aromatic protons are present in two broad peaks centered at 8.58 and 9.22 ppm. The viologen methylene protons appear at 5.10 ppm and as a shoulder accompanying the dendrimer methylene peak at 3.35 ppm, whereas the other methylene peak is eclipsed by the solvent peak at 4.81 ppm. The integrated intensity of the viologen methylene peak at 1.75 ppm can be compared to the integrated intensity of the dendrimer methylene protons to determine the extent of end group functionalization (Table 1). To ensure accuracy of the peak integrations, the NMR spectra were collected at pH 9 to avoid baseline distortions, which were observed under more acidic (pH 6) conditions. It should be noted that over several hours additional peaks in the 8−9.5 ppm region appeared, indicating viologen decomposition under these conditions. Degradation of the PAMAM dendrimers at pH 9 was also indicated by the appearance of peaks in the 5.5−6.5 ppm region. Because these peaks are similar to the alkene proton peaks of methyl acrylate (a starting material in the synthesis of the PAMAM dendrimers), it is likely that a retro-Michael addition reaction is partially responsible for decomposition under basic conditions. For the reasons mentioned above, ^1H NMR spectra of the viologenated dendrimers were obtained immediately after the addition of NaOD to the sample.

MALDI-TOF mass spectra for the G2-$(V^{2+})_x(NH_2)_{16-x}$ and G4-$(V^{2+})_x(NH_2)_{64-x}$ dendrimers are presented in Figure 2. A single broad peak centered around 5400 amu was observed for G2-$(V^{2+})_x(NH_2)_{16-x}$. The peak shape is nearly Gaussian, indicating a symmetric distribution exists in the extent of dendrimer functionalization. The molecular weight of the unfunctionalized G2 amine-terminated PAMAM dendrimer is 3256 amu, as verified by MALDI-TOF MS. The change in molecular weight indicates that on average 5−6 viologen moieties are attached to each dendrimer, assuming the bromide counterions are retained.

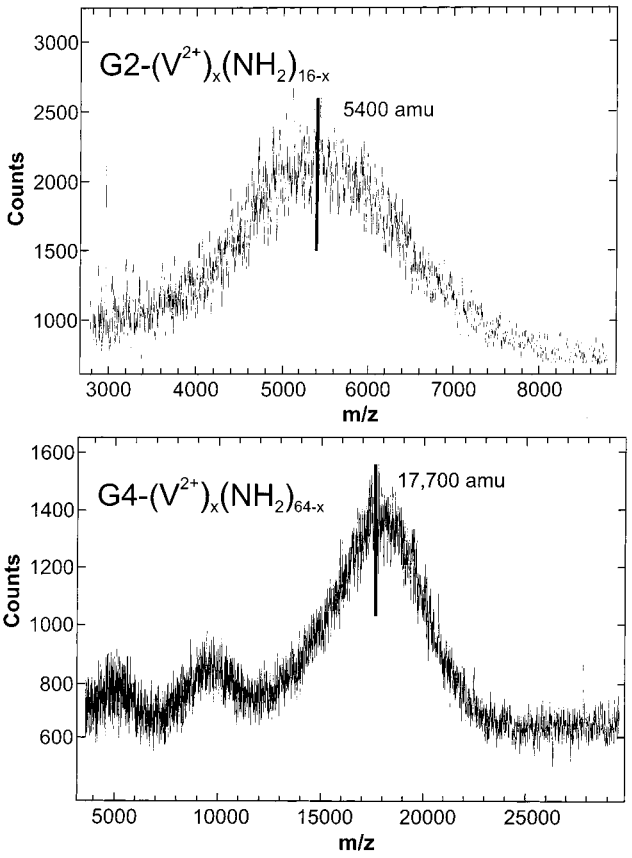


Figure 2. MALDI-TOF MS spectra of the second (G2-$(V^{2+})_x(NH_2)_{16-x}$) and fourth (G4-$(V^{2+})_x(NH_2)_{64-x}$) generation viologenated dendrimers.

The G4-$(V^{2+})_x(NH_2)_{64-x}$ MALDI-TOF spectrum exhibits a peak centered at ~17 700 amu and a series of smaller peaks at lower *m*/*z*. A series of similar peaks was also present in the mass spectrum of the unfunctionalized G4 amine-terminated PAMAM dendrimer. The presence of these peaks in the spectrum of the unfunctionalized-dendrimer indicates that either the dendrimers contain a significant fraction of defects or the fragmentation occurs during the mass spectrometry experiment.[43] More importantly, this finding suggests that the low-*m*/*z* peaks in the viologenated-dendrimer mass spectrum are not caused by dendrimer fragmentation during the functionalization reaction. Because the molecular weight of the unfunctionalized PAMAM dendrimer is 14 215, it can be deduced from the peak centered at 17 700 amu that the mean number of viologens per dendrimer is 8−9. It was not possible to obtain a mass spectrum of G6-$(V^{2+})_x(NH_2)_{256-x}$ by MALDI-TOF analysis due to the high molecular weight of this molecule (58 048 amu for the unfunctionalized G6 dendrimer). Attempts to generate molecular

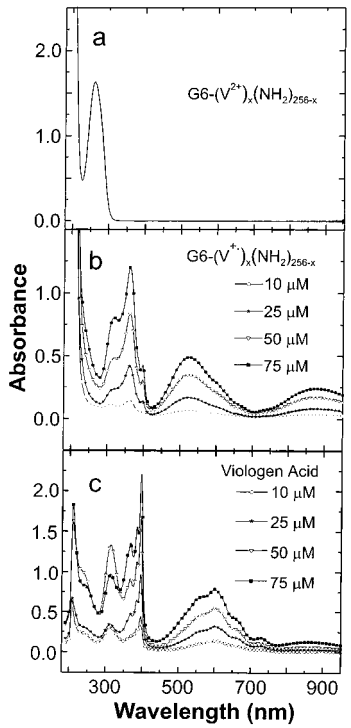


Figure 3. UV−vis spectra of aqueous (a) G6-$(V^{2+})_x(NH_2)_{256-x}$, (b) G6-$(V^{+\cdot})_x(NH_2)_{256-x}$ (pH 8.0), and (c) 1-ethyl-1′-(3-propionic acid)-4,4′-bipyridylium radical cation (pH 8.0).

ion data by electrospray ionization mass spectrometry (ESI-MS) were unsuccessful for all of the viologenated dendrimers.

An additional method for determining the degree of dendrimer-functionalization is to examine the absorbance intensity arising from the bipyridyl unit of the viologen dication. An absorbance maximum is present at 260 nm for the viologen acid (1-ethyl-1′-(3-propionic acid)-4,4′-bipyridylium dibromide) as well as for the viologenated dendrimers. The spectrum of a G6-$(V^{2+})_x(NH_2)_{256-x}$ solution is shown in Figure 3a; this spectrum is typical of the other viologenated dendrimers and the viologen acid. The experimentally determined molar absorptivity of the viologen acid is 20 200 in unbuffered pH 5−6 aqueous solution. This value is nearly identical to that reported for methyl viologen in pH 10 aqueous solution at 257 nm (ϵ = 20 700).[44] Accordingly, we conclude that the molar absorptivity is relatively insensitive to pH and the identity of the alkyl substituents on the viologen. This assumption provides a basis for determining the degree of end group functionalization of the viologenated dendrimers from $A_{260\ nm}$ and gravimetric analysis. The results of these determinations are given in Table 1 for the three generations of dendrimers. The important point is that the percentage functionalization determined by each of the three independent techniques, ^{1}H NMR, MALDI-TOF MS, and UV−vis, are in good agreement.

Figure 3b shows UV−vis spectra of G6-$(V^{2+})_x(NH_2)_{256-x}$ at 10, 25, 50, and 75 μM viologen concentration after chemical reduction with sodium dithionite ($Na_2S_2O_4$). The spectra were obtained in 0.1 M TRIZMA/0.5 M Na_2SO_4 adjusted to pH 8.0 with HCl immediately after preparation and deoxygenation. pH 8.0 was chosen to ensure the pH-sensitive reduction potential of the SO_2^-/HSO_3^- redox couple produced from dissociated $S_2O_4^-$ was negative of the viologen reduction potential.[45] The reduced viologenated-dendrimer solutions were deep purple, and absorbance peaks at 361, 525, and 867 nm indicate dimer formation, whereas a smaller peak at 397 nm corresponds to a less substantial fraction of the monomer radical cation.[46,47]

The dimerization reaction, which occurs at room temperature in aqueous solution only, is promoted by low temperature, high viologen concentration, and increasing alkyl chain length of the bipyridilium substituent.[7] Because the dimer peak intensities in Figure 3b scale linearly with increasing concentration, we conclude that *intra*dendrimer dimerization dominates *inter*dendrimer dimerization within these concentration limits. The spectra of G2-$(V^{2+})_x(NH_2)_{16-x}$ and G4-$(V^{2+})_x(NH_2)_{64-x}$ dendrimers also obeyed Beer's law in this concentration range. The flexible nature of the dendrimer scaffold has previously been shown to promote intramolecular interactions between end group functionalities in TTF-glycol dendrimers,[37] PAMAM dendrimers partially functionalized with naphthalene diimide,[23,24] and in poly(propyleneimine) dendrimers modified with pyrrole [28] and pyrene terminal units.[48] Accordingly, it is likely that the combined effect of high local viologen concentration on the dendrimer periphery and energetically favored solvent−solvent interactions contribute to dimer formation.[7]

UV−vis spectra of the reduced viologen acid (1-ethyl-1′-(3-propionic acid)-4,4′-bipyridylium) are shown in Figure 3c. The strong peaks at 397 and 601 nm, and the blue color of the solution, indicate that monomer formation predominates.[46,47] However, a dimer peak at 867 nm is also present, which exhibits nonlinear growth in the concentration range between 10 and 75 μM, indicating that increased concentration pushes the equilibrium toward the dimer. This is in contradistinction to the linear absorbance change for the dimer peaks of the viologenated dendrimer, which we correlate to intramolecular dimer formation.

Although a precise assignment of the monomer/dimer ratio of viologenated dendrimers and viologen acid is beyond the scope of this work, it is possible to estimate these values using spectroscopic parameters determined for the methyl viologen radical cation monomer and dimer species. The following equations were solved for the percentage dimer by deriving the monomer(c_M) and dimer(c_D) concentrations from absorbance data obtained at λ = 600 nm ($A_{600\ nm}$) and λ = 520 nm ($A_{520\ nm}$)

$$A_{600\ nm} = \epsilon_{M,600\ nm} b c_M + \epsilon_{D,\ 600\ nm} b c_D \quad (1)$$

$$A_{520\ nm} = \epsilon_{M,520\ nm} b c_M + \epsilon_{D,520\ nm} b c_D \quad (2)$$

$$\%\text{dimer} = 2c_D/(c_M + 2c_D)\ x\ 100 \quad (3)$$

The molar absorptivity values ($\epsilon_{M,600\ nm}$ = 14,049, $\epsilon_{D,600\ nm}$ = 11,989, $\epsilon_{M,520\ nm}$ = 4,307, $\epsilon_{D,520\ nm}$ = 23 045) for reduced methyl viologen were reported by Komers.[49] For the three generations of reduced viologenated dendrimer, the percentage dimerization was 90% or greater, provided the ratio of the molar absorptivities of the viologenated dendrimer monomer and dimer are the same as those of methyl viologen. On the basis of the concentrations calculated from the reduced dendrimer spectra, we find that the absolute molar absorptivities at 520 and 600 nm are diminished for the viologenated dendrimer relative to methyl viologen. Specifically, for the three reduced dendrimers the calculated viologen concentrations were at least 25% smaller than expected compared to the other methods shown in Table 1. This may be a consequence of shielding, which is caused by the presence of the large dendrimer substituent. This hypochromic effect has previously been reported for reduced viologens bearing substituents larger than an octyl chain and was attributed to the formation of viologen radical cation multimers.[50] In the case of the viologenated dendrimer radical cations, it is not possible at present to draw a conclusion regarding the presence of higher-

level associations of the reduced terminal group; however, given the close proximity of the viologen groups, such an effect might be anticipated.

On the basis of the concentrations of monomer and dimer calculated from the spectra in Figure 3c, the molar absorptivities of the viologen acid closely approximate those of the methyl viologen cation radical. The spectra indicate 20% dimerization of the reduced viologen acid. This is far less than the 90% dimerization calculated for the dendrimer at the same viologen concentrations and temperature.

Increased monomer-to-dimer peak intensity ratios have been observed in the radical cation spectra of methylheptyl viologen,[51] dibenzyl viologen,[51] and *n*-heptyl viologen[52] in the presence of β-cyclodextrin. An attempt to disrupt dimerization of the viologenated dendrimers by adding a 15-fold excess of β-cyclodextrin resulted in no change in the G2-$(V^{2+})_x(NH_2)_{16-x}$ and G6-$(V^{2+})_x(NH_2)_{256-x}$ spectra and only a slight change in the G4-$(V^{2+})_x(NH_2)_{64-x}$ spectrum. It is unlikely that the bulky dendritic substituent is to blame for the lack of complexation, given that ferrocene-functionalized poly(propyleneimine) dendrimers form inclusion complexes with β-cyclodextrin.[26] In fact, addition of β-cyclodextrin had no observable effect on the UV−vis spectra of the reduced viologen acid, indicating there is a weak host−guest interaction between the viologen ethyl substituent and the inclusion complex, as previously observed in the case of methyl viologen.[53]

Dynamic light scattering (DLS) was used to investigate intermolecular aggregation of the oxidized viologenated-dendrimers. Spectra obtained in neat aqueous solution showed evidence of large aggregate formation (hydrodynamic radii > 300 nm). Aggregates in this size range have previously been reported for unfunctionalized, amine-terminated PAMAM dendrimers in electrolyte-free aqueous solution,[54] a finding supported by our own observations. The aggregation of the viologenated dendrimers was eliminated by adding supporting electrolyte. The DLS-measured average radius of G6-$(V^{2+})_x(NH_2)_{256-x}$ was 4.2 nm in a 17 μM G6-$(V^{2+})_x(NH_2)_{256-x}$/0.1 M K_2SO_4 solution at pH 6.3. The calculated radius of this dendrimer is 3.5 nm, assuming a spherical G6-NH_2 dendrimer modified with 60 viologen groups.[3,55] A G6-NH_2 radius of 3.35 nm, determined by size-exclusion chromatography at an unreported pH,[3] was used for this calculation. Because pH has been shown to influence the hydrodynamic radii of amine-terminated cascade polymers[56] and methanolic solutions of PAMAM dendrimers,[54] it is possible that the small variation in the experimental (4.2 nm) and calculated (3.5 nm) radii may be related to a pH difference in the two experiments. Despite these qualifications, the agreement of the calculated and DLS-determined G6-$(V^{2+})_x(NH_2)_{256-x}$ radii confirm that the G6-viologenated dendrimers are not aggregated in low ionic strength aqueous electrolyte solutions. Poor signal resolution prevented hydrodynamic radii measurements by DLS for G2-$(V^{2+})_x(NH_2)_{16-x}$ and G4-$(V^{2+})_x(NH_2)_{64-x}$ dendrimers; however, the G6-$(V^{2+})_x(NH_2)_{256-x}$ data suggests that aggregation is also unlikely for these materials in aqueous electrolyte solutions.

Cyclic voltammograms of the viologenated dendrimers obtained using a Pt microelectrode are shown in Figure 4. The voltammograms are fully repeatable even after multiple scans through the first reduction wave in 0.1 M K_2SO_4 electrolyte. K_2SO_4 was used as an electrolyte in these experiments because voltammetry in 0.1 M KF or KNO_3 exhibited a less reversible shape and a decrease in current upon repeated scanning. Waveshape analysis of the curves in Figure 4 indicate reversible steady-state voltammetry is obtained in K_2SO_4 electrolyte.

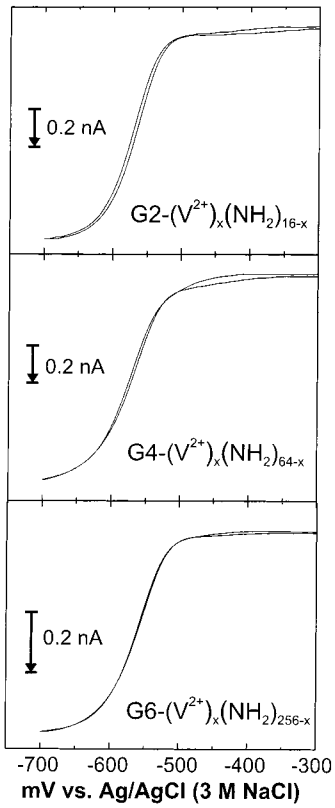


Figure 4. Cyclic voltammograms obtained at a Pt microdisk electrode (radius: 5.2 μm) of the three viologenated dendrimers in 0.1 M K_2SO_4. Viologen concentrations are 5.3 mM, 10.5 mM, and 8.7 mM for G2-$(V^{2+})_x(NH_2)_{16-x}$, G4-$(V^{2+})_x(NH_2)_{64-x}$, and G6-$(V^{2+})_x(NH_2)_{256-x}$, respectively. Scan rate: 2 mV/s.

The voltammograms shown in Figure 4 show little hysteresis at the slow scan rate (2 mV/s) employed. For ideal microelectrode behavior at a disk electrode, the condition $(Dt_c)^{1/2} \gg r$ must be fulfilled, where t_c is the characteristic time of a cyclic voltammetric experiment, r is the radius of the microelectrode, and D is the diffusion coefficient of the electroactive species.[57] The time constant (t_c) is equivalent to $RT/nF\upsilon$, where R is the molar gas constant, T is the absolute temperature, n is the number of electrons transferred, F is the Faraday, and υ is the scan rate. Diffusion coefficients may be calculated using the Stokes−Einstein equation, eq 4, where k is the Boltzmann constant, T is the absolute temperature, η is the viscosity of the solvent, and r_h is the hydrodynamic radius of the diffusing species (r_h values of 1.5, 2.3, and 3.5 nm were used for the three dendrimers).[3] The Stokes−Einstein calculated diffusion coefficients are presented in Table 1. Given the calculated diffusion coefficients and a 2 mV/s scan rate, it can be shown that for the largest dendrimer, G6-$(V^{2+})_x(NH_2)_{256-x}$, $(Dt)^{1/2}$ is a factor of 5 larger than the radius of the electrode (5.2 μm). Accordingly, it is appropriate to employ the equation for the steady-state limiting current at a microdisk electrode to probe for the electrochemical addressability of viologen moieties on the dendrimer periphery.

$$D = kT/6\pi\eta r_h \qquad (4)$$

For a disk electrode the limiting steady-state current, i_{ss}, is given by eq 5, where C is the apparent concentration of the electroactive species, and all other variables are as previously described. Assuming $n = 1$ and that the Stokes−Einstein-calculated diffusion coefficients are correct, the apparent concentrations of electroactive viologens may be determined

and compared to the viologen concentration determined by UV−vis absorbance measurements (which are supported by gravimetry coupled with the NMR and MALDI results). For all three dendrimers, the apparent electrochemical concentrations are smaller than the UV−vis/gravimetric concentration by at least 35%. In fact, the steady-state currents represent the reduction of less than 65, 50, and 55% of the viologen units on the G2-$(V^{2+})_x(NH_2)_{16-x}$, G4-$(V^{2+})_x(NH_2)_{64-x}$, and G6-$(V^{2+})_x(NH_2)_{256-x}$, dendrimers, respectively.

$$i_{SS} = 4nFRCD \tag{5}$$

To ascertain the reliability of the Stokes−Einstein calculated diffusion coefficients, the time-dependent current response at a microelectrode was examined. The experimental diffusion coefficients reported in Table 1 were determined by microelectrode chronoamperometry using a method reported by Baur and Wightman.[39] The following series of equations describes the current response at a microdisk electrode under conditions dominated by radial diffusion.

$$i_{CA} = (8nFR^2D^{1/2}C/\pi^{3/2}t^{1/2}) + i_{SS} \tag{6}$$

$$i_{CA}/i_{SS} = (2R/D^{1/2}\pi^{3/2})\, t^{-1/2} + 1 \tag{7}$$

Here, i_{CA} is the time-dependent current resulting from a mass transfer-limited potential step experiment and t is the time following the potential step.[38] Importantly, eq 7 allows diffusion coefficients to be determined without prior knowledge of concentration, making it a useful tool for investigating the electroactivity of the viologenated dendrimers. i_{ss} was obtained from cyclic voltammograms obtained at 2 mV/s and i_{CA} values were obtained following a potential step from −300 to −700 mV. Data were collected for 3 s, but only data collected between 1 and 3 s were used for the diffusion coefficient calculations to minimize distortions resulting from the finite time constant of the potentiostat. Denuault et al. have reported that use of eq 7 should result in less than 1% error in determination of the diffusion coefficient for the time segment employed.[58] For the linear fit to eq 7, only transients that yielded a correlation coefficient greater than 0.98 and an intercept between 0.99 and 1.1 were used.

Consistent with intuition, the diffusion coefficients reported in Table 1 decrease with increasing dendrimer generation. Importantly, the experimentally determined diffusion coefficients are within 15% of the Stokes−Einstein calculated values, supporting the argument for incomplete reduction of the electroactive groups on the dendrimer periphery. Our results are in accord with those of Abruña and co-workers, who have reported incomplete reduction of the terminal groups of ruthenium-complex modified PAMAM dendrimers.[59] It seems likely that this is a consequence of some of the viologen groups tucking into the dendrimer interior, thereby rendering them electrochemically inaccessible. Similar observations have been made by others for nonelectroactive peripheral groups.[1,60−62]

The electrochemical response of the viologenated dendrimers obtained at a glassy carbon macroelectrode is shown in Figure 5. Like the electrochemical response at the Pt microelectrode, reversible voltammetry was obtained for the first reduction wave in 0.1 M K_2SO_4 electrolyte. However, a nonideal response was obtained in 0.1 M KF and 0.1 M KNO_3. Passivation of the electrode, and a concomitant decrease in current, occurred upon cycling through the second wave. This is clearly shown in the three voltammograms in Figure 5, each of which depicts 10 consecutive cycles. In contrast to results for methyl viologen

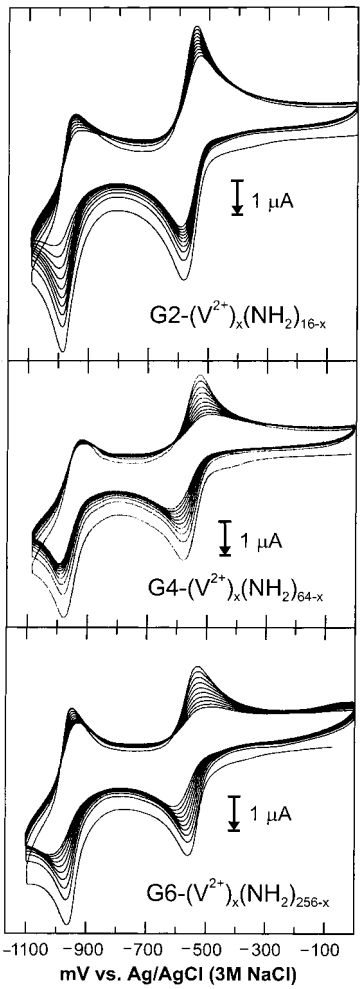


Figure 5. Cyclic voltammograms of the three viologenated dendrimers (G2-$(V^{2+})_x(NH_2)_{16-x}$, G4-$(V^{2+})_x(NH_2)_{64-x}$ and G6-$(V^{2+})_x(NH_2)_{256-x}$) in 0.1 M K_2SO_4 at a glassy carbon electrode (area: 0.0680 cm^2), Scan rate: 50 mV/s. Solutions are 1.0 mM in viologen.

in the presence of equimolar amounts of β-cyclodextrin,[53] passivation of the electrode still occurred despite addition of a 10-fold excess of β-cyclodextrin to the viologenated dendrimer and viologen acid solutions. The half-wave potentials ($E_{1/2}$) and peak separation data for these voltammograms are given in Table 1. The first half-wave potentials ($E(1)_{1/2}$) for the three dendrimers range from −530 mV to −555 mV. The potential of the first reduction wave of the viologen acid is approximately 100 mV negative of the equivalent wave for the viologenated dendrimers. This finding indicates that the dication form is unfavored by the highly charged dendritic microenvironment, consistent with a similar observation reported for viologen oligomers relative to their corresponding monomers.[63]

During the voltammetry experiments a purple plume was observed in the vicinity of the electrode. The color of the electrolyzed solution indicates the formation of radical cation dimers, as supported by the UV−vis results for the chemically reduced viologenated-dendrimers described earlier. On the basis of the parameters given in Table 1, dimer formation does not appear to inhibit the reversibility of the first reduction wave. Peak separation values vary from 54 to 60 mV for the three dendrimers at 1.0 mM total viologen concentration and a scan rate of 50 mV/s. Since the peak separations are less than 58 mV for G2-$(V^{2+})_x(NH_2)_{16-x}$, it is apparent that a layer of electroprecipitated viologenated-dendrimers is contributing to the voltammetric response in this case. The ratio of the anodic and cathodic peak heights (i_{pa1}/i_{pc1}) in Table 1 provides

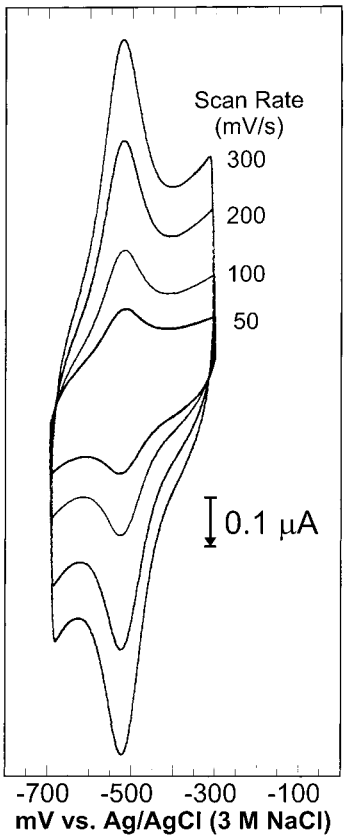


Figure 6. Cyclic voltammograms obtained at a Au electrode (Area: 0.0220 cm^2) after a 20 min soak in 17 μM G6-$(V^{2+})_x(NH_2)_{256-x}$ solution followed by a H_2O rinse. Scan rates: 50, 100, 200, and 300 mV/s.

information about the chemical reversibility of the first redox wave. Since a true anodic baseline could not be established directly from the voltammograms, the peak height ratio was calculated by employing Nicholson's method (eq 8).

$$i_{pa1}/i_{pc1} = ((i_{pa1})_0/i_{pc1}) + (0.485\,(i_{SP1})_0/i_{pc1}) + 0.086 \quad (8)$$

Here, $(i_{pa1})_0$ is the anodic peak current measured relative to the zero-current baseline and $(i_{SP1})_0$ is the cathodic current measured relative to the zero-current baseline at the switching potential.[38] The peak height ratios vary from 1.1 to 1.2 for the three dendrimers at scan rates ranging from 20 to 50 mV/s, indicating relatively good chemical reversibility.

Previous studies have shown that dendrimers adsorb strongly to metal surfaces.[20,27] Accordingly, a film of viologenated dendrimers was examined for stability in aqueous solution. The film was prepared by soaking a Au electrode in an aqueous 17 μM G6-$(V^{2+})_x(NH_2)_{256-x}$ solution for 20 min, followed by extensive rinsing with H_2O. The separation between the anodic and cathodic peaks (ΔE_p), obtained by cyclic voltammetry in a dendrimer-free solution, was found to be less than 10 mV and the magnitude of the adsorption peak scales linearly with scan rate (Figure 6). The reduction potential of the surface-confined species is slightly positive of that of the half-wave potential of the solution-phase species ($E(1)_{surface} = -520$ to -530 mV and $E(1)_{1/2} = -541$ mV). The film is stable when stored in electrolyte solution for up to 10 days and during repeated scanning (>30 scans) between -300 and -700 mV.

Summary and Conclusions

A series of electroactive, water-soluble, partially functionalized, viologenated PAMAM dendrimers was prepared using a simple synthetic procedure. The extent of end-group functionalization determined by ^1H NMR, MALDI-TOF MS and UV−vis spectroscopy was in good agreement for the three dendrimers. The molecules are stable when stored in aqueous solution, and DLS results indicate they are unaggregated in aqueous electrolyte-containing solution.

Spectroscopic studies revealed intramolecular dimerization of the reduced viologen moieties tethered to the viologenated dendrimers. In contrast, the reduced viologen acid employed in the dendrimer functionalization reaction was primarily present in the monomer form.

Electrochemical studies of the viologenated dendrimers resulted in the following five observations. First, repeated scanning through the first reduction wave produces a stable and reproducible electrochemical response in K_2SO_4 electrolyte, whereas electroprecipitation results in electrode passivation upon formation of the direduced species. Second, the half-wave potentials for the first reduction wave become more positive with increasing dendrimer generation, indicating that the cation radical is more favored for the higher generations. This is likely an electrostatic consequence of increased steric crowding of the dication as the dendrimer generation increases. Third, the diffusion coefficients measured by chronoamperometry at a microelectrode scale with dendrimer generation and are in agreement with Stokes−Einstein calculations. Fourth, the magnitude of the steady-state limiting currents and the calculated diffusion coefficients indicate that fewer than 70% of the viologen units on the dendrimer periphery are electrochemically accessible. This is likely a consequence of some of the viologen groups tucking into the interior of the dendrimer. Finally, a stable film of viologenated dendrimers can be formed on a metal substrate by a simple soaking procedure.

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Supporting Information Available: 300 MHz ^1H NMR spectra of G4-$(V^{2+})_x(NH_2)_{64-x}$ and G6-$(V^{2+})_x(NH_2)_{256-x}$ in pH 9 D_2O. This material is available free of charge via the Internet at http://pubs.acs.org.

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