

Synthesis, Characterization, and Electrochemical Behavior of Viologen-Functionalized Poly(Amidoamine) Dendrimers

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Aminoterminated, ethylenediamine core polyamidoamine starburst dendrimers of generation 2 (G2), generation 4 (G4) and generation 6 (G6) have been successfully surface-modified via an amide coupling reaction with 4-ethyl, 4'-(3-propionic) bipyridinium cation and the electrochemical behavior of the resulting dendrimers were investigated in aqueous potassium chloride electrolyte solutions. The 1-[3-(dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride/N-hydroxysuccinimide-mediated reaction resulted in 25-39% end-group functionalization. The water-soluble 4-ethyl, 4'-(3-propylamide) bipyridinium dibromide dendrimers (G2-V2+, G4-V2+ and G6-V2+) were characterized by ¹H NMR and UV-Vis spectroscopic methods. The cyclic voltammetric and chronoamperometric experiments were performed to determine the diffusion coefficient and the number of electrons transferred in the process of the first reduction of the viologen-functionalized dendrimers. Adsorption of viologen-functionalized dendrimers at electrode surface was evidenced in the voltammograms. Experimentally determined diffusion coefficients were in good agreement with the values expected from the Stokes-Einstein relation, while the number of electrons transferred concurred with the extent of functionalization determined by ¹H NMR and UV-Vis spectra.

Key Words : Viologen, Dendrimer, Electrochemistry

Introduction

The synthesis and characterization of dendrimers have been of recent interest due to their well-defined three-dimensional geometry, generational variety, ease of functionalization, and potential for the practical nano particle applications.¹⁻⁶ Monolayers or multilayers of dendrimers can be formed by self-assembly at or through covalent-attachment to the substrate or supporting organic thin film, making them ideal for use in studies of self-assembly (SAMs),⁷ liquid crystalline devices,⁸ and conductive film technology.⁹ Dendritic macromolecules possessing functionalities capable of absorbing and emitting light have been used as molecular light harvesters,¹⁰ and solvatochromic probes.¹¹ The recent reports described the application of an electrostatically bound DNA-dendrimer complexes for use as gene transfer vectors through cell membranes.^{12,13} Dendrimers having redox-active centers including coordinated metal sites are of particular interest because they have potential applications in the field of chemical sensors,¹⁴ multielectron redox catalysts,¹⁵ and molecular electronic devices.^{16,17} In terms of employing dendrimers as electrochemical probes, the preparation of electro-active dendrimers functionalized with redox-active species such as ferrocene,^{18,19} anthraquinone,²⁰ and ruthenium(II) complexes^{21,22} have been described. In this work, we wish to report synthesis and electrochemistry of three different generations of poly(amidoamine) (PAMAM) dendrimers functionalized with a 4-ethyl, 4'-propylamidebi-

pyridinium (viologen) moiety (G2-V2+, G4-V2+ (Figure 1), and G6-V2+), which can be utilized in multi-electron redox catalysts, electrocatalysis, photochemistry and photoelectrochemistry and electrochromic devices.²³⁻²⁸ The water-soluble viologenated-dendrimers were investigated by ¹H NMR, UV-Visible spectroscopy, and electrochemistry. Cyclic voltammetry and chronoamperometry were employed to obtain the number of electrons transferred (*n*) during the first redox process and the diffusion coefficient (*D*) of the three size-differentiated viologen (2+) macromolecules.

Experimental Section

Materials and Apparatus. Amine terminated generation 2, 4, and 6 STARBURSTTM PAMAM dendrimers were supplied by Dendritech, Inc. (Midland, MI). N-hydroxysuccinimide (NHS) and 1-[3-(Dimethylamino)propyl]-3-ethylcarbodiimide hydrochloride (EDC) were purchased from Aldrich. Triethanolamine, bromopropionic acid, bromoethane, K₂SO₄ and KCl salts were purchased from Aldrich and used as received. Ru(NH₃)₆Cl₃ used as standard redox reagent in electrochemical measurement, was purchased from Strem Chemicals. Solutions were prepared from deionized water (Ultrapure Milli-Q water, Millipore Corp.).

¹H NMR and UV-Vis measurements. ¹H NMR spectra were obtained in D₂O (99.9%, Cambridge Isotope Laboratory, Andover, MA) on a Varian 200 (200 MHz) spectrometer. UV-Visible spectra were acquired using a Hewlett-Packard Model 8453 UV-Vis spectrometer.

Electrochemistry. Electrochemical experiments were carried out using a BAS 100A electrochemical analyzer

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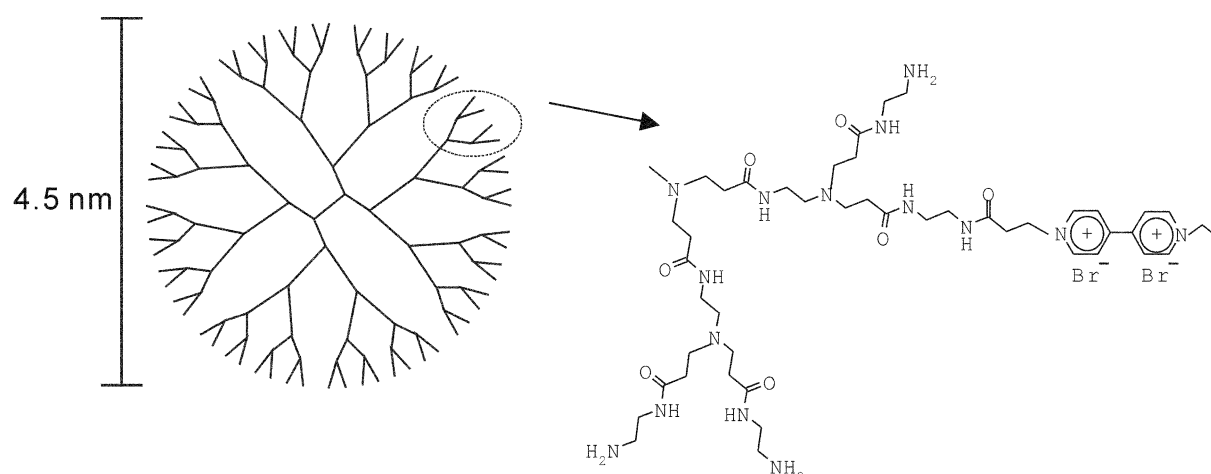
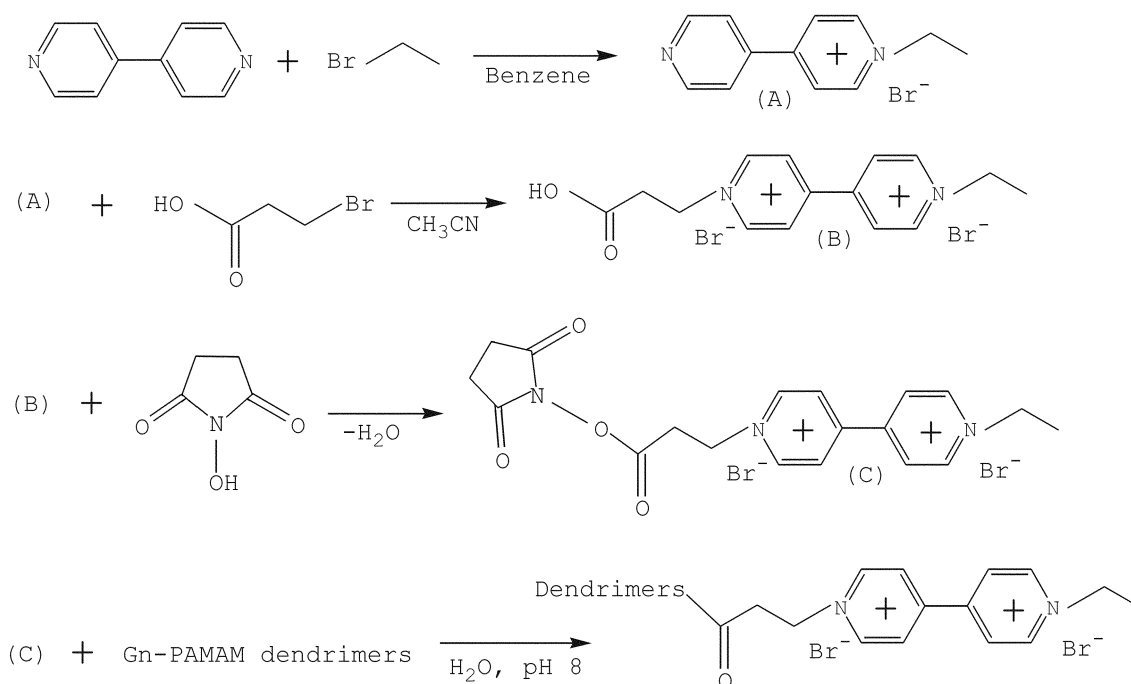


Figure 1. Two dimensional schematic structure of viologen-modified generation 4 PAMAM dendrimer (G4-V2·).

(Bioanalytical Systems, West Lafayette, Inc.), a Pine Instrument AFRDE4 bipotentiostat (Grove City, PA) and Kipp and Zonen XYY' chart recorder (Bohemia, NY). Glassy carbon electrode (GCE, radius: 1.5 mm, BAS), Pt electrode (radius: 1.0 mm, BAS), and Pt microelectrode (radius: 5 μm , BAS) were used as working electrodes. Ag | AgCl (3 M NaCl, BAS) and a Pt-gauze were used as the reference and counter electrodes. Prior to electrochemical experiments, the working electrodes were polished with 1 μm and 0.1 μm - Al_2O_3 on a polishing cloth (Buehler Ltd., Lake Bluff, IL) successively. Following the final polishing step, the electrodes were rinsed thoroughly and sonicated with deionized water and ethanol. All experiments were carried out at 22 ± 2 $^\circ\text{C}$ in deoxygenated aqueous solutions.

Synthesis. The viologen precursor was prepared from 4,4'-bipyridine with bromoethane and 3-bromopropionic acid

in benzene.²⁹ Dendrimers were modified with the viologens according to the EDC/NHS coupling procedure by Vijay, *et al.*³⁰ Scheme 1 outlines the synthetic sequence. An aqueous solution (5 mL) of NHS (150 mg) and viologen precursor (400 mg) was stirred for 1 h at 0 $^\circ\text{C}$. EDC (500 mg) was added, and the mixture was stirred for 10 min at 0 $^\circ\text{C}$, and then at room temperature for an additional 10 min. Next, PAMAM dendrimers dissolved in 4 mL buffer solution (0.1 M TEA adjusted to pH 8 with KOH) were combined with the activated viologen precursor. The amount of dendrimer used was adjusted, according to dendrimer generation, to establish a 1 : 2 : 2 : 10 molar ratio among the dendrimer terminal amines, viologen precursor, NHS, and EDC, respectively. The final solution pH was adjusted to 8.0 by adding dilute KOH, which was then stirred overnight at room temperature and then purified using dialysis for one



Scheme 1. The synthetic sequence of viologen-functionalized PAMAM dendrimers.

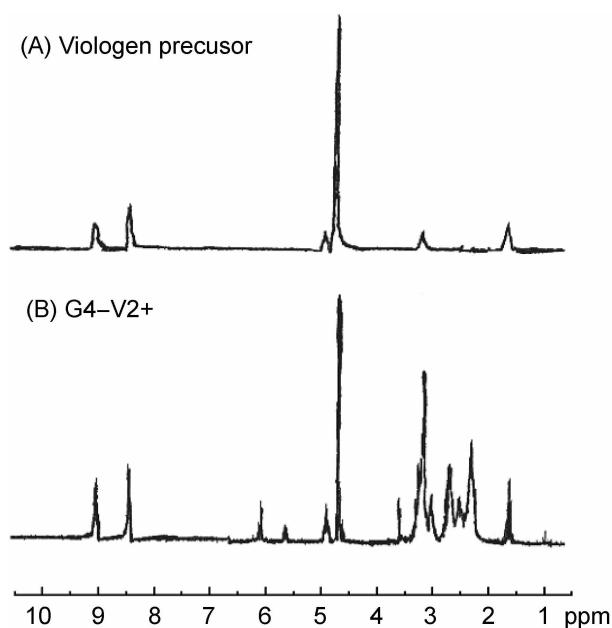


Figure 2. ^1H -NMR spectra of (A) viologen precursor and (B) G2-V2+.

day. A fibrous blue-green powder was formed after 24 h lyophilization (Freezone 6, Labconco, Kansas City, MO).

Results and Discussion

The primary objective of this study was to examine the structural and electrochemical properties of the viologenated-dendrimers (VDs). Figure 2 shows ^1H NMR spectra of the viologen precursor (A) and G2-V2⁻ (B). New signals between 2.1–3.5 ppm (Dendrimer methylene protons³¹) that were absent from the spectra of viologen precursor were shown at the G4-V2⁻ spectrum. The NMR spectra of G4-V2⁺ and G6-V2⁺ also showed the peaks near the same chemical shifts. The 4,4'-bipyridinium unit signals of the viologen precursor and the VDs attached to periphery of dendrimers exhibited a similar shift around 8.4 ppm and 9.0 ppm.³² The number of viologens per dendrimer was established from the ratio of the integrated viologen methylene hydrogens (at 1.7 ppm) to the dendrimer methylene hydrogens (at 3.3 ppm), after normalization with respect to the number of hydrogens per molecule represented within the integral region.

Figure 3 shows UV-Vis spectra of identical molar concentration 2.4 μM of viologen precursor, G2-V2⁺, and G4-V2⁺, and 0.8 μM of G6-V2⁻. The spectra were obtained from the experiments performed after a calculated molar concentration of modified viologen onto dendrimer for using molar extinction coefficient ($21000 \text{ M}^{-1} \text{ cm}^{-1}$ at 259 nm) of viologen precursor (V²⁺).³³ The absorption was attributed to viologen $\pi-\pi^*$ transitions and provides a basis for determining the degree of end group functionalized of viologenated dendrimer and gravimetric analysis. The increase in absorption is due to an increasing number of viologen units attached to the periphery of dendrimers with increasing

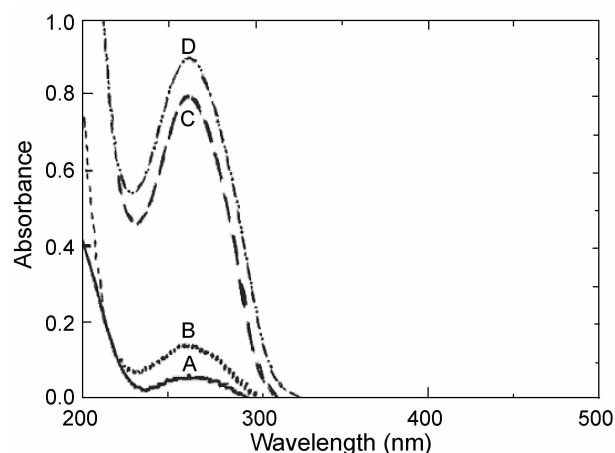


Figure 3. UV-Vis spectra of 2.4 mM (A) viologen precursor, (B) G2-V2⁺ and (C) G4-V2⁺, and 0.8 mM (D) G6-V2⁺ in aqueous solutions.

Table 1. The number of viologens on the three dendrimers surfaces obtained by ^1H -NMR and UV-Vis spectroscopy

Gn	Diameter (Å) ^a	Number of surface groups (g/mol) ^a	Number of viologens on dendrimer surface	
			^1H -NMR	UV-Vis
G2	29	16 (3.256)	4.3 (27%)	4.8 (30%)
G4	45	64 (14.215)	21.8 (34%)	25.5 (39%)
G6	67	256 (58.048)	63.1 (25%)	68.4 (27%)

^aReference: Technology Review by Dendritech, Inc. 1995.

generation. ^1H NMR and UV-Vis spectra could be used to determine the molecular weights and molar concentrations independently. These results indicated that 25–39% viologen functionalization of the dendrimers periphery was accomplished for the dendrimers (G2-V2⁺, G4-V2⁻, and G6-V2⁺). Incomplete functionalization is likely a result of repulsion among positive charges of 4,4'-bipyridinium, and the mild reaction conditions employed. The degree of functionalization determined by both ^1H NMR and UV-Vis was summarized in Table 1 and the results from the two independent methods are in good agreement.

Figure 4 shows cyclic voltammograms of 0.040 mM G2-V2⁺, G4-V2⁺, and G6-V2⁺ in aqueous solutions at the scan rate of 0.1 V/s (vs. Ag | AgCl (3 M NaCl)) by using the glassy carbon electrode. G2-V2⁺ shows a near diffusion shape. On the other hand two peaks were observed on the reverse scan of voltammograms G4-V2⁺. The broad peak results from diffusion of solubilized G4-V⁻, while the sharp peak represents the oxidation of the reduced radical cations that have adsorbed at the electrode surface. G6-V2⁺ has a sharp reverse peak, which indicates stronger adsorption of the reduced VDs at the electrode surface with the change in the oxidation state of the viologen units on the dendritic surface. The facts that methyl viologen (2^{+/-}) does not adsorb at the electrode surface in the similar conditions,²⁵

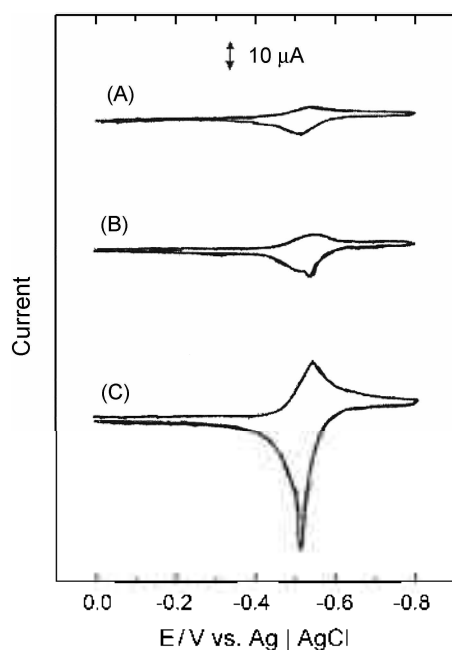


Figure 4. Cyclic voltammograms of 40 μM (A) G2-V2+, (B) G4-V2+, and (C) G6-V2- at a glassy carbon electrode (radius: 1.5 mm). Supporting electrolyte: 0.1 M KCl aqueous solution. Scan rate: 100 mV/s.

that G4-V+ does, and that the extent of adsorption becomes stronger as the size of dendrimer increases reflects that the adsorption of the reduced VDs is promoted by the dendrimer, to which the viologen unit is attached. Figure 5 shows the scan rate dependence of the cyclic voltammetric response (A), the corresponding Randles-Sevcik equation plot for the diffusion process using A (B),³¹ and the Cottrell plot of $I(t)$ vs. $t^{-1/2}$ for the G2-V2- at a Pt planar electrode (C). In the chronoamperometric experiment, the potential was stepped from 0 to -0.6 V and held for 1000 ms to obtain a plot of $I(t)$ vs. $t^{-1/2}$. Similar cyclic voltammograms and chronoamperograms were observed for G4-V2- and G6-V2+. The steady-state voltammograms of G2-V2-, G4-V2+, and G6-V2+ were obtained at the Pt microdisk electrode in 0.1 M KCl aqueous solution (Figure 6). As with the cyclic voltammograms at the Pt planar electrode, G4-V2+ and G6-V2+ have shown an adsorption peak during the reverse scan. The peak intensity increased with increasing generation of dendrimers as was observed at macroelectrode and it did also with increasing the pH as is shown in Figure 7. The solubility of the reduced form increases at low pH because the terminal amine group of dendrimers is protonated.^{35,36} Additionally, the formal potentials (E^0) of three viologen-functionalized dendrimers obtained from curves of the steady-state current are virtually identical at -0.55 (G2-V2+), -0.54 (G4-V2+) and -0.54 V (G6-V2-) vs. Ag | AgCl (3 M NaCl). The similar potential values mean that all of the viologen moieties attached to the periphery of the dendrimers act independently, and the number of dendrimers generation does not affect the redox property of viologen functional group. The electron transfer number (n) and diffusion coefficient (D) of the three VDs can be determined

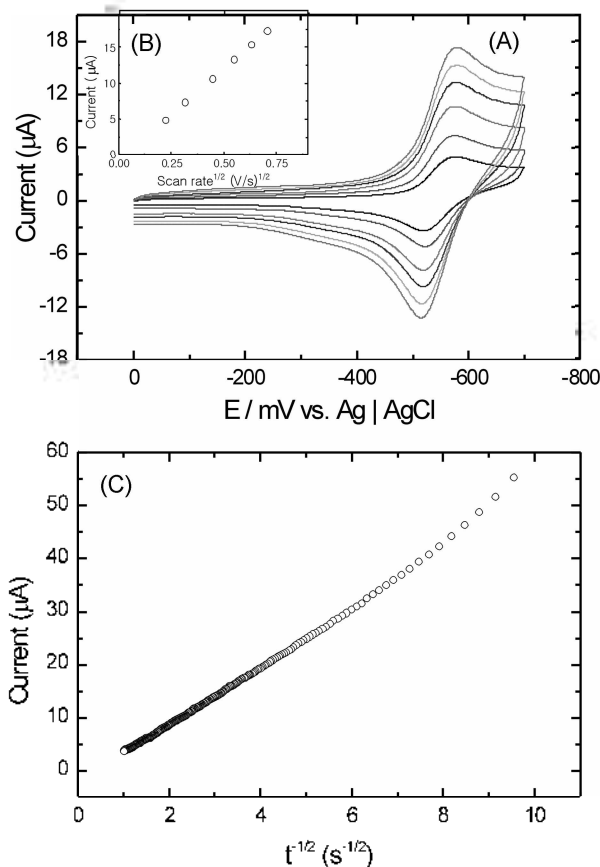


Figure 5. (A) Cyclic voltammograms. Scan rate: 0.05, 0.1, 0.2, 0.3, 0.4, 0.5 V/s. (B) plot of peak current (μA) vs. scan rate (V/s)^{1/2}, and (C) plot of $I(t)$ vs. $t^{-1/2}$ recorded under potential -600 mV of 0.67 mM G2-V2⁺ at a Pt planar electrode (radius: 1.0 mm) in 0.1 M KCl aqueous solution.

from the cyclic voltammograms at a Pt microelectrode and the chronoamperogram³⁷ at a Pt macroelectrode. The values n and D of VDs can be calculated from ratios of the radial and linear diffusion-controlled currents for the unknown and standard reactants.³⁸ $\text{Ru}(\text{NH}_3)_6^{3+}$ was chosen as the electrochemical standard and the diffusion coefficient of $\text{Ru}(\text{NH}_3)_6^{3+}$ was determined to be $5.6 \times 10^{-6} \text{ cm}^2/\text{s}$ by using steady-state and linear diffusion-controlled currents.³⁹ Equation 1 describes the steady-state current (I_∞ is unknown reactant current, $I_{\infty S}$ is standard reactant current) at a microdisk electrode under conditions of radial diffusion.

$$i_\infty = i_{\infty S} = 4rnF c^* D \quad (1)$$

Here, n is the number of electrons transferred, F is the Faraday constant, D is the diffusion coefficient, c^* is the concentration of electroactive species in the solution, r is the radius of the microelectrode. In order to obtain the results for VDs reactions, the standard electrode reaction was performed at the same Pt microelectrode. The ratio of the steady-state currents for the VDs and standards reactant is given by equation 2.

$$\frac{i_\infty}{i_{\infty S}} = \frac{nD_{VD}c_{VD}}{n_S D_S c_S} \quad (2)$$

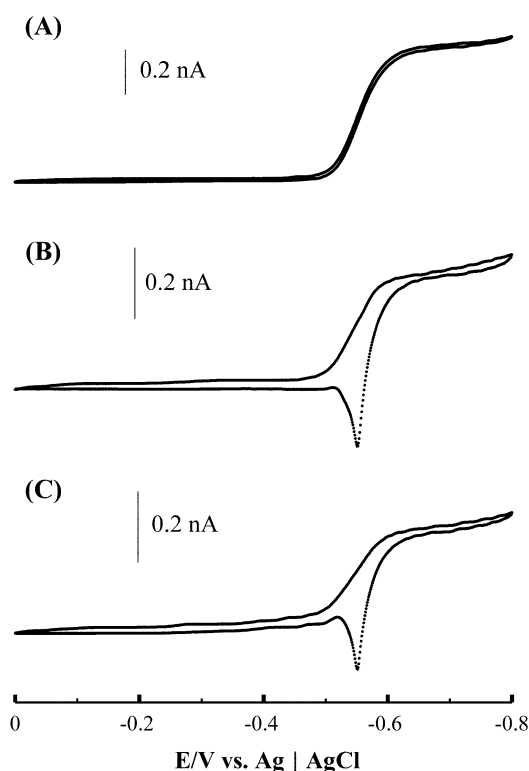


Figure 6. Cyclic voltammograms at 10 μm diameter disk Pt microelectrode in 0.1 M aqueous KCl solution (pH 7.4) containing (A) 0.67 mM G2-V2+, (B) 0.12 mM G4-V2+ and (C) 0.049 mM G6-V2+. Scan rate: 10 mV/s.

Where n_s is the number of electrons transferred, D_s and C_s are the diffusion coefficient and concentration of standard reaction, respectively. Linear diffusion-controlled current at a Pt planar electrode of area A is given by the Cottrell equation (Equation 3). Using equation 3, the ratio of the slopes of I vs. $t^{-1/2}$ for the VDs (S_{VDs}) and for standard reactant (S_s) at the same planar electrode yields (Equation 4)

$$i = \frac{nFA D^{1/2} c}{\pi^{1/2} t^{1/2}} \quad (3)$$

$$\frac{S}{S_s} = \frac{n D_{VDs}^{1/2} c_{VDs}}{n_s D_s^{1/2} c_s} \quad (4)$$

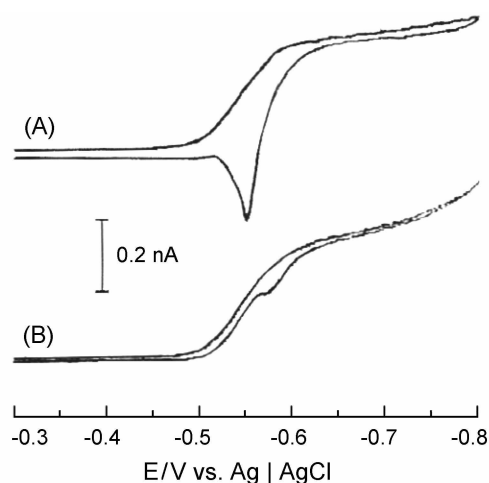


Figure 7. Cyclic voltammograms for 0.12 mM G4-V2+ (A) in 0.1 M aqueous KCl solution (pH 7.4), and (B) in 0.1 M KH₂PO₄ buffer solution (pH 6.3) at 10 μm diameter disk Pt microelectrode. Scan rate: 10 mV/s.

The electron transfer numbers for the unknown may be calculated by combining equations 2 and 4. That is

$$\frac{n}{n_s} = \frac{S^2 i_{\infty s} c_s}{S_{VDs}^2 i_{\infty s} c_{VDs}} \quad (5)$$

Diffusion coefficient can also be obtained separately by equations 2 and 4. The expression is

$$\frac{D_{VDs}}{D_s} = \frac{i_{\infty s}^2 S_s^2}{i_{\infty s}^2 S^2} \quad (6)$$

The results of the electrochemical experiments are summarized in Table 2 together with the diffusion coefficients expected from the Stokes-Einstein equation. The diffusion coefficients determined from the voltammetric experiments, which decrease with increasing the viologen-modified dendrimer generation or with increasing the number of viologen units on the dendrimer periphery, are within the range expected from the Stokes-Einstein equation. The number of electrons involved in the first reduction of the dendrimer viologens is in excellent agreement with those determined by ¹H-NMR and UV-vis spectroscopic methods.

Table 2. Experimental and calculated results for the reductions of G2-V2⁺, G4-V2⁺, and G6-V2⁺ in 0.1 M KCl aqueous solution

Compound (concentration)	Slope × 10 ⁻⁶ ^a	i_{ds} /nA ^b	$D_{1^{\circ}}$ (d. c) × 10 ⁻⁷ cm ² /s	D_{cal}^f × 10 ⁻⁷ cm ² /s	n_{cal}	-E _{cp} (V) ^c	-E _{ap} (V) ^c	-E _{(cp-ap)/2} (V) ^c
Ru(NH ₃) ₆ ³⁺ (5 mM) ^d	20	5.4		56	1	0.25	0.17	0.21
G2-V2 ⁺ (0.67 mM)	5.4	0.61	15 (9.3, 6.7)	9.8	4.8	0.58	0.52	0.55
G4-V2 ⁺ (0.12 mM)	3.5	0.3	9.7 (6.9, 5.3)	5.6	23	0.56	0.52	0.54
G6-V2 ⁺ (0.049 mM)	3.4	0.25	6.6 (5.2, 4.2)	4.1	63.7	0.56	0.52	0.54

^aThe slopes of plot I vs. $t^{-1/2}$ from chronoamperometry on the Pt macroelectrode (diameter = 1.0 mm). ^bSteady-state currents from Pt microelectrode (diameter = 10 μm). ^cTheoretical diffusion coefficients of three non-modified dendrimers were calculated by Stokes-Einstein equation: (D is a diffusivity of a solute molecule, r is the radius of the solute molecule, η is the viscosity of the solvent, and N is Avogadro's number)

$D = \frac{RT}{4\pi\eta N}$. ^dTheoretical diffusion coefficients of three viologen-modified dendrimers were calculated by Stokes-Einstein equation after considering the length of 4-ethyl, 4'-propionic bipyridinium (d: 10 Å, and e: 20 Å). ^eExperimental diffusion coefficients determined by equation 5 and 6. ^fPotentials from cyclic voltammogram on the Pt macroelectrode.

Conclusions

The preparation, characterization and electrochemical behavior of viologen-functionalized second, fourth, and sixth generation PAMAM dendrimers have been described. The numbers of electroactive units determined independently by $^1\text{H-NMR}$ and UV-vis spectroscopies were in good agreement. The present synthetic conditions led to the 25-39 % end-group functionalization. The electron transfer number and the diffusion coefficient of the three dendrimers prepared were determined by cyclic voltammetry and chronoamperometry in aqueous solutions. The diffusion coefficient magnitudes that were obtained from electrochemical methods decreased with increasing dendrimer generation and were in agreement with the values calculated with the Stokes-Einstein equation. Electroreduced forms of G4-V⁺ and G6-V⁺ showed strong adsorption on the electrode surfaces. Additionally, the redox potentials for the first reduction of three viologen-functionalized dendrimers had similar values and all of viologen moieties attached to the periphery of the dendrimer acted independently. Thus these viologen-modified dendrimers may be proved to be useful as molecular electronic devices, electrochromic devices and multi-electron redox catalysts.

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