Complete Charge Pooling is Prevented in Viologen-Based Dendrimers by Self-Protection

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Abstract: We have investigated the electrochemical behavior, and chemical and photosensitized reduction of two dendrimers based on a 1,3,5-trisubstituted benzenoid core, which contain 9 and 21 4,4′-bipyridinium (usually called viologen) units, respectively, in their branches and are terminated with tetraarylmethane groups. For comparison purposes, the behavior of reference compounds that contain a single viologen unit have also been investigated. We have found that only part of the viologen units can be reduced in the dendrimer species. For the larger dendrimer, the number of reducible viologens (out of the 21 present) is 14 in electrochemical experiments (in MeCN), 9 on reduction with bis(benzene)chromium (in MeCN), and 13 by photoinduced electron transfer with 9-methylanthracene as a photosensitizer and triethanolamine as a sacrificial reductant in CH_2Cl_2. The reduced viologen units undergo partial dimerization. The photochemical experiments have shown that only monomeric, one-electron-reduced viologen units are formed at the beginning of the irradiation, followed by dimer formation, until a photostationary state is reached that contains 40% nonreduced, 33% monomeric reduced, and 27% reduced units associated in the dimeric form. The results suggest that, upon reduction of a fraction of the viologen units, the dendrimer structure shrinks, with the result that the bulky terminal groups protect other viologen units from being reduced.

Keywords: bipyridinium units • dendrimers • electrochemistry • photosensitization • redox chemistry • viologen

Introduction

Dendrimers are well-defined, treelike, monodisperse macromolecules, with a high degree of order and the possibility to contain selected functional units in predetermined sites of their structure.[1,2] They are currently attracting the interest of a great number of scientists because of their unusual chemical and physical properties and the wide range of their potential applications. Dendrimers that contain photoactive[3] and/or electroactive[4] units are of particularly interest, since such units 1) offer a handle to probe the intricacies of dendrimer structures and superstructures, 2) allow dendrimers to perform useful functions, such as light harvesting or charge pooling, and 3) can be useful for sensing purposes with signal amplification.

The 4,4′-bipyridinium (usually called viologen) dication is a well-known electroactive unit.[5] It undergoes two successive, reversible, one-electron reduction processes at easily accessible potentials, and its monoreduced form shows a characteristic, very strong absorption in the visible region. Viologen species have been extensively used as electron carriers in reduction processes,[6] as well as in photochemical conversion cycles for hydrogen evolution.[7]

We have previously reported on the synthesis of two dendrimers (**A 9**$^{18+}$ and **A 21**$^{42+}$, Scheme 1) based on a 1,3,5-trisubstituted benzenoid core, containing 9 and 21 viologen units, respectively, in their branches and terminated with tetraarylmethane groups.[8] We have also shown that, in CH_2Cl_2, such highly charged polycationic species give rise to the formation of strong host–guest complexes with the dianionic form of the red dye eosin.[8] Each viologen unit in the dendrimers becomes associated with an eosin molecule,

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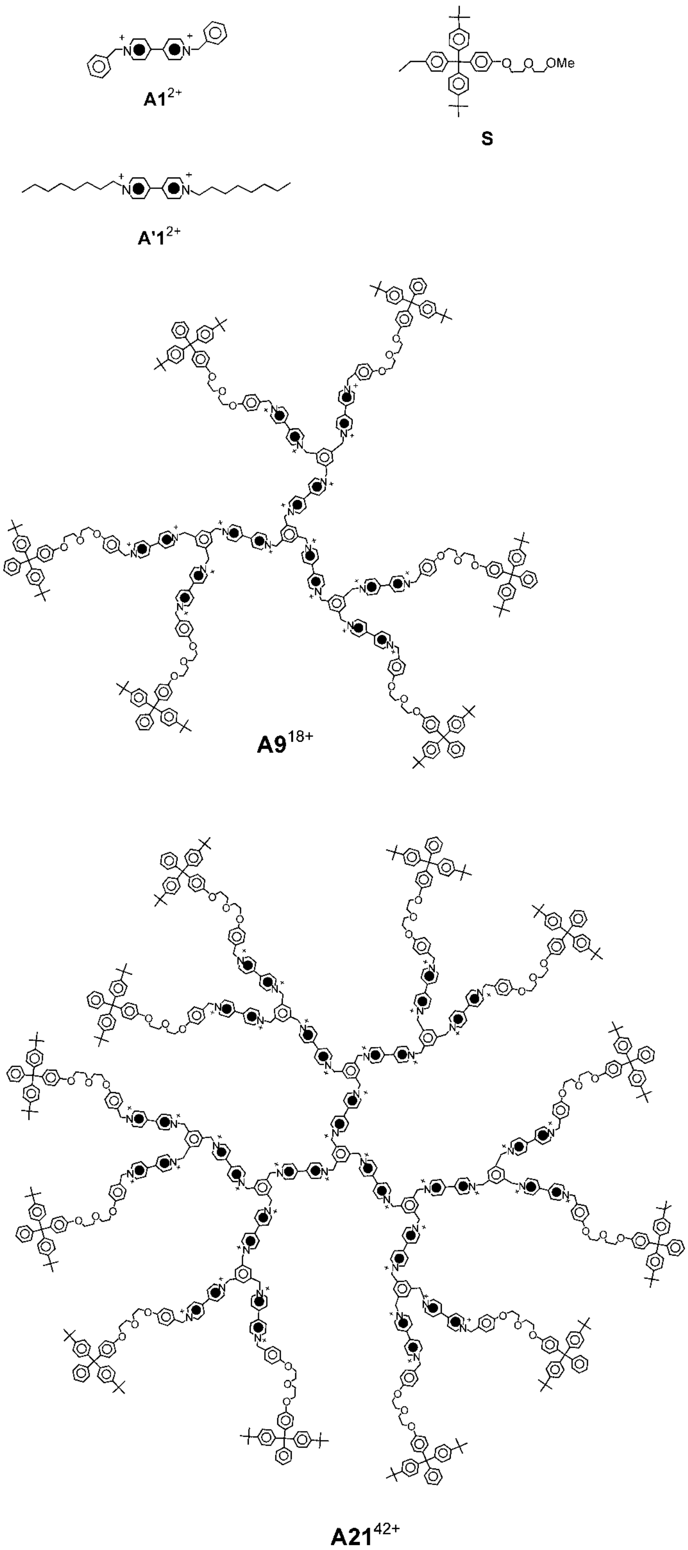
so that the number of positions ("seats") available for the guest molecules in the hosting dendrimer is clearly established; for example, 21 for the larger of the two dendrimers. The host–guest interaction can be destroyed by addition of chloride ions and re-established by successive addition of silver ions, so that eosin molecules can escape from and reenter the dendrimer's interior, a process that can be monitored by fluorescence measurements.

This paper describes the redox reactions of dendrimers **A9**$^{18+}$ and **A21**$^{42+}$. For comparison purposes, we have also investigated the behavior of the simple viologen species **A1**$^{2+}$ and **A′1**$^{2+}$, as reference compounds for the viologen units of the polyviologen dendrimers, and of compound **S**, as a reference for the tetraarylmethane end groups (Scheme 1). Electrochemical investigations on other dendrimers that contain viologen units have recently been reported.[9–12]

Abstract in Italian: *I risultati riportati in questo lavoro riguardano la riduzione elettrochimica, chimica e fotochimica di due dendrimeri formati da un'unità centrale benzenica, da unità periferiche costituite da gruppi tetrafenilmetano e da ramificazioni che contengono rispettivamente 9 e 21 unità di tipo 4,4′-dipiridinio (più comunemente noto come viologeno). Lo studio, nell'ambito del quale è stato anche investigato il comportamento di appropriati composti di riferimento costituiti da una sola unità viologeno, ha messo in evidenza che non è possibile ridurre tutte le unità viologeno contenute nei dendrimeri con nessuna delle metodiche utilizzate e che il numero delle unità riducibili cambia a seconda delle condizioni impiegate. Nel caso del dendrimero più grande, ad esempio, delle 21 unità presenti, quelle che possono essere ridotte per via elettrochimica (in acetonitrile) sono 14, mentre sono solo 9 quelle riducibili chimicamente (usando dibenzenecromo in acetonitrile) e 13 quelle ridotte fotochimicamente (utilizzando 9-metilantracene come fotosensibilizzatore e trietanolammina come agente sacrificale in acetonitrile). I risultati ottenuti hanno anche mostrato che le unità ridotte, almeno in parte, dimerizzano e gli esperimenti fotochimici hanno specificatamente evidenziato che all'inizio dell'irradiamento le unità ridotte sono in forma monomerica e che solo successivamente interviene il processo di dimerizzazione, il cui grado di avanzamento determina poi la composizione dello stato fotostazionario. Ad esempio, per il dendrimero più grande lo stato fotostazionario contiene 40 % delle unità viologeno non ridotte, 33 % di unità ridotte in forma monomerica e 27 % di unità ridotte coinvolte nella dimerizzazione. Il comportamento in riduzione dei due dendrimeri studiati può essere interpretato ammettendo che la riduzione di una certa frazione di unità viologeno induca una contrazione della struttura dendritica a seguito della quale i gruppi terminali, sufficientemente ingombranti, potrebbero svolgere un'azione protettiva nei confronti delle unità viologeno, impedendo così il procedere della riduzione.*



Scheme 1. Formulas of the examined compounds. The **A*n***$^{2n+}$ symbols used indicate the presence of electron-acceptor (**A**) units, their number (n), and, as a superscript, the overall electric charge ($2n$) of each compound.

Results and Discussion

Dendrimers **A9**$^{18+}$ and **A21**$^{42+}$ are slightly soluble in MeCN and CH_2Cl_2. The electrochemical and chemical reductions were carried out in MeCN, with **A1**$^{2+}$ as a reference compound for the viologen units, while the photosensitized reduction experiments were performed in CH_2Cl_2, by using 9-methylanthracene as the photosensitizer and **A′1**$^{2+}$ as a reference compound.

Absorption spectra: Figure 1 shows the absorption spectra in MeCN of reference compounds **A1**$^{2+}$ and **S**. The inset in this figure shows the strong fluorescence band exhibited by **S**, which is no longer present in the dendrimers. This result is an expected one, since the fluorescent excited state of tetraarylmethane derivatives can be quenched by the viologen units through both energy and electron transfer.[13]

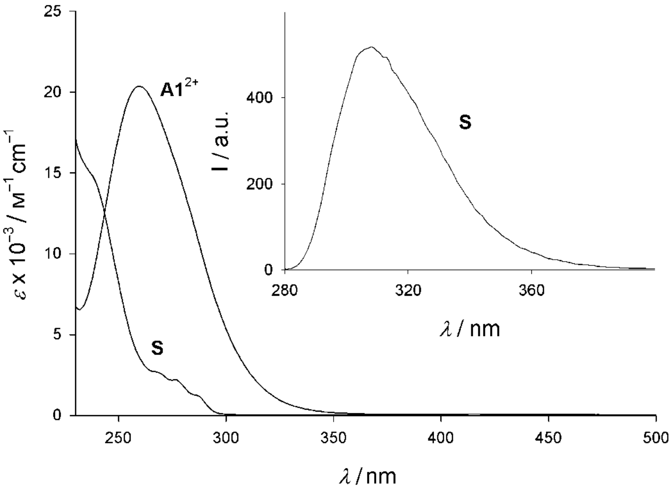


Figure 1. Absorption spectra of the reference compounds **A1**$^{2+}$ and **S** (in MeCN). The inset shows the fluorescence band of **S** (in MeCN, λ_{ex} = 250 nm).

The absorption spectra of dendrimers **A9**$^{18+}$ and **A21**$^{42+}$ are displayed in Figure 2. From this figure it is possible to conclude that the absorption spectrum of **A21**$^{42+}$ is noticeably more intense than the sum of the spectra of 21 **A1**$^{2+}$ and 12 **S** component units, and that broad and weak absorption features emerge in the visible spectral region from the low-energy tail of the intense UV bands. These results confirm that **A1**$^{2+}$ is not a fully satisfactory model, at least from a spectroscopic viewpoint, for the viologen units of **A9**$^{18+}$ and **A21**$^{42+}$. Each viologen unit in the dendrimers shares benzyl groups with other units (Scheme 1) and some benzyl groups carry bismethyleneoxy substituents. The weak charge-transfer bands in the visible region could derive from interactions of the electron-acceptor viologen units with the proximate (through bond) or remote (through space) electron-donor aryloxy units.

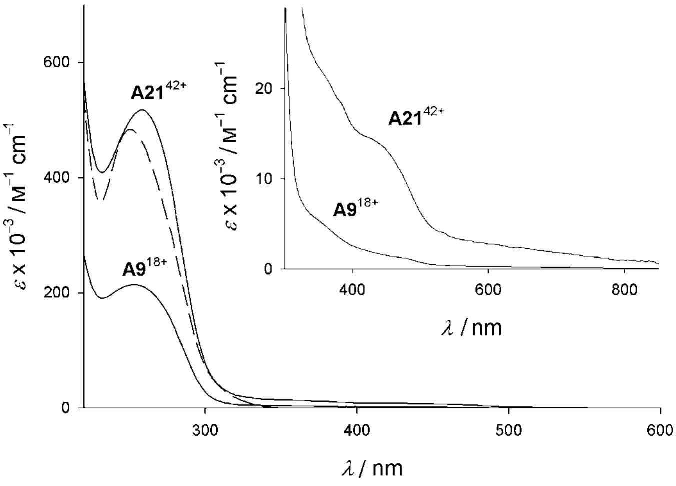


Figure 2. Absorption spectra of the dendrimers **A9**$^{18+}$ and **A21**$^{42+}$ (in MeCN). The dashed curve represents the sum of the spectra of the 21 **A1**$^{2+}$ and 12 **S** component units of the larger dendrimer. The inset shows an enlarged view of the tails of the absorption bands in the visible region.

Electrochemical reduction: Electrochemical experiments were carried out in MeCN. We have examined the electrochemical behavior of the dendrimers **A9**$^{18+}$ and **A21**$^{42+}$, and of 1,1′-dibenzyl-4,4′-bipyridinium (**A1**$^{2+}$) as a reference compound.

The potential values and the number of exchanged electrons are listed in Table 1. Figure 3 displays the cyclic voltammetric patterns of **A1**$^{2+}$, **A9**$^{18+}$, and **A21**$^{42+}$. All the examined compounds show the two reversible reduction processes typical of viologen units.[5] The reduction potential values for the three compounds are similar. In the case of the two dendrimers the reduction scan shows sharp anodic peaks (particularly the second one), indicating adsorption of the reduced species on the electrode. The diffusion coefficients and the number of exchanged electrons have been obtained (Table 1) from chronoamperometric experiments[14] performed at the potential value of the first reduction process. Simulations of the CV curve of the first reduction process for the model compound **A1**$^{2+}$ and the dendrimer **A21**$^{42+}$ are shown in Figure 4. For the dendrimer **A21**$^{42+}$, the simulated curve based on the diffusion coefficient and the number of exchanged electrons found by chronoamperometry fits reasonably well the experimental curve, whereas a very bad match is obtained by using the same diffusion coefficient and 21 exchanged electrons.[15]

Table 1. Reduction potentials, diffusion coefficients and number of exchanged electrons (n).[a,b]

	$E^1_{1/2}$ [V vs SCE]	$E^2_{1/2}$ [V vs SCE]	$D \times 10^5$ [cm^{2}s^{-1}]	n_{el}[c]	n_{chem}[d]	n_{phot}[e,f]	n_{ex}[g]
A1^{2+}	−0.35	−0.77	1.60	1	1	1[h]	1
A9^{18+}	−0.29	−0.75[i]	0.32	5	4	4	9
A21^{42+}	−0.30	−0.76[i]	0.27	14	9	13	21

[a] In MeCN, unless otherwise noted. [b] The estimated error on the number of exchanged electrons is ±20%. [c] From electrochemical experiments. [d] From chemical reductions. [e] From photochemical reduction. [f] In CH_2Cl_2. [g] Expected from the overall number of viologen units present in the compound. [h] For **A′1**$^{2+}$. [i] Estimated value, E_{pc} −30 mV.

The number of exchanged electrons is smaller than that expected on the basis of the number of viologen units, an observation which is also made in the case (Table 1) of the **A9**$^{18+}$ dendrimer.

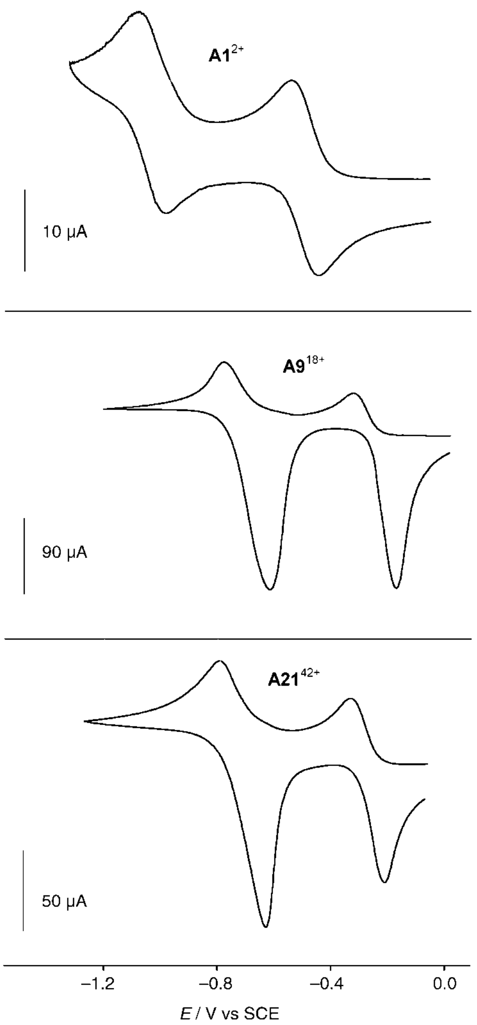


Figure 3. Cyclic voltammetric patterns of **A1**$^{2+}$ (4.6×10^{-4} M), **A9**$^{18+}$ (5.2×10^{-4} M), and **A21**$^{42+}$ (2.2×10^{-4} M) [argon-purged MeCN, scan rate = 200 mV s^{-1}, glassy carbon as working electrode].

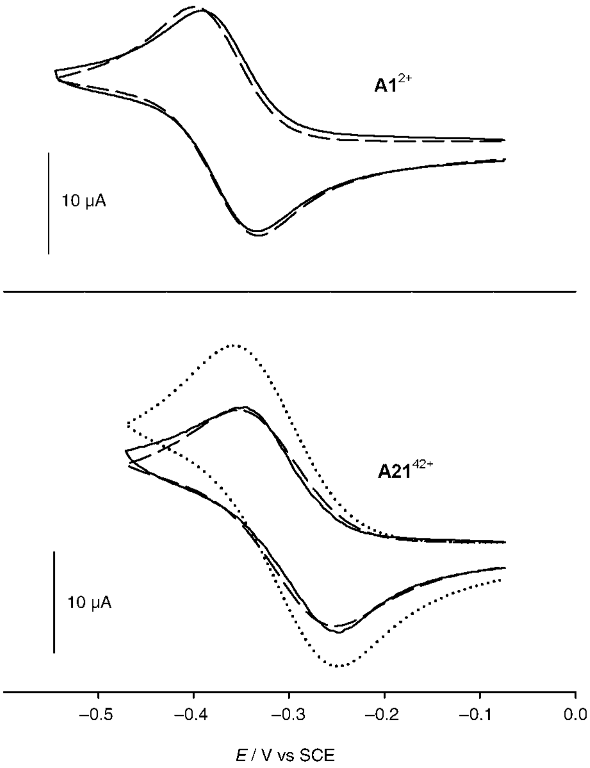


Figure 4. Comparison between observed and simulated cyclic voltammeric waves for the first reduction of **A1**$^{2+}$ (3.5×10^{-4} M) and **A21**$^{42+}$ (5.8×10^{-5} M) [argon-purged MeCN, scan rate = 200 mV s^{-1}, glassy carbon as working electrode]. **A1**$^{2+}$: solid line, observed wave; dashed line, simulated curve based on one-electron reduction. **A21**$^{42+}$: solid line, observed wave; dotted line, simulated curve based on the exchange of 21 electrons; dashed line, simulated curve based on the exchange of 14 electrons. For both the simulated curves, the diffusion coefficient obtained by chronoamperometric experiments (Table 1) has been used.

In conclusion, the results show that in the two dendrimers: 1) the viologen units are reduced at potential values close to that of the **A1**$^{2+}$ model compound, 2) all the reducible units are substantially equivalent, and 3) only a fraction of the viologen units can be reduced. From points 1) and 2), it follows that the charge-transfer interactions between the electron-acceptor viologen units and the electron-donor aryloxy groups in the dendritic structures are very weak. In relation to point 3), however, it is interesting to note that, for similar polyviologen dendrimers carrying $-CH_2-CH_3$ terminal groups in the place of the much longer and bulkier ones that characterize the present dendrimers (Scheme 1), all the viologen units can be reduced.[9] Therefore, the lack of complete reduction for **A9**$^{18+}$ and **A21**$^{42+}$ is apparently related to the presence of such terminal groups.

Chemical reduction: Since reduced viologen is rapidly oxidized by dioxygen, all the experiments were performed in a glove box under a nitrogen atmosphere. The occurrence of the reduction was followed by spectral measurements, taking advantage of the fact that the viologen units are colorless, whereas the one- and two-electron reduced species exhibit distinct absorption bands.[5,16]

Chemical reduction was performed on the dendrimers **A9**$^{18+}$ and **A21**$^{42+}$ and on the reference compound **A1**$^{2+}$. The reduction reactions were performed by addition of a stoichiometric amount (relative to the viologen units) of bis(benzene)chromium $[Cr(\eta^6\text{-}C_6H_6)_2]$,[17] to solutions of **A1**$^{2+}$ (1.0×10^{-4} M), **A9**$^{18+}$ (9.3×10^{-6} M) and **A21**$^{42+}$ (4.0×10^{-6} M) in MeCN; these solutions contained about the same concentration of viologen units. The results obtained are displayed in Figure 5.[18] Reduction of **A1**$^{2+}$ yielded a product whose spectrum (Figure 5a: $\lambda_{max} = 607$ nm, $\varepsilon = 14000\,M^{-1}cm^{-1}$) is that expected[19] for the one-electron reduced form of **A1**$^{2+}$. This result confirms that $[Cr(\eta^6\text{-}C_6H_6)_2]$, used in stoichiometric amount, is indeed a suitable reductant to obtain the monoreduced form of viologen units.[20] Reduction of the solution of **A21**$^{42+}$ in MeCN with $[Cr(\eta^6\text{-}C_6H_6)_2]$ yielded the spectrum displayed in Figure 5b. This spectrum is much less intense than that obtained upon reduction of **A1**$^{2+}$ (Figure 5a) and shows the spectral features for both monomeric (band with maxima at 396 and 607 nm) and dimeric[19] (bands with maxima at 355, 537, and 850 nm) monoreduced viologens. Since each dendrimer con-

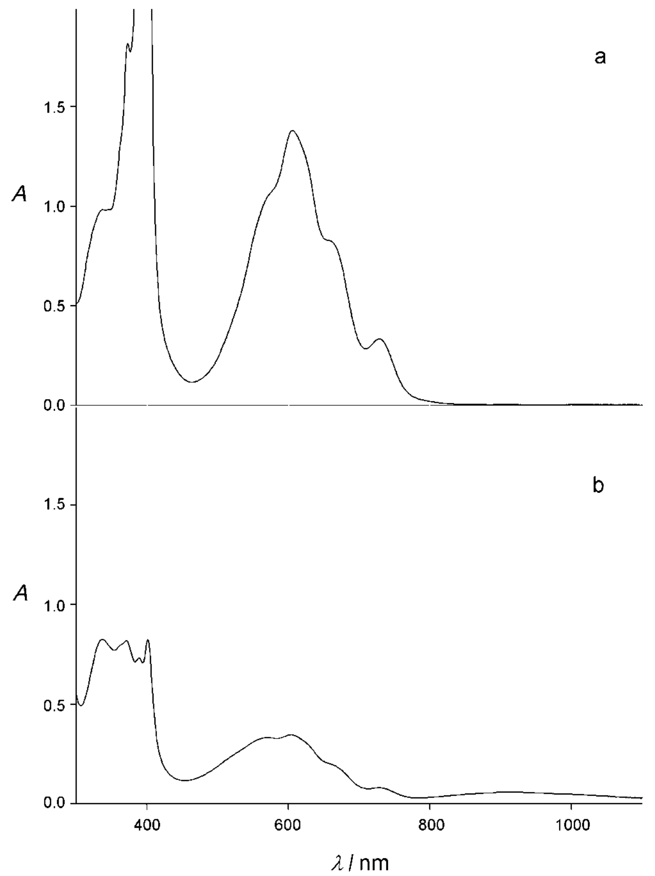


Figure 5. Absorption spectra (optical path = 1 cm) obtained after addition of a stoichiometric amount (relative to the number of viologen units) of $[\mathrm{Cr}(\eta^6\text{-}C_6H_6)_2]$ to deaerated solutions of a) $\mathbf{A1}^{2+}$ (1.0×10^{-4} M) and b) $\mathbf{A21}^{42+}$ (4.0×10^{-6} M) in MeCN. For more details, see the text.

tains different types of viologen units, and, upon one-electron reduction, such units can presumably give rise to different dimers,[21] a complete deconvolution of the spectrum of Figure 5b into its components is impossible. Nevertheless, some interesting pieces of information can be drawn from the spectrum. To a first approximation, we can assume that the spectrum of the reduced form of $\mathbf{A1}^{2+}$ (Figure 5a) and the spectrum of reduced viologen dimers reported by Geuder et al.[19] are reasonably good models for the spectra of the one-electron-reduced viologen monomers and dimers, respectively, in the dendrimer. On this assumption, a quantitative analysis shows that the spectrum of Figure 5b corresponds (Table 2) to the presence of 2.4×10^{-5} M monomeric $V^{\cdot+}$, and 5.0×10^{-6} M dimeric $(V^{\cdot+})_2$ reduced viologen species. For $\mathbf{A21}^{42+}$, 1) only about 9 out of 21 viologen units can be chemically reduced under conditions in which 21 $\mathbf{A1}^{2+}$ species are fully reduced, and 2) several one-electron-reduced viologens of the dendrimer associate to give dimers in common with other polyviologen species.[5,9,19,21,22] Once again, we can conclude that only a fraction of the viologen units contained in the dendrimers can be reduced.

Table 2. Percentages of reduced (monomeric and dimeric species) and not reduced viologen units obtained in the chemical (in MeCN) and photochemical (in CH_2Cl_2) experiments.

	% $V^{\cdot+}$ (monomeric)		% $V^{\cdot+}$ (dimerized)		% V^{2+} (unreduced)	
	chem	phot	chem	phot	chem	phot
$\mathbf{A1}^{2+}$ or $\mathbf{A'1}^{2+}$	100	100	0	0	0	0
$\mathbf{A9}^{18+}$	31	26	12	22	57	52
$\mathbf{A21}^{42+}$	29	33	12	27	59	40

Photosensitized reduction: It is well known that one-electron reduction of viologen compounds can be performed by using suitable photosensitizers, that is, species that become strong reductancts upon light excitation. This kind of photoinduced process has been extensively exploited for hydrogen generation from aqueous solutions,[7]as well as to power artificial molecular machines.[23,24] Photosensitized reduction of viologen requires photoexcitation of a suitable photosensitizer (PS) [Eq. (1)], an electron-transfer reaction during an encounter between the photoexcited molecule and the viologen [Eq. (2)], and fast reaction of the reduced photosensitizer with a sacrificial reductant (RED) [Eq. (3)] to prevent the back-electron-transfer reaction between the oxidized photosensitizer and the reduced viologen [Eq. (4)]:[25]

$$\mathrm{PS} + h\nu \rightarrow {}^{*}\mathrm{PS} \tag{1}$$

$$^{*}\mathrm{PS} + \mathrm{V}^{2+} \rightarrow \mathrm{PS}^{+} + \mathrm{V}^{\cdot+} \tag{2}$$

$$\mathrm{PS}^{+} + \mathrm{RED} \rightarrow \mathrm{PS} + \text{products} \tag{3}$$

$$\mathrm{PS}^{+} + \mathrm{V}^{\cdot+} \rightarrow \mathrm{PS} + \mathrm{V}^{2+} \tag{4}$$

The most common photosensitizer used in this kind of process is $[\mathrm{Ru(bpy)_3}]^{2+}$ and a commonly used sacrificial reductant is triethanolamine (TEOA).[26] We performed some experiments irradiating degassed solutions of $[\mathrm{Ru(bpy)_3}]^{2+}$ (5.0×10^{-5} M), TEOA (1.0×10^{-2} M), and $\mathbf{A1}^{2+}$ (1.0×10^{-4} M) or $\mathbf{A21}^{42}$ (4.7×10^{-6} M)$^{+}$ in MeCN with 450 nm light. In both cases, we observed an increase of absorbance in the near UV and visible spectral regions in line with the formation of one-electron-reduced viologen. The overlap with the $[\mathrm{Ru(bpy)_3}]^{2+}$ absorption bands, however, made it difficult 1) to evaluate the amount of reduced viologen produced by the photoreaction and 2) to distinguish between monomeric and dimeric reduced species.

We have therefore decided to use 9-methylanthracene,[27] which is soluble in CH_2Cl_2, as a sensitizer. In this solvent, we had to use 1,1'-dioctyl-4,4'-bipyridinium, $\mathbf{A'1}^{2+}$ ion (Scheme 1), as a reference species. Figure 6a displays the spectral changes obtained upon irradiation of a degassed solution of 9-methylanthracene (1.2×10^{-4} M), TEOA (5.0×10^{-2} M), and $\mathbf{A'1}^{2+}$ (6.7×10^{-5} M) in CH_2Cl_2 with 365 nm light. The spectral features and the final absorbance values are quite similar to those exhibited by the spectrum of the chemically reduced monomeric form of $\mathbf{A1}^{2+}$ (Figure 5a) and show that all the $\mathbf{A'1}^{2+}$ molecules have been reduced when a plateau is reached. Figure 6b shows the spectral changes obtained under the same conditions for a solution containing $\mathbf{A21}^{42+}$ (4.0×10^{-6} M) in the place of $\mathbf{A'1}^{2+}$ (6.7×10^{-5} M) (so that both solutions contain about the same

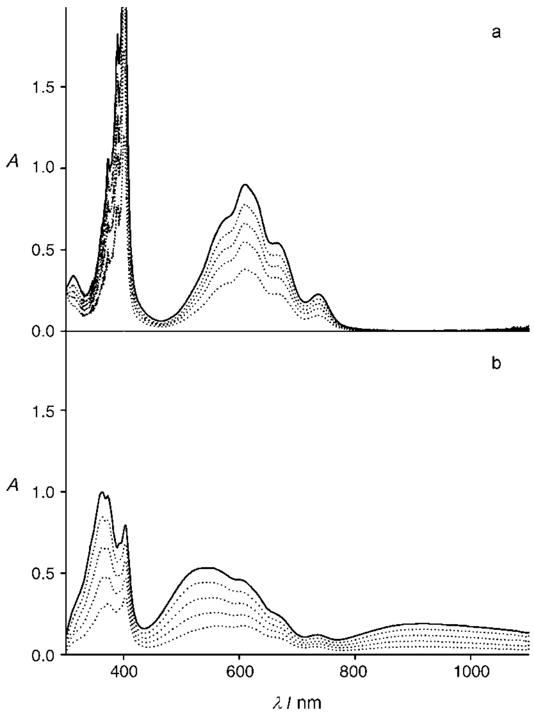


Figure 6. Spectral changes (optical path = 1 cm) observed upon irradiation of degassed solutions of 9-methylanthracene (1.2×10^{-4} M), TEOA (5.0×10^{-2} M), and a) **A′1**$^{2+}$ (6.7×10^{-5} M) and b) **A21**$^{42+}$ (4.0×10^{-6} M) in CH_2Cl_2 with 365 nm light. The solid line corresponds to the photostationary state reached in about ten minutes. A solution containing 1.2×10^{-4} M 9-methylanthracene was used as reference.

number of viologen units). In this experiment, the spectral features that arise upon irradiation (Figure 6b) are quite different from those shown in Figure 6a and recall those obtained upon chemical reduction (Figure 5b). According to the above discussion, we conclude that the photosensitized reaction causes the formation of both monomeric and dimeric reduced viologen species. Looking at the spectral changes at different irradiation times, it is also apparent that the fraction of monomeric and dimeric reduced units changes (Figure 7) with increasing irradiation time. At the photostationary state, only 60 % of the viologen units are reduced, almost equally distributed as monomeric (55 %) and dimerized (45 %) units.

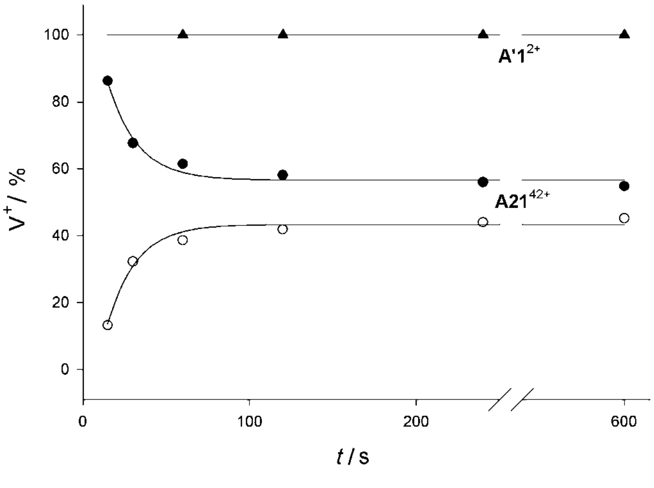


Figure 7. Changes in the percentages of the monomeric (solid circles) and dimerized (open circles) monoreduced viologen units on increasing the irradiation time for the dendrimer **A21**$^{42+}$. For the reference compound **A′1**$^{2+}$ (solid triangles), only the monomeric form is obtained.

Comparison of the spectra in Figures 5b and 6b shows that, at the end of the irradiation, the number of reduced units is slightly higher than that produced by chemical reduction, with a slightly larger dimer/monomer ratio (Table 2).

Conclusions

From the studies reported so far,[9–12,28–33] it is unclear whether or not all the redox units present in a dendrimer can be involved in electron-transfer processes. The results reported in this paper from electrochemical, chemical, and photosensitized reduction experiments concur in showing that only a fraction of the viologen units contained in dendrimers **A9**$^{18+}$ and **A21**$^{42+}$ can be reduced. This finding is consistent with the incomplete reduction of viologen groups appended at the periphery of poly(amidoamine) dendrimers already reported by Crooks et al.[10] Another result pertinent to our discussion, however, is that, in viologen-based dendrimers like those discussed in this paper, but carrying much smaller ($-CH_2-CH_3$) terminal groups, all the viologen units can be reduced.[9]

Incomplete reduction of the dendrimers cannot be attributed to wrong constitutions, since we have previously shown that the **A9**$^{18+}$ and **A21**$^{42+}$ do contain 9 and 21 viologen units, respectively.[8] We have found indeed that, in CH_2Cl_2, **A′1**$^{2+}$ gives rise to a 1:1 complex with eosin, and that **A9**$^{18+}$ and **A21**$^{42+}$ associate with 9 and 21 eosin molecules, respectively. We believe that the lack of complete reduction for **A9**$^{18+}$ and **A21**$^{42+}$ could be related to the presence of the bulky terminal groups. Upon one-electron reduction of a large fraction of the viologen units, the dendrimer structure is expected to shrink for several concomitant reasons, namely: 1) the strong decrease in the electric charge, 2) the decreased number of counterions and polar solvent molecules needed within the dendrimer, 3) the tendency of monoreduced viologens to form dimers, and 4) the occurrence of donor–acceptor interactions between the bulky electron-donating stoppers and the not-yet-reduced viologen units. Structural folding could result in the encapsulation of a fraction of viologen units, thereby preventing their reduction. That the actual number of reducible viologen units is different for different reduction conditions (solvent) and methods (electrochemical, chemical, and photochemical) is not surprising.

Experimental Section

Materials: 1,1′-Dibenzyl-4,4′-bipyridinium (dibenzylviologen, **A1**$^{2+}$) as its hexafluorophosphate salt, 9-methylanthracene, triethanolamine, and bis(benzene)chromium, $[Cr(\eta^6\text{-}C_6H_6)_2]$ were all high-quality commercial products. The tetraarylmethane derivative **D** and the hexafluorophosphate salt of tris(2,2′-bipyridine)ruthenium(II), $[Ru(bpy)_3](PF_6)_2$, were available from previous studies. 1,1′-Dioctyl-4,4′-bipyridinium (dioctylviologen, **A′1**$^{2+}$) as its hexafluorophosphate salt was kindly supplied by

Prof. A. Arduini (University of Parma). The preparation, characterization and properties of dendrimers **A 9**$^{18+}$ and **A 21**$^{42+}$ (all as their hexafluorophosphate salts) have been previously described.[8]

Photophysical experiments: The equipment and procedures used have been previously described.[8,13,23d]

Electrochemical experiments: Cyclic voltammetric (CV) experiments were carried out in argon-purged MeCN (Romil Hi-Dry™) solutions at room temperature with an Autolab 30 multipurpose instrument interfaced to a personal computer. The working electrode was a glassy carbon electrode (0.08 cm^2, Amel); its surface was routinely polished with 0.3 µm alumina-water slurry on a felt surface, immediately prior to use. In all cases, the counter electrode was a Pt spiral, separated from the bulk solution with a fine glass frit, and an Ag wire was used as a quasi-reference electrode. Ferrocene ($E_{1/2} = +0.395$ V vs SCE) was present as an internal standard. In all the electrochemical experiments the concentration of the compounds was in the range 5×10^{-4}–5×10^{-5} M, and tetrabutylammonium hexafluorophosphate with 100 times higher concentration was added as the supporting electrolyte. Cyclic voltammograms were obtained with sweep rates in the range 0.02–1.0 V s^{-1}; the IR compensation implemented within the Autolab 30 was used, and every effort was made throughout the experiments in order to minimize the resistance of the solution. In any instance, the full reversibility of the voltammetric wave of ferrocene was taken as an indicator of the absence of uncompensated resistance effects. The reversibility of the observed processes was established by using the criteria of 1) separation of 60 mV between cathodic and anodic peaks, 2) the close to unity ratio of the intensities of the cathodic and anodic currents, and 3) the constancy of the peak potential on changing sweep rate in the cyclic voltammograms. The experimental error on the potential values was estimated to be ±10 mV.

The diffusion coefficients and the numbers of exchanged electrons were obtained independently by chronoamperometry as described in reference [14]. A Pt disk with a diameter of 50 µm was used as a working electrode and the experiments were carried out for 5 s, with 0.05 s sample time, at the following potential values: −0.40 V for **A 1**$^{2+}$ and −0.35 V for **A 9**$^{18+}$ and **A 21**$^{42+}$. The current intensities in steady-state conditions were determined from CV experiments by using the same working electrode of the chronoamperometric experiments and sweep rate of 10 mV s^{-1}.

Digital simulation of the experimental CVs were obtained by using the software package DigiSim 3.05.[34]

Chemical reduction: The experiments were performed in deaerated MeCN under nitrogen atmosphere in a glove box. Known amounts of bis(benzene)chromium, [Cr(η^6-C$_6$H$_6$)$_2$], were added to solutions of **A 1**$^{2+}$, **A 9**$^{18+}$, or **A 21**$^{42+}$ in MeCN.

Photochemical reduction: The experiments were performed in solutions of **A′1**$^{2+}$, **A 9**$^{18+}$, or **A 21**$^{42+}$ in CH_2Cl_2, with 9-methylanthracene as a photosensitizer and triethanolamine as a sacrificial reductant. The solutions (3 mL) were degassed by repeated freeze-pump-thaw cycles and then irradiated with 365 nm light obtained from a medium pressure Hg lamp and an interference filter.

Concentrations of the monomeric and dimeric forms of the monoreduced viologens: The monomer (c_M) and dimer (c_D) concentrations were determined from the absorbance at 605 and 537 nm (A_{605} and A_{537}, respectively) by using Equations (5) and (6):

$$c_M = (A_{605}\varepsilon_{D537} - A_{537}\varepsilon_{D605})/(\varepsilon_{M605}\varepsilon_{D537} - \varepsilon_{M537}\varepsilon_{D605}) \quad (5)$$

$$c_D = (A_{537}\varepsilon_{M605} - A_{605}\varepsilon_{M537})/(\varepsilon_{M605}\varepsilon_{D537} - \varepsilon_{M537}\varepsilon_{D605}) \quad (6)$$

in which ε_{D537} and ε_{D605} represent the molar absorption coefficients of the dimer at the two selected wavelengths; their values were taken from reference [19] and correspond to 29000 and 2350 M^{-1}cm^{-1}, respectively. For ε_{M605} and ε_{M537}, the molar absorption coefficients of the monomer, the values used were 14000 and 5770 M^{-1} cm^{-1}, respectively, in agreement with those reported in reference [19]. The concentration of the dimerized one-electron-reduced viologen units corresponds to $2\times c_D$.

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