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Published on Web 06/20/2002

A Dendrimer-Based Electron Antenna: Paired Electron-Transfer Reactions in Dendrimers with a 4,4′-Bipyridine Core and Naphthalene Peripheral Groups

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Received January 22, 2002

Abstract: Paired electron transfers (ET) induced by the absorption of two photons by synthetic dendrimers are observed in first-, second-, and third-generation dendrimers comprised of a viologen-like core and an array of naphthalene peripheral groups. Flash photolysis and transient absorption techniques show that the yield of photoinduced double ET depends on laser intensity in the two largest dendrimers, **NBV2**$^{+2}$ and **NBV3**$^{+2}$. Their photochemical behavior thus requires an unusual multiphoton kinetic scheme. These dendrimers constitute the first synthetic models capable of multiple electron redox events deriving from a defined molecular architecture, thus mimicking natural light-collecting antenna systems.

Introduction

Electron transfer (ET) is a key reaction in most natural photosynthetic systems. These reactions are usually driven by an absorbed photon in which sunlight is converted into chemical energy by successive ETs to a precisely positioned chemical redox site. The primary reaction is charge separation, ultimately driving proton pumping and creating an electrochemical potential across a photosynthetic membrane.[1−3] The first critical electron-transfer reaction is initiated by light harvested in a complex array of antenna pigments. The excitation energy then migrates by energy transfer to a primary electron donor with near unit efficiency.[3]

Functionalized dendrimers[4−8] provide an analogous framework in which relatively large numbers of chromophores are chemically bound within a single molecule. As such, they represent potential systems in which multielectron events deriving from multiple excitations can take place in the array of linked chromophores, even at low incident light intensities.[9] Recently, dendrimers with redox cores and/or absorptive periphery-bound chromophores have been studied as models,[10−18] but to our knowledge no demonstration of multiple ET from multiphoton absorption has been achieved. For some time, we have been interested in studying such electron-transfer reactions.[13,19] Here, we report the first observation of electron transfers derived from multiple photon absorptions within a synthetic dendrimer framework containing a viologen marker that serves as an electron trap. Because multiphoton processes are important in several emerging applications, such as fluorescence microscopic imaging[20−23] and optical data storage and microfabrication,[24−26] their demonstration within a well-characterized model establishes a link between fundamental

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studies of biological electron transfer and these exciting new applications.

Experimental Section

Chemicals. All chemicals were purchased from Aldrich. K_2CO_3 was dried in an oven at 130 °C, and 3,5-dihydroxybenzyl alcohol was recrystallized from ethyl acetate prior to use. Methylene chloride (CH_2Cl_2) and tetrahydrofuran (THF) were distilled from CaH_2 and sodium/benzophenone, respectively.

Instrumentation. The NMR spectra were recorded with a Varian Gemini 300 MHz. Absorption spectra were recorded on a Shimadzu PC-3101PC instrument. Fluorescence spectra were measured on a PTI QuantaMaster model C-60/2000 spectrofluorometer. Cyclic voltammetry (CV) was performed with a BAS-100 electrochemical analyzer on a platinum electrode in a standard three-electrode cell. Measurements were reported against a $Ag/AgNO_3$ reference electrode. Solutions were approximately 1 mM in dimethylformamide (DMF) containing 0.1 M $TBAPF_6$.

Time-Resolved Emission and Transient Absorption Measurements. The excitation source for time-resolved emission experiments was the tripled (266 nm) output from a 10 Hz Ti:Sapphire regenerative amplifier (Spectra Physics/Positive Light, Mountain View, CA) which forms part of the laser system for the Laser-Electron Accelerator Facility at Brookhaven National Laboratory. The excitation pulse width was 1 ps fwhm. Energy densities per pulse varied up to 2.3 mJ/cm^2 at 266 nm. The samples were placed in 1 cm square Suprasil fluorescence cuvettes. The axes of the streak camera and photodiode detection systems were placed in opposite directions at right angles to the excitation beam. A 1 mm wide vertical slit was mounted in the excitation beam path to limit the depth (and temporal width) of the emitting region of the sample from the perspective of the detection optics.

The streak camera system consisted of a Hamamatsu Photonics (Japan) C1587 temporal disperser, C4742-95 camera and controller, and HPD-TA control software (Version 3.1). Single shot (M1952) and synchroscan (M1954/5) timebase plug-ins were used as appropriate. The timing signal for synchroscan operation was obtained from the 81.6 MHz Ref Out signal from the Lok-to-Clock cavity length regulation unit attached to the Spectra Physics Tsunami Ti:Sapphire oscillator used to seed the regenerative amplifier. The trigger signal for single-shot operation was obtained by using the 81.6 MHz signal to externally clock a Berkeley Nucleonics Corp. 7050 digital delay generator and setting a suitable delay off of a timing signal from the regenerative amplifier Pockels cell controller. A Hamamatsu C1097-01 passive delay unit was used for fine timing adjustment in both cases. The image of the emitting sample was relayed 1:1 to the horizontal slit of the streak camera with a 100 mm fused silica plano-convex lens. Narrow-band (~8 nm wide) or wide-band (~40 nm wide) interference filters were placed immediately in front of the entrance slit to select the monitoring wavelength. In addition, a 266 nm, normal incidence dichroic mirror was placed in the detection path to reject scattered laser light. Exposures were accumulated over 100, 1000, or 10 000 shots as required. Correction of the streak camera image for time skew between the "early" and "late" sides of the horizontal slit was included in the curvature correction process for each timebase setting used. After baseline and curvature correction, the vertical streak images were summed horizontally to a single intensity/time profile.

For time scales longer than 2.5 ns, the emission was relayed 1:1 with a 25 mm fused silica biconvex lens to a fast photodiode (PD-10, Opto-Electronics, Oakville, Canada). Interference filters and dichroic mirrors were used as described above. The photodiode signal was amplified (Type AC8020H, B+H Electronics Co., Monroe, NY) and collected with a Tektronix (Beaverton, OR) TDS 694C digital storage oscilloscope (3 GHz, 10 GSa). Signals were averaged over 100 shots and corrected by subtracting the average of 100 baselines to remove noise broadcast by the regenerative amplifier's Pockels cells.

Transient absorption spectra and lifetimes were carried out with 260 nm laser pulses from a Continuum Surelite-1 Nd:Yag laser system (6 ns pulse width, 0−50 mJ/pulse). The laser spot size was ~3 mm in diameter at the sample. The change in absorbance was monitored with a PMT, and the output was recorded on a Hewlett-Packard 54510A digital oscilloscope.

Preparation of Dendron NB2. This compound was prepared using the procedure previously described in the literature.[13,19,41]

General Procedure for the Preparation of Dendrimers NBV1^{+2}, NBV2^{+2}, and NBV3^{+2}. 4,4′-Bipyridine (1 equiv) and the corresponding brominated dendron[13,19,41] (2 equiv) in a minimum amount of DMF were heated at 55 °C for 24 h under Ar in the dark. A saturated solution of NH_4PF_6 in water was added slowly to the DMF solution. The resulting solid was filtered, washed with water, and then air-dried. The crude solid was purified by a different method for each dendrimer.

NBV1^{+2} was recrystallized from CH_2Cl_2, and then applied on Sephadex LH-20 and eluted with CH_3CN. Evaporation of the solvent afforded a yellow solid (yield: 85%). ^{1}H NMR (d_6-acetone): δ 5.36 (s, 8H), 6.10 (s, 4H), 6.98−7.01 (m, 6H), 7.50−7.60 (m, 12H), 7.90−7.97 (m, 16H), 8.68 (d, J = 5.2 Hz, 4H), 9.50 (d, J = 5.2 Hz, 4H). ES-MS: m/z 481.1 [M − 2PF_6^-]$^{+2}$.

NBV2^{+2} was purified by flash chromatography (silica gel, 4:1 CH_2Cl_2:ethyl acetate, then with 1−10% methanol). Evaporation of the solvent afforded a yellow solid (yield: 50%). ^{1}H NMR (d_6-acetone): δ 5.12 (s, 8H), 5.28 (s, 16H), 5.98 (s, 4H), 6.75−6.90 (m, 18H), 7.50−7.57 (m, 24H), 7.85−7.94 (m, 32H), 8.60 (d, J = 6.6 Hz, 4H), 9.35 (d, J = 6.6 Hz, 4H). ES-MS: m/z 1006.6 [M − 2PF_6^-]$^{+2}$.

NBV3^{+2} was purified by thin-layer chromatography (TLC) (silica gel, CH_2Cl_2). (Yield: 32%). ^{1}H NMR ($CDCl_3$): δ 4.70 (s, 16H), 5.92 (s, 8H), 5.08 (s, 32H), 6.30 (s, 4H), 6.38−6.65 (m, 42H), 7.31−7.42 (m, 48H), 7.62−7.75 (m, 64H), 8.01 (d, J = 6.6 Hz, 4H), 8.48 (d, J = 6.6 Hz, 4H). MALDI-TOF: m/z 4255.5 [M − PF_6^-]$^+$.

Results and Discussion

The dendrimers (**NBV1^{+2}**, **NBV2^{+2}**, and **NBV3^{+2}**) studied here (Scheme 1) are first-, second-, and third-generation Fréchet-

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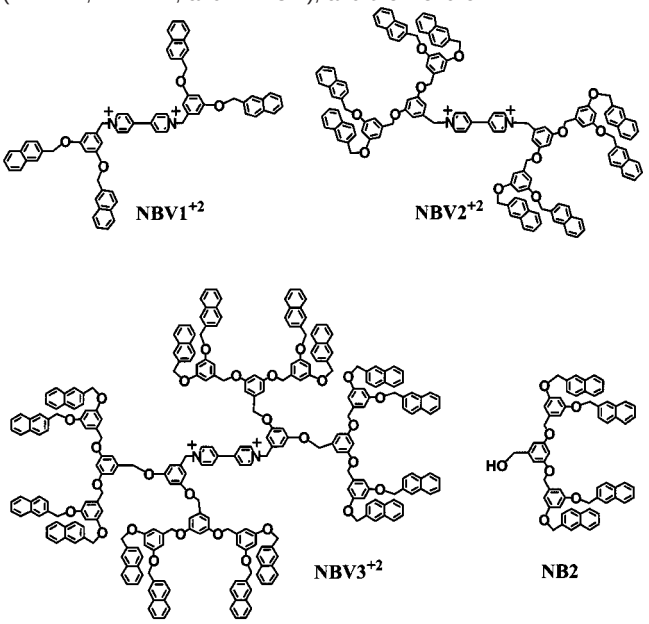
Scheme 1. Structures of the Viologen-Based Dendrimers (**NBV1**$^{+2}$, **NBV2**$^{+2}$, and **NBV3**$^{+2}$), and the Dendron **NB2**



type dendrimers with naphthalene peripheral groups (**N**), benzyl-ether spacers (**B**), and a viologen core (**V**$^{+2}$). Viologen is a well-known two-electron acceptor,[27] but most published work on electron transfer to substituted viologens involves a two-step sequence of one-electron transfers. This result is as expected in systems that contain a one-electron donor and a viologen acceptor.[28,29] In our system, a single viologen-like acceptor can interact with up to 16 naphthyl groups through 14 benzyl spacers (as in the third-generation dendrimer **NBV3**$^{+2}$). All three structural components of the dendrimers have significant absorption at the excitation wavelength of 266 nm. The relative proportions of absorption for each component of a dendrimer are **NB2** 73% **N**, 27% **B**; **NBV1**$^{+2}$ 40% **N**, 10% **B**, 50% **V**$^{+2}$; **NBV2**$^{+2}$ 50% **N**, 19% **B**, 31% **V**$^{+2}$; **NBV3**$^{+2}$ 57% **N**, 25% **B**, 18% **V**$^{+2}$. As a result, rapid multiple electron transfers may be possible, at least in principle.

Steady-state fluorescence measurements of the three dendrimers show strong fluorescence quenching of both the excited naphthyl and the benzyl-ether groups in methylene chloride, Figure 1, as compared with that observed in the nondendrimeric analogue **NB2**. This suggests a forward electron transfer from the excited donor groups (naphthyl and/or benzyl-ether) to the viologen acceptor, because singlet energy transfer is energetically impossible because of the lack of overlapping absorption of the viologen core with either the naphthyl or the benzyl-ether emissions.[30] Streak camera emission measurements (λ_{exc} = 266 nm, λ_{emm} = 334 nm) of the dendron **NB2** show a biphasic fluorescence lifetime decay of τ = 1.7 and 43 ns, where the short-lived component has been previously assigned as the benzyl-ether emission, and the longer-lived component is attributed to the naphthyl emission[14] (Figure 2). The three viologen-based dendrimers **NBV1**$^{+2}$, **NBV2**$^{+2}$, and **NBV3**$^{+2}$ have much faster biphasic fluorescence lifetime decays: a short-lived component τ = 11, 283, and 332 ps, and a longer-lived component τ = 0.77, 1.2, and 1.4 ns, respectively (Figure 2 and Table 1). Fluorescence measurements of the second- and third-generation dendrimers, **NBV2**$^{+2}$ and **NBV3**$^{+2}$ (with laser fluences between 260 MW/cm^2 and 2.3 GW/cm^2, or 7.7−70 μJ per pulse), revealed no significant changes in fluorescence decay profiles upon increasing incident laser pulse power. The photon fractions absorbed per dendrimer at the laser fluences used were calculated to be between 0.05 and 0.5 photon/molecule.[31] Excitation of multiple chromophores in a single dendrimer molecule accounts for only 9% of the absorbed energy at the highest laser power used for the emission measurements.[31] The oxidative quenching rate constant, k_Q, for the dendrimers **NBV1**$^{+2}$, **NBV2**$^{+2}$, and **NBV3**$^{+2}$ was then

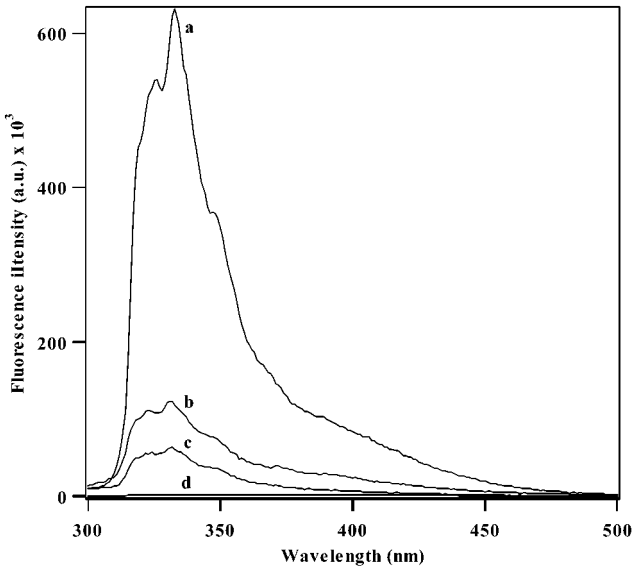


Figure 1. Steady-state fluorescence spectra of the dendrimers: (a) **NB2**; (b) **NBV3**$^{+2}$; (c) **NBV2**$^{+2}$; (d) **NBV1**$^{+2}$ in degassed CH_2Cl_2, λ_{ex} = 266 nm, and absorbance = 0.3 at 266 nm.

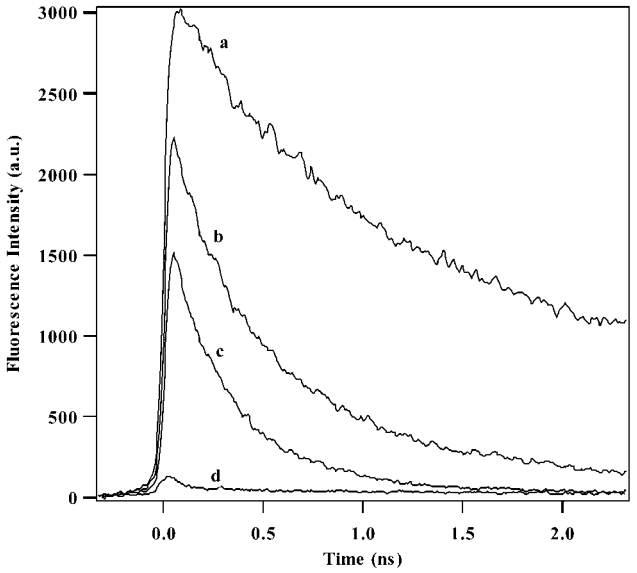


Figure 2. Time-resolved emission at 334 nm of dendrimers: (a) **NB2**; (b) **NBV3**$^{+2}$; (c) **NBV2**$^{+2}$; (d) **NBV1**$^{+2}$ in degassed CH_2Cl_2, λ_{ex} = 266 nm, and absorbance = 0.3 at 266 nm.

Table 1. Rate Constants for Photoinduced Electron Transfer and Fluorescence Lifetime Decays for Dendrimers **NBV1**$^{+2}$, **NBV2**$^{+2}$, and **NBV3**$^{+2}$ [a]

	NBV1^{+2}	**NBV2**$^{+2}$	**NBV3**$^{+2}$
τ (ns)	0.011 (85%), 0.77 (15%)	0.28 (88%), 1.2 (12%)	0.33 (66%), 1.4 (34%)
k_Q s^{-1}	$\geq 8 \times 10^{10}$ [b]	3.6×10^9	3.0×10^9
k_{VB1} s^{-1}	$> 2 \times 10^8$	1.3×10^7	7.1×10^6
k_{VN2} s^{-1}	$> 2 \times 10^8$	2.0×10^5	1.1×10^5
k_{VN1} s^{-1}	$> 2 \times 10^8$	1.4×10^5	6.3×10^4

[a] In degassed CH_2Cl_2, λ_{ex} = 266 nm, and OD $\approx$ 0.3 at 266 nm. Uncorrected for intrinsic decay ($\sim 9 \times 10^8$ s^{-1}). [b] Limited by the resolution of the streak camera.

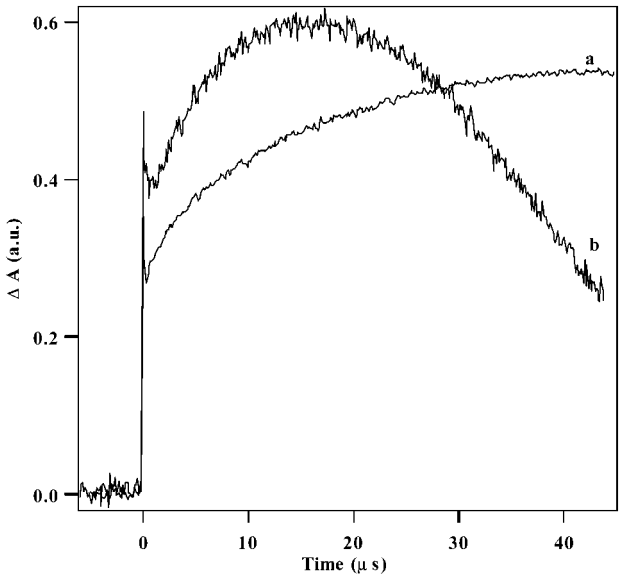


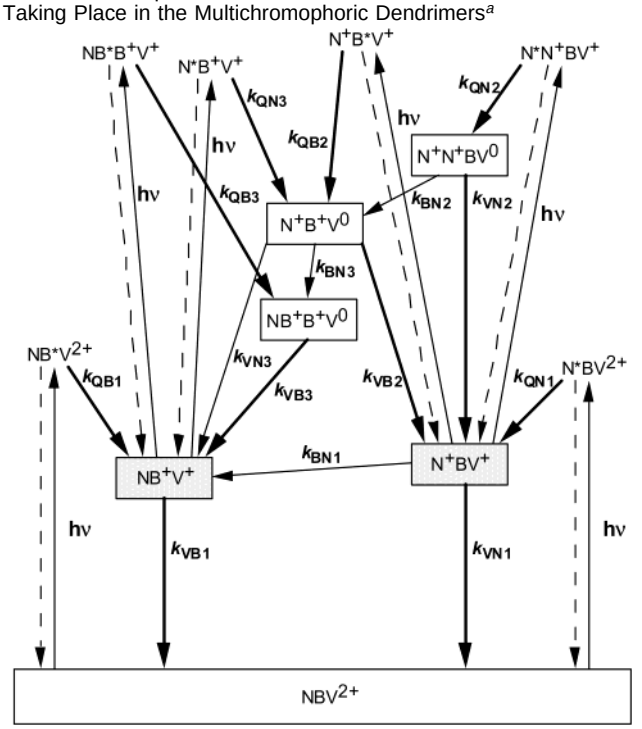
Figure 3. Transient absorption decay profile of dendrimers: (a) **NBV3**$^{+2}$; (b) **NBV2**$^{+2}$ in degassed CH_2Cl_2 at 600 nm; $\lambda_{ex} = 266$ nm, laser fluence = 1.7 MW/cm^2 with a photon fraction = 2.6, and absorbance = 0.3 at 266 nm.

obtained from the observed decay rates for the faster emission transients as $\geq 8 \times 10^{10}$, 3.6×10^9, and 3.0×10^9 s^{-1}, respectively. The longer-lived emission component in dendrimers **NBV1**$^{+2}$, **NBV2**$^{+2}$, and **NBV3**$^{+2}$ decays with roughly the same time constant as the viologen-free dendron **NB2** (Figure 2), although the proportion of the slow component varies with the dendrimer generation number (Table 1).

Vögtle et al.[32] recently reported steady-state emission measurements on first-, second-, and third-generation viologen-benzyl ether dendrimers without naphthyl peripheral groups, where complete loss of the benzyl-ether emission was assigned to oxidative quenching. In the present case, the observed quenching of naphthyl group emission may occur either by direct ET to the viologen core or, at higher laser power, by ET to a cation formed by a previous oxidative quenching event within the dendrimer. These fast electron-transfer rates (10^9–10^{10} s^{-1}) are consistent with rates measured in similar systems.[19,33] The thermodynamic driving force of the forward ET reaction $\Delta G°$ between the excited naphthyl or benzyl-ether and the viologen moiety is derived from electrochemical excited-state potentials to be 1.8 and 2.0 eV, respectively.[32,34–36] Oxidation of a naphthyl group in the second- or third-generation dendrimer likely results in the formation of an intramolecular naphthalene dimer cation radical involving naphthyl groups on neighboring branches. A similar dendrimer with a pentaerythritol core demonstrated emission from naphthalene excimers.[41] For the purposes of this discussion, $\mathbf{N}^+$ will represent a naphthalene monomer or dimer cation.

Transient absorption measurements of the dendrimers were conducted in methylene chloride under anaerobic conditions. The samples were subjected to 6 ns, 266 nm laser pulses (with laser fluence of 357 kW/cm^2 to 1.7 MW/cm^2 or 270 μJ to 1.3 mJ) at 266 nm, and the corresponding transient absorption spectra were recorded between 350 and 750 nm. The first-generation dendrimer **NBV1**$^{+2}$ showed no transient species even at high laser intensities, indicating very fast back ET ($k > 2 \times 10^8$ s^{-1}). The larger dendrimers **NBV2**$^{+2}$ and **NBV3**$^{+2}$ showed multiphasic transient absorption profiles (Figure 3), indicative of several forward (quenching) and back electron-transfer steps. In this system, the transient species with the most significant absorption spectrum is the monoreduced viologen $\mathbf{V}^+$, indicated

Scheme 2. Proposed Kinetic Scheme of the Double ET Reactions Taking Place in the Multichromophoric Dendrimers[a]



[a] Thick arrows indicate the dominant decay of that species. The species in boxes are those persisting after a 6 ns laser pulse during the transient absorption measurements. Energies are not to scale.

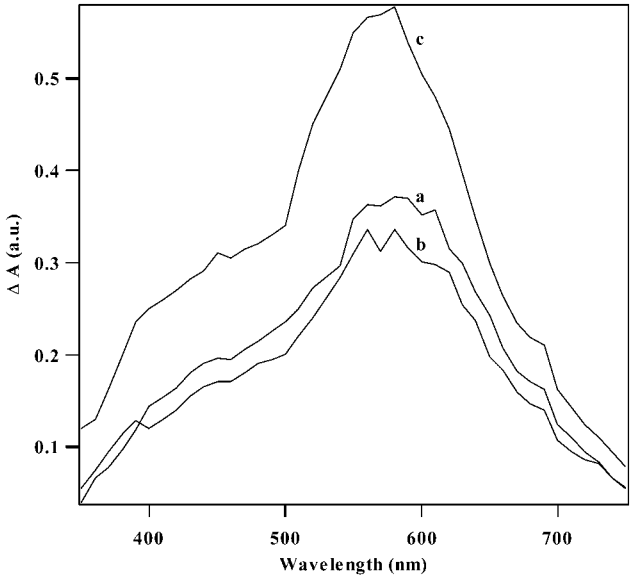


Figure 4. Transient absorption spectra of **NBV3**$^{+2}$ at different delay times after flash excitation: (a) 10 ns; (b) 0.1 μs; (c) 25 μs, in degassed CH_2Cl_2, $\lambda_{ex} = 266$ nm, laser fluence = 1.7 MW/cm^2 with a photon fraction = 2.6, and absorbance = 0.3 at 266 nm.

with shaded boxes in Scheme 2. The observed spectra (Figure 4) show that the concentration of monoreduced viologen varies in a complex way with time and with varying laser pulse energy. The first process is oxidative quenching (k_{QB1}, k_{QN1}) of an excited dendron component by the viologen core to form $\mathbf{NB}^+\mathbf{V}^+$ or $\mathbf{N}^+\mathbf{BV}^+$ as shown in Scheme 2. Some of the monoreduced viologen (likely $\mathbf{NB}^+\mathbf{V}^+$) undergoes back ET with a rate $k_{VB1} = 1.3 \times 10^7$ s^{-1} ($\tau = 77$ ns) and 7.1×10^6 s^{-1} ($\tau = 140$ ns) for dendrimers **NBV2**$^{+2}$ and **NBV3**$^{+2}$, respectively.[37] At higher laser power, dendrimers with monoreduced cores may

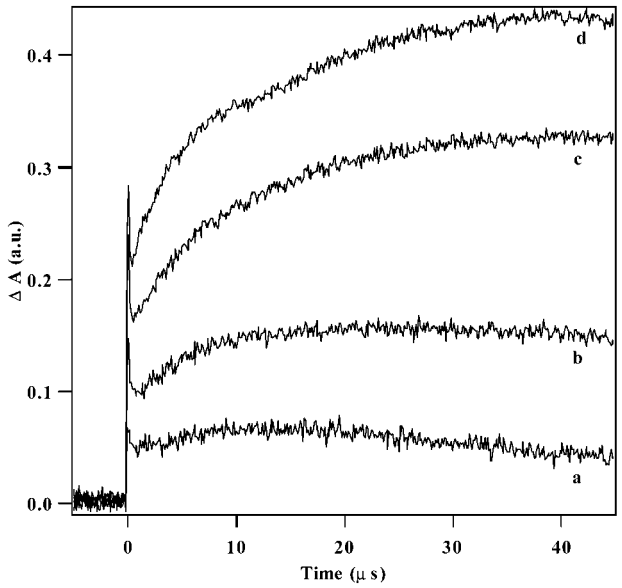


Figure 5. Transient absorption decay profile of **NBV3**$^{+2}$ at different laser power intensities at 600 nm: (a) 270 μJ (357 kW/cm^2 and photon fraction = 0.5); (b) 520 μJ (687 kW/cm^2 and photon fraction = 1.0); (c) 765 μJ (1.0 MW/cm^2 and photon fraction = 1.5); (d) 1.3 mJ (1.7 MW/cm^2 and photon fraction = 2.6).

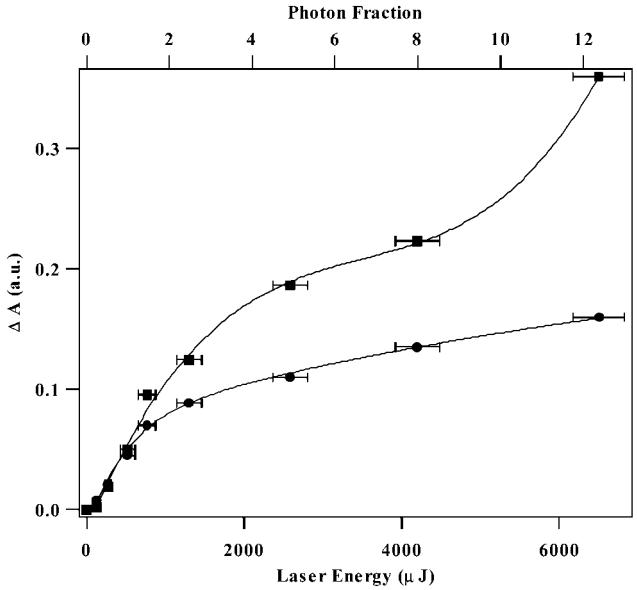


Figure 6. Plot of ΔA of dendrimer **NBV3**$^{+2}$ at 600 nm versus laser power after (●) 10 ns; (■) 20 μs.

undergo a second oxidative quenching event before back ET can occur, to form a weakly absorbing, doubly reduced viologen species $\mathbf{N^+B^+V^0}$, $\mathbf{NB^+B^+V^0}$, or $\mathbf{N^+N^+BV^0}$. The dominant decay pathways of $\mathbf{N^+B^+V^0}$ and $\mathbf{NB^+B^+V^0}$ would be rapid back ET (k_{VB2}, $k_{VB3} \approx 10^7$ s^{-1}) to the monoreduced species $\mathbf{N^+BV^+}$ and $\mathbf{NB^+V^+}$, respectively. $\mathbf{N^+N^+BV^0}$ decays back to the monoreduced viologen $\mathbf{N^+BV^+}$ with rate constants $k_{VN2} = 2.0 \times 10^5$ s^{-1} ($\tau = 5.0$ μs) and 1.1×10^5 s^{-1} ($\tau = 9.4$ μs) for **NBV2**$^{+2}$ and **NBV3**$^{+2}$, respectively. $\mathbf{N^+BV^+}$ then decays back to the initial state (**NBV**$^{+2}$) with rate constants $k_{VN1} = 1.4 \times 10^5$ s^{-1} ($\tau = 7.2$ μs) and 6.3×10^4 s^{-1} ($\tau = 16$ μs) for **NBV2**$^{+2}$ and **NBV3**$^{+2}$, respectively.

This assignment is suggested by the transient spectra of these dendrimers at different time delays, Figure 4. An alternative explanation would invoke **B**-to-**N**$^+$ electron transfer (k_{BN1}, k_{BN2}) as the first, rate-limiting step in the overall transfer from reduced viologen to the naphthyl cation. The driving force for this reaction is small ($\Delta G° \approx 0.2$ eV). The benzyl-ether groups in the dendrimers (**NBV2**$^{+2}$ and **NBV3**$^{+2}$) are known to act as relays, that is, to participate in charge self-exchange as a result of the similar redox potentials of these groups. **B**-to-**N**$^+$ electron transfer could be a reasonable explanation for the substantially slower back ET rates as compared to oxidative quenching (k_{QN1}), even though the respective driving forces for the overall reactions are comparable ($\Delta G° \approx 2$ eV).[32,35,36,38] Conducting the transient absorption experiments in methylene chloride containing 0.1 M $(Bu)_4NPF_6$ did not result in any significant change of the observed rate constants or any discernible shifts in the absorption spectra. Thus, it is unlikely that the PF_6^- counteranion significantly influences the observed kinetics.

To further investigate this system, laser power-dependence studies of the transient absorption spectra were conducted for **NBV3**$^{+2}$ and **NBV2**$^{+2}$. As laser power was increased in the range 28 μJ to 7 mJ per pulse (laser fluences between 37 kW/cm^2 to 9 MW/cm^2) at 266 nm, more of the doubly reduced viologen was produced, Figure 5. A plot of the intensity of the transient absorbance of **NBV3**$^{+2}$ at 10 ns and 20 μs against incident laser intensity (Figure 6) showed that the production of the doubly reduced viologen ($\mathbf{N^+B^+V^0}$) is more sensitive to laser power than is the production of the monoreduced viologen ($\mathbf{NB^+V^+}$). The number of photons absorbed per dendrimer at the highest laser fluences (>6 mJ) was calculated to be more than 12.[31] These findings are fully consistent with the proposed kinetic scheme (Scheme 2), confirming a process that requires two sites of excitation within the same molecule as a route to a two-electron reduction. Further experiments are needed to work out the detailed mechanisms of this complicated system.

In conclusion, the rates of back and forward ET were studied in viologen-based dendrimers containing multiple absorptive chromophores using flash photolysis and transient absorption techniques. These measurements suggest that multiple excitations at two separate sites lead to photoinduced double ET in dendrimers **NBV3**$^{+2}$ and **NBV2**$^{+2}$ (Scheme 2). This mechanism was established by laser power-dependence in both fluorescence and transient absorption measurements. These systems effectively serve, therefore, as antennae for multiple reducing equivalents. Such antenna effects are not only interesting per se, but are also important in light collection for effective signal amplification in optical data storage.[39,40]

Acknowledgment. This work was supported by the U.S. Department of Energy (DE-FG02-98ER14901). The flash photolysis and transient absorption experiments were carried out at Brookhaven National Laboratory under contract DE-AC02-98CH10886 with the U.S. Department of Energy and supported by its Division of Chemical Sciences, Office of Basic Energy Sciences. The authors would like to thank Dr. John Miller and Dr. Bruce Brunschwig at Brookhaven National Laboratory for their helpful discussions.

JA020103C