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Photoreduction of Methyl Viologen Mediated by Tris(bipyridyl)ruthenium(II) in Inert Colloidal Suspensions

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The photoreduction of methyl viologen, covalently attached to a tris(bipyridyl)ruthenium(II) chromophore, in suspensions of positively charged alumina-coated colloidal silica particles, *via* *N*-phenylglycine electron donor, is reported. In the tris(bipyridyl)ruthenium(II) complexes, the central metal atom is coordinated to two 4,4′-dicarboxy-2,2′-bipyridine ligands and thus carries a net 2– charge at pH 5.0. Coadsorption of the *N*-phenylglycine and ruthenium chromophore to the colloidal particles results in rapid production of reduced viologen following visible laser flash excitation of the tris(bipyridyl)ruthenium(II) complex. The yield of the radical was dependent upon the concentration of the electron donor added to the system, but its multiphasic decay was independent of both the *N*-phenylglycine concentration and the initial concentration of the viologen radical cation. Furthermore, both the yield and decay kinetics of the viologen radical cation were relatively independent of the number of intervening methylene units between the ruthenium complex and viologen electron acceptor. The results represent a significant improvement in charge separation yield over those previously reported for the reductive quenching of the carboxylated tris(bipyridyl)ruthenium(II) complex, absent of the covalently attached viologen, by *N*-phenylglycine in alumina-coated silica colloidal suspensions.

Introduction

The utilization of heterogeneous environments, including micellar media[1] and inert inorganic colloidal suspensions,[2] has proven useful in facilitating photoinduced redox processes. In particular, the compartmentalization of electron donor and acceptor can often eliminate the necessary diffusional step in a bimolecular reaction sequence. Such compartmentalization is important in photochemical systems, where the bimolecular donor/acceptor collision competes with the natural radiative and nonradiative decay pathways of the electronically excited donor or acceptor.

We have previously shown that laser flash excitation of an aqueous solution of an anionic tris(bipyridyl)ruthenium(II) complex in the presence of either ascorbate or *N*-phenylglycine electron donor results in the production of the one-electron-reduced metal complex.[3] The cage escape efficiency from this quenching process was moderate, ranging from 20% to 40%, depending on the complex and donor employed. Up to a 50-fold increase in the bimolecular rate constant for this quenching process was observed when the reacting partners were coadsorbed onto positively charged alumina-coated colloidal silica particles. However, the efficiency of the production of redox products was diminished to less than 5% due to the efficient recombination of the radicals within the geminate cage.

The chromophores have been modified in this work to contain a covalent linkage to an electron-accepting viologen moiety. Both the electronically excited state of tris(bipyridyl)ruthenium(II) complexes and the one-electron-reduced complex are capable of reducing methyl viologen.[4,5] Several investigators have demonstrated that both viologen and diquat electron acceptors, when covalently attached to ruthenium(II) diimine and polypyridyl complexes, will quench the lowest energy electronically excited state of the complex.[6–9] The direct spectroscopic observation of the tris(bipyridyl)ruthenium(III)/methyl viologen radical cation charge-transfer state has been reported in some instances.[7a,b] However, the kinetics of both the forward electron transfer and charge recombination are quite dependent upon both the driving force and covalent linkage between the donor and acceptor, and in many cases, the charge-transfer state cannot be directly observed due to very rapid charge recombination. In such cases, redox quenching can only be inferred.

The efficiency of charge separation in the alumina-coated silica colloidal suspensions, in which both the *N*-phenylglycine and carboxylated tris(bipyridyl)ruthenium(II) complexes were electrostatically coadsorbed to the particles, has been measured, and the results are reported herein. The results are compared with those measured in the previous system in which the tris(bipyridyl)ruthenium(II) chromophore was not modified with the covalently attached viologen.

Experimental Section

Materials. *N*-Phenylglycine (Aldrich, 98%) was recrystallized from water several times prior to use. $RuCl_3 \cdot 3H_2O$ (99.9%) and SeO_2 (99.4%) were obtained from Alfa. 4,4′-Dimethyl-2,2′-bipyridine was obtained from Aldrich as 99% pure and recrystallized from ethyl acetate prior to use. 4,4′-Dipyridyl was obtained from Aldrich as 98% pure, recrystallized from water, and then dried in vacuo prior to use. (3-Bromopropyl)ammonium bromide (98%) and (2-bromoethyl)ammonium bromide (99%) were obtained from Aldrich and used as received. Tris(bipyridyl)ruthenium(II) (dichloride salt) was obtained from Aldrich and used as received. The alumina-coated colloidal silica particles (Nalco ISJ-612) were obtained as an aqueous (pH 4.2) suspension and diluted to the desired concentration with 10^{-5} M HCl. Water was deionized and freshly passed through a Sybron/Barnstead Nanopure II purification system prior to use. 4,4′-Dicarboxy-2,2′-bipyridine (dcbpy), 4′-methyl-2,2′-bipyridine-4-carboxylic acid (mcbpy), and $Ru(dcbpy)_2Cl_2 \cdot xH_2O$ were prepared as previously described.[3,10,11]

1-Methyl-4,4′-bipyridinium (iodide). 4,4′-Dipyridyl was stirred with 1 equiv of methyl iodide in a minimal amount of CH_2Cl_2 for 8 h. The yellow precipitate was filtered, washed with CH_2Cl_2, and then recrystallized from ethanol. ^1H-NMR (DMSO-d_6): 9.18 ppm (d, 2H); 8.87 ppm (d, 2H); 8.65 ppm (d, 2H); 8.05 ppm (d, 2H); 4.40 ppm (s, 3H).

1-(3-Ammoniopropyl)-1′-methyl-4,4′-bipyridinium ($3PF_6^-$) (MV_3^{2+}). 1-Methyl-4,4′-bipyridinium was refluxed with 1 equiv

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of (3-bromopropyl)ammonium bromide in CH_3CN for 12 h. The halide salt was filtered from the cooled solution, recrystallized from methanol, and then reprecipitated from water by the addition of NH_4PF_6. ^1H-NMR (CD_3COCD_3/D_2O): 8.93 ppm (d, 2H, 2-H, and 6-H); 8.86 ppm (d, 2H, 2′-H, and 6′-H); 8.43 ppm (d, 2H, 3-H, and 5-H); 8.37 ppm (d, 2H, 3′-H, and 5′-H); 4.69 ppm (t, 2H); 4.40 ppm (s, 3H); 3.09 ppm (t, 2H); 2.36 ppm (pentet, 2H).

1-(2-Ammonioethyl)-1′-methyl-4,4′-bipyridinium (**MV_2^{2+}**). The asymmetric viologen was prepared analogously to the procedure described above for the preparation of MV_3^{2+}, with the substitution of (2-bromoethyl)ammonium bromide. ^1H-NMR (CD_3COCD_3): 9.50 ppm (d, 2H); 9.35 ppm (d, 2H); 8.88 ppm (d, 2H); 8.78 ppm (d, 2H); 8.20 ppm (s (br), 3H); 5.53 ppm (quartet, 2H); 4.70 ppm (s, 3H); 4.30 ppm (t, 2H).

N-(3-(1′-Methyl-4,4′-bipyridinium-1-yl)propyl)-4′-methyl-2,2′-bipyridine-4-carboxamide ($2PF_6^-$) (**LMV_3^{2+}**) and *N-(2-(1′-Methyl-4,4′-bipyridinium-1-yl)ethyl)-4′-methyl-2,2′-bipyridine-4-carboxamide ($2PF_6^-$)* (**LMV_2^{2+}**). Syntheses of the covalently linked 2,2′-bipyridine/viologen ligands were accomplished by the room temperature (dry DMF) coupling of the carboxylic acid, mcbpy, and either MV_3^{2+} or MV_2^{2+} in the presence of 1-hydroxybenzotriazole (1.5 equiv) and 1,3-diisopropylcarbodiimide (excess). The ligands were isolated from the reaction mixture and recrystallized from water. ^1H-NMR (CD_3COCD_3) LMV_3^{2+}: 9.48 ppm (d, 2H); 9.34 ppm (d, 2H); 9.02 ppm (dd, 2H); 8.82 ppm (multiplet, 6H); 8.36 ppm (t, 1H); 8.10 ppm (dd, 2H); 5.05 ppm (t, 2H); 4.72 ppm (s, 3H); 3.65 ppm (quartet, 2H); 2.82 ppm (s, 3H); 2.52 ppm (quintet, 2H). ^1H-NMR (CD_3COCD_3) LMV_2^{2+}: 9.45 ppm (dd, 2H); 9.32 ppm (dd, 2H); 9.00 ppm (dd, 2H); 8.77 ppm (multiplet, 4H); 8.72 ppm (d, 2H); 8.36 ppm (t, 1H); 8.12 ppm (dd, 1H); 8.00 ppm (dd, 1H); 5.32 ppm (t, 2H); 4.72 ppm (s, 3H); 4.33 ppm (quartet, 2H); 2.75 ppm (s, 3H).

$Ru(dcbpy)_2(LMV_3^{2+})$ (**2**) and *$Ru(dcbpy)_2(LMV_2^{2+})$* (**1**). The tris(bipyridyl)ruthenium(II) complexes were prepared by refluxing $Ru(dcbpy)_2Cl_2 \cdot xH_2O$ with either LMV_3^{2+} or LMV_2^{2+} in a minimum amount of aqueous $NaHCO_3$ under argon. The reaction was monitored by UV/vis spectroscopy and the product precipitated by the addition of NH_4PF_6 and acidification with HPF_6. The zwitterionic complexes were purified on a CM-Sephadex gel (Sigma, C-50-120) column.

Methods. All measurements were conducted at ambient temperature (22 ± 2 °C). Ground-state UV/vis absorption spectra were measured using a Perkin-Elmer, Lambda Array 3840 single-beam spectrophotometer. Proton NMR spectra were recorded on a Varian XL-200 FT-NMR spectrometer. Reported chemical shifts were obtained using the resonances of the residual solvent protons which are present as a <0.5% impurity as an internal standard. Nanosecond transient absorption measurements employed the technique of laser flash photolysis. The second harmonic (532 nm) of a Q-switched Nd:YAG laser (Quantel YG-660, pulse width ca. 8 ns) was used for laser flash excitation. The instruments for the time-resolved kinetic spectroscopy and time-correlated single-photon counting have been previously described.[12,13] The double diode array spectrograph utilized for picosecond pump–continuum probe absorption experiments has been previously described.[14] Sample excitation employed the frequency-doubled (532 nm, 25 ps) light from a mode-locked/Q-switched Nd:YAG (Quantel YG571) laser operating at 5 Hz. Typical excitation energies were 5–10 mJ/pulse. Kinetic measurements were obtained by overlapping the excitation and probe beam in a 5-mm cuvette in a quasi-collinear geometry. The probe and reference beam were focused onto the entrance slit of a monochromator (PTI Model 01-002), and the light was detected with a pair of UV-enhanced silicon photodiodes (EG&G Judson UV-100BQ) at the exit slit of the monochromator for kinetic measurements. Spectra were acquired by dispersing the probe and reference beams *via* two fiber optic cables onto a Princeton Instruments DD512 unintensified dual diode array.

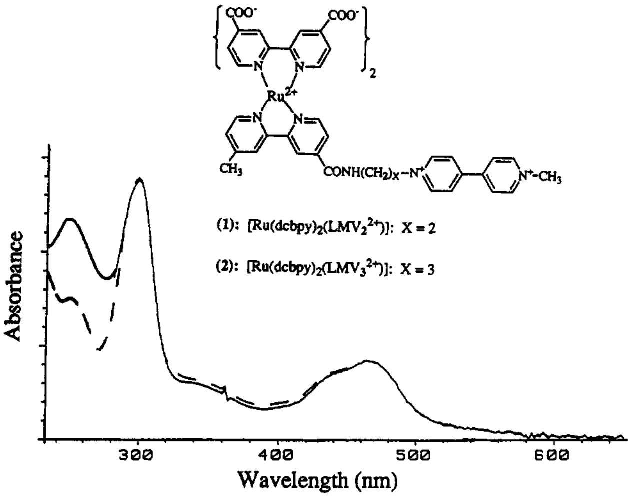

Figure 1. Structures of viologen-linked tris(bipyridyl)ruthenium(II) complexes. Also shown are the UV/vis absorption spectra of **1** (solid line), along with that of the free chromophore [$(Ru(dcbpy)_2(mabpy)^{2-}$] (dashed line) (aqueous solution, pH 7.0).

Results

Shown in Figure 1 are the structures of the covalently linked chromophore/viologen systems. The chromophore portion of both **1** and **2** is identical and is rendered a net 2– charge by the 4,4′-dicarboxy-2,2′-bipyridine (pK_a = 2.8, < 2.0) ligands at pH 5.0. The two systems differ only by the number of intervening methylene units between the 2,2′-bipyridine ligand and the 4,4′-bipyridinium acceptor.

Photophysical Properties in Aqueous Solution and Colloidal Suspensions. The photophysical and redox properties of the tris(bipyridyl)ruthenium(II) chromophores not covalently linked to the viologen electron acceptor have been previously reported.[3] As shown in Figure 1, the ground-state absorption spectra of the viologen-linked chromophores are identical to that of the "free" chromophore not containing the viologen linkage, with the exception of the UV absorbance of methyl viologen. Hence, there is no indication of any ground-state interactions between the donor and acceptor moieties.

Upon laser flash excitation of an aqueous solution of rigorously purified samples of **1** and **2**, the excited-state lifetime is significantly diminished relative to that of the free chromophore, suggesting that oxidative quenching of the excited state is the major deactivation pathway of the excited state. This is shown in Scheme 1, where Ru^{2-} represents the dianionic chromophore portion of either **1** or **2**.

SCHEME 1: Oxidative Quenching of $(Ru^{2-})^*$ by Covalently Attached Viologen (V^{2+})

$$(Ru^{2-})^*\text{-}V^{2+} \xrightarrow{k_{oq}} (Ru^{\bullet-})\text{-}V^{\bullet+} \xrightarrow{k_{bet}} (Ru^{2-})\text{-}V^{2+}$$

$$\xrightarrow{k_d} (Ru^{2-})\text{-}V^{2+}$$

The excited-state lifetime of **2**, measured by time-correlated single-photon counting, was measured from the luminescence decay shown in Figure 2. For complex **1**, only an upper limit of ca. 300 ps could be extracted from the experimental data, as the decay time was shorter than the instrumental response of the system. However, in subsequent picosecond absorption experiments, the viologen radical cation could be clearly observed by its characteristic absorption band at 600 nm as is shown in Figure 3. The spectral features of the picosecond difference spectra are

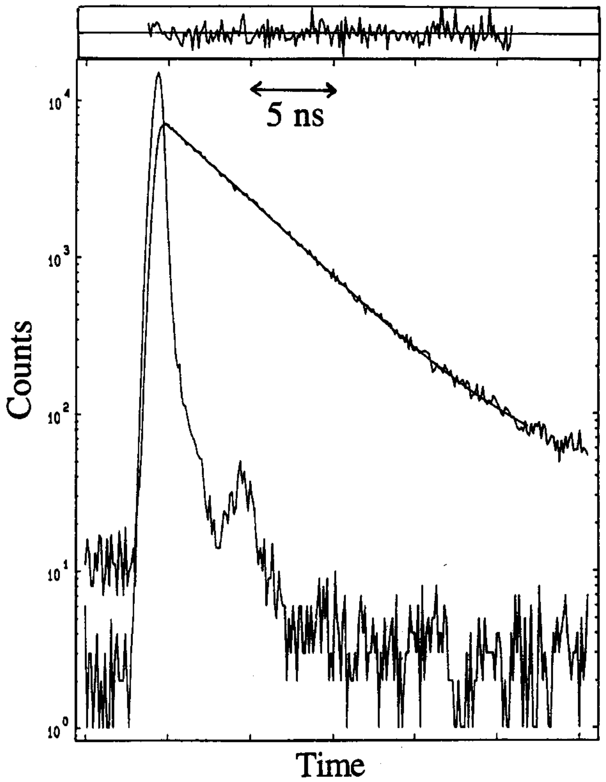

Figure 2. Luminescence decay (630 nm) of **2** in aqueous solution (pH 5.0) measured by time-correlated single-photon counting (λ_{ex} = 295 nm). Solid line shows best fit to a single exponential decay (residuals shown at top). Instrument response function (fwhm ca. 500 ps) is also shown.

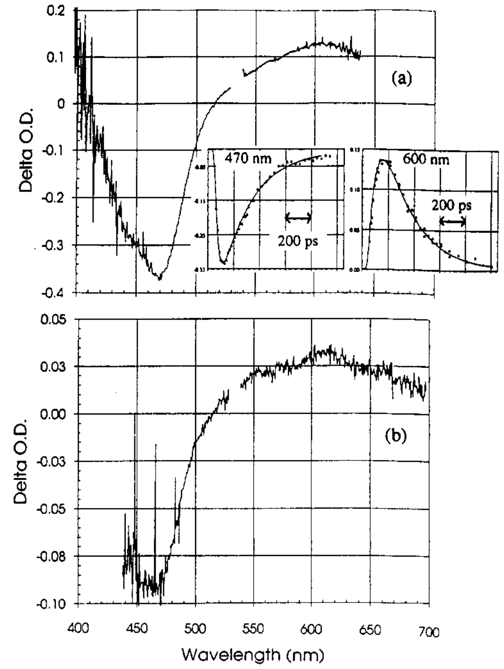

Figure 3. Picosecond absorption spectrum of **1** formed upon excitation with a 25 ps (532 nm) laser pulse in aqueous solution (pH 6.5). The transient spectra resulting from two excitation intensities (a, top and b, bottom) are shown. Both spectra were measured 125 ps after excitation. Inset: Kinetics of viologen radical growth and decay (600 nm), along with the bleaching and recovery of the MLCT absorption band (470 nm). Best fits to eq 1, following deconvolution with the excitation pulse, are shown.

independent of laser excitation intensity in the range employed, ruling out the possibility of viologen radical cation formation *via* biphotonic processes. The kinetics of the growth and decay of the viologen radical cation, monitored at 600 nm, are shown in Figure 3. From the best fit to eq 1, the forward (k_{oq}) and back (k_{bet}) electron-transfer rate constants were determined to be 1.7 × 10^{10} and 4.2 × 10^9 s^{-1}, respectively.

TABLE 1: Summary of Oxidative Quenching Results in Aqueous Solution and Colloidal Suspensions

	aqueous solution			colloidal suspension[c]		
complex	τ^a (ns)	τ_d^a (ns)	$10^{-8}k_{oq}$ (s^{-1})	$\langle\tau\rangle$ (ns)	$\langle\tau_d\rangle$ (ns)	$10^{-7}\langle k_{oq}\rangle$ (s^{-1})
1, $X = 2$	<0.300	558	170[b]	7.0	530	13
2, $X = 3$	4.8	558	2.1	66	530	1.3

[a] Argon-saturated solution (pH > 4.5). [b] From picosecond absorption experiments (see text). [c] Argon-saturated suspensions (pH = 5.0) (2–3 g/L Al_2O_3/SiO_2).

$$[V^{\bullet+}] = [(Ru^{2-})^*]_0\left[\frac{k_{oq}}{k_{bet} - k_{oq}}\right]\{\exp(-k_{oq}t) - \exp(-k_{bet}t)\} \qquad (1)$$

From Scheme 1, k_{oq} can be extracted for **2** from the measured lifetime of $(Ru^{2-})^*$ according to eq 2. In the calculation, τ_d is

$$k_{oq} = 1/\tau - 1/\tau_d \qquad (2)$$

the excited-state lifetime of the complex structurally identical to **1** or **2**, where the alkylamide linkage to the viologen, and hence the viologen, is absent and replaced with an isopropylamide substituent. In argon-saturated aqueous solution, this value was measured to be 558 ns. The unimolecular oxidative quenching rate constants are given in Table 1.

Upon addition of the alumina-coated colloidal silica particles to aqueous solutions of **1** or **2**, the excited-state lifetime of both complexes becomes significantly longer than that measured in homogeneous aqueous solution. At the experimental pH employed (5.0), the particles bear a net positive charge and are capable of electrostatically adsorbing oppositely charged species to the surface. The particles have been previously characterized by electron microscopy and were found to be quite homogeneous with an average diameter of 27.0 nm. In the colloidal suspensions, the luminescence decay of the complexes could no longer be fit to a single exponential decay, reflecting the heterogeneity of the binding sites on the particles.

However, from an estimate of the average lifetime, $\langle\tau\rangle$, of the complexes in the colloidal suspensions, it is apparent that the lowest energy electronically excited state is still quenched by the covalently attached viologen, albeit with a somewhat smaller rate constant. In the heterogeneous systems, k_{oq} was calculated according to eq 2, utilizing average lifetimes, $\langle\tau\rangle$ and $\langle\tau_d\rangle$, from best fits of the luminescence to a double exponential fit: ($I(t) = a_1 \exp(-k_1t) + a_2 \exp(-k_2t)$) according to eq 3. These values are

$$\langle\tau\rangle = (a_1k_1 + a_2k_2)^{-1} \quad \text{with} \quad a_1 + a_2 = 1 \qquad (3)$$

given in Table 1. As in homogeneous aqueous solution, no radicals were observed in the nanosecond transient absorption experiments, suggesting that the back electron transfer rate constant is large compared to k_{oq}.

***N*-Phenylglycine Quenching.** At pH 5.0, the carboxylate groups of the tris(bipyridyl)ruthenium(II) chromophore exist in their basic forms. Furthermore, at this pH, 67% of the *N*-phenylglycine electron donor (pK_a = 4.7 (amino group),[15] 2.35 (carboxylate of glycine)[16]) is in its basic and thus anionic form. It has been previously shown that the organic donor and the anionic tris(bipyridyl)ruthenium(II) complex can be coadsorbed to the surface of cationic alumina-coated colloidal silica particles and the kinetics of the reductive quenching expedited relative to those measured in aqueous solution.[3]

Upon addition of the *N*-phenylglycine electron donor to colloidal suspensions of either **1** or **2**, the laser flash induced transient spectral changes shown in Figure 4 are observed. Immediately

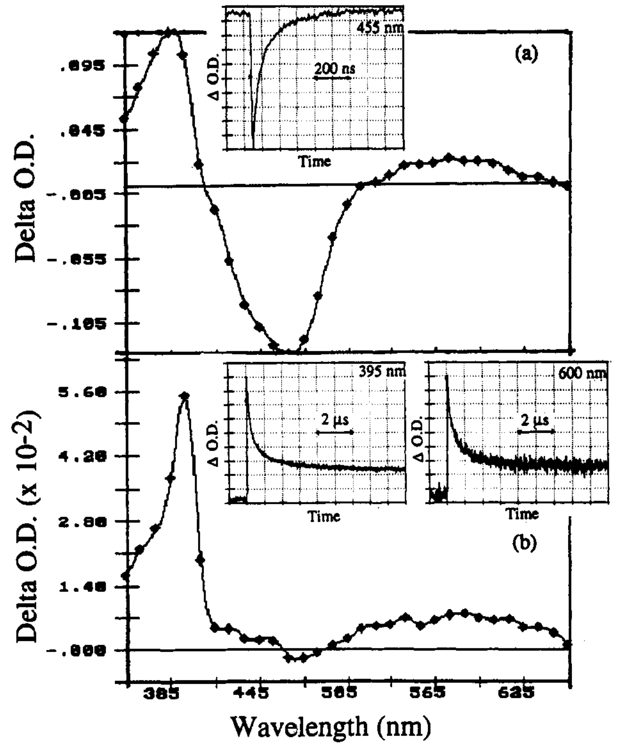

Figure 4. Transient absorption spectrum of **2** measured in suspensions of alumina-coated colloidal silica (2.5 g/L, pH 5.0) containing 0.50 mM *N*-phenylglycine electron donor. (a, top) 43 ns after excitation with an 8 ns (532 nm) laser pulse; (b, bottom) 647 ns after laser flash excitation. Insets: Kinetics of recovery of ground-state bleaching (455 nm) and decay of $V^{\bullet+}$ absorption monitored at 395 and 600 nm (Note different time scales on the insets).

after the laser pulse, absorption bands characteristic of the ruthenium complex $\{^3[Ru^{2-}]^*-[Ru^{2-}]\}$ spectrum are observed, including the triplet absorption at ca. 380 nm, along with the bleaching of the MLCT visible absorption band (460 nm). Superimposed on this is the spectrum characteristic of the viologen radical cation ($V^{\bullet+}$) absorption, which absorbs strongly at 395 nm (ϵ = 42 000 M^{-1} cm^{-1}) and 606 nm (ϵ = 13 700 M^{-1} cm^{-1}).[17] The ground-state bleaching completely recovers ca. 600–700 ns after excitation, as the spectrum evolves to that shown in Figure 4b, characteristic of the viologen radical cation absorption spectrum. However, the viologen radical cation is completely formed during the laser pulse. No further production of the species was observed during the time period in which the ground state of the complex recovers.

As shown in Figure 5, the "instantaneous" absorption change induced by laser flash excitation at both 395 and 600 nm (not shown) increases upon increasing the concentration of added electron donor. Likewise, the magnitude of the ground-state bleaching produced within the 8-ns laser pulse decreases upon increasing the *N*-phenylglycine concentration. Both observations are indicative of a static, or at least very rapid, quenching process resulting in the formation of reduced viologen. As shown in Figures 4 and 5, the kinetics of the decay of the viologen radical cation absorption are multiphasic and independent of the concentration of electron donor.

Efficiency of Viologen Radical Cation Production. Using an aqueous solution of matched optical density (at 532 nm) of $Ru(bpy)_3^{2+}$ as a standard, the concentration of **1*** and **2*** was determined. The previously measured extinction coefficient difference ($\Delta\epsilon_{450}$ = 10 000 M^{-1} cm^{-1})[18] for the triplet minus ground-state MLCT absorption in aqueous solution, along with the absorption change at 450 nm, extrapolated to $t = 0$, was used to determine the $^3[Ru(bpy)_3^{2+}]^*$ concentration. The results are given in Table 2 at different concentrations of *N*-phenylglycine for both **1** and **2**. The concentration of viologen radical was measured from the absorption change extrapolated to $t = 0$ at either 395 or 600 nm.

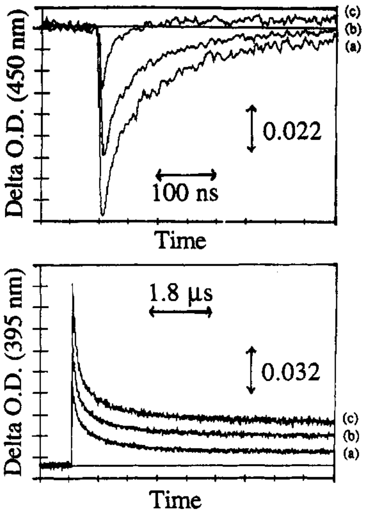

Figure 5. Transient absorption decays monitored at 450 nm (top) and 395 nm (bottom) after excitation of an alumina-coated colloidal suspension (2.2 g/L, pH 5.0) of **2** containing varying amounts of *N*-phenylglycine: (a) 55.1, (b) 164, and (c) 627 μM N-PG.

TABLE 2: Summary of Viologen Radical Cation Yields in Colloidal Suspensions

1		2	
[N-PG] (μM)	$[V^{\bullet+}]/[Ru^*]$	[N-PG] (μM)	$[V^{\bullet+}]/[Ru^*]$
55.1	0.064	55.1	0.10
110	0.094	164	0.14
528	0.17	627	0.23

Discussion

Oxidative Quenching in Aqueous Solution and Colloidal Suspensions. In the absence of *N*-phenylglycine electron donor, the lowest energy electronically excited state of the tris(bipyridyl)-ruthenium(II) chromophore decays primarily *via* unimolecular electron transfer to the covalently attached viologen. The rate constant for this process, in both aqueous solution and colloidal suspensions, is increased 1–2 orders of magnitude in **1**, relative to **2**, where the length of the intervening spacer has been shortened by one methylene unit. From nanosecond and picosecond absorption experiments in homogeneous aqueous solution, no evidence of charge separation in **2** was observed, indicating that $k_{bet} \gg k_{oq}$ in this complex. However, in complex **1**, in which the oxidative rate constant is significantly increased, charge separation was observed by picosecond absorption techniques. Thus, the forward electron transfer rate constant seems to be more dependent upon the number of intervening methylene groups, making charge separation in **1** experimentally observable.

The decreased unimolecular rate constant for oxidative quenching upon introduction of the alumina-coated colloidal particles reflects the adsorption of the carboxylated tris(bipyridyl)-ruthenium(II) complexes to the particle surface. The charged interface could affect the photophysics of the chromophore by either (1) changing the driving force (excitation energy as well as one-electron-oxidation potential of the ruthenium(II) chromophore) of the process or (2) physically extending the flexible donor/acceptor system, thus slowing down any through-space electron-transfer component of the process. The results at hand do not allow these two effects to be discerned. However, the slowing of the intramolecular oxidative quenching in either complex serves to favor the reductive quenching pathway of the electronically excited chromophore.

Mechanism of Viologen Radical Cation Production. The rapid production of viologen radical cation in the colloidal suspensions of **1** or **2** could occur *via* either of the two mechanisms outlined in Scheme 2: (a) Reductive quenching of the electronically excited chromophore by a neighboring adsorbed *N*-phenylglycine quencher. Following formation of the geminate oxidized donor/reduced ruthenium complex, electron transfer to the covalently attached viologen (k_{MV}) could occur in competition with cage recombination (k_{rec}). (b) Oxidative quenching by the covalently attached viologen, followed by rapid electron transfer from a neighboring electron donor ($k_D[D^-]$), in competition with intramolecular charge recombination. In Scheme 2, either step 1 or 2 could account for the *N*-phenylglycine concentration dependence of the viologen radical cation yield. Production of reduced viologen by either mechanism a or b must be rapid (occurring within the 8-ns laser pulse) to account for the "instantaneous" viologen radical cation production. From Figure 4, it is apparent that there is some residual ground-state bleaching which is not responsible for production of any reduced viologen. This is likely due to electronically excited states of the tris(bipyridyl)ruthenium(II) chromophore which are not in the vicinity of any *N*-phenylglycine donors to be quenched and, thus, decay only by intramolecular oxidative quenching followed by rapid back electron transfer. Dissociation of the electrostatically adsorbed complex from the colloidal particle by addition of *N*-phenylglycine would certainly account for the diminished lifetime of the excited state of the complex, as the lifetime in homogeneous solution is more than 10 times shorter than that in the colloidal suspensions. Under the conditions employed, reduced viologen cannot be formed in the aqueous phase, since no charge separation in the covalently linked tris(bipyridyl)ruthenium(II)/viologen system is observed following oxidative quenching ($k_{bet} \gg 2.1 \times 10^8\ s^{-1}$). Furthermore, the bimolecular reaction between *N*-phenylglycine and the oxidized ruthenium complex would not compete effectively with back electron transfer in a homogeneous aqueous solution containing <1 mM electron donor.

SCHEME 2: Mechanism of Viologen Radical Cation Production in Colloidal Suspensions

$$\text{(a)}\quad (\mathrm{Ru}^{2-})^{*}\text{–}\mathrm{V}^{2+} + \mathrm{D}^- \xrightarrow[(1)]{k_{rq}}$$

$$(\mathrm{D}\therefore\mathrm{Ru}^{3-})\text{–}\mathrm{V}^{2+} \xrightarrow{k_{MV}} (\mathrm{Ru}^{2-})\text{–}\mathrm{V}^{\bullet+} + \mathrm{D}^{\bullet}$$

$$\xrightarrow{k_{rec}} (\mathrm{Ru}^{2-})\text{–}\mathrm{V}^{2+} + \mathrm{D}^-$$

$$\text{(b)}\quad (\mathrm{Ru}^{2-})^{*}\text{–}\mathrm{V}^{2+} \xrightarrow{k_{oq}} (\mathrm{Ru}^{\bullet-})\text{–}\mathrm{V}^{\bullet+} \xrightarrow[(2)]{k_D[D^-]} (\mathrm{Ru}^{2-})\text{–}\mathrm{V}^{\bullet+} + \mathrm{D}^{\bullet}$$

$$\xrightarrow{k_{bet}} (\mathrm{Ru}^{2-})\text{–}\mathrm{V}^{2+} + \mathrm{D}^-$$

From Scheme 2, the concentration of viologen radical cation produced by both the reductive and oxidative quenching pathways is given by eq 4.

$$[\mathrm{V}^{\bullet+}] = [\mathrm{Ru}^*]\left\{\frac{k_{rq}[\mathrm{D}^-]}{k_{rq}[\mathrm{D}^-] + k_{oq}}\right\}\left\{\frac{k_{MV}}{k_{MV} + k_{rec}}\right\} + [\mathrm{Ru}^*]\left\{\frac{k_{oq}}{k_{oq} + k_{rq}[\mathrm{D}^-]}\right\}\left\{\frac{k_D[\mathrm{D}^-]}{k_D[\mathrm{D}^-] + k_{bet}}\right\} \quad (4)$$

k_{rq}, the apparent bimolecular rate constant for reductive quenching in the alumina-coated colloidal silica suspensions, has been previously determined to be $5.7 \times 10^9\ M^{-1}\ s^{-1}$.[3] Furthermore, the unimolecular rate constant, k_{oq}, for complexes **1** and **2** has been estimated in the colloidal suspensions and is listed in Table 1. Using these values, at the highest concentration of *N*-phenylglycine employed in the investigations of **2** (0.627 mM), the maximum efficiency of viologen radical cation production ($[\mathrm{V}^{\bullet+}]/[\mathrm{Ru}^*]$) from the reductive quenching pathway, given by the first term in eq 4, is 0.22. The experimentally measured efficiency at this electron donor concentration was 0.23, very close to the theoretical maximum from the reductive quenching pathway only. However, for complex **1**, the same calculation for the viologen radical production from the reductive quenching pathway (at [N-PG] = 0.528 mM) yields a value of only 0.022 for the maximum number of ruthenium excited states which form viologen radical cation *via* the reductive quenching mechanism a. In this case, since the oxidative quenching rate constant is 1 order of magnitude larger than that in complex **2**, all but ca. 2% of the viologen radical cation produced must come from pathway b in Scheme 2 and is given by the second term in eq 4.

Viologen Radical Cation Decay. As shown in Figures 4 and 5, the viologen radical cation is relatively long lived and (not shown) is still present in ca. 15% of its initial concentration 5 ms after the laser pulse. However, the decay kinetics are clearly multiphasic and characteristic of heterogeneous systems. On the time scales shown in the figures, the fast and predominant portion of the decay can be satisfactorily modeled by a single exponential decay with a lifetime of 140 (±10) ns in argon-saturated colloidal suspensions. This value is independent of *N*-phenylglycine concentration and initial concentration of viologen radical cation and is the same for that produced in either **1** or **2**. These observations suggest that the multiphasic decay of the viologen radical cation is geminate in nature and is a result of charge recombination with the same oxidized electron donor which was responsible for producing the viologen radical cation. Any second-order components would manifest themselves as a viologen radical cation yield dependence of the decay.

Conclusions

Thus, we have demonstrated that the photoreduction of methyl viologen, when covalently linked to a tris(bipyridyl)ruthenium(II) complex, can occur with moderate efficiency in colloidal suspensions containing *N*-phenylglycine electron donor. In the reductive quenching scheme, it is crucial that the viologen be covalently attached to the photoreduced chromophore, so that the electron transfer from the one-electron-reduced complex proceeds rapidly, in competition with cage recombination with the oxidized donor. The efficiency of this process is relatively independent of the length of the intervening alkyl group between the metal complex and viologen acceptor. This is most likely a simple coincidence, since the mechanism of viologen reduction must change to that of initial oxidative quenching of the electronically excited chromophore when the unimolecular rate constant for oxidative quenching becomes large.

The adsorption of the complexes to the colloidal particles has several crucial manifestations which make the electron "relay" scheme feasible. Firstly, adsorption of the oppositely charged donor/acceptor system slows down the intramolecular oxidative quenching process, making the "bimolecular" reductive quenching process competitive, at least in the case of complex **1**. Secondly, k_{rq}, the apparent bimolecular rate constant for reductive quenching in the colloidal suspensions is nearly 10 times larger than that in homogeneous aqueous solution, further favoring the reductive quenching pathway.

The efficiency of charge separation has been significantly improved over that previously reported for the reductive quenching of the electronically excited tris(bipyridyl)ruthenium(II) complex, absent of the covalently attached viologen, by coadsorbed *N*-phenylglycine electron donor. This improvement has been accomplished by the covalent attachment of the viologen, capable of "intercepting" the initially formed geminate ion pair in competition with the energy-wasting charge recombination.

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