Supramolecular Assemblies of Metal Complexes: Light-Induced Electron Transfer in the Galleries of α-Zirconium Phosphate

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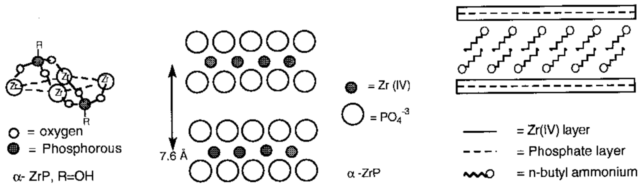
Rapid photoinduced electron transfer was observed with supramolecular assemblies of donor and acceptor metal complexes at the galleries of *n*-butylammonium salt of α-zirconium phosphate ($(C_4H_9NH_3)_2Zr(PO_4)_2 \cdot xH_2O$, abbreviated as BAZrP). Tris(2,2′-bipyridyl)ruthenium(II)$^{2+}$ luminescence, for example, was quenched by tris(2,2′-bipyridyl)cobalt(III)$^{3+}$ with rate constants exceeding 1.6×10^{12} m^2 mol^{-1} s^{-1}, when the metal complexes were intercalated in the galleries of BAZrP. The quenching rates were unaffected when the viscosity of the BAZrP suspensions was increased (2:1 mixture of ethylene glycol−water) or when the loading of the donor was increased 10-fold. Even when cooled to 77 K, as a rigid glass, the electron transfer reactions between the donor and the acceptor proceed at essentially the same rate as at room temperature indicating a very low activation energy for the electron transfer reaction. These activation-less rate constants are faster than anticipated for diffusion controlled electron transfer rates at BAZrP galleries, at low temperatures. Excited-state energy migration from donor to donor (antenna effect) followed by electron transfer between the nearest donor−acceptor pairs is one explanation proposed to account for the above observations.

A number of model systems are being investigated to mimic the photosynthetic apparatus.[1] In particular, supramolecular assemblies of metal complexes and organic chromophores are being explored. Such assemblies may be used for efficient light absorption and subsequent storage of solar energy through charge separation.[2] In this context, two major approaches can be distinguished. Donors were covalently linked to a series of acceptors such that light absorption leads to a sequence of intramolecular electron transfer reactions.[3] Alternatively, reactants may be organized in rigid matrixes to promote forward electron transfer and inhibit the back transfer. When the wasteful back electron transfer is inhibited the overall efficiency is improved. For example, viologen derivatives bound to zirconium phosphonate show high efficiencies for light induced electron transfer.[4] The charge separated products were stabilized in these matrixes, demonstrating the advantages of rigid media in inhibiting the back transfer, and mimicking the photosynthetic apparatus.

Efficient energy and electron transfer was also observed when donors and acceptors were arranged in successive layers of Langmuir−Blodgett films.[5] Donor to donor energy migration (antenna effect) was proposed to occur in these films. Enhanced singlet−singlet energy transfer was observed when organic chromophores were self-assembled at the ionic surfaces of *n*-butylammonium salt of α-zirconium phosphate ($(C_4H_9NH_3)_2Zr(PO_4)_2 \cdot xH_2O$, abbreviated as BAZrP, Scheme 1).[6] Energy hopping from donor to donor, followed by trapping of the energy by the acceptor was proposed to explain the efficient singlet energy transfers. Such antenna systems can be utilized for light harvesting, if the chromophores absorb in the visible region, and the absorbed energy can be used efficiently for charge separation. In this context, we report assemblies of metal complexes intercalated in the galleries of an inorganic phosphate, BAZrP, that show strong light absorption in the visible region followed by rapid electron transfer quenching of excited states.

SCHEME 1: Structure of α-ZrP Layers and Expansion of ZrP Spacings by the Intercalation of Butyl Amine HCl. Binding of the Guest Molecules in the Galleries of BAZrP, at the Edges, and on the Outer Surfaces Is Possible



Layered materials such as α-zirconium phosphate ($Zr(HPO_4)_2) \cdot H_2O$), referred to as α-ZrP (Scheme 1),[7] provide a simple route for the construction of supramolecular assemblies of hydrophobic organic cations and metal complexes.[8] α-ZrP consists of a layer of Zr(IV) ions sandwiched between two layers of phosphate anions (Scheme 1).[9] Each phosphate group in α-ZrP carries one ionizable hydroxyl group, making these materials highly acidic. The hydroxyl groups can be readily deprotonated, and the resulting ionic sites serve to produce supramolecular assemblies of appropriate counterions. Treatment of α-ZrP with *n*-alkylamines, for example, results in the intercalation of alkylammonium ions in the galleries of α-ZrP.[10] The alkylamines are self-assembled as a bilayer at the ionic surfaces of α-ZrP. The ZrP layer spacings, therefore, are expanded from 7.6 Å for α-ZrP to 18.6 Å when *n*-butylamine (BA) is intercalated into the galleries of α-ZrP. The *n*-butylammonium salt of α-ZrP (BAZrP, Scheme 1) thus produced consists of alternate sheets of α-ZrP and bilayers of butylamine hydrochloride.[9−15] The alkyl chains of BA provide hydrophobic regions whereas the ionic headgroups provide highly polar regions to accommodate hydrophobic ionic guests. The butylammonium ions, for example, can be readily ion-exchanged with guest molecules of appropriate size, charge, and

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hydrophobicity.[9,10] The increased interlayer separation in BAZrP, when compared to α-ZrP, is essential for rapid incorporation of large hydrophobic cations into the galleries. On the basis of these observations, self-assembly of chromophores in the galleries of BAZrP can be envisioned to build artificial light harvesting complexes. A number of hydrophobic cations have been self-assembled in the galleries of BAZrP, and these chromophores show enhanced excimer emission, and strong exciton coupling.[12−14] By the use of appropriate substrates, the energy trapped by such assemblies may be stored as chemical potential.[15,16]

Tris(2,2′-bipyridyl)ruthenium(II)$^{2+}$ (abbreviated as Ru(bpy)$_3^{2+}$) was used in the current studies as the light absorbing chromophore (donor), and tris(2,2′-bipyridyl)cobalt(III)$^{3+}$ (Co(bpy)$_3^{3+}$) (acceptor) has been used as the quencher. Ru(bpy)$_3^{2+}$ absorbs in the visible region, and hence, the window of light absorption is shifted to longer wavelengths when compared to the aromatic antenna systems described earlier.[5,6] Ru(bpy)$_3^{2+}$ is quite stable to heat and light, making it a convenient chromophore to construct artificial light-harvesting complexes. Spectroscopic properties of Ru(bpy)$_3^{2+}$ are extensively investigated for its use in solar energy conversion and storage.[17] The excited state of Ru(bpy)$_3^{2+}$ is both an excellent oxidant and a reductant, and therefore, a multitude of energy and electron transfer reactions can be carried out using this chromophore.[18] The photophysical and photochemical properties of Ru(bpy)$_3^{2+}$ is well documented,[19] and Ru(bpy)$_3^{2+}$ has been used as a reporter molecule to investigate a number of organized media.

Ru(bpy)$_3^{2+}$ shows a high affinity for BAZrP and intercalation of Ru(bpy)$_3^{2+}$ into the galleries of BAZrP leads to dramatic changes in Ru(bpy)$_3^{2+}$ photophysical properties.[20] Intercalation of Ru(bpy)$_3^{2+}$ into BAZrP results in a large red shift of metal-to-ligand charge transfer (MLCT) absorption band to 481 nm and blue shift of the luminescence maximum to 590 nm.[20] The spectral maxima were independent of loading of the metal complex, strongly suggesting formation of supramolecular assemblies of the metal complex at the galleries of BAZrP. These assemblies have been thoroughly characterized in a previous report.[20] Blue shift of Ru(bpy)$_3^{2+}$ emission was also observed in rigid matrixes such as ice, or ethanol−methanol glasses at low temperature.[21] Therefore, the microenvironment surrounding Ru(bpy)$_3^{2+}$ in BAZrP is rigid and does not permit the relaxation of the initially produced MLCT excited state. This aspect accounts for the decrease in the energy gap between the initially produced excited state and the luminescent MLCT state. Long lifetimes, and increased MLCT excited-state energy of Ru(bpy)$_3^{2+}$ intercalated in BAZrP, when compared to that of the aqueous solutions, are welcome changes for the use of these assemblies in studies leading to solar energy conversion and storage.

Quenching of Ru(bpy)$_3^{2+}$ luminescence by Co(bpy)$_3^{3+}$ in aqueous solutions is diffusion limited, and involves intermolecular electron transfer.[8] Due to the similarity in size, shape, and hydrophobicity, binding of Co(bpy)$_3^{3+}$ to BAZrP is expected to be similar to that of Ru(bpy)$_3^{2+}$. The donors and the acceptors are, therefore, less likely to segregate at the galleries. Such segregation was observed when methyl viologen was used as a quencher for Ru(bpy)$_3^{2+}$ luminescence in mica type silicates. Binding of Co(bpy)$_3^{3+}$, therefore, in the galleries of BAZrP/Ru(bpy)$_3^{2+}$ is expected to result in mixed assemblies of donor and acceptor metal complexes without segregation. The ease with which the above-mentioned supramolecular assemblies can be prepared, and characterized, provided inspiration for the current work. The bimolecular rate constants for the electron transfer when the above metal complexes were intercalated in the BAZrP layers are in the range $(1-30) \times 10^{11}$ m^2 mol^{-1} s^{-1}. Furthermore, the quenching rates were independent of solvent viscosity, or temperature down to 77 K. The study of energy transport in similar supramolecular assemblies prepared from chromophores that absorb in the visible region of the solar spectrum will be of practical value. The energy trapped by such assemblies may be converted into chemical potential via photoinduced electron transfer reactions, mimicking the photosynthetic apparatus.

Experimental Section

n-Butylammonium salt of α-zirconium phosphate ($(C_4H_9NH_3)_2Zr(PO_4)_2xH_2O$) was a generous gift from Professor G. Rosenthal, formerly at the Department of Chemistry, University of Vermont. Synthesis and characterization of BAZrP were published previously.[22] Concentration of BAZrP is expressed either as the weight percent or as mmol dm^{-3} of exchangeable cationic sites, using 5.4 mmol g^{-1} as the conversion factor, obtained from ion exchange studies.[23] The phosphate suspensions were stirred periodically to prevent sedimentation, and BAZrP concentrations were kept low (0.008%) to minimize scattered light from interfering with the spectral measurements.

Tris(bipyridine)Ru(II) dichloride was obtained from Aldrich Chemical Co., and has been used as received. Ru(bpy)$_3^{2+}$ concentration was varied from 0.5 to 10 μmol dm^{-3} to study the effect of surface coverage on the luminescence quenching of the metal complex. In a typical quenching experiment, aqueous solutions of Ru(bpy)$_3^{2+}$ (donor) and Co(bpy)$_3^{3+}$ (acceptor) were added to a dilute aqueous suspension of BAZrP such that the final concentration of BAZrP has been adjusted to 0.008% (432 μmol dm^{-3} exchangeable cationic sites). After equilibration for 24 h, no further changes in the luminescence properties were noticeable. Powder diffraction patterns of the BAZrP with and without the metal complex were recorded on a Scintag XDS 2000 X-ray diffractometer using Cu Kα radiation ($\lambda = 1.5406$ Å). Samples were spread on a glass slide and were exposed to the X-ray radiation. The powder diffraction patterns of BAZrP matched with the published results.[22] The XRD patterns of BAZrP treated with the metal complexes indicate expansion of the interlayer distances from 18.6 to 19.7 Å consistent with the intercalation of the metal complexes in the BAZrP galleries.[20]

All absorption spectra were recorded on a Perkin-Elmer Lambda-3B spectrophotometer and the luminescence spectra were recorded on a Perkin-Elmer LS-5 Fluorescence spectrometer. Both spectrometers were interfaced with an Apple Macintosh computer, and all the necessary software for the operation of these instruments has been developed in our laboratory. For the luminescence quenching experiments, the BAZrP suspensions, Ru(bpy)$_3^{2+}$, and the quencher were mixed in different proportions and allowed to equilibrate for 24 h. This resulted in a series of suspensions with a constant concentration of BAZrP/Ru(bpy)$_3^{2+}$ but with varying concentrations of Co(bpy)$_3^{3+}$. Air-saturated aqueous suspensions were used without degassing in all experiments unless stated otherwise. Samples were excited at 452 nm, and light absorption by the quencher at low quencher concentrations (1−10 μM) was negligible at this wavelength. The absorption spectra of the BAZrP suspensions containing both the sensitizer and the quencher were similar to the sum of the absorption spectra of individual components bound to BAZrP. Steady-state luminescence quenching data were analyzed using the Stern−Volmer equation,[24]

$$(I_o/I) = 1 + K_{sv}[Q] \qquad (1)$$

where I_o and I are the emission intensities in the absence, and in the presence, of the quencher [Q], respectively. The Stern−Volmer quenching constant (K_{sv}) was obtained from linear plots, using eq 1. The estimated error in the quenching constants did not exceed ± 5%, unless specified otherwise. Data analysis using the Perrin's model[24] did not result in satisfactory fits to the data. Forcing a linear fit to the experimental data ($\ln(I_o/I)$ vs [Q]) resulted in a critical quenching distance of 22 Å.

Luminescence lifetimes were measured on a time-correlated single-photon counting spectrometer, built in our laboratory. A nanosecond flash lamp (Edinburgh Instruments, Model F-199), filled with nitrogen gas, was used to generate light pulses with full widths at half-maximum in the range of 2−3 ns. The data were collected at low rates (<2% of the lamp frequency) to avoid pulse pile-up problems.[25] The luminescence decay traces were deconvoluted using software from PRA, Inc., and by nonlinear least-squares analysis using the Kaleidagraph (v 2.1). Data were collected over several half-lives of the emission using 1024 data points. The data were analyzed using biexponential model, Williams−Watts function of distribution of exponentials,[26] long-distance electron-transfer model used to analyze the electron-transfer data from low-temperature glasses,[27] and by using the subsystem model described by van Damme et al.[28] The subsystem model, for example, can be represented as $P(t) = \exp(-k_o t)\exp\{-n\ [1 - \exp(-k_q t)]\}$, where $P(t)$ is the probability of emission, k_o is the rate constant for the decay of the excited state in the absence of the quencher, k_q is the rate constant for the decay of a probe-quencher pair present within a subsystem, and n is the number of quenchers present per subsystem.[28] The subsystem model has been successfully applied for the quenching of emission from $Ru(bpy)_3^{2+}$ intercalated within the layers of mica type silicates. The goodness of the fits to the experimental data were judged, in all cases, using a number of criteria such as the Durbin−Watson parameter, χ^2, residuals, and the correlation function.[25] Each luminescence lifetime measurement was repeated three times, and each data set has been deconvoluted using different starting guesses to ensure that the fits were unique and reproducible.

Results and Discussion

Emission Spectra. Ion exchange of $Ru(bpy)_3^{2+}$ (10 μM) into the galleries of BAZrP (evident from the interlayer spacings of 19.7 Å) increases $Ru(bpy)_3^{2+}$ emission intensity by nearly 5-fold, and the emission maximum shifts from 610 nm in aqueous solution to 580 nm (Figure 1A) for the BAZrP suspensions. The emission maximum (as well as the absorption maximum) was independent of loading of the metal complex, and suggests the formation of assemblies of the metal complexes that grow in size with increased loading. The large blue shift of the emission maximum suggests a fairly rigid, hydrophobic environment surrounding the metal complex. Such blue-shifted emission was observed for $Ru(bpy)_3^{2+}$ in glassy matrixes at 77 K, in montmorillonite, and in colloidal SiO_2.[21] Solvent reorganization around the metal complex is slow in these rigid media and rigidity may result in the blue-shifted emission. Hydrophobic butyl side chains of BAZrP may interact with the hydrophobic bpy ligands, and the metal complex experiences a hydrophobic environment which does not aid in the relaxation of the initially produced polar, charge transfer state. Such environment may be essential for rapid donor to donor energy migration. If the excited states relax due to solvent reorientation around the excited state, excitation will be trapped and migration may be inhibited. In contrast to the blue-shifted emission observed with BAZrP, the binding of $Ru(bpy)_3^{2+}$ to hectorite,[21] Laponite,[19a] α-Zirconium sulfophenyl phosphonate (ZrPS),[19b] zirconium phosphate,[19d,g] DNA,[19e,f] and smectite clays,[29] results in red-shifted emission. The initially produced excited state is apparently relaxed in these media, and such relaxation could be one of the reasons for the localization of excitation in these systems.

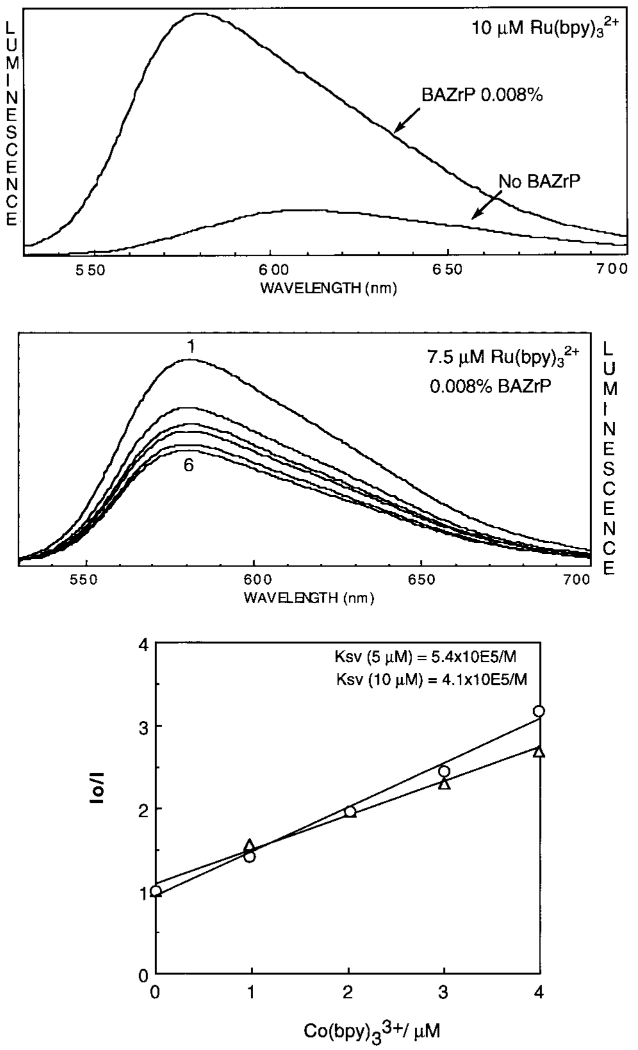

Figure 1. 1. (Top) Luminescence spectra of $Ru(bpy)_3^{2+}$ (10μM) with and without BAZrP (0.008%). Large red shift (30 nm) of the spectral maximum and a nearly 5-fold increase in the intensity are evident. (Middle) Luminescence spectra of $Ru(bpy)_3^{2+}$ (7.5 μM) and 0.008% BAZrP with increasing concentrations of $Co(bpy)_3^{3+}$. Spectra 1−6 correspond to 0, 0.8, 1.6, 2.4, 3.2, and 3.9 μM quencher concentrations, respectively. A gradual decrease in the intensity of the emission spectrum but no change in the position of the emission maximum was observed. (Bottom) Stern−Volmer quenching plots with $Ru(bpy)_3^{2+}$ and $Co(bpy)_3^{3+}$ bound to BAZrP (0.008%). Triangles and circles represent data for 5 and 10 μM $Ru(bpy)_3^{2+}$, and the corresponding quenching constants were 5.4×10^4 and 4.1×10^4 M^{-1}, respectively.

Steady-State Quenching. Ion exchange of $Ru(bpy)_3^{2+}$ along with various concentrations of $Co(bpy)_3^{3+}$ (0.008% BAZrP) resulted in rapid quenching of $Ru(bpy)_3^{2+}$ emission, in steady-state experiments (Figure 1B, 5, and 10 μM $Ru(bpy)_3^{2+}$, 0−3.9 μM of $Co(bpy)_3^{3+}$). Note the low concentrations of the quencher required to quench a large part of the luminescence. No changes in the emission maxima were observed in the presence of the quencher indicating that Ru(bpy)$_3^{2+}$ is not being displaced from the galleries by the quencher ions. Stern−Volmer quenching plots constructed from these data at three different Ru(bpy)$_3^{2+}$ concentrations (5, 7.5, and 10 μM of Ru(bpy)$_3^{2+}$, 0.008% BAZrP) resulted in essentially the same K_{sv} values (with Co(bpy)$_3^{3+}$ as the quencher). The plots were linear (Figure 1C) and the quenching slopes were in the range of (4−5) × 10^4 M^{-1}, independent of ruthenium concentration. These K_{sv} values are much larger than those obtained in aqueous solution ((2−3) × 10^3 M^{-1})[30] indicating enhanced bimolecular electron transfer between the metal complexes due to intercalation in the galleries of BAZrP. Analysis of the data using Perrin's model ($\ln(I_o/I) = VN[Q]$, where V is the critical quenching volume, and N is Avogadro's number), resulted in critical quenching distance (R_o) of 22 Å. The fit to the data was not good and R_o value is too large for these donor−acceptor pairs, in rigid media. If the luminescence quenching was due to displacement of the donors from the matrix by the acceptors, one would have observed a red shift in the emission maximum and the K_{sv} values would have been dependent on the donor concentration. The luminescence quenching was further investigated by measuring excited-state lifetimes.

Time-Resolved Studies. Time-resolved luminescence studies show that the binding of Ru(bpy)$_3^{2+}$ to BAZrP results in enhanced luminescence lifetimes. Deconvolution of the emission data with a sum of two exponentials gave excellent fits to the decay profiles. The lamp profile (full width at half-maximum of 2−3 ns), on these time scales was recorded in a single channel. In the absence of the quencher, the lifetimes and the corresponding amplitudes observed (5 μM Ru(bpy)$_3^{2+}$ and 0.008% BAZrP) were 1472 ± 90 ns, 92%, and 504 ± 56 ns, 8%, respectively. All the ruthenium was bound to BAZrP under these conditions,[31] and the major long-lived component was assigned to excited states originating from the metal complexes intercalated in the galleries. The minor, short-lived component may arise from chromophores bound at the edges of BAZrP platelets. Time-resolved spectra show an emission maximum at 580 nm, independent of the time delay, consistent with the steady-state luminescence spectra. Intercalation of Co(bpy)$_3^{3+}$ into BAZrP galleries rapidly reduces the lifetimes of both the components of Ru(bpy)$_3^{2+}$ emission (Figure 2). The time-resolved decay profile with 5 μM Ru(bpy)$_3^{2+}$ and 5 μM Co(bpy)$_3^{3+}$, in the presence of BAZrP (0.008%) is also shown in Figure 3. Analysis of the decay profile using a sum of two exponentials, under these conditions, resulted in lifetimes 683 ± 26 ns (~49%) and 249 ± 6 ns (~51%). To quantitate the quenching rate constants, luminescence lifetimes of Ru(bpy)$_3^{2+}$ were measured at various concentrations of Co(bpy)$_3^{3+}$ (both intercalated in BAZrP) and the effect of the concentration of Ru(bpy)$_3^{2+}$ on the quenching rates have been investigated. The luminescence decay profiles were analyzed using several different models, such as the subsystem model proposed for layered materials,[28] Williams−Watts function (distribution of exponentials),[26] and the long distance electron-tunneling model[27] in addition to the biexponential model described above.

Attempts to fit the decay profiles at different quencher concentrations to the subsystem model[28] were unsuccessful, and the data could not be fitted until the k_q values were varied nearly 100%. According to this model, k_q should be independent of the quencher concentration. In the case of the tunneling model,[27] the fits to the observed decay traces were poor (Figure 4). The full scale in Figure 4 is 4 orders of magnitude smaller than full scales in Figures 2 and 3. Therefore, the residuals shown in Figure 4 are not acceptable when compared to the residuals for the biexponential fits (Figures 2 and 3). Only at high quencher concentrations (>5 ×b5M), after discarding the initial part of the decay profile, the data could be fitted to the long distance model. Even then the fits were not very good. Also, note that the steady-state data could not be adequately described by the Perrin's model and the estimated critical quenching radius is >20 Å. Hence, the tunneling model was not used for the data analysis. The Williams−Watts function did not result in good fits to the data at any quencher concentration. By the addition of an exponential to the Williams−Watts function, the data can be fitted well but the parameters obtained from the fit reduced the function to a sum of two exponentials (with a beta value of 0.8 and lifetimes close to those obtained from a biexponential function).[26] All decay traces, at all concentrations of the donor and the acceptor, at two temperatures, and at two different solvent viscosities were

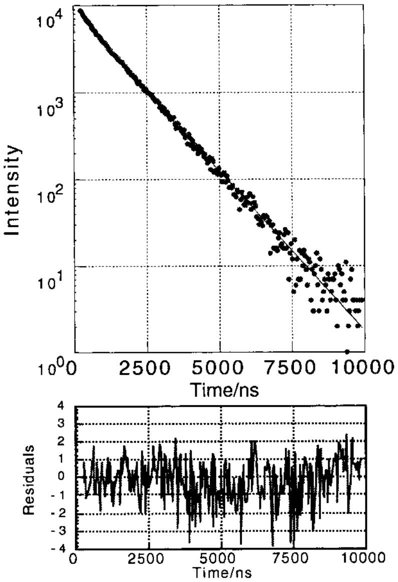

Figure 2. Fluorescence decay profiles for Ru(bpy)$_3^{2+}$ (5 μM) bound to BAZrP (0.008%), in the presence of 1 μM Co(bpy)$_3^{3+}$. The solid line represents the biexponential fit to the experimental data. Shown below is a plot of residuals.

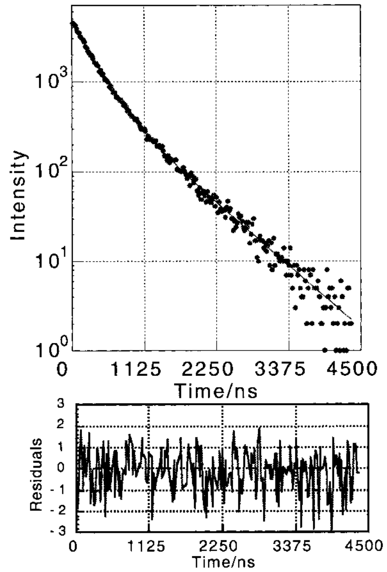

Figure 3. Fluorescence decay profiles for Ru(bpy)$_3^{2+}$ (5 μM) bound to BAZrP (0.008%), in the presence of 5 μM Co(bpy)$_3^{3+}$. The solid line represents the biexponential fit to the experimental data and shown below is a plot of residuals.

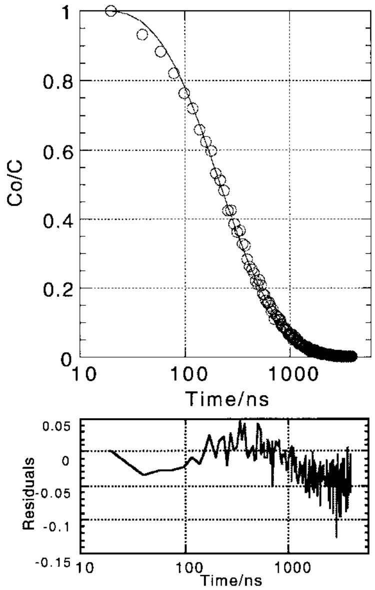

Figure 4. Fluorescence decay profiles for $Ru(bpy)_3^{2+}$ (5 μM) bound to BAZrP (0.008%), in the presence of 6 μM $Co(bpy)_3^{3+}$. The solid line represents fit to long distance tunneling model and the corresponding residuals are shown below the experimental data.

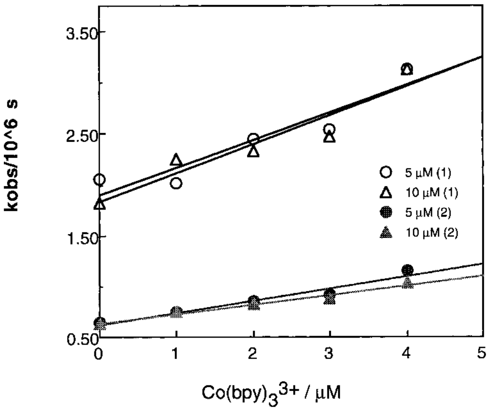

Figure 5. Luminescence quenching of short (open symbols) and long-lived components (closed symbols) of $Ru(bpy)_3^{2+}$ bound to BAZrP (0.008%) by $Co(bpy)_3^{3+}$. Quenching data at 5 μM donor (circles) and 10 μM donor (triangles) are shown. The rate constants for the short (k_1) and long-lived (k_2) components (for 5 μM donor) are 2.1 × 10^{12} and 6.4 × 10^{11} m^2 mol^{-1} s^{-1}, respectively.

satisfactorily fitted to a sum of two exponentials. Therefore, the biexponential model for the decay of donor emission in the absence and in the presence of the quencher was chosen over the other models.

TABLE 1: Bimolecular Electron-Transfer Rate Constants Measured When the Metal Complexes Were Intercalated in BAZrP (0.008% by Weight)[a]

$[Ru(bpy)_3^{2+}]$	medium	temperature/ K	$k_q(1)$/ $m^2\ mol^{-1}\ s^{-1}$	$k_q(2)$/ $m^2\ mol^{-1}\ s^{-1}$
0.5 μM	aqueous	298	1.6 × 10^{12}	4.0 × 10^{11}
5 μM	aqueous	298	2.1 × 10^{12}	6.4 × 10^{11}
10 μM	aqueous	298	2.2 × 10^{12}	7.6 × 10^{11}
5 μM	EG-W (2:1)[b]	298	3.0 × 10^{12}	5.9 × 10^{11}
5 μM	EG-W (2:1)[b]	77	1.8 × 10^{12}	1.4 × 10^{11}

[a] The rate constants $k(1)$, $k(2)$ for the short- and long-lived components were calculated as indicated in the text. [b] EG-W represents a mixture of ethylene glycol and water.

The bimolecular rate constant for luminescence quenching (k_q) was calculated from the observed decay constants (k_{obs}) monitored at various quencher concentrations [Q], using the equation $k_{obs} = k_o + k_q[Q]$. Graphs of k_{obs} vs [Q] resulted in linear plots with slope equal to k_q (Figure 5) for both the long- and short-lived components at two different donor loadings (5 and 10 μM). The quenching data for the two loadings were indistinguishable from each other within our experimental error. Initially, the quenching rate constants were calculated using concentration per unit volume and then converted to concentration per unit area (Table 1). The quencher concentrations per unit area were calculated using the total available surface area for the binding of donors and acceptors (100 m^2 g^{-1} of BAZrP).[19] The k_q values derived from the short and long-lived components are, 2.1 × 10^{12} and 6.4 × 10^{11} m^2 mol^{-1} s^{-1} (5 μM $Ru(bpy)_3^{2+}$, 0.008% BAZrP, ±25% error), respectively (Table 1). The rate constant for the quenching across the ZrP layers was shown to be slow;[29] hence, quenching within each layer is expected to dominate over the quenching across the layers. Hence, total available surface area was used for the calculation of the quencher concentrations and rate constants.

Decreasing the donor concentration (ruthenium concentration) from 5 to 0.5 μM did not change the quenching rate constants to any measurable extent. This later observation indicates the formation of assemblies of the metal complexes at BAZrP galleries and quenching occurs within these assemblies, consistent with the previous spectral studies.[20] The observed rates for electron transfer (Table 1) are faster than anticipated for donors and acceptors intercalated in layered materials.[28] Diffusion was suggested to be 3−4 orders of magnitude slower in the galleries of clay minerals,[28,29] ZrPS,[19b,d] and SiO_2 suspensions[19a] than in solution. $Ru(bpy)_3^{2+}$ adsorpbed on montmorillonite (clay with a low charge density when compared to BAZrP) suspensions was quenched by nitrobenzene with rates in the range of 5 × 10^{10} M^{-1} s^{-1}.[32] Conversion of the units to concentration per unit area, assuming complete binding of the quencher and a surface area of 14 m^2 g^{-1}, results in a rate constant of 7 × 10^{11} m^2 mol^{-1} s^{-1}, a value comparable to the slower rate constant in the current results. In case of montmorillonite, the quenching was diffusion limited. Therefore, if electron transfer were diffusion-limited in the current system, the rates should depend on the viscosity/temperature of the reaction medium.

Viscosity Dependence. The role of diffusion in these reactions was tested by increasing the solvent viscosity using ethylene glycol−water mixtures (2:1).[33] The rate constants for the quenching of short and long-lived components by $Co(bpy)_3^{3+}$ were 3.0 × 10^{12} and 5.9 × 10^{11} m^2 mol^{-1} s^{-1} (5 μM $Ru(bpy)_3^{2+}$), respectively, in glycol−water suspensions of BAZrP. Thus, increased solvent viscosity had no effect on the bimolecular rate constants. This is not surprising if the metal complexes form assemblies at the galleries of BAZrP, and diffusion within these assemblies is already slow to begin with. These observations provide a strong evidence for the nondiffusional nature of the electron transfer in the current system.

Temperature Dependence. The effect of temperature and the role of diffusion at the interlayer regions of BAZrP on the luminescence quenching was further investigated by freezing the samples at liquid nitrogen temperatures. BAZrP suspensions of the metal complexes in ethylene glycol−water mixtures (2:1) were frozen to 77 K to form rigid glasses. The large decrease in the temperature and the dramatic increase in solvent viscosity due to freezing of the samples are expected to drastically reduce collisional electron-transfer rates. On the contrary, the rate constants measured for the short and long-lived components at 77 K were 1.8 × 10^{12} and 1.4 × 10^{11} m^2 mol^{-1} s^{-1} (5 μM $Ru(bpy)_3^{2+}$), respectively. Quenching of the short-lived component is nearly unchanged, and the rate constant for the quenching of the long-lived component decreased by a factor of 4. Such a shallow temperature dependence is either due to a very low barrier for the electron transfer or it may be proceeding by tunneling,[34] and the reaction is not diffusion limited. The tunneling model, however, does not adequately fit the observed decay curves as discussed. The large rate constants as well as their lack of dependence on viscosity or temperature can be explained by proposing excitation migration from donor to donor within the BAZrP matrix, followed by electron transfer between the nearest neighbors. Thus, a diffusion-independent, low activation mechanism can explain the above observations.[5]

Addition of spectator ions such as $Zn(bpy)_3^{2+}$ at low loadings did not have any effect on the electron-transfer rates. If the observed quenching is due to the aggregation of donors induced by the quencher, then addition of a spectator ion such as $Zn(bpy)_3^{2+}$ should dilute such aggregates and decrease the quenching rates. On the contrary, no decrease in the rate constants were observed by the addition of $Zn(bpy)_3^{2+}$ (2 μM $Ru(bpy)_3^{2+}$, 12 μM $Zn(bpy)_3^{2+}$, 0.008% BAZrP) and the rate constants were increased marginally, if any. Nearly identical size, structure, and charge density of $Zn(bpy)_3^{2+}$ makes it an ideal diluent for these experiments.[29]

The blue-shifted emission from the intercalated $Ru(bpy)_3^{2+}$ strongly suggests that the MLCT excited state is not relaxed by the medium surrounding the metal complex in the galleries of BAZrP. Such unrelaxed excited states may participate in donor to donor energy transfers that are nearly isoenergetic. Such excitation migration may be a possible explanation for the observed biexponential decay and the large rate constants. No direct evidence for the excitation migration is currently available. Strong stabilization of the excited state by the solvent may trap the excitation locally and energy migration in such cases will be endothermic and inefficient.

Energy migration in rigid media can be isoenergetic and may have low activation barriers, in contrast to such reactions in solution. The average distance between Ru(II) centers in the galleries of BAZrP is estimated to be 8, 18, and 56 Å for loadings of 10, 5, and 0.6 μM of $Ru(bpy)_3^{2+}$, if the metal complexes are uniformly distributed over the available surface area of BAZrP. Because >90% of emission originates from the long-lived intercalated component, most of the metal complexes are in the galleries as demonstrated earlier.[20] These studies indicate formation of pools of metal complexes within the BAZrP layers and hence the average distances calculated above are not valid, and the intercomplex distances are expected to be independent of loading. This conclusion is supported by the fact that the electron-transfer rates do not depend on Ru loading.

Since the $Ru(bpy)_3^{2+}$ MLCT excited state may be formally represented as a triplet state, donor to donor energy transfer (by Dexter mechanism) can be considered as a double electron-transfer reaction.[35] In such cases the energy transfer would only occur over short distances. Assemblies of metal complexes may provide such short distances between the metal complexes. Such energy transfer was not observed when the donors were immobilized in clays or layered materials where the metal complexes do not form assemblies but rather aggregate. Another characteristic of the current assemblies is the increased MLCT excited-state energy when compared to that of the metal complexes in solution phase. A direct consequence of this fact is that increased MLCT excited-state energy of the donor can result in a lower barrier for electron transfer for a given donor–acceptor pair, when compared to the solution conditions. In a qualitative way, this can be viewed as raising of the reactant potential energy surface with respect to that of the product surface such that the two surfaces cross near the minimum of the reactant surface. In such cases, one anticipates that the reorganization energy be roughly equal to the reaction free energy. Such a scenario describes a reaction with a low energy barrier and hence a shallow temperature dependence. These possibilities are consistent with the present data.

Either the energy migration (donor to donor, if it occurs under these conditions) or the electron-transfer step can be the rate-limiting event. The slow step also shows a very shallow temperature, and viscosity dependence. Quenching is also not inhibited by diluting the assemblies of metal complexes at moderate concentrations of $Zn(bpy)_3^{2+}$. According to the super exchange model,[36] low-energy excited states that can couple with the donor and the acceptor states can accelerate electron-transfer rates. The electronic states of $Zn(bpy)_3^{2+}$ may provide such states. In support of intermetal complex interactions in the assemblies, the absorption spectra of $Ru(bpy)_3^{2+}$ intercalated in BAZrP layers indicate strong excitonic interactions between the bound metal complexes. The metal complexes form pools or assemblies even at low loadings. Energy transfer from Ru(II)* to Co(III), an alternative explanation for the observed rates, is unlikely due to the poor spectral overlap between the donor and the acceptor.[18]

Conclusions

Current results indicate a diffusion-independent, barrier-less, electron transfer between metal complexes promoted by BAZrP. Such electron transfer may be due to donor to donor energy migration followed by electron transfer between the nearest donor–acceptor pairs. Similar fast electron-transfer reactions in frozen media have been reported for the photosynthetic apparatus.[37] Supramolecular assemblies of metal complexes at the BAZrP surfaces may be further developed as model systems to mimic this fascinating biological assembly.

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