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Photoinduced Electron Transfer in Supramolecular Assemblies Composed of Dialkoxybenzene-Tethered Ruthenium(II) Trisbipyridine and Bipyridinium Salts

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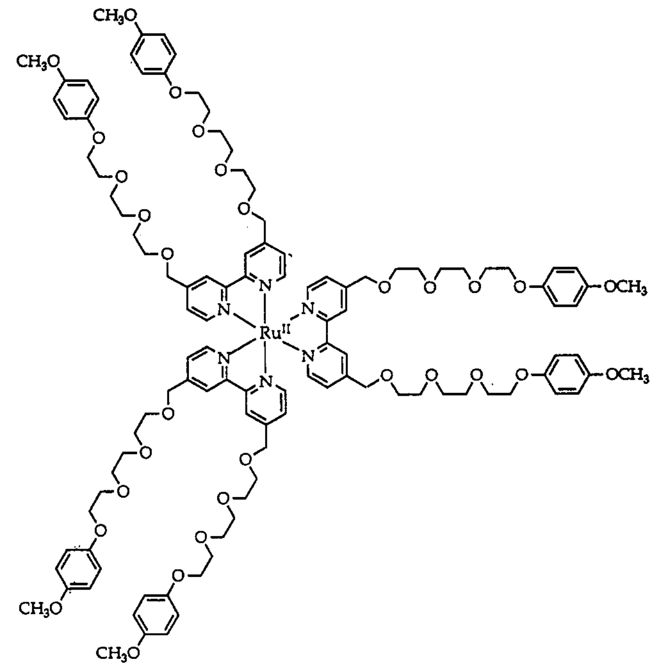
Abstract: Ruthenium(II) tris{4,4′-bis[(methyleneoxy)tris(ethyleneoxy)(4-methoxybenzene)]-2,2′-bipyridine} (**1**), forms supramolecular complexes with *N,N′*-dimethyl-4,4′-bipyridinium, MV^{2+} (**2**), and with cyclo[bis(*N,N′-p*-xylylene-4,4′-bipyridinium)], BXV^{4+} (**3**). The association constants of the complexes generated between the dialkoxybenzene-tethered units of **1** and the electron acceptors **2** and **3** correspond to $K_a = 28 \pm 1$ M^{-1} for MV^{2+} and $K_a = 1200 \pm 100$ M^{-1} for BXV^{4+}. Time-resolved laser flash photolysis and steady-state emission studies show that electron transfer from excited **1** proceeds by an intramolecular pathway to the electron acceptors organized in the supramolecular assemblies, $k_{iq} = 1.7 \times 10^8$ s^{-1} for MV^{2+} and $k_{iq} = 2.9 \times 10^8$ s^{-1} for BXV^{4+}, and by a diffusional route from free-uncomplexed **1**, $k_{dq} = 1.9 \times 10^8$ M^{-1} s^{-1} for MV^{2+} and $k_{dq} = 3.4 \times 10^8$ M^{-1} s^{-1} for BXV^{4+}. Formation of the supramolecular assemblies between **1** and **2** or **3** is supported by the intramolecular electron-transfer quenching of **1** and by the fact that the assemblies dissociate upon addition of β-cyclodextrin.

Substantial efforts are directed toward mimicking the organization of the photosynthetic reaction center.[4] Electron transfer in covalently linked donor–acceptor diads[5] and triads[6] has been extensively studied, and efficient electron transfer followed by charge separation was achieved in these supramolecular assemblies. Here we wish to report on an alternative approach to tailor donor–acceptor complexes based on host–guest interactions. We use as photosensitizer ruthenium(II) tris{4,4′-bis[(methyleneoxy)tris(ethyleneoxy)(4-methoxybenzene)]-2,2′-bipyridine} (**1**). This complex exhibits the common photophysical properties of ruthenium(II) trisbipyridine compounds, but includes in addition covalently tethered *p*-dialkoxybenzene units. Recent studies[7-9] revealed that dialkoxybenzene components form intermolecular complexes with bipyridinium salts such as *N,N′*-dimethyl-4,4′-bipyridinium, MV^{2+} (**2**), and cyclo[bis(*N,N′-p*-xylylene-4,4′-bipyridinium)], BXV^{4+} (**3**). Thus, association of **2** and **3** to the dialkoxybenzene units might organize a sensitizer-acceptor diad. We describe here the formation of these supramolecular assemblies and characterize the electron-transfer properties of the photosensitizer within the complexes as well as by a diffusional path.



(**1**)

Experimental Section

Absorption spectra were recorded with a Uvikon-860 (Kontron) spectrophotometer. Fluorescence spectra were recorded with a SFM-25 (Kontron) spectrofluorimeter. ^1H NMR measurements were performed

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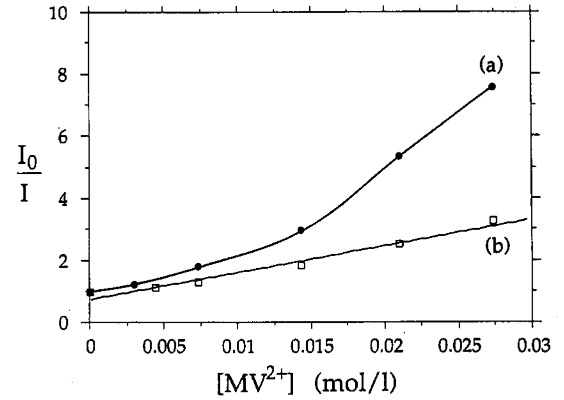


Figure 1. Steady-state Stern–Volmer plots of the luminescence quenching of **1** (a) and **4** (b) by MV^{2+} (**2**) derived from eq 4.

with an AMX 400-MHz spectrometer (Bruker). Flash photolysis experiments were carried out with a Nd-YAG laser (Laser Photonics Model 34-10) coupled to a detection system (Applied Photophysics K-347) that included a monochromator and photomultiplier and is linked to a digitizer (Tektronix 2430 A) and computer for data storage and processing. The resolution of this flash photolysis setup is >30 ns. For shorter time scales of transients (>0.5 ns) a flash photolysis instrument composed of a N_2 laser (PRA, LN-1000) was employed. The detection system consists of a monochromator and a photomultiplier (Applied Photophysics) that is linked to a digitizer (Tektronix 7912 AD) and a computer for data storage and analysis. All materials and solvents were of highest purity from commercial sources (Aldrich, Sigma). The ligand 4,4′-bis[(methyleneoxy)tris(ethyleneoxy)(4-methoxybenzene)]-2,2′-bipyridine was prepared by the reaction of 4,4′-bis(bromomethyl)-2,2′-bipyridine[10] (100 mmol) with mono(4-methoxyphenyl)triethyleneglycol (210 mmol) in the presence of NaH (210 mmol) (toluene, 3 h reflux). The raw material was purified by column chromatography (SiO_2, eluant CH_2Cl_2:CH_3OH/95:5/v:v). The complex ruthenium(II) tris{4,4′-bis[(methyleneoxy)tris(ethyleneoxy)(4-methoxybenzene)]-2,2′-bipyridine} (**1**) was synthesized by the reaction of $Ru(DMSO)_4Cl_2$ (100 mmol) with 4,4′-bis[(methyleneoxy)tris(ethyleneoxy)(4-methoxybenzene)]-2,2′-bipyridine (330 mmol) (ethanol–water, 80:20 as solvent, reflux for 48 h). The resulting raw material was purified by column chromatography (SiO_2, eluent CH_2Cl_2:CH_3OH/85:15/v:v). The ligand 4,4′-bis[(methyleneoxy)bis(ethyleneoxy)ethanol]-2,2′-bipyridine was obtained by the reaction of 4,4′-bis(bromomethyl)-2,2′-bipyridine (100 mmol) with triethyleneglycol (300 mmol) in the presence of NaH (210 mmol) (toluene, 3 h reflux). The raw material was purified by column chromatography (SiO_2, eluent CH_2Cl_2:CH_3OH/90:10/v:v). The complex ruthenium(II)tris{4,4′-bis[(methyleneoxy)bis(ethyleneoxy)ethanol]-2,2′-bipyridine} dichloride was prepared by the reaction of $Ru(DMSO)_4Cl_2$ (100 mmol) with 4,4′-bis[(methyleneoxy)bis(ethyleneoxy)ethanol]-2,2′-bipyridine (330 mmol) (ethanol–water 60:40 as solvent, reflux for 48 h). The resulting raw material was purified by washing five times with 40 mL of distilled CH_2Cl_2. Cyclo[bis(*N*,*N*′-*p*-xylylene-4,4′-bipyridinium)] tetrachloride (**3**) was prepared according to the literature.[11] All compounds gave appropriate ^1H NMR spectra and elemental analyses. All photochemical measurements were performed in triply distilled water.

Time-resolved fluorescence decays and steady-state emission of **1** were recorded in a 0.4 × 1 cm cuvette equipped with a stopper. The aqueous solutions (1 mL) containing **1**, 3.7×10^{-5} M, and different concentrations of **2** or **3** were placed in to the cuvette and deaerated by evacuation followed by bubbling of oxygen-free Ar. The systems were photoexcited at $\lambda_{ex} = 532$ nm (with the Nd-Yag laser) and at $\lambda_{ex} = 337$ nm (with the N_2 laser), and the emission was recorded at $\lambda = 600$ nm. In the inhibition studies, β-CD, 8.75×10^{-4} M was added to the photosystems.

Results and Discussion

The steady-state Stern–Volmer plots of the emission quenching of **1** by MV^{2+}, **2**, and BXV^{4+}, **3**, are shown in Figures 1a and 2a, respectively. Nonlinear Stern–Volmer plots are obtained, and the curvature for the quenching process of **1** by **3** is enhanced as compared to that of **2**. The quenching plots of the reference compound ruthenium(II) tris{4,4′-bis[(methyleneoxy)bis(ethyleneoxy)ethanol]-2,2′-bipyridine} (**4**) by **2** and **3** are also included in these figures. The reference photosensitizer **4** lacks the dialkoxybenzene units, and thus no association of **2** or **3** to this photosensitizer is expected. The Stern–Volmer plots of **4** quenched by **2** and **3** are linear (Figures 1b and 2b). The derived electron-transfer quenching rate constants are $k_q = 1.6 \times 10^8$ $M^{-1} \cdot s^{-1}$ for **2** and $k_q = 2.8 \times 10^8$ $M^{-1} \cdot s^{-1}$ for **3**. The fact that the electron-transfer quenching rate constant by **3** is about 2-fold higher than by **2** is consistent with the availability of two relay

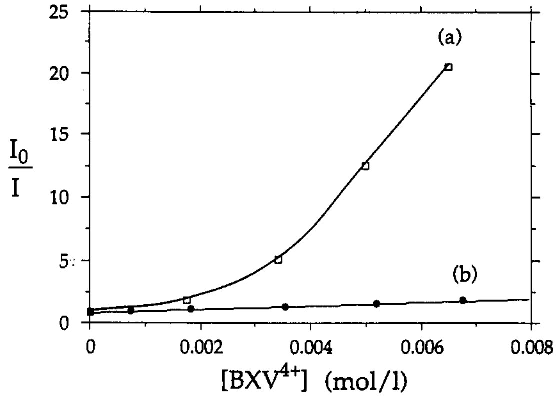
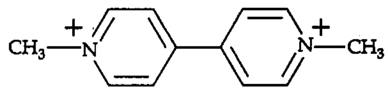


Figure 2. Steady-state Stern–Volmer plots of the luminescence quenching of **1** (a) and **4** (b) by BXV^{4+} (**3**) derived from eq 4.

(2)



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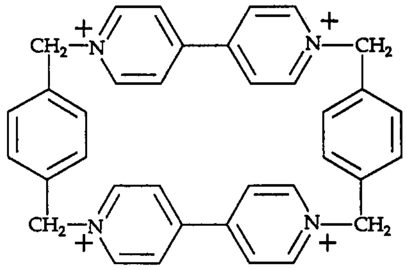

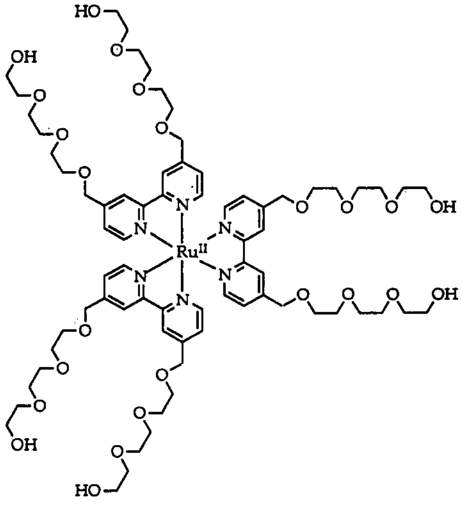

(4)

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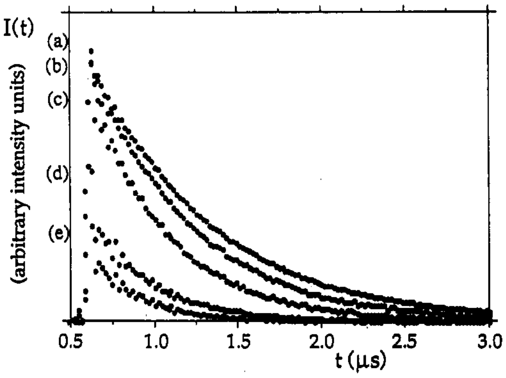

Figure 3. Luminescence intensity decay of **1** with no quencher (a) and after addition of increasing concentrations of BXV^{4+} (**3**): (b) 1.7×10^{-3}, (c) 3.4×10^{-3} (d) 5.1×10^{-3}, (e) 6.5×10^{-3} M.

units in the molecular backbone of **3**. The quenching rate constants are, however, lower than the characteristic electron-transfer quenching of ruthenium(II) trisbipyridine, $Ru(bpy)_3^{2+}$, by MV^{2+} under similar ion-strength conditions and identical counterion ($k_q = 5 \times 10^8$ $M^{-1} \cdot s^{-1}$).[12] This is attributed to the bulkiness of **4**, introduced by the polyethyleneglycol chains that hinder the quenching of the excited state. The nonlinear Stern–Volmer plots of **1** quenched by **2** or **3**, Figures 1a and 2a, might reflect the existence of two complementary electron-transfer quenching pathways of the excited state. One path involves the intramolecular quenching (k_{iq}) within the supramolecular assemblies, while the second route includes the diffusional electron transfer, k_{dq}, (vide infra), Schemes 1 and 2, where K_a is the association constant of the respective supramolecular complex.

The luminescence lifetime of **1** corresponds to τ = 704 ns. Addition of **2** or **3** to **1** influences the fluorescence of **1** in two ways. As the concentration of **2** or **3** is increased, the initial luminescence intensity is reduced, and the emission lifetime is decreased. Figure 3 exemplifies these effects with the addition of **3** to **1**. It should be noted that these luminescence transients were recorded with a laser flash photolysis system with a time resolution corresponding to 30 ns. Thus, only events proceeding on time scales longer than 30 ns can be detected. These results can be rationalized in terms of two-electron-transfer quenching pathways, as schematically outlined in Scheme 3. The photosensitizer, S, undergoes association with the electron acceptor, A, to form the supramolecular assembly [S–A]. K_a is the association constant for the formation of the complex [S–A]. The specific identification of the supramolecular complexes is given in Schemes 1 and 2. Electron-transfer quenching within the supramolecular assembly (k_{iq}) is assumed to be fast, as compared with the experimental time resolution, and hence will be reflected by the decrease in the initial emission intensity. The diffusional electron-transfer quenching of free excited **1** (k_{dq}) is observed in the shortening of the emission lifetime. Figures 4 and 5 show the Stern–Volmer plots derived from the shortening of the lifetime of **1** by addition of **2** or **3**, respectively. The extracted diffusional quenching rate constants, k_{dq}, correspond to 1.9×10^8 $M^{-1} \cdot s^{-1}$ for **2** and 3.4×10^8 $M^{-1} \cdot s^{-1}$ for **3**. These values are very similar to those observed for the reference compound **4** quenced by **2** or **3**. The diffusional electron-transfer rate constant of **1** by **3** is 2-fold higher as compared to the value of **2**. This is consistent with the fact that **3** includes two relay units in the molecular backbone that are capable of participating in the electron transfer, as we already discussed in the diffusional quenching of **4**.

The model outlined in Scheme 3 can be further quantitatively analyzed. The luminescence intensity $I(t)$ decay of S at a time resolution >30 ns is given by eq 1, and τ is expressed by eq 2 where k_{dq} and τ_0 represent the diffusional electron-transfer rate

$$I(t) = Re^{-t/\tau} \tag{1}$$

$$1/\tau = 1/\tau_0 + k_{dq}[A] \tag{2}$$

constant and the lifetime of the free excited photosensitizer, S*, in the absence of quencher, respectively. Since this decay process corresponds only to the diffusional electron transfer, the preexponential coefficient, R, is proportional to the concentration of the free photosensitizer, S ($R \propto$ [S]). The steady-state luminescence intensities of S are given by eq 3. Since R is proportional to [S], the Stern–Volmer equation can be formulated in terms

$$I = \int_0^{\infty} Re^{-t/\tau} dt = R \cdot \tau \tag{3}$$

of eq 4, where $[S]_0$ represents the analytical concentration of S and I_0 its luminescence intensity in the absence of the quencher.

$$I_0/I = \frac{[S]_0}{[S]} \cdot \frac{\tau_0}{\tau} \tag{4}$$

Assuming[13] that S associates with the electron acceptor A with an association constant K_a given by eq 5, the ratio of $[S]_0/[S]$ is given by eq 6. This implies that the steady-state Stern–Volmer plot (eq 4) is nonlinear and depends on the association constant

$$K_a = \frac{[S\text{–}A]}{[S][A]} \tag{5}$$

$$\frac{[S]_0}{[S]} = 1 + K_a[A]_0 \tag{6}$$

K_a.[14] Furthermore, substitution of eq 6 in eq 4 gives eq 7. This relation allows us to derive the association constants of **2** and **3** to **1** from the combined time resolved and steady-state luminescence measurements. Figures 6 and 7 show the modified Stern–Volmer plots according to eq 7 for **2** and **3**, respectively. The derived association constants of the photosensitizer, **1**, are K_a = 28 ± 1 M^{-1} with **2** and K_a = 1200 ± 100 M^{-1} with **3**. We thus conclude that **1** forms supramolecular photosensitizer–acceptor complexes with **2** and **3** and that electron transfer within these assemblies occurs according to Scheme 3. It should be noted that the association constant of **3** to **1** is higher by ca. two orders of magnitude as compared to the association constant of **2** to **1**.

$$\frac{I_0}{I} \cdot \frac{\tau}{\tau_0} = 1 + K_a[A]_0 \tag{7}$$

The discussion implies that electron transfer within the supramolecular assembly [S–A] proceeds rapidly at <30 ns time resolution and is reflected in the decrease of initial fluorescence intensity. The amount of photoexcited species that is quenched within the supramolecular assembly has been monitored indirectly by following the fraction of unbound photosensitizer that decays by the diffusional path and its subtraction from the total photoexcited species concentration, determined by the fluorescence yield of **1** in the absence of any quencher.

Direct insight into the electron-transfer quenching occurring within the supramolecular structures, [S–A], was obtained by laser flash photolysis experiments with a 0.5-ns time resolution. Two photosystems were selected for these studies: one included **1** and MV^{2+} (**2**), 2.7×10^{-2} M and the second photosystem included **1** and BXV^{4+} (**3**), 6.5×10^{-3} M. From our previous

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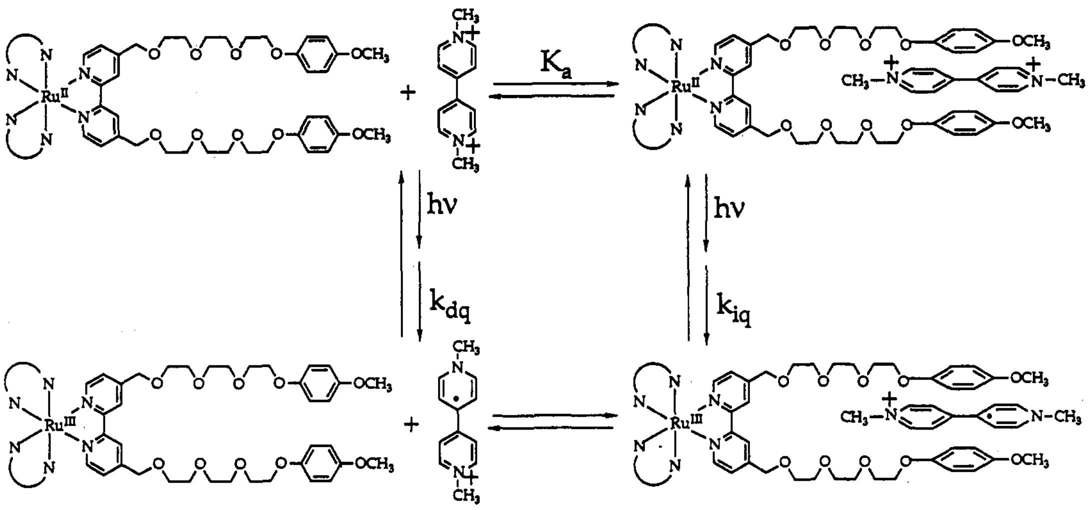
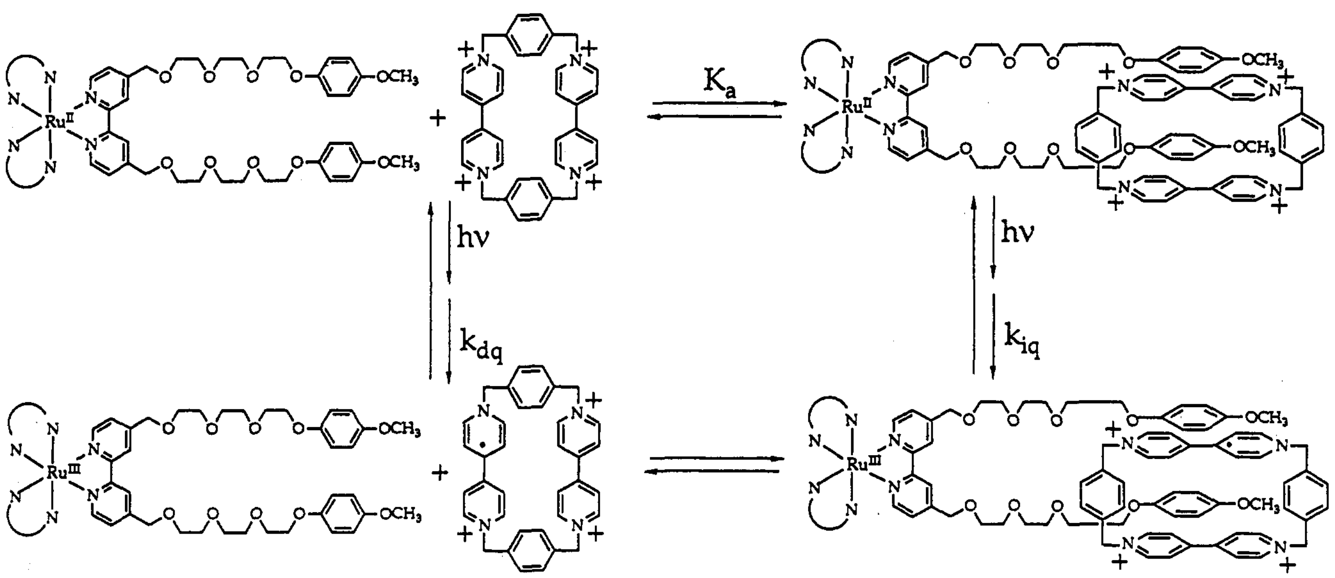
Scheme 1. Electron-Transfer Quenching of **1** by **2** through Diffusional and Intramolecular Pathways



Scheme 2. Electron-Transfer Quenching of **1** by **3** through Diffusional and Intramolecular Pathways



analyses, Figures 6 and 7, the fractions of photosensitizer **1** existing in the supramolecular structure [S–A] at these compositions correspond to 0.4 for MV^{2+} (**2**) and 0.9 for BXV^{4+} (**3**). Figure 8 shows the transient decay of the luminescence emission of **1** in the presence of **2** or **3** (Figure 8 (parts b and c), respectively) using the laser system of 0.5-ns time resolution. The emission transients reveal biexponential decays. For MV^{2+} (**2**) as quencher, Figure 8b, a fast decay corresponding to a time constant of 6 ns is observed, and a substantially slower decay process, $\tau = 160$ ns is extracted. For BXV^{4+} (**3**) as electron acceptor, the fast decay proceeds with a time constant of $\tau = 3.5$ ns and the slow deacy process exhibits a lifetime of $\tau = 270$ ns. The slow decay processes extracted from the biexponential analyses of the luminescence transients are identical to the lifetimes of **1** in the presence of **2** or of **3**, at these quencher concentrations (vide supra). The short lifetimes of luminescence decay of **1** in the presence of **2** or **3** are attributed to the intramolecular electron-transfer quenching of the excited photosensitizer in the supramolecular assemblies, [S–A]. Thus, the intramolecular electron-transfer quenching rate constants, k_{iq}, are estimated to be 1.7×10^8 s^{-1} for MV^{2+} (**2**) and 2.9×10^8 s^{-1} for BMV^{4+} (**3**). The biexponential analyses of the luminescence transients of **1** in the presence of **2** or of **3** allow us to directly extract the amounts of free photosensitizer S and bound photosensitizer, S–A. For the system that includes MV^{2+} (**2**) as quencher, the fast decaying species corresponds to 0.4 of the overall excited-state concentration. For the system that includes BXV^{4+} (**3**) as electron acceptor, the fast decaying component (the supramolecular structure) corresponds to 0.9 of the overall excited-state concentration. These values are in excellent agreement with those derived from the analyses of the long time scale transients of free photosensitizer, Figures 6 and 7. These results nicely support the electron-transfer pathways outlined in Scheme 3. The photosensitizer **1** associates with **2** or **3** to form the supramolecular structures, S–A. The high association constant of **3** to **1** results in a high population of the intermolecular photosensitizer relay complex, [S–A]. Intramolecular electron transfer in this supramolecular configuration proceeds effectively ($\tau = 3.5$ ns). The fraction of free photosensitizer undergoes diffusional electron-transfer quenching ($k_{dq} = 3.4 \times 10^8$ $M^{-1} \cdot s^{-1}$). The relay **2** exhibits a lower affinity toward the binding site of the photosensitizer (**1**), $K_a = 28$ M^{-1}. This results in a lower content of the supramolecular photosensitizer relay complex. The electron-transfer quenching of **1** by **2** proceeds similarly by two routes.

Further insight into the participation of supramolecular structures in electron transfer from **1** to **2** and to **3** is obtained from inhibition experiments. Cyclodextrins (CDs) are cyclic polysugars composed of glucose units linked by 1–4 α-glycoside bonds. These compounds are capable of binding organic compounds and specifically aromatic residues to their hydrophobic cavities.[15,16] The participation of the dialkoxybenzene components of **1** in the generation of the supramolecular structures with **2** or

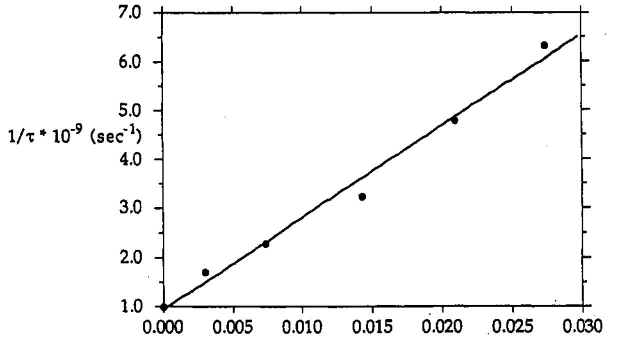


Figure 4. Lifetime Stern–Volmer plot of the luminescence quenching of **1** by MV^{2+} (**2**) derived from eq 2.

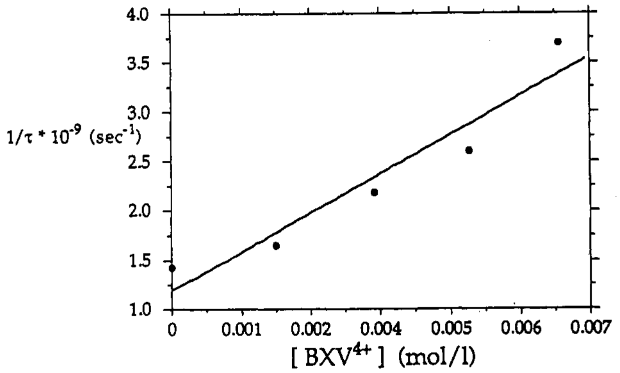


Figure 5. Lifetime Stern–Volmer plot of the luminescence quenching of **1** by BXV^{4+} (**3**) derived from eq 2.

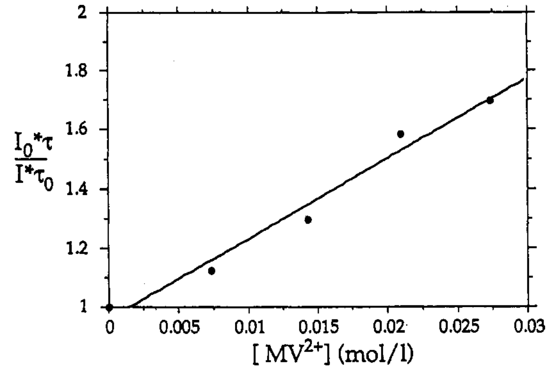


Figure 6. Modified Stern–Volmer plot of the luminescence quenching of **1** by MV^{2+} (**2**) derived from eq 7.

3 suggests that association of CD to the donor sites of **1** would perturb the intermolecular complex formation between **1** and **2** or **3**. The effect of added β-cyclodextrin (β-CD, seven glucose units in the cyclic saccharide) on the electron transfer in these supramolecular assemblies has been examined. Figure 9 shows the transient luminescence decay of **1** in the presence of **3**, 6.0 × 10^{-3} M, in the absence and presence of added β-CD, 8.8 × 10^{-4} M. We see that the intitial luminescence intensity of **1** is higher in the presence of β-CD, but the time constant for the long-lived luminescence decay is unaltered, τ = 270 ns, as compared to the system that lacks β-CD. The decrease in the initial luminescence intensity of **1** upon addition of **3** was attributed to the electron-transfer quenching within the supramolecular complex, while the transient luminescence decay reflected the diffusional electron transfer from free **1** to **3**. Thus, addition of β-CD to the system composed of **1** and **3** results in dissociation of the supramolecular complex. The increase in the free chromophore state is evidenced by the increase in the initial emission intensity. The similar time constants for the long-lived luminescence decay in the two systems implies that in the presence of β-CD a higher fraction of the photosensitizer exists in the free form that is being quenched by the diffusional path. These effects of added β-CD on the luminescence decay of **1** are general in the presence of different concentrations of **2** or **3**. Thus, β-CD dissociates the supramolecular complexes formed between **1** and **2** or **3** by competitive binding of the dialkoxybenzene unit to the β-CD cavity. Quantitative analysis of the competitive association of β-CD and **2** or **3** to the dialkoxybenzene units can be made according to Scheme 4. Here, S–D represents the ruthenium(II) trisbipyridine complex with the tethered dialkoxybenzene units (**1**). This photosensitizer associates with the acceptor components **2** or **3** to form the supramolecular structures [S–D···A], where electron-transfer

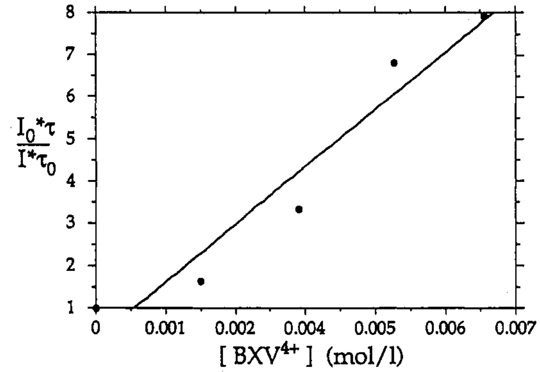


Figure 7. Modified Stern–Volmer plot of the luminescence quenching of **1** by BXV^{4+} (**3**) derived from eq 7.

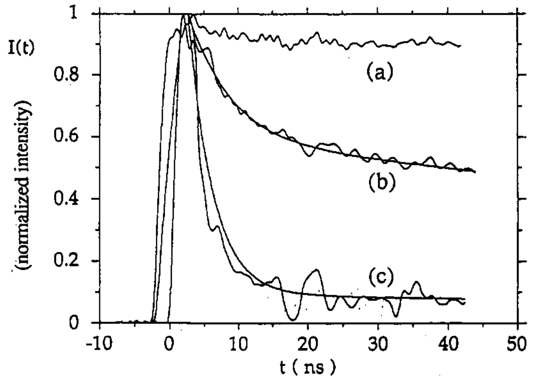
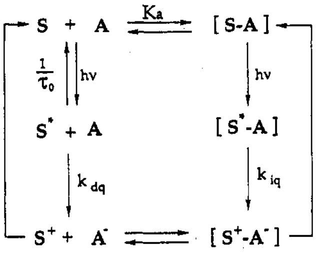


Figure 8. Transient decay of the emission of **1** using the 0.5-ns time-resolution laser: (a) with no quencher, (b) in the presence of MV^{2+} (**2**) 2.7 × 10^{-2} M, and (c) in the presence of BXV^{4+} (**3**) 6.5 × 10^{-3} M.

Scheme 3. Electron-Transfer Quenching and Recombination of Redox Intermediates Following Excitation of the Photosensitizer in the Free and Supramolecular States



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(13) A 1:1 stoichiometry is assumed between **1** and **2** or **3**. The electrostatic repulsions resulting from the 1:1 complex and additional bipyridinium units are assumed to eliminate the formation of supramolecular structures of higher stoichiometries.

(14) Combination of eqs 6, 4, and 2 gives the relation $I_0/I = (1 + K_a[A]_0)(1 + k_{dq}\tau_0[A]_0)$. This reflects a nonlinear Stern–Volmer plot as a result of the formation of the supramolecular structure [S–A].

(15) (a) *Cyclodextrin Chemistry*; Bender, M., Kamiyama, L., Eds.; Springer: 1978. (b) Sanger, A. Q. *Angew. Chrm. Int. Ed. Engl.* **1980**, *19*, 344.

(16) (a) Breslow, R. *Science* (*Washington*, D.C.) **1982**, *218*, 532. (b) Tabushi, I. *Acc. Chem. Res.* **1982**, *15*, 66.

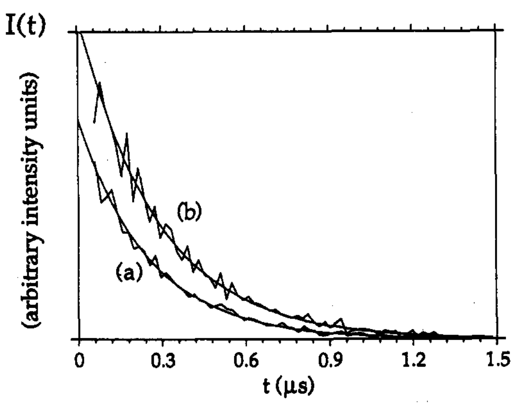
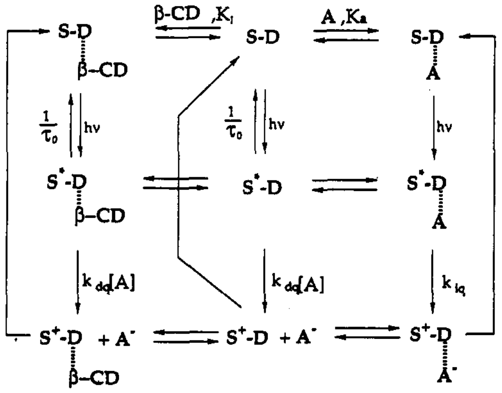
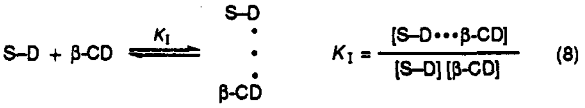


Figure 9. Emission intensity decay of **1** in the presence of BXV^{4+} (**3**) 6.0×10^{-3} M in the absence (a) and presence (b) of β-CD 8.8×10^{-4} M.

Scheme 4. Effects of β-CD on Electron-Transfer Quenching of the Photosensitizer (S), **1**, by the Electron Acceptor (A), **2** or **3**



quenching proceeds by the intramolecular pathway. The free photosensitizer S–D and the fraction of the photosensitizer associated with β-CD, [S–D···β–CD] are quenched by the electron acceptors via the diffusional route. Under these conditions, besides the equilibrium existing between the photosensitizer and the electron acceptor (eq 5), an additional equilibrium process between the donor sites of the photosensitizer and β-CD takes place, eq 8.



$$\text{S–D} + \beta\text{-CD} \overset{K_I}{\rightleftharpoons} \begin{matrix}\text{S–D}\\ \vdots \\ \beta\text{-CD}\end{matrix} \qquad K_I = \frac{[\text{S–D}\cdots\beta\text{-CD}]}{[\text{S–D}][\beta\text{-CD}]} \qquad (8)$$

The concentration of free photosensitizer is thus given by eq 9. The modified Stern–Volmer equation is then expressed in terms of eq 10. Therefore, the modified Stern–Volmer plot in the presence of a constant concentration of β-CD should yield an

$$\frac{[S_0]}{[S]} = 1 + K_I[\beta\text{-CD}]_0 + K_a[A]_0 \qquad (9)$$

$$\frac{I_0}{I}\frac{\tau}{\tau_0} = 1 + \left(\frac{K_a}{1 + K_I[\beta\text{-CD}]_0}\right)[A]_0 \qquad (10)$$

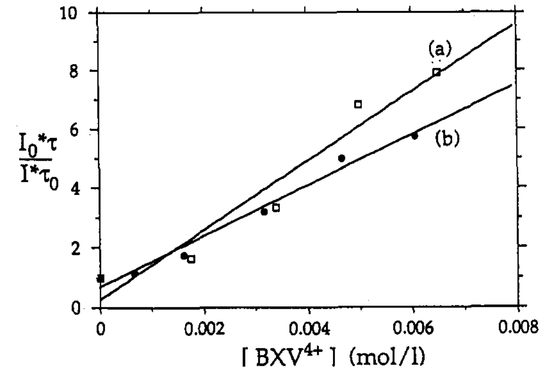


Figure 10. Modified Stern–Volmer plots of the luminescence quenching of **1** by BXV^{4+} (**3**) in the absence (a) and presence (b) of β-CD 8.8×10^{-4} M, derived from eqs 7 and 10, respectively.

apparent association constant K', given by eq 11, which is lowered

$$K' = \frac{K_a}{1 + K_I[\beta\text{-CD}]_0} \qquad (11)$$

by the factor $1 + K_I[\beta\text{-CD}]_0$ as compared to the system that lacks the cyclodextrin receptor. Figure 10 (line b) shows the experimental modified Stern–Volmer plot of the luminescence quenching of **1** by **3** in the presence of β-CD, 8.8×10^{-4} M. The derived K' value for **3** is 850 M^{-1}. From this value we estimate the association constant of β-CD to the dialkoxybenzene sites of the photosensitizer to be $K_I = 360$ M^{-1}.[17]

Conclusions

We have demonstrated a novel approach to generate supramolecular photosensitizer electron relay diads by intermolecular association of the electron acceptor to π-donor units (dialkoxybenzene) tethered to the photosensitizer. Electron-transfer quenching of the excited state of **1** proceeds effectively within the supramolecular assemblies generated with the relay **2** or **3**. We reveal that selection of an appropriate electron relay, BXV^{4+} (**3**) that exhibits a high association constant to the donor binding sites of **1** ($K = 1200$ M^{-1}) yields effectively the supramolecular complex.

The binding properties of the dialkoxybenzene units to β-cyclodextrin provides a means to inhibit the formation of the supramolecular assembly and confirm the intramolecular electron transfer. Nonetheless, the association of **1** to β-cyclodextrin suggests that this latter complex could be further used for electron transfer in organized media, i.e., photosensitization of β-CD stabilized TiO_2 or CdS.[18]

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(17) This value should, however, be considered as a formal association constant rather than the actual thermodynamic value since the photosensitizer includes six binding sites to β-CD, and the existence of stoichiometries higher than 1:1 cannot be excluded.

(18) Willner, I.; Eichen, Y.; Frank, A. J. *J. Am. Chem. Soc.* **1989**, *111*, 1984.