Table IV. Second-Order Rate Constants and Protonation Constants for the Reduction of Acetato and Oxalato Complexes of Ruthenium(III) by Hexaamine- and Aquapentaammineruthenium(II)

reaction	K_s, dm³ mol⁻¹	k_1, dm³ mol⁻¹ s⁻¹	k_2, dm³ mol⁻¹ s⁻¹
$Ru(NH_3)_6^{2+} + Ru(NH_3)_5OAc^{2+} \| Ru(NH_3)_5OAcH^{3+}$	18.9 ± 2.3	4.8 ± 1.4	82.5 ± 7.6
$Ru(NH_3)_5H_2O^{2+} + Ru(NH_3)_5OAc^{2+} \| Ru(NH_3)_5OAcH^{3+}$	20.1 ± 1.9	2.6 ± 0.8	42.8 ± 4.0
$Ru(NH_3)_6^{2+} + Ru(NH_3)_5C_2O_4^+ \| Ru(NH_3)_5C_2O_4H^{2+}$	27.4 ± 3.1	1.3 ± 0.3	13.6 ± 1.2
$Ru(NH_3)_5H_2O^{2+} + Ru(NH_3)_5C_2O_4^+ \| Ru(NH_3)_5C_2O_4H^{2+}$	28.0 ± 3.2	0.5 ± 0.2	7.5 ± 0.7
$Ru(NH_3)_6^{2+} + cis\text{-}Ru(NH_3)_4C_2O_4^+ \| cis\text{-}Ru(NH_3)_4C_2O_4H^{2+}$	11.8 ± 1.4	3.6 ± 0.5	26.4 ± 2.4
$Ru(NH_3)_5H_2O^{2+} + cis\text{-}Ru(NH_3)_4C_2O_4^+ \| cis\text{-}Ru(NH_3)_4C_2O_4H^{2+}$	13.3 ± 1.2	0.8 ± 0.2	12.8 ± 1.3

a common series of closely related cobalt(III) complexes or any pair of oxidants reacting with a common series of reductants. In each case, when a pair of reductants reduces a common series of oxidants by the same mechanism, a linear relationship of the form

$$\log k_a = x \log k_b \pm c \qquad (10)$$

is obtained (where k_a and k_b are the rate constants for the reduction of the common oxidants by reductants a and b and x and c are constants with $x \approx 1$). The data in Table IV have been plotted in this manner (Figure 3), and a relationship of the form

$$\log k_{Ru(NH_3)_6^{2+}} = 0.97 \log k_{Ru(NH_3)_5H_2O^{2+}} + 0.20 \qquad (11)$$

is obtained. $Ru(NH_3)_6^{2+}$ is substitution-inert and must therefore react with the ruthenium(III) species by outer-sphere mechanism.[12,13,17] The good linear log–log correlation obtained here suggests that $Ru(NH_3)_5H_2O^{2+}$, which is more substitution labile[11,12] than $Ru(NH_3)_6^{2+}$, reacts with these ruthenium(III) complexes by an outer-sphere mechanism too. Hexaammineruthenium(II) is more reactive toward the oxalato and acetate complexes of ruthenium(III) than the aquapentaammineruthenium(II) (Table II and IV). This is understandable since the redox potentials of these reductants[11,12] ($Ru(NH_3)_6^{2+}$, -0.10 V; $Ru(NH_3)_5H_2O^{2+}$, -0.16 V) suggest that hexaammineruthenium(II) should be a faster outer-sphere reductant than aquapentaammineruthenium(II).

Aquation of the primary (carboxylato)pentaammineruthenium(II) products of the reactions may be represented by eq 12. Reaction 12 and the reoxidation of Ru-

$$Ru(NH_3)_5X^+ + H_2O \rightarrow Ru(NH_3)_5H_2O^{2+} + X^- \qquad (12)$$
$$(X = OAc^-, C_2O_4^{2-})$$
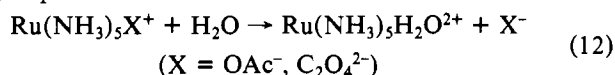
$(NH_3)_5H_2O^{2+}$ by $Ru(NH_3)_5X^{2+}$ ($X = OAc^-$, $C_2O_4^{2-}$) do not affect the reactions studied here since pseudo-first-order rate plots are linear to completion in all cases, otherwise autocatalysis would have been observed in the rate plots. Electron-transfer rate constants (dm³ mol⁻¹ s⁻¹) for the reduction of the (acetato)pentaammineruthenium(III) by Cr(II),[1] V(II),[1] Eu(II),[1] and Ti(III)[6] are 2.6×10^4 (10 °C, $I = 0.10$ mol dm⁻³ (LiClO₄)), 5.6×10^2 (25 °C, $I = 0.10$ mol dm⁻³ (LiClO₄)), 1.7×10^5 (25 °C, $I = 0.10$ mol dm⁻³ (LiClO₄)), and 7.0×10^2 (25 °C, $I = 1.0$ mol dm⁻³ (LiCF₃SO₃)), respectively, and that for the reduction of (oxalato)pentaammineruthenium(III) by Ti(III)[6] is 2.5×10^4 dm³ mol⁻¹ s⁻¹ (25 °C, $I = 0.10$ mol dm⁻³ (LiCl)). When all rate constants are extrapolated to 25 °C and $I = 0.10$ mol dm⁻³ (our experimental conditions for the Ru(II)/Ru(III) systems), they are much higher than the electron-transfer rate constants k_1 and k_2 for the Ru(II)/Ru(III) reactions (Table IV). Competition from the Ru-(II)/Ru(III) cross reactions in the Cr(II), V(II), Eu(II), and Ti(III) reductions[1,6] are probably insignificant and therefore not observed. Reductions using less reactive reductants than those cited above could further access the importance of the Ru(II)/Ru(III) reactions reported here.

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Charge-Transfer Excited States as Molecular Photodiodes

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The results of experiments are described in which a series of sequential electron-transfer reactions are induced by oxidative or reductive quenching of the emitting charge transfer (CT) excited state of $Ru(bpy)_3^{2+}$ (bpy is 2,2′ = bipyridine). The excited state is shown to have the innate properties of electronic charge separation and ability to undergo facile electron and electron-hole loss which allow it to mimic the behavior expected of a photodiode at the molecular level. By adding a chemically linked electron acceptor to the basic chromophore, as in the complex $[(bpy)_2Ru(NC_5H_4C_5H_4NCH_3)_2]^{4+}$, it is possible to introduce a directed charge-transfer character to the excited state.

Introduction

The absorption of light at the molecular level leads to an electronic redistribution and the formation of an excited state. By the nature of the transition, an electron is excited to a higher level where the binding energy is decreased, and a hole is created in a lower level. As a consequence, when compared to the ground state, an excited state has enhanced properties both as oxidant and reductant. For a charge-transfer (CT)

excited state, the absorption of light leads to a transient redox asymmetry where separated oxidizing and reducing sites exist simultaneously within the same molecule. The redox asymmetry inherent in charge-transfer excited states may be of importance in the charge separation step or steps in photosynthesis, in the design of solar energy conversion systems based on molecular excited states, and possibly in the design of molecular level devices. Aviram and Ratner have discussed

the possibility of finding molecules which have properties as rectifiers.[1]

The purpose of this paper is twofold: (1) to elaborate further on a type of experiment reported earlier in a preliminary communication[2] and (2) to show that it is possible to devise experiments where, following the light absorption–charge separation step associated with formation of a CT excited state, electrons and electron holes can be removed from the system in sequential one-electron steps. The net effect is the deactivation of the excited state but with the production of separated oxidized and reduced products in solution. In terms of the sequence of events which occur, such systems have properties commonly associated with a photodiode, and with proper design of the excited state, an element of directional charge transfer can be built into the charge-separation step.

Experimental Section

The PF_6^- salt of the pyridinium complex $[Ru(bpy)_2-(NC_5H_4C_5H_4NCH_3)_2]^{4+}$ was prepared and purified as described earlier.[3] All other chemicals and solvents were purchased or prepared and purified as described in a recent publication.[4a]

Conventional flash photolysis experiments were carried out with use of an apparatus whose construction has been described.[4b,c] The short-time transient absorption measurements were made with use of a dual laser device which will be described in detail in a later publication. The experiment consisted of pumping a chemical dye laser with the use of a molectron UV-400 nitrogen laser and using as probe beam the lines at 514.5 and 488.0 nm from an argon ion laser. The chemical dyes used were either Coumarin 120 (C120, λ_{max} 440 nm) or 7-(diethylamino)-4-methylcoumarin (7D4mc, λ_{max} 450 nm). Light detection was accomplished by using a photodiode whose output was amplified and recorded with use of a Tetronix 7704A oscilloscope with a 7A26 vertical amplifier and a 7B53A dual time base.

All solution samples were degassed either by bubbling with purified N_2 or Ar or by vacuum degassing with use of the freeze–pump–thaw technique.

Transient absorbance decays following flash photolysis were analyzed in terms of either first-order or second-order, equal concentration kinetics by using, respectively, the expressions

$$\ln (\Delta A_t) = kt + \ln (\Delta A_0)$$

$$1/\Delta A_t = kt/\Delta\epsilon b + 1/\Delta A_0$$

where ΔA_t is the optical density change observed after time t, ΔA_0 is the total absorbance change, b is the cell length, and $\Delta\epsilon$ is the difference in molar extinction coefficients between reactants and products at a given wavelength. Difference spectra were obtained by conventional flash photolysis by measuring the change in absorbance before and 100 μs after the flash at a series of wavelengths.

Results and Discussion

Reactions Involving the Emitting Charge-Transfer (CT) Excited State of $Ru(bpy)_3^{2+}$ (bpy is 2,2′-bipyridine). The results of a series of spectroscopic experiments have led to the conclusion that the origin of the intense visible light absorption in the complex $Ru(bpy)_3^{2+}$ is a metal–ligand charge-transfer (MLCT) transition.[5–10] The initially populated CT state is
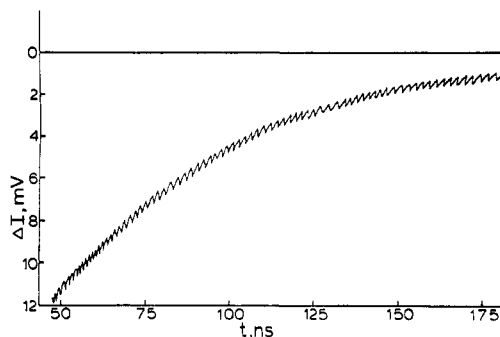

Figure 1. Transient spectral change at 514 nm following 450-nm laser flash photolysis of a solution containing p-$Me_2NC_6H_4CH_3$ (DMT, 1.4×10^{-2} M), $[MeNC_5H_4C_5H_4NMe]^{2+}$ (PQ^{2+}, 3.5×10^{-4} M), and $Ru(bpy)_3^{2+}$ (5.0×10^{-5} M). The decrease in ΔI corresponds to an absorbance increase as $Ru(bpy)_3^+$ is formed by reductive quenching of $Ru(bpy)_3^{2+*}$.
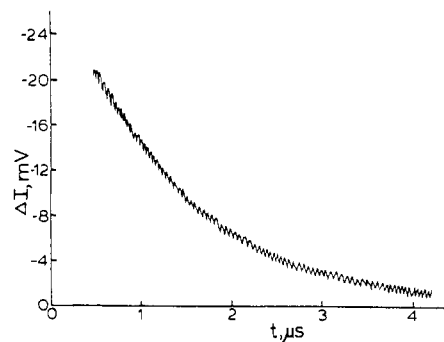

Figure 2. As in Figure 1 but on a longer time scale showing a decrease in absorbance corresponding to the oxidation of $Ru(bpy)_3^+$ by PQ^{2+}.

extremely short-lived[7,8] and decays to give a second, relatively long-lived MLCT state ($\tau_0 = 855$ ns in acetonitrile at 22 ± 2 °C) which is a relatively strong emitter. Although there is some question as to where the excited electron is localized on one ligand or delocalized over all three[5,10] and there appear to be a series of relatively closely spaced states including some d–d in character,[9] it seems clear that in the emitting excited state there is a considerable charge separation (eq 1).

$$Ru^{II}(bpy)_3^{2+} \xrightarrow{h\nu} Ru^{III}(bpy^-)_3^{2+*} \qquad (1)$$
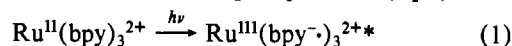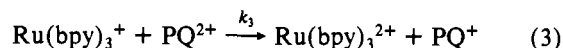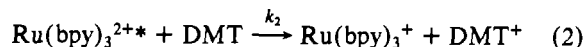
The excited state, $Ru^{III}(bpy^-)_3^{2+*}$, is sufficiently long-lived in solution to undergo bimolecular quenching reactions at relatively low quencher concentrations.[11–13] In Figures 1 and 2 are shown absorption vs. time curves following laser flash photolysis of a solution containing $Ru(bpy)_3^{2+}$ (5.0×10^{-5} M), p-$Me_2NC_6H_4CH_3$ (p-(dimethylamino)toluene (DMT); 1.4×10^{-2} M), and $MeNC_5H_4C_5H_4NMe^{2+}$ (paraquat (PQ^{2+}); 3.5×10^{-4} M) in acetonitrile at 23 ± 2 °C. Figure 1 shows the transient absorbance characteristics of the solution at 514 nm immediately following excitation at 450 nm by a light pulse from a chemical dye laser pumped by a Molectron UV-400 nitrogen laser (~5-ns pulse width). The wavelength observed, 514 nm, is a position of high absorbance for the reduced complex $Ru(bpy)_3^{+}$.[14] The excited state $Ru(bpy)_3^{2+*}$ is

(1) Aviram, A.; Ratner, M. *Chem. Phys. Lett.*, **1974**, *29*, 277.
(2) Young, R. C.; Meyer, T. J.; Whitten, D. G. *J. Am. Chem. Soc.* **1975**, *97*, 4781.
(3) Sullivan, B. P.; Abruna, H.; Finklea, H. O.; Salmon, D. J.; Nagle, J. K.; Meyer, T. J.; Sprintschnik, H. *Chem. Phys. Lett.* **1978**, *58*, 389.
(4) (a) Bock, C. R.; Connor, J. A.; Gutierrez, A. R.; Meyer, T. J.; Whitten, D. G.; Sullivan, B. P.; Nagle, J. K. *J. Am. Chem. Soc.* **1979**, *101*, 4815. (b) Young, R. C. Ph.D. Dissertation, The University of North Carolina, 1976. (c) Nagle, J. K., Ph.D. Dissertation, The University of North Carolina, 1979.
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(9) (a) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *Chem. Phys. Lett.* **1979**, *62*, 153; *J. Am. Chem. Soc.* **1980**, *102*, 4096. (b) Van Houten, J.; Watts, R. J. *Ibid.* **1976**, *98*, 4853; *Inorg. Chem.* **1978**, *17*, 3381. (c) Durham, B.; Caspar, J.; Meyer, T. J., submitted for publication.
(10) Dallinger, R. F.; Woodruff, W. H. *J. Am. Chem. Soc.* **1979**, *101*, 4391.
(11) (a) Meyer, T. J. *Acc. Chem. Res.* **1978**, *11*, 94; (b) *Isr. J. Chem.* **1977**, *15*, 200.
(12) Balzani, V.; Bolletta, F.; Gandolfi, M. T.; Maestri, M. *Top. Curr. Chem.* **1978**, *75*, 1.
(13) Sutin, N. *J. Photochem.* **1979**, *10*, 19.
(14) Anderson, C. P.; Salmon, D. J.; Young, R. C. *J. Am. Chem. Soc.* **1977**, *99*, 1980.

relatively transparent at 514 nm[6] and $Ru(bpy)_3^{2+}$ absorbs, but less strongly. The spectral changes observed at both 514 and 488 nm are consistent with the sequence of reactions in eq 1 and 2. In the sequence, the initial excitation step is followed

$$Ru(bpy)_3^{2+*} + DMT \xrightarrow{k_2} Ru(bpy)_3^+ + DMT^+ \quad (2)$$

$$Ru(bpy)_3^+ + PQ^{2+} \xrightarrow{k_3} Ru(bpy)_3^{2+} + PQ^+ \quad (3)$$

by a diffusional, reductive quenching of the excited state by p-$Me_2NC_6H_4CH_3$ (DMT) which results in an increase in absorbance (a decrease in the transmitted light, ΔI, as shown in Figure 1). On a slightly longer time scale (Figure 2), a transient decrease in absorbance occurs at 514 nm which is accompanied by the appearance of reduced paraquat $(CH_3NC_5H_4C_5H_4CH_3^+, PQ^+)$, showing that the reaction observed is oxidation of the reduced complex $Ru(bpy)_3^+$ by paraquat (eq 3). In competition with eq 3 is recapture of $Ru(bpy)_3^+$ by back electron transfer to DMT^+ (eq 3a).

$$Ru(bpy)_3^+ + DMT^+ \rightarrow Ru(bpy)_3^{2+} + DMT \quad (3a)$$
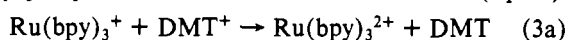
Although rate constants for both eq 3 and eq 3a are near the diffusion-controlled limit,[2,4b,14,15] the competition for $Ru(bpy)_3^+$ between PQ^{2+} (eq 3) and DMT^+ (eq 3a) is heavily balanced in favor of PQ^{2+} because of a large difference in concentration. Under the conditions of our experiments, $[PQ^{2+}] = 3.5 \times 10^{-4}$ M while, following flash photolysis, the maximum concentration of DMT^+ is 5×10^{-5} M, the initial concentration of $Ru(bpy)_3^{2+}$ before the flash (note eq 2).

Since the two sequential one-electron steps in eq 2 and 3 occur under pseudo-first-order conditions in [DMT] and $[PQ^{2+}]$, respectively, it is possible to evaluate electron-transfer rate constants for the two processes by a first-order kinetic analysis of the decay curves in Figures 1 and 2. The results obtained as average values from the results of several experiments were $k_2 = k_{obsd,2}/[DMT] = (1.5 \pm 0.1) \times 10^9$ M^{-1} s^{-1} and $k_3 = k_{obsd,3}/[PQ^{2+}] = 2.3 \times 10^9$ M^{-1} s^{-1} at 22 $\pm$ 2 °C. The value for k_2 is in good agreement with a value obtained earlier by a Stern–Volmer quenching experiment.[4a]

Following the sequence of events outlined in eq 1–3, but on a significantly longer time scale, a further transient absorbance change occurs. From the difference spectrum obtained as the absorption spectral differences which occur before and after conventional flash photolysis (~ 10-μs pulse width), the reaction occurring is clearly back electron transfer between DMT^+ and PQ^+ produced in eq 2 and 3.

The reaction in eq 4 occurs on a time scale which is suf-

$$DMT^+ + PQ^+ \rightarrow DMT + PQ^{2+} \quad (4)$$

ficiently slow to be followed by conventional flash photolysis because DMT^+ and PQ^+, which are electron-transfer products of eq 2 and 3, are formed in small amounts (10^{-5}–10^{-6} M) during the light pulse. As expected from the stoichiometries and coupled nature of eq 2 and 3, the reaction in eq 4 follows second-order, equal-concentration kinetics with $k_4 = (2.3 \pm 0.1) \times 10^9$ M^{-1} s^{-1} at 23 $\pm$ 2 °C in CH_3CN.

Implications of the Electron-Transfer Reactions Based on $Ru(bpy)_3^{2+*}$. It is of value to consider the microscopic details of the individual electron-transfer steps which occur in eq 1–3. The first step is light absorption which is an energy-conversion step in which light energy is converted into the stored, intramolecular chemical energy of a transient excited state. A charge separation has occurred leading to an oxidizing Ru(III) core and a strongly reduced site on the periphery at a ligand. The converted energy remains stored in the excited state until internal recombination of the electron–electron hole pair occurs by a combination of radiative ($\sim 3\%$ at room temperature)

(15) Nagle, J. K.; Young, R. C.; Meyer, T. J. *Inorg. Chem.* **1977**, *16*, 3366.
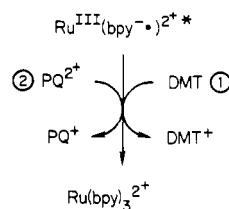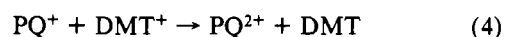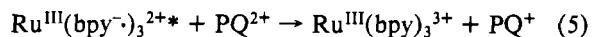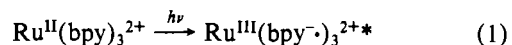
Scheme I

Scheme II
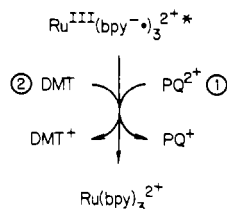
and nonradiative decay ($\sim 97\%$) pathways.[9b,c]

In the context of the theme of excited states as molecular photodiodes, the most important features of the excited state are its internal redox asymmetry and its ability to undergo facile one-electron transfer reactions. Light absorption leads to a charge separation and, in eq 2, an electron is added to the Ru(III) core in the first of two sequential, one-electron transfer reactions. In the second, eq 3, the excited electron generated in the charge-transfer step is also drained from the system, again in a bimolecular, diffusional electron-transfer step.

The net effect of the stepwise electron-transfer reactions is to create a mechanism for conversion of an excited state into its ground state (Scheme I). In most excited-state decay processes, the decay of the excited state leads solely to the production of heat and/or light. However, here an electron-electron hole pair is also produced and stored transiently at separated chemical sites. The net process provides a conceptual basis for the design of a molecular-level photodiode.

In terms of an energy balance, the thermally equilibrated excited state lies at $\Delta G \approx 2.1$ V above the ground state.[4a] Following the sequential electron-transfer steps in Scheme I, 1.2 V of the excited-state energy has been converted into the stored chemical redox energy inherent in the net reaction between PQ^+ and DMT^+ (eq 4) and the remainder is lost to the medium as heat.
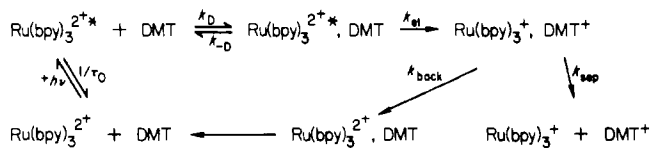
The order in which the electron–electron hole pair is removed from the excited state can be varied simply by changing the reaction conditions. Quenching of $Ru(bpy)_3^{2+*}$ by either PQ^{2+} ($k_q = 2.4 \times 10^9$ M^{-1} s^{-1})[4b] or aromatic amines like DMT ($k_q = 2.5 \times 10^9$ M^{-1} s^{-1}) is rapid and can be varied systematically through a related series of quenchers where there is a variation in redox potentials.[4] Here, the order of events can be controlled simply by varying the relative concentrations of the two redox components. After the concentration of PQ^{2+} is increased relative to that of the amine, the initial quenching step can be made oxidative in nature and the overall sequence of events becomes[2,15]

$$Ru^{II}(bpy)_3^{2+} \xrightarrow{h\nu} Ru^{III}(bpy^-\cdot)_3^{2+*} \quad (1)$$

$$Ru^{III}(bpy^-\cdot)_3^{2+*} + PQ^{2+} \rightarrow Ru^{III}(bpy)_3^{3+} + PQ^+ \quad (5)$$

$$Ru^{III}(bpy)_3^{3+} + DMT \rightarrow Ru^{II}(bpy)_3^{2+} + DMT^+ \quad (6)$$

$$PQ^+ + DMT^+ \rightarrow PQ^{2+} + DMT \quad (4)$$
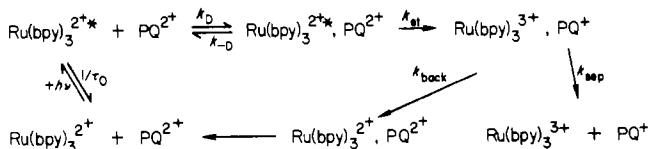
In the net sense, the chemistry remains the same in terms of the redox reaction driven (note eq 7), but the sequence of

$$DMT + PQ^{2+} \xrightarrow{h\nu} DMT^+ + PQ^+ \quad (7)$$

Scheme III

$$Ru(bpy)_3^{2+*} + DMT \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} Ru(bpy)_3^{2+*}, DMT \overset{k_{et}}{\longrightarrow} Ru(bpy)_3^+, DMT^+$$

$$+h\nu \Big\downarrow 1/\tau_0 \qquad\qquad {}^{k_{back}} \nearrow \qquad \Big\downarrow k_{sep}$$

$$Ru(bpy)_3^{2+} + DMT \longleftarrow Ru(bpy)_3^{2+}, DMT \qquad Ru(bpy)_3^+ + DMT^+$$

Scheme IV

$$Ru(bpy)_3^{2+*} + PQ^{2+} \underset{k_{-D}}{\overset{k_D}{\rightleftharpoons}} Ru(bpy)_3^{2+*}, PQ^{2+} \overset{k_{et}}{\longrightarrow} Ru(bpy)_3^{3+}, PQ^+$$

$$+h\nu \Big\downarrow 1/\tau_0 \qquad\qquad {}^{k_{back}} \nearrow \qquad \Big\downarrow k_{sep}$$

$$Ru(bpy)_3^{2+} + PQ^{2+} \longleftarrow Ru(bpy)_3^{2+}, PQ^{2+} \qquad Ru(bpy)_3^{3+} + PQ^+$$
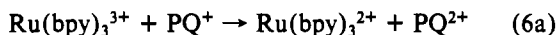
reactions leading to excited-state decay is reversed (note Scheme II).

As in the reductive quenching scheme in the previous section, recapture of $Ru(bpy)_3^{3+}$ by back electron transfer from PQ^+ (eq 6a) can be avoided by having a sufficiently high concen-

$$Ru(bpy)_3^{3+} + PQ^+ \rightarrow Ru(bpy)_3^{2+} + PQ^{2+} \qquad (6a)$$

tration of scavenger, DMT, present in the solution.

We have not followed eq 5 and 6 directly by laser flash photolysis. However, the sequence of reactions in the scheme of eq 1,5,6,4 does occur as shown by conventional flash photolysis experiments.[2,15] In these experiments PQ^+ and DMT^+ are observed following the flash as is their transient decay by the electron transfer reaction in eq 4.

Although the sequences of reactions 1-3 and 1,5,6 lead to the same place, the efficiencies of production of the separated redox products, PQ^+ and DMT^+ are, in general, different because the two schemes involve different chemical reactions. For example, consider the microscopic details of the two quenching steps: reduction (eq 2 and Scheme III) and oxidation (eq 5 and Scheme IV).

Both the quenching schemes are similar in that they involve (1) preassociation (k_D), (2) electron-transfer quenching (k_{et}), and (3) redox product separation (k_{sep}), which is in competition with back electron transfer (k_{back}). In either case, the redox product separation yield after correcting for diffusional effects[4a] is given by eq 8, where $k_q = k_{et}(k_D/k_{-D})$ and [Q] is the

$$\phi_{sep} = \left(\frac{k_q[Q]}{k_q[Q] + 1/\tau_0} \right) \left(\frac{k_{sep}}{k_{sep} + k_{back}} \right) \qquad (8)$$

quencher concentration. At sufficiently high quencher concentrations, excited-state quenching is nearly complete, $k_q[Q] \gg 1/\tau_0$, and eq 8 becomes eq 9. ϕ_{sep} is also the efficiency

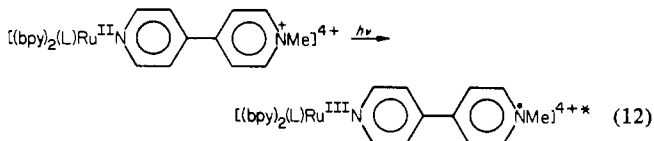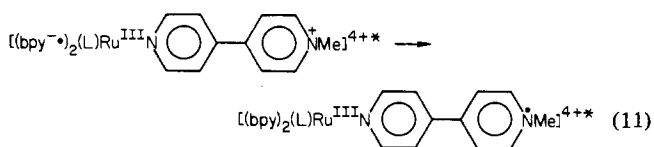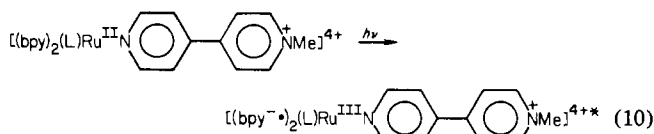$$\phi_{sep} = \frac{k_{sep}}{k_{sep} + k_{back}} \qquad (9)$$

of production of $PQ^+ + DMT^+$ as long as $Ru(bpy)_3^+$ formed by reductive quenching (Scheme III) is completely captured by PQ^{2+} (eq 3 vs. eq 3a) and $Ru(bpy)_3^{3+}$ formed by oxidative quenching (Scheme IV) is completely captured by DMT (eq 6 vs. eq 6a). In either case, ϕ_{sep} will be determined by the ratio of rate constants in eq 9 and, in general, they will be different for the two different quenching steps. For example, in comparing Schemes III and IV, k_{sep} is expected to be larger for PQ^{2+} as quencher than for DMT as quencher because of the greater repulsion between 1+ and 3+ ions ($Ru(bpy)_3^{3+},PQ^+$) compared to that between two 1+ ions ($Ru(bpy)_3^+,DMT^+$).

Reactions Involving the Lowest CT Excited State of *cis*-[(bpy)₂Ru(NC₅H₄C₅H₄NCH₃)₂]⁴⁺. In terms of charge splitting and electron-transfer properties, the MLCT excited state of $Ru(bpy)_3^{2+}$ has been shown to have the requisite electronic

structure and electron-transfer properties needed to mimic the action of a photodiode at the molecular level. However, the system has the innate disadvantage of a lack of directed charge-transfer character. Whether the excited state consists of an electron hole surrounded by an excited electron delocalized over all three ligands or localized on one ligand, in which case rapid electron hopping between ligands would no doubt occur, there is a net symmetrical array in the charge-transfer distribution. The lack of directional CT character in the excited state limits possible applications based on discrete one-electron transfers since there is no way to control charge-transfer directionality following excitation to give the excited state.

It is possible to advance to a higher level of sophistication in terms of molecular design by making appropriate modifications on the basic Ru-bpy unit. We recently reported the preparation and characterization of the complex [*cis*-(bpy)₂Ru(NC₅H₄C₅H₄NCH₃)₂]⁴⁺.[3] Because of the attached pyridinium group, the complex represents an inner-sphere analogue of the $Ru(bpy)_3^{2+}$-PQ^{2+} system which we have exploited extensively in this work. Electrochemical studies show that the pyridinium site is a better electron-acceptor site than the bound 2,2'-bipyridine groups by ~0.5 V.[3] Although the visible absorption and low-temperature emission properties of the system are dominated by the Ru-bpy chromophore, at room temperature in fluid solution, a short-lived ($\tau_0 = 31 \pm 3$ ns in CH₃CN),[4c] red-shifted emission is observed.[3] The origin of the red-shifted emission is a lower lying CT state where the excited electron is on the remote pyridinium site.

For the pyridinium complex, Ru-bpy charge-transfer absorption occurs to give the usual $Ru^{III}bpy^-\cdot$ CT excited state (eq 10). The Ru-bpy CT state is now an upper excited state of the system and decays, at least in part, to the lower CT state (eq 11) which is responsible for the red-shifted emission. The excited-state interconversion process can also be viewed as a ligand to ligand, intramolecular electron-transfer reaction (eq 10 and 11) in which the excited electron is directed away from the Ru-bpy core. The overall effect (eq 12) is to build a high degree of directionality into the net CT process.

$$[(bpy)_2(L)Ru^{II}N\text{-}\langle\text{-}\rangle\text{-}\langle\text{-}\rangle\text{-}NMe]^{4+} \overset{h\nu}{\longrightarrow}$$

$$[(bpy^-\cdot)_2(L)Ru^{III}N\text{-}\langle\text{-}\rangle\text{-}\langle\text{-}\rangle\text{-}NMe]^{4+*} \qquad (10)$$

$$[(bpy^-\cdot)_2(L)Ru^{III}N\text{-}\langle\text{-}\rangle\text{-}\langle\text{-}\rangle\text{-}NMe]^{4+*} \longrightarrow$$

$$[(bpy)_2(L)Ru^{III}N\text{-}\langle\text{-}\rangle\text{-}\langle\text{-}\rangle\text{-}\dot{N}Me]^{4+*} \qquad (11)$$

$$[(bpy)_2(L)Ru^{II}N\text{-}\langle\text{-}\rangle\text{-}\langle\text{-}\rangle\text{-}NMe]^{4+} \overset{h\nu}{\longrightarrow}$$

$$[(bpy)_2(L)Ru^{III}N\text{-}\langle\text{-}\rangle\text{-}\langle\text{-}\rangle\text{-}\dot{N}Me]^{4+*} \qquad (12)$$

Using flash photolysis, it is possible to show that the asymmetric CT state so produced can be deactivated by a sequence of one-electron steps like those used earlier for the deactivation of $Ru(bpy)_3^{2+*}$. Conventional flash photolysis of a solution containing [(bpy)₂Ru(NC₅H₄C₅H₄NCH₃)₂]⁴⁺ $(1.7 \times 10^{-5}$ M), DMT $(1.1 \times 10^{-2}$ M), and PQ^{2+} $(1.1 \times 10^{-2}$ M) resulted in the appearance of DMT^+ and PQ^+ as shown by a difference spectrum in the visible region. Kinetic analysis of the transient absorbance changes following the flash gave the same rate constant $(2.3 \times 10^9$ M⁻¹ s⁻¹) as that observed in the earlier experiment where the reaction DMT + PQ^{2+} $\rightarrow DMT^+ + PQ^+$ was driven by $Ru(bpy)_3^{2+*}$ (note eq 1–3 and

Scheme V
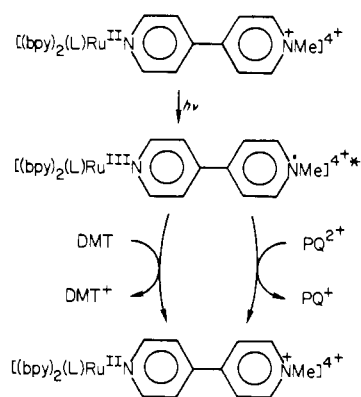
4). As in the case of Ru(bpy)$_3^{2+}$*, a series of one-electron transfer steps leads to net deactivation of the excited state with the production of separated redox products (Scheme V). However, given the properties of the pyridinium CT state, the electron- and electron-hole-loss steps occurs from different parts of the molecule. The directional symmetry of the CT state is transferred to the external redox environment with respect to the internal coordinates of the molecule.

Conclusions and Final Comments

The point of the experiments described here was to show that certain charge-transfer excited states have the innate properties of an electronic-charge separation and the capability of undergoing facile electron and electron-hole loss which mimics the behavior expected for a photodiode at the molecular level. Further, by adding an external electron acceptor to the basic chromophore, as in the complex [(bpy)$_2$Ru-(NC$_5$H$_4$C$_5$H$_4$NCH$_3$)$_2$]$^{4+}$, it is possible to introduce an element of directed charge transfer to the large, transient intramolecular photopotential inherent in the excited state.

In terms of a device-type application, the systems studied here suffer from the inherent disadvantage of any homogeneous system—the isotropic, nondirectional character of the medium. There is no easy way to carry the directed CT character of the excited state to the redox products which appear following electron and electron-hole loss. In order to maintain the CT asymmetry, it will be necessary to imbed the ground-state precursors of appropriately designed excited states into a matrix array perhaps based on electrode attachment, membranes, or monolayer assemblies.

There is an additional point of fundamental interest that should be made. Based on the type of experiments described here and transient absorption measurements, it may be possible to demonstrate long-range, intramolecular electron transfer following optical excitation in properly designed systems and so to develop useful models for the initial charge-splitting step that occurs in photosynthesis.

Intramolecular Energy Transfer in a Rhodium(III) Metalloorganic Bichromophore System. Photochemical and Photoluminescence Studies

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Reported are the photochemical, photoluminescence, and spectral studies of a series of pentaammine(organonitrilo)rhodium(III) compounds, Rh(NH$_3$)$_5$(N≡C—R)$^{3+}$ (where R is a phenyl, benzyl, or 2-phenylethyl group or a substituted derivative). The absorption spectroscopy exhibits features attributable to both $\pi\pi^*$ and ligand field transitions. The luminescence spectra, however, exhibit only ligand field (LF) emissions regardless of whether the $\pi\pi^*$ or LF states are initially populated. The luminescence lifetimes at 77 K are also characteristic of LF states. Irradiation of the $\pi\pi^*$ or LF bands in aqueous solutions leads to photosubstitution of the organonitrile ligand with the quantum yields being somewhat smaller for λ_{irr} = 254 nm ($\pi\pi^*$) than 313 nm (LF) in most cases. The results are discussed in terms of the efficiency of interconfigurational energy transfer between $\pi\pi^*$ and LF states.

Introduction

Since the early investigations of intramolecular energy transfer by Weber[1–3] and by Schnepp and Levy[4] in bichromophoric molecules, there has been much interest in this area.[5] Bimetallic chromophores, organic bichromophores, and metalloorganic systems in which the ligand chromophore is coordinated to the metal chromophore have all received considerable spectral, photochemical, and photophysical atten-

tion.[6–11] The present work is concerned with the last type, complexes of a transition metal ion with a phenyl group containing organonitrile ligand Rh(NH$_3$)$_5$(N≡C—R)$^{3+}$. The presence of distinctly different chromophores, the π-unsaturated phenyl ring, for which $\pi\pi^*$ transitions dominate the spectroscopy, and the low-spin d^6 Rh(III) center, for which

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