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Protonation and Complex Formation of [(2,2′-Bipyrazine)bis(2,2′-bipyridine)ruthenium(II)](2+) in the Lowest Excited State[1]

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$[Ru(bpz)(bpy)_2]^{2+}$ (bpz = 2,2′-bipyrazine; bpy = 2,2′-bipyridine) emits phosphorescence from the lowest "ruthenium-to-bipyrazine" charge-transfer excited triplet state. The absorption spectrum of the complex strongly depends on hydrogen ion concentration $[H^+]$ in the media due to protonation of the peripheral nitrogens of the bipyrazine, while no emission is observed from the protonated species. Even in such a dilute acidic solution where no protonated species can be detected in absorption spectrum, the phosphorescence is partly quenched by H_3O^+ in solution. Two different titration curves were obtained by absorption and luminescence intensity measurements with varied $[H^+]$ in the media. Since the rate of intramolecular nonradiative deactivation is very much promoted in the protonated species, the emission titration curve is shifted depending upon the rate of diffusion-controlled encounter of the excited complex with H_3O^+. The diffusion-controlled protonation is achieved by the fast proton jump initiated from a $H_9O_4^+$ cluster formed in aqueous media. The shift of the emission titration curve is ascribed to the dynamic behavior of excited species in solution but cannot be a direct indication of the enhancement of the excited-state basicity. $[Ru(bpz)(bpy)_2]^{2+}$ forms $[Ru(bpzAg)(bpy)_2]^{3+}$ and $[Ru(bpzAg_2)(bpy)_2]^{4+}$, in which hydrated Ag^+ ions coordinate to bipyrazine peripheral nitrogens. $[Ru(bpzAg)(bpy)_2]^{3+}$ emits at a longer wavelength than $[Ru(bpz)(bpy)_2]^{2+}$. The phosphorescence lifetime of $[Ru(bpzAg)(bpy)_2]^{3+}$ was determined to be 66 ns. From the Stern–Volmer plot of lifetimes, the complex formation constant in the excited state was determined to be $K^* = 130\ M^{-1}$, which is significantly enhanced from $K = 20\ M^{-1}$ of the ground-state complex and is ascribed to an increase of the excited-state basicity of coordinated bipyrazine.

Introduction

Excited-state acid–base reactions and equilibria in organic systems have been extensively studied by luminescence measurements.[2] However, such studies of transition-metal complexes are still quite limited.

Direct evidence of greatly enhanced excited-state acidity was presented with the protonated forms of $[Ru(bpy)_2(CN)_2]$ (bpy = 2,2′-bipyridine).[3,4] The absorption spectrum of the complex strongly depends on $[H^+]$, which is ascribed to protonation of coordinated cyano groups. However, emission from acidified media exhibits a spectrum of the deprotonated species and the emission yield is constant regardless of the variation of $[H^+]$ in solution. This was interpreted by a rapid, complete deprotonation following excitation of the protonated species. The "metal-to-bipyridine" charge-transfer transition results in a decrease in the basicity of coordinated CN groups. Ag^+ ion also coordinates with the cyano groups of $[Ru(bpy)_2(CN)_2]$, however, no dissociation of Ag^+ ion occurs within the excited-state lifetime.[5]

Both protonated and deprotonated forms of $[Ru(bpy)_2$(4,7-dihydroxy-1,10-phenanthroline)$]^{2+}$ are emissive in aqueous solution and thus the proton-dissociation constants in the ground state and the excited state can be determined by spectral and lifetime measurements with varied $[H^+]$ in aqueous media.[6] The complex is more acidic in the excited state. On the other hand, excitation of $[Ru(bpy)_2$(2,2′-bipyridine-4,4′-dicarboxylic acid)$]^{2+}$ results in a decrease in the acidity of carboxylic acid attached to one of coordinated bipyridines. Two different titration curves were obtained by absorption and luminescence intensity measurements with varied $[H^+]$. The displacement of the titration curves has been attributed to a shift of the protonation equilibrium upon electronic excitation.[7] Recently, a two-step protonation of the complex was proposed.[8,9]

$[Ru(bpz)_3]^{2+}$ (bpz = 2,2′-bipyrazine) has six peripheral nitrogen donor atoms available for protonation. With increasing acid concentration in the media, a series of isosbestic points were found in the absorption spectra and the parallel variation of emission maxima and lifetimes were measured. From these observations, it was inferred that the "metal-to-bipyrazine" charge-transfer excitation increases ligand basicity for the first three protonation steps to three different bipyrazine rings on the complex, while it decreases for the second set of three protonation steps.[10] Similar variation of emission spectra was also ascribed to a complex formation of Ag^+ ion with excited $[Ru(bpz)_3]^{2+}$.[11] Recently, exciplex formation with Ag^+ ion was reported on $[Ru(bpy)_3]^{2+}$ which has no peripheral donor atoms.[12]

In the present work, kinetic studies of protonation and complex formation with Ag^+ ion were carried out with $[Ru(bpz)(bpy)_2]^{2+}$, which could avoid the confusion from unresolved successive equilibria on six peripheral nitrogens in $[Ru(bpz)_3]^{2+}$, although a difference of the lifetimes of $[Ru(bpz)(bpy)_2]^{2+}$ (88 ns) and $[Ru(bpz)_3]^{2+}$ (900 ns)[10] in aqueous media should be noted. Since the lowest excited state of $[Ru(bpz)(bpy)_2]^{2+}$ is the "metal-to-bipyrazine" charge-transfer excited state, excitation increases the basicity of coordinated bipyrazine. With $[Ru(bpz)_2(bpy)]^{2+}$ and $[Ru(bpy)(bpm)_2]^{2+}$ (bpm = 2,2′-bipyrimidine), two different titration curves were obtained by absorption and luminescence intensity measurements and their displacement was ascribed to a shift of pK_a caused by electronic excitation.[13] However, the displacement of the titration curves should not necessarily be attributable to an increase of excited-state basicity, when the nonradiative relaxation process in the protonated species is so fast that an equilibrium can not be established during the lifetime of the excited state.

In this paper, we present a kinetics study of protonation and complex formation of $[Ru(bpz)(bpy)_2]^{2+}$ in the lowest excited state.

Experimental Section

Preparation of the Compound. $[Ru(bpz)(bpy)_2]Cl_2{\cdot}5H_2O$[13] was prepared and purified by literature methods. The complex was identified by elemental analyses and absorption, emission, and excitation spectra.

Measurements. Absorption and second-derivative absorption spectra were recorded on a Hitachi spectrophotometer, Model 330. Second-derivative spectra were obtained by measurements of the difference spectra for two different wavelengths with an interval $\Delta\lambda = 10$ nm and a slit width of 6 nm. Emission and excitation spectra and emission second-

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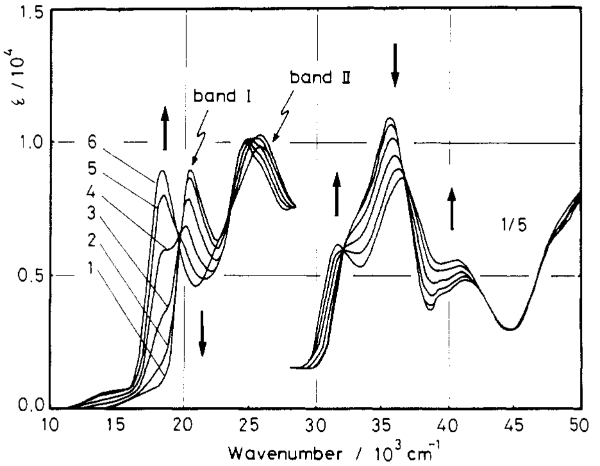

Figure 1. Absorption spectra of $[Ru(bpz)(bpy)_2]^{2+}$ as a function of concentration of $HClO_4$ in aqueous solution ($[H^+]$: 0.0 M (1); 1.2 M (2); 2.3 M (3); 3.5 M (4); 4.6 M (5); 5.8 M (6)).

derivative spectra were measured on a Hitachi 850 spectrofluorometer equipped with a Hamamatsu R928 photomultiplier.

Luminescence lifetimes were measured by means of the single-photon-counting method on a PRA nanosecond fluorometer system. The sample was excited by the 400-nm pulses of 2–5-ns duration from a PRA 510B hydrogen or nitrogen gas lamp through a Jobin-Yvon H-10 monochromator. Photon emission in wavelengths longer than 600 nm was detected through a Toshiba O-59 glass filter by a Hamamatsu R928 photomultiplier and counted on a Norland multichannel analyzer, Model 5300. Lifetimes were determined by fitting the decay curves to single exponentials by using a least-squares method on an NEC PC9801-F2 computer interfaced with the multichannel analyzer.

Concentrations of the complex in solution for emission measurements were typically 10^{-6} M. The temperature of solutions was maintained constant by circulating water in the double wall of cell compartments from a Haake FK thermostat. The solutions were purged with solvent-saturated nitrogen gas for 20–30 min before the measurements. Aqueous solutions were prepared by use of repeatedly distilled water. Ionic strengths and hydrogen ion concentrations were adjusted by addition of NaCl, KCl, or $NaClO_4$ and $HClO_4$, respectively. Deuterated materials including D_2O were Merck products and were used without further purification.

Emission decay was studied in the presence of $[Fe(CN)_6]^{3-}$ as well as hydrated Ag^+ ion. The lifetimes of $[Ru(bpz)(bpy)_2]^{2+}$ in the presence of $[Fe(CN)_6]^{3-}$ were determined by use of 400-nm excitations, while the luminescence yields were measured by means of excitation at 510 nm, which could avoid absorption effect due to $[Fe(CN)_6]^{3-}$. $K_3[Fe(CN)_6]$ was commercially available and purified by recrystallization. For kinetic studies, the concentrations of Ag^+ ion in solution were adjusted by dilution of a stock solution of $AgClO_4$ (pH = 6.0) which was prepared by dissolving Ag_2O in $HClO_4$. The concentrations of Ag^+ ion were determined by Mohr titration.[14] The counterion of the complex was substituted by ClO_4^-.

Results and Discussion

Figure 1 shows the split metal-to-ligand charge-transfer (MLCT) absorption band, which is characteristic of the mixed-ligand complex $[Ru(bpz)(bpy)_2]^{2+}$. The lower energy component band (band I) is ascribed to a metal-to-bipyrazine charge-transfer transition, while the higher energy component (band II) is assigned as a metal-to-bipyridine charge-transfer excitation.[13] In fact, resonance Raman modes of coordinated bipyrazine are observed with $[Ru(bpz)(bpy)_2]^{2+}$ as in $[Ru(bpz)_3]^{2+}$ upon irradiation of the wavelengths within the band I (488.0 nm), while those of coordinated bipyridine in $[Ru(bpz)(bpy)_2]^{2+}$ are detected as in $[Ru(bpy)_3]^{2+}$ upon irradiation in band II (457.9 nm).[15] Figure 1 also presents the variation of the absorption spectrum as a function of concentration of $HClO_4$ in aqueous solution. For hydrogen ion concentrations up to $[H^+] = 3.5$ M, an isosbestic point is observed at 20×10^3 cm^{-1}. Further addition of $HClO_4$ gives rise to a shift of the isosbestic point. The monoprotonated species is predominant in 6.0 M > $[H^+]$ > 3.5 M, while the diprotonated species predominates in $[H^+]$ > 8.0 M. In the case of $[Ru(bpz)_3]^{2+}$, the monoprotonated species forms in 3.5–42.5% H_2SO_4 (11.5 M > $[H^+]$ > 0.7 M), while the diprotonated species, protonated on two different bipyrazines of the complex, predominates in 42.5–48.5% H_2SO_4 (13.7 M > $[H^+]$ > 11.5 M).[10]

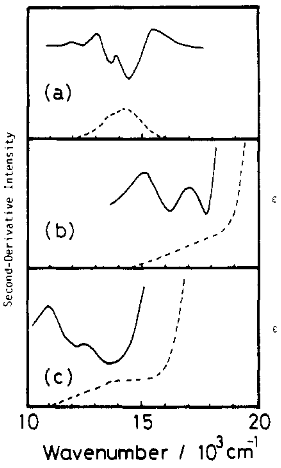

Figure 2. Second-derivative spectra of $[Ru(bpz)(bpy)_2]^{2+}$ (emission (a) and absorption (b)) and $[Ru(bpzH)(bpy)_2]^{3+}$ (absorption (c)) in aqueous media. The minima of second-derivative spectra (—) correspond to the respective maxima of emission or absorption spectra (- - -).

$[Ru(bpz)(bpy)_2]^{2+}$ exhibits emission from the lowest MLCT excited triplet state. The excitation spectrum of the emission conforms to the absorption spectrum taken with solutions of zero hydrogen ion concentration. A single exponential decay of phosphorescence is observed for $[Ru(bpz)(bpy)_2]^{2+}$ in an aqueous medium of $[H^+] = 0.0$ M and $\mu = 0.09$ M. The lifetime of 88 ns was determined by the decay curve. However, the lifetime in propylene carbonate is as long as 400 ns, which is in good agreement with that obtained by Meyer et al.[13]

Figure 2 presents the second-derivative emission (a) and absorption spectra (b) of $[Ru(bpz)(bpy)_2]^{2+}$, whose minima at 695 and 617 nm correspond to emission and absorption maxima, respectively. The second-derivative spectra can detect peaks hidden in a broad band. It is noted that the phosphorescence band (a) is in a mirror-image region of the weak absorption band (b) present to the red of the intense MLCT band (band I). The weak absorption band (b) is assigned as the spin-forbidden S–T (singlet–triplet) absorption band. $[Ru(bpy)_3]^{2+}$ as well as $[Os(bpy)_3]^{2+}$ exhibits a similar S–T absorption to the red of intense MLCT absorption band in the mirror-image region of their emission band.[16] We can also observe the MLCT excited triplet of nonemissive $[Ru(bpzH)(bpy)_2]^{3+}$ as the red-shifted, weak absorption band (c) whose maxima are detected by the second-derivative spectrum.

The ground-state proton dissociation constant of $[Ru(bpzH)(bpy)_2]^{3+}$ was determined by absorption measurements to be $K_a = 1.4$ M at 25 °C, which corresponds to ΔG(at 25 °C) = 1 kJ mol^{-1}. The lowest MLCT excited triplet of nonemissive $[Ru(bpzH)(bpy)_2]^{3+}$ cannot be detected by phosphorescence but is observed as a weak absorption band in a longer wavelength region than the corresponding weak band of $[Ru(bpz)(bpy)_2]^{2+}$ as Figure 2c shows. Thus an energy difference between the lowest MLCT excited triplet states of the protonated and deprotonated complexes is determined to be $\Delta E_T = -47$ kJ mol^{-1} (=3900 cm^{-1}). Assuming an equal entropy change of protonation in the ground state and the excited state, a Förster cycle[17] as illustrated in Figure 3 predicts an exergonic protonation in the excited state. The cycle predicts $K_a^* = 6 \times 10^{-9}$ M for the value of K_a at 25 °C of the

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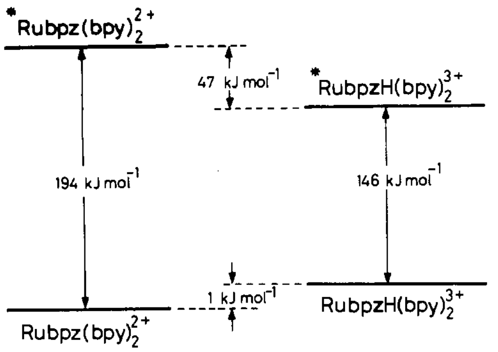


Figure 3. The Förster cycle.

Table I. Rate Constants of Quenching by H_3O^+ and D_3O^+ Determined by Luminescence Lifetime ($k_q(\tau)$) and Yield ($k_q(\phi)$) Measurements

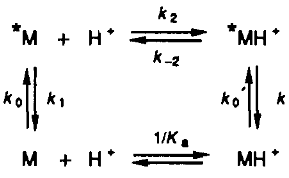
quencher	medium	ionic strength M^a	$k_q(\tau)/10^{10}$ M^{-1} s^{-1}	$k_q(\phi)/10^{10}$ M^{-1} s^{-1}
H_3O^+	H_2O	0.01		1.04
		0.03		1.21
		0.05		1.32
		0.09	1.51	1.52
		0.15		1.58
		0.30	1.77	1.75
		0.90		1.90
D_3O^+	D_2O	0.09	0.94	0.96

^{a}Adjusted by addition of NaCl.

excited monoprotonated species.

$[Ru(bpzH)(bpy)_2]^{3+}$ emits no luminescence. Thus the emission yield (ϕ) and lifetime (τ) of $[Ru(bpz)(bpy)_2]^{2+}$ decrease with increasing [H$^+$] in aqueous media, while no variation of the emission profile is observed. The plot of the ratio of lifetimes in the absence and presence of the quencher τ_0/τ against the quencher concentration [H$^+$] gives a straight line with an intercept of unity which conforms to that obtained with ϕ_0/ϕ for a rather wide range of [H$^+$] (10^{-4} M < [H$^+$] < 10^{-2} M). The plots of τ_0/τ and of ϕ_0/ϕ against [D$^+$] are also coincident. From these Stern–Volmer plots, the quenching rate constants k_q's, 1.5×10^{10} and 0.95×10^{10} M^{-1} s^{-1}, were obtained for H_2O and D_2O media of ionic strength $\mu = 0.09$ M at 25 °C, respectively. The quenching rate constants were also determined as a function of ionic strength in aqueous media as summarized in Table I. The k_q value increases with increasing ionic strength as observed in the rates of cation–cation encounters in aqueous solution,[18] whereas the lifetimes (88 ns in H_2O and 190 ns in D_2O) are rather independent of the ionic strength when [H$^+$] = 0 M or [D$^+$] = 0 M. This suggests that the quenching of $*[Ru(bpz)(bpy)_2]^{2+}$ arises from diffusion-controlled encounters with H_3O^+ or D_3O^+ in solution.

Quenching of the excited complex by H_3O^+ in aqueous media is described as in the following scheme:



where M denotes $[Ru(bpz)(bpy)_2]^{2+}$, *M denotes $*[Ru(bpz)(bpy)_2]^{2+}$, and MH$^+$ and *MH$^+$ are the corresponding protonated species, respectively; k_2* and $k_{-2}*$ are the rate constants of protonation and deprotonation of the excited complex, K_a is the proton-dissociation constant of $[Ru(bpzH)(bpy)_2]^{3+}$ in the ground state, k_1 and k_1' are the reciprocals of the lifetimes of $*[Ru(bpz)(bpy)_2]^{2+}$ and $*[Ru(bpzH)(bpy)_2]^{3+}$, and k_0 and k_0' are the rate constants of photon absorption of $[Ru(bpz)(bpy)_2]^{2+}$ and $[Ru(bpzH)(bpy)_2]^{3+}$, respectively. Upon excitation at the isosbestic points, the constants k_0 and k_0' are equal. In the present work, we used only low hydrogen ion concentrations in which the complex in the ground state is not protonated. Assuming that the concentration of the protonated species, [H$^+$]/K_a, can be ignored, the ratio of emission yields in the absence and presence of hydrogen ion is given by[19]

$$\phi_0/\phi = 1 + \frac{k_2*}{1 + k_{-2}*/k_1'}\tau_0[\mathrm{H}^+] \qquad (1)$$

If $k_1' \ll k_{-2}*$, eq 1 is rewritten as

$$\phi_0/\phi = 1 + (k_1'/K_a*)\tau_0[\mathrm{H}^+] \qquad (2)$$

where K_a* ($\equiv k_{-2}*/k_2*$) is the proton-dissociation constant of the excited complex. The constant K_a* is experimentally determined only when we can measure k_1 ($=1/\tau_0$) and k_1'. On the other hand, if $k_1' \gg k_{-2}*$

$$\phi_0/\phi = 1 + k_2*\tau_0[\mathrm{H}^+] \qquad (3)$$

In this situation, the quenching rate is governed by diffusion-controlled protonation.

The emission yields are measured by use of stationary irradiation, while the lifetimes are determined by means of pulse excitation. The ratio of lifetimes in the absence and presence of H_3O^+ is given by[19]

$$\tau_0/\tau = \tau_0\{\tfrac{1}{2}(k_1' + k_{-2}* + 1/\tau_0 + k_2*[\mathrm{H}^+]) - \tfrac{1}{2}[(k_1' + k_{-2}* - 1/\tau_0 - k_2*[\mathrm{H}^+])^2 + 4k_{-2}*k_2*[\mathrm{H}^+]]^{1/2}\} \qquad (4)$$

It should be noted that the ratio is independent of [H$^+$]/K_a.

As described earlier, an identical straight line $1 + k_q\tau_0[\mathrm{H}^+]$ was obtained by the measurements of both lifetimes and yields

$$\phi_0/\phi = \tau_0/\tau \qquad (5)$$

From substitutions of (1) and (4) into (5), it follows that

$$\frac{4k_{-2}*k_2*[\mathrm{H}^+]}{k_1' + k_{-2}*}\left(1/\tau_0 + k_2*[\mathrm{H}^+] - \frac{k_{-2}*k_2*[\mathrm{H}^+]}{k_1' + k_{-2}*}\right) = 0 \qquad (6)$$

On the other hand, eq 1 can be rewritten as

$$(\phi_0/\phi)(1/\tau_0) = 1/\tau_0 + k_2*[\mathrm{H}^+] - \frac{k_{-2}*k_2*}{k_1' + k_{-2}*}[\mathrm{H}^+] \qquad (7)$$

Substitution of (7) into (6) yields

$$\frac{4k_{-2}*k_2*[\mathrm{H}^+]}{k_1' + k_{-2}*}(\phi_0/\phi)(1/\tau_0) = 0 \qquad (8)$$

Since $(\phi_0/\phi)(1/\tau_0) \neq 0$, $k_{-2}*k_2*[\mathrm{H}^+]/(k_1' + k_{-2}*)$ should be vanishingly small and thus eq 7 is rewritten as follows:

$$(\phi_0/\phi)(1/\tau_0) = 1/\tau_0 + k_2*[\mathrm{H}^+] \qquad (9)$$

Substitution of (1) into (9) proves that eq 5 is valid only if $k_1' \gg k_{-2}*$. In other words, the excited-state lifetime of the protonated species is so short that the protonation-deprotonation equilibrium cannot be established during the excited-state lifetime and thus the deactivation process turns out to be diffusion-controlled. In fact, the concentration of $*[Ru(bpzH)(bpy)_2]^{3+}$ is too low to yield detectable emission.

On the other hand, if $k_1' \ll k_{-2}*$, both protonated and deprotonated species do emit and thus the lifetimes of the deprotonated and monoprotonated species (k_1 and k_1') can experimentally be determined; the excited-state proton-dissociation constant (K_a*) could be determined by eq 2 from the emission titration curve (a plot of ϕ/ϕ_0 versus $-\log$ [H$^+$]). However, the titration curve does not conform to that obtained by lifetime measurements with varied [H$^+$] (τ/τ_0 versus $-\log$ [H$^+$]). If the excited-state equilibrium is established within the time constant characterized by $(1/k_1 - 1/k_1')$, the decay lifetime continuously

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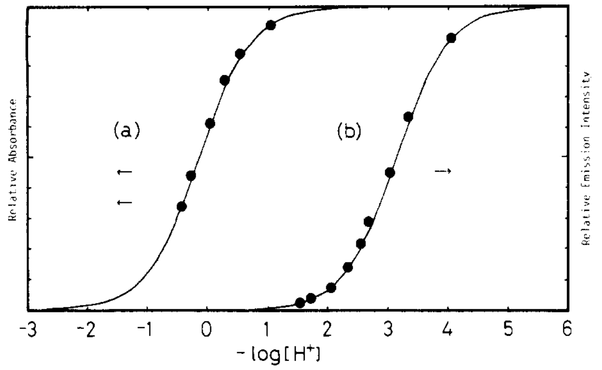

Figure 4. Titration curves obtained by absorption (a) and luminescence (b) intensity measurements. Ionic strengths were set at 3.00 M (a) and 0.09 M (b), respectively.

varies from τ_0 ($=1/k_1$) to τ_∞ ($=1/k_1'$) with increasing [H$^+$] and the titration curve of τ shows a plateau when the complex is exclusively monoprotonated.[2] Note that the excited-state equilibrium constant can be precisely determined by $(\tau_0 - \tau)/(\tau - \tau_\infty) = (\tau_0/\tau_\infty)[\mathrm{H}^+]/K_a$, only when the plateau value τ_∞ is experimentally obtained instead of the lifetimes being taken at arbitrary discrete values of [H$^+$]. Later, the corresponding equation is applied to determine the stability constant of an exciplex with Ag$^+$ ion.

Figure 4 presents the titration curves (a, b) obtained by absorption and luminescence intensity measurements. A remarkable difference between the two titration curves should be noted. Titration curve a is the plot of $\mathrm{OD(M^{2+})/OD_0(M^{2+})}$ ($=1/(1 + [\mathrm{H}^+]/K_a)$) against $-\log$ [H$^+$]: K_a is determined by the equivalent value of [H$^+$] ($K_a = 1.4$ M). The titration curve obtained by luminescence intensity measurements is also the plot of ϕ/ϕ_0 versus $-\log$ [H$^+$], whereas the equivalent point of the titration curve appears at $[\mathrm{H}^+] = (\tau_\infty/\tau_0)K_a^*$ (eq 2) or at $[\mathrm{H}^+] = 1/(k_2^*\tau_0)$ (eq 3) depending upon whether $k_1' \ll k_{-2}^*$ or $k_1' \gg k_{-2}^*$. Since the observation in the present work indicates that k_1' is exceedingly greater than k_{-2}^*, the shift of titration curve b from curve a is to be ascribed to a difference between $1/(k_2^*\tau_0)$ and K_a but not that between $1/(k_2^*\tau_0)$ and $(\tau_\infty/\tau_0)K_a^*$. Thus the observed shift is not a direct indication of the enhancement of excited-state basicity, although the Förster cycle predicts a greater reduction of the proton-dissociation constant in the excited state.

The increase of quenching rate with increasing ionic strength supports a diffusion-controlled mechanism of the positively charged species, *[Ru(bpz)(bpy)$_2$]$^{2+}$ and $\mathrm{H_3O^+}$ (Figure A1). The dependence on the ionic strength is described by[18,20]

$$\ln k_q = \ln k_q^0 + \frac{2'\alpha Z_1 Z_2 \mu^{1/2}}{1 + \beta a \mu^{1/2}} \tag{10}$$

where Z_1 and Z_2 are the charges on the excited complex and the quencher, respectively, $\alpha = (e^2/2\epsilon k_B T)\beta$, $\beta = (8\pi N e^2/1000\epsilon k_B T)^{1/2}$, N is the Avogadro constant, k_B is the Boltzmann constant, and a is the distance between the excited complex and the quencher at extreme approach. An extrapolation down to zero ionic strength by means of the Gauss–Newton method yields the values $k_q^0 = 6 \times 10^9$ M^{-1} s^{-1} and $a = 11$ Å. The value $a = 11$ Å is much greater than expected for the dimension of the protonated complex. This increase of the quenching cross section is attributable to the encounter of the excited complex and a diffusing "four-cluster" structure of the hydrated proton $\mathrm{H_9O_4^+}$ in aqueous solution. The structure of $\mathrm{H_9O_4^+}$ was hypothesized as the most probable hydrating unit of the proton by which a very fast rearrangement of the hydrogen bond in the normal water structure yields the proton-donating cluster.[21] In contrast with the value of $a = 11$ Å for the quenching by $\mathrm{H_3O^+}$, a reasonable sum of the radii was obtained in the case of the quenching by [Fe(CN)$_6$]$^{3-}$.

Table II. Rate Constant of Dynamic Quenching (k_q) and Formation Constant of the Nonluminescent Ion Pair (K) of [Ru(bpz)(bpy)$_2$]$^{2+}$ in the Presence of [Fe(CN)$_6$]$^{3-}$

ionic strength/M^a	$k_q/10^{10}$ M^{-1} s^{-1}	$K/10^2$ M^{-1}
0.003	3.15	12.7
0.01	2.47	7.2
0.02	1.39	3.2
0.09	1.01	1.9
0.16	0.91	0.9

^{a} Adjusted by addition of KCl.

For the quenching by [Fe(CN)$_6$]$^{3-}$, the plot of τ_0/τ gives a straight line, while that of ϕ_0/ϕ curves upward (Figure A2). This suggests a parallel mechanism not only of dynamic quenching but also of static quenching. [Ru(bpz)(bpy)$_2$]$^{2+}$ partly forms a nonemissive contact ion pair with [Fe(CN)$_6$]$^{3-}$. The ratio of lifetimes in the absence and presence of the quencher [Fe(CN)$_6$]$^{3-}$ and the corresponding ratio of emission yields are given respectively by

$$\tau_0/\tau = 1 + k_q\tau_0[\mathrm{Q}] \tag{11}$$

and

$$\phi_0/\phi = 1 + (k_q\tau_0 + K)[\mathrm{Q}] + (k_q\tau_0 K)[\mathrm{Q}]^2 \tag{12}$$

where τ_0 is the lifetime of *[Ru(bpz)(bpy)$_2$]$^{2+}$, [Q] is the concentration of the quencher, k_q is the rate constant of the diffusion-controlled quenching process and K is the formation constant for the nonemissive ion pair. From the best fits, k_q and K were determined as functions of ionic strength μ as summarized in Table II. The plot of $\ln k_q$ against $\mu^{1/2}$ yields $k_q^0 = 6 \times 10^{10}$ M^{-1} s^{-1} and $a = 14$ Å. The distance of extreme approach 14 Å is a reasonable sum of the radii of [Ru(bpz)(bpy)$_2$]$^{2+}$ (7 Å) and [Fe(CN)$_6$]$^{3-}$ (5 Å). Since

$$(\phi_0/\phi)/(\tau_0/\tau) = 1 + K[\mathrm{Q}] \tag{13}$$

the plot depends only on the formation constant K of the nonemissive ion pair. The K varies with ionic strength μ according to the following relationship:[20]

$$\ln K = \ln K^0 + \frac{2\alpha Z_1 Z_2 \mu^{1/2}}{1 + \beta a \mu^{1/2}} \tag{14}$$

where Z_1, Z_2, α, β, and a are the same as defined in eq 10. The plot of $\ln K$ versus $\mu^{1/2}$ yields $K^0 = 3200$ M^{-1} and $a = 12$ Å, the latter of which is consistently closer than the extreme approach (14 Å) obtained from the kinetic data. However, it is concluded that the electron transfer essential to the quenching arises in an ion pair of similar dimension regardless of whether the ion pair is formed by the thermal equilibrium in solution or by the diffusion-controlled encounter.

The kinetics of emission decay of Ag$^+$-containing aqueous solutions were studied. Figure 5b shows a change of the absorption spectrum of [Ru(bpz)(bpy)$_2$]$^{2+}$ with increasing concentration of hydrated Ag$^+$ ion in solution. Band I shows a red shift yielding isosbestic points with increasing [Ag$^+$] up to 6.4×10^{-1} M. The spectral change is ascribed to the formation of [Ru(bpzAg)(bpy)$_2$]$^{3+}$, in which a hydrated Ag$^+$ ion is coordinated to one of the bipyrazine peripheral nitrogens. Further red shift of band I and the slight shift of the isosbestic point observed with increased [Ag$^+$] ($>6.4 \times 10^{-1}$ M) are attributable to the formation of [Ru(bpzAg$_2$)(bpy)$_2$]$^{4+}$. Figure 5a presents the change in the emission spectrum with increasing [Ag$^+$]. Hydrated Ag$^+$ ion gives rise to a red shift of the emission band in contrast with $\mathrm{H_3O^+}$, which only reduces the emission intensity. [Ru(bpzAg)(bpy)$_2$]$^{3+}$ emits at longer wavelengths than [Ru(bpz)(bpy)$_2$]$^{2+}$. The luminescence decays measured with varied [Ag$^+$] are all single exponentials. Emission lifetimes were determined as a function of [Ag$^+$]. The ratio of the lifetimes in the absence and presence of Ag$^+$ ion, τ_0/τ, increases with [Ag$^+$] but the plot of τ_0/τ against log [Ag$^+$] exhibits a plateau when [Ag$^+$] is increased up to (2–4) $\times 10^{-1}$ M. The lifetime of [Ru(bpzAg)(bpy)$_2$]$^{3+}$ at 25 °C was

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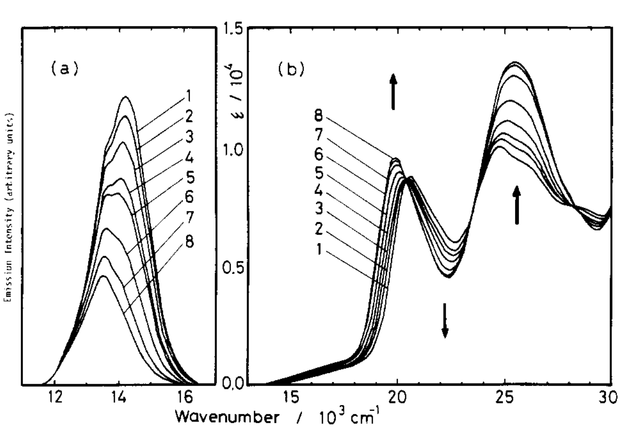

Figure 5. (a) Emission spectra of $[Ru(bpz)(bpy)_2]^{2+}$ in aqueous solution as a function of $[Ag^+]$ ($[Ag^+]$: 0.0 M (1); 5.8×10^{-3} M (2); 1.2×10^{-2} M (3); 2.3×10^{-2} M (4); 2.9×10^{-2} M (5); 5.8×10^{-2} M (6); 1.2×10^{-1} M (7); 2.3×10^{-1} M (8). $\mu = 1.00$ M). (b) Absorption spectra under the same conditions ($[Ag^+]$: 0.0 M (1); 1.6×10^{-2} M (2); 3.2×10^{-2} M (3); 6.4×10^{-2} M (4); 1.6×10^{-1} M (5); 6.4×10^{-1} M (6); 1.9 M (7); 2.6 M (8). $\mu = 3.00$ M).

determined to be 66 ns by the plateau value τ_∞.

The decay lifetime continuously varies from τ_0 to τ_∞ with increasing $[Ag^+]$. The emission spectrum depends on $[Ag^+]$ as shown in Figure 5a but is invariant regardless of whether it is excited in the absorption band of $[Ru(bpz)(bpy)_2]^{2+}$ or that of $[Ru(bpzAg)(bpy)_2]^{3+}$. This indicates that the equilibrium of complex formation is accomplished in a shorter period than the excited-state lifetimes. The ratio τ_0/τ is described by a relationship corresponding to eq 4 as a function of $[Ag^+]$. If the lifetimes of $^*[Ru(bpz)(bpy)_2]^{2+}$ $(1/k_1)$ and $^*[Ru(bpzAg)(bpy)_2]^{3+}$ $(1/k_1')$ are not so much different and thus $k_2^*[Ag^+] + k_{-2}^* \gg k_1' - k_1$, where k_2^* and k_{-2}^* are the rate constants of complex formation and dissociation in the excited state, the excited-state equilibrium is established within the time constant characterized by $(1/k_1 - 1/k_1')$. Provided that $k_2^*[Ag^+] + k_{-2}^* \gg k_1' - k_1$, the equation of τ_0/τ can be rewritten in a simpler form

$$\tau_0/\tau = \frac{k_1'k_2^*[Ag^+] + k_1k_{-2}^*}{k_{-2}^* + k_2^*[Ag^+]}\tau_0 = \frac{1 + (k_1'/k_1)(k_2^*/k_{-2}^*)[Ag^+]}{1 + (k_2^*/k_{-2}^*)[Ag^+]} \qquad (15)$$

The complex-formation constant K^* in the excited state is defined by the ratio k_2^*/k_{-2}^* of the rate constants of complex formation and dissociation, and thus it follows from (15) that

$$(\tau_0 - \tau)/(\tau - \tau_\infty) = (\tau_0/\tau_\infty)K^*[Ag^+] \qquad (16)$$

where τ_0 and τ_∞ are the experimentally determined constants ($\tau_0 = 1/k_1 = 88$ ns; $\tau_\infty = 1/k_1' = 66$ ns). From the decay lifetimes, which continuously vary from τ_0 to τ_∞ with increasing $[Ag^+]$, the complex-formation constant in the excited state was determined by eq 16 to be $K^* = 130$ M^{-1} at 25 °C and $\mu = 3.0$ M. On the other hand, the formation constant in the ground state was obtained to be $K = 20$ M^{-1} at 25 °C and $\mu = 3.0$ M by absorption measurements. It is noted that the complex formation in the excited state is appreciably enhanced as compared with that of the ground state.

Concluding Remarks. $[Ru(bpz)(bpy)_2]^{2+}$ emits phosphorescence at room temperature from the lowest "ruthenium-to-bipyrazine" charge-transfer excited state. However, the protonated complex $[Ru(bpzH)(bpy)_2]^{3+}$ is nonemissive. Even in such dilute acidic media where no protonated species can be detected, the phosphorescence is partly quenched by H_3O^+. A remarkable displacement observed with the titration curves obtained by absorption and emission intensity measurements is to be attributed to a difference between $1/(k_2^*\tau_0)$ and K_a or that of $(\tau_\infty/\tau_0)K_a^*$ and K_a depending upon whether $k_1' \gg k_{-2}^*$ or $k_1' \ll k_{-2}^*$. With the quenching of $^*[Ru(bpz)(bpy)_2]^{2+}$ by H_3O^+, the relation $\phi_0/\phi = \tau_0/\tau$ is observed for a wide range of the quencher concentration, which is valid only when $k_1' \ll k_{-2}^*$, and thus the process is governed by a bimolecular diffusing encounter of the excited complex and the quencher in solution. In fact, the observed value of k_q is a typical diffusion-controlled rate. Therefore, the shift of the emission titration curve is to be ascribed to a difference of $1/(k_2^*\tau_0)$ and K_a but not a direct indication of the reduction of proton-dissociation constant in the excited state. Nevertheless, we do claim that the metal–bipyrazine charge-transfer excitation increases the basicity of peripheral nitrogens of coordinated bipyrazine on the basis of a Förster cycle calculation with the energy value of the lowest triplet state of nonemissive $[Ru(bpzH)(bpy)_2]^{3+}$ detected by the second-derivative absorption spectrum in the present work.

$[Ru(bpzAg)(bpy)_2]^{3+}$ is emissive in contrast with $[Ru(bpzH)(bpy)_2]^{3+}$. This makes it possible to detect a difference in the stability of the complex of hydrated Ag^+ ion with the excited- and ground-state $[Ru(bpz)(bpy)_2]^{2+}$ in solution. An increase in the complex-formation constant of excited $[Ru(bpz)(bpy)_2]^{2+}$ found in the present work is attributable to the enhancement of the excited-state basicity.

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Supplementary Material Available: A plot of the rate constant of quenching of $^*[Ru(bpz)(bpy)_2]^{2+}$ by H_3O^+ as a function of ionic strength (Figure A1) and the Stern–Volmer plots of phosphorescence lifetime (τ) and yield (ϕ) as a function of concentration of $[Fe(CN)_6]^{3-}$ (Figure A2) (2 pages). Ordering information is given on any current masthead page.