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Time-Resolved Emission Spectroscopy of Ru(II) Complexes around the Glass Transition Temperature of the Medium: Counteranion, Ligand, and Solvent Effects

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Time-resolved emission spectroscopy of Ru(II) complexes was conducted around the glass transition temperature of a medium (T_g) focusing on the effects of counteranions ($Ru(bpy)_3X_2$; bpy = 2,2′-bipyridine, X = Cl^-, ClO_4^-, and PF_6^-), bulky ligands (4,4′-diphenyl-2,2′-bipyridine), polar ligands (CN^- and 2,2′-bipyrazine), and solvents on time-dependent (TD) emission shifts. All the Ru(II) complexes examined showed TD emission shifts in ethanol–methanol (4/1 v/v) between 120 and 150 K. $Ru(bpy)_3^{2+}$ showed a TD emission shift in alcoholic solvents (ethanol, 1-propanol, and 1-hexanol) while no TD shift was observed in aprotic solvents (dimethyl sulfoxide, propylene carbonate, and acetonitrile). The TD emission shift of $Ru(bpy)_3^{2+}$ was delayed in the alcoholic solvents when the solvents were deuterized. The amount of TD shift, the relaxation time, and the temperature dependence were shown not to be intrinsic properties of Ru(II) complexes but to be caused by time dependence of solute–solvent interactions. Hydrogen bonding between a solute and solvent molecules is one of important factors determining the TD emission shift of Ru(II) complexes. The anomalous temperature dependence of the excited-state lifetime determined from time evolution of the relative emission quantum yield is also discussed.

Introduction

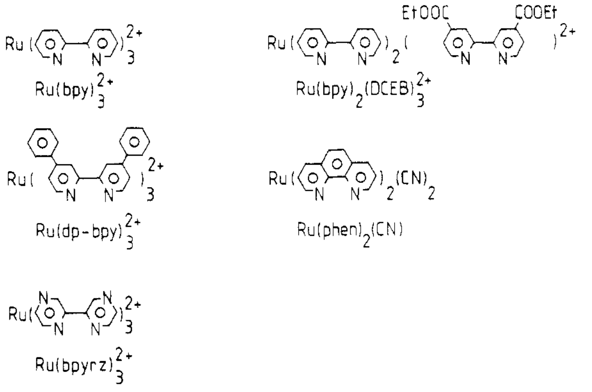
The metal-to-ligand charge-transfer (MLCT) excited state of polypyridyl complexes of d^6 transition metals such as $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ (bpy = 2,2′-bipyridine) are quite characteristic since their spectroscopic and excited-state properties are largely dependent on temperature, solvent, pressure, and so forth.[1] Various factors influencing these properties include thermal repopulation among the excited-state levels,[2-4] the specific solute–solvent interactions (donor–acceptor interaction[5] and/or charge transfer to solvent (CTTS)[6]), the rigidity of the medium,[7] and so forth.

In particular, the excited state of $Ru(bpy)_3^{2+}$ is highly sensitive to temperature variation. In a rigid medium far below its glass-to-fluid transition temperature (T_g), the emission spectrum is sharp and structured with its lifetime of several microseconds. In a fluid medium above T_g, on the other hand, the spectrum becomes broad and structureless, and the lifetime decreases dramatically with increasing temperature.[1,8] Around T_g the emission spectrum strongly depends on time in the nanosecond to microsecond time regime.[9-12] The observation of such a time-dependent (TD) emission shift of $Ru(bpy)_3^{2+}$ by Ferguson et al.[9] and us[10] revealed a possibility of environment-assisted charge localization in the MLCT excited state.

Ferguson et al. have reported that the TD emission shift of $Ru(bpy)_3Cl_2$ is caused by the motion of the surrounding counteranions (Cl^-) in the MLCT excited state.[9] The driving force of such motion is the change in the excited-state dipole moment caused by transition from the charge-delocalized MLCT excited state to the localized one; $Ru^{II}(bpy)_3^{2+}$ ($\sim$0 D) + $h\nu \rightarrow Ru^{III}(bpy^{1/3-})_3^{2+}$ ($\sim$0) $\rightarrow Ru^{III}(bpy)_2(bpy^-)^{2+}$ (14.1).[13] Contrary to Ferguson et al., we suggested that the charge localization was assisted by solvent relaxation but not by the motion of counteranions of $Ru(bpy)_3^{2+}$.[9] However, recent results of resonance Raman[14] and transient absorption spectroscopy[15] showed no spectral change in the picosecond to nanosecond time scale and it was concluded that the charge localization took place in the picosecond to subpicosecond time scale. Therefore, the TD emission shift is not caused by the charge localization process itself.

As an alternative explanation for the TD emission shift, solvent dipole relaxation can be considered. For polar excited molecules, a TD emission shift is a common phenomenon and both experimental and theoretical studies on the solvent relaxation have been active area of research.[16-18] Indeed, photophysical processes and photo/thermal redox processes have been discussed on the basis of solvent relaxation dynamics. For $Ru(bpy)_3^{2+}$ and its related

SCHEME I



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complexes, the excited-state dipole moment exceeds 10 D so that the excited state is susceptible to solvent relaxation. To reveal the photophysical processes of Ru(II) complexes at low temperature, we performed nanosecond time-resolved emission spectroscopy of Ru(II) complexes (Scheme I) from the viewpoints of elucidating the effects of counteranions, bulky ligands, polar ligands, and solvent on the TD low-energy shift of emission.

Experimental Section

Materials. The structures and abbreviations of Ru(II) complexes used in this study were shown in Scheme I.

All the Ru(II) complexes except $Ru(phen)_2(CN)_2$ were prepared as their chloride salts. $Ru(bpy)_3^{2+}$ and $Ru(dp–bpy)_3^{2+}$ were obtained by refluxing $Ru(DMSO)_4Cl_2$ with an excess amount of the ligands in ethanol. $Ru(bpyrz)_3^{2+}$ was prepared according to the method of Crutchley and Lever.[19] $Ru(bpy)_2(DCEB)^{2+}$ was synthesized by refluxing *cis*-$Ru(bpy)_2Cl_2$ with an equimolar amount of DCEB in *N*,*N*-dimethylformamide. The corresponding PF_6^- or ClO_4^- salts were obtained by exchanging the counteranions with NH_4PF_6 or NH_4ClO_4 in aqueous solution, respectively. The crude salts were collected, washed successively with cold water and diethyl ether, and then dried in vacuo. These complexes were purified by column chromatography on alumina (PF_6^- and ClO_4^- salts) or by repeated recrystallizations from water (Cl^- salt). The elemental analyses were in satisfactory agreement (as chloride salts). $Ru(phen)_2(CN)_2$ was the same sample reported previously.[5]

Ethanol, methanol, 1-propanol, 1-hexanol (spectroscopic grade, Tokyo Kasei Kogyo Co., Ltd.), ethanol-*O*-*d*, and methanol-*O*-*d* (99%, *Merck*) were used without further purification. Propylene carbonate and dimethyl sulfoxide were distilled after drying over predried molecular sieve (4A, Merck, 24 h at 200 °C in vacuo). Acetonitrile was purified by the literature method.[20]

Sample solutions were prepared prior to measurements and were deaerated by argon gas purging over 30 min.

Measurements. Nanosecond time-resolved emission spectroscopy was carried out by the system reported previously.[7,10,21] The sample was excited by a Nd:YAG laser (Quanta Ray, DCR-1, 355 nm, pulse width ~6 ns, repetition rate = 0.2 or 0.5 Hz). The emission was detected by a gated multichannel plate/photodiode array detector (Princeton Instruments Inc./Tokyo Instruments Inc., IRY-512G, gate width ~5 ns). The instrumental response of the system was corrected by the use of known emission spectra of $Ru(bpy)_3^{2+}$ and $Ru(phen)_2(CN)_2$ recorded on a Hitachi MPF-4 spectrofluorometer. Data processing was performed by a NEC PC-9801m microcomputer.

Temperature control was achieved by a liquid nitrogen cryostat (Oxford Instrument Inc. DN1704 optical Dewar bottle and 3120 temperature controller). The sample solution was cooled down to T_g or the freezing point (fp) of the solvent. After being kept at the temperature over 1.5 h the sample was cooled down again to 77 K (220 K in acetonitrile or 285 K in dimethyl sulfoxide), kept at the temperature for 1 h, and then slowly heated to a desired temperature. Such procedures resulted in always optically transparent glass and were suitable for emission spectroscopy. The measurements were made after thermal equilibration of the sample solutions by keeping over 30 min at a given temperature.

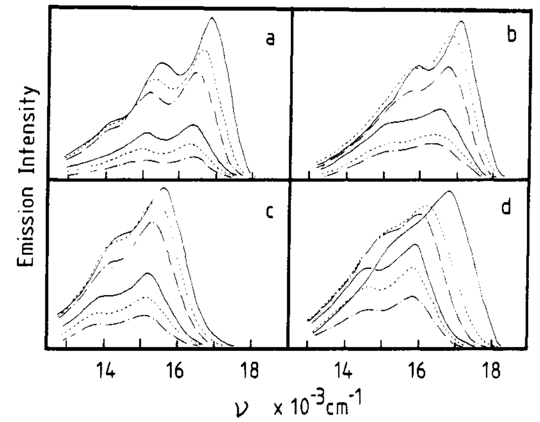

Figure 1. Time-resolved emission spectra of Ru(II) complexes in EtOH-MeOH (4/1 v/v) at 125 K: (a) $Ru(bpy)_3^{2+}$, (b) $Ru(bpyrz)_3^{2+}$, (c) $Ru(bpy)_2(DCEB)^{2+}$, and (d) $Ru(phen)_2(CN)_2$ (gate width 5 ns; delay time 0, 0.2, 0.6, 1.0, 2.0, 3.0, and 4.0 μs after excitation).

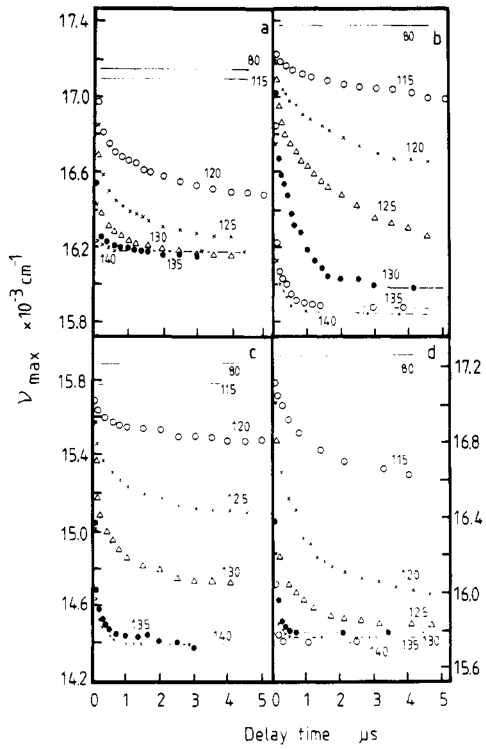

Figure 2. Time and temperature dependence of the emission maximum in EtOH-MeOH (4/1 v/v): (a) $Ru(bpy)_3^{2+}$, (b) $Ru(bpyrz)_3^{2+}$, (c) $Ru(bpy)_2(DCEB)^{2+}$, and (d) $Ru(phen)_2(CN)_2$. Horizontal lines represent the absence of the time-dependent shift.

TABLE I: Counteranion and Ligand Effect on Time-Dependent Emission Maximum and Amount of TD Shift in Ethanol–Methanol (4/1 v/v) at 125 K

	ν_0,[a] 10^3 cm^{-1}	ν_∞,[b] 10^3 cm^{-1}	$\Delta\nu$,[c] cm^{-1}
$Ru(bpy)_3X_2$ (X = Cl^-)	16.84	16.22	620
$Ru(bpy)_3X_2$ (X = ClO_4^-)	16.89	16.25	640
$Ru(bpy)_3X_2$ (X = PF_6^-)	16.88	16.26	620
$Ru(dp–bpy)_3(PF_6)_2$	16.69	16.04	650
$Ru(bpyrz)_3Cl_2$	17.11	16.26	850
$Ru(bpy)_2(DCEB)(PF_6)_2$	15.62	15.09	530
$Ru(phen)_2(CN)_2$	16.83	15.80	1030

[a] Emission maximum immediately after laser excitation. [b] Emission maximum after 3–4 μs. [c] $\Delta\nu = \nu_0 - \nu_\infty$.

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Results and Discussion

General Features of Time-Dependent Emission Spectroscopy. We performed nanosecond time-resolved emission spectroscopy on $Ru(bpy)_3X_2$ ($X = Cl^-$, ClO_4^-, or PF_6^-), $Ru(dp\text{–}bpy)_3(PF_6)_2$, $Ru(bpyrz)_3Cl_2$, $Ru(bpy)_2(DCEB)(PF_6)_2$, and $Ru(phen)_2(CN)_2$ in ethanol–methanol (EtOH–MeOH; 4/1 v/v) at various temperatures (80–298 K). All the complexes exhibited time-dependent (TD) low-energy emission shift in the temperature range between 120 and 150 K (Figure 1). The time dependence of the emission maximum energy (ν_{max}) at a given temperature is shown in Figure 2. Below 110 K, the ν_{max} of each Ru(II) complex was constant regardless of the delay time after laser excitation. Between 120 and 150 K, the TD emission shift becomes faster with increasing temperature, and above 150 K, the TD emission shift is no longer measurable in the nanosecond time scale.

For qualitative discussion, we define ν_0 and ν_∞ as ν_{max} at $t = 0$ and $t = \infty$ (typically, $t = 3\text{–}4\ \mu s$), respectively. $\Delta\nu$ represents $(\nu_0 - \nu_\infty)$ in cm^{-1}. The results in EtOH–MeOH at 125 K are summarized in Table I. Table I clearly indicates that $\Delta\nu$ are comparable at 530–650 cm^{-1} for $Ru(bpy)_3X_2$, $Ru(dp\text{–}bpy)_3^{2+}$, and $Ru(bpy)_2(DCEB)^{2+}$ while the other complexes, $Ru(bpyrz)_3^{2+}$ and $Ru(phen)_2(CN)_2$, show much larger $\Delta\nu$ (850–1030 cm^{-1}).

Effects of Counteranion and Ligand Structure. Ferguson et al. have suggested that the movement of the counteranions (X^-) in $^*Ru(bpy)_3^{2+}$ is the origin of the TD emission shift.[9] X^- in the nonequilibrium position in the Franck–Condon excited state must be relaxed until it reaches the equilibrated state where $^*Ru(bpy)_3^{2+}$ and X^- are in equilibrium electrostatically. Nonetheless, this interpretation emphasizing the role of counteranion is in contradiction to the results in Table I. Table I proves that the nature of X^- in $Ru(bpy)_3X_2$ has almost no effect on the TD emission shift. Much larger $\Delta\nu$ values of $Ru(phen)_2(CN)_2$, which does not possess any counteranion, relative to that of $Ru(bpy)_3^{2+}$ are also against the interpretation by Ferguson.

The presence of bulky substituents on ligands may be expected to influence the TD emission shift. However, $\Delta\nu$ of $Ru(dp\text{–}bpy)_3^{2+}$ is not affected as seen in Table I.

The finding that $\Delta\nu$ (=530 cm^{-1}) of an unsymmetrical complex, $Ru(bpy)_2(DCEB)^{2+}$, is comparable to that of $Ru(bpy)_3^{2+}$ or $Ru(dp\text{–}bpy)_3^{2+}$ also provides key information to the relevancy of $\Delta\nu$ to the symmetry reduction in the MLCT excited state. In $Ru(bpy)_2(DCEB)^{2+}$, an excited electron is localized on the DCEB ligand (C_2 symmetry).[9] If the transition from the delocalized excited state (D_3 symmetry) to the localized one (C_2) is primarily responsible for the present TD emission shift, ν_{max} of $Ru(bpy)_2(DCEB)^{2+}$ should not exhibit the TD shift. Nevertheless, the TD shift was observed for $Ru(bpy)_2(DCEB)^{2+}$ similar to $Ru(bpy)_3^{2+}$. Previously, we suggested that the TD shift of $Ru(bpy)_3^{2+}$ was attributed to the symmetry reduction in the excited state in our preliminary communication.[10] However, our present systematic studies, in addition to the picosecond time-resolved resonance Raman study by Carroll and Brus,[14] nanosecond time-resolved emission polarization experiments by DeArmond and his coworkers,[22] transient CD spectroscopy by Kliger et al.,[23] time-resolved emission spectroscopy for monopyridyl complex ($Os(phen)(1,2\text{-dimethylarsinobenzene})_2^{2+}$) by Meyer et al.,[11] and so forth lead to the conclusion that the origin of TD emission shift of $Ru(bpy)_3^{2+}$ and its analogous complexes between 120 and 150 K is not ascribable to the transition from the charge-delocalized excited state to the charge-localized one in the MLCT excited state.

The MLCT excited state of $Ru(phen)_2(CN)_2$ or $Ru(bpyrz)_3^{2+}$ showing much larger $\Delta\nu$ (850 or 1030 cm^{-1}) strongly interacts with the surrounding solvent molecules, particularly with alcoholic solvents. For $Ru(phen)_2(CN)_2$, both ground and excited states are subjected to electron donor–acceptor interaction with electron-accepting solvents as demonstrated by solvent effects on the spectroscopic (absorption/emission energies and their spectral half-width) and excited-state properties (emission lifetime and its temperature dependence).[5] The 4,4′ nitrogen atoms of bpyrz in $Ru(bpyrz)_3^{2+}$ exhibit intensive interaction with solvent as well.[19] These studies demonstrated that the stronger the interactions between the complex and the solvent molecules, the broader and more featureless the emission spectrum. Close inspection of the spectra in Figure 1 indicates that the vibrational structures of the emission spectrum change with time for $Ru(phen)_2(CN)_2$ and $Ru(bpyrz)_3^{2+}$ while those for the other complexes with $\Delta\nu$ = 530–650 cm^{-1} seem to be almost independent of time.[24] The time-dependent emission band shape of $Ru(phen)_2(CN)_2$ or $Ru(bpyrz)_3^{2+}$ suggests the changes in the excited-state interactions between the complex and solvent molecules with time.[5] The results of counteranion and ligand effects clearly show that the TD emission shift is not an intrinsic property of Ru(II) complex but is caused by time-dependent solute–solvent interaction.

TABLE II: Solvent Effect on Time-Dependent Emission Shift of $Ru(bpy)_3^{2+}$ at 125 K

solvent	fp or T_g, K	ν_0, 10^3 cm^{-1}	ν_∞, 10^3 cm^{-1}	$\Delta\nu$, cm^{-1}	T_{range},[a] K
EtOH–MeOH (4/1)	130	16.88	16.26	620	120–150
EtOD–MeOD (4/1)		17.05	16.47	580	120–160
1-propanol	147	17.27	16.97	300	120–170
EtOH	159	17.15	16.94	210	125–170
1-hexanol	228	17.30	17.30	0[b]	160–230
dimethyl sulfoxide[c]	291	*d*			
acetonitrile[c]	229	*d*			
propylene carbonate[c]	224	17.04	17.04	0	

[a] Temperature range observed time-dependent emission shift. [b] ν_0 = 16.59 × 10^3 cm^{-1}, ν_∞ = 16.27 × 10^3 cm^{-1}, and $\Delta\nu$ = 320 cm^{-1} at 230 K. [c] The emission spectra were independent of delay time in DMSO (285–295 K), ACN (225–298 K), and PC (100–298 K). [d] Emission spectra cannot be measured since DMSO and ACN do not form optically transparent glass.

Solvent Effects on the TD Emission Shift. To confirm the roles of solvent for the TD emission shift, we performed nanosecond time-resolved emission spectroscopy in various solvents, and the data at 125 K are summarized in Table II.

In alcoholic solvents $Ru(bpy)_3^{2+}$ showed the TD emission shift. However, the temperature range (T_{range}) in which the TD emission shift is observable strongly depends on the solvent; the higher fp or T_g of the solvent, higher the T_{range} and also the smaller the $\Delta\nu$ at 125 K. This is easily understandable since the motion of solvent molecules is gradually suppressed upon cooling around fp or T_g and is restricted far below T_g or fp. Consequently, the TD emission shift becomes observed in higher temperature region in the solvent having higher fp or T_g. The decrease in $\Delta\nu$ at 125 K with an increase in fp or T_g is also explainable by the similar context as described above. Increase in the static pressure brings about sharpening and higher energy shift of the $Ru(bpy)_3^{2+}$ emission at low temperature and a smaller $\Delta\nu$ at a given temperature.[7] Delayed solvation owing to increase in viscosity when the pressure is applied is the reason. Thus, temperature and pressure can be considered as relevant parameters in view of viscosity effects on the TD shift of Ru(II).

In nonalcoholic solvent such as dimethyl sulfoxide (DMSO), propylene carbonate (PC), and acetonitrile (ACN), ν_{max} of $Ru(bpy)_3^{2+}$ was independent of time in spite of the similarity in fp (ACN, 229 K; 1-hexanol, 228 K). These results explicitly manifest the specific role of the alcoholic –OH group in the TD emission shift. The fact that solvent deuteration affects both emission lifetime (580 ns in H_2O and 1020 ns in D_2O at 298 K)[25] and the rate of TD shift (relaxation time, discussed later) is in support of the present discussion on the role of the –OH group. Much

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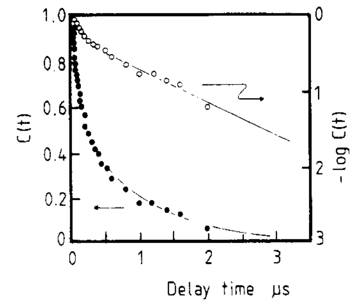

Figure 3. Time dependence of the Stokes correlation function obtained for $Ru(bpy)_3^{2+}$ in EtOH-MeOH (4/1 v/v) at 125 K. ○ and ● are experimental data, and solid lines are best-fit curves by a double-exponential function (eq 2).

TABLE III: Relaxation Times and Their Activation Parameters of Ru(II) Complexes in Ethanol-Methanol (4/1 v/v) at 125 K[a]

	τ_s^1 (int %[b]), ns	τ_s^2, ns	E_a^1 ($\log A^1$), cm^{-1}	E_a^2 ($\log A^2$), cm^{-1}
$Ru(bpy)_3^{2+}$	150 (10.3)	1000	960 (11.7)	1200 (11.8)
$Ru(dp\text{-}bpy)_3^{2+}$	97 (7.0)	1200	790 (11.1)	820 (10.1)
$Ru(bpyrz)_3^{2+}$	140 (2.1)	1900	2200 (16.9)	1400 (13.9)
$Ru(bpy)_2(DCEB)^{2+}$	150 (7.8)	1200	1000 (11.9)	1200 (12.0)
$Ru(phen)_2(CN)_2$	130 (20.5)	940	2500 (19.4)	1600 (14.4)

[a] Uncertainties for the values are τ_s^1, ±15%; τ_s^2, ±10%. [b] Fraction of the component in percent.

larger $\Delta\nu$ values (850–1030 cm^{-1} in Table I) of $Ru(phen)_2(CN)_2$ and $Ru(bpyrz)_3^{2+}$ as compared with those of other Ru(II) complexes ($\Delta\nu$ = 530–650 cm^{-1}) are also in good agreement with the above discussion.

Consequently, the origin of TD emission shift of Ru(II) complexes is concluded to be the time-dependent solute–solvent interaction governed by solvent motion and/or hydrogen-bonding interaction.

Relaxation Time of Ru(II) Complexes. To analyze the present TD emission shift of Ru(II), we introduce the following Stokes shift correlation function:[16-18]

$$C(t) = \frac{\nu_t - \nu_\infty}{\nu_0 - \nu_\infty} \qquad (1)$$

where ν_t is ν_{max} at a given delay time, t. In Figure 3, $C(t)$ of $Ru(bpy)_3^{2+}$ in EtOH-MeOH is shown as a function of t. As clearly seen in Figure 3, $C(t)$ does not decay single exponentially but can be fitted by using a double-exponential function:

$$C(t) = \sum_{i=1}^{2} A^i \exp(-t/\tau_s^i) \qquad (2)$$

Other Ru(II) complexes also gave analogous results. Nonlinear least-squares analysis of $C(t)$ vs t plots yielded sets of the relaxation times, τ_s^1 and τ_s^2, for five Ru(II) complexes. Furthermore, we observed linear Arrhenius plots for both τ_s^1 and τ_s^2 as typically shown in Figure 4. τ_s^1 and τ_s^2 at 125 K and their activation parameters are summarized in Table III.

In a polar solution a TD emission shift is a common phenomenon when the solute has a large dipole moment in the excited state. Theoretical and experimental studies on the phenomena have been active fields, and the microscopic solvation dynamics has been discussed. The solute–solvent system initially produced upon excitation possesses a nonequilibrium configuration and, thus, must relax toward the equilibrium one through rotational and translational motions of the surrounding solvent molecules. Therefore, the analysis of the TD emission shift (i.e., $C(t)$ vs t plot) gives the solvent relaxation time, τ_s.[17,18] Depending on the solvation model, however, the meaning of τ_s is different. In a simple solvation model, it is assumed that a specific solute–solvent interaction is neglected and the solute molecule is considered as a point dipole in a spherical cavity embedded in a dielectric continuum. In this idealized case, $C(t)$ should decay single exponentially with a time constant of the longitudinal relaxation time of the pure solvent. In alcohols two or three time constants are observed and they have been reported to be closely related to hydrogen-bonding interaction.[18] Unfortunately, a sufficient theoretical interpretation has not been put forward yet.

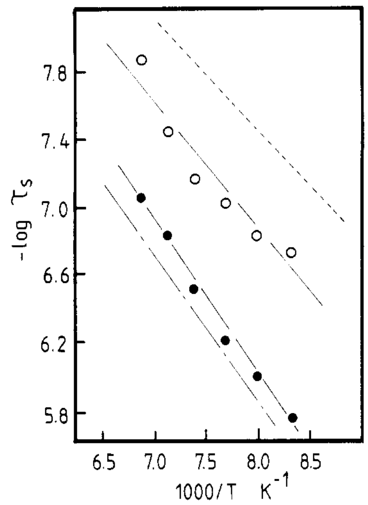

Figure 4. Temperature dependence of τ_s^1 (○) and τ_s^2 (●) of $Ru(bpy)_3^{2+}$ in EtOH-MeOH (4/1 v/v) together with τ_D (— —) and τ_L (- - -) of pure ethanol.

The observed τ_s's and the activation parameters for $Ru(bpy)_3^{2+}$, $Ru(dp\text{-}bpy)_3^{2+}$, and $Ru(bpy)_2(DCEB)^{2+}$ gave similar values (τ_s^1 = 100–150 ns, τ_s^2 = 1000–1200 ns, E_a^1 = 800–1000 cm^{-1}, and E_a^2 = 800–1200 cm^{-1}). These values are almost comparable with Debye (τ_D) and longitudinal (τ_L) relaxation time of pure ethanol at 125 K and their activation energies: 1400 ns (1100 cm^{-1}) and 40 ns (1400 cm^{-1}), respectively.[26] As discussed in the previous section, however, the TD emission shift is closely related to the specific interaction involving the hydroxyl group so that the discussion based on the simple solvent dipole relaxation model will not be adequate. In fact, the activation energies of τ_s for $Ru(phen)_2(CN)_2$ and $Ru(bpyrz)_3^{2+}$ which interact strongly with solvent molecules are much larger (E_a^1 = 2200–2500 cm^{-1} and E_a^2 = 1400–1600 cm^{-1}) than those of other Ru(II) complexes in the same solvent. Furthermore, the TD emission shift of $Ru(bpy)_3^{2+}$ in EtOD-MeOD is slower than that in EtOH-MeOH; τ_s^1 = 100 ns and τ_s^2 = 1700 ns. The results manifest that the motion of –OH (or –OD) or hydrogen bonding is closely related to the relaxation process.

Time-resolved emission spectroscopy of dye molecules in the picosecond to femtosecond time region has been tried to correlate the TD emission shift with τ_L and/or τ_D even in alcoholic solvent.[18] Unambiguous conclusion will not be expected unless the intrinsic nature of solvation dynamics including specific solute–solvent interaction is explored. In this respect, solvent deuteration effect will be very informative.

Excited-State Lifetime of Ru(II) Complexes. The TD emission shift of Ru(II) complexes brings about a complex time evolution of the emission intensity monitored at a fixed frequency, $I_{em}(\nu,t)$. That is, a non-single-exponential emission decay depending on the monitoring frequency should be observed as briefly reported for $Ru(bpy)_3^{2+}$.[12] When the emission was monitored at the higher energy edge of the 0–0 emission band, fast and slow decays were observed while a fast rise and a slow decay of the emission appeared by monitoring the lower energy edge. Analogous results are also obtained for other Ru(II) complexes around fp or T_g of the medium as shown in Figure 5. Under such circumstances, the excited-state lifetime of a complex cannot be determined by $I_{em}(\nu,t)$, which includes an artifact owing to the TD emission shift. We determined the excited-state lifetime based on the time evolution of the relative emission quantum yield, $\Phi_{rel}(t)$, i.e., time evolution of the integrated emission spectrum. $\Phi_{rel}(t)$ decays single

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(26) τ_D and τ_L at 125 K for pure ethanol were extrapolated from the temperature dependence obtained around room temperature.[18]

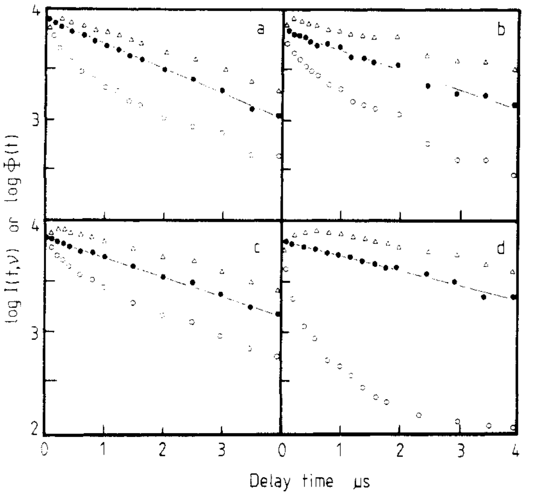

Figure 5. Time evolution of the relative emission quantum yield ($\Phi_{rel}(t)$, ●) and emission intensities monitored at different frequencies (○ = higher energy edge and △ = lower energy edge of 0–0 emission band) of Ru(II) complexes in EtOH–MeOH (4/1 v/v) at 125 K: (a) Ru(bpy)$_3^{2+}$, (b) Ru(bpyrz)$_3^{2+}$, (c) Ru(bpy)$_2$(DCEB)$^{2+}$, and (d) Ru(phen)$_2$(CN)$_2$.

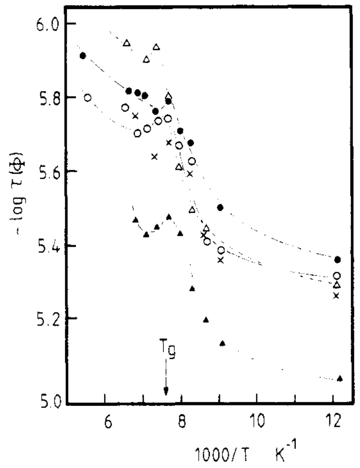

Figure 6. Temperature dependence of $\tau(\Phi)$ in EtOH–MeOH(4/1 v/v): Ru(bpy)$_3^{2+}$ (○), Ru(dp-bpy)$_3^{2+}$ (●), Ru(bpyrz)$_3^{2+}$ (×), Ru(bpy)$_2$(DCEB)$^{2+}$ (△), and Ru(phen)$_2$(CN)$_2$ (▲).

exponentially for all Ru(II) complexes irrespective of the presence and absence of a TD emission shift (Figure 5). The excited-state lifetime ($\tau(\Phi)$) of Ru(II) at various temperatures is now calculated by

$$\Phi_{rel}(t) = \int I_{em}(\nu,t)\, d\nu$$
$$= \Phi_{rel}(0) \exp(-t/\tau(\Phi)) \qquad (3)$$

Temperature dependence of $\tau(\Phi)$ thus determined for several Ru(II) complexes in EtOH–MeOH is shown in Figure 6. With increasing temperature from 110 to 180 K, $\tau(\Phi)$ of Ru(bpy)$_3^{2+}$ decreases dramatically from 3.9 μs to 1.6 μs. Such dramatical decrease in $\tau(\Phi)$ around T_g is very similar to the temperature dependence of the lifetime determined by the decay of the emission at a fixed wavelength. According to Balzani and co-workers,[8] the large temperature dependence of the emission lifetime can be interpreted by thermal repopulation to the highest sublevel in three degenerated triplet MLCT excited states. Also, our recent results revealed the emission lifetime of Ru(bpy)$_3^{2+}$ was almost independent of the applied pressure (i.e., medium viscosity) at a given temperature while the lifetime strongly depends on temperature at a given pressure.[7] Both results are consistent with each other and manifest that the excited-state lifetime of Ru(II) depends directly on temperature, while the emission maximum energy is controlled by temperature through change in the degree of solvation (medium viscosity).

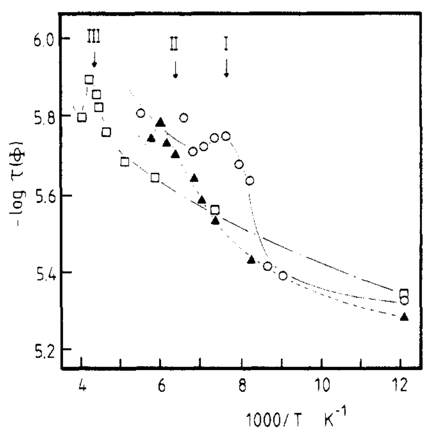

Figure 7. Solvent effects on $\tau(\Phi)$ of Ru(bpy)$_3^{2+}$: EtOH–MeOH (4/1 v/v) (○), 1-propanol (△), and 1-hexanol (□). I, II, and III are T_g (or fp) of EtOH–MeOH, 1-propanol, and 1-hexanol, respectively.

Around T_g of the medium, $\tau(\Phi)$ unexpectedly becomes longer with increasing temperature in EtOH–MeOH and in other alcoholic solvents (Figures 6 and 7). The anomalous $\tau(\Phi)$ vs T^{-1} region is observed around T_g of EtOH–MeOH irrespective of ligands of Ru(II), and the region moves to a higher temperature with increasing fp or T_g of solvent. These results indicate that the phenomena are unequivocally related with medium viscosity.

The phenomena cannot be interpreted by thermal repopulation to other upper lying states such as the fourth short-lived MLCT state[27] and/or nonemissive d–d excited state.[2,4] According to Drickamer et al., the solidification of a medium by applying pressure resulted in sharp drop in the radiative rate constant (k_r) and an increase in the nonradiative rate constant (k_{nr}) for ClRe(CO)$_3$(phen) in non-glass-forming solvents.[28] The temperature dependence of k_r and k_{nr} for Os(bpy)$_3^{2+}$, Os(bpy)$_2$(CO)(py)$^{2+}$,[27] and Ru(3,3′-dihydroxymethyl(bpy))$_3^{2+}$ [29] in EtOH–MeOH around T_g, however, did not show the same trend. Also, an estimation of k_{nr} for Ru(bpy)$_3^{2+}$ around T_g from energy gap law indicates that k_{nr} decreases continuously upon solidification by cooling.[30] Consequently, such solidification effect reported by Drickamer et al. is not at issue for interpretation of the anomalous temperature dependence of $\tau(\Phi)$. The continuous decrease of k_{nr} upon cooling requires that k_r depends on temperature and has a maximum value around T_g as an interpretation of the present anomalous dependence of $\tau(\Phi)$. The estimated values of k_r from emission quantum yield and lifetime usually include large errors, and k_r is treated as a temperature-independent term. However, k_r reported by Meyer et al. for Os(II) complexes depends on temperature around T_g (although small) and has a maximum value, strangely enough, just around T_g.[27] The MLCT state of Ru(bpy)$_3^{2+}$ consists of three degenerated sublevels having different k_r and k_{nr}. Both k_r and k_{nr} of the highest sublevel are largest while the emission quantum yield is highest. Thus, the experimentally estimated value of k_r will include the effect of the thermal repopulation. In support of this, with increasing temperature around T_g the lifetime of Ru(bpy)$_3^{2+}$ decreases while the emission quantum yield increases. This thermal repopulation among the MLCT sublevels may be the origin of the anomalous temperature dependence of $\tau(\Phi)$ around T_g.

Registry No. Ru(bpy)$_3$Cl$_2$, 14323-06-9; Ru(bpy)$_3$(ClO$_4$)$_2$, 15635-95-7; Ru(bpy)$_3$(PF$_6$)$_2$, 60804-74-2; Ru(dp-bpy)$_3$(PF$_6$)$_2$, 123148-14-1; Ru(bpyrz)$_3$Cl$_2$, 80925-50-4; Ru(bpy)$_2$(DCEB)(PF$_6$)$_2$, 83605-49-6; Ru(phen)$_2$(CN)$_2$, 112087-85-1.

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