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Emission Quenching of Double-Complex Salt Crystals of $[RuL_3]_3[Co(bpydc)_3]_2 \cdot nH_2O$ (L: 2,2′-Bipyridine, 2,2′-Bipyrazine or 4,4′-Dimetyl-2,2′-bipyridine, and bpydc: 2,2′-Bipyridine-4,4′-dicarboxylate)

Md. Jamal Uddin, Akio Yoshimura,* and Takeshi Ohno*

Department of Chemistry, Graduate School of Science, Osaka University,
1-16 Machikaneyama, Toyonaka, Osaka 560-0043

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The emission quenching of double-complex salt crystals, $[RuL_3]_3[Co(bpydc)_3]_2 \cdot nH_2O$ (L: 2,2′-bipyridine, 4,4′-dimetyl-2,2′-bipyridine or 2,2′-bipyrazine and bpydc: 2,2′-bipyridine-4,4′-dicarboxylate), were studied over a wide temperature range. Electron-transfer (ET) quenching of the phosphorescent emission of RuL_3^{2+} in the presence of an anionic $Co(bpydc)_3^{3-}$ and the yields of ET-product formation were examined for aqueous solutions by means of laser transient-absorption spectroscopy. The high fraction of ET-product formation in the quenching and the slow rate of the reverse ET reaction establish the mechanism of emission quenching of $Ru(bpy)_3^{2+}$ and $Ru(dmbpy)_3^{2+}$ in the solution. The decreasing rate of uni-molecular quenching within the encounter complexes formed between $^3[RuL_3]^{2+}$ and $Co(bpydc)_3^{3-}$, $Ru(bpy)_3^{2+} > Ru(dmbpy)_3^{2+} > Ru(bpz)_3^{2+}$, was found for emission quenching of double-complex salt crystals. The magnitude and temperature independence of the emission quenching rate for the double-complex salt are discussed from an ET point of view, except for $Ru(bpz)_3^{2+}$.

One-electron redox reactions of Co(III) + e = Co(II) in cobalt complexes are accompanied by changes in the electronic configuration, spin multiplicity, metal-ligand distances, and solvation in solution.[1—4] Studies of laser-induced intramolecular electron-transfer (ET) on covalently linked compounds of $[(bpy)_2Ru^{II}(L\text{-}L)Co^{III}(bpy)_2]^{5+}$ demonstrated that the excited triplet charge-transfer state of the ruthenium(II) moiety (^{3}CT(Ru)) undergoes intramolecular electron-transfer (ET) to produce $[(bpy)_2Ru^{III}(L\text{-}L)Co^{II}(bpy)_2]^{5+}$, in which the spin multiplicity of the cobalt(II) moiety is then converted from a doublet to a quartet, in polar solution (bpy: 2,2′-bipyridine, and L-L: a bridging tetradentate ligand).[5—7] The excited triplet state of $Ru(bpy)_3^{2+}$ ($^3[Ru(bpy)_3]^{2+}$) undergoes a bimolecular ET reaction with $Co(bpy)_3^{3+}$ in solution with a nearly diffusion-controlled rate,

$$^1[Co(bpy)_3]^{3+} + ^3[Ru(bpy)_3]^{2+} \longrightarrow {}^2[Co(bpy)_3]^{2+} + ^2[Ru(bpy)_3]^{3+},$$

while the reverse electron transfer after the spin-conversion of doublet → quartet,

$$^4[Co(bpy)_3]^{2+} + ^2[Ru(bpy)_3]^{3+} \longrightarrow {}^1[Co(bpy)_3]^{3+} + ^1[Ru(bpy)_3]^{2+},$$

is not rapid because of the large inner-sphere reorganization energy (> 1 eV) in addition to the solvent-reorganization energy of ca. 1 eV.[8—10] Meanwhile, few of the ET processes between the metal centers in the solid crystal has been studied for a double-complex salt containing Ru(II) and Co(III),[11] while the energy-transfer rates in solids have been measured for such double-complex salt crystals as $[Ru(bpy)_3]_3[Cr(C_2O_4)_3]_2$[13] and a mixed crystal of $[Ru(bpy)_3](PF_6)_2$ and $[Os(bpy)_3](PF_6)_2$.[14] The ET quenching rate of ^{3}CT(Ru) in $[Ru(bpy)_3]_2[Co(CN)_6]Cl \cdot 8H_2O$ has been observed to be large compared with that in aqueous solution.[11] The short distance between a Ru(II) and a Co(III)[12] is responsible for the large quenching rate (3×10^7 s^{-1}) in a crystal of $[Ru(bpy)_3]_2[Co(CN)_6]Cl \cdot 8H_2O$, while a high activation energy of ET quenching (230 meV) is expected from the small magnitude of ΔG°_{ET} (−0.3 eV) and a large reorganization energy of ET (1.4 eV).

We have examined the quenching of $^3[Ru(bpy)_3]^{2+}$ by a CoL_3^{3-} (L = 2,2′-bipyridine-4,4′-dicarboxylate) in such a double-complex salt crystal as $[Ru(bpy)_3]_3[Co(bpydc)_3]_2 \cdot 39H_2O$ over a wide temperature range of 77—300 K in order to clarify the participation of the ET reaction in emission quenching. Since there is difficulty to identify ET products for the emission quenching of double-complex salt crystals, the quenching reactions have also been examined for aqueous solutions of RuL_3^{2+} and $Co(dcbpy)_3^{3-}$ based on the fraction of electron-transfer product formation in the quenching and the rate of reverse electron transfer between Ru(III) and Co(II) by means of laser kinetic-absorption spectroscopy. The rate of the uni-molecular quenching process for a photo-excited double complex salt crystal is compared with that for an encounter complex formed between an excited RuL_3^{2+} and a $Co(bpydc)_3^{3-}$ in the solution. Uni-molecular quenching in aqueous solution and double-complex salt crystals is discussed with respect to the donor–acceptor interaction and reorganization energy of the quenching process.

Experimental

Preparation of Coordination Compounds and Double-Complex Salt Crystals. A ligand of 2,2′-biyridyl-4,4′-dicarboxy acid ($bpydcH_2$) was prepared by permanganate oxidation of 4,4′-dimethyl-2,2′-bipridine.[1] Anal. $BpydcH_2$: Calcd for $C_{12}H_8N_2O_4$: C, 59.02; H, 3.30; N, 11.47%. Found : C, 59.02; H, 3.32; N, 11.40%.

$[Co(bpydcH)_3]\cdot 8H_2O$: $BpydcH_2$ (0.17 g, 0.7 mmol) in a 4.5 ml NaOH solution (0.2 M, 1 M = 1 mol dm^{-3}) and $CoCl_2\cdot 6H_2O$ (0.05 g, 0.2 mmol) in 3 ml H_2O were mixed, and a brown-color solution was heated at 60 °C for 20 min. the addition of 0.26 ml HCl (6 M) gave yellow precipitates, which was dissolved in 7 ml alkaline solution (pH = 11.8), then treated with chlorine gas for 8 min to oxidize the Co(II) compound. A yellow suspension was formed and dissolved by the addition of a NaOH solution to remove the free ligand. The addition of 0.1 ml HCl (6 M) to the yellow solution produced yellow crystals, which were washed with acetone and air-dried to give a yield of 42%. Anal. $[Co(bpydcH)_3]\cdot 8H_2O$: Calcd for $CoC_{36}H_{37}N_6O_{20}$: C, 46.36; H, 4.00 ; N, 9.01%. Found : C, 46.32; H, 3.99; N, 9.00%.

$[Ru(dmbpy)_3]Cl_2\cdot 9H_2O$ (dmbpy = 4, 4′- dimethyl- 2, 2′- bipyridine) and $[Ru(bpz)_3]Cl_2\cdot 3H_2O$ (bpz = 2,2′-bipyrazine) were synthesized according to literature methods,[16,17] and then purified by Al_2O_3 column-chromatography and recrystallized.

$[Co(bpy)_3]Cl_3\cdot 6H_2O$ and $[Co(bpy)_3]Cl_2$ were prepared by the following literature methods.[18,19]

$[RuL_3]_3[Co(bpydc)_3]_2\cdot mH_2O$ (m = 39 for L = bpy, m = 46 for L = dmbpy, and m = 53 for L = bpz) was prepared from $RuL_3Cl_2\cdot m'H_2O$ and $Co(bpydcH)_3\cdot 8H_2O$ in a mixture of ethanol, 2,6-dimethyl-pyridine, and H_2O (5 : 4 : 1 by volume) in an incubator at 25 °C. Ionic crystals were grown by a slow-evaporation method. Anal. $[Ru(bpy)_3]_3[Co(bpydc)_3]_2\cdot 39H_2O$: Calcd for $C_{162}H_{108}N_{30}O_{24}Ru_3Co_2\cdot 39H_2O$: C, 48.86; H, 4.70; N, 10.55%. Found: C, 48.87; H, 4.60; N, 10.53%. Anal. $[Ru(dmbpy)_3]_3[Co(bpydc)_3]_2\cdot 46H_2O$: Calcd for $C_{180}H_{144}N_{30}O_{24}Ru_3Co_2\cdot 46H_2O$: C, 49.57; H, 5.45; N, 9.63%. Found: C, 49.37; H, 5.30; N, 9.64%. Anal. $[Ru(bpz)_3]_3[Co(bpydc)_3]_2\cdot 53H_2O$: Calcd for $C_{144}H_{90}N_{48}O_{24}Ru_3Co_2\cdot 53H_2O$: C, 40.67; H, 4.65; N, 15.81%. Found : C, 40.59; H, 4.45; N, 15.76%.

Apparatus. The absorption spectra were measured on a Shimadzu spectrophotometer (UV-2500PC). The emission spectra were measured using a Hitachi spectrofluorometer (MPF-4) or a grating monochromator (JASCO CT250) with a silicon diode-array (Hamamatsu S3901-512Q) corrected and a 488 nm line of an argon laser (Coherent Innova 306) for exciting the samples.[20] The decay rate of the emission was measured using the second harmonic Nd^{3+}:YAG laser pulse (532 nm) of Continuum Surelite I-10 or Quantel YG580, as previously described.[21] In the case of crystal samples, the intensity of the exciting laser was sufficiently attenuated by neutral density filters so as to avoid any non-linear processes, such as triplet–triplet annihilation. A crystal sample on a copper holder was retained in a cryostat (Oxford DN1740) controlled by an Oxford ITC4 controller over the temperature range of 77—300 K.

Procedure. Sample solutions were deaerated by bubbling argon gas and adjusted to pH = 10.2 using a 12.5 mM borate buffer. Transient-absorption spectroscopy was carried out to measure the production of ^{3}CT(Ru) and the electron-transfer products, the decay of ^{3}CT(Ru), and the rise-and-decay of the Ru(III) compound. Difference absorption spectra due to the formation of the ^{3}CT(Ru) and Ru(III) compounds were measured using Surelite I-10. The difference molar-absorption coefficients along with excitation to ^{3}CT(Ru) and the conversion of Ru(II) → Ru(III) are available in the literature.[21]

The bimolecular rate constants of reverse electron transfer between photochemical ET products were determined by the following method. The addition of $Co(bpy)_3^{2+}$ increased the recovery of Ru(II), of which the rates were first order with respect to the amount of Co(II). The reverse ET rate constants were evaluated based on the dependence of the recovery rate on the concentration of Co(II) added.

According to Debye–Smoluchowski,[22] the rate constants of encounter complex formation (k_{ass}) can be evaluated by using the following equation:

$$k_{ass} = \frac{2RT}{3\zeta}\left(2+\frac{r_a}{r_b}+\frac{r_b}{r_a}\right)\frac{1}{a\int_a^\infty r^{-2}\exp\left[w(r,\mu)/kT\right]dr}, \quad (1)$$

where ζ, a, and $w(r,\mu)$ are the viscosity of the solvent (0.89 mPa s), the sum of the ion radius of ion_a, and ion_b (r_a and r_b) and the work to bring an ion_a of Z_a-charge and an ion_b of Z_b-charge together at distance of r in an aqueous solution of ionic strength μ,

$$w(r,\mu) = \frac{Z_aZ_be^2}{4\pi\varepsilon 2Dr}\left(\frac{\exp\left(A\sigma_a\sqrt{\mu}\right)}{1+A\sigma_a\sqrt{\mu}}+\frac{\exp\left(A\sigma_b\sqrt{\mu}\right)}{1+A\sigma_b\sqrt{\mu}}\right)\exp\left(-Ar\sqrt{\mu}\right),$$

$$A = \sqrt{\frac{8\pi Ne^2}{4\pi\varepsilon 1000DkT}}, \quad (2)$$

where σ_a, σ_b, and D are the radius of ion_a-pair, ion_b-pair, and the dielectric constant (78) of water. The rate constant of encounter complex dissociation (k_{dis}) are calculated using,

$$k_{dis} = \frac{kT}{2\pi\zeta}\frac{1}{a^2}\left(\frac{1}{r_a}+\frac{1}{r_b}\right)\frac{\exp\left[w(a,\mu)/kT\right]}{a\int_a^\infty r^{-2}\exp\left[w(r,\mu)/kT\right]dr}. \quad (3)$$

The radii of the complex ions are 0.6 nm for $Ru(bpy)_3^{2+}$, $Ru(bpz)_3^{2+}$, $Co(bpy)_3^{3+}$, and 0.8 nm for $Ru(dmbpy)_3^{2+}$, and $Co(bpydc)_3^{3-}$.

Results

Emission Quenching of Double-Complex Salt Crystals. A buffered (pH = 10.2) solution of a double-complex salt crystal, $[RuL_3]_3[Co(bpydc)_3]_2\cdot nH_2O$ (n = 39 for L = bpy, n = 46 for dmbpy, and n = 53 for L = bpz), display an absorption spectrum which is almost the sum of the absorption spectra of the components, RuL_3^{2+} and $Co(bpydc)_3^{3-}$, as shown in Fig. 1. The emission spectra of the double-complex salt crystal are similar in the whole shape to that of the neat crystal of $[RuL_3]Cl_2\cdot 6H_2O$, as shown in Fig. 2. The highest-energy emission peaks of the double-complex salts at 77 K are shifted to 2.08 eV and 2.13 eV for L = bpy and L = bpz from those of the neat crystals (2.17 and 2.08 eV). The emission decays from $^3[Ru(bpy)_3]^{2+}$ and $^3[Ru(dmbpy)_3]^{2+}$ in the single- and double-complex salt crystals are single exponential, while that from $^3[Ru(bpz)_3]^{2+}$ in both crystals is bi-exponential, as Fig. 3 shows. The decay rate of $[Ru(bpy)_3]_3[Co(bpydc)_3]_2\cdot 39H_2O$ ($k_{Ru-Co} = 19\times10^6$ s^{-1}) is much larger than that of the single-salt crystal ($k_{Ru} = 1\times10^6$ s^{-1}), being almost independent of the temperature over the range of 77—300 K as shown in Fig. 4. The difference between k_{Ru-Co} and k_{Ru} is regarded as being the quenching rate given in Table 1. The quenching rate of $[Ru(bpz)_3]_3[Co(bpydc)_3]_2\cdot 53H_2O$ displays a weak dependence on temperature, as shown in Fig. 4.

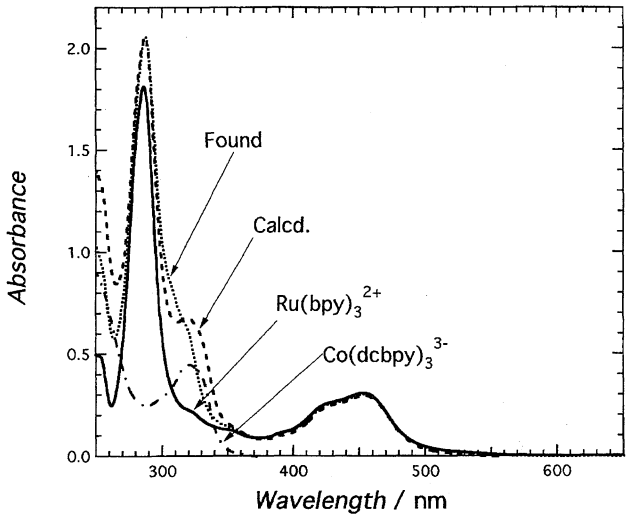


Fig. 1. Absorption spectra of a buffered solution of [Ru(bpy)$_3$]$_3$[Co(bpydc)$_3$]$_2$·39H$_2$O, and the components, Ru(bpy)$_3^{2+}$ and Co(bpydc)$_3^{3-}$, and the calculated sum of Ru(bpy)$_3^{2+}$ and Co(bpydc)$_3^{3-}$.

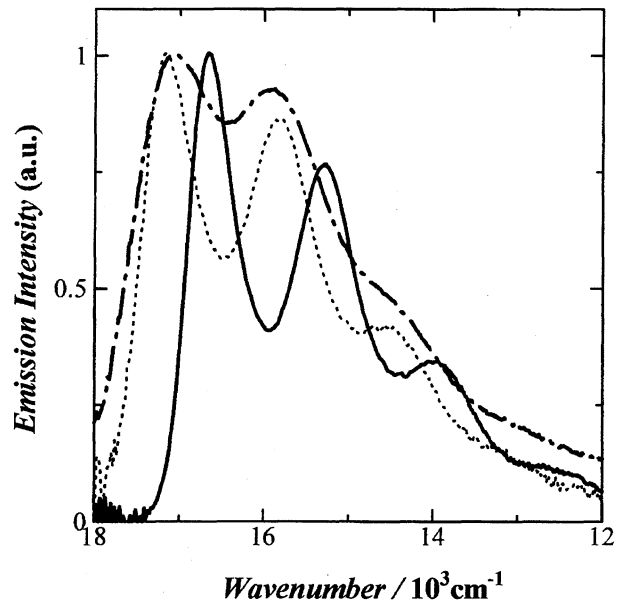


Fig. 2. Emission spectra of crystals of [Ru(bpz)$_3$]$_3$[Co(bpydc)$_3$]$_2$·53H$_2$O and [Ru(bpz)$_3$]Cl$_2$·3H$_2$O and a methanol solution of [Ru(bpz)$_3$]$^{2+}$ at 77 K. The solid line: the neat crystal of [Ru(bpz)$_3$]Cl$_2$·3H$_2$O, the dotted line: the double-complex salt crystal, and the dashed line: the glass solution.

Quenching Rates and Fractions of ET Product Formation in Aqueous Solution Ru(bpy)$_3^{2+}$–Co(bpydc)$_3^{3-}$. A buffered (pH = 10.2) aqueous solution of Ru(bpy)$_3^{2+}$ (40 μM) reveals a difference absorption spectrum on the Nd^{3+}–YAG laser (532 nm) excitation shown in Fig. 5. The transient species is identified as ^{3}CT(Ru) because of the same decay rate ($k_0 = 1.71\times10^6$ s^{-1}) as that of phosphorescence at 620 nm. The difference absorption spectrum with strong bleaching at 455 nm and weak absorption in the red region is typical of that of ^{3}CT(Ru)-formation. The production of ^{3}CT(Ru) ([^{3}CT(Ru)]$_0$) is evaluated to be 40 μM by using the differ-

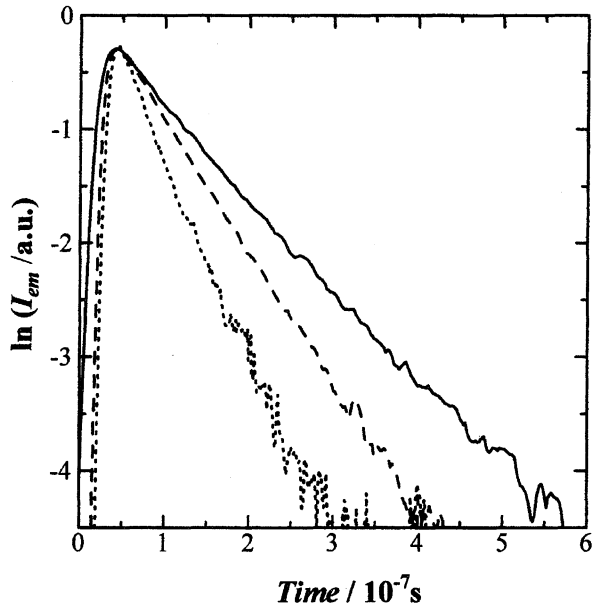


Fig. 3. Emission decays of the double-complex salt crystals at ca. 300 K. The dotted line: [Ru(bpy)$_3$]$_3$[Co(bpydc)$_3$]$_2$, the dashed line: [Ru(dmbpy)$_3$]$_3$[Co(bpydc)$_3$]$_2$ ·46H$_2$O, and the solid line: [Ru(bpz)$_3$]$_3$[Co(bpydc)$_3$]$_2$·53H$_2$O.

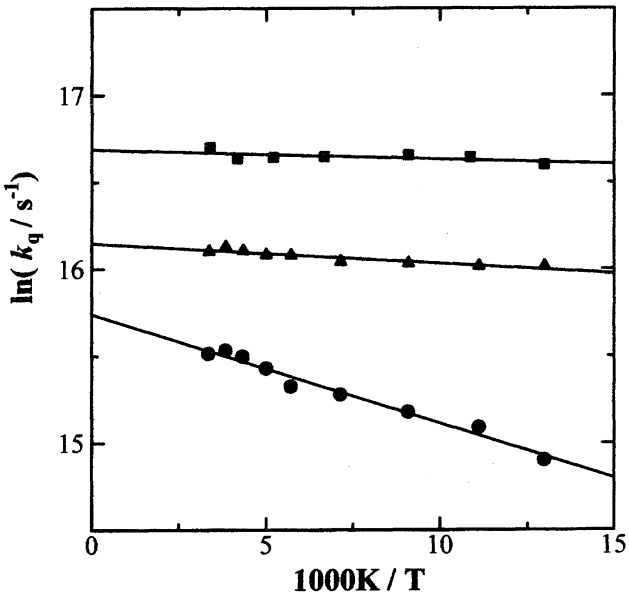


Fig. 4. Temperature dependence of the quenching rate (k_q) of the double-complex salt crystals. ■: [Ru(bpy)$_3$]$_3$[Co(bpydc)$_3$]$_2$·39H$_2$O, ▲: [Ru(dmbpy)$_3$]$_3$[Co(bpydc)$_3$]$_2$·46H$_2$O, and ●: [Ru(bpz)$_3$]$_3$[Co(bpydc)$_3$]$_2$ ·53H$_2$O.

ence molar absorption coefficient (−9800 M^{-1} cm^{-1}). The initial recovery of the transient bleaching (k_d) was very rapid upon the addition of 2—5 mM Co(bpydc)$_3^{3-}$. The bimolecular quenching rate constant (k_q) is estimated to be 9.5×10^9 M^{-1} s^{-1} from the ratio of the increment ($k_d - k_0$) in the decay rate (k_d) to the Co(III) concentration (2 mM), as shown in Table 2. The decay rate of ^{3}CT(Ru(II)) shown in Fig. 6 increased linearly to the concentration of added Co(III).

After a rapid recovery of the ground-state absorption, more

Table 1. Decay Rates (k_{Ru} and k_{Ru-Co}), Quenching Rates (k_q), the Excitation Energy of ^{3}CT(Ru) and Gibbs Energy Change of Electron Transfer Quenching (ΔG°_{ET})

Double complex	$k_{Ru}/10^6$ s^{-1}		$k_{Ru-Co}/10^6$ s^{-1}		$k_q/10^6$ s^{-1}		$E^{a)}$	$\Delta G^\circ_{ET}{}^{b)}$
salt crystal	295 K	77 K	295 K	77 K	295 K	77 K	eV	eV
$[Ru(bpy)_3]_3[Co(bpydc)_3]_2\cdot 39H_2O$	1.0	0.2	19.0	16	18.0	15.8	2.08	−0.92
$[Ru(dmbpy)_3]_3[Co(bpydc)_3]_2\cdot 46H_2O$	2.0	0.3	11.8	9.3	9.8	9.0	2.06	−1.06
$[Ru(bpz)_3]_3[Co(bpydc)_3]_2\cdot 53H_2O$	2.5	0.3	8.0	3.3	5.5	3.0	2.13	−0.42
$[Ru(bpy)_3]_2[Co(CN)_6]Cl\cdot 8H_2O^{c)}$	1.0	0.2	33		32		2.08	−0.32

a) The energy of the first peak of emission in the double-complex salt crystal at 77 K. b) The Gibbs-energy change of electron-transfer quenching are estimated from the redox potentials (shown in Table 3) in the aqueous solution and the excitation energy of ^{3}CT(Ru). c) Ref. 11.

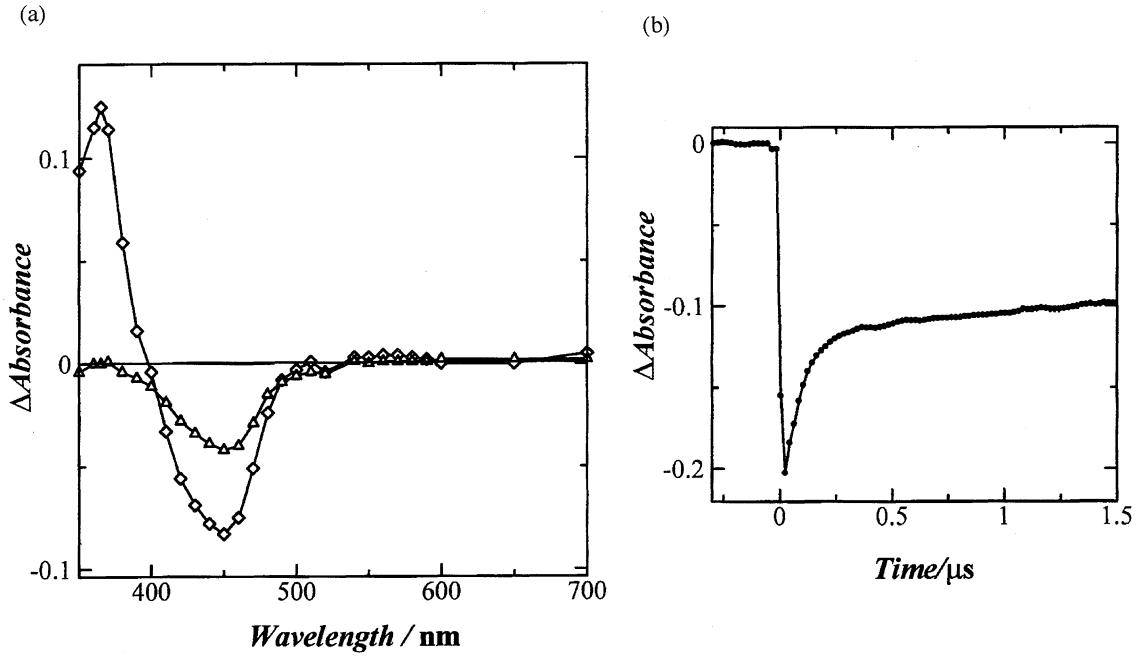


Fig. 5. (a) Transient absorption spectra of an photo-excited solution of $Ru(bpy)_3^{2+}$ containing $Co(bpydc)_3^{3-}$ (0.5 mM) in a low (0.06) ionic-strength solution. (1) immediately after the laser excitation, (2) after the fast recovery of Ru(II) due to the decay of ^{3}CT(Ru). The inset (b) shows the time profile of the absorbance at 450 nm.

Table 2. Fractions of ET Product Formation in the Quenching (F^{obs}_{ET}), Bimolecular Quenching Rate-Constants (k_q), Uni-molecular Quenching Rate-Constants (k^U_q) of an Encounter Complexes Formed between an Excited Ru(II) Complex and a Quencher, Rate Constants of Association (k_{ass}) and Dissociation (k_{dis}) of the Encounter Complex

Excited complex–Quencher	μ	F^{obs}_{ET}	k_q	k^U_q	k_{ass}	k_{dis}	$-\Delta G^\circ_{ET}$
	M		10^9 (M s)$^{-1}$	10^9 (s)$^{-1}$	10^9 (Ms)$^{-1}$	10^9 s^{-1}	eV
$Ru(dmbpy)_3^{2+}$–$Co(bpydc)_3^{3-}$	0.06	0.52	7.0	1.44	8.7	0.35	0.97
$Ru(dmbpy)_3^{2+}$–$Co(bpydc)_3^{3-}$	1.0	0.78	3.7	1.14	6.5	0.86	0.97
$Ru(bpy)_3^{2+}$–$Co(bpydc)_3^{3-}$	0.06	0.48	9.5	8.74	10.0	0.46	0.92
$Ru(bpy)_3^{2+}$–$Co(bpydc)_3^{3-}$	1.0	0.99	3.6	0.76	7.6	0.86	0.92
$Ru(bpz)_3^{2+}$–$Co(bpydc)_3^{3-}$	0.06	0.00	1.41	0.075	10.0	0.46	0.39
$Ru(bpz)_3^{2+}$–$Co(bpydc)_3^{3-}$	1.0	0.00	0.28	0.033	7.6	0.86	0.39
$Ru(dmbpy)_3^{2+}$–$Co(bpy)_3^{3+}$	0.06	0.96	1.33	0.94	4.8	2.38	0.97
$Ru(bpy)_3^{2+}$–$Co(bpy)_3^{3+}$	0.06	0.95	1.2	1.8	5.5	6.4	0.92
$Ru(bpz)_3^{2+}$–$Co(bpy)_3^{3+}$	0.06	0.37	0.015	0.02	5.5	6.4	0.39

than the half of the bleaching was recovered for a time longer than several miliseconds. The difference absorption spectrum due to the longer lifetime species shown in Fig. 5 after the complete disappearance of ^{3}CT(Ru) is in agreement with the difference absorption spectrum of an oxidized sample of $Ru(bpy)_3^{2+}$. The production of Ru(III) ($[Ru(III)]_0$) in the

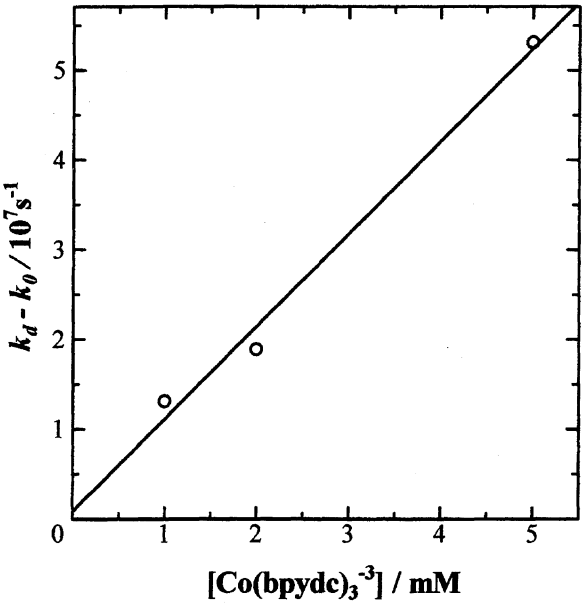


Fig. 6. A plot of k_d–k_0 vs. [Co(bpydc)$_3^{3-}$] for the quenching reaction where k_q and k_0 are the decay rate-constants of ^{3}[Ru(bpy)$_3$]$^{2+}$ in the presence and absence of Co(bpydc)$_3^{3-}$ (μ = 0.06).

presence of the Co(III) compound was evaluated (> 35 μ M) based on the negative absorbance in the later time region. The amount of Ru(III)-production, [Ru(III)]$_0$, can be written in terms of the fraction of product formation (F_{ET}^{obs}) in the bimolecular quenching of ^{3}CT(Ru),

$$[\mathrm{Ru(III)}]_0 = F_{ET}^{obs}\frac{k_d - k_0}{k_d}[^3\mathrm{CT(Ru)}]_0 = F_{ET}^{obs} f_q [^3\mathrm{CT(Ru)}]_0, \quad (4)$$

where k_0, k_d, and f_q are the decay-rate constants of ^{3}CT(Ru) in the absence and presence of a Co(III) compound, and the fraction of quenching in the decay of ^{3}CT(Ru).

$$^3[\mathrm{Ru(bpy)_3}]^{2+} \longrightarrow {}^1[\mathrm{Ru(bpy)_3}]^{2+}, \qquad k_6$$

$$^3[\mathrm{Ru(bpy)_3}]^{2+} + {}^1[\mathrm{Co(bpy)_3}]^{3+} \longrightarrow {}^2[\mathrm{Ru(bpy)_3}]^{3+} + {}^4[\mathrm{Co(bpy)_3}]^{2+}$$

$$\longrightarrow {}^1[\mathrm{Ru(bpy)_3}]^{2+} + {}^1[\mathrm{Co(bpy)_3}]^{3+}, \; k_q$$

$$k_d = k_0 + k_q[\mathrm{Co(III)}]. \quad (5)$$

The fraction of Ru(bpy)$_3^{3+}$ formation in the quenching of ^{3}CT(Ru) by Co(bpydc)$_3^{3-}$ was near to one half (0.48). The addition of KCl (1 M) enhanced F_{ET}^{obs} to 0.99.

Ru(L)$_3^{2+}$ (L = dmbpy, and bpz)–Co(bpydc)$_3^{3-}$. Co(bpydc)$_3^{3-}$ quenched the ^{3}CT of cationic Ru(dmbpy)$_3^{2+}$ with a nearly diffusion-controlled rate of 7×10^9 M^{-1} s^{-1}. The quenching of ^{3}[Ru(bpz)$_3$]$^{2+}$ by Co(bpydc)$_3^{3-}$ occurred at a low rate (1.4×10^9 M^{-1} s^{-1}). However, F_{ET}^{obs} in the quenching of ^{3}[Ru(dmbpy)$_3$]$^{2+}$ is 0.52 for a solution of low ionic strength (0.06); the addition of KCl (1 M) increased the F_{ET}^{obs} up to 0.78. No formation of an electron-transfer product was seen for the quenching of ^{3}[Ru(bpz)$_3$]$^{2+}$ in both the absence and presence of 1 M KCl.

Co(bpy)$_3^{3+}$ quenched ^{3}CT of Ru(bpy)$_3^{2+}$ and Ru(dmbpy)$_3^{2+}$ with a rate constant close to 1×10^9 M^{-1} s^{-1}. The emission quenching rate of [Ru(bpz)$_3$]$^{2+}$ with [Co(bpy)$_3$]$^{3+}$ was two orders of magnitude smaller than those of the other cationic ones. The F_{ET}^{obs} in the emission quenching by Co(bpy)$_3^{3+}$ are high (>0.9), except for ^{3}[Ru(bpz)$_3$]$^{2+}$ (0.37).

Reverse Electron Transfer between Ru(III) and Co(II) in Aqueous Solution. After the complete decay of ^{3}CT(Ru) of Ru(bpy)$_3^{2+}$ and Ru(bpz)$_3^{2+}$ in the presence of Co(bpy)$_3^{3+}$, negative absorbance due to the bleaching of Ru(II) was recovered in several miliseconds. The recovery of Ru(II) occurred almost in a bimolecular reaction between the electron-transfer products, Ru(bpy)$_3^{3+}$ and Co(bpy)$_3^{2+}$. The rate constants of the reverse electron-transfer reactions were determined as a pseudo first-order rate in the presence of excess Co(bpy)$_3^{2+}$. The recovery rate of Ru(II) is linear to the concentration of Co(bpy)$_3^{2+}$ added, as shown in Fig. 7. The line slope shown in Fig. 7 is regarded as being the bimolecular rate constant of reverse electron transfer (0.056×10^9 M^{-1} s^{-1}) for Ru(bpy)$_3^{3+}$.

Discussion

Fractions of ET Quenching in the Quenching and Unimolecular Quenching Rates in the Aqueous Solution. Most transition metal complexes quench an excited state via two mechanisms, electron transfer and energy transfer, because most of metal ions are subjected to a redox reaction, and have a low-lying electronic excited state(s). Though Co(III) complexes have been considered to be acceptors of both the electron and electronic energy for the long-lived excited states of Ru(II)[23–25] and Cr(III) compounds,[26] it has been difficult to obtain clear evidence of any energy transfer involved in the quenching of an excited state, because the excited state of Co(III) does not emit even at low temperatures.[27] Thus, the formation yields of electron-transfer products have been pursued in order to present evidence of electron-transfer

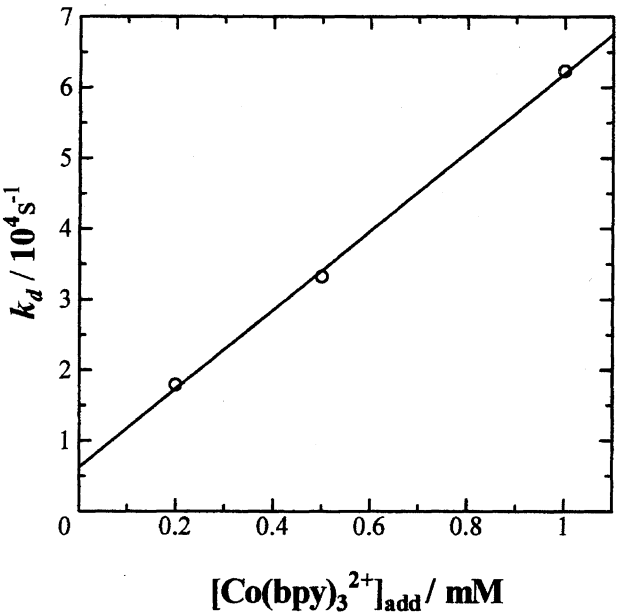


Fig. 7. A plot of the decay rate-constant of [Ru(bpy)$_3^{3+}$] (k_d) vs. [Co(bpy)$_3^{2+}$] in a low (0.06) ionic-strength solution.

quenching.[8,9,23—25,28] Laser photolysis kinetic spectroscopy demonstrated that some Co(III) cage compounds quenched ^{3}CT(Ru) via both ET and energy transfer.[9] A fraction of the electron-transfer reaction in quenching (F_{ET}) could be estimated from the fraction of redox- product formation in the quenching (F_{ET}^{obs}),

$$F_{ET}^{obs} = F_{ET} f_{dis} = F_{ET} \frac{k'_{dis}}{k'_{dis} + k_{ret}^{U}}, \quad (6)$$

where f_{dis} is a fraction of the geminate radical pair dissociating to the bulk, which is written as the ratio of the dissociating rate (k'_{dis}) to the decay rate ($k'_{dis}+k_{ret}^{U}$) of the geminate pair formed in ET quenching, and is called "cage-escape-probability". The reaction mechanism consists of sequential and competitive elementary reactions (Scheme 1): where the spin multiplicities of the Co(II) moiety of a geminate pair are not discriminated, because the intersystem crossing of doublet↔quartet occurs as fast as the dissociation of a geminate pair and the reverse ET within a geminate pair.[5,7] The low fraction (F_{ET}^{obs}) is ascribed to either a slow dissociation rate of the geminate pair to the bulk (k'_{dis}) or a fast reverse electron-transfer (k_{ret}^{U}). The magnitude of f_{dis} can be estimated from the bimolecular-rate constants of the reverse electron-transfer (k_{ret}) and the encounter complex formation (k'_{ass})between the redox products. On assuming that the geminate pair formed in the quenching is the same as the encounter pair formed between the electron-transfer products,[29—31] the bimolecular rate constant of reverse electron-transfer (k_{ret}) can be expressed in terms of the rate constants of elementary processes and f_{dis},

$$k_{ret} = k'_{ass} \frac{k_{ret}^{U}}{k'_{dis} + k_{ret}^{U}} = k'_{ass}(1 - f_{dis}). \quad (7)$$

Consequently, the fraction of the ET reaction (F_{ET}) can be evaluated from the quantities F_{ET}^{obs} and f_{dis}.

Similarly, the bimolecular-rate constant of the quenching reaction is expressed in terms of the rate constants of unimolecular quenching within an encounter complex (k_q^U), association (k_{ass}) and dissociation (k_{dis}) of the encounter complex (Scheme 2),

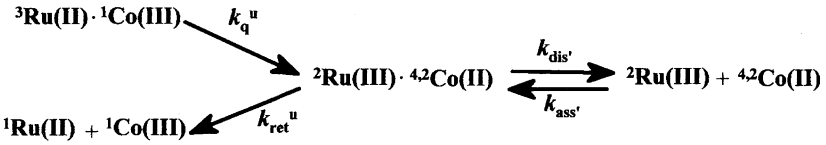
$$k_q = \frac{k_q^U}{k_q^U + k_{dis}} k_{ass}. \quad (8)$$

Since the magnitude of k_{ass} and k_{dis} are oppositely dependent on the product of the reactant charges, it is absolutely necessary to evaluate k_q^U. All of the values of k_q^U are tabulated together with k_q, k_{ass}, and k_{dis} in Table 2.

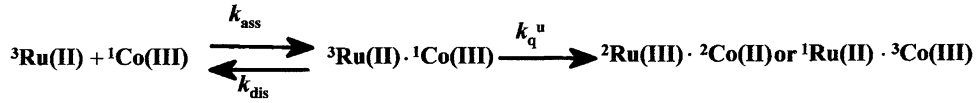
The uni-molecular rates of ET quenching and reverse ET are written as

$$k^U = \varkappa_{el}\varkappa_{nuc} = \frac{2\pi H_{rp}^2}{\hbar\sqrt{4\pi\lambda_o k_B T}} \exp\left(\frac{-(\Delta G_{et}^\circ + \lambda)^2}{4\lambda k_B T}\right), \quad (9)$$

where $\varkappa_{el}$ and $\varkappa_{nuc}$ are the electronic factor and the nuclear factor, respectively; λ and ΔG_{ET}° are the reorganization energy and the standard Gibbs energy change involved in ET processes. The magnitude of the standard Gibbs energy change for the ET reaction of ^{3}CT(Ru) can be evaluated using ,



Scheme 1.



Scheme 2.

Table 3. Redox Potentials of Ru^{3+}/Ru^{2+} (E° ($Ru^{3+/2+}$) and Co^{3+}/Co^{2+} (E° ($Co^{3+/2+}$)) in Solution, Excitation Energy of the Lowest Excited State of Ru(II) Compound (E (^{3}CT(Ru))) and Co(III) compound (E ($^3T_{1g}$)), and Difference Molar-Absorption Coefficients along with the Excitation to ^{3}CT(Ru) ($\Delta\varepsilon_{CT}$) and along with the Conversion of Ru(II) → Ru(III) or Co(III) → Co(II)

Compound	$E^\circ(Ru^{3+/2+})$	$E^\circ(Co^{3+/2+})$	$E(^3CT(Ru))$[a]	$E(^3T_{1g})$	$-\Delta\varepsilon_{CT}$	$-\Delta\varepsilon_{ET}$
	V v.s. SCE	V v.s. SCE	eV	eV	10^3 M^{-1} cm^{-1}	10^3 M^{-1} cm^{-1}
$Ru(bpy)_3^{2+}$	1.26[b]		2.17		9.8[c]	14.1
$Ru(dmbpy)_3^{2+}$	1.10[b]		2.08		9.3[c]	15.0
$Ru(bpz)_3^{2+}$	1.86[d]		2.14		12.0[e]	14.1
$Co(bpy)_3^{3+}$		0.37[g]		1.74[h]		0
$Co(bpydc)_3^{3-}$		0.37[i]		1.74[i]		0

a) The excitation energy of ^{3}CT(Ru) as the first peak of emission at 77 K in the ethanol glass. b) C. -T. Lin, W. Bottcher, M. Chou, C. Creutz, and N. Sutin, *J Am. Chem. Soc.*, **98**, 6536 (1976). c) Ref. 21. d) Ref. 17. e) T. Ohno, A. Yoshimura, N. Mataga, S. Tazuke, Y. Kawanishi, and N. Kitamura, *J. Phys. Chem.*, **93**, 3546 (1989). g) T. J. Przystas and N. Sutin, *J. Am. Chem. Soc.*, **95**, 5545 (1973). h) Ref. 25. i) $E(Co^{3+}/Co^{2+})^\circ$ and E ($^3T_{1g}$) are assumed to be the same as those of $Co(bpy)_3^{3+}$.

$$\Delta G^{\circ}_{ET} = -E^{\circ}(Co^{3+}/Co^{2+}) + E^{\circ}(Ru^{3+}/Ru^{2+}) - E(^3CT) + \Delta G^{\circ}_{4-2}, \quad (10)$$

where E° is the redox potential v.s. SCE in aqueous solution, and $\Delta G^{\circ}_{4-2}$is the Gibbs-energy change involved in a transition from the doublet state of Co(II) to the quartet state, which is assumed to be the same as that (0.2 eV) for Co(bpy)$_3^{2+}$.[5,32] The quantities of ΔG°_{ET}, E° and the excitation energy of ^{3}CT(Ru), $E(^3CT)$ are given in Tables 2 and 3.

Electron-Transfer Quenching in Aqueous Solutions. Ru(bpy)$_3^{2+}$–Co(bpydc)$_3^{3-}$. As for the quenching of ^{3}[Ru(bpy)$_3$]$^{2+}$ by [Co(bpydc)$_3$]$^{3-}$, a low value of F^{obs}_{ET} (0.48) implies that either a rapid reverse electron-transfer within the geminate pair, {Ru(bpy)$_3^{3+}$·Co(bpydc)$_3^{4-}$}, formed in the quenching competes with the dissociation of the geminate pair, or the electron-transfer process competes with the energy-transfer process in quenching. If reverse ET reduces F^{obs}_{ET}, the addition of 1 M KCl to a sample solution would increase the dissociation rate k'_{dis} of the cation-anion geminate pair, {Ru(bpy)$_3^{3+}$·Co(bpydc)$_3^{4-}$} to increase the fraction of ET reaction product formation. This is the case: F^{obs}_{ET} is changed from 0.48 in a low (0.06 M) ionic-strength solution to 0.99 in a high (1 M) ionic-strength solution. Therefore, it is concluded that the geminate pair, {Ru(bpy)$_3^{3+}$·Co(bpydc)$_3^{4-}$}, was uniquely produced in the quenching.

The magnitude of F^{obs}_{ET} (0.95) obtained for the quenching of ^{3}[Ru(bpy)$_3$]$^{2+}$ with Co(bpy)$_3^{3+}$ at low (0.06) ionic strength is much higher than that[25] at high (1 M) ionic-strength. The fast dissociation of the cationic ET products at the low ionic-strength is responsible for the large value of F^{obs}_{ET}, which undoubtedly indicates that the quenching occurs as an ET process. Since the extent of f_{dis} is high (0.98), evaluated from the ratio of observed bimolecular rate (k_{ret}) to the diffusion-controlled encounter rate (k'_{ass}) evaluated, the fraction of the ET reaction in the quenching (F_{ET}) is estimated to be unity. The pseudo first-order rate constant (0.056×10^9 M^{-1} s^{-1}) of the bimolecular ET between Ru(bpy)$_3^{3+}$ and Co(bpy)$_3^{2+}$ is slightly smaller than that (0.24×10^9 M^{-1} s^{-1}) obtained from the second-order decay of Ru(bpy)$_3^{3+}$,[8] both of which give rise to a similarly large value of f_{dis}.

The rate constants of the uni-molecular quenching of ^{3}[Ru(bpy)$_3$]$^{2+}$ within an encounter complex were evaluated to be 8.7×10^9 s^{-1} for Co(bpydc)$_3^{3-}$ and 1.8×10^9 s^{-1} for Co(bpy)$_3^{3+}$, respectively. The carboxylate groups of 2,2′-bipyridine-4,4′-carboxylate probably enhance the electronic factor ($\varkappa_{el}$) or electronic interaction between ^{3}[Ru(bpy)$_3$]$^{2+}$ and Co(III). Nevertheless, the magnitudes are much smaller than those ($>4\times10^{10}$ s^{-1}) within excited bridged Ru(II)–Co(III) compounds.[5–7] The reduction of k^U_q at high (1 M) ionic strength (8.7×10^9 s^{-1} → 0.76×10^9 s^{-1}) suggests that K$^+$ and/or Cl$^-$ incorporated into the encounter complex diminishes the electronic interaction between the metal ions.

Ru(dmbpy)$_3^{2+}$–Co(bpydc)$_3^{3-}$. A high fraction (0.78) of F^{obs}_{ET} in the quenching of ^{3}Ru(dmbpy)$_3^{2+}$ in a higher ionic-strength (1 M) solution uniquely shows that ET is the main quenching mechanism, and that the reverse electron-transfer within the geminate pair, {Ru(bpy)$_3^{3+}$·Co(bpydc)$_3^{4-}$}, is competitive with dissociation of the geminate pair. ET exclusively occurs in the quenching of ^{3}[Ru(dmbpy)$_3$]$^{2+}$ by Co(bpy)$_3^{3+}$. The carboxylate substitution of 2,2′-bipyridine enhances the value of k^U_q from 0.94×10^9 to 1.44×10^9 s^{-1}.

Ru(bpz)$_3^{2+}$–Co(bpydc)$_3^{3-}$. The slow quenching (1.5×10^7 M^{-1} s^{-1}) process of ^{3}[Ru(bpz)$_3$]$^{2+}$ with Co(bpy)$_3^{3+}$ gave electron-transfer products with a fraction of 0.37. The low fraction can be ascribed to non-ET quenching, as Gafney[25] suggested concerning the emission quenching of Ru(bpy)$_3^{2+}$ with Co(1,10-phenanthroline)$_3^{3+}$. The null value of F^{obs}_{ET} for the quenching of Ru(bpz)$_3^{2+}$ with Co(bpydc)$_3^{3-}$ indicates that non-ET quenching is predominant, while f_{dis} is unknown for reverse ET within the geminate pair of ET products.

Carboxylate groups of Co(bpydc)$_3^{3-}$ increased the uni-molecular quenching rate of ^{3}[Ru(bpz)$_3$]$^{2+}$ from 2×10^7 to 7.5×10^7 s^{-1}. The slow rate of uni-molecular quenching (7.5×10^7 s^{-1}) can be interpreted in terms of the ΔG°_{ET} dependence of the electron-transfer rate; ΔG°_{ET} is less negative (−0.39 eV) than that of Ru(bpy)$_3^{2+}$ (−0.92 eV). However, since redox products on the carboxylate substitution are not formed in the presence and absence of KCl (1 M), the quenching mechanism may be switched over from ET to non-ET.

Emission Quenching of the Double-Complex Salt Crystals. A rate constant of intermolecular quenching of the excited Ru(II) compound without a molecular displacement was determined as a uni-molecular rate for three double-complex salt crystals. For the sake of comparison, the uni-molecular rate constants of quenching (k^U_q) are estimated for the encounter complexes between a ^{3}CT(Ru) and a Co(III) complex ion in an aqueous solution. Co(bpydc)$_3^{3-}$ quenched both ^{3}[Ru(bpy)$_3$]$^{2+}$ and ^{3}[Ru(dmbpy)$_3$]$^{2+}$ more rapidly than did Co(bpy)$_3^{3+}$. Thus, the uni-molecular quenching rates in the encounter complexes are evidently enhanced by introducing carboxylate groups in 2,2′-bipyridine. This may be due to carboxylate groups enhancing the intermolecular interaction between ^{3}[Ru(bpy)$_3$]$^{2+}$ and Co(III). Meanwhile, the ethyl-2-carboxylate groups of 1,1′-bis(2-carboxyethyl)-4,4′-bipyridinium reduce the rates of the ET quenching of ^{3}[Ru(bpy)$_3$]$^{2+}$.[33]

Short-life emissions of the double-complex salt crystals compared to that of a neat crystal of [RuL$_3$]Cl$_2$, indicate the occurrence of electron- or energy-transfer quenching of ^{3}CT(Ru). The quenching rate of ^{3}CT(Ru) by Co(bpydc)$_3^{3-}$ decreases in the same order (Ru(bpy)$_3^{2+}$ > Ru(dmbpy)$_3^{2+}$ > Ru(bpz)$_3^{2+}$), as that of the ET reaction in aqueous solution. Since it is likely that the contribution of the ET reaction of ^{3}[Ru(bpz)$_3$]$^{2+}$ in a crystal is as small as it is in solution, the rate of the ET reaction in [Ru(bpz)$_3$]$_3$[Co(bpydc)$_3$]$_2$·53H$_2$O is much smaller than that in [Ru(bpy)$_3$]$_3$[Co(bpydc)$_3$]$_2$·39H$_2$O. Consequently, the decrease in the ET rate in the crystal (Ru(bpy)$_3^{2+}$ ≫ Ru(bpz)$_3^{2+}$) can be ascribed to a decrease (0.92 → 0.42) in $-\Delta G^{\circ}_{ET}$. The ET rates for double-complex salt crystals, [RuL$_3$]$_3$[Co(bpydc)$_3$]$_2$·nH$_2$O, are 10-times as slow as the

uni-molecular rates within the encounter complexes. The ET rate might be ascribed to the small extent of H_{rp} between $^3[Ru(bpy)_3]^{2+}$ and $Co(bpydc)_3^{3-}$ compared with the encounter-pair in solution.

The weak temperature dependence of the emission quenching of the double-complex salt crystal can be interpreted based on Marcus's theory of electron transfer. The rate of electron transfer is the optimum and independent of temperature when the extent of $-\Delta G^\circ_{ET}$ is close to that of the reorganization energy. In a region of small exo-ergonicity, the rate decreases and becomes dependent on temperature along with a decrease in $-\Delta G^\circ_{ET}$. The weak dependence of the ET rate on temperature for $[RuL_3]_3[Co(bpydc)_3]_2 \cdot nH_2O$ ($n = 39$ for L = bpy and $n = 46$ for L = dmbpy) implies that the extent of $-\Delta G^\circ_{ET}$ (1 eV) is close to that of the reorganization energy, while the photo-induced electron transfer of $-\Delta G^\circ_{ET}$ of 1 eV within a covalently linked compound of $[(bpy)_2Ru^{II}(L\text{-}L)Co^{III}(bpy)_2]^{5+}$ in polar solution exhibits a considerable amount of activation energy (54 meV) due to the reorganization energy of 1.6 eV.[6,7] This is because the contribution of the solvent-reorganization energy (1.1 eV) is lacking in the crystalline state. The estimated magnitude of the inner-sphere reorganization energy is smaller than that of a redox couple, $[Co(CN)_6]^{4-}/[Co(CN)_6]^{3-}$ and slightly larger than the Franck–Condon energy (0.7—0.8 eV) of $^3T_1$-emission of a isoelectronic Rh(III) in the solid state,[34,35] in which the LUMO of $d\sigma^*$ is singly occupied, as in the spin-doublet state of Co(II). The small activation energy (5 meV) of quenching for $[Ru(bpz)_3]_3[Co(bpydc)_3]_2 \cdot 53H_2O$ compared with $[Ru(bpy)_3]_2[Co(CN)_6]Cl \cdot 8H_2O$ (230 meV) might be ascribed to non-ET quenching.

Conclusion

The lifetimes of the emission of double-complex salt crystals, $[RuL_3]_3[Co(bpydc)_3]_2 \cdot nH_2O$, are short compared with those of the neat crystal of $[RuL_3]Cl_2$ over a wide temperature range of 77—300 K. The same decreasing order of the uni-molecular quenching rate, $Ru(bpy)_3^{2+} > Ru(dmbpy)_3^{2+} > Ru(bpz)_3^{2+}$, is observed for both the double-complex salt crystals and the encounter complexes formed between $^3[RuL_3]^{2+}$ and $Co(bpydc)_3^{3-}$ in aqueous solution. The high fraction of ET product formation in the quenching of encounter complex and the high fraction of cage escape demonstrate that emission quenching in aqueous solution occurs as an ET process. These findings strongly suggest that the Ru(II)-to-Co(III) ET process shortens the emission lifetimes of double-complex salt crystals, $[RuL_3]_3[Co(bpydc)_3]_2 \cdot nH_2O$. The carboxylate groups of 2,2′-bipyridine-4,4′-dicarboxylate enhance the intermolecular interaction between $^3[Ru(bpy)_3]^{2+}$ or $^3[Ru(dmbpy)_3]^{2+}$ and $Co(bpydc)_3^{3-}$ so as to increase the uni-molecular ET quenching rate in both the crystal and aqueous solution. A very weak dependence of the quenching rate on temperature in the crystal is accounted for by a small reorganization energy (1 eV).

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