Energy Transfer from $[Ru(bpy)_3]^{2+}$ to $[Cr(ox)_3]^{3-}$ in a Crystal of Double Complex Salt: $Na[Ru(bpy)_3][Cr(ox)_3]$

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In a crystal of double complex salt $Na[Ru(bpy)_3][Cr(ox)_3]$ (bpy=2,2'-bipyridine, $ox^{2-}=C_2O_4{}^{2-}$) obtained by mixing aqueous solutions of $Na_3[Cr(ox)_3]•5H_2O$ and $[Ru(bpy)_3]Cl_2•6H_2O$, both luminescence from ^3CT (metal-to-ligand charge-transfer) state of $[Ru(bpy)_3]^{2+}$ and ^2E_g state of $[Cr(ox)_3]^{3-}$ could be observed at 77 K, although the luminescence from ^3CT was extremely small. Lifetime of the luminescence from ^3CT becomes far shorter than that of single complex salts $[Ru(bpy)_3]X•nH_2O$ ($X=2Cl^-$, $SO_4{}^{2-}$). The large lifetime reduction of ^3CT state indicates that the excitation energy transfer occurs via ^3CT state of $[Ru(bpy)_3]^{2+}$ moiety in the double complex salt.

It has been known that photo-excitation energy absorbed by ruthenium(II) complex transfers to chromate(III) complex in a crystal of double complex salt composed of ruthenium(II) and chromate(III) complexes.[1,2] I.Fujita and H.Kobayashi reported that the luminescence from ^3CT state of $[Ru(bpy)_3]^{2+}$ was completely quenched and the strong emission from ^2E_g state of $[Cr(ox)_3]^{3-}$ was observed in the double complex salt $[Ru(bpy)_3]_3[Cr(ox)_3]_2•nH_2O$ obtained by mixing aqueous solutions of $K_3[Cr(ox)_3]•3H_2O$ and $[Ru(bpy)_3]Cl_2•6H_2O$. On the contrary, in the salt of $[Ru(bpy)_3]_3[Cr(CN)_6]_2•nH_2O$, the luminescence of $[Ru(bpy)_3]^{2+}$ was partially quenched and the emission of $[Cr(CN)_6]^{3-}$ was also observed. From these experimental results, transition energy of (d,d*) states of Cr(III) complexes and the electron spin conservation rule, they concluded that the excitation energy transferred via ^1CT state of $[Ru(bpy)_3]^{2+}$ to $^4T_{2g}$ state of $[Cr(ox)_3]^{3-}$ in $[Ru(bpy)_3]_3[Cr(ox)_3]_2•nH_2O$, whereas via ^3CT to ^2E_g in $[Ru(bpy)_3]_3[Cr(CN)_6]_2•nH_2O$.[1] In aqueous solutions, luminescence of $[Ru(bpy)_3]^{2+}$ is quenched by $[Cr(ox)_3]^{3-}$ and $[Cr(CN)_6]^{3-}$. The quenching is brought about by energy transfer from ^3CT state of $[Ru(bpy)_3]^{2+}$ to ^2E_g state of chromate(III) complexes because of the very fast internal conversion from ^1CT to ^3CT states in $[Ru(bpy)_3]^{2+}$.[3]

In this paper, we report that a very weak luminescence from ^3CT state of $[Ru(bpy)_3]^{2+}$ could be observed in the crystal of $Na[Ru(bpy)_3][Cr(ox)_3]$ which is obtained by mixing aqueous solutions of $Na_3[Cr(ox)_3]•5H_2O$ and $[Ru(bpy)_3]Cl_2•6H_2O$ and we could estimate the energy transfer rate constant from ^3CT state of $[Ru(bpy)_3]^{2+}$ to ^2E_g state of $[Cr(ox)_3]^{3-}$ in the double complex salt. Moreover, we propose the path of energy transfer from ^3CT to ^2E_g instead of the path from ^1CT to $^4T_{2g}$ in the salt.

$[Ru(bpy)_3]Cl_2•6H_2O$ and $Na_3[Cr(ox)_3]•5H_2O$ were prepared according to the literature.[3,4] Micro-crystals of the double complex salt precipitated readily by mixing aqueous solutions of $Na_3[Cr(ox)_3]•5H_2O$ with that of $[Ru(bpy)_3]Cl_2•6H_2O$. The double complex salt was identified by elemental analysis.[5] Unfortunately, single crystals of the double complex salt did not grow to the right size for performing X-ray structure analysis. Pure crystals of $[Ru(bpy)_3]_3[Cr(ox)_3]_2•nH_2O$ could not be obtained. By mixing aqueous solutions of $K_3[Cr(ox)_3]•3H_2O$ with that of $[Ru(bpy)_3]Cl_2•6H_2O$, a mixture of $[Ru(bpy)_3]_3[Cr(ox)_3]_2•nH_2O$ and $K[Ru(bpy)_3][Cr(ox)_3]$ was precipitated.

The method measuring luminescence and excitation spectra at 77 K was described elsewhere.[2] Luminescence decay of the double complex salt at 77 K was determined by means of the two-dimensional photon-counting method (Hamamatsu Photonics model C4780 and Hamamatsu Photonics streak-scope model C4334) with the optical fiber optics. Excitation was used at 525 nm obtained by a Laser Photonics, INC., model LN120C nitrogen laser pumped dye laser. Lifetimes were calculated by fitting the decays to a single or double exponential function.

In visible region, $[Ru(bpy)_3]^{2+}$ shows a strong ^1CT band at 21700 cm^{-1} (molar extinction coefficient $\varepsilon = 13000\ M^{-1}cm^{-1}$). The luminescence from ^3CT state appears at 17500 cm^{-1} (see Figure 1(a)).[2] $[Cr(ox)_3]^{3-}$ has absorption bands at 17500 cm^{-1} ($^4T_{2g}$) and 23800 cm^{-1} ($^4T_{1g}$) and these ε are very small (about 100 $M^{-1}cm^{-1}$). The phosphorescence from ^2E_g state is observed at 14400 cm^{-1} (see Figure 1(b)).[6] Figure 2 shows energy diagram of each complex.

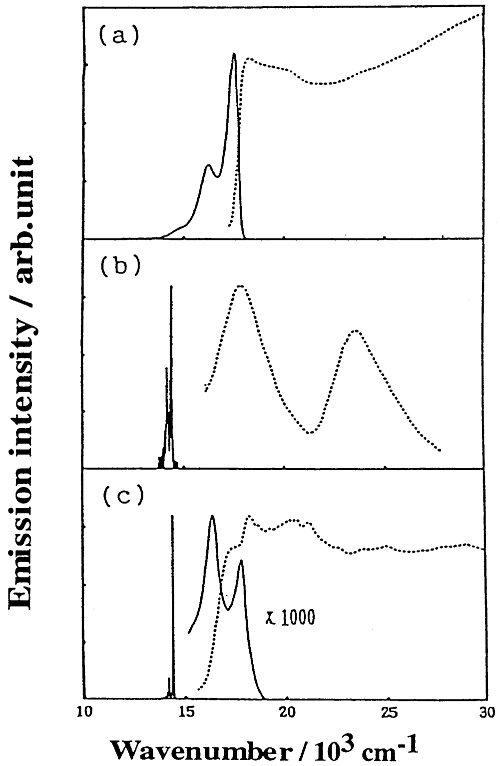

Figure 1. Luminescence (solid line) and excitation (dot line) spectra at 77K; (a) $[Ru(bpy)_3]Cl_2•6H_2O$ (excited at 21700 cm^{-1} and monitored at 17500 cm^{-1}), (b) $Na_3[Cr(ox)_3]•5H_2O$ (excited at 17500 cm^{-1} and monitored at 14400 cm^{-1}), (c) $Na[Ru(bpy)_3][Cr(ox)_3]$ (excited at 21700 cm^{-1} and monitored at 14400 cm^{-1}).

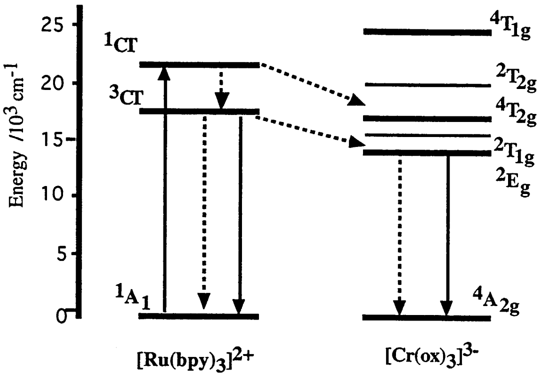

Figure 2. Energy diagram of $[Ru(bpy)_3]^{2+}$ and $[Cr(ox)_3]^{3-}$; radiative transition (bold arrow), nonradiative transition (fine arrow).

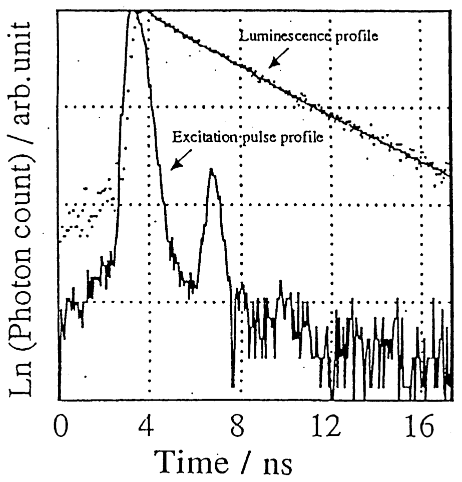

Figure 3. Log plot of luminescence intensity of $[Ru(bpy)_3]^{2+}$ in $Na[Ru(bpy)_3][Cr(ox)_3]$ at 77K. The lifetime τ=1.4 and 4.0 ns was determined by the best fit method considering the profile of the excitation pulse.

Table 1. Lifetime (τ) and energy transfer rate (k_{ET}) of $[Ru(bpy)_3]^{2+}$ in various crystals at 77K

Sample	τ / ns	k_{ET} / 10^6 s^{-1}
$Na[Ru(bpy)_3][Cr(ox)_3]$	1.4, 4.0 [a]	250 ,714 [a]
$[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\bullet}8H_2O$	160 [b]	6.0 [b]
$Na[Ru(bpy)_3][Al(ox)_3]$	3100 [a]	
$[Ru(bpy)_3]Cl_2{\bullet}6H_2O$	5500 [b]	
$[Ru(bpy)_3]SO_4{\bullet}6H_2O$	3800 [b]	

[a] This work. [b] Reference 2.

At 19000 cm^{-1} (525 nm) which is excitation wavenumber in this work, ε of $[Ru(bpy)_3]^{2+}$ is about 10000 $M^{-1}cm^{-1}$, while that of $[Cr(ox)_3]^{3-}$ is at the most 10 $M^{-1}cm^{-1}$. Thus, only $[Ru(bpy)_3]^{2+}$ complex absorbs the excitation light. Figure 1(c) shows the luminescence spectrum of the double complex salt excited at 19000 cm^{-1}. The salt emits a very narrow and strong phosphorescence from ^2E_g state of $[Cr(ox)_3]^{3-}$ (at 14400 cm^{-1}) although only $[Ru(bpy)_3]^{2+}$ is excited.

Figures 1(a) and (b) show the excitation spectra of the single complex salts of $[Ru(bpy)_3]Cl_2{\bullet}6H_2O$ and $Na_3[Cr(ox)_3]{\bullet}5H_2O$ at 77 K, respectively. Figure 1(c) shows the excitation spectrum on monitoring the luminescence maximum of $[Cr(ox)_3]^{3-}$ in the crystal of $Na[Ru(bpy)_3][Cr(ox)_3]$ at 77 K. By comparing Figure 1(c) with 1(a) and 1(b), it is clear that the energy transfer surely occurs from $[Ru(bpy)_3]^{2+}$ to $[Cr(ox)_3]^{3-}$.

Moreover, a broad and extremely weak phosphorescence from ^3CT state of $[Ru(bpy)_3]^{2+}$ (at 17800 cm^{-1}) could be observed. The luminescence decayed double exponentially (see Figure 3) and the lifetime could be evaluated as about 1.4 and 4.0 ns. The shorter lifetime is a minor component and the longer one is a major one. The shorter lifetime may be caused by a little restruction of a part of the crystal surface in air. It should be noted that the two lifetimes (1.4 and 4.0 ns) are very close to each other and very short compared with those of single complex salts and $Na[Ru(bpy)_3][Al(ox)_3]$ in which excitation energy can not transfer to a counter anion. As listed in Table 1, the lifetimes of these salts are in micro seconds (3.1—5.5 μs). By the results of powder X-ray structure analysis, a crystal structure of $Na[Ru(bpy)_3][Al(ox)_3]$ is the same as that of $Na[Ru(bpy)_3][Cr(ox)_3]$. Thus, quenching of the luminescence from $[Ru(bpy)_3]^{2+}$ in $Na[Ru(bpy)_3][Cr(ox)_3]$ is brought about by not the crystal structure but energy transfer from ^3CT state of $[Ru(bpy)_3]^{2+}$ to ^2E_g state of $[Cr(ox)_3]^{3-}$. The transfer rate can be evaluated with the reciprocal of the luminescence lifetime because the lifetime of $[Ru(bpy)_3]^{2+}$ in $Na[Ru(bpy)_3][Cr(ox)_3]$ is far shorter than those in the salts where energy transfer can not occur. Luminescence lifetimes and energy transfer rates in various crystals are listed in Table 1. The $^3CT \rightarrow {}^2E_g$ rate from $[Ru(bpy)_3]^{2+}$ to $[Cr(ox)_3]^{3-}$ is larger than that from $[Ru(bpy)_3]^{2+}$ to $[Cr(CN)_6]^{3-}$ in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\bullet}8H_2O$.[2] The difference may be due to the energy gap and spectral overlap integral between ^3CT and ^2E_g states. The gap in $Na[Ru(bpy)_3][Cr(ox)_3]$ (3000 cm^{-1}) is much smaller than that in $[Ru(bpy)_3]_2[Cr(CN)_6]Cl{\bullet}8H_2O$ (5000 cm^{-1}).

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References and Notes

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