6158 *J. Phys. Chem. A* **2000,** *104,* 6158−6164

Hopping and Annihilation of ^{3}MLCT in the Crystalline Solid of $[Ru(bpy)_3]X_2$ ($X = Cl^-$, ClO_4^- and PF_6^-)

Noriaki Ikeda,* Akio Yoshimura, Minoru Tsushima, and Takeshi Ohno*

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

Received: January 14, 2000; In Final Form: March 29, 2000

Emission decay measurements under various excitation intensities and time-resolved absorption spectroscopy were applied to investigate the bimolecular reactions of the triplet lowest excited metal-to-ligand charge-transfer state (^{3}MLCT) in the neat crystals or doped crystals with energy acceptor. The rate of hopping to the nearest-neighbor site in the energy migration of ^{3}MLCT in $[Ru(bpy)_3](PF_6)_2$ was determined to be $(3.5 \pm 0.5) \times 10^8$ s^{-1} from the dependence of emission decay rates on the doping concentration of Os^{2+} and the rate constant of triplet−triplet (T−T) annihilation in the emission decay for the single-crystal or transparent mixed-crystal ground with KCl. The rate constants of hopping to the nearest-neighbor sites obtained for the crystals of $[Ru(bpy)_3]X_2$ ($X = Cl^-$, ClO_4^-, and PF_6^-) showed a distance dependence. The diffusion constants of triplet exciton in the crystals were also estimated. Time-resolved absorption spectroscopy revealed that T−T annihilation produced the one-electron transferred products. The rate of electron transfer between ^{3}MLCT in the crystal of $[Ru(bpy)_3](PF_6)_2$ was estimated to be $\geq 5 \times 10^{10}$ s^{-1} by time-resolved absorption spectroscopy.

Introduction

Solid-state photoreactions such as bimolecular reactions of energy transfer and electron transfer and monomolecular reactions of isomerization have been attractive subjects from various points of view.[1−8] Both the mode and the rate of chemical reaction in crystalline solids are expected to be quantitatively related to the distance and orientation among reactants and surrounding molecules. Understanding of the bimolecular rates of chemical reaction in crystalline solid might be crucially important to interpret the rates of biochemical reactions between molecules well spatially oriented without involving water molecules in living cells.

Several difficulties are, however, involved in the study of the photochemical reactions in the solid state. A very small portion of the emission quenching causes a permanent change of the chemical species because the separation process of the reaction products is too slow to be free from the reverse reaction. Nevertheless, transient absorption spectroscopy of the excited state and reaction intermediates formed has been rarely applied to the photochemical reactions in optically dense materials such as crystals because most of the molecules excited by a high dose of laser pulse undergo annihilation in a very short time and produce a lot of heat burning themselves. Some heat absorber in the crystal sample is necessary to detect an optical change of the crystal. Since most of the emission decays might not be single exponential because of its extraordinary sensitivity to quenching impurities nearby, a highly purified crystal is required.

On the photochemistry and photophysics of $[Ru(bpy)_3]^{2+}$ (Ru(II)) in the various media, much attention has been paid to excited-state redox chemistry.[9,10] Especially, to figure out the interchromophoric interaction and reaction of Ru(II) in the concentrated system, several studies on annihilation or electron-transfer reaction between Ru(II) chromophores have been carried out for the Ru(II) adsorbed on heterogeneous systems such as silicate surfaces, etc.[11−14]

Spectroscopic studies of the triplet excited metal-to-ligand charge-transfer state (^{3}MLCT) of Ru(II) in the crystalline state have been performed at very low temperatures to identify the lowest excited state and to figure out the emission mechanism from the excited state.[10,15−17] There are some arguments whether the ^{3}MLCT state of Ru(II) as a luminophore in the concentrated or neat crystal is localized or its excitation energy can migrate.[18−21] There have been few studies on excitation energy migration of the ^{3}MLCT in neat crystal. If the triplet excited state of Ru(II) is almost localized (or slow migration), the excited state would be not severely sensitive to both the defect and the impurity of crystal when those concentrations are low. Such features in the metal complex ion of octahedral coordination compounds where the counterions keep a moderate distance between chromophores are much less understood. When the crystal of $[Ru(bpy)_3](PF_6)_2$ is excited by a pulse laser even if the intensity is as weak as 0.01 mJ/cm^2, some portion of the second-order decay in the emission is observed, and it could be ascribed to the annihilation of ^{3}MLCT.[17] Migration of the excitation energy through the crystal might be responsible for the annihilation of ^{3}MLCT and the impurity quenching. To know these features, an energy-transfer process in a crystal of $[Ru(bpy)_3](PF_6)_2$ doped with $[Os(bpy)_3]^{2+}$ (Os(II)) is a good target to elucidate the distance dependence on the rate of excitation energy transfer between donor and acceptor ions and of energy migration in the crystal. In the present paper, we evaluated a diffusion constant of the ^{3}MLCT state of Ru(II) and the rate of Ru(II)−Ru(II) excitation migration in the crystal from the rate dependence of energy transfer to Os(II) on the acceptor concentration. Furthermore, the emission decay measurements under various excitation intensities and time-resolved difference absorption spectroscopy have been applied to reveal a couple of bimolecular processes in the crystal. The former was applied to energy-transfer and migration processes of ^{3}MLCT in the crystal of $[Ru(bpy)_3]X_2$ ($X = PF_6^-$, ClO_4^-, and Cl^-) doped with an acceptor or dispersed in KCl solid. The latter was applied to annihilation reaction of ^{3}MLCT in the transparent solid of [Ru-

10.1021/jp0002188 CCC: $19.00

(bpy)$_3$](PF$_6$)$_2$ ground with KCl crystal. KCl is not only an index-matching medium but also a heat absorber preventing from burning the crystal itself.

Experimental Section

Materials. The compounds, [M(bpy)$_3$](PF$_6$)$_2$ (M = Ru, Os, Zn), were prepared by metathesis from [Ru(bpy)$_3$]Cl$_2$·6H$_2$O,[22] [Os(bpy)$_3$]I$_2$·3H$_2$O,[23] and [Zn(bpy)$_3$]Cl$_2$·7H$_2$O[13,22] salts that were synthesized according to literature methods and then recrystallized from acetonitrile−ethanol solution. The crystals of [Ru(bpy)$_3$](PF$_6$)$_2$ doped with [Os(bpy)$_3$](PF$_6$)$_2$ were prepared from acetonitrile−ethanol solution after mixing the solution of each component in the stoichiometric molar ratio. Since the crystal structure of [Os(bpy)$_3$](PF$_6$)$_2$ as a guest molecule is isomorphous with that of [Ru(bpy)$_3$](PF$_6$)$_2$ as a host crystal and those cell parameters are almost the same,[24,25] it is assumed that doping and mixing between these two compounds to form crystals is homogeneous. [Ru(bpy)$_3$](ClO$_4$)$_2$ and [Ru(bpy)$_3$](B(C$_6$H$_5$)$_4$)$_2$ were also prepared by metathesis from the chloride salt. For Ru(bpy)$_3$Cl$_2$, it is generally known as hexahydrate; the crystals obtained are usually analyzed to have 5−6 H$_2$O as a content of crystal water. Single crystals as heptahydrate[26] have been obtained by slow evaporation from the concentrated aqueous solution. Data of elementary analysis for the complexes agreed with those calculated except for tetraphenylborate salt that might contain solvents for recrystallization. Large single crystals of [Ru(bpy)$_3$](PF$_6$)$_2$, [Ru(bpy)$_3$](ClO$_4$)$_2$, and [Ru(bpy)$_3$]Cl$_2$·7H$_2$O were used for the annihilation measurement.

Transparent disks of KCl containing crystals of the Ru(II) compound were prepared in the following way. The ground microcrystals of Ru(II) compounds (1 mg) were dispersed in the ground crystals of KCl (1 g). The ground mixture (60 mg) was pressed to be transparent under vacuum. An island of the red crystal was invisible under magnification.

Apparatus and Measurements. Absorption spectra were recorded on Shimadzu MPS-2000 or UV2500PC spectrophotometers. Emission spectra of the crystals were measured by using a grating polychromator (Jasco CT250) with a silicon diode array (Hamamatsu S3901-512Q). The 488 nm line of an Ar laser was used for the excitation. Crystal samples were normally contained in quartz cells with 2 mm diameter under atmosphere. For measuring the emission spectra of a single crystal at room temperature, the only front surface of the crystal, which was placed on a fine glass tip with an angle of ~45° against the excitation light, was excited by using an objective lens (×10), and the emission from the same surface of the crystal was detected. The detector sensitivity was corrected by using a bromine lamp (Ushio JPD 100V500WCS). For the emission decay measurements under high laser excitation intensities, the SHG (532 nm, fwhm 6−10 ns) pulse of a Q-switched Nd^{3+}:YAG laser (Quantel YG580 or Continuum Surelite I-10) was used for excitation of the sample crystals. The intensity of laser was attenuated by using neutral density (ND) filters under lower pumping-flash voltage of the laser. Furthermore, a hard aperture (typically 2 mm diameter) just before the samples was also used to cut and determine the irradiated intensity of laser output energy. Laser power was monitored by a power meter (Gentic ED100A). Final energies irradiated to the sample were in the range of 1−3000 μJ/pulse. To avoid any thermal effect in the samples, measurements for the emission decay were done by one-shot laser excitation as far as possible.[27] Emission from the crystals under atmosphere was detected by using a monochromator (Jovin Yvon HR-320) with a photomultiplier (Hamamatsu R636) and a digitizing oscilloscope (HP 54510A, 8 bit, 250 MHz 1 G sampling/s). In the case of a large single crystal, the crystal was placed on a fine glass tip, and the emission from the same aria of the crystal was detected. When the laser intensity was high, the emission intensity from the sample was also attenuated by ND filters with known transmittance at monitoring wavelength to avoid the saturation of photomultiplier output. For measuring the emission decays under weak excitation power with high time resolution, the time-correlated single-photon counting system with a cavity-dumped Ti^{3+}:sapphire laser was used. The details are described elsewhere.[8] The frequency-doubled output of the laser (400 nm, 100 fs, 200 kHz, few nJ/pulse) was used for excitation. The instrumental response function is typically 40 ps.

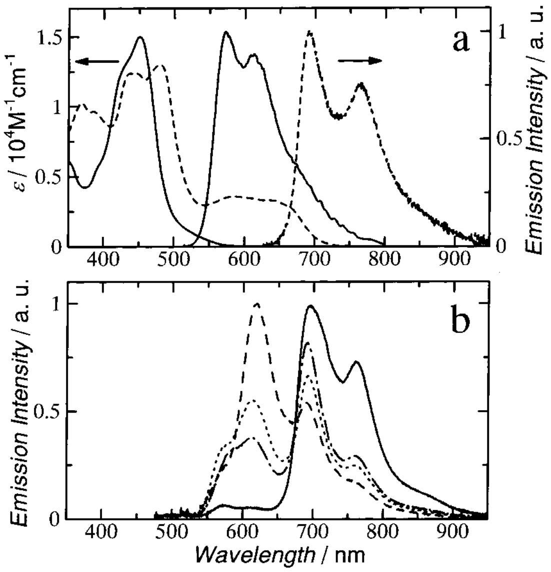

Figure 1. (a) Absorption spectra in acetonitrile solution and emission spectra in the single crystal of [Ru(bpy)$_3$](PF$_6$)$_2$ (—) and Os(bpy)$_3$(PF$_6$)$_2$ (---). (b) Emission spectra in the doped crystals of Os$_x$Ru$_{1-x}$(bpy)$_3$(PF$_6$)$_2$; $x = 10^{-4}$ (---), 5×10^{-4} (···), 10^{-3} (—·—), 10^{-2} (—). Intensities of emission are arbitrary.

A picosecond Nd^{3+}:YAG laser system for the time-resolved absorption measurement was reported elsewhere.[28] For the selective excitation of Os(II) in the doped crystals, a homemade dye laser (cresyl violet; 636 nm, 8 ns pulse width) pumped by the SHG pulse of a Q-switched Nd^{3+}:YAG laser was used. All the decay measurements were done at 298 K.

Results and Discussion

(1). Migration and Energy Transfer of ^{3}MLCT in the Crystal of [Ru(bpy)$_3$](PF$_6$)$_2$ Doped with Os(II). Figure 1a shows absorption spectra of acetonitrile solution and emission spectra of the single crystal of [M(bpy)$_3$](PF$_6$)$_2$ (M = Ru, Os). An absorption spectrum of [Ru(bpy)$_3$](PF$_6$)$_2$ diluted by [Zn(bpy)$_3$](PF$_6$)$_2$ in a single crystal was close to that of the solution.[29] A weak absorption tail at the lower energy side (500−580 nm) of the ^{1}MLCT band for [Ru(bpy)$_3$]$^{2+}$ and absorption bands with moderate intensity around 550−700 nm for [Os(bpy)$_3$]$^{2+}$ are considered to have a triplet character (^{3}MLCT) to some extent.[30]

The emission spectra of the Ru(II) and the Os(II) in the single crystal at 77 and 298 K show vibronic bands originating from the electronic excited states, which are assigned to a phosphorescence from the ^{3}MLCT state. When all the surfaces of the crystal were irradiated, the highest energy band of emission was weakened resulting in a small shift of the peak to the lower energy. This deformation of the emission spectra at room

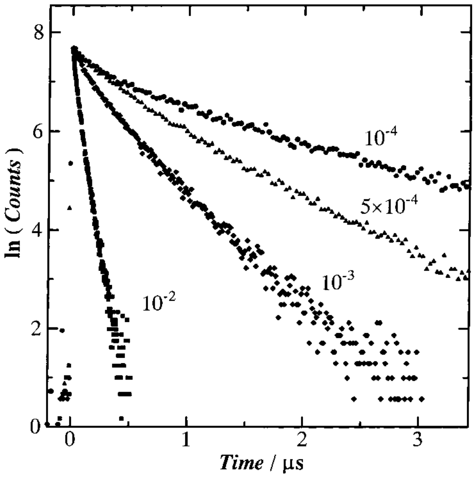

Figure 2. Decay curves of emission at 600 nm in the doped crystals of $Os_xRu_{1-x}(bpy)_3(PF_6)_2$: a, $x = 10^{-4}$; b, 5×10^{-4}; c, 10^{-3} d, 10^{-2}.

temperature is ascribed to reabsorption,[20] since there is some spectral overlap between absorption and emission of the compound. This suggests a possibility of energy migration in the neat crystal. The position of the highest energy band of emission was nearly constant between 77 and 300 K for a single neat crystal of $[M(bpy)_3](PF_6)_2$ as well as a diluted crystal of $[M_xZn_{1-x}(bpy)_3](PF_6)_2$ (M = Ru, Os; $x = 10^{-3}$) although the bandwidth increases with temperature raising.[29] The energy level of the ^{3}MLCT state of Os(II) is about 3500 cm^{-1} lower than that of Ru(II). There is a good spectral overlap between the Ru(II) emission and the Os(II) absorption, as can be seen from Figure 1a.

The occurrence of energy transfer from a Ru(II) to an Os(II) in the doped crystal can be detected by observing the emission spectra and the decay profiles. Figure 1b shows the enhancement of the Os(II) emission along with a decrease of the Ru(II) emission when the doping concentration of Os(II) was increased. Seeming peak shifts observed in the Ru(II) and Os(II) emissions of doped crystals reflect the different extent of reabsorption by each component. It should be noted here that a relatively high concentration of Os(II) is needed to effectively quench the Ru(II) emission.

For measuring the emission decays of Ru(II) crystal doped with Os(II), the time-correlated single-photon counting method was used under weak excitation power. A laser pulse with relatively high power causes another decay channel such as annihilation (see next section).[31] Figure 2 shows the decay curves of the Ru(II) emission band at 600 nm in the doped crystals of $[Os_xRu_{1-x}(bpy)_3](PF_6)_2$ with various doping concentrations at room temperature. When the doping concentration is equal to or less than 1%, the emission decay curves observed can be simply described by using two exponential terms

$$I(t) = I(0)[A_1 \exp(-k_1 t) + A_2 \exp(-k_2 t)] \tag{1}$$

where A_i and k_i stand for the preexponential factor (amplitude) and the time constant of the ith (i = 1 and 2) component, respectively. A deconvolution analysis of the decay profiles affords the best fit by biexponential decay for the Ru(II) emission and a single-exponential decay with one rise component for the Os(II) emission. Values of A_i and τ_i (=$1/k_i$) for the lightly doped crystals studied here are summarized in Table 1. The rise of the Os(II) emission occurred in 150 ns when the fast decay component of the Ru(II) emission was observed. The lifetimes ($1/k_{slow}$) of the slow component of the Ru(II) emission decreased with an increase of the doping concentration of Os(II), which were almost the same as those of the Os(II) emission. Because the intrinsic lifetime of Os(II) in the doped crystal measured by direct excitation at 646 nm using a dye laser was 200 ns, the lifetime of precursors (Ru(II)*) is reflected on the apparent lifetime of the Os(II) emission longer than 200 ns. This behavior tells us the presence of relatively slow energy transfer mediated by donor−donor energy migration. Although this was observed in early studies[19] at low temperature, any quantitative data on the migration was still not revealed. Since the Os(II) emission contains a directly excited component to some extent with the energy-transferred component from Ru(II)* when the crystal is excited at 400 nm, a rise component factor of A_1 is smaller than A_2 and there is some uncertainty in the decay analysis of the Os(II) emission. Therefore, only decay analysis of the Ru(II) emission was considered.

TABLE 1: Decay Parameters of Emissions of $Os_xRu_{1-x}(bpy)_3(PF_6)_2$ Doped Crystals with Various Mole Fraction (x) of Os^{2+} at 298 K

mole fraction		Ru emission (600 nm)		Os emission (720 nm)	
x	i	A_i/%	τ_i/ns	A_i/%	τ_i/ns
10^{-4}	1	7.0	470	−41.9	95
	2	93.0	1980	100	1970
5×10^{-4}	1	7.0	178	−66.5	142
	2	93.0	938	100	947
10^{-3}	1	43.7	127	−79.2	106
	2	56.3	426	100	405
9.9×10^{-3}	1		44.0[a]	−87.0	46.2
	2	41.8	77.0	100	187
0.048	1		5.1[a]	−58.2	5.8
	2	21.6	11.3	100	160
0.115	1		0.73[a]	−61.2	0.67
	2	40.3	3.27	100	130
0.231	1		0.29[a]	−47.7	0.30
	2	4.5	2.32	100	101

[a] Decay curves are essentially multiexponential, therefore only times of the emission decaying to $I(0)/e$ are shown. A detailed analysis for the fast multiexponential component is described elsewhere.[8]

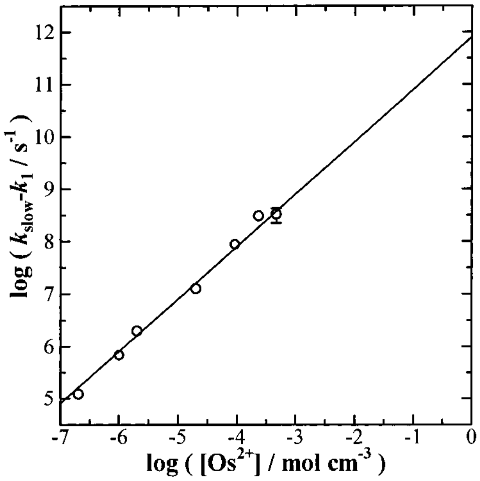

Figure 3. Log−log plot of the quenching rate constants ($k_{slow} - k_1$) of the emission of Ru(II) vs the concentrations of Os(II) in the doped crystals of $Os_xRu_{1-x}(bpy)_3(PF_6)_2$.

The rate constant of the slowest decay component ($k_{slow} = 1/\tau_{slow}$) increased with an increase in the doping concentration of Os(II) from 10^{-4} to 0.23. Since the decay rate constant was linear to the concentration of Os(II) (Figure 3), the excited state of Ru(II) migrates through the crystal to encounter an energy acceptor of Os(II) as in the solution.[32] The slowest rate constant is expressed by the following equation

$$k_{slow} = k_1 + k_2[Os^{2+}] \quad (2)$$

where k_1 and k_2 are the intrinsic decay rate constant of ^{3}MLCT and the apparent bimolecular quenching rate constant of energy transfer, respectively. A plot of log($k_{slow} - k_1$) versus log[Os^{2+}] gives a fairly good straight line even in the high doping region as shown in Figure 3. The rate constant of the energy transfer was evaluated from the intercept of the straight line in Figure 3 to be 1.4×10^{-12} cm^3 s^{-1} (=8.4×10^8 M^{-1} s^{-1}).

On increasing the concentration of Os(II) more than 1%, the decay curves of Ru(II) emission cannot be described in biexponential term. The fast decays in an early time region (<1 ns) were too complicated to determine the lifetime. This is due to fast and direct energy transfer to Os(II) at short distances. A detailed analysis for multiexponential decay at an early time region by Monte Carlo simulation is published elsewhere.[8]

(2) Annihilations of ^{3}MLCT in the Crystalline Solid of [$Ru(bpy)_3$]X_2. The emission of the irradiated single crystals of [$Ru(bpy)_3$]$(PF_6)_2$ decayed in a single-exponential mode of $k_1 = 3.2 \times 10^5$ s^{-1} on the excitation of a weak power laser less than 5 $\mu J/cm^2$. As the laser intensity exceeded 5 $\mu J/cm^2$, the emission rapidly decayed at the beginning of the emission decay and the rapid decay component increased with the increase in the laser intensity (Figure 4). The fast process can be assigned to the annihilation of ^{3}MLCT

$$^3[Ru(bpy)_3]^{2+} + {}^3[Ru(bpy)_3]^{2+} \rightarrow X + Y \quad (3)$$

Similar features have been observed in the systems of [$Ru(bpy)_3$]$^{2+}$ concentrated on micelle,[33] cellulose film,[11] porous silicate,[12] clay,[13] zeolite Y,[14] and the Ru(II) crystal[17] or in the crystals of Pt compound such as Pt(II) diphosphite.[34,35] On the assumption that the short-lived component of emission decays following the second-order rate formula, an integrated equation for the ^{3}MLCT concentration ($n(t)$) of Ru(II) at a time after excitation is obtained

$$n(t) = \frac{n(0)\exp(-k_1 t)}{1 + \frac{k_2}{k_1} n(0)[1 - \exp(-k_1 t)]} \quad (4)$$

where $n(0)$, k_1, and k_2 are the ^{3}MLCT concentration of Ru(II) immediately after excitation and the monomolecular and bimolecular rate constants of the phosphorescent state of Ru(II), respectively. By plotting the inverse of the ^{3}MLCT concentration in an arbitrary unit versus $\exp(k_1 t)$,[34−37] straight lines with an intercept were obtained under various excitation intensities as shown in Figure 5.

$$1/n(t) = [1/n(0) + k_2/k_1]\exp(k_1 t) - k_2/k_1 \quad (4')$$

If we estimate the $n(0)$, the T−T annihilation rate of ^{3}MLCT in the crystal can be obtained. For an estimation of the initial concentration of ^{3}MLCT in the crystal, the following equation was used.[37]

$$n(0) = [N_0 L(1 - e^{-1})]/(\Delta S \Delta l) = 1.455(N_0 L/\Delta S)\epsilon C \quad (5)$$

where N_0, ΔS, and L are, respectively, the number of photons irradiated, the irradiated area on the sample crystal, and the light transmittance of measuring system (a photon-loss factor of lenses and cell windows etc.). Δl is defined as the absorption depth, which an excitation light decreases to $1/e$ and has a relation of $(2.303\epsilon C)^{-1}$, where ϵ and C are the molar extinction coefficient and the molar concentration of the Ru(II) in the crystalline state, respectively. The irradiated area on the sample crystal was typically 0.06 cm^2. The molar extinction coefficient at excitation wavelength (532 nm) was assumed to be ca. 800 M^{-1} cm^{-1} for all $Ru(bpy)_3(X)_2$ crystals considering the reference data.[22,38] The data of the crystal structure were used to estimate C to be 2.02 M for hexafluorophosphate salt,[24] 2.2 M for perchlorate salt,[39] and 1.92 M for chloride salt.[26] By applying these values to eq 5, $n(0)$ was 1.7×10^{-3} M (=1×10^{18} cm^{-3}) typically for $Ru(bpy)_3(PF_6)_2$ when the laser intensity was 10 $\mu J/cm_2$. The mole fraction of the excited state (10^{-3}) is too low to form a contact pair of ^{3}MLCT because the number of the nearest neighbors of ^{3}MLCT is less than eight for all the crystals studied here. Therefore, the migration of excitation energy is necessary to undergo bimolecular annihilation. From the intercept in Figure 5, the bimolecular rate constants for annihilation, k_2, was obtained to be $(1.8 \pm 0.3) \times 10^{-12}$ cm^3 s^{-1} (=1.1×10^9 M^{-1} s^{-1}) for the crystal of [$Ru(bpy)_3$]$(PF_6)_2$. The rate of T−T annihilation in the crystal of [$Ru(bpy)_3$]$(ClO_4)_2$, $(6.2 \pm 3) \times 10^{-12}$ cm^3 s^{-1}, is larger than those of [$Ru(bpy)_3$]$(PF_6)_2$. The rate constant of the second-order decay for [$Ru(bpy)_3$]$Cl_2 \cdot nH_2O$ (n = 6 and 7) is in the range of $(6-12) \times 10^{-12}$ cm^3 s^{-1} as shown in Table 2.

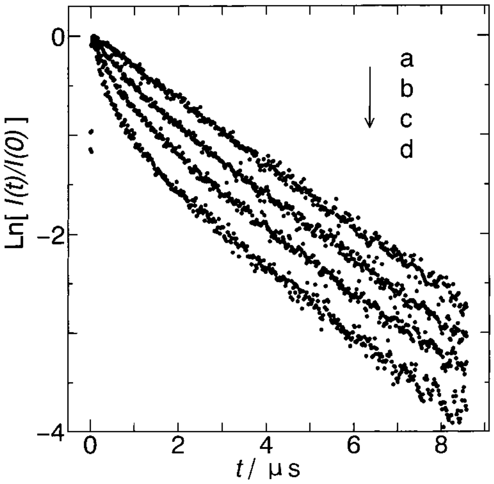

Figure 4. Emission decay curves of $Ru(bpy)_3(PF_6)_2$ in the single crystal under various laser excitation intensities: a, 1.1 $\mu J/cm^2$; b, 17 $\mu J/cm^2$; c, 68 $\mu J/cm^2$; d, 280 $\mu J/cm^2$. Each of initial intensities was normalized. Observed wavelength is 620 nm.

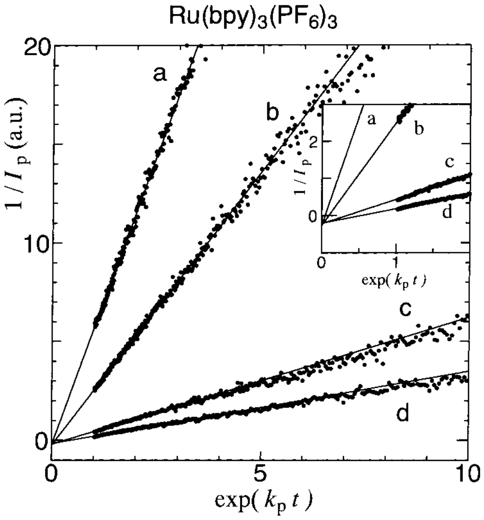

Figure 5. Plots of the reciprocal of emission intensity for $Ru(bpy)_3(PF_6)_2$ crystal vs $\exp(k_1t)$ under different exciting light intensities: a, 1.1 $\mu J/cm^2$; b, 2.8 $\mu J/cm^2$; c, 17 $\mu J/cm^2$; d, 68 $\mu J/cm^2$. Inset shows an enlargement around intercept.

TABLE 2: Three Kinds of the Closest Metal−Metal Distances (R_1, R_2, R_3) in the Crystal of $[Ru(bpy)_3]X_2$ and the Number of Sites (in Parentheses), the Intrinsic Decay Rate Constants (k_1), Bimolecular Rate Constants of T−T Annihilation or Energy Transfer (k_2), Diffusion Constants of ^{3}MLCT, and Rate Constants of Hopping (k_{hop})

X	R_1/nm	R_2/nm	R_3/nm	$k_1/10^5\ s^{-1}$	$k_2/10^{-12}\ cm^3\ s^{-1}$	$D_m/10^{-6}\ cm^2\ s^{-1}$	$k_{hop}/10^8\ s^{-1}$
PF_6^-	0.820(2)[e]	1.076(6)	1.352(12)	3.2[a]	1.8 ± 0.3,[a] 1.5 ± 0.3,[b] 1.4[c]	1.3,[a] 1.1,[b] 1.0[c]	4.0,[a] 3.3,[b] 3.1[c]
ClO_4^-	0.797(2)[f]	1.032(4),1.075(2)	1.279−1.374(10)	3.7[a]	6.2 ± 3,[a] 3 ± 0.5[b]	4.6,[a] 2.2[b]	14,[a] 7[b]
Cl^-	0.761(2)[g]	0.781(1)	1.129(1), 1.249(2)	10−50[a,d]	6−12,[a] 23 ± 7[b]	9,[a] 23[b]	29,[a] 80[b]

[a] The single crystal. [b] The transparent solid sample ground with KCl. [c] The doped crystal with Os(II). [d] The decay rate constant of the chloride salt depends on the number of crystal water.[29] [e] Reference 24, [f] Reference 39, [g] Reference 26.

When the diluted crystal of $[Ru_{0.1}Zn_{0.9}(bpy)_3](PF_6)_2$ was excited, no deviation of exponential decay of the emission was observed up to the laser intensity of 1 mJ/cm^2. A rough estimation of k_2 gave a smaller value of 2.4×10^{-14} cm^3 s^{-1} in 2 orders of magnitude than that of $[Ru(bpy)_3](PF_6)_2$. The same feature was also observed for the crystal of $[Ru(bpy)_3](B(C_6H_5)_4)_2$. The presence of the bulky counterion of $B(C_6H_5)_4^-$ seems to keep larger distance between Ru chromophores as in the diluted crystal.

To estimate the formation of ^{3}MLCT more exactly, a transparent solid-disk sample composed from ground crystal of $[Ru(bpy)_3]X_2$ and KCl with a thickness of 0.5 mm was also examined. The thin crystal was prepared by mixing the ground crystal of $[Ru(bpy)_3]X_2$ with that of KCl. The formation of ^{3}MLCT for the transparent and thin crystal was assumed to be the same as ^{3}MLCT production for the aqueous solution of the same absorbance, the latter of which is easily determined by means of transient absorption spectroscopy. The laser excitation of 60 and 300 μJ/cm^2 converted the Ru(II) compound of 0.03% and 0.15% to ^{3}MLCT, respectively. Since the mole fractions of ^{3}MLCT are too small to form a contact pair of ^{3}MLCT in these cases, only the excitation migration through the crystal via hopping (k_{hop}) give a chance of encounter. A biexponential decay was observed for the thin crystal of $[Ru(bpy)_3]X_2$ ground with KCl even on the laser excitation with weak power less than a few μJ/cm^2. The rate constants (k_1 and k'_1) of the fast and slow decay components are 8×10^6 and 2×10^6 s^{-1} and may be ascribed to the bulk and the surface of the thin crystals of $[Ru(bpy)_3](PF_6)_2$, respectively. As the laser intensity exceeded 100 μJ/cm^2, a rapid decay appeared at the beginning of the emission decay and the rapid decay component increased with the increase in the laser intensity. Assuming a common bimolecular rate constant for annihilation for the decay components, the rate constant for annihilation was estimated by means of simulation using the following equation

$$n(t) + n'(t) = \frac{fn(0)\exp(-k_1 t)}{1 + \dfrac{k_2}{k_1}n(0)[1 - \exp(-k_1 t)]} + \frac{(1 - f)n'(0)\exp(-k'_1 t)}{1 + \dfrac{k_2}{k_1}n'(0)[1 - \exp(-k'_1 t)]} \qquad (6)$$

where $n(t)$ and $n'(t)$ are the concentration of excited complexes ion in the bulk and near to the surface of the ground crystal, respectively, and f is a fraction of the bulk component. The estimated values of k_2 are $(1.5 \pm 0.3) \times 10^{-12}$ cm^3 s^{-1}, $(3 \pm 0.5) \times 10^{-12}$ cm^3 s^{-1}, and $(23 \pm 7) \times 10^{-12}$ cm^3 s^{-1} for the diluted crystals of $[Ru(bpy)_3](PF_6)_2$, $[Ru(bpy)_3](ClO_4)_2$, and $[Ru(bpy)_3]Cl_2\cdot 7H_2O$, respectively. These values are in good agreement with those obtained for the single crystals except for $[Ru(bpy)_3]Cl_2\cdot 7H_2O$. It is noteworthy that the values obtained by using three different methods for $[Ru(bpy)_3](PF_6)_2$ coincide with each other. The much larger value of k_2 in $[Ru(bpy)_3]Cl_2\cdot 7H_2O$ could be ascribed to the chemical instability of the hydrated crystal dispersed in KCl.

(3) Diffusion Constants of the Excitation Migration. Since the migration of excitation energy is the net result of sequential hopping to the adjacent sites of Ru(II) ion, the bimolecular rate of collision (energy transfer) to Os(II) (or ^{3}MLCT) can be written assuming the Smoluchowski type equation as follows

$$k_2[Os^{2+}] = 4\pi R_{eff} D_m N_A\,[Os^{2+}] \qquad (7)$$

where D_m is a diffusion constant of the excitation energy in the crystal and N_A is Avogadro's number. R_{eff} is an effective D−A distance at which energy transfer occurs much more efficiently than energy hopping to the nearest-neighbor site. D_m is evaluated to 1.04×10^{-6} cm^2 s^{-1} assuming R_{eff} to be the second closest distance. This assumption is valid for the energy transfer from ^{3}MLCT(Ru) to Os(II) in the PF_6 salt crystal, where there are two of the closest sites ($R_1 = 0.82$ nm)[24] in the adjacent layers and six of the second closest sites ($R_2 = 1.076$ nm)[8,24] in the layer containing the excited ion. The rate of energy transfer to Os(II) at the distance shorter than 1.076 nm (7×10^9 s^{-1}) is much faster than the rate of hopping to the two adjacent sites with 0.82 nm,[8] which is faster than the energy transfer to the third closest sites (see also the next section).

The bimolecular rate of the T−T annihilation is also written as follows

$$k_2 n(t) = 4\pi R'_{eff} D_m n(t) \qquad (8)$$

where $n(t)$ is the molecular concentration of ^{3}MLCT of Ru(II) in cm^{-3} that is produced by laser excitation and R'_{eff} is an effective site−site distance at which the T−T annihilation occurs much more efficiently than energy hopping. Since the k_2 values observed for the T−T annihilation were almost similar to that for the energy transfer of ^{3}MLCT to Os(II), it was assumed that both effective reaction distances are the same. Using this assumption, D_m is again evaluated to be $(1.1{-}1.3) \times 10^{-6}$ cm^2 s^{-1} from the results of T−T annihilation observed in the neat crystal and the diluted crystals of $[Ru(bpy)_3](PF_6)_2$. The values of R'_{eff} in the crystals of $[Ru(bpy)_3](ClO_4)_2$ and $[Ru(bpy)_3]Cl_2\cdot 7H_2O$ were assumed to be the distance to the second closest metal sites (1.075[39] and 0.781 nm,[26] respectively), as in $[Ru(bpy)_3](PF_6)_2$.

The diffusion constants are calculated to be $(1.2 \pm 0.2) \times 10^{-6}$ cm^2 s^{-1}, $(3.4 \pm 2) \times 10^{-6}$ cm^2 s^{-1}, and $(16 \pm 7) \times 10^{-6}$ cm^2 s^{-1} for $[Ru(bpy)_3](PF_6)_2$, $[Ru(bpy)_3](ClO_4)_2$, and $[Ru(bpy)_3]Cl_2\cdot 7H_2O$, respectively, by using the values of R'_{eff} in each crystal (Table 2). The crystal structure of $[Ru(bpy)_3]Cl_2\cdot 7H_2O$ is very different from the others owing to the presence of hydrated water. According to our recent study[26] on the crystal structure, there is a network of hydrogen bonding consisting of water molecules and chloride ions above and below the layer of metal ions, in which the Ru^{2+} ions are at the two closest sites at 0.761 nm and one site at 0.781 nm. The third closest site lies at a distance of 1.129 nm in the different layer of metal ion. If the annihilation rate of ^{3}MLCT with ^{3}MLCT at the third closest sites is comparable to that of the hopping, the value of D_m is smaller than the evaluated one to some extent. This may be true for the crystal of [Ru(bpy)$_3$]Cl$_2$•7H$_2$O.

It is interesting to compare the reported values of diffusion constants for the triplet exciton in various crystals. The magnitude of the diffusion constant of the triplet state in the crystal of uranyl nitrate (5.5×10^{-6} cm^2 s^{-1})[37a] is similar to those determined here. Meanwhile, the diffusion constants of rare-earth metal salt such as EuAl$_3$B$_4$O$_{12}$ (8×10^{-10} cm^2 s^{-1})[40] are much smaller, and those of molecular crystals such as anthracene (2×10^{-4} cm^2 s^{-1})[36,41] are larger than those of the Ru(II) salts. Delocalization of the excited electron decreasing in the order of 2p > 4d > 5f may be responsible for the magnitude of the diffusion constants.

(4) Hopping Rate of the Excited State in [Ru(bpy)$_3$]X$_2$. On the assumption that Einstein−Smoluchowski relation, $k_{hop} = 2D_m/R_1^2$, is valid for the hopping to the closest site at R_1, the monomolecular rate constant of hopping, k_{hop}, can be estimated from the values of D_m and R_1. The calculated values of hopping rate constant in the crystal of [Ru(bpy)$_3$](PF$_6$)$_2$ are $(3.1-4.0) \times 10^8$ s^{-1} for the single crystal and the ground crystal as is shown in Table 2. The rate is very close to that (3.1×10^8 s^{-1}) estimated from the rate of bimolecular energy transfer to Os(II). The obtained value was again verified by comparing with the energy-transfer rate to various neighboring sites (see previous section). In a recent our paper,[8] furthermore, it was shown that a stochastic simulation using this hopping rate constant quite reasonably reproduced the multiexponential decay observed for highly doped crystals with Os(II).

As a mechanism of hopping leading to energy migration, only electronic exchange interaction between the Ru(II) in the excited and ground states allows the fast energy transfer since the rate of energy transfer estimated by the dipole−dipole interaction is too small.[8] The hopping rate for [Ru(bpy)$_3$](ClO$_4$)$_2$ was estimated to $(7-14) \times 10^8$ s^{-1} as shown in Table 2 for the ground crystal and the single crystal. The larger rate of hopping in [Ru(bpy)$_3$](ClO$_4$)$_2$ than in [Ru(bpy)$_3$](PF$_6$)$_2$ can be accounted for by the shorter distances to the closest sites shown in Table 2. The largest rate of hopping $(29-80) \times 10^8$ s^{-1} was evaluated for the crystal of [Ru(bpy)$_3$]Cl$_2$•7H$_2$O. It was assumed that the annihilation with ^{3}MLCT between the three closest sites in the layer occurs more efficiently than the hopping to the two closest sites. The largest rate of hopping may be reasonable on account of the shortest site−site distance among the three crystals.

The hopping rate should be dependent on the site-to-site distance as shown in the following equation

$$\ln k_{hop} = \ln k^0_{hop} - \beta(R - R_0) \qquad (9)$$

where β, R, and k^0_{hop} are an attenuation factor, the center-to-center distance of the metal site, and the hopping rate at the van der Waals distance (R_0). Although the range of distance examined in this study is small, a tentative plot shows a large value of $\beta = 45$ nm^{-1} (Figure 6), which leads the rate estimation of hopping to Ru(II) at the van der Waals distance (6.8×10^{12} s^{-1}). The limiting rate of hopping might not be realistic because the emission−absorption overlap integral required for the hopping is so small compared with the energy transfer to Os(II) ($k_{en} = 2 \times 10^{12}$ s^{-1}).[8] It should be reexamined in a wide range of the distance by changing the counterions.

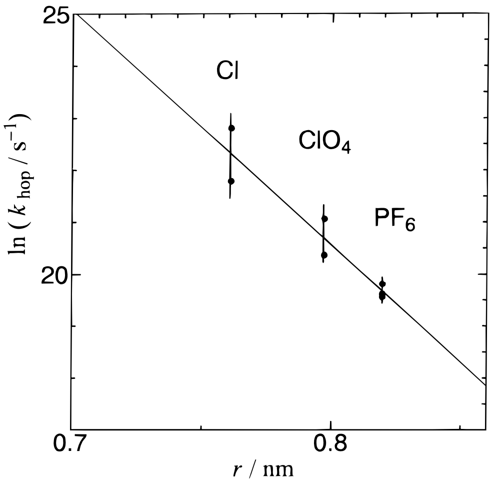

Figure 6. Dependence of hopping rate on the distance of the closest site in the Ru(bpy)$_3$X$_2$.

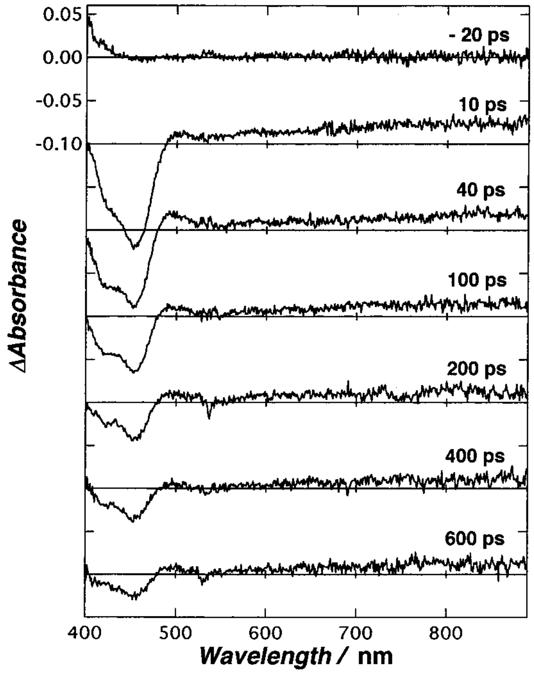

Figure 7. Time-resolved absorption spectra of the transparent solid of [Ru(bpy)$_3$](PF$_6$)$_2$ ground with KCl after the laser excitation.

(5) Transient Absorption Change in the Annihilation of ^{3}MLCT. A high-energy-laser excitation of the transparent solid of [Ru(bpy)$_3$](PF$_6$)$_2$ ground with KCl gave rise to time-resolved absorption spectra, the initial one of which is assigned to the ^{3}MLCT as is shown in Figure 7. A new transient absorption spectrum appeared in 40 ps and decayed within a couple of 100 ps. Since the peak of a new absorption band at 510 nm is characteristic of the one-electron-reduced species, [Ru(bpy)$_3$]$^+$, the following reaction could be involved in the annihilation[11]

$$^3[\mathrm{Ru(bpy)_3}]^{2+} + {}^3[\mathrm{Ru(bpy)_3}]^{2+} \rightarrow {}^2[\mathrm{Ru(bpy)_3}]^{3+} + {}^2[\mathrm{Ru(bpy)_3}]^{+} \qquad (3')$$

The probabilities of excited-state formation at the closest site and the second closest site are 0.19 and 0.53, respectively, when the laser intensity was so strong as to convert 10% of the Ru(II) to the excited state. Since the rate constant of T−T annihilation between the nearest neighbors at 0.82 nm might be 30 times larger than that at 1.076 nm at least, the fast rise of the [Ru(bpy)$_3$]$^+$ can be ascribed to the T−T annihilation between the nearest neighbors. The rate constant of the T−T annihilation is inferred to be 5×10^{10} s^{-1} from the rise time, which is not so far from that of Ru(II) to Os(II) energy transfer between the next neighbors. The decay of the one-electron reduced species was not single exponential so that the distances between the reaction products are various (0.82, 1.076, or 1.352 nm). Time-resolved absorption spectroscopy of a concentrated aqueous solution of $^3[Ru(bpy)_3]^{2+}$ revealed that the reaction products are the same as those in the crystal as shown in Figure 7. The bimolecular rate constant of annihilation (8×10^{-11} cm^3 s^{-1}) was almost the diffusion-controlled one.

Conclusion

Photophysical behavior of ^{3}MLCT states in $Ru(bpy)_3X_2$ was studied in view of the energy migration in neat crystals and doped crystals with energy acceptor. Rates of the energy transfer and the annihilation in the crystalline solids were determined by means of a single-photon counting of emission and transient absorption spectroscopy. The rates of bimolecular processes were determined from the dependence of emission decay rate on the concentration of either Os(II) or ^{3}MLCT of Ru(II) in $[Ru(bpy)_3](PF_6)_2$, and also the rate constant of T−T annihilation in the emission decay for the single-crystal or transparent mixed-crystal ground together with KCl. The diffusion constants of excitation migration were estimated from the bimolecular rates, the former of which affords the rates of hopping. Three different methods gave quite similar values of $(3.5 \pm 0.5) \times 10^8$ s^{-1} as a hopping rate constant to the closest distance of 0.82 nm. The rates of the hopping were estimated ($3 \times 10^8 \sim 8 \times 10^9$ s^{-1}), on the assumption that random hopping of the excitation energy occurs along the axis of the shortest site−site distance, which is dependent on the shortest site−site distance in the three kinds of crystals.

Luminescence decays in neat crystals observed under pulse laser excitation (532 nm) showed power dependence. The decay curves fitted the kinetics derived for processes with first- and second-order components. The second-order component that depended on the excitation intensity was attributed to exciton annihilation and not to the thermal effects. From an estimation of the initial concentration of the triplet excited state in the crystal, the rate constant of bimolecular annihilation was determined to be $10^8 - 10^9$ M^{-1} s^{-1} (ca. 10^{-12} cm^3 s^{-1}) at room temperature. This value is large enough to affect the excitation dynamics of neat crystals when the intensity of exciting light pulses such as lasers is above few μJ/cm^{-2}. Furthermore, the migration process between the Ru(II) sites would become a rate-determining step when a fast reaction with any site in the crystal of the Ru(II) is concerned.

Finally, transient absorption spectroscopy revealed that the annihilation between two ^{3}MLCT in a ground crystal of $[Ru(bpy)_3](PF_6)_2$ together with KCl gave rise to the electron-transferred products within 40 ps in the crystal as in the aqueous solution.

Acknowledgment. The present work was partially supported by Grants-in-Aid from the Japanese Ministry of Education, Science, Sports, and Culture to N.I.

References and Notes

(1) *Electron Transfer in Biology and the Solid State*; Johnson, M. K., King, R. B., Kurtz, D. M., Jr.; Kutal, C., Norton, M. L., Scott, R. A., Eds.; Advances in Chemistry Series 226; American Chemical Society, Washington, D.C., 1990.

(2) Mikkelsen, K. V.; Ratner, M. A. *Chem. Rev.* **1994**, *94*, 993.

(3) Henderson, B.; Imbusch, G. F. *Optical Spectroscopy of Inorganic Solids*; Clarendon Press: Oxford, 1989.

(4) (a) Fujita, I.; Kobayashi, H. *J. Chem. Phys.* **1973**, *59*, 2902. (b) Otsuka, T.; Takahashi, N.; Fujagasaki, N.; Sekine, A.; Ohashi, Y.; Kaizu, Y. *Inorg. Chem.* **1999**, *38*, 1340.

(5) Schmidtke, H.-H.; Mink, H. J. *Z. Naturforsch., A* **1990**, *45*, 771.

(6) Iguro, T.; Ikeda, N.; Ohno, T. *Inorg. Chim. Acta* **1994**, *226*, 203.

(7) Hauser, A.; von Arx, M. E.; Pellaux, R.; Decurtins, S. *Mol. Cryst. Liq. Cryst.* **1996**, *286*, 225.

(8) Tsushima, M.; Ikeda, N.; Nozaki, K.; Ohno, T. *J. Phys. Chem. A*, in press.

(9) Kalyanasundaram, K. *Coord. Chem. Rev.* **1982**, *46*, 159.

(10) Krausz, E.; Ferguson, J. *Prog. Inorg. Chem.* **1989**, *37*, 293.

(11) Milosavljevic, B. H.; Thomas, J. K. *J. Phys. Chem.* **1983**, *87*, 616.

(12) Gafney, H. D. *Coord. Chem. Rev.* **1990**, *104*, 113.

(13) Kamat, P. V.; Gopidas, K. R.; Mukherjee, T.; Joshi, V.; Kotkar, D.; Pathak, V. S.; Ghosh, P. K. *J. Phys. Chem.* **1991**, *95*, 10009.

(14) Sykora, M.; Kincaid, J. R.; Dutta, P. K.; Castagnola, N. B. *J. Phys. Chem. B* **1999**, *103*, 309.

(15) Yersin, H.; Braun, D. *Coord. Chem. Rev.* **1991**, *111*, 39.

(16) Krausz, E.; Riesen, H. *Coord. Chem. Rev.* **1997**, *159*, 9.

(17) Komada, Y.; Yamauchi, S.; Hirota, N. *J. Phys. Chem.* **1988**, *92*, 6511.

(18) Krol, D. M.; Blasse, G. *Chem. Phys. Lett.* **1981**, *77*, 253.

(19) (a)Yersin, H.; Braun, D.; Gallhuber, E.; Hensler, G. *Ber. Bunsen-Ges. Phys. Chem.* **1987**, *91*, 1228. (b) Yersin, H.; Hensler, G.; Gallhuber, E. *Inorg. Chim. Acta* **1987**, *132*, 187.

(20) Yersin, H.; Hensler, G.; Gallhuber, E.; Rettig, W.; Schwan, L. O. *Inorg. Chim. Acta* **1987**, *105*, 201.

(21) Krausz, E.; Nightingale, T. *Inorg. Chim. Acta* **1986**, *120*, 37.

(22) Palmer, R. A.; Piper, T. S. *Inorg. Chem.* **1966**, *5*, 864.

(23) Burstall, F. P.; Dwyer, F. P.; Gyarfus, E. C. *J. Chem. Soc*, **1950**, 953.

(24) (a) Rillema, D. P.; Jones, D. S. *J. Chem. Soc., Chem. Commun.* **1979**, 849. (b) Biner, M.; Burgi, H.-B.; Ludi, A.; Rohr, C. *J. Am. Chem. Soc.* **1992**, *114*, 5197.

(25) (a) Constable, E. C.; Raithby, P. R.; Smit, D. N. *Polyhedron* **1989**, *8*, 367. (b)Richter, M. M.; Scott, B., Brewer, K. J.; Willett, R. D. *Acta Crystallogr.* **1991**, *C47*, 2443.

(26) Ikeda, N.; Kuma, H.; Kawamoto, T.; Kushi, Y.; Ohno, T. Unpublished results. The crystal structure has been determined by X-ray diffraction. $[Ru(bpy)_3]Cl_2 \cdot 7H_2O$ crystallized in the monoclinic space group *C*2/*c* with $a = 23.08(1)$ Å, $b = 13.217(5)$ Å, $c = 22.820(8)$ Å, $\boldsymbol{\beta} = 96.67(3)°$, and $Z = 8$.

(27) Some possibility of thermal effects by laser excitation was also considered. The heat capacity of $Ru(bpy)_3(PF_6)_2$ crystal was determined to be $C_P = 890$ J K^{-1} mol^{-1} = 1.03 J K^{-1} g^{-1} by thermal analysis (DSC) on comparison with standard α-alumina powder. By using this value, the extinction coefficient, and the density of crystal ($\rho = 1.737$ g cm^{-3}), a degree of heating in the temperature of the sample is estimated to be only 0.89 K when the intensity of laser excitation is 1 mJ/cm^2.

(28) Yoshimura, A.; Nozaki, K.; Ikeda, N.; Ohno, T. *J. Phys. Chem.* **1996**, *100*, 1630.

(29) (a) Islam, A.; Ikeda, N.; Nozaki, K.; Ohno, T. *Chem. Phys. Lett.* **1996**, *263*, 209. (b) Ikeda, N.; Islam, A.; Ohno, T. unpublished results.

(30) Kober, E. M.; Meyer, T. J. *Inorg. Chem.* **1982**, *21*, 3967.

(31) The laser intensity for excitation should be attenuated to less than about a few μJ/cm^2 pulse by neutral density filters to avoid nonlinear photoprocesses. When the excitation intensity of laser pulse is high in the case of using a Q-switch YAG laser, a exponential decay of the Ru(II) emission becomes multicomponents and no rise of the Os(II) emission is observed.

(32) Creutz, C.; Chou, M.;. Netzel, T. L.; Okamura, M.; Sutin, N. *J. Am. Chem. Soc.* **1982**, *102*, 1309.

(33) Lachish, U.; Ottolenghi, M.; Rabani, J. *J. Am. Chem. Soc.* **1977**, *99*, 8062.

(34) Tanaka, Y.; Azumi, T. *Inorg. Chem.* **1986**, *25*, 247.

(35) Uchida, T.; Kim, H.-B.; Hiraga, T.; Tazuke, S. *J. Am. Chem. Soc.* **1989**, *111*, 8265.

(36) Birks, J. B. *Photophysics of Aromatic Molecules*; Wiley-Interscience: London, 1970.

(37) (a) Kobayashi, T. *Bull. Chem. Soc. Jpn.* **1978**, *51*, 349. (b) Kobayashi, T.; Hirota, N. *Bull. Chem. Soc. Jpn.* **1977**, *70*, 1743.

(38) Felix, F.; Ferguson, J.; Güdel, H. U.; Ludi, A. *Chem. Phys. Lett.* **1979**, *62*, 153.

(39) (a) Harrowfield, J. M.; Sobolev, A. N. *Aust. J. Chem*. **1994**, *47*, 763. (b) Krausz, E.; Riesen, H.; Rae, A. D. *Aust. J. Chem.* **1995**, *48*, 929.

(40) (a) Kellendonk, F.; Blasse, G. *J. Chem. Phys.* **1981**, *75*, 561 (b) van Schaik, W.; Lizzo, S.; Smit, W.; Blasse, G. *J. Electrochem. Soc.* **1993**, *140*, 216.

(41) Avakian, P.; Merrifield, R. E. *Mol. Cryst.* **1968**, *33*, 25.