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Solid-state photochemistry: energy-transfer and electron-transfer of ^{3}CT in crystals of $[Os_xRu_{1-x}(bpy)_3]X_2$ ($x = 0$–0.23)

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Abstract

Time-correlated single-photon counting method and time-resolved absorption-spectroscopy were applied to bimolecular reactions of energy-transfer and electron-transfer in the crystals of $[Os_xRu_{1-x}(bpy)_3]X_2$ (bpy = 2,2′-bipyridine). Migration of the triplet excited charge-transfer state (^{3}CT) of $[Ru(bpy)_3](PF_6)_2$ gave rise to either energy-transfer to a small amount of $[Os(bpy)_3]^{2+}$ or bimolecular annihilation with the ^{3}CT. The rate of hopping in the migration of ^{3}CT ($(2-24)\times 10^8$ s^{-1}) was determined from the bimolecular rate-constants of the energy-transfer and ^{3}CT–^{3}CT annihilation in the single crystal of $[Ru(bpy)_3]X_2$ ($X = Cl^-$, ClO_4^- and PF_6^-) or the transparent crystal of $[Ru(bpy)_3]X_2$ ground together with KCl. Rate of the energy-transfer from ^{3}CT(Ru) to an Os(II) without energy-migration was determined to be 1.7×10^{11} s^{-1} for the crystal heavily doped with Os^{2+}. Time-resolved absorption spectroscopy revealed that the annihilation of the ^{3}CT in the transparent crystal of $[Ru(bpy)_3]X_2$ ground together with KCl formed the one-electron-transferred products in 40 ps.

Keywords: Solid-state photochemistry; Energy-transfer; Electron-transfer

1. Introduction

Bimolecular reactions such as energy-transfer and electron-transfer in crystalline solids have been an attractive subject from various points of view. Rate-constants of chemical reactions in crystalline solids are expected to be quantitatively related to the distance and orientation between reactants. Understanding of the rates of chemical reactions in crystalline solids could be of crucial importance in interpreting the rates of biochemical reactions between molecules well spatially orientated, without involving water molecules in living cells.

Studies on a photochemical reaction in crystalline solids have met with several difficulties in the detection of quantum yield and reaction-intermediate, though photochemical reactions have been studied in qualitative ways [1,2]. A very small portion of the emission quenching brings about a permanent change of the chemical species, because the reverse reaction occurs more rapidly than the separation process of the reaction products. Time-resolved absorption spectroscopy of the excited state and reaction intermediates formed, however, have been rarely applied to the photochemical reactions in the solid state, because most of the molecules excited by a high dose of laser pulse, undergo annihilation of the excited states in a very short time, and produce a lot of heat burning themselves. Moreover, much of the emission decay in the crystalline solid is not always single exponential so that quantitative studies on the emission quenching have rarely been performed. It is believed that the extraordinary sensitivity to quenching by nearby impurities and the rapid annihilation of the excited states might be responsible for the multi-exponential decay of the emission.

Ikeda and Ohno reported that the second-order decay of the triplet excited charge-transfer state (^{3}CT) for the microcrystal of $[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2′-

bipyridine) was ascribed to the migration of ^{3}CT through the crystal, followed by the annihilation of ^{3}CT [3]. When the intensity of the excitation laser is as low as 5 μJ cm^{-2}, the emission decays were single-exponential for the crystal sample of $[RuL_3]X_2$ (L = 2,2′-biquinoline), or $[Ru(L')_2]X_2$ (L′ = 2,2′:6′,2″-terpyridine), which were carefully purified [4]. In this work, both time-correlated single-photon counting of emission and time-resolved difference absorption spectroscopy have been applied to a couple of bimolecular processes. The former was applied to both energy-transfer and annihilation of ^{3}CT in the crystals of $[Os_xRu_{1-x}(bpy)_3](PF_6)_2$ and $[Ru(bpy)_3]X_2$ ($X = PF_6^-$, ClO_4^-, and Cl^-) and in transparent solids of $[Ru(bpy)_3]X_2$ ($X = PF_6^-$, ClO_4^-, and Cl^-) ground with KCl. The latter was applied to electron-transfer in the transparent solid of either $[Ru(bpy)_3](PF_6)_2$ or a donor–acceptor compound, ground together with a KCl crystal.

2. Experimental

2.1. Materials

$[Ru(bpy)_3](PF_6)_2$, and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$ were synthesized and purified according to literature methods. $RuCl_3 \cdot 3H_2O$ and ligands were purchased commercially and used without further purification. Elementary analyses for the complexes are in agreement with those calculated.

Transparent discs of KCl-containing crystals of the Ru(II) compound were prepared in the following way. The ground microcrystal of an Ru(II) compound (1 mg) was dispersed in ground KCl (2 g). The ground mixture (120 mg) was pressed to be transparent under vacuum. An island of the red crystal was invisible under magnification [5].

2.2. Apparatus and measurements

The emission spectra were measured by using a grating monochromator (Jasco CT250) with a silicon diode-array (Hamamatsu S3901-512Q). A 488 line of an Ar laser (Coherent Innova 306) was used for the excitation of crystal samples. The sensitivity of emission measurement was corrected by using a bromine lamp, Ushio JPD100V500WCS. A Kerr lens mode-locked Ti^{3+}-Sapphire laser with a cavity-dumper and a BBO crystal for the frequency-doubling [6] was used for excitation. The output energy and repetition rate of the 400 nm laser were 5 nJ pulse^{-1} and 200 kHz, respectively. A time-correlated single-photon counting system [6] was used to measure the decay of emission. The FWHM of instrumental response function (IRF) is typically 40 ps. Another laser for the decay measurement was a Nd^{3+}-YAG laser of Continuum Surelite I-10, whose intensity was attenuated to 1–3000 μJ pulse^{-1} by neutral density filters. Picosecond time-resolved absorption spectra were obtained using a picosecond laser photolysis system with a mode-locked Nd^{3+}-YAG laser (Continuum PY61C-10) of 2 mJ [7].

3. Results and discussion

3.1. Annihilation of ^{3}CT of $[Ru(bpy)_3]X_2$ in the crystalline solid [8]

3.1.1. Rate constants of bimolecular annihilation

Emission at 600 nm from the triplet excited charge-transfer state (^{3}CT) of $[Ru(bpy)_3](PF_6)_2$ in a crystalline solid, was observed to decay in a single exponential mode ($k_1 = 3 \times 10^5$ s^{-1}) with laser-excitation of less than 5 μJ cm^{-2}. As the laser-intensity exceeded 10 μJ cm^{-2}, a rapid decay component appeared at the beginning of the decay of emission. The rapid process can be the bimolecular annihilation of ^{3}CT,

$$^3[Ru(bpy)_3]^{2+} + {}^3[Ru(bpy)_3]^{2+} \rightarrow X + Y \tag{1}$$

With the assumption that the emission decays via uni- and bimolecular processes, the rate-constant of the bimolecular decay (k_{ann}) was determined by using an integrated equation for the mixed-order decay of excited state,

$$\frac{1}{C(t)} = \left[\frac{1}{C(0)} + \frac{k_{ann}}{k_1}\right]\exp(k_1 t) - \frac{k_{ann}}{k_1} \tag{2}$$

where $C(t)$ and $C(0)$ are the concentrations of ^{3}CT in the crystal at an arbitrary time and just after the laser excitation; the latter of which is estimated from the dose of SHG of the laser and the molar absorption coefficient of $Ru(bpy)_3^{2+}$ to be constant, independent of the depth from the surface. The rate constant of k_{ann} is $1.4–1.8 \times 10^{-12}$ cm^3 s^{-1}.

A biexponential decay was observed for the transparent solid of $[Ru(bpy)_3](PF_6)_2$ ground with KCl even with excitation by a weak-power laser of less than 10 μJ cm^{-2}. The rate-constants (k_1 and k'_1) of the fast and slow components are 8×10^6 and 2×10^6 s^{-1}, respectively, which are at least ten times faster than observed for the single crystal. The rate-constant (k_{ann}) was determined to be 1.7×10^{-12} cm^3 s^{-1} by numerical integration of the following differential rate-equation,

$$\frac{\partial(C(t) + C'(t))}{\partial t} = -(k_1 C(t) + k'_1 C'(t) + k_2 C(t)^2) \tag{3}$$

where $C(t)$ and $C'(t)$ are the concentrations of ^{3}CT in the bulk and near to the surface of the crystal, ground together with KCl, respectively. The formation of ^{3}CT for the transparent solid ground with KCl ($C(0)$) is assumed to be the same as that of ^{3}CT for the aqueous solution of the same absorbance as the solid, which is easily determined by means of time-resolved absorption spectroscopy. The exposure of Ru(II) to a laser beam of 20 and 100 μJ pulse^{-1} converted 0.03 and 0.15% of the Ru(II) compound to ^{3}CT, respectively. The formation of ^{3}CT is too small to produce a contact pair of ^{3}CT and ^{3}CT within 1.4 nm, because the number of the nearest neighbors of a ^{3}CT is only 20 for all the crystals studied here. Only excitation–migration through the crystal via hopping provides a chance for encounter. The rate constants of the ^{3}CT–^{3}CT annihilation in the crystal are $(1.4–1.8) \times 10^{-12}$ cm^3 s^{-1}, $(6–9) \times 10^{-12}$ cm^3 s^{-1}, and $(6–40) \times 10^{-12}$ cm^3 s^{-1} in the crystals of $[Ru(bpy)_3](PF_6)_2$, $[Ru(bpy)_3](ClO_4)_2$, and $[Ru(bpy)_3]Cl_2 \cdot 6H_2O$, respectively.

3.1.2. Hopping rate of energy-migration

The bimolecular rate constant of diffusional annihilation can be written in terms of the diffusion constant of excitation in the crystal (see Table 1),

$$k_{\mathrm{ann}} = 4\pi RD \tag{4}$$

where R is the largest reaction-diameter of annihilation occurring before the next hop of the excitation to neighboring sites. On the assumption that the diameter is presumed to be the distance of the second closest site (1.08 nm), the diffusion constant is estimated to be $(1.4\text{–}1.8) \times 10^{-12}/(4\pi \times 1.08 \times 10^{-7}) = (1.0\text{–}1.3) \times 10^{-6}$ cm^2 s^{-1} for $[\mathrm{Ru(bpy)_3}](\mathrm{PF_6})_2$. As the diffusion of excitation-energy is the net result of sequential hopping, the rate-constant of either the energy-transfer or the annihilation, is related to the rate-constant of hopping to the adjacent sites of $\mathrm{Ru(bpy)_3^{2+}}$ at the distance (r), k_{hop}.

$$r = \sqrt{2D(1/k_{\mathrm{hop}})}$$

The rate-constant for hopping in the crystals of $[\mathrm{Ru(bpy)_3}]\mathrm{X_2}$ is estimated in the range $(3\text{–}39) \times 10^8$ s^{-1} from the bimolecular rate-constants of energy-transfer or annihilation, increasing in the following order, $[\mathrm{Ru(bpy)_3}](\mathrm{PF_6})_2 < [\mathrm{Ru(bpy)_3}](\mathrm{ClO_4})_2 < [\mathrm{Ru(bpy)_3}]\mathrm{Cl_2{\cdot}6H_2O}$. The increasing order is in agreement with the decreasing order of the closest site–site distance (r) in the crystals, $[\mathrm{Ru(bpy)_3}](\mathrm{PF_6})_2$ (0.82 nm [9]) $>$ $[\mathrm{Ru(bpy)_3}](\mathrm{ClO_4})_2$ (0.80 nm [10]) $>$ $[\mathrm{Ru(bpy)_3}]\mathrm{Cl_2{\cdot}7H_2O}$ (0.76 nm [8]).

3.1.3. Mechanism of annihilation of ^{3}CT [8]

A high-energy laser excitation of the transparent solid of $[\mathrm{Ru(bpy)_3}](\mathrm{PF_6})_2$ ground with KCl gave rise to a time-resolved absorption spectrum as shown in Fig. 1. There were two transient absorption spectra observed within 3 ns. One of them is assigned to ^{3}CT(Ru) [11], which is clearly seen at 0 ps. The other seen at 50 ps, exhibits an absorption peak at 510 nm, which is assigned to $[\mathrm{Ru(bpy)_3}]^+$ by

Table 1
Bimolecular rate constants of T–T annihilation (k_{ann}), and rate constant of hopping (k_{hop}), the metal–metal distances (r_1 and r_2) between $[\mathrm{Ru(bpy)_3}]\mathrm{X_2}$, and the diffusion constant (D)

X	r_1 (nm)^a	r_2 (nm)^a	k_{ann} (10^{-12} cm^3 s^{-1})	D (10^{-6} cm^2 s^{-1})	k_{hop} (10^8 s^{-1})
$\mathrm{Cl^-}$	0.76(2), 0.78(1)^b	1.13(1), 1.25(2)^b	40^c, 6–12^d	6.1–12.2^d	19–39^d
$\mathrm{ClO_4^-}$	0.80(2)^e	1.03(4), 1.08(2)^e	8.3^c, 6.2^d	6.1^c, 4.6^d	19^c, 14^d
$\mathrm{PF_6^-}$	0.82(2)^f	1.08(6)^f	1.7^c, 1.4–1.8^d	1.3^c, 1.0–1.3^d	4^c, 3.1–4.0^d

[a] The number of identical sites is shown in parantheses.
[b] Ref. [8].
[c] The transparent solid ground with KCl.
[d] The single crystal.
[e] Refs. [8,10].
[f] Ref. [9].

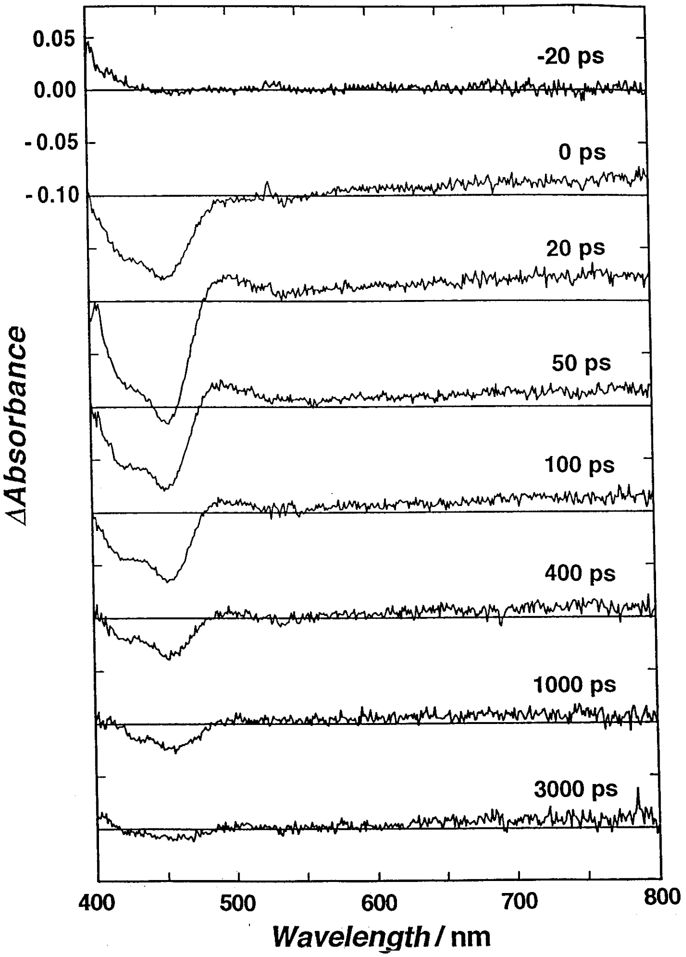

Fig. 1. Time-resolved absorption spectra for the crystalline solid of $[Ru(bpy)_3](PF_4)_2$ ground with solid KCl, exposed to a 15 ps laser of 532 nm (100 mJ cm^{-2}). The absorption spectra at 0 and 50 ps are assigned to $^3CT(Ru)$ and $[Ru(bpy)_3]^+$, respectively. The remaining negative absorbance at 450 nm after 400 ps, was due to $^3CT(Ru)$ free from the annihilation.

referring to its known absorption spectrum [12]. The $[Ru(bpy)_3]^+$ was produced along with the fast decay of the ^3CT within 50 ps and is inferred to decay through the recombination between the $[Ru(bpy)_3]^+$ and $[Ru(bpy)_3]^{3+}$ within 400 ps; the latter of which was not seen in the time-resolved absorption spectrum. Consequently, some of the annihilation can be the process of one-electron transfer,

$$^3[Ru(bpy)_3]^{2+} + {}^3[Ru(bpy)_3]^{2+} \rightarrow {}^2[Ru(bpy)_3]^{3+} + {}^2[Ru(bpy)_3]^+ \qquad (5)$$

The rate-constant of the annihilation between the next neighbors is inferred to be $5 \times 10^{10}\ s^{-1}$.

3.2. Energy transfer of ^{3}CT in the crystal of $[Ru_{1-x}Os_x(bpy)_3](PF_6)_2$ [6]

3.2.1. Migration assisted energy-transfer

The emission of the single crystal of $[Ru_{1-x}Os_x(bpy)_3](PF_6)_2$ consists of two peaks at 16 600 and 14 300 cm^{-1}, which are assigned to the phosphorescence from the ^{3}CT(Ru) and ^{3}CT(Os) states, respectively. A slow rise of the Os(II)-emission ca. 10^{-9} s after the laser excitation, confirmed the energy-transfer. The presence of Os^{2+} in the crystal of $[Os_xRu_{1-x}(bpy)_3](PF_6)_2$ shortened the duration of emission at 600 nm as the doping concentration increased. As far as the slowest decay-component is concerned, good linearity of the decay-rate-constant to the concentration of Os^{2+} implies that ^{3}CT migrates to meet a doped Os^{2+} instead of another ^{3}CT, as shown in Fig. 2. The rate constant of bimolecular energy-transfer (k_{en}) is estimated to be 1.4×10^{-12} cm^3 s^{-1},

$$k_d = k_1 + k_{en}[Os^{2+}] \tag{6}$$

where k_1 is the rate constant of intrinsic emission-decay. The magnitude of k_{en} is very close to that of ^{3}CT–^{3}CT annihilation in the crystal of $[Ru(bpy)_3](PF_6)_2$.

3.2.2. Direct energy-transfer

The total decay of Ru(II)-emission of $[Os_xRu_{1-x}(bpy)_3](PF_6)_2$ is never single exponential even if the excitation laser is as low as 0.01 μJ cm^{-2}. The decay-rates in an early time-region (< 1 ns) could not be determined by means of biexponential analysis for the crystal of $[Os_xRu_{1-x}(bpy)_3](PF_6)_2$ ($x > 1\%$). The time for the emission intensity of the fast decay component ($I(0)$) to decrease to $I(0)/e$ were

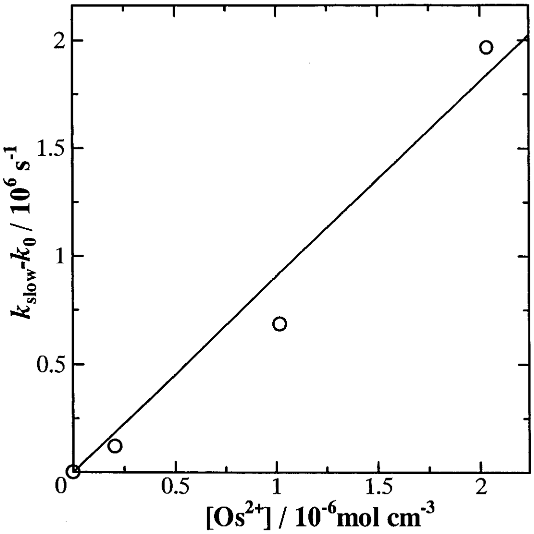

Fig. 2. Plots for the slowest first-order decay rates of the emission observed at 610 nm vs. the doping concentration of Os^{2+} in the doped crystals of $[Ru_{1-x}Os_x(bpy)_3](PF_6)_2$ at 298 K.

evaluated to be 470, 178, 127, 44, 5.1, 0.73 and 0.29 ns for the crystals containing the mole-fraction (0.01, 0.05, 0.10, 0.99, 4.8, 10.8 and 23%) of Os^{2+}, respectively. The fast-decay-component can be ascribed to energy transfer to Os^{2+} without excitation–migration.

The decay of emission-intensity without excitation–migration can be written in terms of occupation probability (x) of Os(II) in the Ru(II) sites and the rate-constants of energy-transfer depending on the distance between a ^{3}CT(Ru) and an Os(II),

$$\begin{aligned} I(t) = {} & I(0)\exp(-k_0 t) \\ & \times [1-x+x\exp(-k_{\mathrm{en}}(0.82)t]^2[1-x+x\exp(-k_{\mathrm{en}}(1.076)t)]^6 \\ & \times [1-x+x\exp(-k_{\mathrm{en}}(1.352)t)]^{12}\cdots[1-x+x\exp(-k_{\mathrm{en}}(R_{\mathrm{DA}})t)]^{z}\cdots \end{aligned} \tag{7}$$

where z is the number of sites with the same distance in the crystal. The first term of the right-hand side stands for the intrinsic decay in a neat crystal. In an early stage of time, ^{3}CT surrounded by Os^{2+} at short distances, undergoes energy transfer to the Os^{2+}. ^{3}CT surrounded by Os^{2+} at long distances are left to decay slowly in a later stage of time. If ^{3}CT surrounded by Os^{2+} at long distances migrates to meet with an Os^{2+}, the rate of energy transfer in a later stage of time is enhanced. This is the case, because the rate of the hopping to the nearest metal-ion sites is estimated to be much larger (3.5×10^8 s^{-1}) than the intrinsic decay-rate as mentioned later. The simple statistical equation (Eq. (7)) is not valid any more.

In order to reconstitute the decay-profile of emission, the time for deactivation of a ^{3}CT was calculated on the basis of the rate constants of intrinsic decay, energy-transfer and hopping. Monte Carlo simulation of the emission-decay was performed by assuming the stochastic processes of intrinsic decay, energy-transfer to an Os^{2+} and excitation-hopping to the closest Ru^{2+} sites of crystal. The Ru(II) are randomly excited to ^{3}CT(Ru) in a volume of 1.25×10^5 lattices based on the crystallographic data, where a periodic boundary condition is introduced and the Os^{2+} are also randomly distributed in the same volume. The occurrence of deactivation of every ^{3}CT for instance, was stochastically determined based on the presumed rate constants of energy-transfer ($k_n(r)$) to Os^{2+} at distance (r) and the intrinsic decay of ^{3}CT as follows. If a random number generated between 0 and 1 is smaller than the probability of deactivation, $1-\exp[-(k_0+k_{\mathrm{en}}(r))\delta t]$, the excited donor can be regarded as being deactivated in a time interval of δt (6 ps). Energy-transfer was considered until the 10th nearest metal-ion site. Once the excited donor was determined to undergo excitation-hopping to the nearest metal-ion site in a time interval based on the k_{hop} rate-constant, the rates of energy-transfer to Os^{2+} in the subsequent time are based on the recalculated distances between the ^{3}CT(Ru) and Os^{2+}. The distance-dependent rate constant of energy-transfer is given by the following equation,

$$k_{\mathrm{en}}(r) = k_{\mathrm{en}}^{0}\exp[-\beta(r-r_0)] \tag{8}$$

where β and k^0_{en} are a distance-attenuation factor and the rate-constant of energy-transfer to an Os^{2+} at the contact distance (r_0). The contact distance was set to the van der Waals radius of the complex cation (0.6 nm). Summing the lifetimes over all the ^{3}CT (1.25×10^3) gives rise to the decay-profile of emission as shown in Fig. 3.

By means of Monte Carlo simulation, a parameter set of β (12.5 nm^{-1}) and k^0_{en} (2.7×10^{12} s^{-1}) gives the best fit to the emission-decays of the crystals doped with Os^{2+} at different concentrations ($x = 0.231$, 0.108, 0.048, and 0.0099), as shown for the doped crystal of $x = 0.108$ in Fig. 3. The rate-constants of energy-transfer were estimated to be 1.7×10^{11} and 7×10^9 s^{-1} for the energy-transfer to the closest Os(II) at 0.82 nm [9] and to the second closest Os(II) at 10.8 nm [9], respectively.

4. Conclusions

Rates of the energy-transfer and the electron-transfer in the crystalline solids were determined by means of time-correlated single-photon counting of emission and time-resolved absorption spectroscopy. The rate of energy-transfer from a Ru(II) ion to an Os(II) ion at the closest proximity was determined to be 1.7×10^{11} s^{-1} by means of a Monte Carlo simulation of the emission-decay profile. The hopping rate of the excitation–migration was determined to be 3.5×10^8 s^{-1} from the dependence of emission decay-rate on the concentration of Os^{2+} doped into

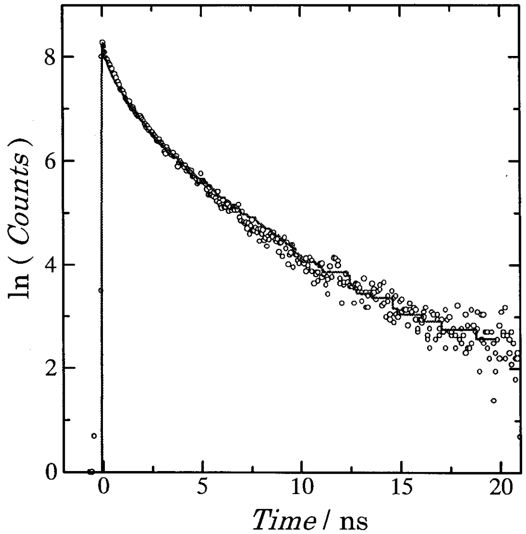

Fig. 3. Emission decay of the $[\mathrm{Ru}_{0.892}\mathrm{Os}_{0.108}(\mathrm{bpy})_3](\mathrm{PF}_6)_2$ crystal. The observed decay (open circles) is compared with the stochastically simulated decay (solid line) by using a set of parameters, k_{en} and k_{hop} evaluated by using Eq. (8), $k^0_{\mathrm{en}} = 2.7 \times 10^{12}$ s^{-1}, $\beta = 12.5$ nm^{-1}, and $r_0 = 0.6$ nm for the close pairs of Ru(II)–Os(II) and $k^0_{\mathrm{hop}} = 7.2 \times 10^9$ s^{-1}, $\beta = 10.8$ nm^{-1}, and $r_0 = 0.6$ nm for the close pairs of Ru(II)–Ru(II). The simulated curves were convoluted by using the IRF.

$[Ru(bpy)_3](PF_6)_2$ and from the ^3CT–^3CT annihilation rate of the crystal ground with KCl exposed to a high energy laser. The rates of electron-transfer and the reverse process in the crystal of a donor–acceptor compound ground together with KCl, was measured by means of time-resolved absorption spectroscopy.

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