Intermolecular Energy-Transfer Dynamics in $\{\Delta$-$[Ru(bpy)_3]\}\{\Lambda$-$[Os(bpy)_3]\}(PF_6)_4$ and rac-$[Os(bpy)_3](PF_6)_2$ Crystals

Kazuteru Shinozaki,* Yasutake Hotta, Takuhiro Otsuka,† and Youkoh Kaizu†
Department of Chemistry, Faculty of Science, Yokohama City University, Seto, Yokohama 236-0027
†Department of Chemistry, Faculty of Science, Tokyo Institute of Technology, O-okayama, Meguro-ku, Tokyo 152-0033

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In the crystal composed of Δ-$[Ru(bpy)_3]^{2+}$ and Λ-$[Os(bpy)_3]^{2+}$ complexes which were pseudo enantiomers the photo-excitation energy was effectively transferred from $[Ru(bpy)_3]^{2+}$ to $[Os(bpy)_3]^{2+}$ ($k_{ET} > 1.1\times10^8$ s^{-1}). In rac-$[Os(bpy)_3](PF_6)_2$ crystal the energy-transfer rates from Λ-$[Os(bpy)_3]^{2+}$ to Λ-$[Os(bpy)_3]^{2+}$ and from Λ-$[Os(bpy)_3]^{2+}$ to Δ-$[Os(bpy)_3]^{2+}$ were estimated as $k_\perp = 1.8\times10^6$ s^{-1} and $k_{//} = 7.9\times10^5$ s^{-1}, respectively.

The molecular arrangement of complex ion in the single crystal of $[Ru(bpy)_3](PF_6)_2$ (bpy = 2,2'-bipyridine) was clarified by an X-ray crystallography (trigonal, $P\bar{3}c1$, a = 10.760(1) Å, c = 16.391(3) Å, V = 1644(1) Å^3, and Z = 2).[1] According to the report the complex ions with the three fold axis which is pallarel to the crystal needle axis (c-axis) formed a complex layer perpendicular to the c-axis. Surprisingly the single layer was composed of only optically active Δ-$[Ru(bpy)_3]^{2+}$ and the next layer was composed of Λ-$[Ru(bpy)_3]^{2+}$. The shortest metal-metal distance between Δ-$[Ru(bpy)_3]^{2+}$ and Λ-$[Ru(bpy)_3]^{2+}$ was 10.76 Å while that between Δ-isomers or Λ-isomers was 8.20 Å. Many investigations on the $[Ru(bpy)_3](PF_6)_2$ single crystal were performed in terms of photophysical properties.[2,3,4] Yersin et al reported a radaiationless energy transfer from $[Ru(bpy)_3]^{2+}$ to $[Os(bpy)_3]^{2+}$ in a crystal of $[Ru(bpy)_3]X_2$ containing $[Os(bpy)_3]^{2+}$.[5] Intermolecular energy-transfer in a salt composed of ruthenium(II) and chromium(III) have been investigated.[6] The crystal structure of the double complex salt was identified.[7] Electron-transfer quenching in $[Ru(bpy)_3]_2[M(CN)_6]Cl\cdot8H_2O$ (M = Co^{3+} or Fe^{3+}) was also reported by Ikeda and Ohno.[8] Recently en energy-transfer reaction from ruthenium(II) to osmium(II) in a mixed crystal of $\{\Delta$-$[Ru(phen)_3]\}\{\Lambda$-$[Os(phen)_3]\}(PF_6)_4$ (phen = 1,10-phnanthroline) was studied on the basis of an X-ray crystallographic data of the crystal (Monoclinic Cc, a = 37.372(6) Å, b = 15.962(6) Å, c = 12.266(4) Å, β = 101.46(2), V = 7171(3) Å^3, and Z = 4).[9] The cell parameters were shown to be the same as those of rac-$[Ru(phen)_3](PF_6)_2$.[10] In the present paper we report on intermolecular energy-transfer dynamics in a pseudo-racemic crystal composed of a pair of tris(2,2'-bipyridine)complexes (Δ-$[Ru(bpy)_3]^{2+}$ and Λ-$[Os(bpy)_3]^{2+}$). It is expected that the crystal is formed by the mutually stacking layers composed of Δ-$[Ru(bpy)_3]^{2+}$ and Λ-$[Os(bpy)_3]^{2+}$, respectively, on the analogy of the crystallographic data of $[Ru(bpy)_3](PF_6)_2$ and $[Os(bpy)_3](PF_6)_2$ in which the complex ions are shown to be completely isostructural.[1,11]

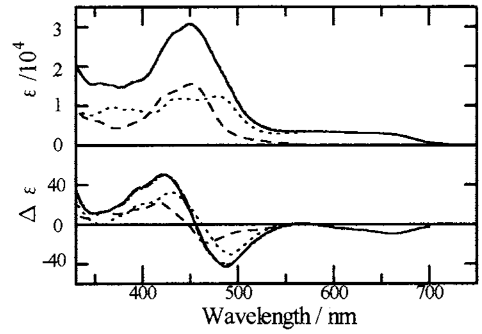

Figure 1. Absorption (upper) and circular dichroism (below) spectra of $\{\Delta$-$[Ru(bpy)_3]\}\{\Lambda$-$[Os(bpy)_3]\}(PF_6)_4$ (solid lines), Δ-$[Ru(bpy)_3](PF_6)_2$ (broken lines), and Λ-$[Os(bpy)_3](PF_6)_2$ (dotted lines) dissolved in acetone. The solid lines were in good agreement with composite spectra of Δ-$[Ru(bpy)_3](PF_6)_2$ and Λ-$[Os(bpy)_3](PF_6)_2$ (dashed lines).

The novel mixed-crystal of $[Ru(bpy)_3]^{2+}$ and $[Os(bpy)_3]^{2+}$ was given by slow evaporation of solvent from an acetone-ethanol solution containing both Δ-$[Ru(bpy)_3]^{2+}$ and Λ-$[Os(bpy)_3]^{2+}$ which were obtained by the resolution of racemic ruthenium and osmium complexes, respectively, by use of a silver antimonyl tartrate.[12] Since the pseudo racemic crystal of $\{\Delta$-$[Ru(bpy)_3]\}\{\Lambda$-$[Os(bpy)_3]\}(PF_6)_4$ was less soluble than Δ-$[Ru(bpy)_3](PF_6)_2$ and Λ-$[Os(bpy)_3](PF_6)_2$ it was selectively precipitated by evaporation of solvent. It seemed that Δ-$[Ru(bpy)_3]^{2+}$ was able to recognize the absolute configuration of the optical isomer regardless the kind of central metal. The composition of the salt was confirmed by absorption spectra and by circular dichroism (CD) spectra as shown in Figure 1. Absorption spectrum of the mixed complex salt in acetone was in good agreement with the composite spectrum of Δ-$[Ru(bpy)_3]^{2+}$ and Λ-$[Os(bpy)_3]^{2+}$. The same result was given in CD spectra. $[Os(bpy)_3]^{2+}$ was a good energy-acceptor of $[Ru(bpy)_3]^{2+}$ because emission spectrum of $[Ru(bpy)_3]^{2+}$ was observed at around 600nm where $[Os(bpy)_3]^{2+}$ was able to absorb the photon from $[Ru(bpy)_3]^{2+}$ moiety.[5] Luminescence quenching of Δ-$[Ru(bpy)_3]^{2+}$ and luminescence sensitization of Λ-$[Os(bpy)_3]^{2+}$ were observed in $\{\Delta$-$[Ru(bpy)_3]\}\{\Lambda$-$[Os(bpy)_3]\}(PF_6)_4$. In the case of the powder sample obtained from a mixture of $[Ru(bpy)_3](PF_6)_2$ and $[Os(bpy)_3](PF_6)_2$

Table 1. Luminescence lifetime[a] (τ / ns) at 77 K

Sample	τ (700 nm)[b]	τ (600 nm)[b]
rac-$[Ru(bpy)_3](PF_6)_2$	—	4100
rac-$[Os(bpy)_3](PF_6)_2$	280	—
Δ-Ru/Λ-Os[c]	550	2.2, 9.3[e]
Os/$[Zn(bpy)_3](PF_6)_2$[d]	970	—

[a] Excited at 523 nm. [b] Monitoring wavelength. [c] $\{\Delta$-$[Ru(bpy)_3]\}\{\Lambda$-$[Os(bpy)_3]\}(PF_6)_4$. [d] 0.1% $[Os(bpy)_3](PF_6)_2$ doped in $[Zn(bpy)_3](PF_6)_2$.
[e] Photon emission was detected in wavelengths from 620 to 670nm. A fast component (2.2 ns) was predominant.

microcrystals, however, they could not be observed. The emission lifetime of Λ-$[Os(bpy)_3]^{2+}$ moiety was evaluated as τ = 550 ns at 77 K and was two times as large as that of the neat rac-$[Os(bpy)_3](PF_6)_2$ as listed in Table 1. A rise profile due to the energy-transfer from Δ-$[Ru(bpy)_3]^{2+}$ to Λ-$[Os(bpy)_3]^{2+}$ was not detected in the emission decay of Λ-$[Os(bpy)_3]^{2+}$ moiety because the energy-transfer rate was presumably fast. Extremely weak emission from Δ-$[Ru(bpy)_3]^{2+}$ moiety was detected by means of a single photon counting method using a streak-scope. Since the emission decay was exhibited as a non-exponential curve the lifetimes were estimated as τ = 2.2 ns and τ = 9.3 ns from a double-exponential analysis. Because the lifetimes were considerably shorter than that of neat rac-$[Ru(bpy)_3](PF_6)_2$ (τ = 4.10 μs) the energy-transfer rate (k_{ET}) from Δ-$[Ru(bpy)_3]^{2+}$ to Λ-$[Os(bpy)_3]^{2+}$ was considered to be faster than 1.1×10^8 s^{-1} evaluated as a reciprocal of the slow component of the lifetime. With increasing the concentration of $[Os(bpy)_3]^{2+}$ in a crystal composed of ruthenium and osmium complexes emission decay-rate at 700 nm was monotonically increased. The fastest decay-rate was obtained as 3.6×10^6 s^{-1} (τ = 280 ns) for a neat $[Os(bpy)_3](PF_6)_2$ crystal.

The excitation energy of Λ-$[Os(bpy)_3]^{2+}$ is converted into a photon and a phonon or trapped in the surface state or the dislocation resulted from the energy-migration. We can describe the luminescence decay-rate ($1/\tau$) of Λ-$[Os(bpy)_3]^{2+}$ moiety as a following equation;

$$1/\tau = k_0 + k_1 + k_2 + \cdots + k_1' + k_2' + \cdots,$$

where k_0 denotes a decay rate of Λ-$[Os(bpy)_3]^{2+}$ in the absence of the energy acceptor, $k_1 + k_2 + \cdots$ ($= k_\perp$) is a sum of the energy-transfer rate to Λ-isomers in the complex layer of the crystal, and $k_1' + k_2' + \cdots$ ($= k_{//}$) is a sum of the energy-transfer rate to Δ-isomers in the next complex layers of the crystal. k_0 is determined as 1.0×10^6 s^{-1} (τ = 970 ns) from the lifetime measurement of a dilute $[Os(bpy)_3]^{2+}$ ion (0.1%) doped in a $[Zn(bpy)_3](PF_6)_2$ host crystal. Since the energy-transfer from Λ-$[Os(bpy)_3]^{2+}$ to Δ-$[Ru(bpy)_3)]^{2+}$ is forbidden because of the high energy-gap $k_1' + k_2' + \cdots$ in the above equation are neglected in the case of {Δ-$[Ru(bpy)_3]$}{Λ-$[Os(bpy)_3]$}$(PF_6)_4$. The energy-transfer rate in a Λ-$[Os(bpy)_3](PF_6)_2$ layer is obtained as $k_\perp = 1.8 \times 10^6$ s^{-1}. A $k_\perp$ value in rac-$[Os(bpy)_3](PF_6)_2$ is given as the same figure because the crystal structure of the mixed complex is suggested to be the same as that of rac-$[Os(bpy)_3](PF_6)_2$ on the analogy of the case of {Δ-$[Ru(phen)_3]$}{Λ-$[Os(phen)_3]$}$(PF_6)_4$. We conclude that an energy-transfer rate between complex layers is estimated as $k_{//} = 7.9 \times 10^5$ s^{-1}. Despite the distance between a Λ-isomer and a Δ-isomer is shorter than that between the closest Λ-isomers, the inter-layer energy-transfer rate ($k_{//}$) is slower than the intra-layer energy-transfer rate ($k_\perp$).

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References and Notes

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