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Doublet−Quartet Intersystem Crossing and Electron Transfer of Cobalt(II) Moieties in [LRu^{III}(L−L)Co^{II}L]$^{5+}$ (L = 2,2′:6′,2″-Terpyridine and L−L = A Bridging Ligand)

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Return electron transfer (RET) and intersystem crossing (ISC) of [(tpy)Ru^{III}(tpy-ph-tpy)^{2,4}Co^{II}(tpy)]$^{5+}$ (tpy = 2,2′:6′,2″-terpyridine and tpy-ph-tpy = 1,4-bis[2,2′:6′,2″-terpyridine-4′-yl]benzene) and [(tpy)Ru^{II}(tpy-tpy)-Co^{III}(tpy)]$^{5+}$ (tpy-tpy = 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quarter-pyridyne) produced on the subpicosecond laser excitation have been investigated in a wide temperature range. A biexponential recovery process of [(tpy)Ru^{II}(tpy-ph-tpy)Co^{III}(tpy)]$^{5+}$ and $[\mathrm{Co^{III}}(t)] = [{}^2\mathrm{Co^{II}}(0)](1 - [f_\alpha \exp(-k_\alpha t) + f_\beta \exp(-k_\beta t)])$ occurs immediately after the production of [^{2}Ru^{III}(tpy)(tpy-pph-tpy)^{2}Co^{II}(tpy)]$^{5+}$ in the excited-state electron-transfer quenching of [(tpy)Ru^{II}(tpy-ph-tpy)Co^{III}(tpy)]$^{5+}$. Four parameters of biexponential recovery, k_α, f_α, k_β, and f_β in a range of 180−300 K, are interpreted in terms of RET and ISC reactions among three states: [(tpy)^{2}Ru^{III}(tpy-ph-tpy)^{2}Co^{II}(tpy)]$^{5+}$, [(tpy)^{2}Ru^{III}(tpy-tpy)^{4}Co^{II}(tpy)]$^{5+}$, and [(tpy)Ru^{II}(tpy-ph-tpy)Co^{III}(tpy)]$^{5+}$. RET of [(tpy)^{2}Ru^{III}(tpy-ph-tpy)^{2}Co^{II}(tpy)]$^{5+}$ regenerating [(tpy)Ru^{II}(tpy-ph-tpy)Co^{III}(tpy)]$^{5+}$ with $k_{\mathrm{RET(D)}}$ of $\sim 4 \times 10^{10}$ s^{-1} competes with doublet−quartet ISC with k_{QD} of 0.20×10^{10} s^{-1} at $\Delta G^\circ_{\mathrm{QD}}$ of 0.044 eV and 2.8×10^{10} s^{-1} at $\Delta G^\circ_{\mathrm{QD}}$ of −0.01 eV. Meanwhile, the rate constant of the quartet−doublet ISC, k_{DQ} ($\sim 1.6 \times 10^{10}$ s^{-1}at $\Delta G^\circ_{\mathrm{DQ}}$ of −0.01 eV), is much larger than RET of [(tpy)^{2}Ru^{III}(tpy-ph-tpy)^{4}Co^{II}(tpy)]$^{5+}$. Dependences of k_{QD} on $\Delta G^\circ_{\mathrm{QD}}$ give rise to a rough estimation of reorganizational free energy (0.03 eV). As for [(tpy)Ru^{II}tpy-tpy)Co^{III}(tpy)]$^{5+}$, $k_{\mathrm{RET(D)}}$, k_{DQ}, and k_{QD} are evaluated to be 2.3×10^{11} s^{-1}, 1.5×10^{11} s^{-1} and 1.5×10^{11} s^{-1} at $\Delta G^\circ_{\mathrm{QD}}$ of −0.01 eV.

Introduction

A spin-inverted transition between electronic states with different spin multiplicities, intersystem crossing (ISC), is frequently involved in transitions of excited states of not only transition-metal compounds but also aromatic compounds. ISC of a fluorescent state to a lower lying phosphorescent state is too rapid to emit a fluorescence in aromatic ketones and in hexacoordinated compounds of transition-metal ion. Most compounds of Cr(III), Ru(II), Re(I), Os(II), and Ir(III) never emit fluorescence from an excited state lying above the lowest phosphorescent state. Singlet metal-to-ligand charge-transfer state (^{1}MLCT) of Fe(II) compounds[1,2] underwent exothermic ISC to quintet d−d* excited state(s) within 100 fs. A large spin−orbit coupling constant of Fe(II) is considered to promote the singlet−quintet ISCs via a closely lying triplet state.[1,2] A tremendous change of the coordination structure of Fe(II) ion reduced the rate of quintet−singlet ISC of spin crossover compounds to 10^6 s^{-1} to 10^7 s^{-1}.[3−10]

^{1}MLCT of Ru(II) compounds underwent exothermic ISC to ^{3}MLCT within 100 fs.[11,12] However, it was more recently shown that low-symmetry compounds of Cu(I) and Pt(0) emit a weak fluorescence.[13−16] The slow rate of ISC between ^{1}MLCT and ^{3}MLCT in tetracoordinated compounds of Cu(I) and Pt(0) (8×10^{10} s^{-1} and 5×10^{11} s^{-1}, respectively) was ascribed to the complete quenching of the angular momenta of d-orbitals in their low (C_2) symmetry of the metal moiety.[15,16] ISC of closely lying d−d* states between $^4(d\pi^5 d\sigma^{*2})$ and $^2(d\pi^6 d\sigma^*)$ of hexacoordinated Co(II) compounds has been rarely observed.[3,17−19] Though noisy transient absorption change following the laser stimulated Raman T-jump of [Co^{II}(*N*-*R*-2,6-pyridinedicarbonaldimine)$_2$] with 10^7 s^{-1} was ascribed to ISC,[17a] no signal of transient absorption or ultrasonic relaxation has been observed for a similar compound of [Co(tpy)$_2$]$^{2+}$.[17b] Fast ISCs of Co(II) compounds have been ascribed to a small structural change involving ISC of Co(II) compounds compared with Fe(II) compounds.[3−10,17−20] More recently, the laser excitation of [(bpy)$_2$Ru^{II}(L−L)Co^{III}(bpy)$_2$]$^{5+}$ (L−L = 1,2-bis(2,2′-bipyridyl-4′-yl)ethan[18] and 2,6-bis(2-pyridyl)benzodiimidazole[19]) formed an excited-state electron-transfer (EET) product with a yield close to unity, which exhibited a decay of transient absorption with a rate constant of 9×10^8 s^{-1} and 10^{10} s^{-1}, respectively, and return electron transfer (RET) with a rate constant of $\sim 2 \times 10^8$ s^{-1} to regenerate the original reactants. Both of the transient absorptions were tentatively assigned to a higher lying doublet state of EET product. Most recently, Torieda et al.[21] demonstrated that the RET with a rate constant of 10^{10} to 10^{11} s^{-1} took place from the doublet ground state of [(tpy)^{2}Ru^{III}(L−L)^{2}Co^{II}(tpy)]$^{2+}$ (tpy = 2,2′:6′,2″-terpyridine and L−L = 1,4-bis[2,2′:6′,2″-terpyridine-4′-yl]benzene and 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quarter-pyridyne), of which the symmetry of coordination structure around Co(II) is lower than that of D_{4h}. The temperature dependence of RETs and the quantum chemical calculation using density functional theory (DFT) showed that the big difference in the RET rate between the doublet and the quartet ground state of Co(II) moiety originated from the difference in the intramolecular reorganizational free energy of RET (0.28 and 0.90 eV, respectively).[21,22] If an RET between ^{2}Co(II) and ^{2}Ru(III) is such a rapid process as seen in the lower symmetry compounds, a high yield of the ^{4}Co(II) moiety in the

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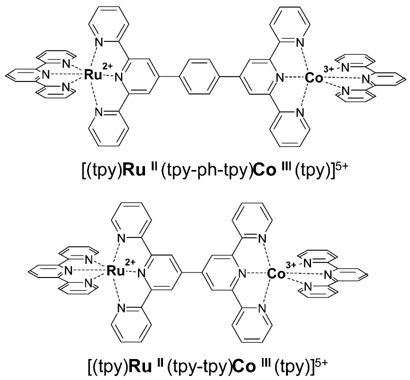

Figure 1. Molecular structures.

EET demonstrates that the ISC of ^{2}Co(II) moiety to the low lying quartet state takes place much faster than RET of the ^{2}Co(II).[23]

In this study, RET between Co(tpy)$_2$$^{2+}$ and Ru(tpy)$_2$$^{3+}$ as well as doublet−quartet ISC of Co(tpy)$_2$$^{2+}$ moiety are reinvestigated for chemically linked Co(III)−Ru(II) compounds shown in Figure 1. Doublet states of Co^{II}(tpy)$_2$$^{2+}$ moiety of [(tpy)Ru^{III}(tpy-ph-tpy)Co^{II}(tpy)](PF$_6$)$_5$ and [(tpy)(Ru^{III}(tpy-tpy)Co^{II}(tpy))(PF$_6$)$_5$ were produced in pulse-laser-induced intramolecular EET reaction, which partially carried out ISC to the isoenergetic quartet state.[21,24] The RET of [(tpy)Ru^{III}(L−L)^{2}Co^{II}(tpy)]$^{5+}$ regenerating the original reactant was examined by means of laser kinetic spectroscopy. A similar rate of RET to that of doublet−quartet ISC made the recovery process of the original reactant biphasic. As for the doublet−quartet ISC of [(tpy)^{2}Ru^{III}(tpy-ph-tpy)^{2}Co^{II}(tpy)](PF$_6$)$_5$, a good correlation between the ISC rate and the Gibbs free-energy difference between the doublet and the quartet states was found in a temperature range of 180−300 K.

Experimental Section

Materials. [(tpy)Ru(tpy-ph-tpy)Co(tpy))(PF$_6$)$_5$·6H$_2$O and [(tpy)Ru(tpy-tpy)Co(tpy)](PF$_6$)$_5$.

The preparation and the purification of these compounds were described in a previous article.[21]

Measurement. Preparation of the Sample Solutions. Butyronitrile was used as a solvent for the measurement in a region of 170−350 K. Solvents of butyronitrile and acetonitrile were purified by distillation. Propylene carbonate was used without further purification. The sample solutions were prepared just before the measurements.

Absorption Spectra and Emission Spectra. Absorption spectra were measured by using a Shimadzu spectrophotometer (UV-2500PC). Emission spectra were recorded by using a grating monochromator (Jasco CT25-C) with a photodiode image sensor (Hamamatsu C4351) whose sensitivity of detection was corrected by using a bromine lamp (Ushio JPD 100V, 500W). A YVO$_4$ laser (fwhm: 5ns) was used as a light pulser for the lifetime measurements.

Time-Resolved Difference Absorption Spectra. Time-resolved difference absorption spectra were obtained by using the second harmonic (SHG) of Nd^{3+}:YAG laser (Continuum Surelite I-10, $\lambda_{ex} = 532$ nm, fwhm 4 ns) and the SHG of Mode-lock Nd^{3+}:YAG laser ($\lambda_{ex} = 532$ nm, fwhm 20 ps) for the excitation. A white light of Xe-arc lamp was used for acquisition of absorption spectra of species living longer than 10 ns.[19] A white light pulse with a delay of 20−6000 ps for the excitation was produced by focusing the fundamental oscillation laser light into a flowing H$_2$O/D$_2$O (1:1 by volume) solution.[25]

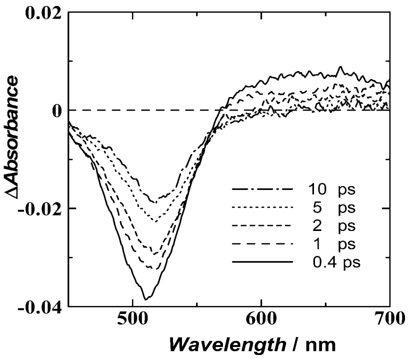

Figure 2. Difference absorption spectra of [(tpy)Ru(tpy-tpy)Co(tpy)]$^{5+}$ in AN and at 298 K at various delay times. Solid, 0.4 ps; long dash, 1 ps; dash, 2 ps; dot, 5 ps; and dash−dot−dash, 10 ps.

Subpicosecond Laser Photolysis. Laser pulses with a repetition rate of 200 kHz were generated by a Ti^{3+}:sapphire laser with an oscillator and a regenerative amplifier (Tsunami and Spitfire, Spectra Physics, Inc.). The amplified laser has characteristics of 100 fs width and energy of 0.4 mJ with a wavelength centered at 800 nm. The fundamental beam was frequency-doubled by using a 1 mm β-BBO crystal to obtain a 400-nm pump pulse, which was used to excite the sample solutions in a 1-mm quartz cell. The remainder of the fundamental beam was focused into an 8-mm flow cell containing water to generate a white light continuum. A polarizer was used to attain a linear polarization of the probe light and to rotate the polarization to 54.7° (magic angle) relative to that of the pump beam for excitation. Before passing through the sample, the probe beam was divided into a signal and reference beam by a 3-mm beam splitter inserted at 45°. The typical energy of the pump pulse was 50 μJ/pulse with the diameter of 1 mm at the sample. The signal beam through the sample solution and the reference were detected by using image sensors (Chromex) attached to a polychromator (Hamamatsu). The fwhm of instrument response function was ca. 300 fs.[26]

TA Spectra at Various Temperatures. The temperature of the sample solutions (77−300 K) was controlled by the use of a cryostat (Oxford DN1704) and a controller (Oxford ITC4).

Results

Time Profile of Transient Absorption Spectra. 1. [(tpy)Ru(tpy-tpy)Co^{III}(tpy)]$^{5+}$. A subpicosecond laser excitation of a N$_2$-bubbled butyronitrile solution of [(tpy)Ru^{II}(tpy-tpy)Co^{III}(tpy)]$^{5+}$ produced a difference absorption spectrum with a negative absorbance below 540 nm and a positive and broad band with the maximum at 650 nm.[21] In 3 ps, as is shown in Figure 2, most of the positive band above 570 nm disappeared, and one-third of the MLCT absorption band bleached around 515 nm was recovered. The rate constant of the fast decay monitored at 620 nm, 1.0×10^{12} s^{-1}, is ascribed to the decay of ^{3}MLCT of [(tpy)Ru^{II}(tpy-tpy)Co^{III}(tpy)]$^{5+}$ (Figure 3). The fast recovery of MLCT absorption band bleached was a little slower than the decay of ^{3}MLCT with a rate constant of 1.0×10^{12} s^{-1}, as is shown in Figure 3. The recovery of MLCT band in 100 ps was decomposed into three processes: the fast one is the decay of ^{3}MLCT and the intermediate and slow recoveries of MLCT band are due to RET of [(tpy)Ru^{III}(tpy-tpy)Co^{II}(tpy)]$^{5+}$. The rate constant of the slow recovery, 2.8×10^{10} s^{-1}, was directly determined, and the rate constant of an intermediate recovery was determined to be 5.2×10^{11} s^{-1} from a time profile of difference absorption on the basis of the decay rate constants of ^{3}MLCT (1.0×10^{12} s^{-1}) and the slow recovery

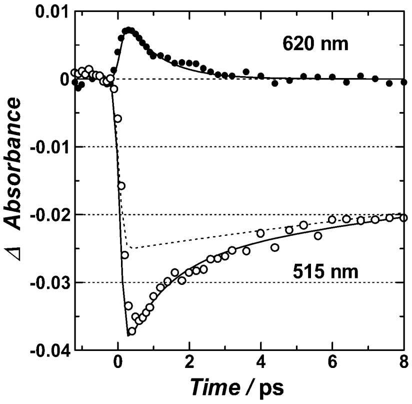

Figure 3. Decay of the excited-state absorption at 620 nm (●) and the recovery of MLCT absorption at 515 nm (○) of $[(tpy)Ru(tpy\text{-}tpy)\text{-}Co(tpy)]^{5+}$ in AN and at 298 K. A solid line at the top represents the exponential decay of the excited-state absorption (1×10^{12} s^{-1}) and a solid line at the bottom represents the sum of exponential recoveries (1×10^{12} s^{-1}, 8.1×10^{10} s^{-1}, and 4.9×10^{9} s^{-1}). A dotted line at the bottom stands for the slow component of the exponential recovery (4.9×10^{9} s^{-1}).

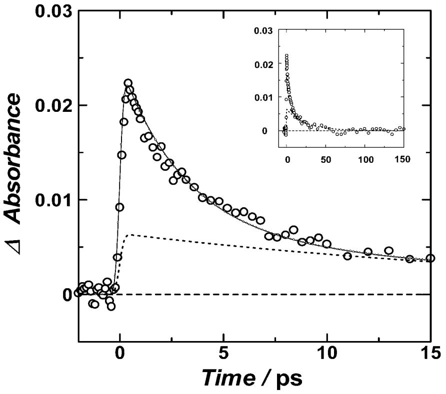

Figure 4. Decay of the excited-state absorption (3.2×10^{11} s^{-1}) monitored at 565 nm of $[(tpy)Ru(tpy\text{-}ph\text{-}tpy)Co(tpy)]^{5+}$ in BN and at 298 K. A dotted line stands for another slow component of decay, which is shown on 10 times wider time ordinate in the inset.

of MLCT band (2.8×10^{10} s^{-1}), respectively. The solvents of acetonitrile and propylene carbonate did not vary the rate constants of the intermediate and the slow recoveries: 44×10^{10} s^{-1} and 2.7×10^{10} s^{-1} on the average, respectively.

2. $[(tpy)Ru^{II}(tpy\text{-}ph\text{-}tpy)Co^{III}(tpy)]^{5+}$. As for $[(tpy)Ru^{II}(tpy\text{-}ph\text{-}tpy)Co^{III}(tpy)]^{5+}$ in butyronitrile, the subpicosecond laser excitation produced a difference absorption spectrum with a negative band in a region of 420−520 nm and a positive one with the peak at 650 nm, which is characteristic of ^{3}MLCT-(Ru).[21] In 10 ps, three-quarters of the difference absorption in the red region disappeared with a rate constant of 3.2×10^{11} s^{-1}, as Figure 4 shows. A consequent difference absorption spectrum composed of the bleached MLCT band and a broad and weak band with a peak at 650 nm is characteristic of the formation of electron-transfer product, $[(tpy)Ru^{III}(tpy\text{-}ph\text{-}tpy)\text{-}Co^{II}(tpy)]^{5+}$.[21] The bleached MLCT band at 490 nm was recovered in the following two processes. The rate constant of the slow recovery was directly determined to be 4.9×10^{9} s^{-1} at 298 K (Figure 5). The rate of an intermediate recovery was determined to be 8.1×10^{10} s^{-1}, as in the case of $[(tpy)Ru\text{-}(tpy\text{-}tpy)Co(tpy)]^{5+}$. As the temperature decreased, the rate constant of the slow recovery process increased to 2.2×10^{10} s^{-1} at 180 K, as shown in Figure 5. A decrease in the decay rate constant of ^{3}MLCT at 180 K was small, as shown in Table 1, where the rate constants and the initial amplitudes of the recovery processes are shown. The rate constants of the intermediate and the slow recoveries in acetonitrile and propylene carbonate were independent of solvents at 298 K; the averaged rate constants are 7.4×10^{10} s^{-1} and 0.41×10^{10} s^{-1}, respectively.

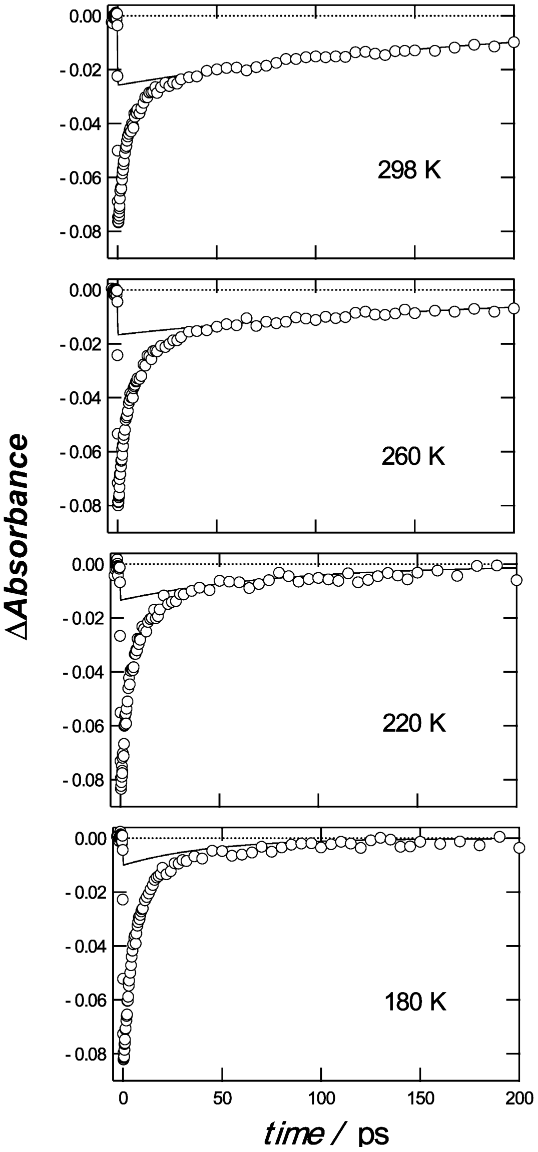

Figure 5. Recoveries of the MLCT absorption band of $[(tpy)Ru(tpy\text{-}ph\text{-}tpy)Co(tpy)]^{5+}$ in BN, monitored at 490 nm and at 298, 260, 220, or 180 K. The solid lines stand for the slow component of the recovery (4.9×10^{9} s^{-1} at 298 K, 5.2×10^{9} s^{-1} at 260 K, and 16×10^{9} s^{-1} and 22×10^{9} s^{-1} at 180 K).

Discussion

Reexamination of Reaction Mechanism. A time profile of difference absorption spectra is interpreted in the following. The initial absorption change on the photoexcitation of $[(tpy)Ru^{II}\text{-}(tpy\text{-}tpy)Co^{III}(tpy)]^{5+}$ has been ascribed to the formation of ^{3}MLCT(Ru) with the bleaching of MLCT absorption band and a weak broad absorption of reduced ligand in the whole spectral region (eq 1).[21] ^{3}MLCT(Ru) was monitored at 620 nm to decay with a rate constant of 1.0×10^{12} s^{-1} and to produce $[(tpy)\text{-}Ru^{III}(tpy\text{-}ph\text{-}tpy)^2Co^{II}(tpy)]^{5+}$ with a fraction (0.57[24]) (eq 2) and the reactant at the ground state (0.43[24])). The recovery of MLCT absorption band in 10 ps took place differently from the decay of ^{3}MLCT monitored at 620 nm, as Figure 3 shows. Disagree-

TABLE 1: Temperature Dependence of the Decay Rate Constant (k_1) of ^{3}CT(Ru) and the Rate Constants (k_α and k_β) and the Fractions (f_α and f_β) of the Recovery Processes of the Ground State Absorption of [(tpy)Ru(tpy-ph-tpy)Co(tpy)]$^{5+}$ and [(tpy)Ru(tpy-tpy)Co(tpy)]$^{5+}$ in Butyronitrile

compound	T (K)	k_1 (10^{10} s^{-1})	$-\Delta G^\circ_{\mathrm{RET}}$ (eV)^a	k_α (10^{10} s^{-1})	f_α	k_β (10^{10} s^{-1})	f_β
[(tpy)Ru(tpy-ph-tpy)Co(tpy)]$^{5+}$	298	32	0.99	8.1	0.45	0.49	0.55
	260	32	1.02	6.7	0.64	0.52	0.36
	180	25	1.07	6.1	0.63	1.6	0.37
[(tpy)Ru(tpy-tpy)Co(tpy)]$^{5+}$	298	100	0.97	52	0.59	2.8	0.41

[a] $\Delta G^\circ_{\mathrm{RET}} = \Delta H^\circ_{\mathrm{RET}} - T\Delta S^\circ_{\mathrm{RET}} = -1.20$ eV $+ T \times 0.70$ meV/K.[21]

TABLE 2: Gibbs Free Energy Change, $-\Delta G^\circ_{\mathrm{RET(D)}}$, Rate Constant of RET, $k_{\mathrm{RET(D)}}$, Reorganizational Free Energy, λ_{RET}, and Matrix Element, H_{RET}, of RET at 298 K

Ru$^{\mathrm{III}}$−Co$^{\mathrm{II}}$ compounds	$-\Delta G^\circ_{\mathrm{RET}}$ (eV)	$k_{\mathrm{RET(D)}}$ (10^{10} s^{-1})	λ_{RET} (eV)	H_{RET} (meV)
[(tpy)Ru(tpy-ph-tpy)Co(tpy)]$^{5+}$	−0.99	3.9	1.1	1.9
[(tpy)Ru(tpy-tpy)Co(tpy)]$^{5+}$	−0.97	23	0.95	4.6

ment between the decay of ^{3}MLCT monitored at 620 nm and the recovery of the MLCT absorption band monitored at 515 nm demonstrates that the recovery of the MLCT absorption band occurs in an intermediate process with a rate constant of 5.2 × 10^{11} s^{-1} in addition to the slow one with a rate constant of 2.8 × 10^{10} s^{-1}.

As for [(tpy)Ru(tpy-ph-tpy)Co(tpy)]$^{5+}$, the fast recovery of the MLCT absorption band at 490 nm is presumed to occur with the same rate constant of 3.2 × 10^{11} s^{-1} of ^{3}MLCT(Ru) monitored at 565 nm. The quantum yield of the EET reaction (0.41[24]) was given by a fraction of the EET product formation in the ET quenching of ^{3}MLCT. The rate constant of the slow recovery of the MLCT band was determined to be 4.9 × 10^9 s^{-1} at 298 K. Since the time profile of MLCT band at 490 nm is not reconstituted in terms of the fast quenching of ^{3}MLCT (3.2 × 10^{11} s^{-1}) and the slow RET of the ^{2}Co (II) moiety (4.9 × 10^9 s^{-1}), an intermediate recovery process of the MLCT band with a rate constant of 8.1 × 10^{10} s^{-1} is required. The process of the intermediate recovery exhibits a larger fraction f_α than the slow one of the MLCT band as will be mentioned later.

The doublet state of Co(II) moiety in [(tpy)Ru$^{\mathrm{III}}$(tpy-ph-tpy)-Co$^{\mathrm{II}}$(tpy)]$^{5+}$ undergoes both RET (eq 5) with a rate constant of $k_{\mathrm{RET(D)}}$ and ISC to a higher lying quartet state, ^{4}Co(II), (eq 3) with a rate constant of k_{QD} immediately after the production. ^{4}Co(II) at the latter stage undergoes both RET (eq 6) with a rate constant of $k_{\mathrm{RET(Q)}}$ and ISC to the low lying doublet state with a rate constant of k_{DQ}.

$$[(\mathrm{tpy})\mathrm{Ru}(\mathrm{tpy\text{-}ph\text{-}tpy})\mathrm{Co}(\mathrm{tpy})]^{5+} + h\nu \rightarrow {}^3\mathrm{MLCT(Ru)} \tag{1}$$

$$^3\mathrm{MLCT(Ru)} \rightarrow [(\mathrm{tpy})\,{}^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^2\mathrm{Co^{II}}(\mathrm{tpy})]^{5+} \; k_{\mathrm{EET}} \tag{2}$$

$$[(\mathrm{tpy})^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^2\mathrm{Co^{II}}(\mathrm{tpy})]^{5+} \rightarrow [(\mathrm{tpy})\,{}^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^4\mathrm{Co^{II}}(\mathrm{tpy})]^{5+} \; k_{\mathrm{QD}} \tag{3}$$

$$[(\mathrm{tpy})^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^4\mathrm{Co^{II}}(\mathrm{tpy})]^{5+} \rightarrow [(\mathrm{tpy})\,{}^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^2\mathrm{Co^{II}}(\mathrm{tpy})]^{5+} \; k_{\mathrm{DQ}} \tag{4}$$

$$[(\mathrm{tpy})^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^2\mathrm{Co^{II}}(\mathrm{tpy})]^{5+} \rightarrow [(\mathrm{tpy})\,\mathrm{Ru^{II}}(\mathrm{tpy\text{-}ph\text{-}tpy})\mathrm{Co^{III}}(\mathrm{tpy})]^{5+} \; k_{\mathrm{RET(D)}} \tag{5}$$

$$[(\mathrm{tpy})^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^4\mathrm{Co^{II}}(\mathrm{tpy})]^{5+} \rightarrow [(\mathrm{tpy})\,\mathrm{Ru^{II}}(\mathrm{tpy\text{-}ph\text{-}tpy})\mathrm{Co^{III}}(\mathrm{tpy})]^{5+} \; k_{\mathrm{RET(Q)}} \tag{6}$$

In our previous paper,[21] the recovery of [(tpy)Ru$^{\mathrm{II}}$(tpy-ph-tpy)Co$^{\mathrm{III}}$(tpy)]$^{5+}$ was differently analyzed on the time profile of the MLCT band recovery only. The recovery of the MLCT absorption band was observed to take place during the decay of ^{3}MLCT and through the RET of [(tpy)Ru$^{\mathrm{III}}$(tpy-ph-tpy)Co$^{\mathrm{II}}$-(tpy)]$^{5+}$ with a rate constant of 4.9 × 10^9 s^{-1}. The reaction mechanism postulated[21] was the following: (1) ^{2}Co(II) carried out rapid doublet−quartet ISC and (2) ^{2}Co(II) in equilibrium with ^{4}Co(II) underwent RET with an apparent rate constant of $k_{\mathrm{RET(D)}} \times (1 + K_{\mathrm{DQ}})^{-1}$, where $k_{\mathrm{RET(D)}}$ and K_{DQ} were the rate constants of RET from ^{2}Co(II) moiety and the equilibrium constant of ^{4}Co(II) formation expressed as a ratio of k_{QD} to the rate constant of quartet−doublet ISC (eq 4). The magnitude of $k_{\mathrm{RET(D)}}$ was evaluated to be 1.3 × 10^{10} s^{-1} at 310 K from K_{DQ} and the apparent recovery rate.

The doublet state of Co(II) moiety may be partially converted to a higher lying quartet state with some delay, because the equilibrium constant of ^{4}Co(II) formation, K^{298}_{DQ}, is near 1 at 298 K.[21,24] The doublet−quartet ISC was not reflected on the time profile of transient absorption in the region below 520 nm,[21] because a small difference in the molar absorption coefficient between the doublet and the quartet (3500 M^{-1} cm^{-1} at 515 nm) was completely hidden by the recovery process, causing a big absorption change (34200 M^{-1} cm^{-1} at 490 nm) between the original reactant and the EET product.

Return Electron-Transfer and Intersystem Crossing. Each decay of [(^{2}Ru$^{\mathrm{III}}$(L−L)^{2}Co$^{\mathrm{II}}$)(t)] and [(^{2}Ru$^{\mathrm{III}}$(L−L)^{4}Co$^{\mathrm{II}}$)(t)] is written in terms of biexponential decays (eqs 7 and 8):

$$[(^2\mathrm{Ru^{III}}(\mathrm{L{-}L})^2\mathrm{Co^{II}})(t)] = \frac{(k_{\mathrm{RET(D)}} + k_{\mathrm{QD}} - k_\beta)D(0)}{k_\alpha - k_\beta} \times \exp(-k_\alpha t) + \frac{(k_\alpha - k_{\mathrm{RET(D)}} - k_{\mathrm{QD}})D(0)}{k_\alpha - k_\beta}\exp(-k_\beta t) \tag{7}$$

$$[(^2\mathrm{Ru^{III}}(\mathrm{L{-}L})^4\mathrm{Co^{II}})(t)] = \frac{k_{\mathrm{QD}}D(0)}{k_\alpha - k_\beta}[\exp(-k_\beta t) - \exp(-k_\alpha t)] \tag{8}$$

where $D(0)$, k_α, and k_β are the initial formation of EET product shown as [(^{2}Ru$^{\mathrm{III}}$(L−L)^{2}Co$^{\mathrm{II}}$)(0)], the apparent rate constant of the intermediate recovery, and that of the slow recovery, respectively.

$$k_\alpha = \frac{1}{2}[(k_{\mathrm{DQ}} + k_{\mathrm{QD}} + k_{\mathrm{RET(D)}} + k_{\mathrm{RET(Q)}}) + \{(k_{\mathrm{DQ}} - k_{\mathrm{QD}} + k_{\mathrm{RET(Q)}} - k_{\mathrm{RET(D)}})^2 + 4k_{\mathrm{QD}}k_{\mathrm{DQ}}\}^{1/2}] \tag{9}$$

$$k_\beta = \frac{1}{2}[(k_{\mathrm{DQ}} + k_{\mathrm{QD}} + k_{\mathrm{RET(D)}} + k_{\mathrm{RET(Q)}}) - \{(k_{\mathrm{DQ}} - k_{\mathrm{QD}} + k_{\mathrm{RET(Q)}} - k_{\mathrm{RET(D)}})^2 + 4k_{\mathrm{QD}}k_{\mathrm{DQ}}\}^{1/2}] \tag{10}$$

The sum of apparent rate constants is equal to the sum of the rate constants of eqs 3−6.

$$k_\alpha + k_\beta = k_{\mathrm{DQ}} + k_{\mathrm{QD}} + k_{\mathrm{RET(D)}} + k_{\mathrm{RET(Q)}} \tag{11}$$

Since the recovery rate of the reactant, $[(\mathrm{tpy})\mathrm{Ru^{II}(L{-}L)Co^{III}}(\mathrm{tpy})]^{5+}$, is given by the following equation

$$\frac{\mathrm{d}[(\mathrm{Ru^{II}(L{-}L)Co^{III}})(t)]}{\mathrm{d}t} = k_{\mathrm{RET(D)}}[(^{2}\mathrm{Ru^{III}(L{-}L)^{2}Co^{II}})(t)] + k_{\mathrm{RET(Q)}}[(^{2}\mathrm{Ru^{III}(L{-}L)^{4}Co^{II}})(t)] \quad (12)$$

the integration of eq 12 gives the time profile of the reactant recovered:

$$[(\mathrm{Ru^{II}(L{-}L)Co^{III}})(t)] = [(^{2}\mathrm{Ru^{III}(L{-}L)^{2}Co^{II}})(0)][1 - (f_{\alpha}\exp(-k_{\alpha}t) + f_{\beta}\exp(-k_{\beta}t))] = [(^{2}\mathrm{Ru^{III}(L{-}L)^{2}Co^{II}})(0)][1 - ([(^{2}\mathrm{Ru^{III}(L{-}L)^{2}Co^{II}})(t)] + [(^{2}\mathrm{Ru^{III}(L{-}L)^{4}Co^{II}})(t)])] \quad (13)$$

$$f_{\alpha} = \frac{(k_{\mathrm{RET(D)}} - k_{\beta})}{(k_{\alpha} - k_{\beta})} \quad (14)$$

$$f_{\beta} = \frac{(k_{\alpha} - k_{\mathrm{RET(D)}})}{(k_{\alpha} - k_{\beta})} \quad (15)$$

From eqs 14 and 15, the following equation is derived:

$$k_{\mathrm{RET(D)}} = f_{\alpha}k_{\alpha} + f_{\beta}k_{\beta} \quad (16)$$

RET. By using eq 16, the $k_{\mathrm{RET(D)}}$ of $[(\mathrm{tpy})\mathrm{Ru}(\mathrm{tpy\text{-}ph\text{-}tpy})\mathrm{Co}(\mathrm{tpy})]^{5+}$ is calculated to decrease from $4.6 \times 10^{10}\ \mathrm{s^{-1}}$ at 180 K to $3.9 \times 10^{10}\ \mathrm{s^{-1}}$ at 298 K, as shown in Table 2, which is three times as large as that previously estimated.[21] The negative temperature change of $k_{\mathrm{RET(D)}}$ comes from the decrease of $-\Delta G^{\circ}_{\mathrm{RET}}$ (1.07 eV at 180 K to 0.97 eV at 298 K) due to the positive entropy change of RET. The $\Delta G^{\circ}_{\mathrm{RET}}$ dependence of $k_{\mathrm{RET(D)}}$ suggests that λ_{RET} is larger than 1.0 eV. It is in agreement with the sum of solvent reorganizational free energy (0.85 eV[21,28]) and intramolecular reorganizational free energy (0.28 eV[21]). That of the electronic coupling matrix element H_{RET} of RET is evaluated to be 1.9 meV by putting λ_{RET} (1.1 eV) and $\Delta G^{\circ}_{\mathrm{RET}}$ (−0.99 eV) in

$$\frac{2\pi {H_{\mathrm{RET}}}^{2}}{\hbar\sqrt{4\pi\lambda_{\mathrm{RET}}k_{\mathrm{B}}T}}\exp\left(-\frac{(\Delta G^{\circ}_{\mathrm{RET}} + \lambda_{\mathrm{RET}})^{2}}{4\lambda_{\mathrm{RET}}k_{\mathrm{B}}T}\right)$$

As for $[(\mathrm{tpy})\mathrm{Ru}(\mathrm{tpy\text{-}tpy})\mathrm{Co}(\mathrm{tpy})]^{5+}$, $k_{\mathrm{RET(D)}}$ is evaluated to be $2.3 \times 10^{11}\ \mathrm{s^{-1}}$, which is 3.8 times larger than the previous one.[21] The magnitudes of λ_{RET} and H_{RET} are evaluated to be 0.95 eV and 4.6 meV, respectively.

Each of the other three rate constants, $k_{\mathrm{RET(Q)}}$, k_{QD}, and k_{DQ}, cannot be determined from two quantities of k_{α} and k_{β} empirically assessed. A relation of $K_{\mathrm{QD}} = k_{\mathrm{QD}}/k_{\mathrm{DQ}}$, however, allows one to evaluate the rate constants of three processes, as is shown in Table 3. Since the magnitude of $k_{\mathrm{RET(Q)}}$ at the temperatures are calculated to be scattered from minus to plus by using eq 11, $k_{\mathrm{RET(Q)}}$ is small compared with others ($k_{\mathrm{RET(D)}}$ and k_{DQ}).

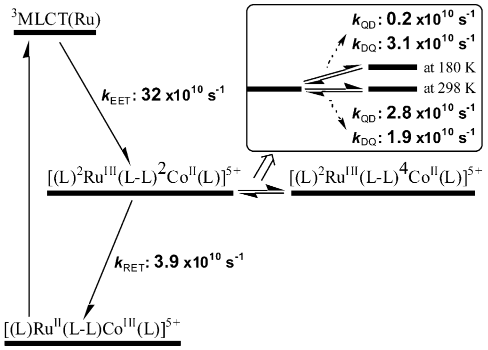

Figure 6. Transition rates of EET and RET at 298 K and ISC rates of doublet−quartet and quartet−doublet at 298 and 180 K of $[(\mathrm{tpy})\mathrm{Ru}(\mathrm{tpy\text{-}ph\text{-}tpy})\ \mathrm{Co}(\mathrm{tpy})]^{5+}$. The Gibbs free energy of the ^{4}Co(II) moiety at 180 K is higher by 0.054 eV than that at 298 K.

ISC. The dependence of the magnitude of k_{QD} on the temperature can be seen in Table 3; all the magnitudes of $k_{\mathrm{RET(Q)}}$ and k_{DQ} are almost independent of temperature. The temperature dependence of k_{QD} can be understood as follows. As Figure 6 shows, the Gibbs free-energy change of doublet−quartet ISC, $\Delta G^{\circ}_{\mathrm{QD}} = \Delta H^{\circ}_{\mathrm{QD}} - T\Delta S^{\circ}_{\mathrm{QD}}$, becomes small as the temperature increases (from 0.044 eV at 180 K to −0.01 eV at 298 K) because of the positive entropy change of the ISC (0.044 eV $\mathrm{K^{-1}}$).[21,28] The extent of k_{QD} became comparable with k_{DQ} at higher temperatures. This temperature dependence of k_{QD} is responsible for the temperature dependence of k_{α}, k_{β}, f_{α}, and f_{β}. As a result of the temperature dependence of k_{QD}, k_{α} is the smallest and f_{α} is the largest at 180 K.

By employing the relation of $K_{\mathrm{QD}} = k_{\mathrm{QD}}/k_{\mathrm{DQ}}$ and eq 11, the magnitudes of k_{QD} and k_{DQ} at each temperature are evaluated to be $0.20 \times 10^{10}\ \mathrm{s^{-1}}$ to $2.8 \times 10^{10}\ \mathrm{s^{-1}}$ from k_{α}, k_{β}, f_{α} and f_{β}, as shown in Table 3. The ISC occurs through an intersection between quadratic potential-energy surfaces of the doublet and quartet states. The rate constants of doublet−quartet ISC and quartet−doublet ISC can be written in the following equation:

$$k_{\mathrm{QD}} = k^{\circ}_{\mathrm{QD}}\exp\left[-\frac{(\Delta G^{\circ}_{\mathrm{QD}} + \lambda_{\mathrm{QD}})^{2}}{4\lambda_{\mathrm{QD}}RT}\right] \quad (17)$$

where $\Delta G^{\circ}_{\mathrm{QD}}$ and λ_{QD} are the Gibbs free-energy change and reorganizational free energy of doublet−quartet ISC. The rate of quartet−doublet ISC increases with increase in the temperature kinetically, too, unless $\Delta G^{\circ}_{\mathrm{QD}}$ is close to λ_{QD}. By using least-squares fits to a quadratic function of $\Delta G^{\circ}_{\mathrm{QD}}$, we roughly determined that λ_{QD} was 0.03 eV from the ΔG° dependence of k_{QD} on the assumption that the ISC exhibits a small activation energy ($E_{\mathrm{a}}^{\mathrm{QD}}$) of 0.01 eV (Figure 7). The λ_{QD} of doublet−quartet ISC is reasonably small compared with those (λ_{SQ}: 0.58 and 0.29 eV) of quintet−singlet ISC of the spin crossover Fe(II) compounds, $[\mathrm{Fe(1\text{-}propyl\text{-}tetrazole)_{6}}]$ and Fe(hydrotris(pyrazo-

TABLE 3: Rate Constants of Intersystem Crossing, k_{DQ} and k_{QD}, and Gibbs Free Energy Change of Intersystem Crossing, $\Delta G^{\circ}_{\mathrm{DQ}}$ and $\Delta G^{\circ}_{\mathrm{QD}}$, in Butyronitrile at Various Temperatures

compound	T (K)	$\Delta G^{\circ}_{\mathrm{QD}}$ (meV)	k_{QD} ($10^{10}\ \mathrm{s^{-1}}$)	$\Delta G^{\circ}_{\mathrm{DQ}}$ (meV)	k_{DQ} ($10^{10}\ \mathrm{s^{-1}}$)	$-\Delta G^{\circ}_{\mathrm{RET}}$ (eV)	$k_{\mathrm{RET(D)}}$ ($10^{10}\ \mathrm{s^{-1}}$)
	298	−10	2.8	10	1.9	0.99	3.9
$[(\mathrm{tpy})\mathrm{Ru}(\mathrm{tpy\text{-}ph\text{-}tpy})\mathrm{Co}(\mathrm{tpy})]^{5+}$	260	7	1.1	−7	1.6	1.02	4.4
	220	25	0.69	−25	2.6	1.05	4.5
	180	44	0.20	−44	3.1	1.07	4.6
$[(\mathrm{tpy})\mathrm{Ru}(\mathrm{tpy\text{-}tpy})\mathrm{Co}(\mathrm{tpy})]^{5+}$	298	−10	15	10	15	0.97	23

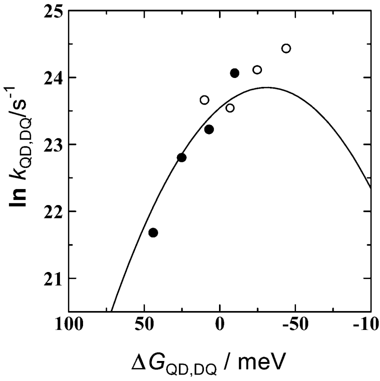

Figure 7. Dependence of the temperature-corrected intersystem crossing rate, k_{DQ} (○) and k_{QD} (●), on ΔG°_{DQ} or ΔG°_{QD} for [(tpy)Ru^{III}-(tpy-ph-tpy)Co^{II}(tpy)]$^{5+}$ at 298 K. A solid line is the least-squares fit to eq 17, $k_{QD} = 2.3 \times 10^{10} \exp(-(\Delta G^\circ_{QD} + 0.030)^2/(0.12 \times k_B \times 298))$.

ly)borato)$_2$, which were roughly calculated from E_a^{SQ} of quintet−singlet ISC (0.145 eV[9] and 0.077 eV[4], respectively) on the assumption that $\lambda_{SQ} = 4 \times E_a^{SQ}$ at $\Delta G^\circ_{SQ} = 0$. It was suggested that a rapid transient absorption change of the EET product of [(bpy)$_2$Ru^{III}(2,6-bis(2- pyridyl)dibenzimidazole)^{4}Co^{II}(bpy)$_2$]$^{5+}$ could be ascribed to downhill doublet−quartet ISC with $\Delta G^\circ_{QD} = -0.20$ eV at 298 K.[19] By employing the fixed value (−0.20 eV) of ΔG°_{QD}, λ_{QD} of the ISC was estimated to be either 0.52 or 0.08 eV from an activation energy (E_a^{QD}: 0.052 eV) of a rapid transient absorption change process,[29] in which a strong transient absorption in near ultra-violet region decayed to form a stable EET product of [(bpy)$_2$Ru^{III}(2,6-bis(2-pyridyl)dibenzimidazole)^{4}Co^{II}(bpy)$_2$]$^{5+}$ though the strong transient absorption was left for assignment. Since such a strong transient absorption change was not observed just after the EET of [(bpy)$_2$Ru^{II}-(tpphz)Co^{III}(bpy)$_2$]$^{5+}$,[23] further study on it is in progress.

Conclusion

Excited-state electron transfer (EET) of [Ru^{II}(L−L)Co^{III}]$^{5+}$ and the following return electron transfer (RET) of [Ru^{III}(L−L)^{2}Co^{II}]$^{5+}$ (L−L = tpy-ph-tpy and tpy-tpy) produced on the subpicosecond laser excitation have been investigated in a wide temperature range. Biexponential recovery process of [(tpy)-Ru^{II}(L−L)Co^{III}(tpy)]$^{5+}$ in butyronitrile, $[(\mathrm{Ru^{II}(L{-}L)Co^{III}})(t)] = (^2\mathrm{Ru^{III}(L{-}L)^2Co^{II}})(0)[1 - f_\alpha \exp(-k_\alpha t) - f_\beta \exp(-k_\beta t)]$, occurred immediately after the production of [(tpy)^{2}Ru^{III}(L−L)^2-Co^{II}(tpy)]$^{5+}$ in the electron-transfer quenching of ^{3}CT(Ru). Four parameters of biexponential recovery, k_α, f_α, k_β, and f_β, weakly depend on temperature in a range of 180−300 K. The biexponential recovery of the reactant is interpreted in terms of three states model, in which [Ru^{II}(L−L)Co^{III}]$^{5+}$ is reproduced with a rate constant of $k_{RET(D)}$ from [^{2}Ru^{III}(L−L)^{2}Co^{II}]$^{5+}$ and with $k_{RET(Q)}$ from a little higher lying [^{2}Ru^{III}(L−L)^{4}Co^{II}]$^{5+}$, and both ^{2}Co(II) and ^{4}Co(II) are exchangeable via ISC with k_{QD} and k_{DQ}. The rate constants of $k_{RET(D)}$ for [(tpy)Ru(tpy-ph-tpy)Co(tpy)]$^{5+}$ and [(tpy)Ru^{II}(tpy-tpy)Co^{III}(tpy)]$^{5+}$ were evaluated to be 3.9×10^{10} s^{-1} and 2.3×10^{11} s^{-1}, respectively, at 298 K. The extent of $k_{RET(D)}$ is 3 times as large as those obtained by assuming the occurrence of doublet−quartet equilibrium before RET.[21] The rate constant of uphill doublet−quartet ISC of [(tpy)Ru^{II}(tpy-ph-tpy)Co^{III}(tpy)]$^{5+}$, k_{QD}, increases from 0.2×10^{10} s^{-1} at 180 K to 2.8×10^{10} s^{-1} at 298 K as ΔG°_{QD} decreases from 0.044 eV at 180 K to −0.010 eV at 298 K. A small reorganizational free energy (0.03 eV) for the doublet−quartet ISC was evaluated from the dependence of the doublet−quartet ISC rate on the Gibbs free-energy change. Meanwhile, that of k_{DQ} is estimated to be independent of temperature (2×10^{10} s^{-1}). As for [(tpy)-Ru^{II}(tpy-tpy)Co^{III}(tpy)]$^{5+}$, the rate constants of k_{DQ} and k_{QD} at 298 K are evaluated to be 1.5×10^{11} s^{-1}.

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