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ARTICLES

Low Quantum Yields of Relaxed Electron Transfer Products of Moderately Coupled Ruthenium(II)−Cobalt(III) Compounds on the Subpicosecond Laser Excitation

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Photoinduced electron-transfer reactions of [(tpy)Ru^{II}(tpy-tpy)Co^{III}(tpy)]5+ (tpy = 2,2′:6′,2″-terpyridine and tpy-tpy = 6′,6″-bis(2-pyridyl)-2,2′:4′,4″:2″,2‴-quarterpyridyne), [(tpy)Ru^{II}(tpy-ph-tpy)Co^{III}(tpy)]$^{5+}$ (tpy-ph-tpy = 1,4-bis[2,2′:6′,2″-terpyridine-4′-yl]benzene), and [(bpy)$_2$Ru^{II}(tpphz)Co^{III}(bpy)$_2$]$^{5+}$ (bpy = 2,2′-bipyridine, and tpphz = tetrapyrido[3,2-*a*:2′,3′-*c*:3″,2″-*h*::2‴,3‴-*j*]phenazine) were studied in the range 140−298 K by means of subpicosecond transient absorption spectroscopy. ^{3}MLCT(Ru) of [(tpy)Ru^{II}(L−L)Co^{III}(tpy)]$^{5+}$ (L−L: tpy-tpy and tpy-ph-tpy) underwent intramolecular electron-transfer (EET) reaction to form [^{2}Ru^{III}(tpy)(L−L)^{2}Co^{II}(tpy)]$^{5+}$ in a shorter time than 10 ps. Low quantum yields of the EET products (0.53 for tpy-tpy and 0.41 for tpy-ph-tpy in butyronitrile at 298 K) measured before the fast return electron-transfer were found as in the intermolecular electron-transfer quenching of ^{3}MLCT(Ru) by [Co(tpy)$_2$]$^{3+}$. The quantum yield of [(tpy)-Ru^{III}(tpy-tpy)Co^{II}(tpy)]$^{5+}$ (Φ) decreases to 0.38 in a slowly reorganizing solvent of propylene carbonate and that of [(tpy)Ru^{II}(tpy-ph-tpy)Co^{III}(tpy)]$^{5+}$ to 0.21 at 180 K. The reductions in the EET yields, $1 - \Phi$, can be ascribed to a fast transition of the nonrelaxed EET product to the lowest triplet d−d* state of [Co^{III}(tpy)$_2$] moiety during the solvent reorganization. A tunneling transition of the nonrelaxed EET products to the lowest lying d−d excited-state of [Co^{III}(tpy)$_2$] moiety takes place as a hole transfer, HT, from the dπ-orbital of Ru(III) to that of Co(II) with a configuration of dπ^6dσ*. An electronic coupling of dπ(Ru)−dπ(Co) estimated from the intensity of inter-valence transition of [(tpy)Ru^{III}(L−L)Ru^{II}(tpy)]$^{5+}$ (Collin, J.-P.; Laine, P.; Launay, J.-P.; Sauvage, J.-P.; Sour, A. *J. Chem. Soc., Chem. Commun.* **1993**, 434) is large enough to carry out the HT. The weak coupling of dπ(Ru)−dπ(Co) in the case of [(bpy)$_2$Ru(tpphz)Co(bpy)$_2$]$^{5+}$ attenuates the HT rate to bring about a high yield of EET (0.8). The possibility that energy-transfer of ^{3}MLCT(Ru) to the Co(III) moiety via an intermediate super-exchange coupling between dπ(Ru) and dπ(Co) occurs in competition with the EET of [(tpy)Ru^{III}(tpy-ph-tpy)Co^{II}(tpy)]$^{5+}$ is also pursued.

Introduction

Reaction products of excited-state electron-transfer (EET) are likely to undergo return electron-transfer (RET) reducing apparent quantum yield of EET product formation. A transient absorption spectroscopy has revealed that fast RET occurs within geminate radical pairs formed in bimolecular quenching of excited molecule[1−4] and in photoexcitation of charge-transfer compounds.[5,6] Provided that EET within a chemically linked donor−acceptor compound takes place faster than 10^{12} s^{-1}, electronic coupling between an oxidized donor and a reduced acceptor is expected to be large enough to carry out a fast RET. Furthermore, the Gibbs free energy surface of EET product could have an intersection with that of the reactant not only at the ground state but also at the electronic excited state.[7] According to theories of tunneling transition between potential-energy surfaces, a fraction of the tunneling transition depends on the strength of electronic coupling between diabatic states, the intersection angle between diabatic states, and the excess

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thermal energy of the nonrelaxed state.[8,9] EETs of donor−acceptor compounds in solution are followed by reorganization of atoms in the product and of surrounding solvent molecules to redistribute the change of standard Gibbs free energy to many vibrational modes of the product and kinetic or solvation mode of surrounding solvent molecules. Some extent of entropy change is involved in the reorganization. It takes less than a couple of picoseconds to redistribute the thermal energy among low-frequency modes of vibration and solvation.[10−12] Furthermore, the nonrelaxed product of EET could undergo a tunneling transition to lower lying states in competition with the thermal relaxation.

Small yields of the relaxed ET product demonstrate the occurrence of either RET on the way to the relaxed product or competing processes of the excited-state such as excitation energy transfer. Quantum yields of intramolecular reactions in the fast quenching of excited state Φ_{EET} have, however, been rarely determined,[13] because the lifetimes of excited states are too short to determine the formation of excited-state undergoing EET even on using a subpicosecond transient photometry. In this paper, the number of photon absorbed by a chromophore is counted for by employing a transient actinometer of $[Ru(bpy)_3]^{2+}$, which is converted to the countable lowest excited state, ^{3}MLCT(Ru), in 100 fs.[14,15] Low quantum yields of electron-transfer products in a bimolecular electron-transfer quenching of ^{3}MLCT(Ru) of $[RuL_3]^{2+}$ (L:2,2′-bipyridine and 2,2′-bipyridine-4,4′-dicarboxylate) with $[Co(tpy)_2]^{3+}$ (tpy:2,2′:6′,2′′-terpyridine) have been ascribed to either RET of geminate radical-pair formed in the electron-transfer quenching or a rapid radiationless transition of exciplex formed.[16] A previous paper revealed that both EET and RET with a temperature-independent rate of $10^{10}-10^{12}$ s^{-1} occurred in $[(tpy)Ru(tpy\text{-}ph\text{-}tpy)Co(tpy)]^{5+}$ and $[(tpy)Ru(tpy\text{-}tpy)Co(tpy)]^{5+}$ containing a $[Co(tpy)_2]^{2+}$ moiety.[17] The fast processes of EET and RET have been accounted for in terms of through-ligand electronic coupling between localized d-orbitals of metal centers and small structural change of the Co(II) moiety. Quantum yields of $[Ru^{III}(L{-}L)Co^{II}]^{5+}$ formation, however, have not been determined for these compounds because EET quenching of ^{3}MLCT(Ru) was too rapid to determine the production of ^{3}MLCT(Ru).

In this study, quantum yields of excited-state ET reactions, Φ_{EET}, for rigid donor−acceptor compounds, $[Ru(bpy)_2(tpphz)Co(bpy)_2](PF_6)_5$ (bpy = 2,2′-bipyridine, tpphz = tetrapyrido[3,2-*a*:2′,3′-*c*:3′′,2′′-*h*::2′′′,3′′′-*j*]phenazine), $[Ru(tpy)(tpy\text{-}ph\text{-}tpy)Co(tpy)](PF_6)_5$(tpy = 2,2′:6′,2′′-terpyridine, tpy-ph-tpy = 1,4-bis[2,2′:6′,2′′-terpyridine-4′-yl]benzene) and $[Ru(tpy)(tpy\text{-}tpy)Co(tpy)]$ $(PF_6)_5$ (tpy-tpy = 6′,6′′-bis (2-pyridyl)-2,2′:4′,4′′:2′′,2′′′-quarterpyridyne) were determined by means of transient actinometry. Time-resolved absorption spectroscopy after the laser excitation in the region $10^{-13}-10^{-7}$s will reveal a different reaction sequence for $[Ru^{II}(bpy)_2(tpphz)Co^{III}(bpy)_2]^{5+}$ from those for $[Ru^{II}(tpy)(tpy\text{-}ph\text{-}tpy)Co^{III}(tpy)]^{5+}$ and $[Ru^{II}(tpy)(tpy\text{-}tpy)Co^{III}(tpy)]^{5+}$. Solvent and temperature dependence of the ET reaction yield were also investigated.

Experimental Section

Materials. $[Ru(tpy)(tpy\text{-}ph\text{-}tpy)Co(tpy)](PF_6)_5 \cdot 6H_2O$ and $[(tpy)Ru(tpy\text{-}tpy)Co(tpy)](PF_6)_5$. The preparation of these compounds was described in the previous paper.[17]

$[Ru(bpy)_2(tpphz)Co(bpy)_2](PF_6)_5$ and $[Ru(bpy)_2(tpphz)Ru(bpy)_2](PF_6)_4$. The ligand 1,10-phenanthroline-5,6-dione was prepared as follows. 5-Nitro-6-amino-1,10-phenanthroline was prepared by refluxing 5-nitro-1,10-phenanthroline with hydroxylamine hydrochrolide in ethanol and then was converted to 5,6-diamino-1,10-phenanthroline, which gave rise to 1,10-phenanthroline-5,6-dione.[18,19] $[Ru(bpy)_2$(1,10-phenanthroline-5,6-dione)$](PF_6)_2 \cdot 2H_2O$ was prepared from *cis*-$[Ru(bpy)_2Cl_2] \cdot 3H_2O$ and 1,10-phenanthroline-5,6-dione by refluxing for 3 h. $[Ru(bpy)_2(tpphz)](PF_6)_2 \cdot 2H_2O$ was prepared from $[Ru(bpy)_2$(1,10-phenanthroline-5,6-dion)$]^{2+}$ and 5,6-diamino-1,10-phenanthroline by refluxing for 2 h.[19] *cis*-$[Co(bpy)_2Cl_2]Cl \cdot 2H_2O$ was prepared according to the literature.[20]

$[Ru(bpy)_2(tpphz)Co(bpy)_2](PF_6)_5$ was prepared from a solution of $[Ru(bpy)_2(tpphz)](PF_6)_2 \cdot 2H_2O$ (26 mg) and $[Co(bpy)_2Cl_2]Cl \cdot 2H_2O$ (16 mg) in 1:1 ethanol−acetonitrile (40 mL) by refluxing for 2 h, and then the solvent was evaporated. The residue was dissolved in water and then excess amount of NH_4PF_6 was added. The solid product was filtered out and purified through CM Sephadex C-25 column and Sephadex LH-20 column. Yield: 7 mg (16%). $[Ru(bpy)_2(tpphz)Ru(bpy)_2](PF_6)_4$ was prepared according to the literature.[20]

Measurement. Preparation of the Sample Solutions. Acetonitrile (AN) and propylene carbonate (PC) were used as a solvent for the measurement at 298 K. Butyronitrile (BN) was used as a solvent for the measurement in the region 170−298 K. The solvents were purified by distillation. The sample solutions were prepared just before the measurements.

Cyclic Voltammetry. Redox potentials of the metal complexes were measured by means of differencial-pulse voltammetry using a dc pulse polarograph (Huso, HECS-312B). Voltamograms were recorded by using a platinum disk electrode (diameter 0.5 mm) in a solution of the complex containing 0.05 M of tetraethylammonium perchlorate as a supporting electrolyte.

Determination of the Quantum Yields of Electron-Transfer Product. The quantum yield of excited-state formation or excited-state reactions on the laser excitation was determined in the following procedures, provided that the conversion took place during the excitation pulse. Rates of reactant disappearance are proportional to the laser flux absorbed by the reactant, I_{abs}, and the quantum yield of excited-state formation or reaction, Φ. The ET-reaction rate of a reactant in a cell with path length of d cm is written in terms of laser flux irradiated to the reactant,$I(t)$, and the absorbance of the sample, $\alpha C(t)d$,

$$-\frac{dC(t)}{dt} = \Phi\, I_{abs}\frac{10^3}{d} = \Phi\, I(t)(1-\exp(-\,\alpha C(t)d))\times\frac{10^3}{d} \tag{1}$$

Provided that the formation of either the reacting excited state or the ET product occurs during the laser pulse to decrease the concentration of reactant at the ground-state, integrations of the left-hand term over the concentration and of the right-hand term over time during the laser pulse give the following equation

$$\ln(e^{\alpha c_a d}-1) = \ln(e^{\alpha c_b d}-1) - 10^3\,\Phi\alpha I \tag{2}$$

where c_a, c_b, α, d, and I are the concentration after and before the laser excitation, the molar absorption coefficient of a reactant at the wavelength of the excitation laser, the optical length, and the integrated laser flux, respectively. By employing $[Ru(bpy)_3]^{2+}$ as a chemical actinometer, the integrated laser flux, I, can be determined using, d, $\Phi_1(=1)$, α_1, c_{1a}, and c_{1b}, the last of which was calculated from the formation of ^{3}MLCT on the basis of $\Delta Abs_{450\ nm}$ by using the difference molar absorption coefficient $\Delta\epsilon = -9800$ M^{-1} cm^{-1} at 450 nm.[21] Provided that the width of the laser pulse is long enough to produce the ET product, the quantum yield of ET product, $[Ru^{III}(L{-}L)Co^{II}]^{5+}$, Φ_2, can be estimated by plotting $\ln(e^{\alpha_2 c_{2a} d}-1)$ against $10^3\alpha_2 I$.

Provided that EET takes place after a laser pulse, the formation of ^{3}MLCT(Ru), $c_{2b} - c_{2a}$, can be calculated from α_2, c_{2a} and I.

Formations of the ET product,$c_{2b} - c_{2a}$, were obtained from a difference absorbance at the peak wavelength of MLCT absorption right after the disappearance of ^{3}MLCT. The molar absorption coefficient of the ET product was determined as the sum of those of $[\mathrm{Ru^{III}(L{-}L)}]^{3+}$ and $[\mathrm{Co^{II}(L{-}L)}]^{2+}$, of which the former was prepared by means of electrochemical oxidation of $[\mathrm{Ru^{II}(L{-}L)}]^{2+}$. Differences in the molar absorption coefficient between the reactant and the product are the following, $\Delta\epsilon_{490} = -34400$ M^{-1} cm^{-1} for $[\mathrm{Ru^{II}(tpy)(tpy\text{-}ph\text{-}tpy)Co^{III}(tpy)}]^{5+}$, $\Delta\epsilon_{515} = -24400$ M^{-1} cm^{-1} for $[\mathrm{Ru^{II}(tpy)(tpy\text{-}tpy)Co^{III}(tpy)}]^{5+}$, and $\Delta\epsilon_{450} = -30\,000$ M^{-1} cm^{-1} for $[\mathrm{Ru^{III}(bpy)_2(tpphz)\ Co^{II}(bpy)_2}]^{5+}$.

Time-Resolved Difference Absorption Spectra. Time-resolved difference absorption spectra were obtained by using the second harmonic (SHG) of Q-switched $\mathrm{Nd^{3+}}$:YAG laser (Continuum Surelite I-10, $\lambda_{ex} = 532$ nm, fwhm 4 ns) and the SHG of a mode-locked $\mathrm{Nd^{3+}}$:YAG laser ($\lambda_{ex} = 532$ nm, fwhm 17 ps) for the excitation.

White light from a Xe-arc lamp was used for acquisition of absorption spectra of longer-living species than 10 ns.[21] 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 $\mathrm{H_2O/D_2O}$ (1:1 by volume) solution.[21] The experimental setup and the characteristics of a subpicosencond laser was shown in ref 22. 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

$[\mathrm{Ru^{III}(tpy)(L{-}L)Co^{II}(tpy)}]^{5+}$ (L—L: tpyp-py-tpy and tpy-tpy). 1. Transient Absorption Changes and Sequential Reactions. A subpicosecond laser excitation of a $\mathrm{N_2}$-bubbled BN solution of $[\mathrm{Ru^{III}(tpy)(tpy\text{-}ph\text{-}tpy)Co^{II}(tpy)}]^{5+}$ produced a negative absorbance below 540 nm due to the smaller molar extinction coefficient of ^{3}MLCT of Ru(II) moiety than the ground state and a broad band of ^{3}MLCT with the maximum at 650 nm in a red and near infrared region. The broad band due to ^{3}MLCT of Ru(II) moiety decayed in 2 ps with a rate constant of $(3.2 \pm 0.5) \times 10^{11}\mathrm{s^{-1}}$. $[\mathrm{(tpy)^2Ru^{III}(tpy\text{-}ph\text{-}tpy)^2Co^{II}\ (tpy)}]^{5+}$ in eqs 4 and 5.[17] The resultant difference absorption consisted of a negative band below 570 nm and a weak and broad band in a red region, both of which were ascribed to the bleaching of the MLCT band and the formation of the LMCT band, respectively. The recovery of the MLCT absorption band during the disappearance of ^{3}MLCT (eq 5) demonstrates a low yield of $[\mathrm{(tpy)^2Ru^{III}(tpy\text{-}ph\text{-}tpy)^2Co^{II}(tpy)}]^{5+}$. The subsequent biexponential recovery of the MLCT band was a result of RET of $[\mathrm{Co^{II}(tpy)_2}]$ moiety with rate constants of 8.1×10^{10} and 0.49×10^{10} s^{-1}.[17] The production of the $[\mathrm{Ru^{III}(tpy)_2}]$ moiety was determined from the absorbance recovered of MLCT band from the EET product.

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

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

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

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

$$[\mathrm{(tpy)\,{}^2Ru^{III}(tpy\text{-}ph\text{-}tpy)^2Co^{II}(tpy)}]^{5+} \rightarrow [\mathrm{(tpy)\,Ru^{II}(tpy\text{-}ph\text{-}tpy)Co^{III}(tpy)}]^{5+} \quad (7)$$

TABLE 1: Phosphoresence Peaks at 77 K and the Decay Rate Constants of ^{3}CT(Ru), k_1, and $[\mathrm{Ru^{III}(L{-}L)Co^{II}}]$, k_{RET}, at 298 K

compounds	$\tilde{\nu}^{\mathrm{phos}}_{\mathrm{max}}$/cm^{-1}	$k_1/10^9$ s^{-1}	$k_{\mathrm{RET}}/10^9$ s^{-1}
$[\mathrm{Ru(tpy)(tpy\text{-}ph\text{-}tpy)Ru(tpy)}]^{5+}$	15 500[a]	0.30[b]	
$[\mathrm{Ru(tpy)(tpy\text{-}ph\text{-}tpy)Co(tpy)}]^{5+}$		320[b]	81, 4.9[b]
$[\mathrm{Ru(tpy)(tpy\text{-}tpy)Ru(tpy)}]^{5+}$	14 900[a]	0.20[a]	
$[\mathrm{Ru(tpy)(tpy\text{-}tpy)Co(tpy)}]^{5+}$		1000[b]	520, 28[b]
$[\mathrm{Ru(bpy)_2(tpphz)}]^{2+}$	16 730	0.0009*	
$[\mathrm{Ru(bpy)_2(tpphz)Ru(bpy)_2}]^{4+}$	16 680	0.013*	
$[\mathrm{Ru(bpy)_2(tpphz)Co(bpy)_2}]^{5+}$		1400	0.02

[a] Reference 16. [b] Reference 17.

TABLE 2: Redox Potentials of the Component Compounds and Gibbs Free Energy Change of the Return Electron-Transfer Process in BN at 298 K

compounds	$E^{\mathrm{o}}(\mathrm{Ru^{3+/2+}})$[a]	$E^{\mathrm{o}}(\mathrm{Co^{3+/2+}})$[a]	$\Delta G^{\circ}_{\mathrm{RET}}$[b]
$[\mathrm{Co(bpy)_3}]^{3+}$		0.28	
$[\mathrm{Co(tpy)_2}]^{3+}$		0.25[b]	
$[\mathrm{(tpy)Ru(tpy\text{-}ph\text{-}tpy)Co(tpy)}]^{5+}$	1.24[b]	0.25[b]	−0.99[b]
$[\mathrm{(tpy)Ru(tpy\text{-}tpy)Co(tpy)}]^{5+}$	1.26[b]	(0.25)[c]	−0.97[b]
$[\mathrm{Ru(bpy)_2(tpphz)}]^{2+}$	1.24		
$[\mathrm{Ru(bpy)_2(tpphz)Ru(bpy)_2}]^{4+}$	1.3		
$[\mathrm{Ru(bpy)_2(tpphz)Co(bpy)_2}]^{5+}$	1.3	(0.25)[c]	−1.02[b]

[a] Vs SCN in AN containing 0.1 M tetraethylammonium perchlorate. [b] Reference 17. [c] $E^{\mathrm{o}}(\mathrm{Co^{3+/2+}})$ is assumed to be either that of $[\mathrm{Co(bpy)_3}]^{3+}$ or $[\mathrm{Co(tpy)_2}]^{3+}$.

TABLE 3: Temperature Dependence of the Decay Rate Constant (k_1) of ^{3}CT(Ru), the Quantum Yield of ET Product Formation (Φ_{EET}) and the Rate Constants (k_{RET}) of the Recovery Processes of the Ground State Absorption of $[\mathrm{(tpy)Ru(tpy\text{-}ph\text{-}tpy)Co(tpy)}]^{5+}$ in BN

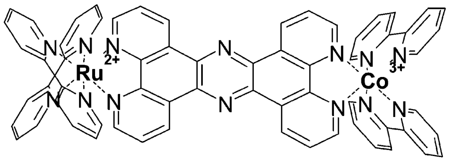
T/K	$\Delta G^{\circ}_{\mathrm{RET}}$/eV	k_1s/10^{12}[a]	Φ_{EET}	$k_{\mathrm{RET}}/10^{10}$ s^{-1} [a]
297	0.99	0.32	0.41	3.9
260	1.03	0.32	0.31	4.4
220	1.05	0.28	0.23	4.5
180	1.07	0.25	0.21	4.6

[a] Reference 17.

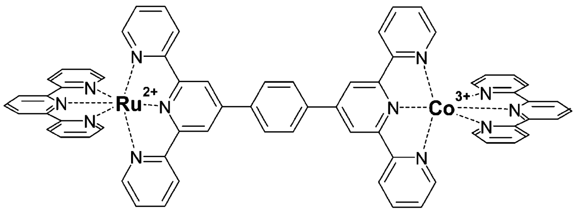
As for $[\mathrm{(tpy)Ru^{II}(tpy\text{-}tpy)Co^{III}(tpy)}]^{5+}$ in BN, the subpicosecond laser excitation produced a difference absorption spectrum characteristic of ^{3}MLCT, of which a broad band at 620 nm was monitored to decay with a rate constant of 1.0×10^{12} s^{-1}. The MLCT absorption band bleached was multiexponentially recovered in 100 ps. The rate constant of the slow recovery was 2.8×10^{10} s^{-1}. That of the intermediate recovery was determined to be 1.5×10^{11} s^{-1} on the basis of the fastest recovery rate (1.0×10^{12} s^{-1}) of MLCT band from ^{3}MLCT and the slow one (2.8×10^{10} s^{-1}) from EET product. The production of $[\mathrm{Ru(III){-}Co(II)}]^{5+}$ was determined from the absorbance-bleached MLCT band.

2. Formation Quantum Yield of the Electron-Transfer Product. The formation of the EET product was determined by extrapolating the recovery of the MLCT band from EET product. The formation of the excited state (4.5×10^{-5} M) of $[\mathrm{(tpy)Ru(tpy\text{-}ph\text{-}tpy)Co(tpy)}]^{5+}$ was evaluated by using eq 2 from the absorbances before and after the excitation ($\epsilon C_b d$ and $\epsilon C_a d$) and the integrated laser flux (0.90×10^{-7} mol/cm^2), the latter of which was obtained by using $[\mathrm{Ru(bpy)_3}]^{2+}$ (6.4×10^{-5} M) as a chemical actinometer. The quantum yields of $[\mathrm{(tpy)Ru^{III}(tpy\text{-}ph\text{-}tpy)Co^{II}(tpy)}]^{5+}$ were independent of the solvents, 0.39 in AN, 0.41 in BN, and 0.39 in PC. Lowering the temperature to 180 K reduced the yield to 0.21 in BN as is shown in Table 3.

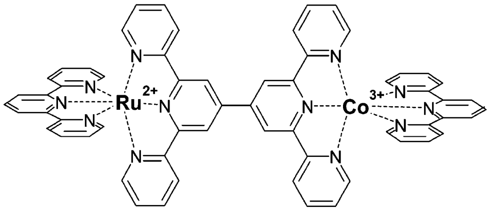
The quantum yield of $[\mathrm{(tpy)Ru^{III}(tpy\text{-}tpy)Co^{II}(tpy)}]^{5+}$ on the subpicosecond excitation was determined in a similar way. The



$[(bpy)_2\mathbf{Ru}^{II}(tpphz)\mathbf{Co}^{III}(bpy)_2]^{5+}$



$[(tpy)\mathbf{Ru}^{II}(tpy\text{-}ph\text{-}tpy)\mathbf{Co}^{III}(tpy)]^{5+}$



$[(tpy)\mathbf{Ru}^{II}(tpy\text{-}tpy)\mathbf{Co}^{III}(tpy)]^{5+}$

Figure 1. Molecular structures.

formation of the ^{3}CT (2.0×10^{-5} M) was evaluated from the absorbance of the reactant before and after the laser excitation at 400 nm, molar absorption coefficient (α) and the integrated laser flux (0.90×10^{-7} mo/lcm^2). The formation of $[(tpy)Ru^{III}(tpy\text{-}tpy)Co^{II}(tpy)]^{5+}$, 1.1×10^{-5} M, was determined by extrapolating the recovery of MLCT band from the EET product.. The quantum yield of $[(tpy)Ru^{III}(tpy\text{-}tpy)Co^{II}(tpy)]^{5+}$ was 0.65 in AN, 0.53 in BN, and 0.38 in PC.

The initial difference absorbance at 490 or 515 nm at the peak time of the laser pulse can be ascribed to a difference in the absorbance between the ground state and ^{3}MLCT(Ru). By employing the production of ^{3}MLCT determined above, one calculates the difference in the molar extinction coefficient, $\Delta\epsilon$, to be 17 100 M^{-1} cm^{-1} at 490 nm and 19 300 M^{-1} cm^{-1} at 515 nm for $[(tpy)Ru^{III}(tpy\text{-}ph\text{-}tpy)Co^{II}(tpy)]^{5+}$ and $[(tpy)Ru^{III}(tpy\text{-}tpy)Co^{II}(tpy)]^{5+}$, respectively.

$[(bpy)_2Ru^{II}(tpphz)Co^{III}(bpy)_2]^{5+}$. 1. Absorption Spectra and Redox Potentials. The peak potentials of differencial pulse voltamograms (DPV) vs Fc$^+$/Fc for $[Ru(bpy)_2(tpphz)]^{2+}$, $[Co(bpy)_2(tpphz)]^{3+}$, and $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$ were obtained at 298 K and are shown as the redox potential in Table 2. For the binuclear compounds, the peaks in the higher and the lower potential region of DPV correspond to $E°(Co^{3+/2+})$ and $E°(Ru^{3+/2+})$, respectively.

An absorption spectrum of $[Ru^{II}(bpy)_2(tpphz)]^{2+}$ consists of three bands, a broad MLCT band with the peak at 445 nm, a structured $\pi-\pi$ band of tpphz with two peaks at 380 and 360 nm and a sharp $\pi-\pi$ band of bpy coordinating to a divalent cation at 290 nm as is shown in Figure 2. $[Co(bpy)_2Cl_2]^+$ displays a structured $\pi-\pi$ band around 310 nm, which is characteristic of bpy coordinating to a trivalent cation. The absorption spectrum of $[Ru^{II}(bpy)_2(tpphz)Co^{III}(bpy)_2]^{5+}$ is nearly equal to the sum of those of the components mentioned above.

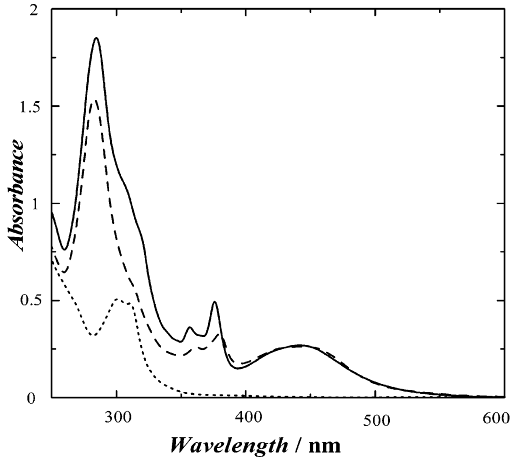


Figure 2. Absorption spectra of $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$ and its components in AN. Solid line: $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$. Dashed line: $[(bpy)_2Ru(tpphz)]^{2+}$. Dotted line: $[Co(bpy)_2Cl_2]^+$.

The coordination of tpphz to $[Co^{III}(bpy)_2]$ moiety enhances the molar absorption coefficients (ϵ) of the $\pi-\pi$ transition of tpphz at 350−400 nm compared with $[Ru(tpy)(tpphz)]^{2+}$.

2. Transient Absorption Change and Sequential Reaction. A N$_2$-bubbled AN solution of $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$ under the laser excitation displayed the bleaching of the MLCT band below 520 nm and the formation of a positive band with the maximum at 610 nm in the red and nearinfrared regions as Figure 3 shows. Each of the spectral changes was obtained as a difference absorption spectrum referred to the spectrum before the excitation. The transient difference spectrum observed immediately after the subpicosecond laser excitation of $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$ was similar to the primary excited-state (^{3}CT(Ru)) absorption spectrum of $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$, which was very rapidly converted to an absorption spectrum of differently solvated charge-transfer state in polar solvent.[24,25] A partial bleaching of the MLCT band and the formation of a broad band in a longer wave wavelength than 530 nm are characteristic of ^{3}CT(Ru) excited states, though the intensity and width of a broad band are sensitive to the polarity of solvents for $[(bpy)_2M(tpphz)M'(bpy)_2]^{4+}$ (M = Ru(II) and M′ = Ru(II) or Os(II)). In 2 ps, the initial difference absorbance of −0.08 at 450 nm became more negative (−0.175) at 450 nm and that of 0.04 at 600 nm was reduced to 0.02 at 600 nm, respectively, with a rate constant of 1.4×10^{12} s^{-1}. Moreover, the difference absorbance at 450 nm became slightly more negative (−0.185) in 20 ps with a rate constant of 1.3×10^{11} s^{-1}. The slight absorption change monitored at 450 nm may be somewhat of a relaxation process of molecular vibration, spin-multiplicity, or solvent reorganization that produces a stable form of the electron-transfer product. The reaction product exhibited an absorption spectrum similar to the sum of the absorption spectra of $[(bpy)_2Ru^{III}(tpphz)]^{3+}$ electronically prepared and $[Co^{II}(bpy)_2Cl_2]$, indicating that the reaction is the following

$$^3[(bpy)_2Ru^{II}(tpphz)Co^{III}(bpy)_2]^{5+} \rightarrow {}^3[(bpy)_2{}^2Ru^{III}(tpphz){}^2Co^{II}(bpy)_2]^{5+} \quad (8)$$

The recovery of the MLCT band of the original reactant took place with a rate constant of 2.1×10^7 s^{-1} at 298 K. The rate constant decreased as the temperature decreased down to 170 K as is shown in Figure 4.

3. Formation Yield of ET Product. The formation quantum yield of ET product, $[(bpy)_2Ru^{III}(tpphz)Co^{II}(bpy)_2]^{5+}$, on the nanosecond laser excitation was evaluated by plotting the left-

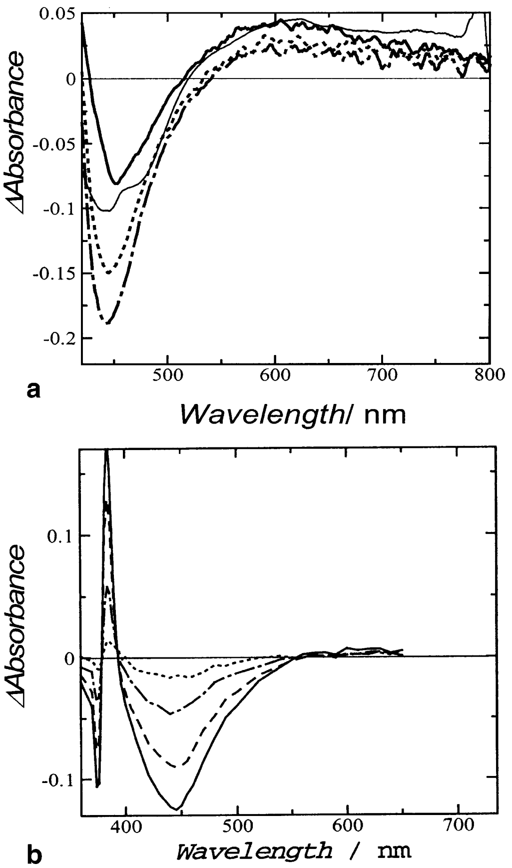


Figure 3. (a) Subpicosecond transient absorption spectra of $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$ at 0.25 (solid line), 1 (dot), and 10 ps (dash−dot−dash) and $[(bpy)_2Ru(tpphz)Ru(bpy)_2]^{4+}$ at 0.3 ps (fine solid line). (b) Difference absorption spectra of $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$ in AN on the nanosecond laser excitation. Solid line: at 20 ns. Dashed line: at 50 ns. Dash−dot−dashed line: at 100 ns. Dotted line: at 200 ns.

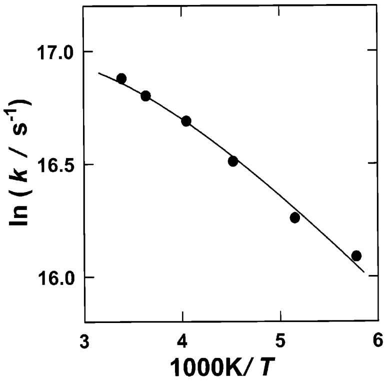


Figure 4. Temperature dependence of the recovery rate of $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$ in BN. A solid line is the least-squares fit to the equation,

$$\ln k_{\mathrm{RET}} = \ln \frac{2\pi H^2_{\mathrm{RET}}}{\hbar\sqrt{4\pi k_{\mathrm{B}} T\lambda}} - \frac{(\Delta H^\circ_{\mathrm{RET}} - T\Delta S^\circ_{\mathrm{RET}} + \lambda)^2}{4\lambda k_{\mathrm{B}} T},$$

$\Delta H^\circ_{\mathrm{RET}}$, $\Delta S^\circ_{\mathrm{RET}}$, H_{RET}, and λ are −1.4 eV, 1.3 meV/K, 0.51 meV, and 2.05 eV, respectively.

hand term of eq 2, $\ln(e^{\alpha_2 c_{2a} d} - 1)$, against $10^3\alpha_2 I$ as is shown in Figure 5. The integrated laser flux ($I = 4.77 \times 10^{-7}$ mol/cm^2) was obtained by inserting the unity formation-yield of ^{3}CT(Ru) of $[Ru(bpy)_3]^{2+}$ and the absorbances before and after the laser excitation into eq 2. The quantum yield of the long-living ET product, $[(bpy)_2Ru^{III}(tpphz)Co^{II}(bpy)_2]^{5+}$, is estimated to be 0.77.

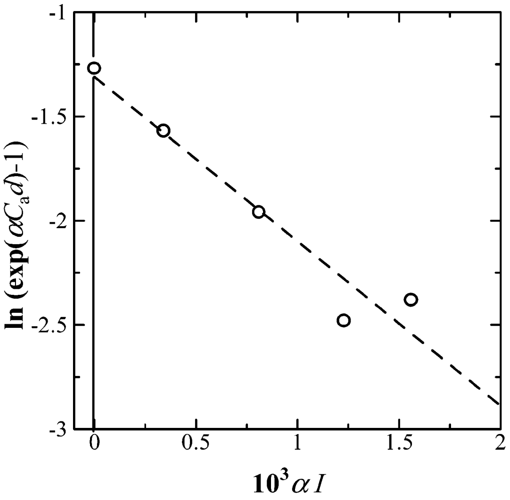


Figure 5. Plot of $\ln(\exp(\alpha d C_a) - 1)$, against $10^3\alpha I$ for a solution of $[(bpy)_2Ru^{I}(tpphz)Co^{III}(bpy)_2]^{5+}$.

The formation of ^{3}CT(Ru) of $[Ru(bpy)_2(tpphz)Co(bpy)_2]^{5+}$ on the subpicosecond laser excitation was also estimated by using eq 2. The integrated laser flux (0.9×10^{-7} mol/cm^2) was obtained by using $[Ru(bpy)_3]^{2+}$ as an actinometer. The product formation of $[(bpy)_2Ru^{III}(tpphz)Co^{II}(bpy)_2]^{5+}$, $C_b - C_a$, was determined from the difference absorbance at 450 nm and at 100 ps. The quantum yield of $[(bpy)_2Ru^{III}(tpphz)Co^{II}(bpy)_2]^{5+}$ formation in BN Φ_{EET} at 298 K was 0.84, which slightly decreased to 0.77 at 173 K.

Discussion

1. Formation and decay of $[Ru^{III}(bpy)_2(tpphz)Co^{II}(bpy)_2]^{5+}$. The primary difference absorption spectrum on the subpicosecond laser excitation of $[(bpy)_2Ru(tpphz)Co(bpy)_2]^{5+}$ is ascribed to the formation of ^{3}CT(Ru) by comparing the primary excited-state absorption of $[Ru(bpy)_2(tpphz)Ru(bpy)_2]^{4+}$.[24,25] The ^{3}MLCT(Ru) decayed with a rate constant of 1.4×10^{12} s^{-1} to produce the second transient species, which is assigned to the EET product, $^3[(bpy)_2{}^2Ru^{III}(tpphz){}^2Co^{II}(bpy)_2]^{5+}$, from the difference absorption spectrum. The absorption spectrum of the stable EET product, $[(bpy)_2{}^2Ru^{III}(tpphz){}^4Co^{II}(bpy)_2]^{5+}$, with a lifetime of 480 ns on the 532 nm nanosecond laser excitation was indifferent from the nascent EET product on the subpicosecond excitation. The quantum yield of the EET product, $[{}^2Ru^{III}(bpy)_2(tpphz){}^4Co^{II}(bpy)_2]^{5+}$, on the 4 ns laser excitation (0.77) is in agreement with that on the 400 nm subpicosecond laser excitation (0.84). The high yield is consistent with the reported quantum yields for intermolecular EET product of ^{4}Co(II) moiety.[4,26] High yields of geminate-radical pairs ($\Phi_{\mathrm{EET}} = 0.94{-}1.0$) were obtained in the intermolecular quenching of ^{3}MLCT(Ru) of $[Ru(bpy)_3]^{2+}$ by either $[Co(phen)_3]^{3+}$ or $[Co(bpy)_3]^{2+}$, where the high quantum yields were calculated from the yields of ET product formation in the bulk ($\Phi_{\mathrm{EET}}f_{\mathrm{CE}} = 0.93$) and the cage-escape fractions ($f_{\mathrm{CE}} = 0.99$).[4] A unity yield for the intramolecular redox reaction of $[(bpy)_2Ru(bpy\text{-}(CH_2)_2\text{-}bpy)Co(bpy)_2]^{5+}$ was also observed.[26]

The ^{3}MLCT(Ru) of $[Ru^{II}(bpy)_2(tpphz)Co^{III}(bpy)_2]^{5+}$ in BN undergoes EET with a much faster rate of 1.4×10^{12} s^{-1} than $[(bpy)_2Ru^{II}(tpphz)Os^{III}(bpy)_2]^{5+}$ with a rate of 0.13×10^{10} s^{-1}.[24,25] The nuclear factor κ_n for EET to the $[Co^{III}(bpy)_2]$ moiety is much larger than that for EET to the $[Os^{III}(bpy)_2]$ moiety, since the ergonicity of the former (−1 eV) is much favorable compared with the latter (−1.7 eV).

TABLE 4: Dielectric Constants and Longitudinal Relaxation Time of Solvents, Solvent Reorganization Energy of RET, and Decay Rate Constants (k_1) of ^{3}CT(Ru) and the Formation Yields (Φ_{EET}) of [(tpy)Ru^{III}(L−L)Co^{II}(tpy)]$^{5+}$ (L−L: tpy-ph-tpy and tpy-tpy) at 298 K

	L-L					
	tpy•tpy•tpy			tpy•tpy		
solvent	AN	BN	PC	AN	BN	PC
τ_l/ps^a	0.9	3.6	4.9	0.9	3.6	4.9
ϵ_s	36	24	65	36	24	65
ϵ_{op}	1.78	1.91	2.02	1.78	1.91	2.02
λ_o/eV^b	1.1	1.0	0.95	0.88	0.81	0.80
k_1/10^{10} s^{-1}	32	32	76	>200	100	190
Φ_{EET}	0.39	0.41	0.39	0.65	0.53	0.38

[a] Reference 27. [b] Calculated by using the two-sphere model and presuming the distances of electron transfer, 1.3 and 0.94 nm, for the tpy-ph-tpy compound and the tpy-tpy compound, respectively. λ_o values in acetonitrile are larger than the transition energy of the intervalence band by 0.1 e.[29]

TABLE 5: Temperature Dependence of the Decay Rate Constant (k_1) of ^{3}CT(Ru), the Quantum Yield of ET Product Formation (Φ_{ET}), and the Rate Constants (k_{RET}) of the Recovery Processes of the Ground State Absorption of [(bpy)$_2$Ru(tpphz)Co(bpy)$_2$]$^{5+}$ in BN

T/K	$-\Delta G^\circ_{RET}$/eV	k_1/10^{12} s^{-1}	Φ_{ET}	k_{RET}/10^9 s^{-1}
295	0.97	1.4	0.84	0.021
275	1.03		0.82	0.020
247	1.07		0.78	0.0175
221	1.13		0.78	0.014
194				0.011
173	1.17		0.75	0.0097

2. Quantum Yields of EET Products of [(tpy)Ru^{II}(L—L)-Co^{III}(tpy)]$^{5+}$ (L—L: tpy-ph-tpy and tpy-tpy). ^{3}MLCT(Ru) of [(tpy)Ru^{II}(L−L)Co^{III}(tpy)]$^{5+}$ (L−L:tpy-ph-tpy and tpy-tpy) underwent EET from the π* orbital of L−L to one of the dσ* orbitals of [Co^{III}(tpy)$_2$] moiety. The thermally relaxed products of the EET reaction, [(tpy)Ru^{III}(L−L)^{2}Co^{II}(tpy)]$^{5+}$, have lifetimes of 25 and 3 ps, respectively,[17] for which the production yields were determined from the absorbance-bleached MLCT band by means of transient photometry. The numbers of photon absorbed by the solute were determined by means of transient actinometry. The quantum yields of an electron-transfer reaction product, [(tpy)^{2}Ru^{III}(tpy-tpy)^{2}Co^{II}(tpy)]$^{5+}$, 0.65 in AN, 0.53 in BN, and 0.40 in PC look to be in correlation with not the dielectric constants of solvents (ϵ = 36, 24, and 65 for AN, BN, and PN, respectively) but the dielectric relaxation times of solvent (τ_l = 0.38, 2, and 10 ps, for AN, BN, and PN, respectively) as is shown in Table 4. The transition of the nonrelaxed EET product to the original reactant is suggested to occur during the solvent relaxation. The product yield of [(tpy)-Ru^{III}(tpy-ph-tpy)Co^{II}(tpy)]$^{5+}$ decreased from 0.41 at 300 K to 0.21 at 180 K, while it was independent of the solvents. Not only the figures but also the temperature dependence of the quantum yields of [(tpy)^{2}Ru^{III}(L−L)^{2}Co^{II}(tpy)]$^{5+}$ (L−L:tpy-ph-tpy and tpy-tpy) are in contrast to those of [L$_2$Ru^{III}(L−L)-CoL$_2$]$^{5+}$ (L−L: tpphz, and bpy-(CH$_2$)$_2$-bpy[26]). Nonunity yields of geminate-radical pairs of Ru^{3+}−Co^{2+} (Φ = 0.60−0.80) were only observed in the intermolecular quenching of ^{3}MLCT(Ru) of [RuL$_3$]$^{2+}$ (L = 2,2′-bipyridine-4,4′-dicarboxylato or bpy) by [Co(tpy)$_2$]$^{3+}$.[4]

It should be noticed that the low quantum yields were met in the EET quenching of ^{3}MLCT(Ru) by [Co^{III}(tpy)$_2$] moiety. Several different features of Co(tpy)$_2$$^{3+/2+}$ from those of Co(bpy)$_3$$^{3+/2+}$ might be related to the low yields of EET product formation. (1) Co(tpy)$_2$$^{3+/2+}$ has a distorted square-bipyramidal structure with a weak ligand field on average and splitting of dπ and dσ*, while Co(bpy)$_3$$^{2+}$ has an octahedral structure. (2) The lowest state of Co(tpy)$_2$$^{2+}$ has a doublet configuration of dπ^6dσ*, while Co(bpy)$_3$$^{2+}$ a quartet d-electron configuration of dπ^5dσ^{*2}. (3) The reorganization energy of ET is 0.28 eV for [Co(tpy)$_2$]$^{3+/2+}$ and 0.9 eV for [Co(bpy)$_3$]$^{3+/2+}$, respectively.[17]

3. Gibbs Free Energy Surfaces of the Excited State and the Ground State of Reactant and EET Product. The ^{3}MLCT of [(tpy)Ru^{II}(tpy-tpy)Co^{III}(tpy)]$^{5+}$ was subjected to rapid intramolecular quenching in 1 ps, followed by frequency changes of the molecular vibration modes and the solvation modes and displacement of atoms in the product and of surrounding solvent molecules in a couple of picoseconds. The intermolecular flow of thermal energy achieves the entropy change of EET product. The vertical energy gap of EET, $\Delta G^\circ_{EET} + \lambda_{EET}$, between ^{3}MLCT and EET product before the nonvertical reorganization is slightly positive on the basis of ΔG°_{EET} (−1.0 eV), intramolecular reorganization energy around the ruthenium (0.2 eV) and the cobalt (0.28 eV[17]), and solvent reorganization (0.72 eV). Then, the Gibbs free energy surface of ^{3}MLCT at 298 K has an intersection with that of EET product, [(tpy)Ru^{III}(tpy-tpy)^{2}Co^{II}-(tpy)]$^{5+}$, around the bottom of the surfaces along with both of the intramolecular coordinate and solvent coordinate, as shown in Figure 6. In Figure 6, a Gibbs free energy surface of the EET product, [^{2}Ru^{III}−^{2}Co^{II}]$^{5+}$, is shown in black dash−dot−dash line as a function of one coordinate with the other coordinate fixed and a Gibbs energy surface of the EET product fully relaxed is shown in gray dash−dot−dash line. The solvent reorganization energy was estimated on the basis of the two-sphere model[27] with a shorter electron-transfer distance of 0.84 nm than the metal−metal distance by 0.3 nm because of the far location of the excited electron from the Ru(III) of ^{3}CT-(Ru) state. As for [(tpy)Ru^{II}(tpy-ph-tpy)Co^{III}(tpy)]$^{5+}$, the Gibbs free energy surface of ^{3}MLCT has an intersection with the displaced free energy surface of EET product because of the larger solvent reorganization energy (0.85 eV) than that of [(tpy)Ru^{II}(tpy-tpy)Co^{III}(tpy)]$^{5+}$.

Nascent EET products of [(tpy)^{2}Ru^{III}(L−L)^{2}Co^{II}(tpy)]$^{5+}$ just formed in the quenching of ^{3}MLCT have a chance of transition to the reactant not only at the ground state but also at the excited states lying intermediately between ^{3}MLCT(Ru) and the ground state during the thermal relaxation, where the nitrogen atoms of pyridyl groups coordinating to Co(II) get far from the cobalt, from 196[30] to 202 pm[31] on the average. The Gibbs free energy surface of relaxed EET product is horizontally and vertically displayed with a reorganization energy of 0.28 eV along with the intramolecular coordinate and of 0.81 eV along with the solvent coordinate referring to the ground state of reactant (open circles in Figure 7).[16,17,22] The Gibbs free energy surface of the EET product with a relaxed solvation has an intersection with that of reactant around the bottom as is shown in Figure 7, because the Gibbs free energy change (−1.0 eV) is close to the net reorganization energy (1.1 eV). The lowest energy surface in gray is drawn for the reactant fully relaxed.

As for [(bpy)$_2$Ru^{II}(tpphz)Co^{III}(bpy)$_2$]$^{5+}$, the Gibbs free energy surface of EET product is horizontally and vertically displaced along with both the solvent coordinate and the intramolecular coordinate as referring to that of reactant as shown in Figure 8. After a transition to the Gibbs free energy surface of reactant, the nitrogen atoms of pyridyl groups get closer to the cobalt during its oxidation from 213 pm[32] to 193 pm[33] and the surrounding solvent molecules are reorganized to the inverted electric dipole of Ru^{2+}−Co^{3+} to accomplish the entropy change of 1.3 meV/K. The reorganization energy of RET with an

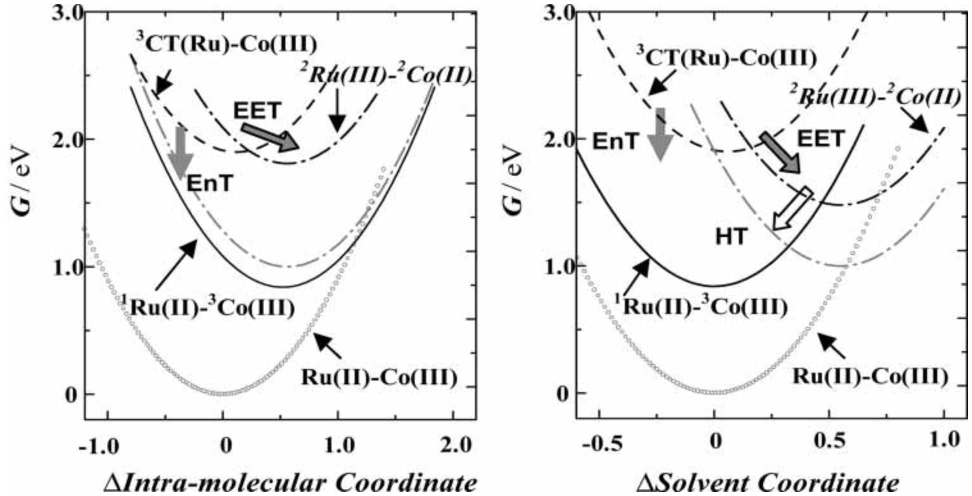


Figure 6. Schematic Gibbs free energy surfaces of ^{3}CT(Ru), EET product and excitation energy-transfer product of the triplet (d−d) state of $[(tpy)Ru^{II}(tpy\text{-}tpy)Co^{III}(bpy)]^{5+}$. A Gibbs free energy surface of EET product is vertically relaxed to the surface of fully relaxed product (gray line) within a couple of picoseconds. Transitions EET, EnT, and HT are shown as gray, fine gray, and white arrows, respectively.

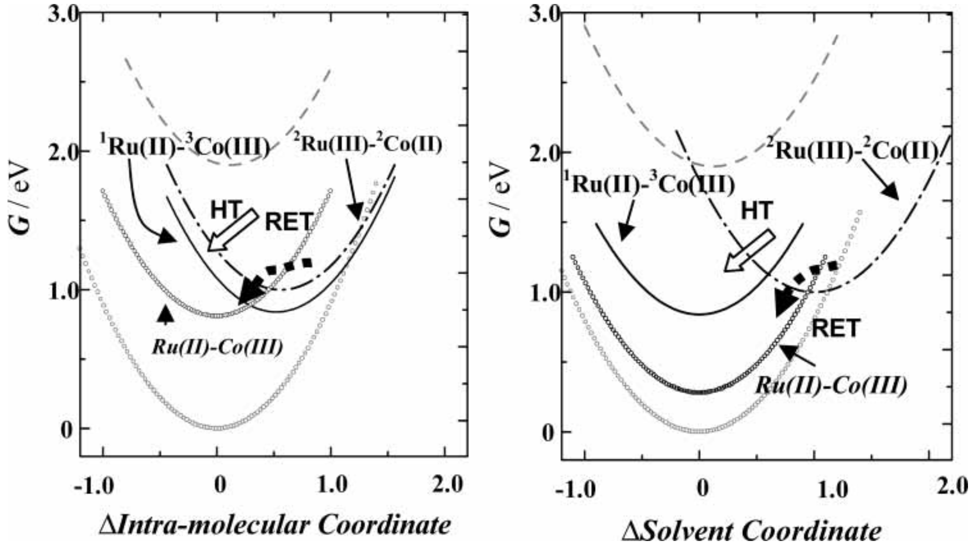


Figure 7. Schematic Gibbs free energy surfaces of EET product ($[(tpy)^2Ru^{III}(tpy\text{-}tpy)^2Co^{II}(tpy)]^{5+}$) thermally relaxed, triplet excited hole-transfer product ($[(tpy)Ru^{II}(tpy\text{-}tpy)^3Co^{III}(tpy)]^{5+}$) with electronic configurations of $^1(d\pi^6)$ for Ru(II) and $^3(d\pi^5 d\sigma^*)$ of Co(III) and RET product. The Gibbs free energy surface of the RET product is vertically relaxed to that of fully relaxed product (gray line) within a couple of picoseconds. Transitions are shown as in Figure 6.

electron-transfer distance of 1.1 nm in BN is 0.92 eV along with the solvent coordinate and 0.9 eV along with the intramolecular coordinate, respectively.

There are triplet d−d excited-states of $[Co^{III}(tpy)_2]$ moiety below ^{3}MLCT(Ru). An optical transition to the lowest triplet d−d excited state of $[Co^{III}(tpy)_2]$ with a configuration of $d\pi^5 d\sigma^*$ is expected to emerge at lower energy than the corresponding one of $[Co(bpy)_3]^{3+}$ (1.8 eV[34]), because the equatorial ligand field of $[Co(tpy)_2]^{3+}$ is much weaker than that of $[Co(bpy)_3]^{3+}$. The peak energy of the lowest d−d singlet−triplet band of $[Co(tpy)_2]^{3+}$ is inferred to be lower (1.35 eV) than the singlet−triplet absorption-band peak observed of $[Co(bpy)_3]^{3+}$ on the basis of the difference (0.7 eV) in the energy of the lowest triplet d−d excited state between $[Ru(tpy)_2]^{2+}$ and $[Ru(bpy)_3]^{2+}$, which was estimated to be 2.1 and 2.8 eV, respectively, from the temperature dependence of radiation-less transition rate of ^{3}CT(Ru).[35,36] The peak energy of the triplet excited d−d transition of $[Co(tpy)_2]^{3+}$ is shifted from the 0−0 energy by the Franck−Condon energy of optical transition, which is estimated to be 0.75 eV from the Stokes shift (1.5 eV = 3.2 eV (the absorption peak) − 1.7 eV (the phosphorescence)) in the case of $[Co(CN)_6]^{3-}$.[37] Since the weaker ligand-field of $[Co(tpy)_2]^{3+}$ than $[Co(CN)_6]^{3-}$ is assumed to reduce the Franck−Condon energy of the optical singlet−triplet d−d transition to 0.4 eV, the enthalpy of the formation of lowest triplet state is close to 1 eV. The Gibbs free energy change of the formation of $^3[Co^{III}(tpy)_2]$, $\Delta G^\circ_{3_{(d-d)}}$, is estimated to be ≈ 0.82 eV, because the entropy change, $\Delta S_{3_{(d-d)}}$, of $^3[Co^{III}(tpy)_2]$ with highly dense vibrational states is as large as the entropy change of $^2[Co^{II}(tpy)_2]$ formation (0.6 meV/K[22])) with a similar configuration of $d\pi^6 d\sigma^*$. The Gibbs free energy surface of $^3(d\pi^5 d\sigma^*)$ has a similar displacement to that of the EET product along with the intramolecular coordinate, while Franck−Condon energy of optical transition (0.4 eV) is similar to the reorganization energy of RET.

It is noteworthy that the triplet d−d excited states of $[Co^{III}(tpy)_2]$ moiety are considerably displaced from the EET products along with the solvent coordinate as is shown in Figures 6 and 7. The transition to $^3(d\pi^5 d\sigma^*)$ occurs as a HT from $^2[Ru^{III}(tpy)_2]$ with an electronic configuration of $d\pi^5$ to $^2[Co^{II}(tpy)_2]$ with an electronic configuration of $d\pi^6 d\sigma^*$. The solvent reorganization

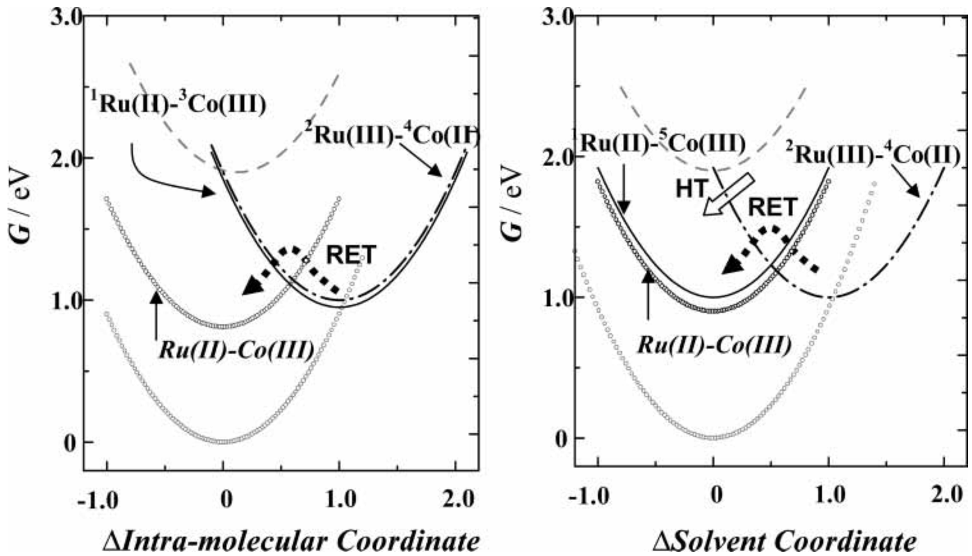


Figure 8. Schematic Gibbs free energy surface of ^{3}CT(Ru), EET product of $[(\mathrm{bpy})_2{}^2\mathrm{Ru^{II}}(\mathrm{tpphz})^4\mathrm{Co^{II}}(\mathrm{bpy})_2]^{5+}$, excitation energy-transfer product of triplet (d−d) state with electronic configurations of $^1(\mathrm{d}\pi^6)$ for Ru(II) and $^5(\mathrm{d}\pi^4\mathrm{d}\sigma^{*2})$ of Co(III), and RET product. The Gibbs free energy surface of the RET product is vertically relaxed to that fully relaxed (gray line). Transitions are shown as in Figure 6.

energy of the HT between the EET product and $^3(\mathrm{d}\pi^5\mathrm{d}\sigma^*)$ is the same as the RET (0.9−1.0 eV) as is shown in Figure 7. The solvents may vary both the reorganization energy of HT and the rate of solvent relaxation, which considerably affect the transition rate of EET product to $^3(\mathrm{d}\pi^5\mathrm{d}\sigma^*)$.

In the case of $[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{tpphz})\mathrm{Co}(\mathrm{bpy})_2]^{5+}$, the Gibbs free energy change of lowest d−d triplet excited state formations of $^3[\mathrm{Co^{III}}(\mathrm{bpy})_2]$ moiety is inferred to be 1.0 eV by taking into account the absorption peak of optical transition to triplet d−d excited-state (1.8 eV), the entropy change of 1.3 meV/K, and the Franck−Condon energy (0.4−0.5 eV). A HT from $^2[\mathrm{Ru^{III}}(\mathrm{bpy})_2]$ to $^4[\mathrm{Co^{II}}(\mathrm{bpy})_2]$ produces the quintet d−d excited state with an electronic configuration of $^5(\mathrm{d}\pi^4\mathrm{d}\sigma^{*2})$, whose energy level may be close to the lowest triplet state. The Gibbs free energy surface of the quintet lowest excited state is largely displaced from the EET product along with the solvent coordinate as shown in Figure 8.

A quantum chemical calculation of the energies of ^{3}MLCT, EET product, and ^{3,5}(d−d) of the $[\mathrm{Co^{III}L_2}]$ moiety and the tunneling transition among them is in progress to give insight into the phosphorescence quenching, RET, and HT in the case of $[(\mathrm{tpy})\mathrm{Ru^{III}}(\mathrm{tpy\text{-}tpy})\mathrm{Co^{II}}(\mathrm{tpy})]^{5+}$, and $[(\mathrm{bpy})_2\mathrm{Ru}(\mathrm{tpphz})\mathrm{Co}(\mathrm{bpy})_2]^{5+}$.

4. RET of the EET Product To Form the Ground State of $[\mathrm{Ru^{II}(L{-}L)Co^{III}}]$. The EET products are thermally relaxed to the bottom of the Gibbs free energy surface within a couple of picoseconds to accomplish the entropy change. The recovery of the ground-state-absorption of $[\mathrm{Ru^{II}}(\mathrm{bpy})_2(\mathrm{tpphz})\mathrm{Co^{III}}(\mathrm{bpy})_2]^{5+}$ occurred with a rate constant of $2.1 \times 10^7\ \mathrm{s^{-1}}$ at 298 K as follows, $[\mathrm{Ru^{III}}(\mathrm{bpy})_2(\mathrm{tpphz})^4\mathrm{Co^{II}}(\mathrm{bpy})_2]^{5+} \rightarrow [\mathrm{Ru^{II}}(\mathrm{bpy})_2(\mathrm{tpphz})\mathrm{Co^{III}}(\mathrm{bpy})_2]^{5+}$. The slow recovery of $[\mathrm{Ru^{II}}(\mathrm{bpy})_2(\mathrm{tpphz})\mathrm{Co^{III}}(\mathrm{bpy})_2]^{5+}$ is written using an effective frequency, ν_n, a nuclear coefficient, χ_n, and an electronic transmission coefficient, χ_{el},

$$k_{\mathrm{RET}}(T) = \nu_n\chi_n\chi_{\mathrm{el}} = \frac{2\pi}{\hbar}\frac{H_{\mathrm{RET}}{}^2}{\sqrt{4\pi k_B T\lambda_{\mathrm{RET}}}}\exp\left[-\frac{(\Delta G^\circ_{\mathrm{RET}}+\lambda_{\mathrm{RET}})^2}{2\lambda_{\mathrm{RET}}k_B T}\right] \quad (9)$$

the second of which is expressed in terms of vertical energy difference, $\Delta G^\circ_{\mathrm{RET}} + \lambda_{\mathrm{RET}}$, of electron-transfer process in the Marcus normal region. Provided that the product of rate-controlled process is the reactant at the ground-state, the ergonicity $\Delta G^\circ_{\mathrm{RET}}$ is −0.97 eV and the reorganization energy λ_{RET} is the difference in the Gibbs free energy of $[\mathrm{Ru^{II}}(\mathrm{tpphz})\mathrm{Co^{III}}]^{5+}$ between the minimum energy point and the point corresponding to the minimum energy of $[\mathrm{Ru^{III}}(\mathrm{tpphz})\mathrm{Co^{II}}]^{5+}$. The less negative values of $\Delta G^\circ_{\mathrm{RET}}$ at high temperatures due to negative entropy change ($\Delta S^\circ_{\mathrm{RET}} = -1.3$ meV) of the RET process attenuates the temperature effect on the RET rate, reducing the apparent energy of activation (0.028 eV). By means of simulation, the optimized value of λ_{RET} (2.05 eV) and H_{RET} (0.51 mV) were obtained by assuming the same magnitude of $\Delta S^\circ_{\mathrm{RET}}$ as that ($\Delta S^\circ_{\mathrm{RET}} = -1.3\ \mathrm{meV\ K^{-1}}$) of the redox pair, $[\mathrm{Ru}(\mathrm{bpy})_2(2,6\text{-bis}(2\text{-pyridyl})\mathrm{benzodiimidazole})\mathrm{Co}(\mathrm{bpy})_2]^{5+}$.[22] The large value of λ_{RET} can be the sum of the reorganization energies of the products and the surrounding solvent in the RET. Since the solvent reorganization energy in BN is estimated to be 0.91 eV by using two-sphere model with a donor−acceptor distance of 1.1 nm, the rest of the reorganization energy (1.14 eV) is assigned as the Gibbs energy difference of $[\mathrm{Ru^{II}}(\mathrm{tpphz})\mathrm{Co^{III}}]^{5+}$ between the minimum energy point ($r_{\mathrm{Co}}{}^{\mathrm{III}} - N = 0.193$ pm) and the point ($r_{\mathrm{Co}}{}^{\mathrm{II}} - N = 0.213$ pm) corresponding to the minimum energy of $[\mathrm{Ru^{III}}(\mathrm{tpphz})\mathrm{Co^{II}}]^{5+}$. The intramolecular reorganization energy for the oxidation of $\mathrm{Co^{II}}$ is in agreement with the quantum chemically calculated one (0.87−0.90 eV) for $[\mathrm{Co}(\mathrm{bpy})_3]^{3+/2+}$ using a density functional theory (DFT).[17]

It is instructive to compare the RET rate of $[^2\mathrm{Ru^{III}}(\mathrm{tpphz})^4\mathrm{Co^{II}}]^{5+}$ with $[^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^2\mathrm{Co^{II}}]^{5+}$ and $[^2\mathrm{Ru^{III}}(\mathrm{tpphz})^1\mathrm{Os^{II}}]^{5+}$. The small magnitude of the nuclear factor (4.6×10^{-3}) is ascribed to the large intramolecular reorganization energy (1.1 eV) compared with $[(\mathrm{tpy})^2\mathrm{Ru^{III}}(\mathrm{tpy\text{-}ph\text{-}tpy})^2\mathrm{Co^{II}}(\mathrm{tpy})]^{5+}$ (0.28 eV). If the lifetime of $^2[\mathrm{Co^{II}}(\mathrm{bpy})_2]$ moiety were long enough, the RET of the doublet cobalt(II) moiety in $[(\mathrm{bpy})_2\mathrm{Ru^{III}}(\mathrm{tpphz})^2\mathrm{Co^{II}}(\mathrm{bpy})_2]^{5+}$ could occur with a rate of $4.6 \times 10^9\ \mathrm{s^{-1}}$, which is calculated by assuming the same electronic coupling strength (0.51 meV) as that of $[(\mathrm{bpy})_2\mathrm{Ru^{III}}(\mathrm{tpphz})^4\mathrm{Co^{II}}(\mathrm{bpy})_2]^{5+}$ and the zero intramolecular reorganization energy. The extent of the electronic coupling (0.51 meV) for RET of $[^2\mathrm{Ru^{III}}(\mathrm{tpphz})^4\mathrm{Co^{II}}]^{5+}$ is not so small compared with $[^2\mathrm{Ru^{III}}(\mathrm{tpphz})^1\mathrm{Os^{II}}]^{5+}$ (1.6 meV),[24] while through-ligand superexchange coupling between $\mathrm{d}_\pi(\mathrm{Ru^{III}})$ and $\mathrm{d}_\sigma{}^*(\mathrm{Co^{II}})$ is thought to be much smaller than $\mathrm{d}_\pi(\mathrm{Ru^{III}})-\mathrm{d}_\pi(\mathrm{Os^{II}})$.

The relaxed EET products of $[(\text{tpy})\text{Ru}^{\text{III}}(\text{tpy-tpy})\text{Co}^{\text{II}}(\text{tpy})]^{5+}$ and $[(\text{tpy})\text{Ru}^{\text{III}}(\text{tpy-ph-tpy})\text{Co}^{\text{II}}(\text{tpy})]^{5+}$ disappear to recover the reactant at the ground state with $3.2 \times 10^{11}\text{s}^{-1}$ and 4×10^{10} s^{-1}, respectively, at 298 K.[17] The absence of temperature dependence of the recovery rate demonstrates that the relaxed product carries out a transition to either the ground or the excited state of the original reactant near to the bottom of free energy surface. The slow rate constant, $10^{10}-10^{11}$ s^{-1}, of an activationless process suggests a low transmission coefficient of the intersurface transition. Provided that the final state of RET is the reactant at the ground state, the magnitudes of H_{RET}s are evaluated to be 1.9 and 4.6 meV, respectively, from the temperature dependence of the recovery rate of the original reactant, $\Delta G^{\circ}_{\text{RET}}$ ($-$ 0.99 eV)and λ_{RET} (1.1 eV for the tpy-ph-tpy compound and 1.0 eV for the tpy-tpy compound). The difference in the rate constants ($3.2 \times 10^{11}\text{s}^{-1}$, 3.9×10^{10} s^{-1}, and $4.6 \times 10^{9}\text{s}^{-1}$) among $[^2\text{Ru}(\text{L}-\text{L})^2\text{Co}]^{5+}$ (L$-$L: tpy-tpy, tpy-ph-tpy and tpphz) originates from those in the square of $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}}) - \text{d}_{(x^2-y^2)}(\text{Co}^{\text{II}})$ coupling (4.6, 1.9, and 0.51 meV). The electronic coupling between $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}})$ and $\text{d}_{(x^2-y^2)}(\text{Co}^{\text{II}})$ is thought to be smaller than $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}})-\text{d}_{yz(xy)}(\text{Co}^{\text{II}})$ coupling, because $\text{d}_{(x^2-y^2)}(\text{Co}^{\text{II}})$ are unable to overlap with $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}})$ via delocalized π-orbitals of the bridging ligand without any vibronic coupling. Actually, the extents of electronic coupling between $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}})$ and $\text{d}_{yz(xy)}(\text{Ru}^{\text{II}})$ in $[(\text{tpy})\text{Ru}^{\text{II}}(\text{L}-\text{L})\text{Ru}^{\text{III}}(\text{tpy})]^{5+}$ or $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}})$ and $\text{d}_{yz(xy)}(\text{Os}^{\text{II}})$ in $[(\text{bpy})_2\text{Ru}^{\text{III}}(\text{L}-\text{L})\text{Os}^{\text{II}}(\text{bpy})_2]^{5+}$ were evaluated to be 47 meV[37] for the tpy-tpy compound, 30 meV[37] for the tpy-ph-tpy compound, and 1.6 meV[23] for the tpphz compound, respectively. The involving of $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}})-\text{d}_{yz(xy)}(\text{Co}^{\text{II}})$ coupling in $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}})-\text{d}_{(x^2-y^2)}(\text{Co}^{\text{II}})$ coupling via vibronic coupling might enhances the rate of RET. The extents of $\text{d}_{yz(xy)}(\text{Ru}^{\text{III}})-\text{d}_{(x^2-y^2)}(\text{Co}^{\text{II}})$ coupling (4.6, 1.9, and 0.51 meV) are too small for the RET of nonrelaxed EET product to compete with thermal relaxation.

5. Hole-Transfer of $^2\text{Ru}^{\text{III}}(\text{L—L})^2\text{Co}^{\text{II}}$ To Form Excited States of $[^1\text{Ru}^{\text{II}}(\text{L—L})^3\text{Co}^{\text{III}}]$. Another possible process for the reactant recovery consists of the formation of a triplet d$-$d excited state $^3(\text{d}\pi^5\text{d}\sigma^*)$ of the Co(III) moiety followed by a rapid radiationless transition of the triplet excited state. The transition to the triplet state, $^3(\text{d}\pi^5\text{d}\sigma^*)$, occurs as a HT between ^{2}Ru(III) with $\text{d}\pi^5$ and ^{2}Co(II) with $\text{d}\pi^6\text{d}\sigma^*$. By employing $\Delta G^{\circ}_{\text{HT}}$ of -0.15 eV and $\lambda_{\text{HT,s}}$ of $+0.82$ eV for $[(\text{tpy})\text{Ru}(\text{tpy-tpy})\text{Co}(\text{tpy})]^{5+}$, the extent of H_{HT} is estimated to be large (57 meV) from the recovery rate of the relaxed product at 298 K. The activation-less recovery from the relaxed product is inconsistent with the activation energy of HT (0.16 eV) calculated on the based of eq 9, $\Delta G^{\circ}_{\text{HT}}$ of -0.15 eV, and $\lambda_{\text{HT,s}}$ of 1 eV. Since a more negative value of $\Delta G^{\circ}_{\text{HT}}$ only allows the activationless transition, the HT is able to develop from the nonrelaxed product of EET.

The thermal relaxation of the nascent EET product is controlled by the rates of solvent relaxation, intramolecular vibration redistribution IVR, and intermolecular energy transfer IET between a solute molecule and surrounding solvent molecules. Since most of solvents are relaxed in not a single-exponential mode but multiexponential one,[39] the effective relaxation time of viscous solvent for the formation of a charged solute is longer than the average one depending on the coupling between the modes of intramolecular vibration and solvation. Time-resolved spectroscopy of electronic transition[10b,38] and anti-Stokes resonance Raman[10a,12] revealed that the thermal relaxation of vibrationally excited molecule in the condensed phase occur in a shorter time than a couple of picoseconds. Thermal energy released during the relaxation is redistributed into the low-frequency vibrations of the product molecule and of the surrounding solvent to accomplish the entropy change. Consequently, nonequilibrium free energy of the reorganization[41] consists of entropic term, too. The nonrelaxed EET product in PC with a long relaxation time conceivably has many chances of intersurface tunneling with that of $^3(\text{d}\pi^5\text{d}\sigma^*)$ of the $[\text{Co}^{\text{III}}(\text{tpy})_2]$ moiety. The temperature dependence of Φ_{EET} in BN is understood in terms of longer relaxation time at lower temperatures.

Intramolecular HT needs the large strength of electronic coupling between Ru(III) and Co(II). Both $\text{d}\pi-\text{d}\pi$ interaction of $\text{d}_{yz}(\text{Ru}^{\text{III}})-\text{d}_{yz}(\text{Co}^{\text{II}})$ and $\text{d}_{xy}(\text{Ru}^{\text{III}})-\text{d}_{xy}(\text{Co}^{\text{II}})$ are thought to be strong enough to cause the HT of the EET product, $[^2\text{Ru}^{\text{III}}(\text{d}\pi^5)-{}^2\text{Co}^{\text{II}}(\text{d}\pi^6\text{d}\sigma^*)]^{5+}$, due to a superexchange interaction via the p_y electrons of bridging ligand of tpy-tpy and tpy-ph-tpy. The strong $\text{d}\pi-\text{d}\pi$ interaction can be seen in the intensity of the MMCT transition. The intensive MMCT bands between Ru(II) and Ru(III) in $[(\text{tpy})\text{Ru}^{\text{II}}(\text{L}-\text{L})\text{Ru}^{\text{III}}(\text{tpy})]^{5+}$ ($H_{\text{II}-\text{III}} = 30$ meV for tpy-ph-tpy and 47 meV for tpy-tpy)[37] demonstrate the $\text{d}\pi-\text{d}\pi$ interaction is intermediate. Though the replacement of $^1\text{Ru}^{\text{II}}$ by $^2\text{Co}^{\text{II}}$ might reduce $\text{d}\pi-\text{d}\pi$ interaction to some extent, a HT from $^2\text{Ru}^{\text{III}}$ to $^2\text{Co}^{\text{II}}$ forming the triplet d$-$d excited states of $[\text{Co}^{\text{III}}(\text{tpy})_2]$ moiety with an electronic configuration of $\text{d}\pi^5\text{d}\sigma^*$ much more efficiently occurs via strong $\text{d}\pi-\text{d}\pi$ interaction than RET of $[(\text{tpy})\text{Ru}^{\text{III}}(\text{tpy-tpy})\text{Co}^{\text{II}}(\text{tpy})]^{5+}$ via weak $\text{d}\pi-\text{d}\sigma^*$ interaction. The triplet d$-$d excited state of the $[\text{Co}^{\text{III}}(\text{tpy})_2]$ moiety, $^3(\text{d}\pi^5\text{d}\sigma^*)$, might decay via nonradiative transition immediately after the formation of the triplet d$-$d excited state.

Intersurface tunneling transition between adiabatic states depends on the intersecting angle between adiabatic states and strength of electronic coupling between diabatic states as well as thermal relaxation rate. According to Nakamura and Zhu,[7,8] the probability of tunneling transition between adiabatic states increases as the thermal energy of the product increases. Moreover, the greater coupling between the energy surfaces in a strong coupling region makes the energy surfaces more distant and the intersurface tunneling difficult where the energy surfaces intersect with the same sign of slopes (Landau$-$Zener crossing),[7,8] while the more coupling between the energy surfaces in a weak coupling region increases the tunneling rate. Such a strong $\text{d}\pi-\text{d}\pi$ interaction in $[(\text{tpy})\text{Ru}^{\text{III}}(\text{tpy-tpy})\text{Co}^{\text{II}}(\text{tpy})]^{5+}$ could make the adiabatic energy surface more distant from that of ^{3}(d$-$d) (Co(III)) to prevent the tunneling transition. This effect on the fraction of tunneling transition might account for the higher yield of $[(\text{tpy})\text{Ru}^{\text{III}}(\text{tpy-tpy})\text{Co}^{\text{II}}(\text{tpy})]^{5+}$ than $[(\text{tpy})\text{Ru}^{\text{III}}(\text{tpy-ph-tpy})\text{Co}^{\text{II}}(\text{tpy})]^{5+}$.

In the case of $[(\text{bpy})_2\text{Ru}^{\text{III}}(\text{tpphz})\text{Co}^{\text{II}}(\text{bpy})_2]^{5+}$, a transition to the reactant at the ground state is retarded by the large intramolecular reorganization energy (0.9 eV) of ET in addition to the solvent reorganization energy (0.92 eV) as is shown in Figure 8. The nascent doublet state of EET product is able to undergo HT before the thermal relaxation, only if superexchange interaction of $\text{d}\pi-\text{d}\pi$ between Ru^{III} and Co^{II} is strong enough. The extent of $\text{d}\pi-\text{d}\pi$ interaction between Ru^{III} and Os^{II} was estimated to be as small (1.6 meV) for $[\text{Ru}^{\text{III}}(\text{tpphz})\text{Os}^{\text{II}}]^{5+}$ from the rate of RET based on eq 9. The absence of an intervalence optical transition of $[\text{Ru}^{\text{III}}(\text{tpphz})\text{Ru}^{\text{II}}]^{5+}$ [24] indicates that the $\text{d}\pi-\text{d}\pi$ coupling between Ru^{III} and Ru^{II} via tpphz is much smaller. It turns out that weak $\text{d}\pi-\text{d}\pi$ superexchange interaction through tpphz between Ru^{III} and Co^{II} may be unable to open the channel of HT during the thermal relaxation of nonrelaxed EET product reducing the quantum yield of EET product in the case of $[(\text{bpy})_2\text{Ru}(\text{tpphz})\text{Co}(\text{bpy})_2]^{5+}$.

6. Competing Process with Electron Transfer. Provided that the excitation energy transfer (EnT) of ^{3}MLCT(Ru) occurs in competition with EET, the yield of EET product is reduced. Yields Smaller than 0.5 were given for the formation of $[(dmb)_2Ru^{III}(L\text{-}(CH_2)_n\text{-}L)Os^{II}(bpy)_2]^{5+}$ (dmb, 4,7-dimethyl-2,2′-bipyridine; L, 2-(2-pyridyl)-1-benzimidazolyl; $n = 3, 4, 5$) in the intramolecular phosphorescence quenching of $[(dmb)_2Ru^{II}\text{-}(L\text{-}(CH_2)_n\text{-}L)Os^{III}(bpy)_2]^{5+}$,[13b] where the energy accepting level of $[Os^{III}(bpy)_2]$ moiety was the triplet ligand-to-metal charge transfer state. Excitation energy transfer of ^{3}MLCT(Ru) to the cobalt(III) moiety is able to be in competition with EET, since the triplet d−d excited-states of the $[Co^{III}(tpy)_2]$ moiety of $[(tpy)Ru^{II}(tpy\text{-}ph\text{-}tpy)Co^{III}(tpy)]^{5+}$ and $[(tpy)Ru^{II}(tpy\text{-}tpy)Co^{III}(tpy)]^{5+}$ are low enough (−1.04 and −0.94 eV, respectively). Since the optical transitions to the triplet excited-states of $[Co^{III}(tpy)_2]$ moiety are spin-forbidden, only exchange interaction is able to cause the EnT. The interactions not only between $\pi^*(L^-)$ and $d\sigma^*(Co^{III})$but also between $d\pi(Ru^{III})$ and $d\pi(Co^{II})$ are required for the EnT, of which the former and the latter are necessary for the EET of ^{3}MLCT(Ru) to $[Co^{III}(tpy)_2]$ moiety and for the HT of Ru^{III} to $[Co^{II}(tpy)_2]$ moiety, respectively. Consequently, the interaction between $\pi^*(L^-)$ and $d\sigma^*(Co^{III})$ necessary for the EET of ^{3}MLCT(Ru) is more favorably satisfied than both the interactions of $\pi^*(L^-)\text{−}d\sigma^*(Co^{III})$ and $d\pi(Ru^{III})\text{−}d\pi(Co^{II})$ for the EnT of ^{3}MLCT(Ru).

The rate of the EnT can be comparable with that of the EET, only when the Franck−Condon factor of the EET process is less favorable than that of the EnT. Following energy-gap law of nonradiative transitions, Franck−Condon factors of EET and EnT decrease as the vertical free-energy gaps of EET $(-\ \Delta G^\circ_{EET} - \lambda_{EET,i} - \lambda_{EET,s})$ and EnT $(-\ \Delta G^\circ_{EnT} - \lambda_{EnT,i} - \lambda_{EnT,s})$, respectively. As the magnitudes of ΔG°_{EnT}, $\lambda_{EnT,i}$, and $\lambda_{EnT,s}$ are −1.15, +0.45,[42] and 0 eV, respectively, and those of ΔG°_{EET}, $\lambda_{EET,i}$ and $\lambda_{EET,s}$ are −0.93, 0.38,[42] and 0.85 eV,[17] respectively, for $[(tpy)Ru^{II}(tpy\text{-}ph\text{-}tpy)Co^{III}(tpy)]^{5+}$, the EnT with a vertical free-energy gap of 0.7 eV is more preferable than EET with the negative energy gap (−0.30 eV). It is probable that the second lowest triplet state of $[Co^{III}(tpy)_2]$ moiety as an energy acceptor improves the Franck−Condon factor of EnT more. The small solvent reorganization (0.72 eV) of EET for $[(tpy)Ru(tpy\text{-}tpy)Co(tpy)]^{5+}$ due to a small Ru−Co distance is expected to shift the vertical free-energy gap of EET to the less negative (−0.22 eV). This might lead the more contribution of EET to the decay of ^{3}MLCT resulting in the larger EET yield of $[(tpy)Ru^{II}(tpy\text{-}tpy)Co^{III}(tpy)]^{5+}$ than that of $[(tpy)Ru^{II}(tpy\text{-}ph\text{-}tpy)Co^{III}(tpy)]^{5+}$.

Conclusion

EET reaction products of $[Ru^{II}(L\text{−}L)Co^{III}]^{5+}$ (L−L: tpy-ph-tpy, tpy-tpy, and tpphz) were formed in the intramolecular electron-transfer quenching of ^{3}MLCT(Ru) in a time shorter than 10 ps for subpicosecond laser excitation. A transient actinometry using $[Ru(bpy)_3]^{2+}$ was applied to evaluate the quantum yield of EET product. The yields of the EET reaction products in BN, Φ_{EET}, were 0.41 and 0.53 for L−L = tpy-ph-tpy and for L−L = tpy-tpy of $[^2Ru^{III}(tpy)(L\text{−}L)^2Co^{II}(tpy)]^{5+}$, respectively. The ET yield of $[(bpy)_2{}^2Ru^{III}(tpphz)^4Co^{II}(bpy)_2]^{5+}$ was 0.77−0.84. The smaller yields of EET product in PC with a slow relaxation time and at lower temperatures suggest that the triplet d−d excited state of $[Co^{III}(tpy)_2]$ moiety is formed during the solvent relaxation. A tunneling transition of the nonrelaxed EET products to the lowest d−d excited-states of $[Co^{III}(tpy)_2]$ moiety takes place as a hole-transfer from $[Ru^{III}(tpy)_2]$ to $[Co^{II}(tpy)_2]$ generating an electronic configuration of $d\pi^6 d\sigma^*$. A strong through-ligand electronic coupling of $d\pi(Ru)\text{−}d\pi(Co)$, which was estimated from the strong intensity of inter-valence transition of $[(tpy)Ru^{III}(L\text{−}L)Ru^{II}(tpy)]^{5+}$,[38] allows the hole-transfer between $[Ru^{III}(tpy)_2]$ and $[Co^{II}(tpy)_2]$. The possibility that the lower lying d−d excited-states are produced in competition with the ET of $[(tpy)Ru^{III}(tpy\text{-}ph\text{-}tpy)Co^{II}(tpy)]^{5+}$ is also pursued. In the case of $[(bpy)_2Ru^{III}(tpphz)\text{-}Co^{II}(bpy)_2]^{5+}$, both RET and HT are retarded very much by a small superexchange electronic interaction between $d\pi(Ru^{III})$ and $d\pi(Co^{II})$.

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