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Intramolecular Electron-Transfer of Covalently-Linked Polypyridine Ruthenium(II)/Rhodium(III) Binuclear Complexes in the Excited State. Observation of the Marcus Inverted Region

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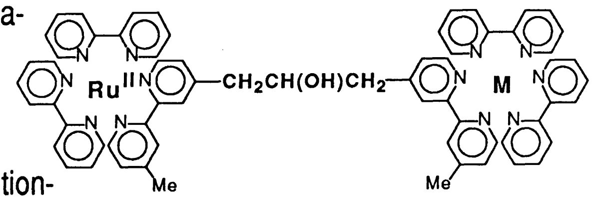
Ru(II)bpy$_2$Mebpy-CH$_2$CH(OH)CH$_2$-MebpyRh(III)L$_2$ (L = bpy. phen) (**1**) were newly synthesized. Intramolecular electron-transfer in excited **1** was studied with a time-correlated single photon counting method. In H_2O, the excited Ru(II) complex exhibits a biexponential decay. The presence of a slow component suggests that the excited state can be repopulated by thermal activation from the Ru(III)-Rh(II) and the direct process to the ground state lies in the Marcus Inverted region



1(L=bpy) : M= Rh(III), **2** : M= Os(II)

The evaluation of the rate constants of the intramolecular step is crucial to understand the role of the various molecular parameters in determining reaction rates.1) Recently there have been examined excited decay processes in a variety of weakly coupled transition-metal-complex dimers. Such systems allow us to study the effects of distance and driving force on electron/energy transfer rates and afford a valuable opportunity for testing theoretical models.2)

Polymethylene-linked dimers of Ru(bpy)$_3^{2+}$ exhibited no intramolecular interaction leading to the enhanced quenching between the excited and ground states.3a,b) However, the efficient intramolecular triplet-triplet annihilation process was found under the high intensity irradiation of laser light.4) In the heterobinuclear system consisting of polypyridine-ruthenium(II) and -osmium(II) complexes (**2**) the efficient intramolecular energy transfer from excited Ru(II) complex to Os(II) complex occurs through a dipole-dipole interaction, i.e., the Förster mechanism.5)

This work presents the preparation of novel covalently-linked polypyridine Ru(II)/Rh(III) binuclear complexes (**1**), their spectroscopic and electrochemical properties, and the kinetic study of intramolecular electron-transfer (ET) by a time-correlated single-photon counting method. Initial excitation of **1** is followed by intramolecular ET from excited Ru(II) complex to Rh(III) complex with exergonicity of ≈0.1 V. Kinetic analysis provides the evidence that the subsequent ET process to the ground state with exergonicity of ≈2.0 V lies in the Marcus inverted region.

The synthesis of **1** is outlined in Scheme 1. The preparation of the bridging ligand is described elsewhere.3b) The bridging ligand was first coupled with 1/10 equimolar Rh(III)L$_2$Cl$_3$ (L=bpy, phen) and

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purified by repeated Sephadex LH-20 chromatography to remove unreacted ligand dimer and Rh(III)L_2Mebpy-$CH_2CH(OH)CH_2$-MebpyRh(III)L_2. Treatment of Rh(III)L_2Mebpy-$CH_2CH(OH)CH_2$-Mebpy with $Rubpy_2Cl_2$ and ammonium hexafluorophosphate affords **1** as a PF_6 salt. Purification of **1** was achieved by repeated chromatography using Sephadex LH-20 and methanol as an eluent.6)

$$\mathrm{HCOOEt} \xrightarrow{\mathrm{MebpyCH_2Li}} \mathrm{MebpyCH_2CH(OH)CH_2bpyMe} \xrightarrow{\mathrm{RhL_2Cl_3}} [\mathrm{RhL_2MebpyCH_2CH(OH)CH_2bpyMe}]^{3+}$$

$$[\mathrm{RhL_2MebpyCH_2CH(OH)CH_2bpyMe}]^{3+} \xrightarrow{\mathrm{Rubpy_2Cl_2/NH_4PF_6}} [\mathrm{RhL_2MebpyCH_2CH(OH)CH_2bpyMe(bpy)Ru}]^{5+}$$

Scheme 1. **1**(L=bpy, phen)

The redox and electronic properties of **1** were compared with those of its component complexes, 4,4'-dimethyl-2,2'-bipyridine-bis(2,2'-bipyridine)ruthenium(II), **3**, and -rhodium(III), **4**, and a 1:1 mixture of **3** and **4**. Redox potentials in acetonitrile (MeCN) were measured by cyclic voltammetry using a platinum electrode and tetrabutylammonium perchlorate as a supporting electrolyte.Cyclic voltammetry of **1**(L=bpy, phen) exhibited a single reversible wave at 1.27 V vs. SCE in the 0.0-1.5 V range that can be assigned to the oxidation of Ru(II) to Ru(III). In the negative potential range, an irreversible wave at ≈-0.7 V (vs. SCE) corresponds to reduction of Rh(III) to Rh(II), as inferred from the known behavior of poly(pyridine)rhodium(III) complexes.7)

As shown in Fig. 1, the electronic absorption spectrum of **1**(L=phen) was identical with the superimposed spectra of equimolar **3** and **4**(L=phen). The characteristic absorption bands of **1**(L=bpy) are 456, 318, 302(sh), 286, 242, and 211 nm corresponding to those of **3** and **4**(L=bpy). Thus, comparison of redox and electronic properties of **1** with its component complexes gave no evidence for interaction between Ru(II)- and Rh(III)-moieties in the ground state.

The luminescence spectra of **1** (excitation wavelength : 455 nm) were recorded with argon-gas bubbled solutions at room temperature and compared with that of **3** at the same substrate concentration. The emission intensities of **1**(L=bpy) and **1**(L=phen) decreased to 1/8 and 1/6 in water, and 7/8 and 3/4 in methanol, respectively. In the equimolar mixture of **3** and **4**, there could not be observed such a quenching process because of the low substrate concentrations (1.5 x 10^{-5}M). Therefore, the quenching reactions in **1** are intramolecular in nature.

As for the quenching mechanism, oxidative electron transfer from *Ru(II) to Rh(III) is conceivable. In acetonitrile, the first oxidation potential of Ru is +1.27V and the first reduction potential of Rh is ≈-0.7 V vs.SCE (by cyclic voltammetry). Since substitution of one bpy-ligand of $Ru(bpy)_3^{2+}$ with 4,4'-dimethyl-2,2'-bipyridine does not show a marked difference in absorption and emission maxima, the excited energy of Ru-complex of **1** can be estimated to be almost the same (2.10 V) with that of $Ru(bpy)_3^{2+}$.8) The energy level diagram deduced from the above considerations for **1** can allow us to estimate the ergonicity of excited-state ET. The oxidative quenching of excited Ru-complex is slightly exergonic (-ΔG ≈ 0.1 V). The luminescence decay at 610 nm for **1** was measured in three

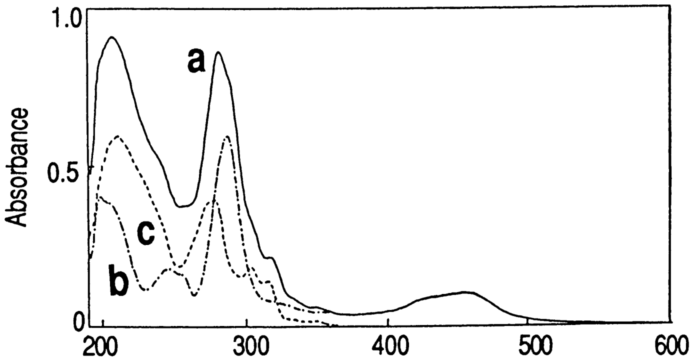
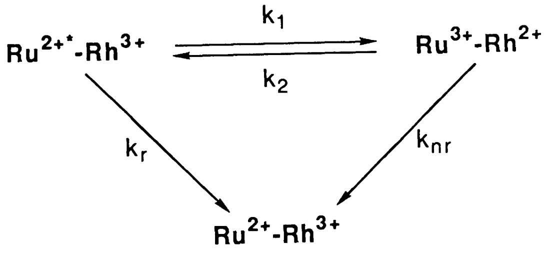


Fig. 1. Absorption spectra of **1**(L=phen)(a), **3**(b), and **4**(c) in MeCN. [Complex] = 7.8 μM



Scheme 2.

different solvents (H_2O, MeOH, MeCN) with use of time-correlated single photon counting (excitation wavelength at 457.9 nm and an instrumental width of 300 ps).9) As illustrated in Fig. 2 with the computer calculated fit, the emission decay profiles of **1**(L=bpy) and **1**(L=phen) in water disclosed a biexponential decay consisting of a fast and a slow components. Deconvolution of emission profiles afforded the best fit by the sum of two exponential decays. The amplitude of the slow component remained constant irrespective of the degree of purification of the sample by repeated chromatography.

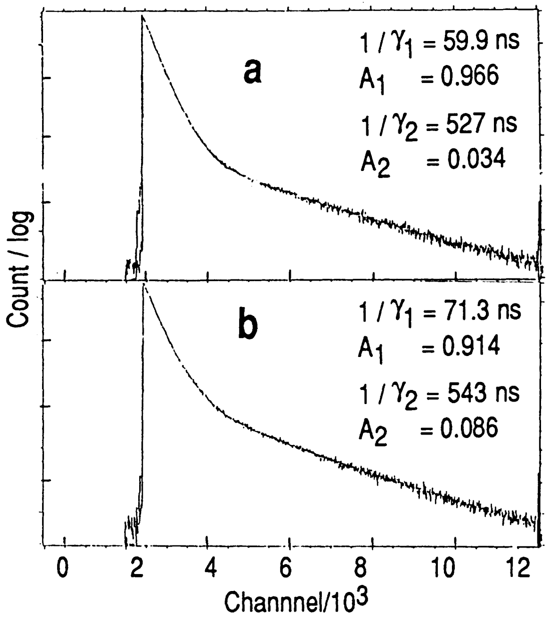


Fig. 2. Emission profiles of **1**(L=bpy)(a) and **1**(L=phen)(b) in water. [**1**] = 15 μM, 1.62 ns / channel.

On the condition that the decay of Ru(III)-Rh(II) to Ru(II)-Rh(III) is sufficiently slow, the excited state *Ru(II)-Rh(III) can be repopulated by thermal activation from the Ru(III)-Rh(II). The excited-state decay in **1** can be described by Scheme 2. The rate equations for Scheme 2 are

$$\frac{d[^*\mathrm{Ru(II)\text{-}Rh(III)}]}{dt} = -(k_r + k_1)\,[^*\mathrm{Ru(II)\text{-}Rh(III)}] + k_2[\mathrm{Ru(III)\text{-}Rh(II)}] \qquad (1)$$

$$\frac{d[\mathrm{Ru(III)\text{-}Rh(II)}]}{dt} = +k_1[^*\mathrm{Ru(II)\text{-}Rh(III)}] - (k_{nr} + k_2)\,[\mathrm{Ru(III)\text{-}Rh(II)}] \qquad (2)$$

The solution of these equations for the concentration of [*Ru(II)-Rh(III)] is

$$[^*\mathrm{Ru(II)\text{-}Rh(III)}] = [^*\mathrm{Ru(II)\text{-}Rh(III)}]_0\left[A_1e^{-\gamma_1 t} + A_2e^{-\gamma_2 t}\right] \qquad (3)$$

where $[^*\mathrm{Ru(II)\text{-}Rh(III)}]_0$ means the initial concentration, $A_1 = (X - \gamma_2) / (\gamma_1 - \gamma_2)$; $A_2 = -(X - \gamma_1) / (\gamma_1 - \gamma_2)$; $\gamma_1 = \{(X+Y) + [(X-Y)^2 + 4k_1k_2]^{1/2}\} / 2$: $\gamma_2 = \{(X+Y) - [(X-Y)^2 + 4k_1k_2]^{1/2}\} / 2$; $X = k_r + k_1$; $Y = k_{nr} + k_2$.10) Rate constants k_1, k_2, and k_{nr} were calculated by eq 3 where k_r is the value from the emission lifetime of **3** and A_1, A_2, γ_1, and γ_2 are the parameters for the computer fits of the experimental decay profiles. As presented in Table 1, the rate constants k_1 depend strongly on solvent and k_{nr} are 1.6-1.9 x 10^6 s^{-1}.

Table I. Kinetic data for intramolcular ET in **1**

Solvent	k_1	k_2	k_{nr}	k_r
L=bpy	$10^6 s^{-1}$	$10^6 s^{-1}$	$10^6 s^{-1}$	$10^6 s^{-1}$
H_2O	14	0.5	1.9	1.9
MeCN	1.2	1.6	1.6	1.1
MeOH	1.1	1.1	1.7	1.2
L=phen				
H_2O	11	1.1	1.8	1.9
MeCN	2.1	0.9	1.6	1.1
MeOH	1.1	1.0	1.8	1.2

In semiclassical theory 11) the rate constant for a (first order) ET reaction is given by

$$k = \kappa_{el}\nu_n\exp\left[\frac{-(\Delta G^\circ + \lambda)^2}{4\lambda RT}\right] \qquad (4)$$

where κ_{el} is the electronic coupling between the donor and acceptor, ν_n is the frequency factor of the nuclear motion that takes the system over the barrier, $\Delta G°$ is the free-energy change for the reaction, λ (= $\lambda_{in} + \lambda_{out}$) is a parameter related to the extent of inner-shell (λ_{in}) and solvent nuclear reorganization (λ_{out}) accompanying the reaction, R is the gas constant, and T is the absolute temperature. The solvent is assumed to behave as a dielectric continuum and λ_{out} is given by

$$\lambda_{out} = (\Delta e)^2\left(\frac{1}{2a_1} + \frac{1}{2a_2} - \frac{1}{r}\right)\left(\frac{1}{D_{op}} - \frac{1}{D_s}\right) \qquad (5)$$

where Δe is the charge transferred, a_1 and a_2 are radii of the donor and acceptor, r is the distance between their centers, D_{op} is the square of refractive index, and D_s is the dielectric constant.

Expression 5 was evaluated by taking $(\Delta e)^2(1/D_{op} - 1/D_s) = 0.79$Å V for water and by using the molecular radius 5Å for the radii a_1 and a_2 and the distance r=15Å. The structures of polypyridyl Ru and Rh complexes are expected to be essentially identical so that the results of an X-ray crystallographic structure for $Ru(bpy)_3^{2+}$ can be used for estimating a_1 and a_2.[12)] The resultant solvent reorganization energy λ_{out} is 1.06 V for **1**. The value of λ_{in} is estimated to be less than 0.04 V, since the Ru-N and, possibly, Rh-N[13)] bond length changes expected upon redox reactions are very small.[14a,b)]

The value of $-\Delta G°$ for the process from Ru(III)-Rh(II) to Ru(II)-Rh(III) is ≈2.0 V which is greater than λ. As predicted by Eq 4, this reaction is well within the inverted region and, as a consequence, proceeds relatively slow. On the other hand, the reaction to form *Ru(II)-Rh(III) is endergonic($\Delta G° \approx 0.1$ eV). Because of its smaller endergonicity, it lies still in the normal free energy region ($-\Delta G° < \lambda$) and can become competitive to the former process. The kinetic data in water in Table 1 demonstrate explicitly that *Ru(II)-Rh(III) can be repopulated by thermal activation from the Ru(III)-Rh(II) and the direct process to the ground state lies in the Marcus inverted region. The observed solvent dependence of k_1 can not be rationalized by the change of λ. A subtle change of $\Delta G°$in this process may bring about a significant effect on the rate.

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