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Intramolecular Energy Transfer in Covalently Linked Polypyridine Rhenium(I)/Ruthenium(II) Complexes

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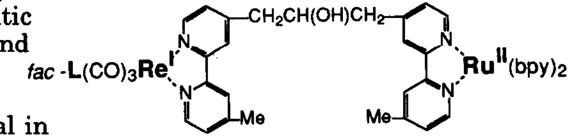
Abstract

A novel series of covalently-linked polypyridine Re(I)/Ru(II) binuclear complexes [LRe(I)(CO)$_3$MebpyCH$_2$CH(OH)CH$_2$MebpyRu(II)(bpy)$_2$] (L = Cl, 4-methylpyridine, N-methylimidazole, or acetonitrile) **1**, has been synthesized. The emission spectra of **1** (excitation wavelength:360 nm) showed a nearly complete quenching of $Re^{I} \rightarrow \pi^*$(bpy) MLCT emission and the enhancement of $Ru^{II} \rightarrow \pi^*$(bpy) MLCT emission. The rate constants (k_{en}) of the intramolecular energy transfer ranged from 1.7×10^8 to 1.2×10^9 s^{-1}. The relation between k_{en} and the energy gap was discussed in terms of the energy gap law.

1. Introduction

Recently, the excited-state properties of d^6 transition-metal complexes such as polypyridine Ru(II), Os(II), and Re(I) complexes have been increasingly investigated. Since the metal, ligands, and solvent environment can all affect excited-state properties, variations of one or more of these factors can be used to tune the photophysical and photochemical properties [1]. Similar to Ru(bpy)$_3^{2+}$ and Os(bpy)$_3^{2+}$ (bpy = 2,2'-bipyridine), the lowest excited state of Re(bpy)(CO)$_3$L is MLCT (metal-to-ligand charge transfer) in character. Replacement of L by various ligands affords a variety of excited states [2].

We have undertaken a systematic study of photoinduced energy and electron transfer among polymethylene-bridged binuclear complexes of d^6 transition-metal in order to evaluate the molecular parameter for the donor-acceptor interactions of the weakly coupled system [3-6]. This work presents 1) the preparation of covalently-linked heterobinuclear complexes comprising the polypyridine rhenium(I)/ruthenium(II) complex [LRe(I)(CO)$_3$MebpyCH$_2$CH(OH)CH$_2$MebpyRu(II)(bpy)$_2$] (L = Cl, 4-methylpyridine, 1-methylimidazole, or acetonitrile) **1**, 2) the spectroscopic and



1: L = Cl, 1-MeIm, 4-MePy, MeCN

electrochemical properties, and 3) a kinetic study of intramolecular energy transfer in excited **1** by a time-correlated single-photon counting method. For these complexes, the rate constant of the intramolecular energy transfer (k_{en}) increases with increasing the energy gap between two chromophores. Electron localization in the excited MLCT state is discussed in conjunction with the reorganization energy in the energy gap dependency.

2. Experimental

The synthesis of **1** is outlined in Scheme 1. Details concerning the synthesis and characterization of all compounds described herein are available as supplementary information. Spectral and electrochemical measurements were made in acetonitrile (MeCN) or methanol (MeOH) by using instrumentation and procedures that have been described elsewhere [6].

Scheme 1.

$$\text{4,4'-Me2bpy} \xrightarrow{\text{LiN(2-Pr)}_2} \text{MebpyCH}_2\text{Li} \xrightarrow{\text{HCOOEt}} \text{MebpyCH}_2\text{CH(OH)CH}_2\text{bpyMe}$$

$$\xrightarrow{\text{Rubpy}_2\text{Cl}_2\,/\,\text{NH}_4\text{PF}_6} [\text{Ru(bpy)}_2\text{Mebpy-CH}_2\text{CH(OH)CH}_2\text{-Mebpy](PF}_6)_2$$

$$\xrightarrow{\text{Re(CO)}_5\text{Cl}} [\textit{fac}\text{-Re(CO)}_3\text{Cl-Mebpy-CH}_2\text{CH(OH)CH}_2\text{-Mebpy-Ru(bpy)}_2](\text{PF}_6)_2$$

$$\xrightarrow[\text{AgPF}_6\,/\,\text{L}]{\text{AgSO}_3\text{CF}_3\text{ or}} [\textit{fac}\text{-Re(I)(CO)}_3\text{(L)-Mebpy-CH}_2\text{CH(OH)CH}_2\text{-Mebpy-Ru(II)(bpy)}_2]$$

L = Cl, 1-Methylimidazole, 4-Methylpyridine, acetonitrile

3. Results and Discussion

The electrochemical properties of **1** were compared with those of its component complexes, Ru(II)(dmb)(bpy)$_2$, **2**, and Re(dmb)(CO)$_3$L, **3** (dmb=4,4'-dimethyl-2,2'-bipyridine). Redox potentials in acetonitrile (MeCN) were measured by cyclic voltammetry using a glassy carbon or a platinum electrode. For **1** (L = Cl), two oxidation waves associated with metal-centered reactions of Ru(II)$\rightarrow$Ru(III) and Re(I)$\rightarrow$Re(II) are present at 1.23 and 1.36 V vs. SCE, respectively. The peak-to-peak splitting for the reversible wave is 60-70 mV, indicating that in **1**, two successive one-electron oxidation processes take place. The first two reversible reduction waves are assigned to reductions of the bridged ligand of the rhenium metal and the bpy ligand of ruthenium metal at -1.3~-1.5 V. The splittings between the one electron bridged-Mebpy$^{0/-}$ couple of rhenium complex and the one electron bpy$^{0/-}$ couple of ruthenium complex are too small to resolve.

As shown in Figure 1, the electronic absorption spectrum of **1** (L = Cl) is identical with the superimposed spectrum of equimolar **2** and **3**(L = Cl). This was also observed in **1**(L = 4-MePy, 1-MeIm, MeCN). Thus, a comparison of the redox and electronic properties of **1** with its component complexes gave no evidence of an interaction between the ruthenium and rhenium moieties of **1** in

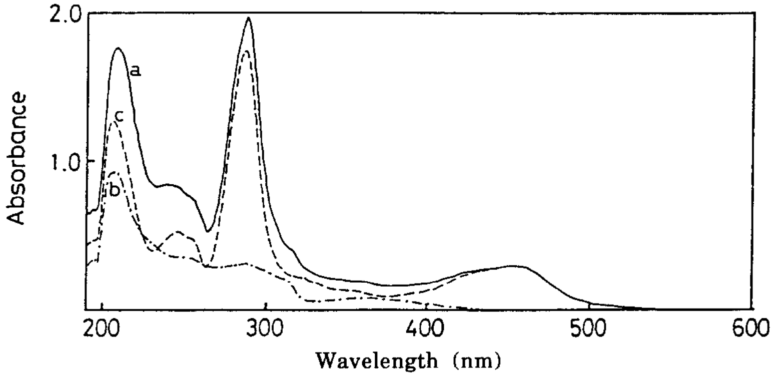


Figure. 1 Absorption spectra of a : **1** (L = Cl), b : **3** (L = Cl) and c : **2**, Ru(II)(dmb)(bpy)$_2$, in MeOH. [Substrate] = 2.3 x 10^{-5} M.

the ground state. This represents a general trend in the covalently linked dimers of polypyridine transition metals [3-7].

The emission spectrum of **1** (excitation wavelength : 360 nm) was recorded with an argon-gas bubbled MeCN solution at room temperature and compared with that of **3** at the same substrate concentration. As an illustration, the emission spectrum of **1**(L = 4-MePy) is shown in Figure 2. The efficient quenching of emission at 550 nm from a rhenium complex and the enhancement of emission intensity at 613 nm from ruthenium complex were observed in **1**. In a mixture of **2** and **3**, no such quenching process could be observed because of the low substrate concentration. The enhancement of emission at 613 nm indicates that the sensitization of the ruthenium complex by an excited rhenium complex occurs through an intramolecular process in **1**. Irrespective of L, a nearly complete quenching of $Re^{I}\rightarrow\pi^{*}$(bpy) MLCT emission and the enhancement of $Ru^{II}\rightarrow\pi^{*}$(bpy) MLCT emission were observed. In Table 1 are summarized uv-vis, emission, and electrochmical data for **3** and electrochemical data for **1**.

Table 1. Spectral and Electrochemical$^{a)}$ Data for [LRe(I)(CO)$_3$(dmb)] and **1**

	[LRe(I)(CO)$_3$(dmb)]				**1**	
L	$\lambda_{abs}$$^{b)}$	$\lambda_{em}$$^{b)}$	$E_{1/2}^{ox}$	$E_{1/2}^{red}$	$E_{1/2}^{ox}$	$E_{1/2}^{red c)}$
Cl	361	600	1.36	-1.43	1.23, 1.36	-1.3~-1.5
1-MeIm	345	580	1.62	-1.29	1.24, 1.60	-1.3~-1.5
4-MePy	338	557	1.73	-1.24	1.24, 1.72	-1.3~-1.5
MeCN	335	534	1.65	-1.41	1.24, 1.59	-1.3~-1.5

a) V vs. SCE, $E_{1/2} = (E_{pa} + E_{pc})/2$. Solvent :MeCN. b) nm in MeCN. C) not well-defined.

The photophysical behavior of **1** can be described in terms of an energy level diagram that is simply made by superimposing the low-lying excited states of the Ru(dmb)(bpy)$_2$$^{2+}$ and Re(dmb)(CO)$_3$L units on the redox potentials in the ground state. The reductive and oxidative quenching of the excited Re-complex is endergonic based on a comparison of the redox potential for the excited Re-complex with that for the Ru-complex. On the other hand, energy transfer can be more favorable by 0.41-0.66 eV, which is derived from the observed differences in the emission maxima and the Stokes shifts of the Re-complex and the Ru-complex of **1**. Therefore, the thermodynamical aspect allows us to conclude that energy transfer from *Re(I) to Ru(II) instead of electron transfer constitutes the quenching mechanism. The occurrence of energy transfer was detected by observing the enhancement of Ru^{II}→π*(bpy) MLCT emission along with a decrease in Re^{I}→π*(bpy) MLCT emission.

The measurement of luminescence lifetimes was performed to evaluate the quenching on a quantitative basis by a time-correlated single-photon counting method [8]. The decay of Re^{II}→π*(bpy) MLCT emission at the wavelength of the emission maximum was measured in acetonitrile (excitation wavelength at 307 nm and instrumental width of 300 ps). Deconvolution of the luminescence profiles afforded the best fit by double exponential decay. The fast exponential decay is attributed to a deactivation of the rhenium-excited state by an intramolecular energy transfer to the ruthenium complex. A minor, long-lived component represents a deactivation of the ruthenium-excited state due to the overlap of the emission spectrum. Figure 3 shows the emission decay profile of an excited Re-complex of 1(L = 4-MePy) in MeCN, with which a computer-calculated fit is superimposed.

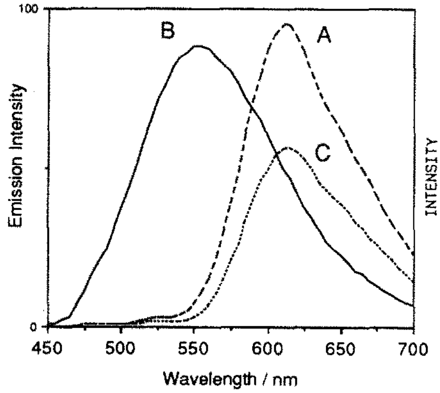


Figure 2. Emission spectra of **1**(A) and **3**(B) in MeCN. L = 4-MePy. (C) : The estimated contribution due to the direct excitation of the ruthenium complex. [Substrate] = 1.5 x 10^{-5}M. Excitation at 360 nm.

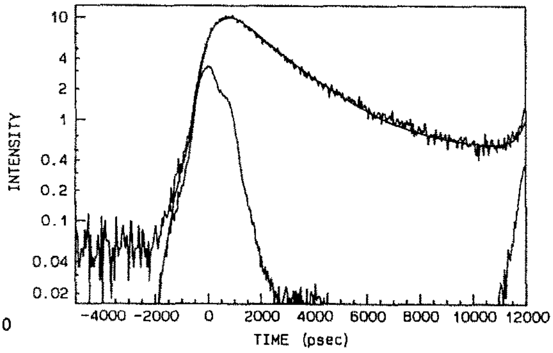


Figure 3. Emission decay for **1**(L=4-MePy) in MeCN. Monitored at 540 nm. Excitation at 307 nm. A computer calculated fit is superimposed. The parameter for double exponential fit : lifetime τ_1 = 1.8 ns (preexponential factor A_1 = 0.97) and τ_2 = 390 ns (A_2 = 0.03).

The rate constant, k_{en}, of energy-transfer can then be calculated via $k_{en} = k_{obs} - k_0$ where k_{obs} and k_0 are evaluated from the observed lifetime (τ_{obs}) of **1** at 610 nm and the emission lifetime of the corresponding rhenium complex **3**, respectively. As presented in Table 2, the rate constant (k_{en}) of the intramolecular energy transfer depends on ΔG° (*vide infra*).

The mechanisms available for the transfer of electronic energy are based on remote dipole-dipole or dipole-multipole electronic interactions (the Förster mechanism) [9] and on a collisional mechanism that involves electronic exchange (the Dexter mechanism) [10].

A quantitative treatment of the Förster mechanism leads to the following expression for k_{en}:[9]

$$k_{en} = \frac{9000 \ln 10 \kappa^2 \phi_D}{128 \pi^5 n^4 N \tau_D R^6} \int_0^\infty F_D(\nu) \varepsilon_A(\nu) \frac{d\nu}{\nu^4} \qquad (1)$$

Here, ν is the wave number, $\Phi_D(\nu)$ is the spectral distribution of the donor emission in quanta normalized to unity, $\varepsilon_A(\nu)$ is the molar extinction coefficient for the acceptor absorption, n is the refractive index of the solvent, κ is an orientation factor which equals $(2/3)^{1/2}$ for a random distribution of donor and acceptor molecules, ϕ_D is the quantum yield of donor emission, τ_D is the actual donor emission lifetime, N is Avogadro's number, and R is the distance between the donor and acceptor molecules. The overlap integral was calculated from numerical integration over the emission of **3**(L = MeCN) and the absorption of **2** in MeCN and the value was 8.29×10^{-15} mol^{-1} cm^6. Based on the observed values of $\phi_D = 0.103$ and $\tau_D = 4.60 \times 10^{-7}$ s and assuming $\kappa^2 = 2/3$ and R = 12.8Å for **1**(L = MeCN), the calculated k_{en} value was 7.6×10^7s^{-1}, which was more than one order slower than the actually observed value (1.2×10^9s^{-1}). Thus, at room temperature, the Förster mechanism is not likely to explain the fact. The electronic exchange interaction can be the main pathway for the intramolecular energy transfer in **1**, namely the Dexter mechanism. Compared with polypyridine Ru(II)/Os(II) complexes in which the Förster mechanism operates [6], the donor-acceptor spectral overlap is very small in **1**. The energy transfer is dominated by an electron exchange mechanism which is most readily related to electron-transfer processes. It can be treated formally with the theoretical formalism describing electron-transfer pathway.

Table 2. Intramolecular Energy-Transfer in **1**, in acetonitrile at 20°C

	LRe(I)(CO)$_3$(dmb)		**1**		
L	λ_{em}(nm)	τ_0(ns)	$-\Delta G$(eV)$^{a)}$	τ_{obs}(ns)	k_{en}(10^8s^{-1})
Cl	600	37	0.41	6.0	1.7
1-MeIm	580	61	0.48	4.0	2.7
4-Mepy	557	240	0.57	1.4	5.5
MeCN	536	460	0.66	0.80	12

a) estimated from $\Delta E_{em} + \Delta E_{ss}/2$. **2** : $E_{em} = 1.64 \times 10^4$ cm^{-1}, $E_{ss} = 0.58 \times 10^4$ cm^{-1}. **3** : $E_{em} = 1/\lambda_{em}$, $E_{ss} = 1.14 \pm 0.04 \times 10^4$ cm^{-1}

In semiclassical theory [11], the rate constant for a (first order) energy-transfer reaction can be given by

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

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, ΔG° is the energy gap for the reaction, λ is a reorganizational parameter, R is the gas constant, and T is the absolute temperature.

The energy gap $\Delta G°$ can be evaluated from the difference in the zero-zero emission energies of the corresponding ruthenium and rhenium complexes E_{00}. The spectroscopic Stokes shifts E_{ss} for **3** are nearly the same ($1.14 \pm 0.04 \times 10^4$ cm^{-1}) irrespective of the ligand L (Table 1) and E_{ss} for **2** is 5.8×10^3 cm^{-1}. Provided E_{00} equals the energy of emission maximum $E_{em} + E_{ss}/2$. $\Delta G°$ will be obtained from the energy differences between the donor and acceptor emission maxima and the Stokes shifts, that is $\Delta E_{em} + \Delta E_{ss}/2$.

As shown in Table 2, $\Delta G°$ varies between 0.41 and 0.61 eV. The value k_{en} increases with increasing $\Delta G°$, indicating that the process lies in the normal free energy region. Although too few data are available to discuss the relationship between the rate constant and the energy gap quantitatively, there is no evidence for any inverted behavior up to a themodynamic driving force of 0.88 eV[12]. The reorganization energy λ is expected to be similar to those in the electron-transfer processes. In equation 2, the solvent is assumed to behave as a dielectric continuum. The energy of the solvent nuclear reorganization λ_{out} for acetonitrile can be estimated to be 1.02 eV by using 15Å for the center-to-center distance and the molecular radius 5Å for the corresponding Re(I) and Ru(II) complexes. The MLCT excited state of **1** can be also described as the $M^+(bpy^{\bullet -})$-based state and there is an electronic displacement of ca 3Å from M to the center of bpy ligand [13]. In these respects, the large energy (>0.9 eV) will be needed to achieve the reorganization in the present energy transfer process. The results indicate that there is a similarity between energy-transfer and electron-transfer processes when the energy-transfer proceeds by the electronic exchange mechanism.

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