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Intramolecular Energy Transfer in Covalently Linked Ruthenium(II)/Osmium(II) Binuclear Complex. $Ru(II)bpy_2Mebpy\text{-}CH_2CH(OH)CH_2\text{-}MebpyOs(II)bpy_2$

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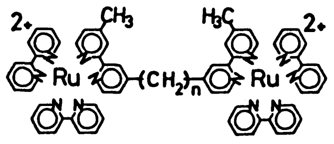
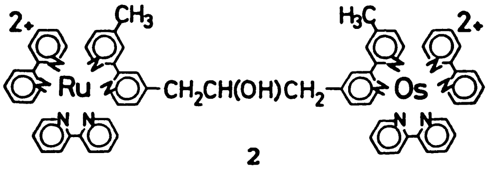
A novel polypyridine ruthenium(II)/osmium(II) heterobinuclear complex (2) was synthesized. The luminescence properties of 2 were compared with those of its component complex. In 2, the efficient intramolecular energy transfer from excited Ru(II) to Os(II) complex was observed and interpreted by Foerster mechanism.

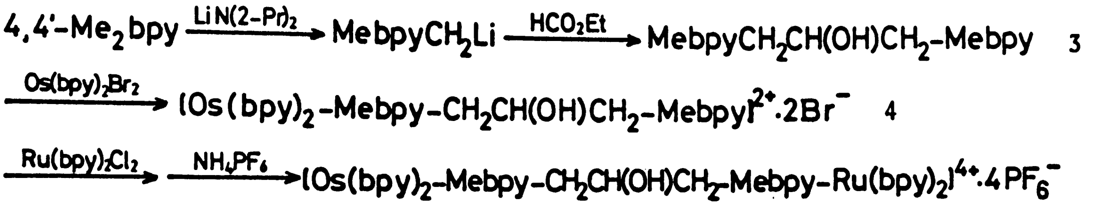


1(n=2&3)



2

Molecular assemblies consisting of polypyridine and porphyrin complexes of transition metals are of interest in view of systems capable of photochemical energy conversion analogous to photosynthesis.[1)] A possible use of these materials is to control photochemical processes in which optical excitation is followed by a spatially directed energy or electron transfer.[2)] We have studied photochemical and photophysical properties of $Ru(bpy)_3^{2+}$ complexes which were covalently incorporated into a vinyl polymer.[3)] In a recent study, we reported the photophysical properties of covalently linked dimers of $Ru(bpy)_3^{2+}$ (complex **1**) as a dimer model for $Ru(bpy)_3^{2+}$ containing polymers.[4)] We have found a rather different photophysical behavior of **1** in comparison with those of aromatic hydrocarbon- and porphyrin-dimers.[5-7)] In excited **1**, the intramolecular interaction leading to the enhanced quenching between the excited and ground states was not found. However, the efficient intramolecular triplet-triplet annihilation process was found under the high intensity irradiation of laser light. These findings aroused our interest in the heterobinuclear system. In this letter, we wish to communicate the synthesis and luminescence properties of a novel polypyridine heterobinuclear transition metal complex **2**, in which polypyridine-ruthenium(II) and -osmium(II) complexes were connected by a three-carbon chain. The synthesis of **2** is outlined in Scheme 1. 4,4'-Dimethyl-2,2'-bipyridine was lithiated by an equimolar amount of lithium diisopropylamide in tetrahydrofuran and then allowed to react with ethyl formate at room temperature to yield a new dimeric ligand **3**.[8)] **4** was obtained by refluxing a mixture (10:1) of **3** and $Os(bpy)_2Br_2$ in methanol. After the isolation of **4** by chromatography on Sephadex LH-20 with a



$$\text{4,4'-Me}_2\text{bpy} \xrightarrow{\text{LiN(2-Pr)}_2} \text{MebpyCH}_2\text{Li} \xrightarrow{\text{HCO}_2\text{Et}} \text{MebpyCH}_2\text{CH(OH)CH}_2\text{-Mebpy} \quad 3$$

$$\xrightarrow{\text{Os(bpy)}_2\text{Br}_2} [\text{Os(bpy)}_2\text{-Mebpy-CH}_2\text{CH(OH)CH}_2\text{-Mebpy}]^{2+}\cdot 2\text{Br}^- \quad 4$$

$$\xrightarrow{\text{Ru(bpy)}_2\text{Cl}_2} \xrightarrow{\text{NH}_4\text{PF}_6} [\text{Os(bpy)}_2\text{-Mebpy-CH}_2\text{CH(OH)CH}_2\text{-Mebpy-Ru(bpy)}_2]^{4+}\cdot 4\text{PF}_6^- \quad 2$$

Scheme 1. Synthesis of Polypyridine Ru(II)/Os(II) Binuclear Complex 2.

methanol eluent, treatment of **4** with $\text{Ru(bpy)}_2\text{Cl}_2$ in methanol under reflux and then with ammonium hexafluorophosphate in water afforded **2**. **2** was purified by the same procedure with **4** and was recrystallized from water as a PF_6^- salt.[8)]

The redox and electronic properties of **2** in the ground state were compared with those of its component complexes, 4,4'-dimethyl-2,2'-bipyridine-bis(2,2'-bipyridine)ruthenium(II) complex **5** and -osmium(II) complex **6**, and a 1:1 mixture of **5** and **6**. Redox potentials in acetonitrile (MeCN) were measured by cyclic voltammetry using a platinum electrode and tetrabutylammonium perchlorate (TBAP) as a supporting electrolyte. As shown in Fig. 1, two reversible oxidation waves appears at 0.77 V and 1.21 V vs. SCE for the Os(III)/Os(II) and Ru(III)/Ru(II) couples which correspond to those of **5** and **6**, respectively. The peak to peak splitting for these waves is 60 mV. This indicates that in **2**, two successive 1-electron oxidation processes take place. As shown in Fig. 2, electronic absorption spectra of **2** in methanol was identical with the superimposed spectra of equimolar **5** and **6**. Thus, comparison of redox and electronic properties of **2** with its component complexes provided no evidences for interaction between the ruthenium and osmium moieties of **2** in the ground state. This is a marked difference with the covalently linked porphyrin dimers where the interaction between porphyrin rings has been reported.[6,7)]

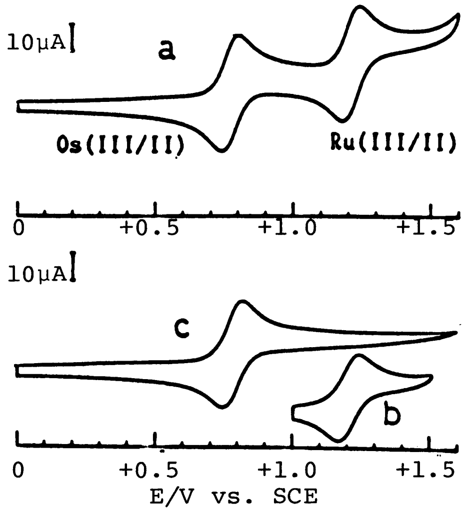


Fig. 1. Cyclic voltammograms of **2**(a), **5**(b), and **6**(c) in MeCN/ 0.1 M TBAP at scan rate of 200 mV/s. [complex]=1×10^{-3}M.

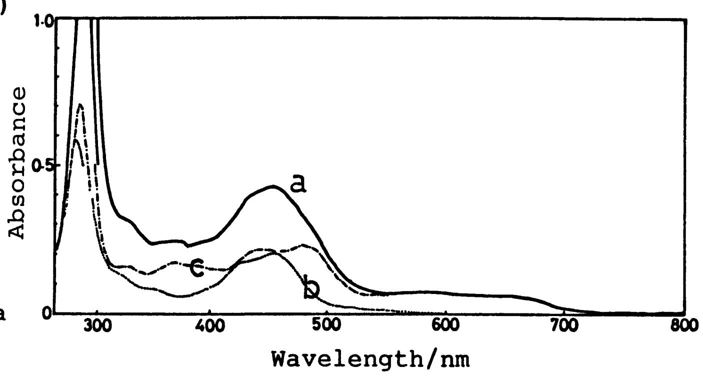


Fig. 2. Absorption spectra of **2**(a), **5**(b), and **6**(c) in methanol. [complex]=1.5×10^{-5}M.

The luminescence spectra of **2** (excitation wavelength : 455 nm) was recorded with an argon-gas bubbled methanol solution at room temperature and compared with that of a 1:1 mixture of **5** and **6** at the same substrate concentration. As shown in Fig. 3, the efficient quenching of emission at 615 nm from ruthenium complex and the enhancement of emission intensity at 720 nm from osmium complex were observed. In the mixture of **5** and **6**, there could not be observed such a quenching process because of the low substrate concentrations (1.5×10^{-5}M). Therefore, one can conclude that the intramolecular quenching process takes place very efficiently in **2**. The quenching rate constant was estimated to be $>1 \times 10^{8}$ s^{-1} from the relative value of **2** to the luminescence intensity of **5** at the same concentration. As for the quenching mechanism, energy transfer from *Ru(II) to Os(II) and reductive electron transfer from Os(II) to *Ru(II) are conceivable. On the thermodynamic ground, energy transfer ($-\Delta G = 0.27$ eV) can be more favorable than electron transfer ($-\Delta G = -0.05$ V). To distinguish these processes, it is necessary to work on the luminescence lifetime measurements of **2**. The luminescence decay at 610 nm of the ruthenium moiety (Fig. 4a) and the luminescence rise and decay at 800 nm of the osmium moiety (Fig. 4b) were measured by the time-correlated single photon counting method[10] (excitation wavelength at 458 nm and instrumental width of 300 ps). Deconvolution of luminescence profiles at 610nm afforded the best fit by the sum of two exponential decays. In this case, a minor, long-lived component was present (2-0.6%). The amplitude of this component was sensitive to the degree of purification of the sample, and therefore most probably represents an impurity. The major fast exponential decay (2.1 ns : 4.7×10^{8} s^{-1}) was attributed to the deactivation of the ruthenium-excited state by intramolecular energy transfer to the osmium complex. The double exponential analysis for the rise and decay of excited-osmium complex at 800 nm gave 2.1 ns (4.7×10^{8} s^{-1}) for the rise which corresponded to the decay of excited ruthenium complex and 18.5 ns (5.4×10^{7} s^{-1}) for the decay, respectively. The ratio of pre-exponential factor of the two processes was almost 2 which corresponded to the ratio of absorbance of ruthenium and osmium moieties at the excitation wavelength (458 nm). This means that the quantum efficiency of energy transfer is almost 1 and therefore the electron transfer process can be ruled out. Creutz and Sutin reported that the bimolecular quenching rate constant between excited $Ru(bpy)_3^{2+}$ and $Os(bpy)_3^{2+}$ was 1.5×10^{9} $M^{-1}s^{-1}$ which is almost diffusion-controlled.[11] The observed first order rate constant for **2** was unexpectedly small. This fact might come from the electrostatic repulsion between two chromophores of **2** which prevented the collisional quenching

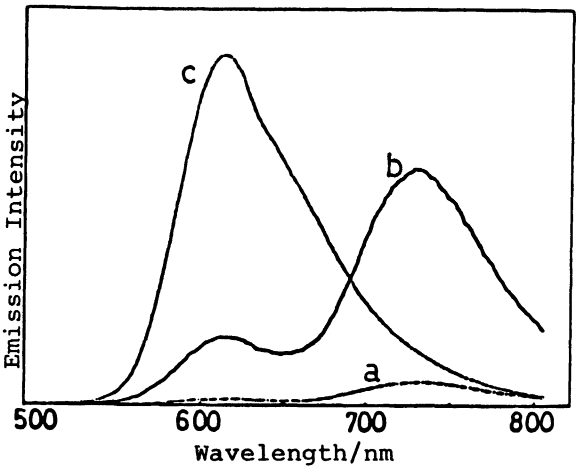


Fig. 3. Emission spectra of 2 [**a**, **b**(ax10)] and [5 +6](**c**) in MeOH (1.5×10^{-5}M). Excitation at 455 nm.

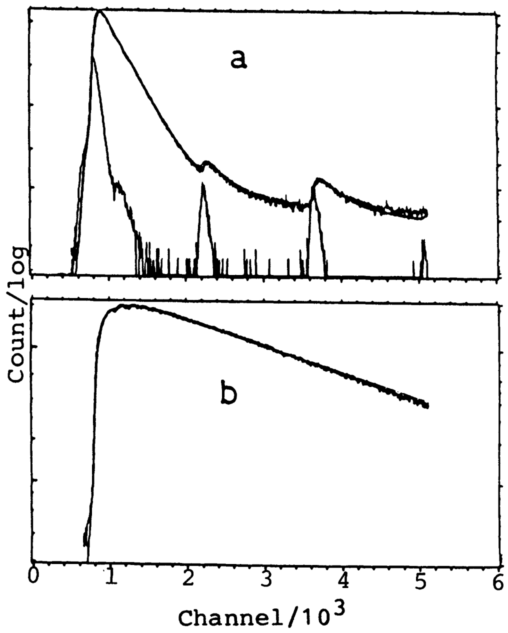


Fig. 4. Emission rise and decay for 2 monitored at 610 nm (**a**) and 800 nm (**b**). 814 ps/channel, [2]=1×10^{-4}M, solvent : 0.17 M Na_2SO_4 aq. soln.

process based on the electron exchange (Dexter mechanism).[12)] On the other hands, the dipole-dipole interaction mechanism depends on the magnitude of the molar absorptivity of the acceptor absorption in the region of the overlap of the donor emission and acceptor absorptions.[13)] The emission spectrum (λ_{max}=615 nm) of 5 overlaps the absorption spectrum of 6 (λ_{max}=590 and 650 nm; ε=~4000 $M^{-1}cm^{-1}$), so that energy transfer due to the dipole-dipole interaction by Foerster mechanism is conceivable. According to the Foerster formulation, the calculated value for energy transfer in 2 was $1.8 \times 10^9\ s^{-1}$ which was reasonably close to the observed value ($4.7 \times 10^8\ s^{-1}$). It is known that the intramolecular electron transfer via collisional processes in tri-methylene linked donor-acceptor was influenced by the solvent viscosity.[14)] To confirm the electronic dipole-dipole interaction mechanism, the dependency of solvent viscosity on the energy transfer rate (k_{en}) was examined. When the energy transfer takes place through the collisional process (electron exchange mechanism), solvent viscosity should reflect on the rate. k_{en} was measured in ethanol (0.012), ethylene glycol (0.17), and glycerol (10.7) (in parentheses : viscosity in poise). In spite of the large difference of viscosity, the observed k_{en} were in good agreement, that is, $4.2 \times 10^8\ s^{-1}$ irrespective to the solvent used. These facts strongly suggest that the intramolecular energy transfer in 2 takes place through Foerster mechanism.

In the case of the three-methylene linked dimers of porphyrins and aromatic hydrocarbons, the interactions in the excited state are in general resulted from the cofacial alignment of planar rings. Polypyridine complexes are spherical molecules and are charged positively. From the geometric and electrostatic viewpoints, their photophysical properties may be different from those of porphyrin complexes and aromatic hydrocarbons.

References

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9) Anal. Found: C,40.34; H, 3.18; N, 8.57%. Calcd for $OsRuC_{65}H_{56}F_{24}N_{12}OP_4 2H_2O$: C, 40.48; H, 3.13; N, 8.72%.
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