PHOTOCHEMICAL PROPERTY OF PORPHYRIN DERIVATIVES ASSEMBLED ON DIRUTHENIUM COMPLEX HAVING A SIMILAR FRAME OF HEMERYTHRIN

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$K[Ru_2(dhpta)(\mu\text{-}O_2C\text{-}p\text{-}Zn\text{-}TPP)_2]$ (1) (H_5dhpta = 1,3-diamino-2-hydroxypropanetetraacetic acid, ZnTPP-p-COOH = 5-(4-carboxylphenyl)-10, 15, 20-triphenylporphyrin) was synthesized and characterized by elemental analysis, mass spectroscopy, electronic absorption, NMR spectroscopies, and EXAFS analysis. The electronic and photochemical properties were studied by CV and time-resolved fluorescence measurement. The mixed valence complex of (1) was prepared by potentiostatic electrolysis. This mixed-valence complex exhibited an intervalence transfer (IT) band, and its value was closed to that of typical class II complexes.. The result of time-resolved fluorescence measurement indicated that the excited porphyrin moieties could be quenched through the intramolecular electron transfer of (1). The free energy change for the intramolecular charge recombination process from ruthenium moieties to porphyrin radical cation was estimated from cyclic voltanograms. The date and the exited singlet state energy of porphyrin moieties of (1) suggested possibility of the charge separation of (1) by excited porphyrin moieties.

Keyword: ruthenium, mixed valence complex, photoinduced electron transfer, porphyrin

INTRODUCTION

Photo-induced charge separation is of great interest in connection with artificial photosynthetic systems. Recently we have reported (μ-alcoxo)bis(μ-carboxylato)diruthenium complexes having the similar frame to that of Hemerytherin [1]. These complexes have stable mixed-valence state, suggesting its potentially catalytic activive for redox reaction. We also found that the ligand substitution reaction of $K[Ru_2(dhpta)(\mu\text{-}O_2CCH_3)_2]$ (2) with benzoic acid to give $K[Ru_2(dhpta)(\mu\text{-}O_2CC_6H_5)_2]$ (3) [1]. While porphyrin and its derivatives are used as the light-harvesting antenna systems, porphyrins are arranged suitable for photoinduced charge separation. Porphyrin have been expected to apply in molecular photonics and electronics. Thus, introduction of porphyrin moiety to metal complexes with catalytic activity produces photofunctionality.

In this report, we reported the synthesis of $K[Ru_2(dhpta)(\mu\text{-}O_2C\text{-}p\text{-}Zn\text{-}TPP)_2]$ and its electronic and photochemical properties [2].
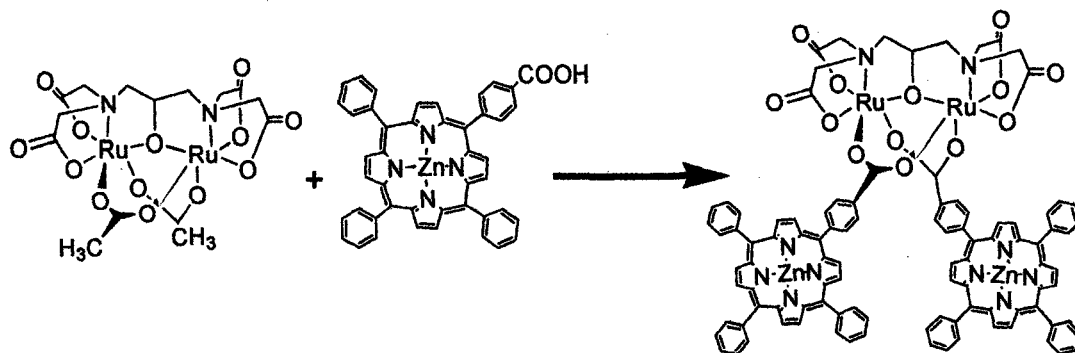
Figure 1 The synthesis of $K[Ru_2(dhpta)(\mu\text{-}O_2C\text{-}p\text{-}ZnTPP)_2]$

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Photochemical Property of Porphyrin Derivatives
Assembled on Diruthenium Complex Having a Similar Frame of Hemerythrin

MATERIALS AND METHODS

The commercially available were used as received. K[Ru₂(dhpta)(μ-O₂CCH₃)₂] was prepared according to the previous paper [1]. ZnTPP-p-COOH were prepared according to the literature [2].

To methanol solution (200ml) of K[Ru₂(dhpta)(μ-O₂CCH₃)₂] (**2**) (86mg, 0.125mmol), ZnTPP-p-COOH (360mg, 0.50mmol) was added and the

mixture was hearted at 80 °C for 8 days. The mixture was purified by gel permeation chromatography (sephadex RH-20 eluted by methanol). Yield, 125mg (0.0063mmol, 50%). K[Ru₂(dhpta)(*μ*-O₂C-*p*-ZnTPP)₂] (**1**) was characterized by elemental analysis, mass spectroscopy, electronic absorption, NMR spectroscopy and EXAFS analysis.
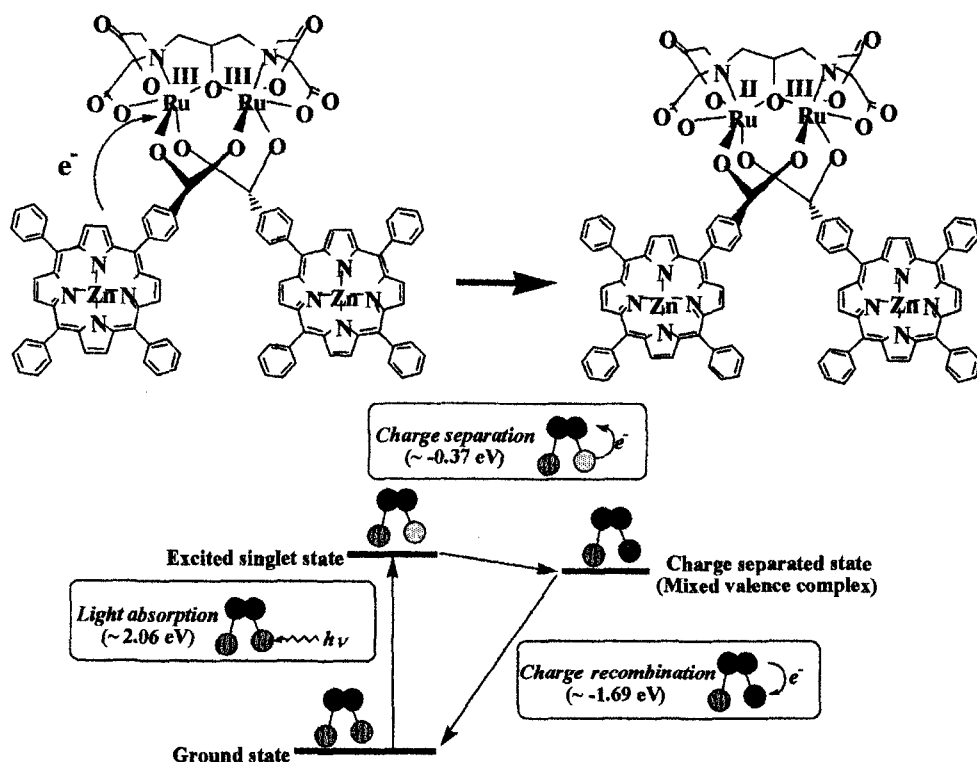

Figure 2. intermolecular electron transfer model of 1

RESULT AND DISSCUTION

The complexes **1**,**2**, and **3** were subject to EXAFS analysis. The Fourier transform of the EXAFS shows three peaks, at 1.6, 2.3, and 3.0 Å, which were assigned to the back-scattering contributions from the coordinated nitrogen and oxygen atoms, carbon atoms, including five-membered chelate ringsfrom other ruthenium atoms. The *r* values for **1** agreed quite closely with **2** that were characterized by X-ray crystallography. This result indicated that the complex **1** also has Hemerythrin-like frame.

The electronic absorption spectrum of **1** resemble to that of ZnTPP-*p*-COOH. Soret band appears at 429 nm and two Q bands appear at 561 and 602 nm. The molar extinction coefficient of **1** for Soret (andQ) band(s) is almost twice that of Zn-*p*-COOH. The mixed valence complex of **1** was prepared by controlled-potential electrolysis. The resultant mixed valence species of **1** exhibits two absorption peaks in

the near Infrared region. The peak around 5500cm⁻¹ was assigned to intervalence charge transfer (IT) band, and the peak around 11000cm⁻¹ was assigned to LMCT band. These two bands were analyzed and separated by Gauss fitting, and peak positions and half-height widths were obtained. Using the parameters, the electron exchange integral of **1** was calculated to H_{ad}=0.4 × 10³cm⁻¹, which is determined by Hush theory. The obtained value for H_{ad} was similar to that of the complex **2**, **3** and other typical Class II complexes. As a result, complex **1** was classified to Class II mixed valence state.

The magnetic susceptibility and effective magnetic moment of **1** was measured at 50~300K. The large decrease of effective magnetic moment of **1** on low temperature indicates that there is strong antiferromagnetic interaction between Ru atoms. The coupling constant, J value was calculated to J = -404cm⁻¹ by Bleany-Bowers formula.

The electrochemistry of **1** was studied by cyclic

voltammetry. The complex **1**, **3**, and ZnTPP-*p*-COOH were measured in DMF using glassy carbon working and Ag/AgPF$_6$ reference electrodes at room temperature. The scan rate was 100mVs^{-1}. For **3**, a reversible oxidation peak and two reversible reduction peaks were appeared in between -2.0~1.0V vs. Ag/Ag$^+$. The oxidation peak was assigned to Ru(III)-Ru(III), the two reduction peaks were assigned Ru(III)-Ru(II) and Ru(II)-Ru(II) respectively.(I can not understand the description. If Ru(III)-Ru(III) exist in the solution, the oxidation peak should be Ru(III)-Ru(III)/Ru(III)-Ru(IV) and reductios peaks should be Ru(III)-Ru(II)/Ru(III)-Ru(III) and Ru(III)-Ru(II)/Ru(II)-Ru(II) For ZnTPP-*p*-COOH, the two reversible oxidation peaks and two reversible reduction peaks were found in between–2.5V~1.0V which were characterized as one electron processes. For **1** there are two reversible oxidation peak and three reversible reduction peaks, i.e., the two-electron oxidation peaks which originated with two porphyrin moieties were found at 0.51V, the three-electron oxidation peaks which were assigned to one-electron oxidation of Ru(III)-Ru (IV) and two-electron oxidation of two porphyrin moieties was found at 0.72V.

In the cathodic scan, the one-electron redaction peak was appeared at −1.2 V which was Ru (III)-Ru (II) reduction, the three-electron reduction peak was appeared at −1.7 V which was the combination of the reduction of two porphyrin moieties and the reduction of Ru(II)-Ru(II), and two-electron reduction peak was appeared at −2.1 V which was reduction of two porphyrin moieties. This result suggests that there is no electronic interaction between Ru atoms and porphyrin moieties. From the CV result, the free energy change for the intramolecular charge recombination process from the ruthenium moiety to the porphyrin cation was evaluated to $\Delta G_{ET(CR)}$ = -1.69eV, Where the exited singlet state energy of porhyrin moieties was evaluated to ΔE_{0-0} = 2.06 eV, based on the absorption and fluorescence spectra. Figure 2 represents the whole scope of these processes, including excitation, charge separation, and recombination. The free energy change during the electron transfer from porphyrin cation to Ru(II)-Ru(III) was ca. 1.69eV. The porphytin moieties of **1** was excited to S$_1$ state (2.06eV) by light, and the electron transfer from excited porhyrin to Ru(II)-Ru(III) was occurred with diminishing the energy about –0.37eV. The assumption shown in the figure 2 suggests the possibility of charge separation by the excitation of porphyrin moiety in complex **1**.
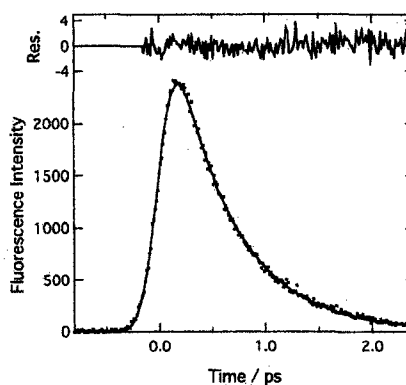

Figure 3. The S$_2$ fluorescence decay curve of **1**

The photochemical process of **1** was measured by time-resolved fluorescence using by femto second fluorescence up-conversion system. The complex **1** was measured in MeOH, and the S$_2$ and S$_1$ fluorescence were observed at 470nm and 600nm, respectively. The fluorescencet from S$_2$ state was clearly observed due to the large energy gap between S$_1$ and S$_2$. Figure 3 presents the fluorescence decay curve of **1**.

When the complex **1** was excited at 422nm, the S$_2$ fluorescence decay was measured about 450nm. The S$_2$ fluorescence decayed very quickly with the lifetime of 570fs. The rapid decay of the S$_2$ fluorescence plausibly due to the inter conversion to the S$_1$ state, as well as the electron transfer to ruthenium.

Figure 4 shows the time resolved fluorescence from S$_1$ state of complex **1**. The S$_1$ florescence was observed at 600nm by the irradiation at 422nm. The curvature of fluorescent for S1 indicates the presence of multi decay process for S$_1$. The S$_1$ fluorescence lifetime of ZnTPP was reported to 2ns. Even though very short life time of 36 ps was obtained which strongly indicate the presence of the charge separation process.
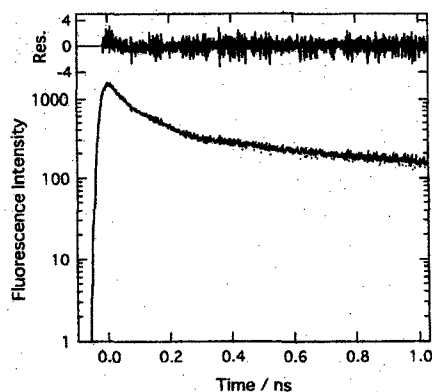

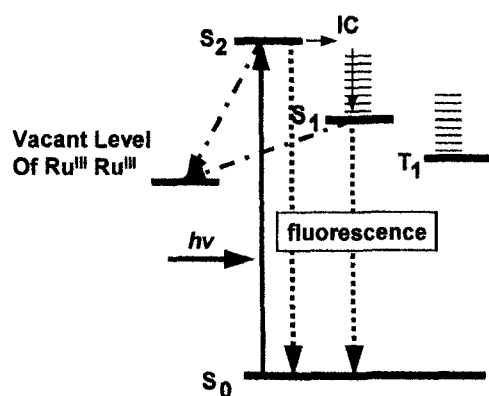**Figure 4.** The S1 fluorescence decay curve of **1**

Figure 5. The energy diagram of 1

CONCLUTION

$K[Ru_2(dhpta)(\mu-O_2C-p-ZnTPP)_2]$ (1) was synthesized from $K[Ru_2(dhpta)(\mu-O_2CCH_3)_2]$which has hemerythtin frame in both solid and liquid state and the structure was confirmed by EXSAFS and ^1H NMR. The mixed valence complex of 1 was assigned Class II. The CV measurement with the combination of photophysical results indicates the charge separation of 1 taken place during the excitation   process.

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