Noncovalently Linked Zinc Porphyrin-Ru(bpy)$_3$ Dyad Assembled via Axial Coordination

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Received August 4, 2003

Noncovalently linked electron donor-acceptor dyad consisting of zinc tetratolylporphyrin and pyridine-appended ruthenium trisbipyridine complex was prepared, *via* axial coordination of pyridine moiety in ruthenium trisbipyridine complex on zinc tetratolylporphyrin. For the purpose of comparison, axial coordination of pyridine-appended 2,2'-bipyridine on zinc tetratolylporphyrin was also investigated. The K values were determined based on absorption or fluorescence studies. The fluorescence of zinc tetratolylporphyrin was efficiently quenched upon axial coordination of pyridine moiety, probably due to the photoinduced electron transfer from zinc tetratolylporphyrin to ruthenium trisbipyridine, supported by free energy estimation.

Key Words : Noncovalently-linked donor-acceptor dyad, Porphyrin, Ru(bpy)$_3^{2+}$, Axial coordination, Photo-induced electron transfer

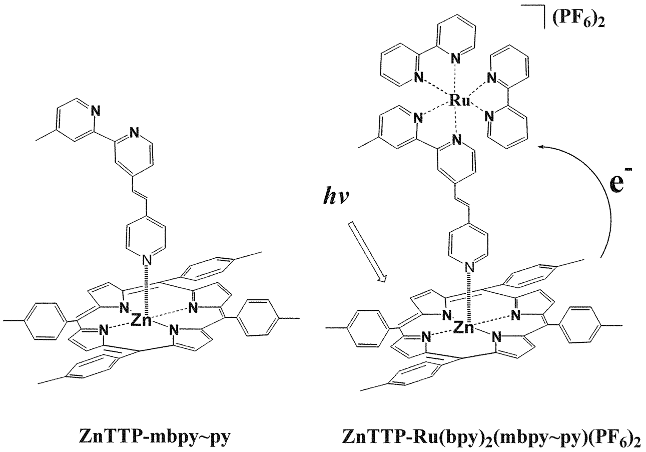
Introduction

Multicomponent donor-acceptor systems and their photo-induced energy or electron transfer processes have been received great attention with the goals of understanding the primary processes in natural photosynthesis and of designing photochemical molecular devices for energy conversion and information processing.[1-9] Porphyrins[1-4,9] and ruthenium trisbipyridine derivatives[5-9] are popularly employed as suitable photoactive components in multicomponent systems. Some porphyrin derivatives linked covalently to ruthenium polypyridyl complexes have also been reported.[10-18]

Recently, a number of covalently linked donor-acceptor systems have been extensively studied, but sometimes require time-consuming laborious synthetic works. Fortunately, a variety of donor-acceptor systems can be also assembled easily through noncovalent interactions such as ion-pairing,[19] H-bonding in DNA base-pairing,[20] or ligand binding on transition metal.[21]

Actually, naturally occurring photosynthetic reaction center is a kind of non-covalently linked donor-acceptor system.[22-23] Self-assembly[24] has been achieved by hydrogen bonding, salt bridges, axial ligation through the central metal ion by using functionalized acceptor molecules, and hydrophobic interactions, and applied recently to arrange multicomponent donor-acceptor systems. The non-covalent approach offers some advantages such as reduced synthetic efforts and modulation of the electronic interaction by solvent, temperature and concentration of the components, although there are several disadvantages such that the low association constants often prevent photophysical studies for which high-dilution conditions are required.[25] Complex formation is confirmed by red-shift of absorption spectrum and emission spectrum, down-field shift of ^{1}H-NMR spectrum, or shift of cyclic voltammogram, *etc*.

We report here the preparation of ruthenium trisbipyridine complex containing a pyridine pendant group, Ru(bpy)$_2$(mbpy~py)$^{2+}$, and its axial coordination on zinc 5,10,15,20-tetra-*p*-tolylporphyrin (ZnTTP) leading to the formation of noncovalently linked donor-acceptor system, and discuss the photoinduced electron transfer from ZnTTP to Ru(bpy)$_2$(mbpypy)$^{2+}$ (Scheme 1).



Scheme 1. Structures of the coordinated complexes between ZnTTP and mbpy~py or Ru(bpy)$_2$(mbpy~py).

Experimental Section

Materials. Ru(bpy)$_3$(PF$_6$)$_2$ was prepared from Ru(bpy)$_3$Cl$_2$ by adding saturated aqueous NH$_4$PF$_6$. Triphenylphosphonium salt of 4-(bromomethyl)-4'-methyl-2,2'-bipyridine was prepared according to the literature.[26-28] Zinc 5,10,15,20-tetra-*p*-tolylporphyrin (ZnTTP) was prepared by addition of zinc acetate to dichloromethane solution of 5,10,15,20-tetra-*p*-tolylporphyrin (TTP).

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Synthesis of 4'-methyl-4-(2-(4-pyridyl)ethenyl)-2,2'-bipyridine [mbpy~py]. Triphenylphosphonium salt of 4-(bromomethyl)-4'-methyl-2,2'-bipyridine (224 mg, 0.43 mmol) and 4-pyridinecarboxaldehyde (60 μL, 0.43 mmol) were dissolved in 10 mL methanol and stirred under nitrogen atmosphere at 0 °C for 20 min. A 1.4 mL solution of 0.3 M sodium methoxide in methanol was added dropwise over 2 min, and the solution was allowed to warm to room temperature. After stirring for 5 hrs the solvent was removed under vacuum and dichloromethane (20 mL) was added. The solution was filtered and the filtrate was concentrated with rotary evaporator. The concentrate was chromatographed on silica gel column using chloroform and chloroform/methanol (v/v = 9/1), successively, as eluents. The solution was evaporated and the resulting solid was recrystallized with hexane/toluene. Mbpy~py was obtained as white solid (52 mg, 44% yield) and characterized by absorption, emission, IR, ^{1}H-NMR, and mass spectral data. UV-VIS (CH_2Cl_2): λ_a^{max} 281 nm. Emission (CH_2Cl_2): λ_f^{max} 363 nm. IR: 3566, 3471, 3419, 1595, 1553, 1458, 1437, 823 cm^{-1}. ^{1}H-NMR ($CDCl_3$): δ (ppm) 2.46 (3H, s, CH_3), 7.18 (1H, m, H5'), 7.34 (2H, d, J = 5.7 Hz, ethenyl), 7.39 (1H, m, H5), 7.41 (2H, dd, J = 1.5 & 4.5 Hz, pyridyl-ortho H), 8.28 (1H, s, H3'), 8.56-8.59 (2H, m, H3 and H6'), 8.63 (2H, dd, J = 1.5 & 4.5 Hz, pyridyl-meta H), 8.69 (1H, d, J = 5.1 Hz, H6). EI-MS: *m/e* 273 (M$^+$).

Synthesis of bis(2,2'-bipyridine)[4'-methyl-4-(2-(4-pyridyl)ethenyl)-2,2'-bipyridine]ruthenium (II) bis(hexafluorophosphate) [Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$]. To a solution of mbpy~py (15 mg, 0.12 mmol) in methanol (20 mL) was added *cis*-Ru(bpy)$_2$Cl$_2$·2H$_2$O (30 mg, 0.12 mol) under nitrogen atmosphere. The resulting brown solution was stirring for 2 days and then turned to orange color. The solvent was evaporated under vacuum. The residue was redissolved in water of 15 mL, and the unreacted mbpy~py was removed by filtration. 0.3 M sodium carbonate solution (10 mL) was added into the filtrate. The solution gave a red precipitate on the addition of a saturated ammonium hexafluorophosphate solution and the precipitate was filtered. The red solid was recrystallized from ethyl ether/methanol to give Ru(bpy)$_2$-(bpy~py)(PF$_6$)$_2$ (76 mg, 65% yield). Structure was identified with absorption, emission, and FAB-mass spectra. UV-VIS (CH_2Cl_2): λ_a^{max} 291, 461 nm. Emission (CH_2Cl_2): λ_e^{max} 661 nm. FAB-Mass (NBA): *m/e* 832 (M$^+$-PF$_6$), 687 (M$^+$-2PF$_6$).

Spectroscopic and electrochemical measurements. Absorption spectra were recorded on a Simadzu UV-2401PC spectrometer. ^{1}H NMR spectra were measured on 300 MHz Varian UNITY plus 300. Infrared spectra were obtained on a Midac Prospect FT-IR spectrometer. EI-Mass and FAB-Mass spectra were measured on Mircomass (UK) Platform GC/LC Mass Spectrometer and Jeol LTD JMS-HX110/110A High Resolution Tandem Mass Spectrometer, respectively. Electrochemical measurements were made using a Bioanalytical Systems (BAS) CV-50W potentiostat. Cyclic voltammetry was carried out in dichloromethane using the conventional three electrodes arrangement, consisting of a gold or platinum or glassy carbon working electrode, a caromel or Ag/AgCl in 0.3 M KCl solution reference electrode and a coiled platinum counter electrode. A 0.1 M tetrabutylammonium perchlorate (TBAP) solution was used as a supporting electrolyte. Fluorescence spectra were obtained on an Aminco-Bowman Series 2 luminescence spectrometer at 590 nm of excitation wavelength.

Results and Discussion

A 2,2'-bipyridine derivative containing pyridine ring was prepared to study noncovalently linked dyad formed by coordination of ligand on ZnTTP. As shown in Figure 1(a), upon addition of mbpy~py, absorption bands of ZnTTP in dichloromethane were red-shifted with the appearance of isosbestic points, indicating the formation of 1 : 1 complex by the axial coordination on ZnTTP. It was observed that the intense Soret band was shifted from 420 to 428 nm and two Q bands at visible region were shifted from 549 and 588 nm to 563 and 603 nm (Table 1). Table 1 summarized absorption maxima, emission maxima and quantum yields, and half-wave potentials for ZnTTP, mbpy~py, Ru(bpy)$_2$(mbpy~py)-

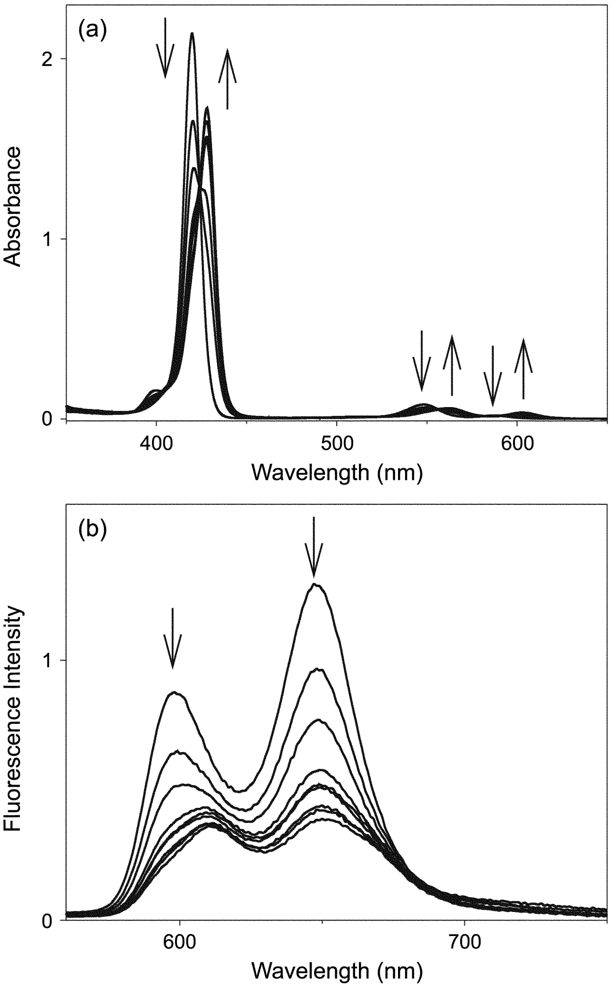

Figure 1. Absorption (a) and fluorescence (b) spectral changes of ZnTTP in dichloromethane on the addition of mbp~ypy: [ZnTTP] = 3.0×10^{-6} M, [mbpy~py] = 0, 6.0×10^{-5}, 1.2×10^{-4}, 1.8×10^{-4}, 2.4×10^{-4}, 3.0×10^{-4}, 3.6×10^{-4}, 4.2×10^{-4}, 4.8×10^{-4} M.

Table 1. Absorption maxima (λ_a^{max}), emission maxima (λ_e^{max}), and emission quantum yields (Φ_e), and half-wave potentials ($E_{1/2}$) for ZnTTP, mbpy~py, Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$, and their coordinated complexes in dichloromethane at room temperature

Compounds	λ_a^{max}/nm	λ_e^{max}/nm	Φ_e	$E_{1/2}$, V	
				Ox.	Red.
ZnTTP	420, 549, 588	598, 648	0.049	0.74	-1.24
mbpy~py	281	363	0.031	–	-2.62
Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$	291, 461	661	0.001	1.26	-1.25 -1.32 -1.63
ZnTTP-mbpy~py	428, 563, 603	611, 652	0.021	–	–
ZnTTP-Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$	291, 429, 461	609, 651	0.033	–	–

Table 2. The formation constants K_f (for ground state) and K_f* (for excited state), and the photoinduced electron transfer rate constants k_{et} and free energy changes ΔG_{et} for coordinated complexes ZnTTP-mbpy~py and ZnTTP-Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$ in dichloromethane at room temperature

Compound	K_f/M^{-1}	K_f*/M^{-1}	k_{et}/s^{-1}	ΔG_{et}/eV
ZnTTP-mbpy~py	6.6×10^3	6.4×10^3	–	+1.30
ZnTTP-Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$	–	5.3×10^3	8.7×10^7	-0.07

(PF$_6$)$_2$, and their coordinated complexes in dichloromethane at room temperature. The formation constant K_f (Table 2) for axial coordination of mbpy~py on ZnTTP was estimated to be 6.6×10^3 M^{-1} from the absorption spectral data by using Benesi-Hildebrand plot[29] (Figure 2) and showed the formation of a fairly stable complex.

$$1/(A_0-A_x) = 1/(A_0-A) + 1/(A_0-A) \times 1/K_f \times 1/[L]$$

where, A_0 is the absorbance when [L] = 0, A_x is the absorbance of the solution with [L] and A is the absorbance when the concentration of ligand is very high, and we have practically only pure coordinated complex.

Upon excitation at 548 nm, one of two Q bands, ZnTTP itself shows two major fluorescence bands at 598 and 648 nm. The fluorescence emission of ZnTTP was not only red-shifted upto 13 nm but also significantly quenched with addition of mbpy~py as shown in Figure 1(b). Fluorescence maxima were shifted from 598 and 648 nm to 611 and 652 nm (Table 1). Efficient fluorescence quenching may be due to the photoinduced electron transfer from ZnTTP to mbpy~py. The formation constant K_f^* for the excited state was obtained to be 6.4×10^3 M^{-1} from the fluorescence spectral data (Figure 3), in good agreement with the value of 6.6×10^3 M^{-1} from the absorption spectral data.

$$1/(I_0-I_x) = 1/(I_0-I) + 1/(I_0-I) \times 1/K_f^* \times 1/[L]$$

where, I_0 is the fluorescence intensity when [L] = 0, I_x is the fluorescence intensity of the solution with [L] and I is the fluorescence intensity when the concentration of ligand is very high, and we have practically only pure coordinated complex. The formation constants K_f for ground state and K_f* for excited state, and the photoinduced electron transfer constants k_{et} for coordinated complexes of mbpy~py and Ru(bpy)$_2$(mbpy~py)$^{2+}$ on ZnTTP in dichloromethane at room temperature were represented in Table 2.

As pyridine-tethered ruthenium complex, Ru(bpy)$_2$(mbpy~

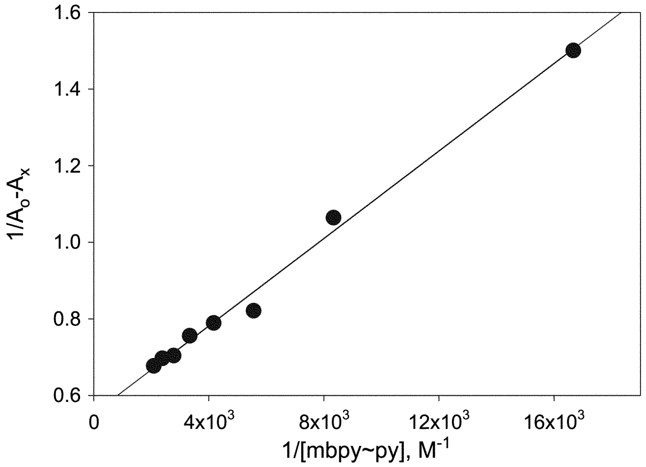

Figure 2. Benesi-Hildebrand plot for absorption spectral change of ZnTTP in dichloromethane on the addition of mbpy~py.

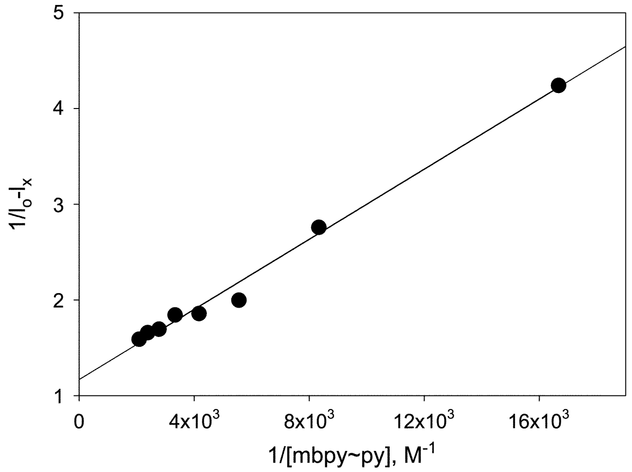

Figure 3. Benesi-Hildebrand plot for the fluorescence quenching of ZnTTP in dichloromethane on the addition of mbpy~py.

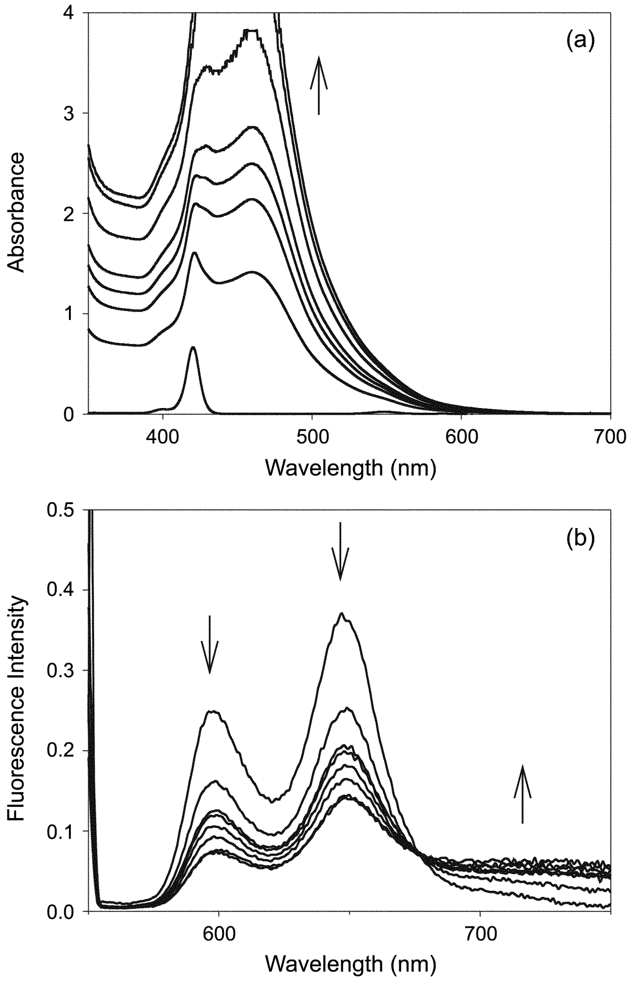

Figure 4. Absorption (a) and fluorescence (b) spectral changes of ZnTTP in dichloromethane on the addition of Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$: [ZnTTP] = 1.0×10^{-6} M, [Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$] = 0, 8.0×10^{-5}, 1.2×10^{-4}, 1.4×10^{-4}, 1.6×10^{-4}, 2.0×10^{-4}, 2.6×10^{-4}, 2.8×10^{-4} M.

py)(PF$_6$)$_2$, was added, the absorption bands of ZnTTP were obscured by overlapping with those of ruthenium complex and spectral shift was difficult to observe (Figure 4(a)). Therefore, the formation constant K$_f$ could not be determined from the absorption spectral data. As shown in Figure 4(b) and Table 1, the fluorescence emission of ZnTTP was not only red-shifted (598 and 648 nm → 609 and 651 nm), but also significantly quenched with addition of Ru(bpy)$_2$-(mbpy~py)(PF$_6$)$_2$, probably due to the photoinduced electron transfer from the excited ZnTTP moiety to Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$. The formation constant K_f^* (Table 2) for the excited state was obtained to be 5.3×10^3 M^{-1} from the fluorescence quenching data on the addition of Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$ (Figure 5).

To demonstrate the energetics for fluorescence quenching of ZnTTP, the electrochemical study was carried out in addition to spectroscopic measurements. The half-wave potentials for oxidation and reduction processes found from cyclic voltammograms for ZnTTP, mbpy~py, and Ru(bpy)$_2$-(mbpy~py)(PF$_6$)$_2$ in dichloromethane were given in Table 1.

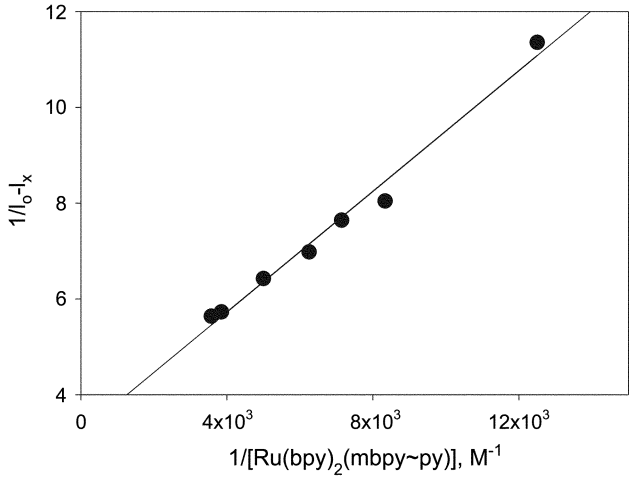

Figure 5. Benesi-Hildebrand plot for the fluorescence quenching of ZnTTP in dichloromethane on the addition of Ru(bpy)$_2$(mbpy~py).

The energy of the lowest excited singlet state of ZnTTP coordinated with mbpy~py, E$_S$(^{1}ZnTTP), was calculated to be 2.06 eV from the average of the frequencies of the longest-wavelength absorption maximum and shortest-wavelength emission maximum. The half-wave potential for the oxidation of ZnTTP, $E_{1/2}^{ox}$(ZnTTP$^{+/0}$), is 0.74 V *vs* SCE[30] and the half-wave potential for the reduction of mbpy~py, $E_{1/2}^{red}$(mbpy~py$^{0/-}$), is -2.62 V *vs* SCE. Therefore, the photoinduced electron transfer from the excited singlet state of ZnTTP to mbpy~py, forming the charge transfer state (ZnTTP$^{\bullet+}$-mbpy~py$^{\bullet-}$), is thermodynamically unfavorable. Therefore, significant reduction of fluorescence quantum yield in ZnTTP-mbpy~py dyad in comparison with those of ZnTTP cannot be due to electron transfer. It is most likely associated with the change in electron density and in the lowering of the energy gap.

The half-wave potentials for the reduction of Ru(bpy)$_2$-(mbpy~py)(PF$_6$)$_2$, $E_{1/2}$(Ru$^{0/-}$), is -1.25 V *vs* SCE (Table 1). On the basis of the spectroscopic and electrochemical data in Table 1, a charge transfer state corresponding to the electron transfer from the excited ZnTTP moiety to the Ru(bpy)$_2$-(mbpy~py)$^{2+}$ moiety, indicated by ZnTTP$^{\bullet+}$-Ru$^{\bullet-}$, can be placed around 1.99 eV, *i.e.* slightly below the S$_1$ excited state of the ZnTTP moiety (2.06 eV) and between the S$_1$ level of the ZnTTP moiety and the ^{3}MLCT level of the Ru(bpy)$_2$-(mbpy~py)(PF$_6$)$_2$ (1.98 eV). Therefore, the photoinduced electron transfer from the excited singlet state of ZnTTP to Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$, forming the charge transfer state (ZnTTP$^{\bullet+}$-Ru$^{\bullet-}$), is thermodynamically favored by *ca*. 0.07 eV.

The free energy change values indicate that the fluorescence quenching of ZnTTP could be attributed to the photoinduced oxidative electron transfer from the excited ZnTTP to the axially coordinated Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$ (ΔG_{et} = -0.07 eV). Therefore, the electron transfer from the excited ZnTTP moiety to Ru(bpy)$_2$(mbpy~py) moiety is most likely quenching mechanism for fluorescence from ZnTTP.

The rate constant of the photoinduced electron transfer, k$_{et}$, was estimated using the fluorescence lifetime and quantum yields:

$$k_{et} = 1/\tau^o\ (\Phi_f^o/\Phi_f - 1)$$

where τ^o is the fluorescence lifetime of ZnTTP in the absence of quencher, and Φ_f^o and Φ_f are the fluorescence quantum yields of ZnTTP in the absence and presence of quencher, respectively.

From the data in Table 1, the electron transfer quenching rate constant for noncovalently linked dyad ZnTTP-Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$ has been estimated to be 8.7×10^7 s^{-1} and the values are shown in Table 2. Since this rate is slower than the intrinsic deactivation rate (2.0×10^8 s^{-1}) of the S$_1$ level, estimated from the fluorescence lifetime of ZnTTP,[18] it is inferred that the electron-transfer process is not 100% efficient. The understanding for the detailed deactivation processes of the excited state in the dyads needs further works including transient spectroscopic study.

These results show that it is possible to obtain photoinduced charge separation from the well-defined design for noncovalently linked dyads based on zinc porphyrins as donor and Ru complexes as acceptors.

Summary

Noncovalently linked ZnTTP-mbpy~py and ZnTTP-Ru(bpy)$_2$-(mbpy~py)(PF$_6$)$_2$ dyads assembled via axial coordination were prepared. Absorption and emission spectra in dichloromethane revealed the complex formation between ZnTTP and mbpy~py or Ru(bpy)$_2$(mbpy~py). The formation constants, K_f for ground state and K_f^* for excited state, were determined with absorption and fluorescence studies by Benesi-Hildebrand equation. K_f and K_f^* was determined to be 6.6×10^3 and 6.4×10^3 for ZnTTP-mbpy~py, and only K_f^* was obtained 5.3×10^3 for ZnTTP-Ru(bpy)$_2$(mbpy~py)-(PF$_6$)$_2$. The fluorescence of zinc tetratolylporphyrin was efficiently quenched upon axial coordination of pyridine moiety in Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$, probably due to the photoinduced electron transfer from ZnTTP to coordinated Ru complex, as supported by free energy estimation. The free energy change ΔG_{et} for photoinduced electron transfer was calculated to be -0.07 eV for ZnTTP-Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$. The free energy change indicated that the photoinduced intramolecular electron transfer from the excited ZnTTP to the axially coordinated Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$ is exergonic. The electron transfer rate constant, k_{et}, was calculated to be 8.7×10^7 s^{-1} for ZnTTP-Ru(bpy)$_2$(mbpy~py)(PF$_6$)$_2$.

It is concluded that the efficient photoinduced electron transfer was successfully achieved through noncovalent assembly more readily prepared than covalently-linked donor-acceptor dyad[31,32] based on porphyrin.[33] The S$_1$ excited state of ZnTTP was quenched through photoinduced electron transfer to generate a ZnTTP$^{\bullet+}$-Ru(bpy)$_2$(mbpypy)(PF$_6$)$_2^{\bullet-}$ charge transfer state.

Acknowledgement. The authors thank to Korea Basic Science Institute for ^{1}H-NMR and mass spectral measurements. This work was supported by a grant No. R04-2002-000-00014-0 (2002) from Korea Science & Engineering Foundation.

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