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Preparation and Photoinduced Electron Transfer in Porphyrin-Ruthenium Complex and Zinc Porphyrin-Ruthenium Complex Dyads

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Photoinduced electron transfer processes in multicomponent donor-acceptor systems, in which electron donor and acceptor are chemically linked, have received much attention with the goal of understanding the primary processes in natural photosynthesis and of designing photochemical molecular devices for energy conversion and information processing.[1-7] A number of porphyrin systems covalently linked to various electron acceptors and donors has been extensively studied.[1-3,7] Ruthenium polypyridyl complexes have also been widely used as suitable photoactive components in multicomponent systems.[4-7] Porphyrins connected to ruthenium polypyridyl complexes have also been reported.[8-11]

We have prepared a dyad (TTP-CH₂NHCO-Ru(bpy)₃, TTP-Ru) composed of 5,10,15,20-tetra(*p*-tolyl)porphyrin (TTP) and ruthenium tris(2,2'-bipyridyl) complex (Ru(bpy)₃) subunits, which are functionalized for connection by an amide linkage. Hammarstrom and co-workers has recently reported similar dyad (TTP-NHCO-Ru(bpy)₃).[11] We report here the preparation and fluorescence properties of TTP-Ru and ZnTTP-Ru dyads and photoinduced electron transfer from S₁ state of ZnTTP to a covalently linked Ru(bpy)₃.

Experimental Section

Synthesis

5-(4-Cyanophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (TTP-CN). TTP-CN was prepared according to synthetic procedure reported for closely related tetraarylporphyrin systems.[12-13] ¹H NMR in CDCl₃ (300 MHz): δ 8.70-90 (8H, m, pyrrole), 8.33 (2H, d, J = 8.3 Hz, 5Ar2-H and 6-H), 8.08 (6H, d, J = 8.0 Hz, 10,15,20Ar2-H and 6-H), 8.04 (2H, d, J = 8.3 Hz, 5Ar3-H and 5-H), 7.55 (6H, d, J = 8.0 Hz, 10,15,20Ar3-H and 5-H), 2.70 (9H, s, Ar-CH₃), -2.78 (2H, s, pyrrole-NH).

5-(4-Aminomethylphenyl)-10,15,20-tris(4-methylphenyl)porphyrin(TTP-CH₂NH₂). TTP-CN (400 mg, 0.59 mmol) was dissolved in 100 mL of dry THF and LiAlH₄ (67 mg, 1.77 mmol) in small amount (3-4 mL) of dry THF was added. The solution was refluxed under an argon atmosphere for 1 hr. Reaction mixture was poured into saturated aqueous

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NaHCO₃ solution and then extracted with dichloromethane. Dichloromethane layer was evaporated and dried under vacuum. The resulting purple solid was purified by column chromatography with dichloromethane and acetone. Disappearance of IR band at *ca.* 2230 cm⁻¹ indicates absence of CN functional group and N-H stretch band at *ca.* 3300 cm⁻¹ is observed. ¹H NMR in CDCl₃ (300 MHz): δ 8.86 (8H, m, pyrrole-NH), 8.10 (8H, d, J = 7.6 Hz, Ar2-H and 6-H), 7.52 (8H, d, J = 7.6 Hz, Ar3-H and 5-H), 4.18 (2H, s, Ar-CH₂NH₂), and 2.67 ppm (9H, s, Ar-CH₃), -2.63 (2H, s, pyrrole-NH).

5-(4-(4'-Methyl-2,2'-bipyridine-4-carboxamido)methylphenyl)-10,15,20-tris(4-methylphenyl)-porphyrin (TTP-CH₂NHCO-mbpy). A 21.4 mg (0.1 mmol) portion of mbpy-COOH[14] was dissolved in 5 mL of dry toluene and 0.5 mL of dry pyridine, and 2 mL of thionyl chloride was added. After stirring the solution under argon for 40 min, the solvent was evaporated to dryness under vacuum to remove the excess thionyl chloride. To the residue were added 20 mL of freshly distilled dichloromethane and 0.1 mL of dry pyridine. Subsequently, 68.6 mg (0.1 mmol) of TTP-CH₂NH₂ was added and the solution was refluxed under argon for 30 min. The reaction mixture was evaporated and redissolved with 30 mL of dichloromethane and washed with a saturated aqueous solution of sodium bicarbonate and once with water and dried with sodium sulfate. The solvent was evaporated and the crude product was purified by column chromatography on silica gel with 3% methanol/dichloromethane to afford 44 mg (0.05 mmol, 50% yield) of pure TTP-CH₂NHCO-mbpy. ¹H NMR in CDCl₃ (300 MHz): δ 8.76-8.91 (9H, m, TTP pyrrole and mbpy 6-H), 8.55 (2H, s and d, J = 4.1 Hz, mbpy 3-H and 6'-H), 8.30 (s, 1H, mbpy 3'-H), 8.22 (2H, d, J = 7.8 Hz, TTP 5Ar 2-H and 6-H), 8.09 (6H, d, J = 7.8 Hz, TTP 10,15,20Ar 2-H and 6-H), 7.81 (1H, m, mbpy 5-H), 7.77 (2H, d, J = 7.8 Hz, TTP 5Ar 3-H and 5-H), 7.55 (6H, d, J = 7.8 Hz, TTP 10,15,20Ar 3-H and 5-H), 7.23 (1H, d, J = 4.1 Hz, mbpy 5'-H), 2.77 (2H, s, -CH₂NH-), 2.70 (9H, s, TTP Ar-CH₃), 2.50 (s, 3H, mbpy 4'-CH₃), -2.63 (2H, s, TTP pyrrole-NH).

Bis(2,2'-bipyridine) (5-(4-N-(4'-methyl-2,2'-bipyridine-4-carboxy)aminomethylphenyl)-10,15,20-tris(4-methylphenyl)porphyrin)ruthenium(II) bis(hexafluorophosphate) (TTP-Ru dyad). 13 mg (0.025 mmol) of Ru(bpy)₂Cl₂·2H₂O[15] and 22 mg (0.025 mmol) of TTP-CH₂NHCO-mbpy were sus-

pended in 50 mL of 70% ethanol. The mixture was refluxed for 10 hr. The reaction mixture was cooled to room temperature and the ethanol was evaporated. After standing overnight, the mixture was filtered and the remaining solid was washed with water. The product was precipitated from water as its PF_6^- salt by adding saturated aqueous NH_4PF_6, and then filtered and dried in vacuum. Red-brown solid; IR: 1592, 1505, 1424, 1116, 988, 885, 846, 818, 778, 737 cm^{-1}. ^1H NMR in $CDCl_3$ (300 MHz): δ 8.74-8.90 (13H, m, 8x TTP pyrrole, 4x bpy 3-H, and mbpy 3-H), 8.59 (1H, m, mbpy 3'-H), 8.21 (2H, d, $J = 8.1$ Hz, TTP 5Ar 2-H and 6-H), 8.09 (6H, d, $J = 7.8$ Hz, TTP 10,15,20Ar 2-H and 6-H), 7.96-8.05 (5H, m, 4x bpy 4-H and mbpy 6-H), 7.75 (2H, d, $J = 8.1$ Hz, TTP 5Ar 3-H and 5-H), 7.70 (1H, m, mbpy 6'-H), 7.55 (6H, d, $J = 7.8$ Hz, TTP 10,15,20Ar 3-H and 5-H), 7.52-7.61 (5H, m, 4x bpy 6-H and mbpy 5-H), 7.46-7.48 (4H, m, 4x bpy 5-H), 7.31-7.35 (1H, m, mbpy 5'-H), 2.71 (9H, s, TTP Ar-CH_3), 2.68 (2H, s, $-CH_2NH-$), 2.63 (s, 3H, mbpy 4'-CH_3), -2.79 (2H, s, TTP pyrrole-NH).

ZnTTP-Ru dyad. A 1 : 4 methanol:dichloromethane solution of TTP-Ru dyad with an excess of zinc acetate was stirred at room temperature for 24 hrs. Dark-brown solid; IR: 1617, 1594, 1501, 1307, 1114, 1014, 892, 836, 810, 788, 770, 734 cm^{-1}.

Spectroscopic and photochemical measurements. ^1H NMR spectra were measured on 300 MHz Varian UNITY plus 300 spectrometer in chloroform-d_1. IR spectra were obtained in KBr pellets on Midac Prospect-IR spectrometer. Absorption spectra were recorded on a Hitachi U-3210 spectrophotometer. Steady state emission spectra were recorded on a SLM-AMINCO AB2 luminescence spectrometer. Fluorescence decay measurements were performed using the time-correlated single photon counting method.

Results and Discussion

Absorption spectra. As shown in Table 1, the TTP-Ru dyad features a Soret absorption at 420 nm and four Q bands at 500-650 nm attributable to the TTP moiety.[7,16] The 456 nm band is due to metal-to-ligand charge-transfer (MLCT) band of Ru moiety.[7,17] For the ZnTTP-Ru dyad, a Soret absorption at 420 nm and two Q bands at 549 and 587 nm are from ZnTTP moiety.[7,13] The 456 nm band is due to MLCT band of Ru moiety. The absoprtion spectra of two dyads are similar to the sum of the absorption spectra of the component chromophores. This suggests a negligible electronic interaction between its individual component porphyrin and Ru moieties.

Fluorescence properties. As shown in Table 2, the fluorescence spectral shape of TTP-Ru dyad, with maxima at 653 and 720 nm is identical, within experimental error, to that of the reference compound TTP. The excitation of either the porphyrin Q-bands (S_1 band) or the Soret band (S_2 band) of the TTP-Ru dyad gives similar fluorescence spectral shapes as well as similar Φ_f of 0.12 ($\lambda_{ex}=515$ nm) and 0.13 ($\lambda_{ex}=410$ nm). The fluorescence lifetimes are determined to be 8.5 ns for TTP-Ru dyad which is similar to 8.6 ns for the reference

Table 1. Absorption maxima (λ_a^{max}), lowest singlet state energy (E_s), and half-wave potentials ($E_{1/2}$) for TTP-Ru, ZnTTP-Ru and the reference compounds TTP, ZnTTP, and Ru[a] in dichloromethane at room temperature

Compound	λ_a^{max}, nm			E_s, eV	$E_{1/2}$, V	
	Porphyrin		Ru		ox	red
	Soret band	Q band				
TTP-Ru	420	516,552,592,648	456	1.90	-	-
ZnTTP-Ru	420	549, 587	456	2.09	-	-
TTP	420	516,552,594,650	-	1.90	0.93^b	-1.20^b
ZnTTP	420	549, 589	-	2.09	0.74^c	-1.36^c
Ru[a]	-	-	456	2.00	1.27	-1.28

[a]Ru=[Ru(II)(bpy)$_2$(mbpy-CONHCH$_3$)](PF$_6$)$_2$, where mbpy-CONHCH$_3$ is 4'-methyl-2,2'-bipyridine-4-carboxyamidomethane. Data from references 17 and 29. ^{b}Data from reference 18. ^{c}Data for zinc 5,15-bis(4-aceamido-phenyl)-10,20-bis(4-methylphenyl)porphyrin from reference 15.

compound TTP.

The fluorescence spectrum of ZnTTP-Ru dyad shows a structured band with maxima at 598 and 648 nm and is quenched compared to that of the reference compound ZnTTP, but the spectral shape is the same. The excitation of either the porphyrin Q-bands or the Soret band of the ZnTTP-Ru dyad gives similar fluorescence spectral shapes and shows no emission contributed from the Ru moiety, implying that energy transfer from ZnTTP moiety to Ru moiety may not be significant. Therefore, electron transfer is most likely quenching mechanism. The excitation into the porphyrin Q-bands (S_1 band) of the ZnTTP-Ru dyad gives rise to the reduction of fluorescence quantum yield ($\Phi_f=0.028$) relative to that of ZnTTP ($\Phi_f=0.049$), presumably due to quenching by electron transfer from excited Zn porphyrin moiety to Ru complex moiety.

The S_2 fluorescence of metalloporphyrins was observed due to relatively large energy differences between the S_1 and S_2 states as well as very intense $S_0 \rightarrow S_2$ absorption, while no S_2 fluorescence has been detected from the free base porphyrins was observed due to a small energy gap.[7] On excitation into the Soret band (S_2 band) ($\lambda_{ex}=410$ nm) in the reference compound ZnTTP, fluorescence quantum yield ($\Phi_f=0.046$)

Table 2. Fluorescence maxima (λ_f^{max}), quantum yields (Φ_f), lifetimes (τ_f) for TTP-Ru, ZnTTP-Ru and the reference compounds TTP, ZnTTP, and Ru[a] in dichloromethane at room temperature

Compound	λ_f^{max}, nm	Φ_f		τ_f, ns
		λ_{ex}=Soret band	λ_{ex}=Q band	
TTP-Ru	653, 720	0.13	0.12	8.5^c
ZnTTP-Ru	598, 648	0.017	0.028	2.3^d
TTP	653, 719	0.15^b		8.6^c
ZnTTP	598, 648	0.046	0.049	5.1^d
Ru[a]	645	0.087		1380

[a]Ru=[Ru(II)(bpy)$_2$(mbpy-CONHCH$_3$)](PF$_6$)$_2$, where mbpy-CONHCH$_3$ is 4'-methyl-2,2'-bipyridine-4-carboxyamidomethane. For Ru, data in this table are not related to fluorescence but luminescence, and from reference 19. ^{b}Data from reference 13. $^c\lambda_{ex}=592$ nm, $\lambda_{em}=720$ nm. $^d\lambda_{ex}=587$ nm, $\lambda_{em}=648$ nm.

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is only slightly decreased compared with that on excitation of S_1 band (Φ_f=0.049). When S_2 band (λ_{ex}=410 nm) in the ZnTTP-Ru dyad is excited, fluorescence quantum yield (Φ_f= 0.017) is further decreased to *ca.* 60% of that on excitation of S_1 band (Φ_f=0.028). This suggests that only 60% of the S_2 population convert to S_1, as demonstrated for similar dyad system.[11] It is tentatively inferred that there is an additional deactivation channel from S_2 state, such as intramolecular photoinduced electron transfer from S_2 state of ZnTTP moiety to Ru moiety.

The fluorescence lifetimes in dichloromethane are determined to be 2.3 ns for ZnTTP-Ru dyad, which is significantly decreased in comparison with 5.1 ns for ZnTTP. This is consistent with the results of fluorescence quantum yield, suggesting that there are some quenching processes such as electron transfer from excited Zn porphyrin moiety to Ru complex moiety.

Photoinduced Electron Transfer

TTP-Ru dyad. The energy of the excited singlet state of TTP is calculated to be 1.90 eV and the energy of the ^{3}MLCT excited state of Ru(bpy)$_2$(mabpy) (PF$_6$)$_2$ complex (mabpy= N-isopropyl-4methyl-2,2-bipyridine-4-carboxamide), a model compound of Ru(bpy)$_3$ moiety in TTP-Ru dyad, was calculated to be 2.00 eV.[18] The energy of TTP$^{•+}$-Ru$^{•-}$ and TTP$^{•-}$-Ru$^{•+}$ charge separated states can be roughly estimated to be 2.21 eV and 2.47 eV, respectively, from the electrochemical data in Table 1.

Photoinitiated electron transfer is endergonic by about 0.31 eV for electron transfer from the excited ^{1}TTP moiety to Ru moiety, and by about 0.47 eV for electron transfer from the excited ^{3}MLCT Ru moiety to TTP moiety. Therefore, reductive or oxidative electron transfer quenching is thermodynamically unfavorable. This is consistent with the fact that neither significant reduction of fluorescence quantum yield nor shortening of fluorescence lifetime in TTP-Ru dyad in comparison with those of TTP has been observed.

ZnTTP-Ru dyad. On the basis of the electrochemical data (Table 2), ZnTTP$^+$-Ru$^-$ charge transfer state can be placed around 2.02 eV, *i.e.* slightly below the S_1 excited state of the ZnTTP moiety (2.09 eV)[13] and slightly above the ^{3}MLCT level of the Ru-based moiety (2.00 eV). The situation is therefore substantially different from that exhibited by TTP-Ru. The oxidative electron transfer quenching is thermodynamically favorable. On the other hand, reductive quenching is energetically unfavorable, because the energies of ZnTTP$^{•-}$-Ru$^{•+}$ charge separated state can be estimated to 2.63 eV. Therefore, electron transfer from the excited ZnTTP moiety to Ru moiety is most likely quenching mechanism. However, other quenching mechanism or a possibility of intermolecular electron transfer cannot be excluded. The electron transfer quenching rate constant for the ZnTTP-Ru dyad has been estimated to be 2.4×10^8 s^{-1}. Since this rate is only

slightly faster than the intrinsic deactivation rate of the S_1 level (2.0×10^8 s^{-1}), estimated from the fluorescence lifetime of the model compound ZnTTP, it is inferred that the electron-transfer process is not 100% efficient.

The understanding for the detailed deactivation processes of the excited state in ZnTTP dyad needs further work including transient spectroscopic study.

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