Synthesis of a Porphyrin Derivative Covalently linked to Nickel Aza-macrocycle Complex[†]

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A porphyrin derivative covalently linked to Ni aza-macrocycle complex has been prepared. Absorption spectrum of porphyrin-Ni aza-macrocycle dyad (λ_a^{max} =230, 416 nm) was observed to similar to a sum of those of tetratolylporphyrin (λ_a^{max} =419 nm) and Ni aza-macrocycle (λ_a^{max} =227 nm), indicating no electronic interaction between porphyrin and Ni aza-macrocycle moieties. Fluorescence quantum yield of dyad (Φ_f=0.10) was same to that of tetratolylporphyrin (Φ_f=0.10). Photoinduced intramolecular electron transfer or energy transfer from excited porphyrin moiety to Ni(II) aza-macrocycle moiety should be very inefficient in dyad.

key words: fluorescence, dyad, porphyrin, Ni aza-macrocycle

INTRODUCTION

Photoinduced electron transfer processes in multicomponent donor-acceptor systems, in which electron donor and acceptor are chemically linked, have been received much attention with the goals of understanding the primary processes in natural photosynthesis and of designing photochemical molecular devices for energy conversion and information processing [1-8]. One approach to find photoactive components is mimicking natural system. In natural photosynthetic systems, the primary electron transfer step following light absorption occurs from a porphyrin-based complex [1,2,4]. A number of porphyrin systems covalently linked to various electron acceptor and donor has been extensively studied [1-3,7]. In most cases, porphyrin has been employed as both a photon absorber and an electron donor. Numerous electron acceptors such as quinone, viologen, C_{60}, other porphyrin and ruthenium trisbipyridine were used in the covalently linked donor-acceptor system [1-8]. However, dyad molecule Porphyrin-Ni macrocycle, in which Ni macrocycle is covalently attached to a photosensitizer porphyrin, has been scarcely reported [9]. Bimetallic porphyrin complexes have been received much attention not only as multicomponent photoinduced electron transfer system, but also as synthetic analogues of active sites in biological processes such as polymetallic enzyme.

In this point of view, we have prepared a dyad, TTP-Ni aza-macrocycle, composed of 5,10,15-tris(*p*-tolyl)-20-(*p*-carboxyphenyl) porphyrin and nickel aza-macrocycle complex subunits. We report here the preparation and fluorescence properties of TTP-Ni aza-macrocycle dyad and the photoinduced electron

transfer from S_1 state of TTP to a covalently linked Ni aza-macrocycle will be discussed.

MATERIALS AND METHODS

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 [10-12]. To 25 g (0.19 mol) of 4-cyanobenzaldehyde and 25 mL(0.23 mol) of p-tolualdehyde in 1.2 L of propionic acid at 90 °C was added 26.5 mL(0.38 mol) of pyrrole. The mixture was refluxed for 2 hrs and then cooled to room temperature. The reaction mixture was evaporated and dried under vacuum. Column chromatography on silica gel with dichloromethane and hexane gave successively 5,10,15,20-tetra(4-methylphenyl)porphyrin (TTP), 5-(4-cyanophenyl)-10,15,20-tris(4-methylphenyl)porphyrin (TTP-CN), 5,15-bis(4-cyanophenyl)-10,20-bis(4-methylphenyl)porphyrin, 5,10-bis(4-cyanophenyl)-15,20-bis(4-methylphenyl)porphyrin, 5,10,15-tris(4-cyanophenyl)-20-(4-methylphenyl)porphyrin, 5,10,15, 20-tetra(4-cyanophenyl)porphyrin. TTP-CN was obtained in ca. 1% yield. UV-Vis λ_a^{max} in dichloromethane: 420, 516, 552, 594, 650 nm. Fluorescence λ_f^{max} in dichloromethane: 653, 720 nm. ^{1}H NMR in CDCl$_3$(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, 10,15,20 Ar2-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-CH$_3$), -2.78(2H, s, pyrrole-NH) ppm.

5-(4-Carboxyphenyl)-10,15,20-tris(4-methylphenyl)porphyrin (TTP-COOH) 5-(4-Carboxyphenyl)-10,15,20-tris(4-methylphenyl) porphyrin was prepared by hydrolysis of 5-(4-cyanophenyl)-10,15,20-tris(4-methylphenyl)porphyrin with strong acid. 5-(4-cyanophenyl)-10,15,20-tris(4-methylphenyl)porphyrin(300 mg, 0.44 mmol) was dissolved in 12 mL of conc. HCl and 20 mL of CF$_3$COOH. The solution was refluxed under an argon atmosphere

for 2 days. The reaction progress was monitored by TLC with 3% methanol/chloroform. NaHCO₃ lump was added into the reaction mixture until color changes from green to purple. Purple solid was filtered and rinsed with distilled water and dried. The yield was 87%. The structure was identified by spectral data. Disappearance of IR band at ca. 2230 cm⁻¹ indicates absence of CN functional group and C=O and O-H stretch band at ca. 1700 and 3300 cm⁻¹ was observed. UV-Vis λ_a^{max} in dichloromethane: 419, 517, 552, 592, 648 nm. Fluorescence λ_f^{max} in dichloromethane: 655, 720 nm. ¹H NMR in DMSO-d₆(300 MHz): δ 8.7-8.9 (8H, m, pyrrole-H), 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), -2.63 (2H, s, pyrrole-NH) ppm.

TTP-Ni aza-macrocycle dyad 1 A 100 mg (0.14 mmol) portion of TTP-COOH was dissolved in 40 mL of dry benzene and 0.16 mL of dry pyridine, and 72 µL of thionyl chloride was added. The initial purple suspension was rapidly converted into dark green solution. 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, 57.5 mg (0.14 mmol) of Ni aza-macrocycle prepared by the literature method [13], 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 dehydrated 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 21 mg (0.02 mmol, 14% yield) of TTP-Ni aza-macrocycle dyad 1. FAB-Mass: m/z 1111.

Spectroscopic measurements ¹H-NMR spectra were measured on 300 MHz Varian UNITY plus 300 spectrometer in chloroform-d₁. FAB-Mass spectra were obtained on JEOL JMS HX-110/110A Tandem Mass Spectrometer. Absorption spectra were recorded on a Hitachi U-3210 spectrophotometer. Steady state fluorescence spectra were recorded on a SLM-AMINCO AB2 luminescence spectrometer. Fluorescence quantum yields Φ_f were determined using 5,10,15,20-tetra(4-methylphenyl)porphyrin (TTP) as a standard (Φ_f=0.12 in benzene) [14].

RESULTS AND DISCUSSION

The absorption spectrum of TTP-Ni aza-macrocycle dyad 1 in acetonitrile is represented along with those of model compounds TTP, TTP-COOH, and Ni aza-macrocycle 2 in Figure 1. Their structures are represented in Scheme 1. The absorption spectrum of the reference compound TTP-COOH in acetonitrile shows the very intense Soret band with a maximum at 416 nm and the weaker four Q bands in the range of 500-650 nm. The absorption spectrum of the TTP-Ni aza-macrocycle dyad 2 in dichloromethane (λ_a^{max} =230, 416 nm)
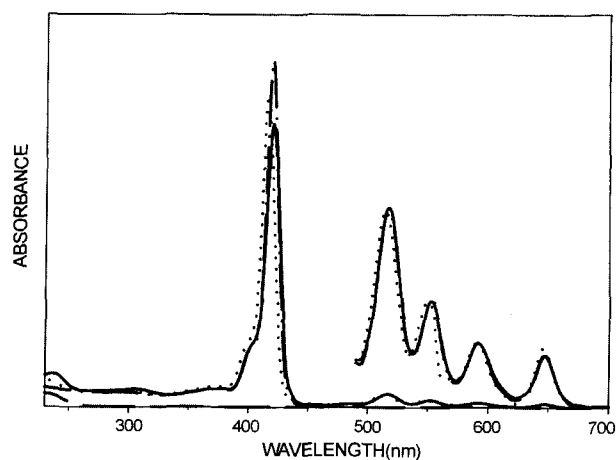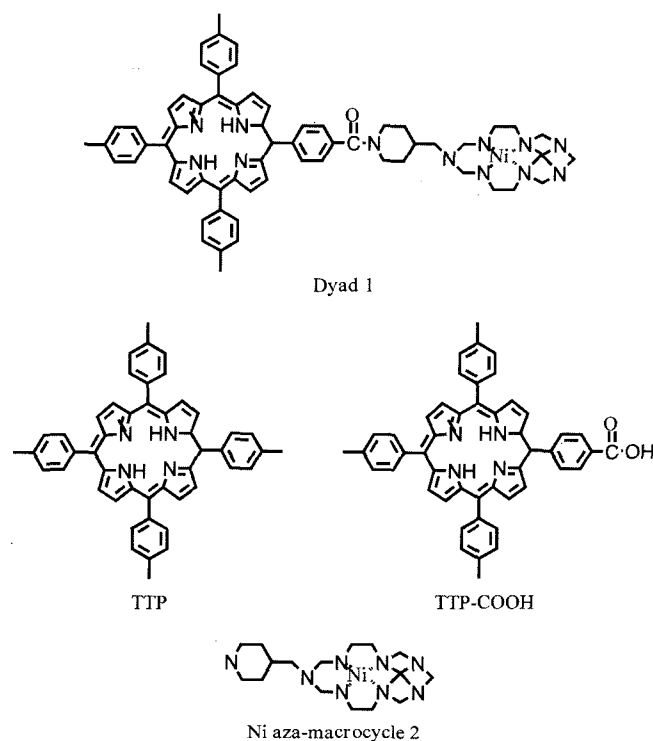

Figure 1. Absorption spectra of TTP-Ni aza-macrocycle dyad 1 (solid line) and the reference compounds, TTP (dash-dotted line) in dichloromethane, TTP-COOH (dotted line), and Ni aza-macrocycle 2 (dashed line) in acetonitrile.

Scheme 1. Structures of TTP-Ni aza-macrocycle dyad 1 and the reference compounds TTP, TTP-COOH, Ni aza-macrocycle complex 2.

features a Soret absorption band at 416 nm attributable to the TTP moiety and an absorption band at 230 nm attributable to Ni aza-macrocycle moiety. The absorption spectrum of dyad is superimposed to a sum of those of TTP and Ni aza-macrocycle 2, indicating no electronic interaction between two moieties in dyad. Absorption and fluorescence data for TTP-Ni aza-macrocycle dyad 1 and the reference compounds TTP, TTP-COOH, and Ni aza-macrocycle 2 in dichloromethane

Table 1. Absorption maxima(λ_a^{max}), fluorescence maxima(λ_f^{max}), fluorescence quantum yields(Φ_f), lowest singlet state energy(E_s), and half-wave potentials($E_{1/2}$) for TTP-Ni aza-macrocycle dyad along with the model compounds TTP, TTP-COOH, and Ni aza-macrocycle in dichloromethane at room temperature

Compound	λ_a^{max}, nm	λ_f^{max}, nm	Φ_f	E_s, eV	$E_{1/2}$, V	
					ox	red
TTP	419, 516, 552, 592, 646	654, 720	0.10	1.90	+0.93[3]	-1.20[3]
TTP-COOH[1]	416, 514, 548, 590, 646	651, 717	0.11	1.90	-	-
Ni complex 2[1]	206, 227, 441	n. d.[2]	n. d.[2]	-	+1.43[4]	-1.39[4]
Dyad 1	230, 419, 516, 552, 592, 646	653, 720	0.10	-	-	-

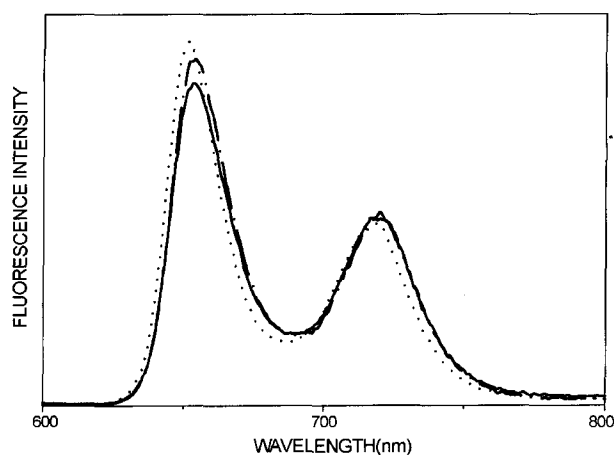[1]In acetonitrile. [2]n.d.=not detected. [3]From ref. 14. [4]From ref. 15.

Figure 2. Fluorescence spectra of TTP-Ni aza-macrocycle dyad 1 (solid line) and the reference compounds, TTP (dash-dotted line) in dichloromethane, and TTP-COOH (dotted line) in acetonitrile.

at room temperature are collected in Table 1. Absorption of Ni aza-macrocycle 2 at 441 nm is extremely weak. The extinction coefficients of absorption bands for Ni aza-macrocycle 2 are 14,040 M^{-1} cm^{-1} at 206 nm, 13,770 M^{-1} cm^{-1} at 227 nm, and 71 M^{-1} cm^{-1} at 441 nm.

Figure 2 shows the fluorescence spectra for TTP-Ni aza-macrocycle dyad 1 and the reference compounds TTP, TTP-COOH, and Ni aza-macrocycle 2 in dichloromethane. Fluorescence maxima of dyad 1 appear at 653 and 720 nm (see Table 1). The fluorescence spectral shape is identical to that of the reference compound TTP or TTP-COOH. Ni aza-macrocycle 2 shows no emission. Fluorescence quantum yield for TTP-Ni aza-macrocycle dyad in dichloromethane (Φ_f=0.10) at the excitation wavelength of 590 nm is determined relative to that of TTP in benzene (Φ_f=0.12) [14].

The energy of the excited singlet state of TTP is calculated to be 1.90 eV from the average of the frequencies of the longest-wavelength absorption maximum and shortest-wavelength emission maximum. The energy of TTP*+-Ni aza-macrocycle*− charge separated state can be roughly estimated to be 2.32 eV from the electrochemical data (Table 1) by using following equation [7].

$$\Delta G^\circ = E_{1/2}(TTP^{+/0}) - E_{1/2}(Ni^{+2/+1})$$

where the half-wave potentials for the oxidation of TTP, $E_{1/2}$ (TTP$^{+/0}$), is 0.93 V vs SCE [15] and the half-wave potentials for the reduction of Ni aza-macrocycle, $E_{1/2}(Ni^{+2/+1})$, is -1.37 V vs Ag/AgCl electrode (-1.39 V vs. SCE) [13]. The half-wave potentials for oxidation and reduction processes found for TTP and Ni aza-macrocycle, the model compounds of TTP-Ni aza-macrocycle dyad, are summarized in Table 1. The half-wave potential for the reduction of TTP, $E_{1/2}(TTP^{0/-})$, is -1.20 V vs. SCE [14]. The half-wave potential for the oxidation of Ni aza-macrocycle, $E_{1/2}(Ni^{+3/+2})$, in acetonitrile is +1.45 V vs. Ag/AgCl electrode (+1.43 V vs. SCE) [13]. By using these values, the energy of TTP*−-Ni aza-macrocycle*+ charge separated state is roughly estimated to be 2.65 eV. Photoinitiated electron transfer is endergonic by about 0.42 eV for oxidative electron transfer from the excited ^{1}TTP moiety to Ni aza-macrocycle moiety, and by about 0.75 eV for reductive electron transfer from the excited ^{1}TTP moiety to Ni aza-macrocycle moiety. Therefore, either oxidative or reductive electron transfer quenching is thermodynamically unfavorable. This is consistent with the fact that no significant reduction of fluorescence quantum yield in TTP-Ni aza-macrocycle dyad 1 in comparison with that of TTP has been observed.

Modulation of redox potential by the structural modification for porphyrin moiety and/or Ni aza-macrocycle moiety may lead to lower the charge-separated state energy and, therefore, to find out mono-/bi-metallic porphyrin-Ni aza-macrocycle dyad performing efficient photoinduced intramolecular electron transfer.

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