Self-Assembly of Zincporphyrin Dimer and Pyromellitimide Using Two Coordination Bonds and Photoinduced Intramolecular Electron Transfer

Koji Yamada, Hiroshi Imahori,* Eiichi Yoshizawa, David Gosztola,† Michael R. Wasielewski,*†,†† and Yoshiteru Sakata*
The Institute of Scientific and Industrial Research (ISIR), Osaka University, 8-1 Mihoga-oka, Ibaraki, Osaka 567-0047
†*Chemistry Division, Argonne National Laboratory, Argonne, Illinois 60439-4831, U.S.A.*
††*Department of Chemistry, Northwestern University, Evanston, Illinois 60208-3113, U.S.A.*

(Received December 3, 1998; CL-980900)

Zincporphyrin dimer-pyromellitimide supramolecule has been designed and assembled using two coordination bonds. Photoinduced charge separation and charge recombination in the supramolecule were observed by picosecond time-resolved transient absorption measurements.

The primary electron transfer (ET) events in the photosynthesis take place unidirectionally along an array of chromophores embedded in the protein matrix.[1] Donor (D) and acceptor (A) have been covalently linked to understand the factors controlling ET in the biological systems. Considering that weak molecular interactions such as hydrogen-bonds, coordination bonds, and electrostatic interactions are employed for molecular assembly in nature, it is important to develop non-covalently linked D-A systems. So far there have been a number of reports about hydrogen-bonded D-A systems,[2] while less attention has been paid for non-covalent systems using coordination bonds.[3-9] We have already reported self-assembly of zincporphyrin dimer **1** and benzoquinone with two pyridyl groups **2** as shown in Figure 1.[7,8] The two-point coordination-bond approach allows selective formation of the 1:1 bridging supramolecule with the relatively rigid geometry in solution. However, owing to the instability of the quinone as well as the lack of strong bands due to the resulting anion radical produced *via* photoinduced ET, it was difficult to investigate the photodynamics of the supramolecule **1-2**. Bearing these in mind, we designed a new acceptor **3** where the acceptor moiety in **2** is replaced by a pyromellitimide. Advantage of the complex **1-3** over other complexes **1-2**, **7-3**, and **7-5** is the following two points. First, combination of **1** and **3** will make it possible to generate the high concentration of the supramolecule **1-3** in solution exclusively. Second, it is well established that pyromellitimide anion radical (Im$^-$) has a characteristic intense band at around 700 nm.[10] Thus, it is expected that photoinduced charge separation (CS) and charge recombination (CR) processes in the complex **1-3** can be monitored and accurately analyzed using picosecond time-resolved absorption spectroscopy.

Zincporphyrin dimer **1** and the reference **4** and **7** were prepared as described in the previous paper.[7,8] The synthesis of pyromellitimides **3**, **5**, and **6** was carried out according to the literature[4] by refluxing a mixture of pyromellitic dianhydride and the corresponding amines in DMF. The molecular structures of these compounds were confirmed on the basis of spectroscopic data.[11]

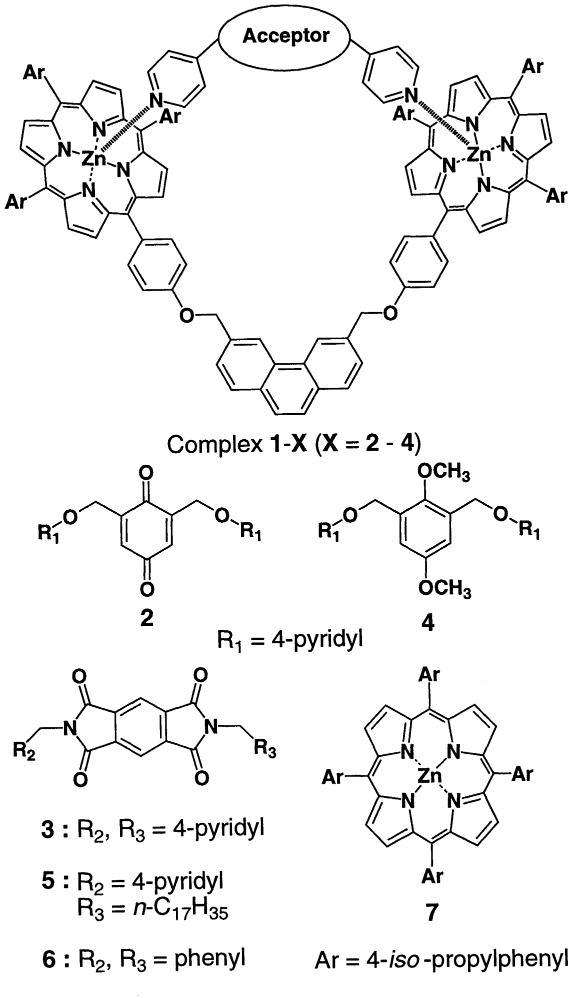

Figure 1.

The structure of the complex **1-3** was established by UV-visible spectrophotometric titrations of **1** (8.0×10^{-7} mol dm^{-3}) with **3** and **5** (10^{-7} to 10^{-4} mol dm^{-3}) in CH_2Cl_2 using the band shift in Soret absorption on ligation.[12] The binding constant (K_1) of **1** and **3** was determined to be 2.6×10^6 dm^3 mol^{-1}. The value is at least two orders of magnitude larger than that for **1** and **5** ($K_1 = 1.8 \times 10^4$ dm^3 mol^{-1}, $K_2 = 4.2 \times 10^3$ dm^3 mol^{-1}) and that for **7** and **5** ($K_1 = 7.6 \times 10^3$ dm^3 mol^{-1}), and 1/4 times smaller than that for **1** and **4** ($K_1 = 1.1 \times 10^7$ dm^3 mol^{-1}).[13] These results show that **1** and **3** form the 1:1 bridged structure exclusively, while **1** and **5** as well as **7** and **5** make the weaker complexation. However, the structure of the complex **1-3** is somewhat unstabilized compared with that of the complex **1-4**. This may be attributed to the difference in the distance between the two binding sites in **3** and **4** as well as in the electron donating ability between the spacer in **3** and **4**.

The fluorescence quenching of **1** (8.0×10^{-7} mol dm^{-3}) in CH_2Cl_2 with excitation at 428 nm was investigated by the addition of 50 equivalent of **3** or **4**. After the addition, the peak positions of α and β-emission bands are red-shifted by about 20 nm, implying that the two pyridine ligands in **3** or **4** remain coordinated to both the zincporphyrins in the excited states. The relative intensity for the fluorescence of **1**-**3** versus **1**-**4** is 0.08, which is similar to that (0.06) of **1**-**2** versus **1**-**4**. These results indicate that intramolecular ET occurs from the excited singlet state of the porphyrin to the pyromellitimide.[14] We can rule out the possibility of intermolecular photoinduced ET because of no fluorescence quenching of **1** by the addition of **6**.

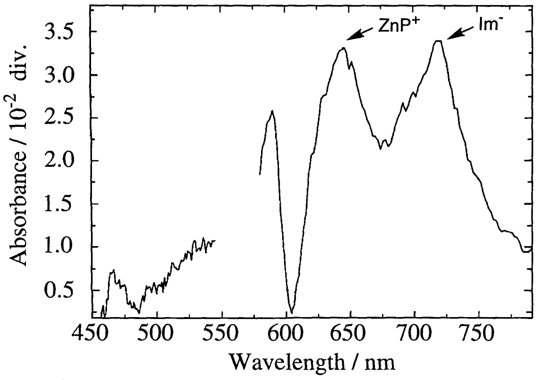

Figure 2. Time-resolved transient absorption spectrum of the complex **1**-**3** at time delay of 45 ps excited at 560 nm in CH_2Cl_2.

Transient absorption spectrum of the complex **1**-**3** (1.2×10^{-4} mol dm^{-3}) in CH_2Cl_2 at 45 ps following excitation with 560 nm laser pulse displays characteristic bands due to zincporphyrin cation radical (ZnP^+) and Im^- at 644 nm and 719 nm, respectively (Figure 2). The time profile of the absorbance at 720 nm was analyzed by a rise with a time constant with 47 ps and a decay with that of 78 ps (Figure 3). On the basis of these values, the rate constants for photoinduced CS (k_{CS}) and CR (k_{CR}) are estimated to be 2.1×10^{10} s^{-1} and 1.3×10^{10} s^{-1}, respectively. Similarly, the ET rates for the complex **7**-**5** were found to be $k_{CS} = 2.5 \times 10^{10}$ s^{-1} and $k_{CR} = 9.4 \times 10^9$ s^{-1}. Considering that the rates for the complex **7**-**5** are almost the same as those for the complex **1**-**3**, we can conclude that the difference of the supramolecular structures between the two systems does not affect the ET process substantially. The CS rate for the complex **1**-**3** is similar to that (1.6×10^{10} s^{-1}) for the complex **1**-**2**. The changes in $-\Delta G_{CS}$ and the electronic coupling would compensate one another in the k_{CS} and therefore, the CS rates do not vary much. Sanders et al. reported photoinduced ET in the similar zinctetraphenylporphyrin monomer-pyromellitimide system using a coordination bond.[4] The CS and CR values in the present system are larger by a factor of 4-5 and 10-14 than their values ($k_{CS} = 5.33 \times 10^9$ s^{-1} and $k_{CR} = 9.40 \times 10^8$ s^{-1}), respectively. The discrepancy can be explained by the difference in their monitoring wavelength region (420 - 540 nm) where the characteristic bands due to ZnP^+ and Im^- do not appear.[15] Thus, lack of observing the characteristic bands in their system may lead to the wrong conclusion.

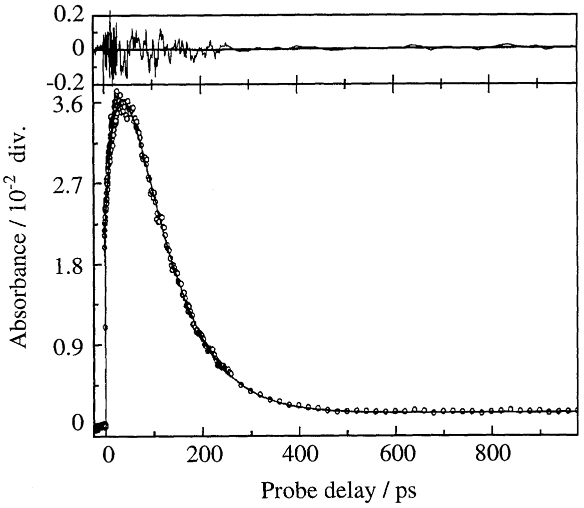

Figure 3. Transient kinetics of the complex **1**-**3** at 720 nm in CH_2Cl_2 excited at 560 nm.

In conclusion, we have developed photoactive supramolecule consisting of zincporphyrin dimer and pyromellitimide with two coordination bonds. Intramolecular photoinduced CS and CR were detected clearly using picosecond time-resolved transient absorption spectroscopy. Our study will provide a new approach in the design of photoactive devices.

References and Notes

1 "The Photosynthetic Reaction Center," ed by J. Deisenhofer and J. R. Norris, Academic Press, CA (1993).

2 P. Wallimann, T. Marti, A. Fürer, and F. Diederich, *Chem. Rev.*, **97**, 1567 (1997).

3 H. L. Anderson, C. A. Hunter, and J. K. M. Sanders, *J. Chem. Soc., Chem. Commun.*, **1989**, 226.

4 C. A. Hunter, J. K. M. Sanders, G. S. Beddard, and S. Evans, *J. Chem. Soc., Chem. Commun.*, **1989**, 1765.

5 C. A. Hunter and R. J. Shannon, *Chem. Commun.*, **1996**, 1361.

6 C. A. Hunter and R. K. Hyde, *Angew. Chem., Int. Ed. Engl.*, **35**, 1936 (1996).

7 H. Imahori, E. Yoshizawa, K. Yamada, K. Hagiwara, T. Okada, and Y. Sakata, *J. Chem. Soc., Chem. Commun.*, **1995**, 1133.

8 H. Imahori, K. Yamada, E. Yoshizawa, K. Hagiwara, T. Okada, and Y. Sakata, *J. Porphyrins Phthalocyanines*, **1**, 55 (1997).

9 J. Otsuki, K. Harada, K. Toyama, Y. Hirose, K. Araki, M. Seno, K. Takatera, and T. Watanabe, *Chem. Commun.*, **1998**, 1515.

10 A. Osuka, S. Nakajima, K. Maruyama, N. Mataga, and T. Asahi, *Chem. Lett.*, **1991**, 1003.

11 **3**: mp >300 °C; MS(EI) m/z, 398 (M^+); Anal. Found: C, 66.07; H, 3.50; N, 14.04%. Calcd for $C_{22}H_{14}N_4O_4$: C, 66.33; H, 3.54; N, 14.06%; ^1H NMR (270 MHz, $CDCl_3$) δ 8.59 (4H, d, J=6 Hz), 8.34 (2H, s), 7.30 (4H, d, J=6 Hz), 4.90 (4H, s). **5**: mp >205-6 °C; MS(EI) m/z, 559 (M^+); Anal. Found: C, 73.18; H, 8.20; N, 7.28%. Calcd for $C_{34}H_{45}N_3O_4$: C, 72.96; H, 8.10; N, 7.51%; ^1H NMR (270 MHz, $CDCl_3$) δ 8.59 (4H, d, J=6 Hz), 8.30 (2H, s), 7.30 (2H, d, J=6 Hz), 4.89 (2H, s), 3.74 (2H, t, J=7 Hz), 1.69 (2H, m), 1.24-1.32 (30H, m), 0.88 (3H, t, J=7 Hz).

12 ^1H NMR titrations of **1** with **3** could not be carried out because of low solubility of **3**.

13 K_1 = [porphyrin-ligand 1:1 complex] / ([porphyrin] [ligand]), K_2 = [porphyrin-ligand 1:2 complex] / ([porphyrin-ligand 1:1 complex] [ligand]).

14 The free energy changes for photoinduced CS ($-\Delta G_{CS}$) and CR ($-\Delta G_{CR}$) in CH_2Cl_2 are calculated to be 1.28 and 0.76 eV in the complex **1**-**2** and 0.95 and 1.09 eV in the complex **1**-**3**, respectively.

15 R. J. Harrison, B. Pearce, G. S. Beddard, J. A. Cowan, and J. K. M. Sanders, *Chem. Phys.*, **116**, 429 (1987).