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Nonameric Porphyrin Assembly: Antenna Effect on Energy Transfer

Yasuhisa Kuroda,* Kenji Sugou, and Ken Sasaki

Department of Polymer Science
Kyoto Institute of Technology
Matsugasaki, Sakyo-ku, Kyoto 606-8585, Japan

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Photosynthetic systems have been attracting significant attention of many biomimetic chemists because of their functions of effective energy conversion and tremendously ingenious structures. One of the most impressive structural characteristics of the proposed total structure of the bacterium photosynthetic system is that the reaction center is surrounded by many antenna pigments to collect and transmit light energy effectively.[1] Many artificial multiporphyrin systems have been developed to mimic the function of such energy transmittance between multipigment systems.[2] In construction of these multiporphyrin systems, the methodology of "self-assembling" becomes more important especially when the number of porphyrins contained in the system is large.[3] In this work we report the new porphyrin assembly containing eight antenna porphyrin and one energy acceptor porphyrin. The system is self-assembled by using specific complexation between the dimeric zinc porphyrin assembly and pyrazine derivative which we reported previously.[4]

The new porphyrin (**1**) was synthesized as the central energy acceptor by condensation of *meso*-tetrakis(4-aminophenyl)-porphyrin with 5-(2-pyrazinyl)pentanoic acid. The self-assembling processes of **1** to incorporate dimeric [*meso*-tetrakis(2-carboxy-4-nonylphenyl)porphyrinato]zinc(II) (**2**) as the antenna moiety are examined by visible spectroscopic titration in CH_2Cl_2 shown in Figure 1. Although there are no strict isosbestic points due to the small absorbance of the titrant porphyrin **1** even at its low concentration region, the spectroscopic behavior in the Q-band region is quite similar to that of complexation of **2** with simple pyrazine derivatives.[4] The titration curve obtained from absorption change at 566 nm shows a sharp bend at the concentration ratio of **2**/**1** = 4/1, where the spectrum is practically identical with the combined spectra of **1** + 4 × **2**·pyrazine complex. The observations indicate that **1** forms the 1:4 assembly with **2** through four independent binding processes with an identical binding constant *K* (see Scheme 1)[5] and electronic interaction between porphyrins in the resulting assembly is weak. The theoretical curve-fitting analysis of the absorbance changes, assuming the molar extinction coefficient of **1** + 4 × **2**·pyrazine complex as that of the final assembly shows the excellent agreement between the calculated and observed values to give $K = (4 \pm 1) \times 10^7$ M^{-1} as shown in Figure 1b. The results suggest that the over 92% of **2** in the solution of 1:4 mixture of these porphyrins is bound to **1** under the present experimental conditions.[6] Thus, present complexation effectively gives the nonameric porphyrin assembly **1**·(**2**)$_4$ where the one free base porphyrin is surrounded by eight zinc porphyrin complexes.[7] The center-to-center distance between the free base and zinc porphyins in extended conformations of the alkyl chains supporting the pyrazinyl moieties is estimated to lie in the range 16−21 Å.

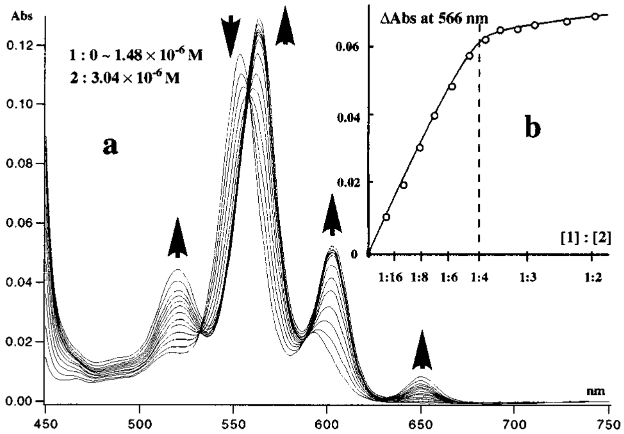
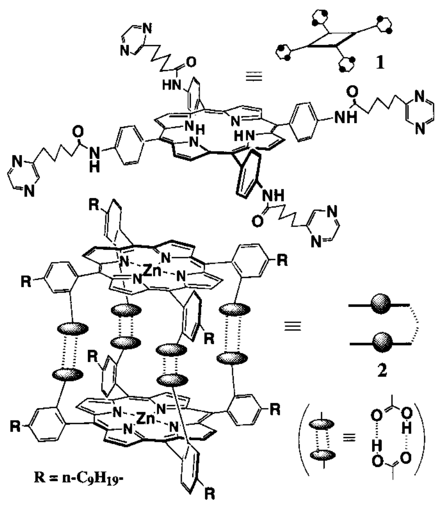


Figure 1. UV/vis spectroscopic titration of **2** with **1** in CH_2Cl_2. (a) Spectral change at 296 K. [**2**] = 3.04 × 10^{-6} M (6.08 × 10^{-6} M as the Zn porphyrin), [**1**] = 0, 1.17, 2.33, 3.46, 4.58, 5.68, 6.76, 7.83, 8.88, 9.91, 10.9, 12.9, 14.8 × 10^{-7} M. (b) Absorption changes at 566 nm observed for the titration; (○) observed points, (—) theoretical curves calculated with $K = 4 \times 10^7$ M^{-1}.



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* To whom correspondence should be addressed.

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[3] For examples of trimeric or larger porphyrin assemblies, see: (a) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H.; Hamilton, A. D. *J. Am. Chem. Soc.* **1990**, *112*, 9408. (b) Brun, A. M.; Atherton, S. J.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc.* **1992**, *114*, 4632. (c) Odobel, F.; Sauvage, J.-P. *New J. Chem.* **1994**, *18*, 1139. (d) Anderson, S.; Anderson, H. L.; Bashall, A.; Mcpartlin, M.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1096. (e) Chernook, A. V.; Rempel, U.; von Borczyskowski, C.; Shulgam, A. M.; Zenkevich, E. I. *Chem. Phys. Lett.* **1996**, *254*, 229. (f) Hunter, C. A.; Hyde, R. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1936. (g) Drain, C. M.; Russell, K. C.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun.* **1996**, 337. (h) Kuroda, Y.; Kato, Y.; Ogoshi, H. *J. Chem. Soc., Chem. Commun.* **1997**, 469. (i) Kuroda, Y.; Shiraishi, N.; Sugou, K.; Sasaki, K.; Ogoshi, H. *Tetrahedron Lett.* **1998**, *39*, 2993.

[4] (a) Kuroda, Y.; Kawashima, A.; Urai, T.; Ogoshi, H. *Tetrahedron Lett.* **1995**, *36*, 8449. (b)Kuroda, Y.; Kawashima, A.; Ogoshi, H. *Chem. Lett.* **1996**, 57. (c) Kuroda, Y.; Kawashima, A.; Hayashi, Y.; Ogoshi, H. *J. Am. Chem. Soc.* **1997**, *119*, 4929.

[5] For the theoretical treatment of the multiple equiribrium processes, see Tanford, C. *Physical Chemistry of Macromolecules*; John Wiley & Sons: New York, 1961.

[6] The distributions of **1**·(**2**)$_4$, **1**·(**2**)$_3$, **1**·(**2**)$_2$, and **1**·**2** complexes in the 1:4 mixture of **1** (7.8 × 10^{-7} M) and **2** (3.1 × 10^{-6} M) are estimated to be ∼70, 25, 4, and <1%, respectively.

[7] The data of Job plot analysis of the present system show maximum assembly formation at ∼0.8 of the molar fraction of **2** which is consistent with the nonameric assembly.

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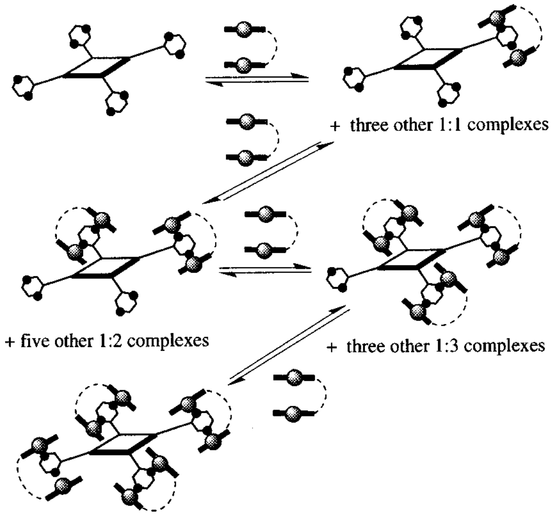
Scheme 1



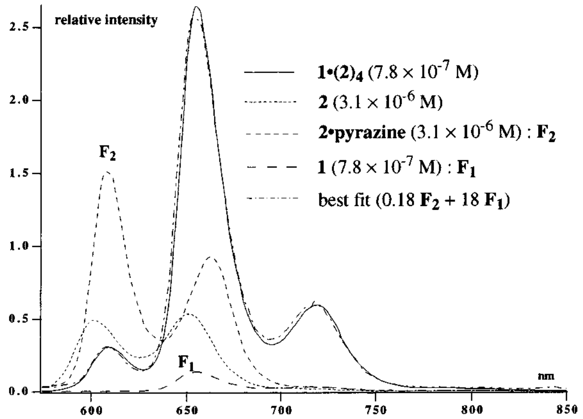


Figure 2. Fluorescence spectra of the assembly and each component in CH_2Cl_2 at 296 K excited at 564 nm. The spectrum of the **2**·pyrazine complex is measured for the solution of **2** in the presence of slight excess of pyrazine. The best fit spectrum is simulated by simply adding two weighted spectra of F_1 and F_2.

The similar titration behavior is observed also in the fluorescence spectra ($\lambda_{ex} = 564$ nm), that is, on addition of **1** into the solution of **2**, the total fluorescence intensity rapidly increases until the ratio **2**/**1** = 4/1 and further addition results in only weak emission increase proportionating to the concentration of **1** and the spectrum at the end of titration is attributed mainly to that of **1** despite existence of large excess of the zinc porphyrin complex, suggesting effective energy transfer within the assembly. Addition of excess amounts of **2** into the solution of **1**·(**2**)$_4$ also results in no further enhancement of the fluorescence intensity of **1**. These results indicate that the energy transfer in an isotropic solution is negligible under the present conditions. The fluorescence spectra of each component and the resulting assembly are shown in Figure 2, where all spectra are measured at the same concentrations of **1** (7.8×10^{-7} M) and **2** (3.1×10^{-6} M). The freebase porphyrin **1** without **2** shows only weak emission F_1 at the present low concentration compared with the relatively strong emission F_2 of **2**·pyrazine complex. The observations are corresponding to the fact that the absorbance ratio of the free base porphyrin and the **2**·pyrazine complex at 564 nm is 1/22 and the ratio of their quantum yields $\phi_{\mathbf{2}\cdot\mathrm{pyrazine}}/\phi_{\mathbf{1}}$ is 0.71 under the present conditions.[8] In contrast with each fluorescence spectrum of the components, the 1:4 mixture of **1** and **2** exhibits a strong emission mainly consisted of that of **1**. The best fit analysis for the observed spectrum indicates that the resulting spectra contains 18% of F_1 and 1800% of F_2 as shown in Figure 2, which corresponds to 82% efficiency of the energy transfer from the **2**·pyrazine complex to the free base porphyrin of **1** in the assembly.[9] Although the observed efficiency of the energy transfer is not so high compared with those previously reported for the covalently linked multiporphyrin systems,[10] the 18 times enhanced fluorescence of **1** is interesting enough to demonstrate the antenna effect of eight zinc porphyrins arranged around the central energy acceptor, which enhance the light absorption efficiency of the system rather than the energy transfer efficiency.

Since the synthetic variation for the structures of the pyrazine linker in **1** is widely open, the present assemblies provide excellent systems to examine dependencies of the antenna effect on the number of the antenna pigments or the donor−acceptor distance. The investigations on these subjects are now under way in this laboratory.

Supporting Information Available: Synthetic procedures for **1** and details of the electronic and emission spectroscopic titration (PDF). The material is available free of charge via the Internet at http://pubs.acs.org.

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[8] The relative quantum yield is determined by the reported method, see: Hsiao, J.-S.; Krueger, B. K.; Wagner, R. W.; Johnson, T. E.; Delaney, J. K.; Mauzerall, D. C.; Fleming, G. R.; Lindsey, J. E.; Bocian, D. F.; Donohoe, R. J. *J. Am. Chem. Soc.* **1996**, *118*, 11181.

[9] The contribution of the fluorescence of uncomplexed **2** to the resulting emmission is estimated to be less than 1%. For present estimation of the energy transfer efficiency, multiply excited assemblies containing two or more excited porphyrins are not taken into consideration.

[10] The energy transfer is less efficient than that observed for covalently linked multi-porphyrin systems (>0.9) where the through-bond mechanism of energy transfer is proposed, see, for example: Wagner, R. W.; Lindsey, J. S. *J. Am. Chem. Soc.* **1994**, *116*, 9759, but more efficient than that for assemblies linked with hydrogen bonds (~0.6) where the through-space mechanism is proposed, see: Sessler, J. L.; Wang, B.; Harriman, A. *J. Am. Chem. Soc.* **1995**, *117*, 704. The preliminary estimation, assuming Förster mechanism and using spectroscopic data and typical known lifetime data, indicates that the observed efficiency corresponds to 17−18 Å center-to-center separation between the donor−acceptor porphyrins.