J|A|C|S
COMMUNICATIONS

Published on Web 01/25/2002

Light-Harvesting Heptadecameric Porphyrin Assemblies

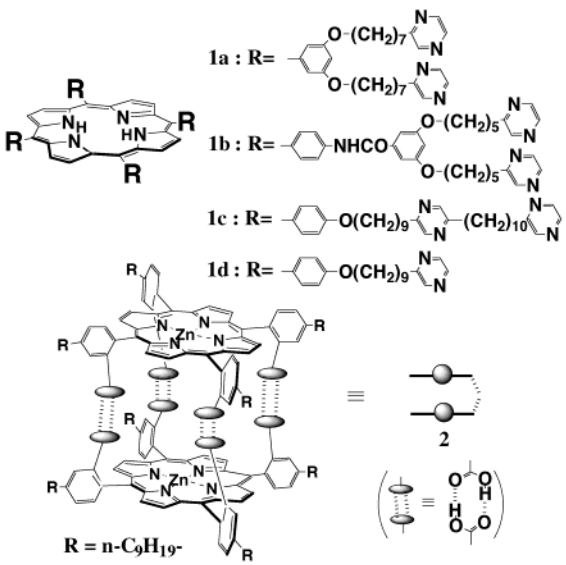
Kenji Sugou, Ken Sasaki, Koji Kitajima, Toru Iwaki, and Yasuhisa Kuroda*

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

Received November 5, 2001

The antenna complex in the photosynthetic light-harvesting system is one of the largest porphyrin assemblies in Nature. To utilize the photon energy given in a unit area as effectively as possible, Nature has developed the gigantic antenna complexes rather than increase the number of photosynthetic centers. The recent model of the antenna system suggests that over 50 antenna bacteriochlorophyll molecules belong to one photoreaction center to cover a large sunshine surface area.[1] Since the molecular design using self-assembling systems is one of the most promising approaches to construct such large chemical structures, it is important to examine the limitations and possibilities of this methodology.[2] We have been attempting to construct such molecular systems of the porphyrin by using noncovalent interactions.[3] In this contribution we report porphyrin assemblies containing 17 porphyrin molecules, in which the photoenergy absorbed by the entire system is effectively converted to the emission of the single central porphyrin. The systems also show an interesting dependency of energy-transfer efficiencies on the topological arrangement of the antenna elements.

The basic concept for the construction of assemblies is the same as that for the previous nonameric assembly where the central porphyrin has the pyrazine arms to hook the zinc porphyrin dimers.[3c] Three types of central free base porphyrins having eight pyrazine sites, the direct parallel type **1a**, the spaced parallel type **1b**, and the serial type **1c**, were newly synthesized in this work. The porphyrin **1d** is also synthesized as the reference template for the nonameric assembly. In the syntheses of these porphyrins, the



pyrazine moieties are attached by the reaction of the corresponding phenolic compounds with the corresponding bromoalkylpyrazine prepared from the methylpyrazine and dibromoalkanes.[4] The HRMS and NMR spectra of all compounds show satisfactory agreement with the expected structures. The spectroscopic behavior of these porphyrins is summarized in Table 1.

Table 1. Spectroscopic data of **1a**−**d** and the corresponding assemblies[a]

porphyrin	UV λ_{max} (nm (log ϵ))	fluorescence λ_{max} (nm)	r_{564}[b]	ϕ_1[c]	f_a[d]	f_b[e]
1a	516 (4.30), 550 (3.77), 589 (3.77), 645 (3.49)	649, 714	127	0.077	77	0.39
1b	519 (4.30), 557 (4.19), 595 (3.84), 650 (3.84)	655, 717	25	0.128	20	0.20
1c	519 (4.30), 557 (4.22), 596 (3.86), 651 (3.85)	656, 720	24	0.113	12	0.45
1d	519 (4.10), 556 (3.97), 595 (3.59), 651 (3.67)	658, 720	21	0.120	16	0.24

[a] In CH_2Cl_2, at 298 K. [b] The absorption ratio at 564 nm of the central porphyrins, **1a**−**d**, and the **2**·pyrazine complex in the heptadecameric- for **1a**−**c** and nonameric- for **1d** assemblies. [c] Fluorescence quantum yield. [d] The fluorescence amplifying factor for **1a**−**d** (see text and Figure 1). [e] The fluorescence quenching factor for the **2**·pyrazine complex in the assembly.

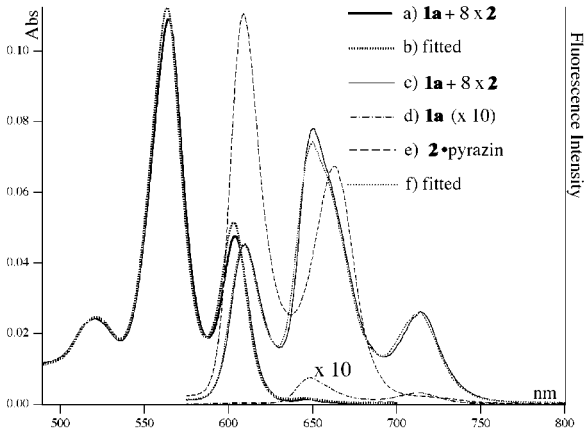
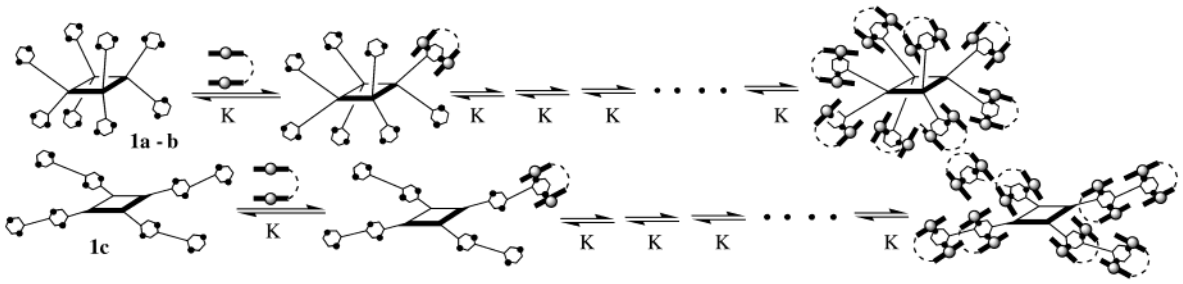


Figure 1. Electronic absorption and fluorescence spectra of the assembly **1a**·(**2**)$_8$ and its components in CH_2Cl_2. (a) Electronic spectrum of the mixture of **1a** (3.52×10^{-7} M) and **2** (2.89×10^{-6} M). (b) Simulated spectra composed of each spectrum of **1a** (3.52×10^{-7} M) and **2**·pyrazine (2.89×10^{-6}M). (c) Fluorescence spectrum of **1a** (3.52×10^{-7} M) and **2** (2.89×10^{-6} M). (d) 10 times expanded fluorescence spectrum F_1 of **1a** (3.52×10^{-7} M). (e) the fluorescence spectrum F_2 of **2**·pyrazine (2.89×10^{-6} M). (f) Simulated spectra, $77F_1 + 0.39F_2$.

The formation of the heptadecameric porphyrin assemblies is confirmed by spectroscopic titration of dimeric [*meso*-tetrakis(2-carboxy-4-nonylphenyl)porphyrinato]zinc(II) (**2**) with **1** as described previously.[3c] All titration curves for central free base porphyrins **1a**, **1b** and **1c** are sharply bent at the concentration ratio of **2**/**1** = 8/1, where the spectrum shows simple additivity for those of the component porphyrins (**1** and **2**·pyrazine complex)[5] indicating weak electronic interactions between the pigments. The spectrum of **1a**·(**2**)$_8$ is shown in Figure 1 as the typical example of the assembly. The processes of the assembly formation seem to be monotonic

10.1021/ja017470t CCC: $22.00

Scheme 1



and may be analyzed as eight independent equilibrium processes with an identical binding constant to give excellent agreement between observed and theoretical titration behavior (see Scheme 1).[6] Interestingly, not only the parallel type porphyrins, **1a** and **1b**, but also the serial type one, **1c**, show similar monotonic titration behavior and the binding constants for the inner pyrazine and the outer one could not be practically separated from each other. The observation may indicate a relatively free shuttle movement of the antenna porphyrins between the inner and outer pyrazine sites in **1c**. All binding constants are larger than 5×10^7 M^{-1} which is the determinable upper limit of the present titration method.[7] The results suggest that under the typical experimental condition of [**1**] = 3.75×10^{-7} M and [**2**] = 3.0×10^{-6} M, free **2** is estimated to be less than 8% at the utmost.

The photoabsorption and following energy transfer in the assemblies are examined by measurements of the fluorescence spectra. The fluorescence titration experiments (λ_{ex} = 564 nm) using **1a**−**c** as the titrant for the constant concentration of **2** also show the sharp saturation behavior of the fluorescence intensities of the free base porphyrins at the concentration ratio of **2**/**1** = 8/1. Further addition of **1** results in only weak emission increase proportionate to the concentration of **1**, indicating negligible energy transfer between nonassembled components in an homogeneous solution under the present conditions. In all cases, the fluorescence spectrum of the 1:8 mixture of **1** and **2** consists of the major fluorescence of **1** and the minor one of **2**·pyrazine complex even in the presence of the large excess of the antenna pigments. The obeserved spectra are well reconstructed by the form of $f_aF_1 + f_bF_2$, where F_1 and F_2 are the fluorescence of **1** and the **2**·pyrazine complex, respectively, measured separately at the corresponding concentrations (see Figure 1). The amplifying factor, f_a, for the acceptor emission and the quenching factor, f_b, for the antenna fluorescence are also summarized in Table 1 together with the absorption ratios of the **2**· pyrazine moiety and the central free base porphyrin in the assemblies at 564 nm, r_{564}, where the antenna moiety shows largest absorption in the Q-band region. It is very interesting to note the general trend that values of f_a are nearly equal to those of $r_{564} \times (1 - f_b)$ in all cases, which indicates the excitation of the central porphyrin is directly enhanced by the absorption of the antenna pigments even in such large-scale assemblies. Thus the antenna effect for **1a** having largest r_{564} results in 77 times fluorescence enhancement of the central free base porphyrin. The apparent energy-transfer efficiencies ($1 - f_b$) seem to be rather insensitive to the nature of different type bonding of linker such as amide, phenyl, or ether moieties, suggesting the major contribution of the Förster-type energy-transfer mechanism. Another interesting result is the unexpectedly low efficiency of the energy transfer observed for **1c** which has a serial arrangement of the antenna pigments. The observed lowest efficiency of **1c** is notable even compared with that of **1d**. The comparison indicates that the outer antenna pigments in **1c** appear to act as an interfering factor for the energy transfer even though they absorb the photoenergy normally. There are two temporary explanations for the low energy-transfer efficiency of **1c**: (a) the linker chain rigidified by attachment of two highly bulky antenna pigments in the single strand makes the position of the antenna pigments fixed at the longer distance from the central porphyrin, and (b) the energy transfer between inner and outer antenna pigments as observed in the natural photosynthetic system operates in **1c** to interfere with the energy transfer from the antenna to the central porphyrin.[8] Although a conclusion cannot be drawn in the present stage, the results give important suggestions for the design of effective photoabsorption systems. Further investigations containing the fast kinetic analyses for the present energy transfer are now under way and will be soon reported.

Supporting Information Available: Characterization data of **1a**−**d** and a typical example of the titration data of the present eight independent equilibrium processes (PDF). This material is available free of charge via the Internet at http://pubs.asc.org.

References

(1) (a) Deisenhofer, J.; Epp. O.; Miki, K.; Huber, R.; Michel, H. *Nature* **1985**, *318*, 618. (b) McDermott, G.; Prince, S. M.; Freer, A. A.; Hawthornthwaite-Lawless, A. M.; Papiz, M. Z.; Cogdell, R. J.; Isaacs, N. W. *Nature* **1995**, *374*, 517. (c) Pullerits, T.; Sundstrom, V. *Acc. Chem. Res.* **1996**, *29*, 381.

(2) For recent review of the porphyrin assemblies, see: (a) Ogoshi, H.; Mizutani, T.; Hayashi, T.; Kuroda, Y. In *The Porphyrin Handbook*; Kadish, K. M.; Smith, K. M.; Guilard, R., Eds.; Applications: Past, Present and Future, Vol. 6; Academic Press: New York, 2000; pp 279−340. For examples of trimeric or larger porphyrin assemblies, see: (b) Tecilla, P.; Dixon, R. P.; Slobodkin, G.; Alavi, D. S.; Waldeck, D. H.; Hamilton, A. D. *J. Am. Chem. Soc*. **1990**, *112*, 9408. (c) Brun, A. M.; Atherton, S. J.; Harriman, A.; Heitz, V.; Sauvage, J.-P. *J. Am. Chem. Soc*. **1992**, *114*, 4632. (d) Odobel, F.; Sauvage, J.-P. *New. J. Chem*. **1994**, *18*, 1139. (e) Anderson, S.; Anderson, H. L.; Bashall, A.; Mcpartlin, M.; Sanders, J. K. M. *Angew. Chem., Int. Ed. Engl*. **1995**, *34*, 1096. (f) Chernook, A. V.; Rempel, U.; von Borczyskowski, C.; Shulgam, A. M.; Zenkevich, E. I. *Chem. Phys. Lett*. **1996**, *254*, 229. (g) Hunter, C. A.; Hyde, R. K. *Angew. Chem., Int. Ed. Engl.* **1996**, *35*, 1936. (h) Drain, C. M.; Russell, K. C.; Lehn, J.-M. *J. Chem. Soc., Chem. Commun*. **1996**, 337.

(3) (a) Kuroda, Y.; Kato, Y.; Ogoshi, H. *J. Chem. Soc., Chem. Commun*. **1997**, 469. (b) Kuroda, Y.; Shiraishi, N.; Sugou, K.; Sasaki, K.; Ogoshi, H. *Tetrahedron Lett*. **1998**, *39*, 2993. (c) Kuroda, Y.; Sugou, K.; Sasaki, K. *J. Am. Chem. Soc.* **2000**, *122*, 7833.

(4) Houminer, Y.; Fenner, R. A.; Secor, H. V.; Seemann, J. I. *J. Org. Chem.* **1987**, *52*, 3971.

(5) (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.

(6) For the theoretical treatment of the multiple equilibrium processes, see: Tanford, C. *Physical Chemistry of Macromolecules*; John Wiley & Sons: New York, 1961. See Supporting Information.

(7) Since the larger value of the binding constant gives practically the same theoretical curve-fitting, the value determined by the present titration is regarded as a minimum estimate.

(8) Hess, S.; Visscher, K. J.; Pullerits, T.; Sundstrom, V.; Fowler, G. J. S.; Hunter, C. N. *Biochemistry* **1994**, *33*, 8300; Pullerits, T.; Visscher, K. J.; Hess, S.; Sundstrom, V.; Freiberg, A.; Timpmann, K.; Van Grondelle, R. *Biophys. J.* **1994**, *66*, 236.

JA017470T