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COMMUNICATIONS

Published on Web 01/29/2003

Hexameric Macroring of Gable-Porphyrins as a Light-Harvesting Antenna Mimic

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Photosynthetic organisms convert solar energy into chemical energy with excellent efficiencies. The first event starts when light is absorbed by light-harvesting complexes around the reaction center complex. The structures of the light-harvesting complexes (LH1, LH2, and LH3) in photosynthetic bacteria have been determined by X-ray crystallographies[1] and electron microscopies.[2] Their special features may refer to the higher ordered barrel structure of complete beauty and scientific significance. The key functional unit is composed of a bacteriochlorophyll-*a* dimer in a slipped-cofacial orientation by coordination from imidazolyl residue to the central magnesium ion. These dimers are further arranged into a macroring form. Until now, several oligomeric porphyrin rings have been synthesized through both covalent[3] and supramolecular[3b,4] approaches toward antenna mimics. To the best of our knowledge, however, there is no example of a porphyrin macroring composed of dimer units. Here we report a novel artificial ring by connecting slipped-cofacial dimer units. This model is a self-assembled supramolecule that has distances and orientations of metal porphyrin units in close analogy to those of the natural light-harvesting complexes.

We designed the molecular model keeping two basic points in mind. First, we employed imidazolylporphyrinatozinc(II) dimer,[5] as the basic construction unit, because it satisfies perfectly the functional requisites of the light-harvesting dimer unit, in view of the distance and the orientation of chromophores, and imidazolyl to zinc coordination free from excitation energy quenching. Second, the ring structure was provided by connecting two imidazolylporphyrinatozinc(II) dimers with a 1,3-phenylene spacer.[6] In contrast to the *meso*-*meso*-coupled imidazolylporphyrinatozinc(II), which grows linearly into a giant porphyrin array,[5b] the spatial orientation of 120° is expected to give a closed ring under appropriate conditions. If all of these designs work perfectly, a dodecaporphyrin barrel structure with center-to-center distances of 6.1 and 11.0 Å, in close analogy to those of the light-harvesting complexes of photosynthetic purple bacteria,[1,2] will result (Figure 1). *N*-Heptyl groups were attached at four remaining *meso*-positions to improve poor solubility of the porphyrin oligomers.

According to Scheme S1 in the Supporting Information, acid-catalyzed condensation of *meso*-(*n*-heptyl)dipyrromethane with two aldehydes, isophthalaldehyde and 1-methyl-2-imidazolecarbaldehyde, followed by oxidation afforded a free base porphyrin mixture: 5,15-bis(imidazolyl)porphyrin **3**, 5-imidazolyl-15-(*m*-formylphenyl)porphyrin **4**, and 5,5′-*m*-phenylene-bridged gable-porphyrin[6] with 15,15′-bis(imidazolyl) groups **5** as the main porphyrin products. The porphyrin mixture was separated by using column chromatography, and the intermediate porphyrin **4** was treated again with dipyrromethane and imidazolecarbaldehyde to afford a second crop of gable-porphyrin **5** in a combined yield of 2.1%. The structural proof of **5** was obtained by nuclear magnetic resonance and mass spectrometers.

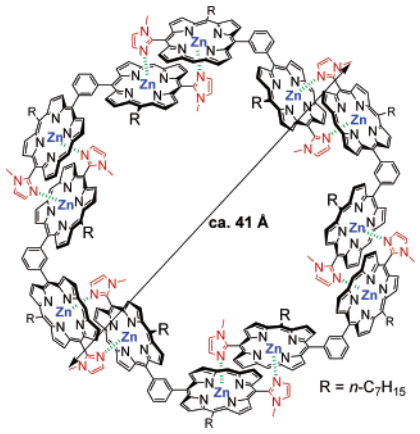

Figure 1. A structural model of the target cyclic hexamer. Some *n*-heptyl groups on each porphyrin are omitted for visual clarity.

Zinc insertion converted free base porphyrins (**3** and **5**) to the corresponding zinc complexes **6** and **7**, respectively. The size distribution of **7** was analyzed by gel permeation chromatography (GPC) and was observed as a polymeric mixture with broad distributions of molecular weight. The elution curve was totally different from that of the *meso*-*meso*-coupled porphyrin dimer zinc complex, which gave giant linear arrays.[5b] Although the distribution of **7** was broad, the curve showed a distinctly longer elution time, indicating the oligomer formation of much smaller molecular weight. The fact suggests that the terminal imidazolyl tends to find the zinc porphyrin counterpart at the other chain end, leading to intramolecular cyclization rather than zigzag chain elongation.

To dominate then the intramolecular cyclization, we applied the reorganization principle established previously:[5b] The coordination bond is formed in nonpolar solvents, while it is broken in polar solvents by competitive coordination, and the process is reversible, but in this case under high-dilution conditions. The reorganization processes are as follows: (1) Cleavage of the coordinate bond and dilution; **7** was dissolved at 5 μM in $CHCl_3$/methanol = 7/3 (v/v). (2) Further cleavage and dilution; methanol was added to make a 3.5 μM solution in $CHCl_3$/methanol = 1/1 (v/v). (3) Finally, the solvent was evaporated at 25 ± 1 °C. The GPC chart of the sample after the reorganization processes showed a dramatic change. In the reorganized sample, **8**, the larger molecular weight part was eliminated almost completely, and the peaks converged to the two of smallest molecular weights (Figure 2).

Atomic force microscope (AFM) measurements of **8** on flat mica substrate demonstrated the presence of round-shaped particles of uniform height (ca. 1.5 nm). The size, after correction of the radius curvature of the AFM probe (ca. 10 nm), provides the net diameter of the particles as a few nanometers (Figure 3). These particles,

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10.1021/ja028325y CCC: $25.00

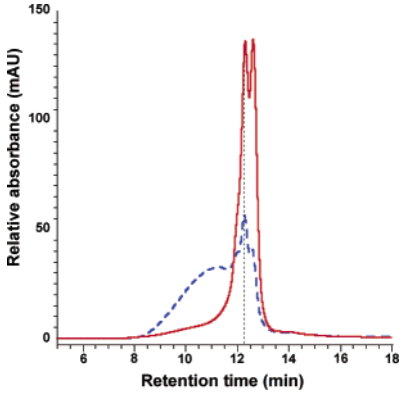
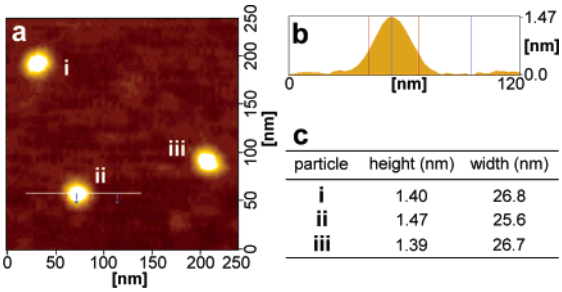


Figure 2. Gel permeation chromatograms for **7** (dashed curve) and **8** (solid curve) with a column exclusion volume of 7×10^4 daltons. Each eluent is chloroform, and 150 μM solutions were injected.



particle	height (nm)	width (nm)
i	1.40	26.8
ii	1.47	25.6
iii	1.39	26.7

Figure 3. Results of AFM measurements. (a) AFM image of **8** spin coated on mica substrate. (b) Cross section profile of particle **ii**. (c) Height and width of each particle.

corresponding to the barrel shaped macroring, are main components of the minimum size, although they are accompanied by larger ones presumably of their aggregates. Therefore, the reorganization processes converted completely the polymeric assemblies **7** to a barrel structured mixture **8**. Separation of **8** by preparative GPC afforded finally **1** and **2** as the first and second eluting components, respectively. It should be noted that each component (**1** and **2**) is very stable both in solid states and in solution unless coordinating solvents are used.

To determine the exact aggregation number, we applied small-angle X-ray scattering (SAXS) measurements for **1** with synchrotron radiation. The plot of scattering intensity versus the square scattering vector (Guinier analysis) provided a radius of gyration (R_g) of 15.59 $\pm$ 0.34 Å for the predominant (98%) component. This R_g corresponds to diameters of 42.36 and 40.26 Å according to sphere and cylinder approximations, respectively. These values agree well with the estimation of ca. 41 Å for the outer diameter of cyclic hexamer from the molecular mechanics calculation.[7] In a wide-angle region of the scattering profile, the first minimum peak of **1** appeared at 0.17 Å^{-1} followed by a rise of the intensity. The scattering intensity plot is best expressed by a theoretical calculation[8] for the cyclic hexamer with a minimum at 0.18 Å^{-1}, in contrast to other cyclic oligomers, the minimum being 0.23 and 0.30 Å^{-1} for a cyclic pentamer and a tetramer, respectively (Figure S2).[9] We conclude that **1** is a hexameric macroring of gable-porphyrins as previously shown in Figure 1.

The UV−vis absorption spectrum of **1** gave a large split of the Soret bands (strong absorption in the near-UV region), 2073 cm^{-1}, which corresponds to the sum of each contribution of the splitting energy from slipped-cofacial and phenylene-bridged interactions,[10] 1310 and 775 cm^{-1}, respectively, the values of dimer **6** (zinc complex of **3**) and of the monomeric bis-zinc gable-porphyrin (measured in 1-methylimidazole). The fluorescence quantum yield of **1** relative to that of the monomeric bis-zinc gable-porphyrin was 0.51 (excited at the longer wavelength band of the Soret bands, respectively). Similar relations have been observed between the natural light-harvesting complex and its dimeric subunit constituent.[11] Detailed studies on photophysics of the porphyrin macroring **1** will be of profound interest from the viewpoint of elucidating the relation between structure and function.

In summary, we succeeded in constructing the porphyrin macroring by interlocking *m*-gable-porphyrins by slipped-cofacial dimer formation without any protein matrices. This model must be a major milestone for further investigation to elucidate the mechanism of highly efficient light harvesting as well as the evolutional strategy of such ring structures in the natural photosynthetic system.

Acknowledgment. We thank Prof. M. Kataoka and his laboratory members for technical assistance and helpful discussions with the SAXS measurements. This work was supported by CREST (Core Research for Evolutional Science and Technology) of the Japan Science and Technology Corporation (JST).

Note Added after ASAP: In the version published on the Web 1/29/2003, the UV−vis spectral assignments for **1** were incorrect. The final version published 2/04/2003 and the print version are correct.

Supporting Information Available: Experimental details for synthetic procedures, reorganization procedure under high dilution conditions, GPC, synchrotron SAXS, and theoretical calculations (PDF). This material is available free of charge via the Internet at http://pubs.acs.org.

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JA028325Y