

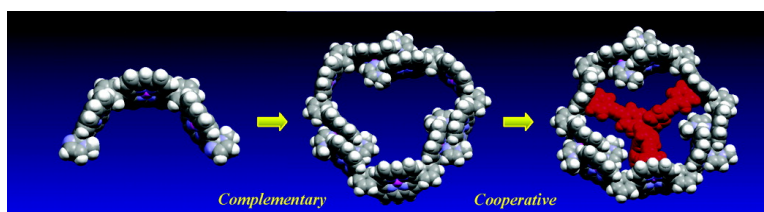
Communication

**Light-Harvesting Macroring Accommodating a Tetrapodal Ligand
 Based on Complementary and Cooperative Coordinations**

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Light-Harvesting Macroring Accommodating a Tetrapodal Ligand Based on Complementary and Cooperative Coordinations

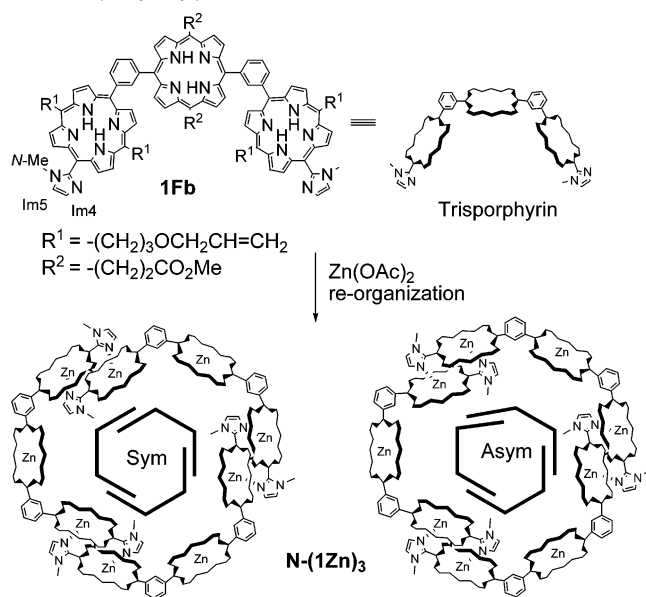
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Light-harvesting complexes (LHs) contained in photosynthetic purple bacteria are some of the most beautiful and efficient molecular structures found in nature. These complexes exist in two types of cyclic arrangements of Bchl *a*: the LH1 arrangement, which includes the reaction center,¹ and the LH2 arrangement around the periphery of LH1.² The most fascinating basic structure is the higher-ordered barrel structure of LH1 and B850 in LH2.³ These chromophore arrays exist as strongly coupled excitons and play important roles in the rapid and efficient transfer of absorbed solar energy to the reaction center. Various types of multiporphyrin systems have been described by investigations into the high efficiency of the energy transfer process and for application to artificial photosynthetic systems.⁴ However, light-harvesting cyclic arrays of porphyrins showing strong excitonic coupling such as LH systems have hardly been described so far. Under these circumstances, we have recently reported that hexameric and pentameric macrorings, which exhibited large split Soret bands ($\Delta E \sim 2000 \text{ cm}^{-1}$), mimicked the structure of B850 in LH2 by assembling gable-porphyrinatoZn(II) complexes with imidazolyl groups in a supramolecular fashion based on the complementary coordination of imidazolyl to Zn(II).^{5,6}

Scheme 1. Formation of Self-assembled Cyclic Trisporphyrin Trimers, $(\text{N}-(\mathbf{1Zn})_3)^a$



^a Two topological isomers, one D_{3h} -symmetric (left bottom) and one asymmetric (right bottom), exist.

We have now applied this supramolecular methodology to trisporphyrin **1** and have constructed a novel light-harvesting cyclic trimer of **1Zn**. Only the terminal two porphyrins in **1Zn** are used in the ring-forming complementary coordination. Three noncoor-

ordinated porphyrinatoZn(II) sites in the cyclic trimer afford scaffolds that can accommodate a functional molecule corresponding to the reaction center. Furthermore, this molecule is composed of three porphyrin units connected at an angle of 120° by *m*-phenylene moieties. Therefore, its cyclic trimer, $(\mathbf{1Zn})_3$, should be strain-free, whereas dimer or tetramer formation will be improbable because of high angle strain energies, and expected as a specific product on supramolecular cyclization.

Free-base trisporphyrin **1Fb** was synthesized in 20% yield by condensation of 5-(1-methylimidazol-2-yl)-10,15-bis(3-allyloxypropyl)-20-(3-formylphenyl)porphyrin **3Fb** with *meso*-methoxycarbonylethylidipyromethane **4**. Zn(II) metal ion was introduced into **1Fb** by treatment with a methanol solution of $\text{Zn}(\text{OAc})_2$ in CHCl_3 . GPC analysis of the as-prepared (before reorganized) mixture showed a sharp peak accompanied by a broad shoulder at a shorter retention time (Figure S1, Supporting Information). To turn the mixture into a single product, it was diluted to 0.02 mM in $\text{CHCl}_3/\text{MeOH} = 9/1$ (v/v) and allowed to stand at 27°C for 1 day in the dark. The equilibrium of the complementary coordination of imidazolyl to Zn(II) is expected to drive linear oligomers and any larger ring compounds to form the more stable cyclic trimers.⁶ After this reorganization, the broad shoulder disappeared completely, leaving the sharp peak as the sole product in the GPC chromatogram. This cyclic trimer was stable for at least several days⁷ even under extremely dilute conditions ($\sim 10^{-7}$ M) in nonpolar solvents such as CHCl_3 (including 0.5% EtOH as a stabilizer) and toluene. To determine the structure of the complex by mass spectrometry, the coordination pairs were covalently linked by a multisite ring-closing metathesis reaction.⁸ After covalent linking, the mass spectrum showed only a single peak corresponding to the **1Zn** trimer, $\text{C}-(\mathbf{1Zn})_3$ (m/z found 5816.4, calcd for $[\text{M} + \text{H}]^+$ 5816.5) (Figure S2, Supporting Information). The covalently linked trimer $\text{C}-(\mathbf{1Zn})_3$ maintains its cyclic structure even in highly coordinating solvents such as pyridine. This feature enables us to evaluate the photo-physical properties of the complex in polar media, facilitating the electron-transfer reaction.

The proton NMR spectra of the noncovalently linked cyclic trimer, $\text{N}-(\mathbf{1Zn})_3$, were complex. However, use of HH-COSY, TOCSY, and HMQC measurements allowed the assignment of all the signals as a 2:3 mixture of two topological isomers, D_{3h} -symmetric and asymmetric. The key signals were protons inside and outside the ring. In the reference dimer, **5Zn** (whose structure was illustrated in Supporting Information Scheme 1), the corresponding *Im-4* protons were observed around 2.1 ppm, with an upper field shift of 5.7 ppm from 7.8 ppm in the free base **5Fb**. In the case of $\text{N}-(\mathbf{1Zn})_3$, the outside *Im-4* protons appeared at 2.26 ppm in the D_{3h} -symmetric isomer and at 2.30, 2.23, and 2.20 ppm in the asymmetric isomer. The inside *Im-4* protons appeared at 1.72 ppm in the D_{3h} -symmetric isomer and 1.89, 1.86, and 1.69 ppm in the asymmetric. The inside protons are discriminated from the

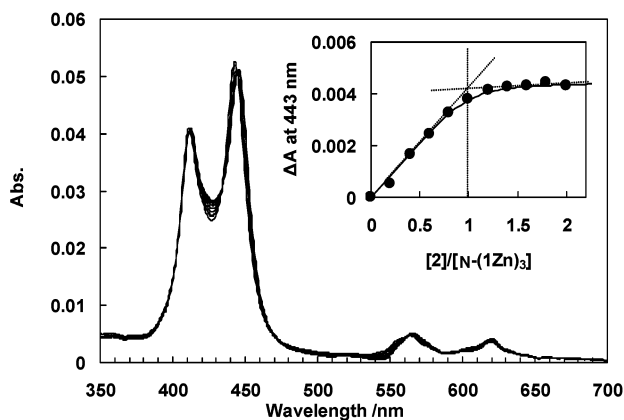
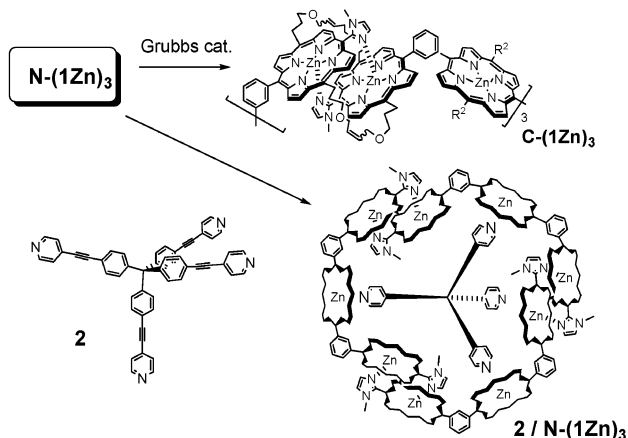


Figure 1. UV-vis titration of $N-(1Zn)_3$ (4×10^{-8} M) in toluene with tetrapodal ligand **2**. Inset: Plot of ΔA at 443 nm as a function of ratio $[2]/[N-(1Zn)_3]$.

outside protons by further shifts of 0.4–0.5 ppm caused by anisotropic effects from other porphyrin members. Similar behavior was observed for *Im-5* and *N-Me* protons (see Supporting Information, Figures S3 and S4). The clear differentiation of these protons into a single species or three different species assigns the ring structures as D_{3h} -symmetric and asymmetric topological isomers, respectively.

The incorporation of a guest-molecule into the inner sphere of $N-(1Zn)_3$ was examined by UV-vis titration. For this purpose, the tetrapodal guest **2** was synthesized from tetra(4-iodophenyl)methane⁹ and 4-ethynylpyridine by Sonogashira coupling.¹⁰ When a $N-(1Zn)_3$ solution (4×10^{-8} M) in toluene was titrated by guest **2**, the Soret band at 443 nm and the Q-band at 564 nm were shifted to longer wavelengths. Figure 1 shows the spectral change during the titration and the plot of ΔA at 443 nm as a function of the ratio $[2]/[N-(1Zn)_3]$. A Job plot (Supporting Information, Figure S6) and the clear bending behavior observed at $[2]/[N-(1Zn)_3] = 1$ (Figure 1 inset) indicate the formation of a strong 1:1 complex. Heterogeneity of the two topological isomers was not observed in the titration, and both isomers similarly accommodated guest **2**. The association constants obtained by curve fitting analysis were 8×10^8 M⁻¹ in toluene and 1.2×10^7 M⁻¹ in CHCl₃ (including 0.5% EtOH as a stabilizer). Such large association constants for the composite reflect the cooperative nature of the three coordination sites. Furthermore, these high-stability constants are of great advantage in such a supramolecular architecture in homogeneous solution because simple mixing is sufficient to generate the desired product.

Scheme 2. Covalent Linking of $N-(1Zn)_3$ (Upper) and Incorporation of **2** (Lower)



The fluorescence quantum yields (Φ_f) of Znporphyrin monomer,¹¹ dimer ($5Zn$)₂, and nonameric ring $N-(1Zn)_3$ in toluene were 3.4, 4.9, and 5.1%, respectively. It is noteworthy that the enhanced fluorescence of the dimer ($5Zn$)₂ compared to the monomer was not quenched at all and was maintained even for $N-(1Zn)_3$ by the accumulation of nine chromophores in close vicinity. These facts suggest that macroring formation is an excellent way to harvest light. Extensive investigations of other photophysical properties are now underway.

In conclusion, we have successfully synthesized a new model of light-harvesting complexes by specific trimerization of the trisporphyrin, **1Zn**, in a supramolecular fashion. A tetrapodal ligand was incorporated into the cavity of the macroring with excellent cooperativity. The residual arm of **2** in the composite **2/(1Zn)₃** can be further modified with energy and electron acceptors. This simple method, based on complementary and cooperative coordination, seems to be an efficient way to construct LH1 and its composites with reaction centers.

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Supporting Information Available: Synthetic details, GPC, MS, and NMR spectra, and UV-vis titration in CHCl₃ and Job plots of $N-(1Zn)_3$ with **2** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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