A Self-Assembled Light-Harvesting Array of Seven Porphyrins in a Wheel and Spoke Architecture
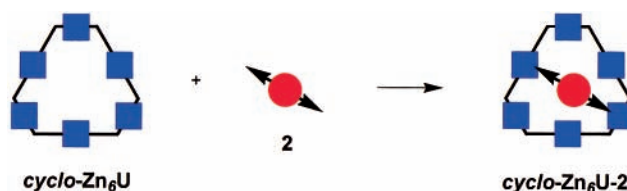
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ABSTRACT

A shape-persistent cyclic array of six zinc porphyrins provides an effective host for a dipyridyl-substituted free base porphyrin, yielding a self-assembled structure for studies of light harvesting. Energy transfer occurs essentially quantitatively from uncoordinated to pyridyl-coordinated zinc porphyrins in the cyclic array. Energy transfer from the coordinated zinc porphyrin to the guest free base porphyrin is less efficient ($\Phi_{trans} \sim 40\%$) and is attributed to a Förster through-space process.

The design and synthesis of light-harvesting complexes that rival those in photosynthesis poses stringent challenges, requiring the organization of numerous pigments in a three-dimensional architecture such that light is absorbed strongly and the resulting excited state energy flows efficiently to a designated site.[1] Synthetic arrays in diverse architectures have been prepared via stepwise synthesis,[1,2] polymerization chemistry,[3] and noncovalent self-assembly[4−8] approaches. An

attraction of self-assembly is the opportunity to mix and match different components within a given structural framework, thereby creating sets of closely related assemblies without relying on independent manual syntheses. Among striking examples of self-assembled multiporphyrin systems, Sanders has shown that a cyclic tetramer of zinc porphyrins and a complementary free base tetrapyridylporphyrin form a host−guest complex with very high affinity ($K_{assoc} \sim 10^{10}$ M^{-1}),[5] Hunter has shown that dipyridyl-substituted cobalt porphyrins undergo indefinite association,[6] Drain has demonstrated tessellation of nine porphyrins,[7] and Tamiaki has devised light-harvesting arrays composed of hydroporphyrins.[8]

We recently developed a template-directed synthesis of a covalent array of six porphyrins in a wheel-like architecture having 3-fold symmetry (Figure 1).[9] The cyclic array is available with alternating zinc and free base porphyrins

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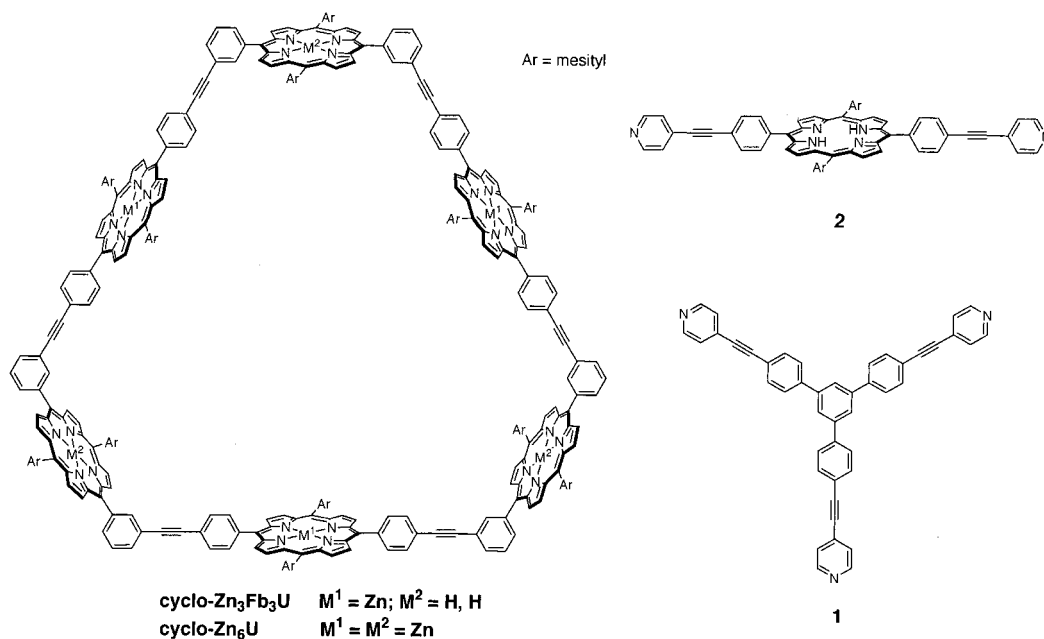
Figure 1. Structure of cyclic hosts and complementary guests.

(*cyclo*-Zn$_3$Fb$_3$U) or with all zinc porphyrins (*cyclo*-Zn$_6$U). The macrocycle is shape persistent with an inner cavity diameter of ~35 Å. We sought to determine whether this cyclic array could be used as a host to bind a guest molecule, thereby generating a light-harvesting complex. For these studies, we employed the tripyridyl template (**1**) used to synthesize the cyclic arrays, as well as a dipyridyl-substituted free base porphyrin (**2**) (see Supporting Information for
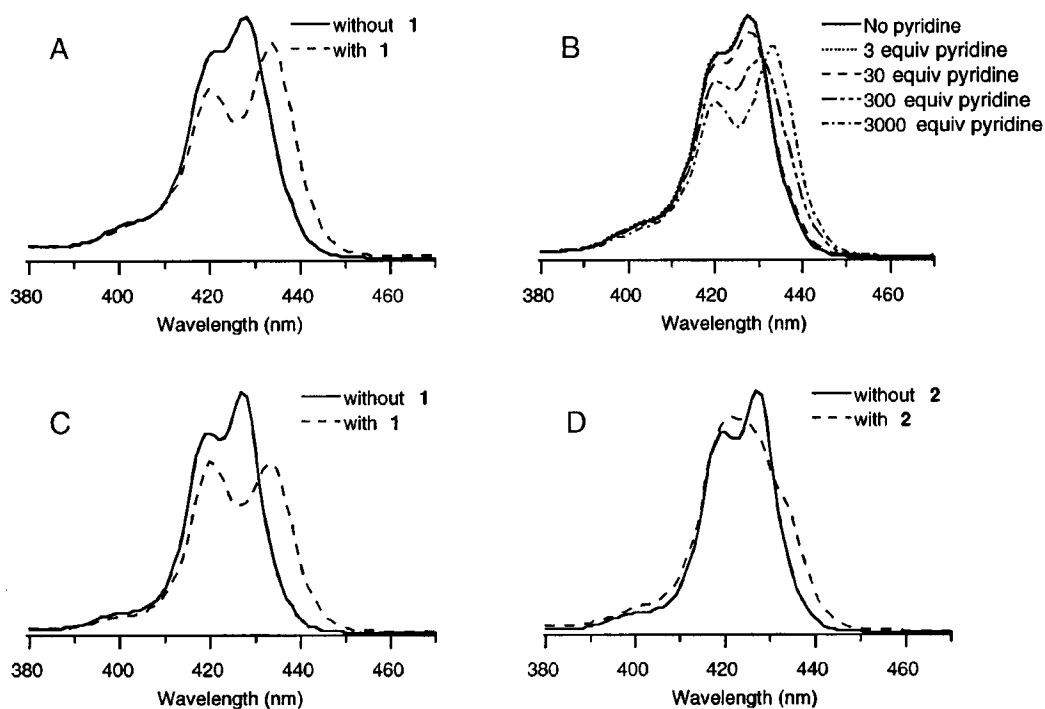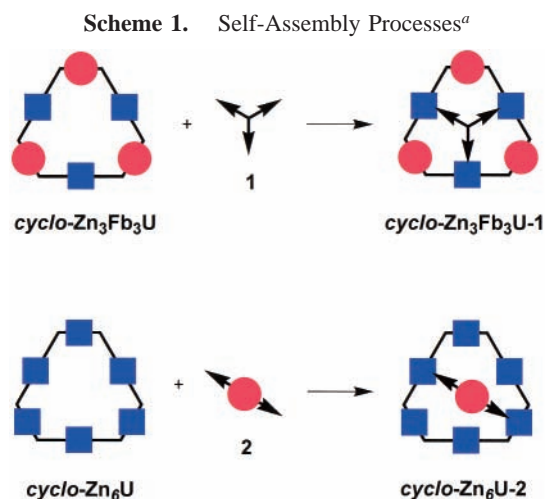

Figure 2. Absorption spectra at room temperature: (A) *cyclo*-Zn$_3$Fb$_3$U with and without template **1** (3.0×10^{-7} M each) in toluene; (B) titration of *cyclo*-Zn$_3$Fb$_3$U (3.3×10^{-7} M) in toluene with 3–3000 molar equiv of pyridine; (C) *cyclo*-Zn$_6$U with and without template **1** (3.8×10^{-7} M each) in CHCl$_3$; (D) *cyclo*-Zn$_6$U with and without template **2** (4.5×10^{-7} M each) in CHCl$_3$.

synthesis). Porphyrin **2** exhibited poor solubility in toluene but was sufficiently soluble in CHCl$_3$ for spectroscopic studies.

The absorption spectrum in the Soret region of *cyclo*-Zn$_3$Fb$_3$U in toluene is shown in Figure 2A. Upon addition of 1 equiv of the tripyridyl template (**1**) to *cyclo*-Zn$_3$Fb$_3$U in toluene (3.0 × 10^{-7} M each), a red shift occurs reflecting the > 90% binding of the template (K_{assoc} > 3 × 10^8 M^{-1}). For comparison, the titration of *cyclo*-Zn$_3$Fb$_3$U with pyridine in toluene required approximately 300 times as many moles of pyridine to give about half as much binding as occurs with 1 molar equiv of **1** (Figure 2B). A spectral change similar to that in Figure 2A occurred upon addition of **1** to a solution of *cyclo*-Zn$_6$U, again reflecting tight binding of the template (Figure 2C). Upon addition of 1 molar equiv of free base dipyridylporphyrin (**2**) to *cyclo*-Zn$_6$U (4.5 × 10^{-7} M each), a similar red shift in the Soret region was observed, indicating very high binding (Figure 2D).[10] These self-assembly processes are illustrated in Scheme 1.

Figure 3. Fluorescence emission spectrum of *cyclo*-Zn$_6$U (solid line) and *cyclo*-Zn$_6$U−**1** (dashed line) in CHCl$_3$ at room temperature (corrected for equal absorbance at λ_{exc} = 550 nm).

Scheme 1. Self-Assembly Processes^a

cyclo-Zn$_3$Fb$_3$U   *cyclo*-Zn$_3$Fb$_3$U-1

cyclo-Zn$_6$U   *cyclo*-Zn$_6$U-2

^{a} Blue squares indicates zinc porphyrins; red spheres indicates free base porphyrins.

Photoinduced energy transfer in the arrays was investigated using static fluorescence spectroscopy. We previously showed that illumination of *cyclo*-Zn$_3$Fb$_3$U at 550 nm (where the zinc porphyrin absorbs preferentially) in toluene results in emission almost exclusively from the free base porphyrin. The rate of energy transfer from zinc to free base porphyrin is (34 ps)$^{-1}$ and the yield is 99.2% as determined from time-resolved measurements.[9] The fluorescence spectrum of *cyclo*-Zn$_6$U in CHCl$_3$ shows the typical zinc porphyrin emission (597, 644 nm; Φ_f = 0.040). However, illumination at 550 nm of the complex derived from *cyclo*-Zn$_6$U and tripyridyl template **1** (*cyclo*-Zn$_6$U−**1**) results in red-shifted emission (614, 664 nm) characteristic of a pyridine-coordinated zinc porphyrin, with no emission observed that is characteristic of the uncoordinated zinc porphyrin (Figure 3). The slight

increase in intensity is characteristic of pyridyl-coordinated zinc porphyrins.[11] These data indicate essentially quantitative energy transfer from uncoordinated zinc porphyrin to the pyridyl-coordinated zinc porphyrin.

Upon illumination at 550 nm of the complex derived from *cyclo*-Zn$_6$U and **2** (*cyclo*-Zn$_6$U−**2**), where the zinc porphyrin absorption is 14.1 times that of the free base porphyrin,[12] the emission spectrum shows a large contribution from the free base porphyrin (Figure 4). The emission from the zinc
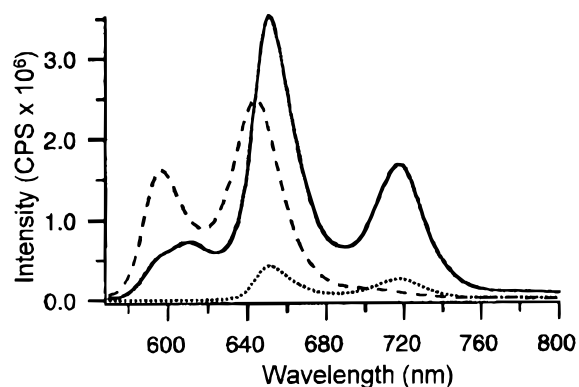
Figure 4. Fluorescence emission spectrum of equal concentrations of *cyclo*-Zn$_6$U (dashed line), *cyclo*-Zn$_6$U−**2** (solid line), and **2** (dotted line) in CHCl$_3$ at room temperature upon illumination at λ_{exc} = 550 nm (not corrected for unequal absorbances).

porphyrin is diminished by 43%, and the peak shifts from 597 to 610 nm.[13] These spectral changes are due to the bis-ligation of **2** in the cavity of *cyclo*-Zn$_6$U, forming a wheel and spoke architecture.[14] Figure 4 shows the emission spectra of samples of *cyclo*-Zn$_6$U, the complex of *cyclo*-Zn$_6$U−**2**, and **2** at identical concentrations (not identical absorbances at 550 nm). Note that the emission from the free base porphyrin (720 nm) in *cyclo*-Zn$_6$U−**2** is 6.6 times that of **2** alone. The 6.6-fold increase in emission is consistent with

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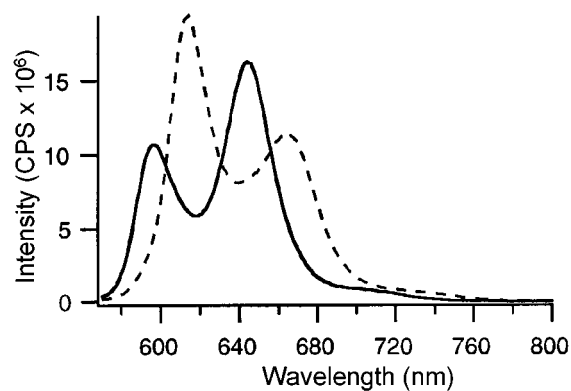
(1) a 14.1-fold increase in absorption at 550 nm due to the presence of the six zinc porphyrins and (2) a net transfer efficiency from the zinc porphyrins to the free base porphyrin commensurate with the amount of quenching of the zinc porphyrins (43%). This analysis assumes no quenching of the free base porphyrin upon docking in the hub of the wheel. Indeed, illumination at 647 nm, where the free base porphyrin **2** absorbs exclusively, resulted in no change in the emission intensity ($\Phi_f = 0.13$) upon binding to *cyclo*-Zn$_6$U. These results are supported by comparison of the absorption and fluorescence excitation spectra (λ_{em} 720 nm) of *cyclo*-Zn$_6$U−**2**, which shows that absorption by the zinc porphyrins contributes to emission by the free base porphyrin.

While more detailed analyses of the energy-transfer dynamics must await time-resolved measurements, the results in hand show that energy flows efficiently from uncoordinated to pyridyl-coordinated zinc porphyrins but transfer from the coordinated zinc porphyrin to the core free base porphyrin is rather inefficient (Φ_{trans} ~40%).[15] We have previously shown that the energy-transfer process in diphenylethyne-linked arrays, including *cyclo*-Zn$_3$Fb$_3$U, is dominated by a through-bond rather than a through-space mechanism.[9,16] The expected Förster through-space energy-transfer efficiency from the coordinated zinc porphyrin to the core free base porphyrin is 44%.[17] These results imply that the through-bond energy-transfer process via the ligated zinc porphyrin is exceptionally inefficient compared with that in covalent diphenylethyne-linked porphyrins. The inefficiency likely reflects insufficient electronic communication of the pyridyl moiety with the porphyrin orbitals at the zinc atom.

In summary, the cyclic hexameric porphyrin arrays bind complementary guests and can be used to construct a self-assembled light-harvesting system. These assemblies provide a means of studying energy transfer in novel arrangements, including (1) from uncoordinated to coordinated metalloporphyrins which differ slightly in energy and (2) from a coordinated zinc porphyrin to a free base porphyrin where the planes of the porphyrins are orthogonal. Further studies and refinement of these wheel and spoke architectures should prove useful in learning how to design more efficient light-harvesting systems.

Supporting Information Available: Description of spectroscopic measurements, procedure for the synthesis of **2**, and ^{1}H NMR and LD-MS spectra of **2**. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Though the spectral shift was quite clear upon formation of *cyclo*-Zn$_6$U−**2**, multicomponent analysis was difficult given that (1) only two of the six zinc porphyrins are coordinated and (2) the absorption λ_{max} of **2** appears at 422 nm which lies between the Soret bands of the zinc porphyrins (420, 434 nm). Regardless, $K_{assoc} > 3 \times 10^8$ M^{-1}, implying >90% binding under the conditions of the energy-transfer experiments (see Supporting Information).

(11) ZnTPP exhibits $\Phi_f = 0.033$ in toluene and 0.038 in pyridine.

(12) The ratio of absorption of zinc porphyrins (coordinated and uncoordinated) to the free base porphyrin (14.1) in *cyclo*-Zn$_6$U−**2** is less than that (17.9) based on the molar absorption coefficients in the separate species (*cyclo*-Zn$_6$U, **2**). The addition of 1 equiv of **2** to a solution of *cyclo*-Zn$_6$U (forming *cyclo*-Zn$_6$U−**2**) causes a net 15% *decline* in absorption at 550 nm, stemming from a 6% increase due to **2** and a 21% decrease due to the red shift of the two pyridyl-coordinated zinc porphyrins.

(13) Addition of 2 or 10 equiv of **2** resulted in negligible further decline in zinc porphyrin emission, reflecting the tight binding inferred from absorption measurements.

(14) A control experiment with a mono-pyridyl substituted free base porphyrin (analogous to **2**) and zinc tetraphenylporphyrin each at 3.6×10^{-6} M, which is 10 times the concentration at which the self-assembly process occurs with the cyclic hexameric arrays and a suitable guest (**1** or **2**), resulted in no detectable binding or energy transfer between the two porphyrins.

(15) The estimate of Φ_{trans} is based on the upper limit set by the zinc porphyrin quenching experiment (43%) and consideration of the errors inherent in quantitative analyses of static absorption and fluorescence spectra.

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(17) Förster calculation based on $\kappa^2 = 0.25$, $R = 20.0$ Å, and $\Phi_f = 0.038$, giving $J = 2.8 \times 10^{-14}$ cm^{6}mmol^{-1}, $R_o = 19.2$ Å, and $\Phi_{trans} = 43.9\%$ (performed on model porphyrin monomers using PhotochemCAD: Du, H.; Fuh, R.-C. A.; Li, J.; Corkan, L. A.; Lindsey, J. S. *Photochem. Photobiol.* **1998**, *68*, 141−142).