

A Dodecameric Porphyrin Wheel

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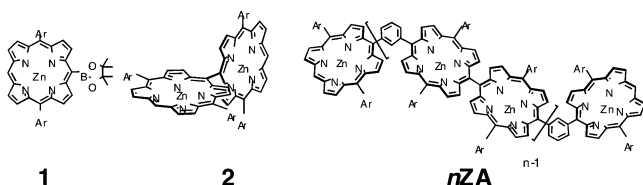
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The design and synthesis of light-harvesting systems that rival those in photosynthesis has been an important issue, which may require the organization of many pigments in an elaborate arrangement. Inspired by the wheel-like architectures of photosynthetic pigments (LH2 and LH1),¹ particular attention has been focused on the construction of covalently linked cyclic porphyrin arrays, which may aid the understanding of the mechanisms of the energy transfer or find new applications as optoelectronic material.² The synthetic arrays prepared thus far contain at most six porphyrins,³ whereas B800 and B850 in LH2 consist of eight or nine bacteriochlorophyll *a* (Bchl*a*) molecules and eight or nine dimeric subunits of Bchl*a*, respectively, and B870 in LH1 has recently shown to consist of 15 pairs of dimeric Bchl*a*,^{1c} hence posing a further synthetic challenge.

Recently we have explored the Ag(I)-promoted meso–meso coupling reaction of 5,15-diaryl Zn(II)-porphyrins,^{4a} which is useful, enabling the syntheses of a variety of porphyrin arrays including 3D-extending windmill porphyrin arrays^{4b} and extremely long porphyrin arrays.^{4c} In this communication, we report the synthesis of a dodecameric porphyrin wheel.

Chart 1



To program curvature in the porphyrin array, we employed 1,3-phenylene-bridged diporphyrin **ZA** as a building block in the coupling reaction. **ZA** was prepared in 56% yield from Suzuki coupling of boronate **1** with 1,3-diiodobenzene.⁵ Coupling reaction of **ZA** with AgPF₆ (1.0 equiv) followed by separation over size-exclusion chromatography gave porphyrin tetramer **2ZA** (16%), hexamer **3ZA** (8%), and octamer **4ZA** (3%). Similar coupling reaction of **2ZA** gave **4ZA** (18%), **6ZA** (9%), and **8ZA** (4%). The coupling reaction proceeded with high regioselectivity only at meso–meso positions. All these products were characterized by ¹H NMR, MALDI-TOF mass, UV–vis, and fluorescence spectra.

Then, we attempted the intramolecular cyclization of the linear porphyrin 12-mer **6ZA**. Under very dilute conditions (9×10^{-7}

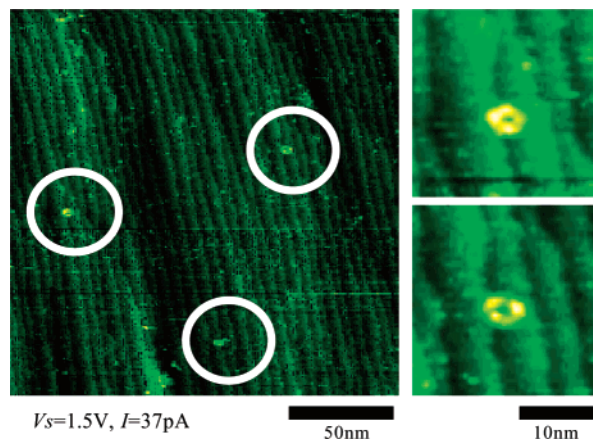


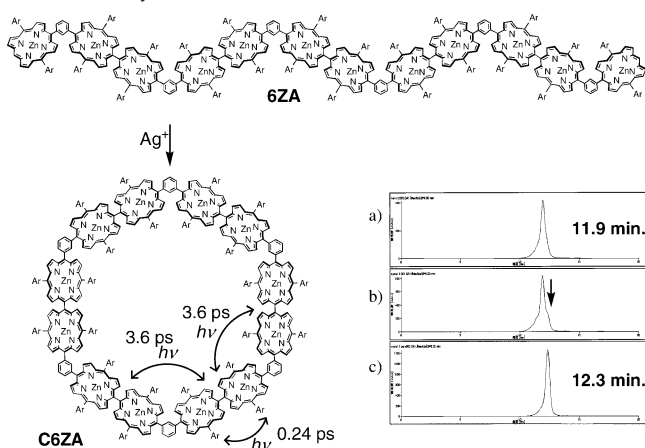
Figure 1. STM images of **C6ZA** on Cu(100).

M), **6ZA** was treated with 0.5 equiv of AgPF₆ for 48 h at room temperature. Progress of the reaction was monitored by analytical GPC–HPLC, which revealed the formation of a discrete product that eluted as a shoulder at 12.3 min, later than **6ZA** (11.9 min) (Figure 1, inset). This product isolated by repeated preparative GPC–HPLC in 12% yield together with the recovery of **6ZA** (51%) was assigned to a wheel-like dodecameric porphyrin array, **C6ZA**, on the basis of the following facts. (1) The product exhibits the parent ion peak at 11167 (calcd for C₇₀₈H₈₁₆N₄₈O₂₄Zn₁₂, *m/z* = 11167) in MALDI-TOF mass, indicating its dodecameric porphyrin constitution. (2) Despite a small difference in the molecular weight, a distinct difference in the retention time on GPC–HPLC from **6ZA** indicates a substantial difference in the hydrodynamic volume, which may arise from an overall drastic change in molecular shape. (3) The ¹H NMR spectrum is quite simple, featuring only a single set of a porphyrin subunit without the edge meso-protons (Supporting Information). Importantly, the outer and inner porphyrinic β-protons and the eight aromatic protons on the meso-aryl substituents are all distinguished because of restricted rotation. (4) Finally, the scanning tunneling microscopy (STM) image exhibits a clear wheel-like structure. A dilute solution of **C6ZA** in CH₂Cl₂ was sprayed by using a pulse injection method onto a clean flat Cu(100) surface obtained by cycles of annealing and Ar-ion sputtering.^{6,7} In situ STM measurements were performed at room temperature in ultrahigh vacuum ($<10^{-10}$ mbar) in a constant height mode. The STM images of **C6ZA** taken at *V_s* (sample bias voltage) = 1.5 V and *I* (tunneling current) = 37 pA reveal ring spots with discrete hollow. An average height of the STM images estimated on the basis of the height histogram is ca. 2.9 ± 1.2 Å,⁸ and an average

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Scheme 1. Synthesis of **C6ZA** from **6ZA**^a

^a Ar = *p*-dodecyloxyphenyl. Inset: GPC-HPLC chromatographic charts: (a) **6ZA**, (b) reaction mixture of **6ZA**, and (c) purified **C6ZA**.

diameter is $35 \pm 6.7 \text{ \AA}$, being similar to a calculated diameter of ca. $36\text{--}38 \text{ \AA}$ (Figure 1).

The absorption spectrum of **C6ZA** exhibits split Soret band at 420 and 472 nm and Q-bands at 567 and 610 nm, which are red-shifted compared with that of **2** as a consequence of exciton coupling with the neighboring porphyrins. The wheel **C6ZA** emits its fluorescence with nearly the same quantum yield (0.04) as those of linear arrays, indicating no serious quenching in the singlet excited state.

The excited-state dynamics of **C6ZA** have been examined in comparison to those of **2** and **3ZA** using the time-correlated single-photon counting (TCSPC), fluorescence anisotropy decay, and femtosecond transient absorption anisotropy (TAA) measurements. The average fluorescence lifetimes measured by TCSPC technique are 1.56 ns for **C6ZA** and 2.02 ns for **2**, respectively. The fluorescence anisotropy decay by TCSPC measurement revealed the decay components: $<50 \text{ ps}$ (17%) and 5.4 ns (83%) for **C6ZA**, 500 ps (100%) for **2**, and 4.3 ns (100%) for **3ZA**, while the femtosecond time-resolved TAA measurements taken by excitation at 570 nm (Q-band excitation) revealed the decay components: 240 fs (65%) and 1.2 ps (35%) for **C6ZA**, 340 fs (72%) and 3.7 ps (28%) for **3ZA**, and only a 180-fs short component for **2**. With much better time resolution for the TAA measurement, the shortest anisotropy decays of ca. 180–340 fs for **C6ZA**, **3ZA**, and **2** have been assigned to the incoherent exciton hopping within meso-meso-linked diporphyrin. On the other hand, the longest decay times have been assigned to the rotational diffusion time constant, 5.4 and 4.3 ns for **C6ZA** and **3ZA**, while the corresponding time constant of 500 ps was observed for **2**. Finally, 1.2- and 3.7-ps TAA decay components for **C6ZA** and **3ZA** have been assigned to the energy migration processes between meso-meso-linked diporphyrins bridged by a 1,3-phenylene spacer. Since each meso-meso-linked diporphyrin in **C6ZA** is connected with two adjacent diporphyrins with an angle of 120° in a cyclic form, the excitation energy hopping rate constant may be taken to be $(1.2 \text{ ps} \times 3 = 3.6 \text{ ps})^{-1}$ (Scheme 1),⁹ which is accidentally similar to the TAA decay time of **3ZA**.

In summary, the intramolecular Ag(I)-promoted coupling of **6ZA** afforded the dodecameric porphyrin array **C6ZA**, whose wheel structure was observed by STM. The wheel **C6ZA**, as investigated by the fluorescence and transient absorption anisotropy decay measurements, has been shown to be pertinent as a model of photosynthetic antenna in terms of very efficient excitation energy hopping along the array without energy sink. Exploration of even larger porphyrin wheels and fabrication of these arrays with appropriate electron acceptor are subjects of further investigation.

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Supporting Information Available: Experimental details for synthesis of **nZA** and **C6ZA**. MALDI-TOF mass and ¹H NMR spectra, TCSPS and TAA data, and STM height histogram of **C6ZA** (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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