Exploration of electronically interactive cyclic porphyrin arrays

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Abstract

We have explored a variety of covalently and non-covalently assembled cyclic porphyrin arrays mainly as biomimetic models of light harvesting antenna in photosynthetic systems. The key reaction is Ag(I)-promoted coupling reaction of 5,15-diaryl zinc(II) porphyrin that provides a *meso–meso* linked diporphyrin. An advantage of this coupling reaction is its extremely easy extension to higher porphyrin arrays, since longer porphyrin arrays have practically the same reactivity as that of the monomer. On the basis of this strategy, we have prepared cyclic porphyrin arrays including directly *meso–meso* linked porphyrin rings **CZ4–CZ8**, large porphyrin wheels **C12ZA** and **C24ZB**, and three-dimensional porphyrin boxes **D1–D3**. Efficient excitation energy transfer along these cyclic porphyrin arrays has been revealed by the time-resolved transient absorption and fluorescence measurements.
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Keywords: Porphyrinoids; Oligomerization; Photosynthetic antenna; Nanostructures

1. Introduction

In the last two decades, covalently and non-covalently linked multi-(metallo)porphyrin arrays have been extensively explored for their numerous applications such as artificial photosynthetic system, molecular wire, sensor, and nonlinear optical (NLO) device [1–3]. The electronic coupling between the constituent porphyrin chromophores is a key parameter that controls various important functions of porphyrin arrays [4]. In most cases, porphyrin arrays are not conjugated and only weakly coupled via through-space and through-bond interactions [5]. For example, porphyrin dimers bridged by rigid aromatic spacers, in which the geometry of two porphyrin rings is precisely controlled, have been shown to be useful for the tuning of the exciton coupling and the rates of intramolecular energy- and electron-transfer reactions [5]. Among these, the design and synthesis of light-harvesting antenna systems have been a long-standing issue, which require the

organization of many pigments in a regular arrangement. Inspired by the wheel-like giant architecture of photosynthetic pigments (LH2 and LH1) [6], a particular attention has been focused on the construction of cyclic porphyrin arrays, which may aid the understanding of the fundamental mechanisms of excitation energy transfer (EET) in the natural photosynthetic antenna and/or find new applications as an optoelectronic material [7–13]. LH2 consists of two wheel-like pigment arrays; B800 with nine bacteriochlorophyll *a* (Bchl *a*) and B850 with nine dimeric subunits (totally 18 pigments) of Bchl *a*. Initial process of photosynthesis events is a light-harvesting process which occurs in antenna complex that consists of regularly arranged photosynthetic pigments as seen in LH1 and LH2. While several cyclic oligomeric porphyrins have been synthesized through both covalent and supramolecular approaches toward light-harvesting antenna mimics so far, there were no studies on covalently linked cyclic porphyrin arrays in which the number of porphyrins was changed in a systematic manner.

This paper deals with the synthesis of cyclic arranged porphyrin assemblies that have recently been developed

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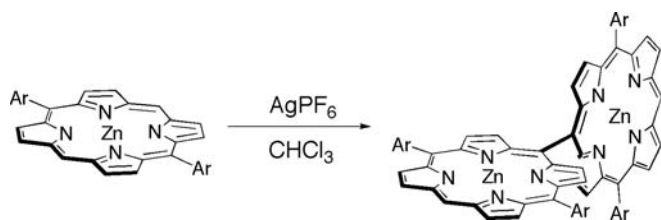
Scheme 1. The key reaction scheme.

by us. Synthesis of *meso–meso* linked diporphyrins by Ag(I)-promoted oxidation of 5,15-diaryl substituted Zn(II) porphyrins [14] opened a new synthetic porphyrin chemistry, in which metalloporphyrins with free *meso*-positions are converted under appropriate oxidation conditions into a variety of directly linked porphyrin arrays with varying electronic interactions (Scheme 1). We have prepared a wide range of covalently linked diporphyrins and porphyrin arrays, including *meso–meso* linked linear porphyrin arrays [14a,14b,14c,14d], two-dimensional windmill arrays [14e], three-dimensional grid-like arrays [14f], and cyclic arrays [15–18], which are interesting as artificial antenna models in terms of the well-defined arrangement of many porphyrins.

2. Background

Ag(I)-promoted *meso–meso* coupling reaction of a 5,15-diaryl Zn(II)-porphyrin has following advantages: (1) the

regioselectivity of the *meso–meso* coupling reaction is always quite high; (2) the molecular length grows rapidly at a rate of 2^n, where n is the number of iterations; (3) the porphyrin array products are highly soluble owing to orthogonal conformations, which allows the manipulation of very long porphyrin arrays; (4) the separation of the coupling products is easy on a recycling preparative GPC–HPLC chromatography as a result of a large difference in the molecular weights of the porphyrin products, and finally (5) the long coupling products still bear two free *meso*-positions that are available for next reaction as long as the porphyrin array is soluble in reaction solvent. Taking advantage of these features, we synthesized a series of *meso–meso* linked porphyrin arrays up to its 1024-mer that have been the longest discrete molecule [14d].

3. Directly linked porphyrin rings [15]

Cyclic porphyrin architectures, in which the constituent porphyrins are all directly linked at *meso–meso* positions, are an attractive target in view of synthetic challenge, higher molecular symmetry, and large and regular electronic interaction between neighboring porphyrins that will lead to efficient EET. Such molecules can be regarded as a genuine porphyrin ring whose electronic π-network consists of only porphyrins, and thus may be interesting also in view of belt-shape aromatic molecules that consist of only aromatic segments. In addition, these molecules will allow direct comparison of molecular morphology effects,
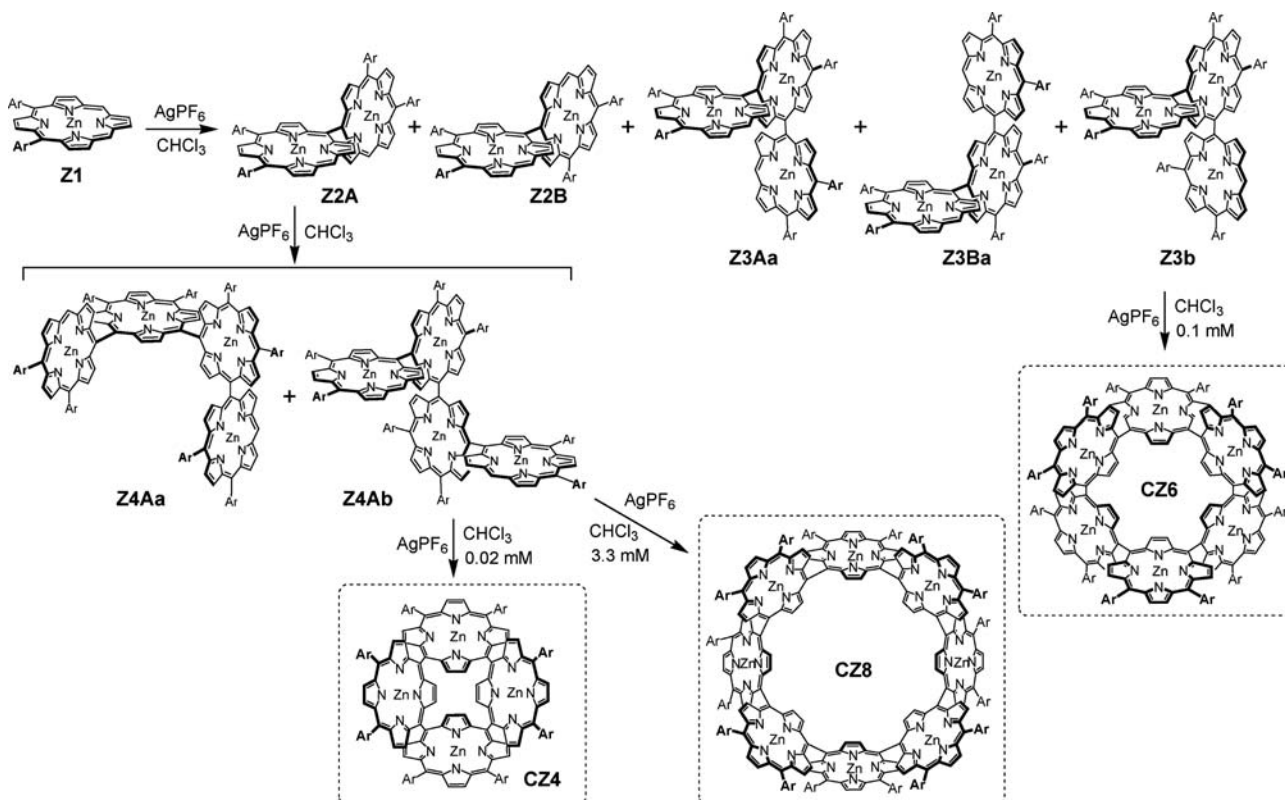
Scheme 2. Synthesis of directly linked porphyrin rings. Ar = 3,5-di-*tert*-butylphenyl.

linear versus *cyclic*, upon the overall photophysical properties of *meso–meso* linked porphyrin arrays.

Directly *meso–meso* linked porphyrin rings **CZ4**, **CZ6**, and **CZ8** that are respectively comprised of four, six, and eight porphyrins have been synthesized in a stepwise manner from a 5,10-bis(3,5-di-*tert*-butylphenyl) zinc(II)-porphyrin building block as follows (Scheme 2). Coupling reaction of **Z1** with AgPF$_6$ in CHCl$_3$ afforded dimer **Z2** (24%), trimer **Z3** (7%) and higher oligomers (Scheme 2). Since a free rotation around the *meso–meso* bond is strictly prohibited, **Z2** is chiral and **Z3** is diastereoisomeric, which will make higher coupling products complicated. In order to avoid this situation, **Z2** was optically separated into two enantiomers **Z2A** and **Z2B** through a chiral HPLC column.

Then, the optically pure **Z2A** was coupled to tetraporphyrin **Z4** (40%), hexaporphyrin **Z6** (10%), and higher oligomers (ca. 6%). The **Z4A** products were then separated by chromatography over a silica gel column into two diastereoisomers **Z4Aa** and **Z4Ab**. Upon treatment with AgPF$_6$, the intramolecular cyclization of **Z4Ab** under dilute conditions (0.02 mM) gave tetrameric porphyrin ring **CZ4** preferentially in 74% yield. Interestingly, oxidative

coupling reaction of a tetramer **Z4Ab** in CHCl$_3$ under higher concentration (3.3 mM) gave octameric porphyrin ring **CZ8** in 29% together with other non-cyclic oligomers.

The triporphyrin fraction **Z3** was separated into two diastereoisomers, an enantiomeric pair of **Z3Aa** and **Z3Ba** and *meso*-isomer **Z3b**, by chromatography over a silica gel column. Upon treatment with AgPF$_6$ at 0.1 mM in CHCl$_3$ for 2 h, **Z3b** gave coupling products, from which hexameric porphyrin ring **CZ6** was isolated in 22% yield as a first eluting fraction.

The structures of **CZ4**, **CZ6**, and **CZ8** were characterized by ESI mass and ^{1}H NMR spectroscopies. The symmetric cyclic structures have been indicated by their very simple ^{1}H NMR spectra, which all exhibit only a single set of porphyrin. Four β-peripheral protons are differentiated in these porphyrin rings. Among them, the chemical shifts of protons that are adjacent to the *meso–meso* linkage exhibit large changes depending on the molecule. To explain these observations, theoretical calculations at the B3LYP/6-31G* level were performed to get respective energy minimized structures (Fig. 1). The calculations have revealed that the dihedral angles between neighboring porphyrins (C_α–C_{meso}–C_{meso}–C_α) are 90° in **CZ6**, 76° (inner)
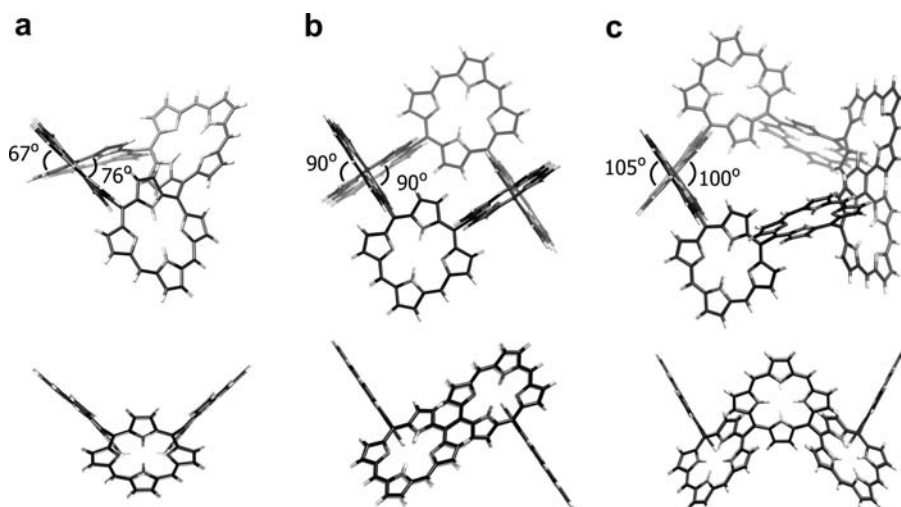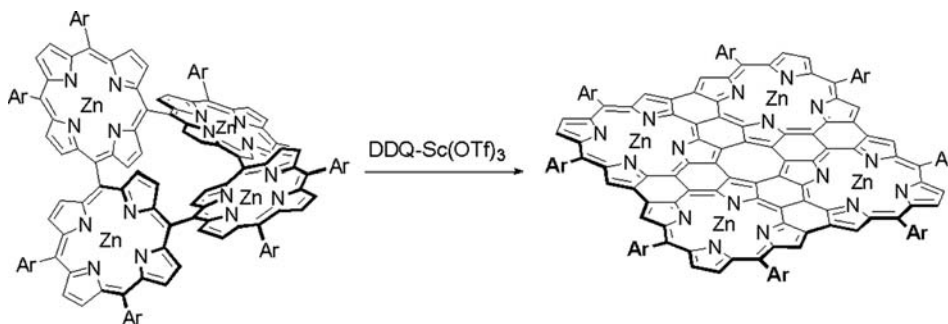

Fig. 1. Energy minimized structures of simplified (a) **CZ4**, (b) **CZ6**, and (c) **CZ8**, in which *meso*-substituents were omitted and zinc atoms were substituted for H2. The dihedral angle between neighboring porphyrins is defined as C_α–C_{meso}–C_{meso}–C_α.

Scheme 3. Synthesis of directly fused porphyrin sheet. Ar = 3,5-di-*tert*-butylphenyl.

and 67° (outer) in **CZ4**, and 100° (inner) and 105° (outer) in **CZ8**.

Characteristically, these cyclic porphyrin arrays exhibit broad non-split Soret absorption band around 460 nm. The excitation energy hopping rates have been estimated for **CZ4** $(119 \pm 2 \text{ fs})^{-1}$, **CZ6** $(342 \pm 59 \text{ fs})^{-1}$, and **CZ8** $(236 \pm 31 \text{ fs})^{-1}$, which reflect the magnitude of the electronic coupling between the neighboring porphyrins. Overall, these porphyrin rings serve as a well-defined wheel-shaped light harvesting antenna model in light of very efficient excitation energy hopping along the ring. Very recently we succeeded in the synthesis of a square planar porphyrin sheet by strong oxidation of **CZ4**, which exhibits a strong paratropic ring current detected above the central cyclooctatetraene core (Scheme 3) [19].

4. *m*-Phenylene linked porphyrin wheels [16,17]

On the basis of Ag(I)-promoted coupling reaction, a dodecameric porphyrin wheel **C12ZA** has been explored, in which six *meso–meso* linked zinc(II) diporphyrin sub-units are bridged by 1,3-phenylene spacers [16]. The synthetic scheme of **C12ZA** is shown in Scheme 4. **2ZA** as a building block was prepared in 56% yield from Suzuki–Miyaura coupling of boronated porphyrin with 1,3-diiodobenzene. Coupling reaction of **2ZA** in freshly distilled CHCl₃ (0.2 mM) with AgPF₆ (1.0 equiv.) for 5 min followed by separation over size-exclusion chromatography gave porphyrin tetramer **4ZA** (28%), hexamer **6ZA** (11%), and octamer **8ZA** (3–5%). Similar coupling reaction of **4ZA** gave **8ZA** (29%), and **12ZA** (14%). Then, we attempted the intramolecular cyclization of the linear porphyrin 12-mer **12ZA**. Under very dilute conditions $(1 \times 10^{-6} \text{ M})$, **12ZA** was treated with 3.0 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 **12ZA** (11.9 min).

This product was isolated by preparative GPC–HPLC in 60% yield together with the recovery of **12ZA** (25%), and was assigned to a wheel-like dodecameric porphyrin array **C12ZA** on the basis of the following facts: (1) the
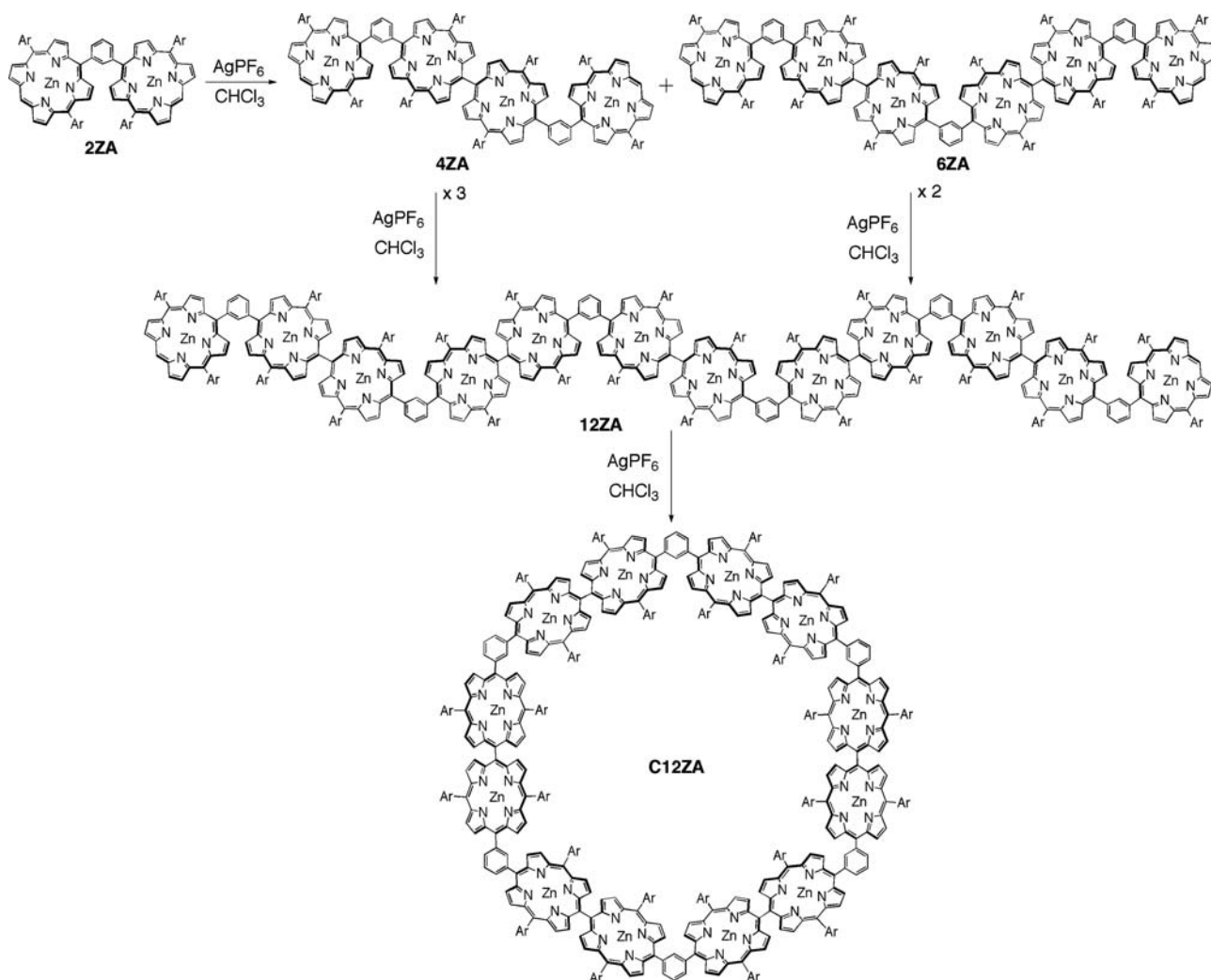
Scheme 4. Synthesis of **C12ZA** from **2ZA**. Ar = 4-dodecyloxyphenyl.

product exhibits the parent ion peak at 11167 (calcd for $C_{708}H_{816}N_{48}O_{24}Zn_{12}$, $m/z = 11167$) in MALDI-TOF mass, indicating its twelve porphyrin units; (2) despite a small difference in the molecular weight, a distinct difference in the retention time on the GPC–HPLC chromatography from **12ZA** indicates a substantial difference in the hydrodynamic volume, which may be arising from an overall drastic change in molecular shape; (3) the ^{1}H NMR spectrum is quite simple, featuring only a single set of a porphyrin subunit, and finally (4) the scanning tunneling microscopy (STM) image of **C12ZA** adsorbed on Cu(100) surface exhibits a clear wheel-like structure. Fig. 2a shows the STM images of **C12ZA** taken at $V_s = 1.5$ V and $I = 37$ pA that reveal a ring spot with discrete hollow. An averaged height of the STM images estimated on the basis of the height histogram is ca. 2.9 ± 1.2 Å. An averaged STM-detected diameter of 35 ± 6.7 Å is consistent with a calculated diameter of ca. 36–38 Å.

According to successful synthesis of **C12ZA**, this synthetic strategy has been applied to a 1,3-phenylene linked tetraporphyrin to produce larger cyclic porphyrin wheel as an extension [17]. Synthetic route to **24ZB** is shown in Scheme 5.

1,3-Phenylene-bridged tetraporphyrin **4ZB** was prepared in 46% yield by Suzuki–Miyaura coupling of a borylated diporphyrin with 1,3-diiodobenzene. To a solution of **4ZB** in CHCl$_3$ (1.0 mM), AgPF$_6$ (0.7 equiv.) was added and the resulting mixture was stirred for 2 min at room temperature. After the usual workup, the products were separated by size-exclusion chromatography to give porphyrin octamer **8ZB** (29%) and dodecamer **12ZB** (10%). In the next step, a solution of **8ZB** (1.0 mM) was treated with AgPF$_6$ (0.7 equiv.) for 2 min at room temperature. The separation over preparative GPC–HPLC gave

hexadecamer **16ZB** (27%), and tetracosamer **24ZB** (10%). All these products have been also characterized by ^{1}H NMR, MALDI-TOF mass, UV–Vis, and fluorescence spectra as well as GPC analysis. Especially MALDI technique is a powerful analytical tool for confirmation of molecular structures of this size.

Then, we examined the intramolecular cyclization of **24ZB** to **C24ZB**. Under highly dilute conditions (1×10^{-6} M), **24ZB** was treated with 3.0 equiv. of AgPF$_6$ for 60 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 new peak at 17.8 min slower than **24ZB** at 17.1 min, hence indicating its smaller hydrodynamic volume. This product was isolated by repeated preparative GPC–HPLC in 34% yield and has been assigned to a wheel-like tetracosameric porphyrin array **C24ZB** on the basis of the same reason for **C12ZA** synthesis, while the ^{1}H NMR spectrum is considerably broad, presumably reflecting an existence of several pseudo-stable conformations in solution. ^{1}H NMR spectra are independent of temperature in the range of $-50\,°C$ to $100\,°C$.

The STM images of **C24ZB** exhibit mostly ellipsoidal shapes, indicating its conformational flexibility of **C24ZB** as compared with rather uniform **C12ZA** (Fig. 2b). The averaged diameter of the STM images of **C24ZB** is 45–70 Å, which matches roughly with its estimated diameter (ca. 70 Å).

Efficient EET along **C12ZA** is aided by large electronic coupling between the neighboring *meso–meso* linked diporphyrin subunits. Similar to the case of **C12ZA**, the efficient EET along the ring has been confirmed for **C24ZB** by the time-correlated measurements, which occurs with a rate of $(35\,ps)^{-1}$ for energy hops between neighboring
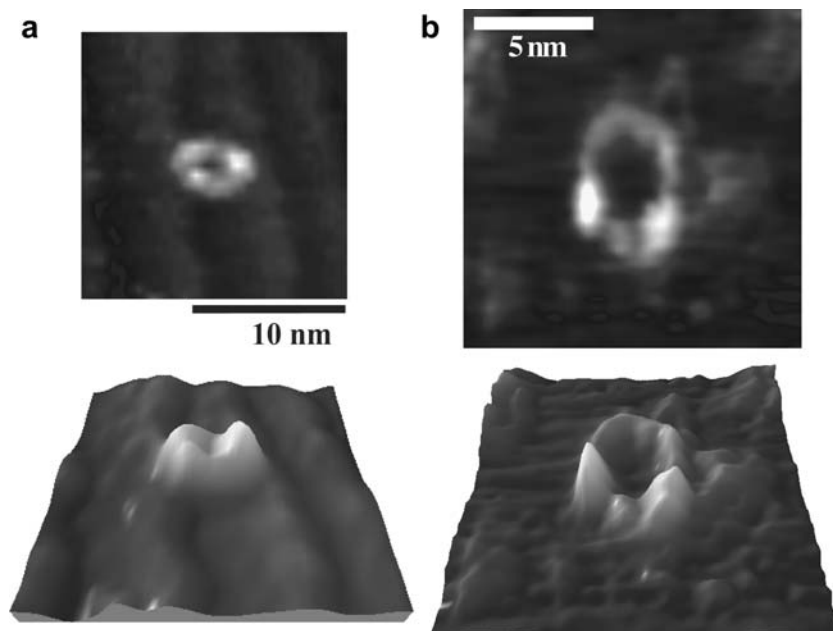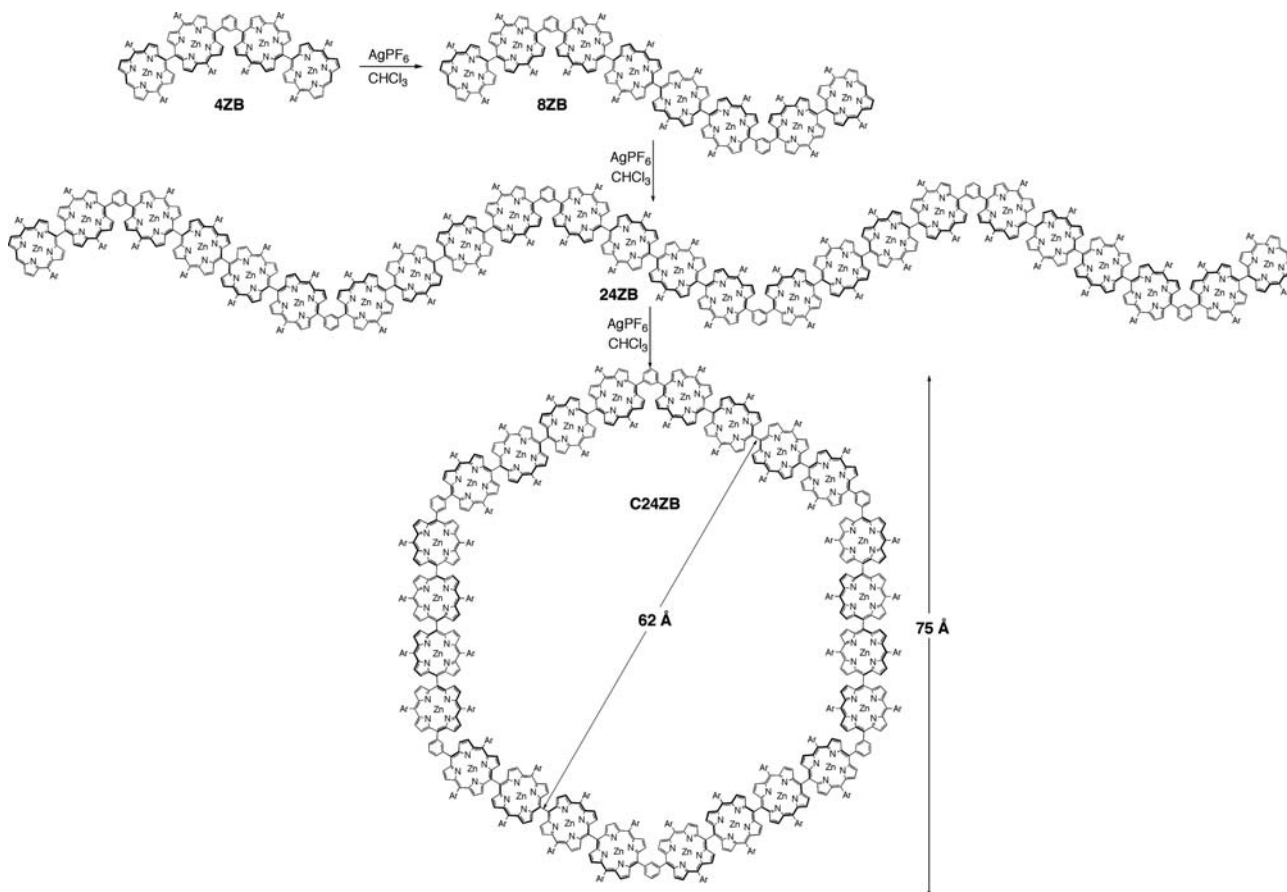

Fig. 2. STM images of (a) **C12ZA** and (b) **C24ZB**.

Scheme 5. Synthesis of **C24ZB** from **4ZB**. Ar = 4-dodecyloxyphenyl.

tetraporphyrin subunits. Collectively, the present work provides an important step for the construction of large cyclic arranged porphyrin arrays with ample electronic interactions as a model of light-harvesting antenna.

## 5. Three-dimensional supramolecular porphyrin boxes [18]

Supramolecular chemistry, using a strategy of non-covalent self-assembly of molecular units, has been developed as a highly promising means for the construction of two- or three-dimensional architectures that have specific structures, properties, and functions [20]. The coordination interaction between zinc(II) porphyrin and pyridine is particularly useful for its easy manipulation, relatively large association constant, and a favorable tendency not to spoil the photo-excited-state dynamics of porphyrins [21]. Large porphyrin wheels as a model of light-harvesting antenna reported by Kobuke and co-workers are excellent examples, where an imidazolyl substituent is used instead of a pyridyl substituent [13].

Spatial control of porphyrinic pigments is crucial in supramolecular design of an artificial photosynthetic antenna, since it directly leads to control of the electronic interactions between chromophores. Molecular self-assembly can translate the covalent connectivity and molecular shape of the components into tertiary architectures. In this

context, a *meso–meso* linked diporphyrin is quite attractive because of its perpendicular conformation, which may lead to unique structures.

We have reported self-assembly behaviors of *meso*-pyridine appended zinc(II) porphyrins **M1**–**M3** and their *meso–meso* linked dimers **D1**–**D3** (Scheme 6). Ag(I)-promoted coupling reaction of **M1** gave **D1** by refluxing the reaction mixture for a longer time. The Ag(I)-promoted coupling reaction of **M2** gave *meso–meso* coupled diporphyrin **D2** along with triporphyrin **T2**. Since the separation of these oligomers was practically impossible due to serious self-aggregation, these zinc(II) complexes were once demetalated to the corresponding free-base porphyrin oligomers, which were separated over preparative GPC to provide diporphyrin and triporphyrin in 32% and 14% yields, respectively. Similarly the Ag(I)-promoted coupling of **M3** gave **D3** in 20% yield. In non-coordinating solvents, the monomeric porphyrins **M1**–**M3** and the dimeric porphyrins **D1**–**D3** spontaneously assemble into porphyrin squares **S1**–**S3** and three-dimensional porphyrin boxes **B1**–**B3**, respectively. Interestingly, formation of **Bn** from **Dn** proceeds via homochiral self-sorting assembly, which has been verified by optical separations of **B1** and **B2**.

Quantitative self-assembly of **D1** as its tetramer **B1** was confirmed by ^1H NMR spectroscopy in CDCl$_3$. On the
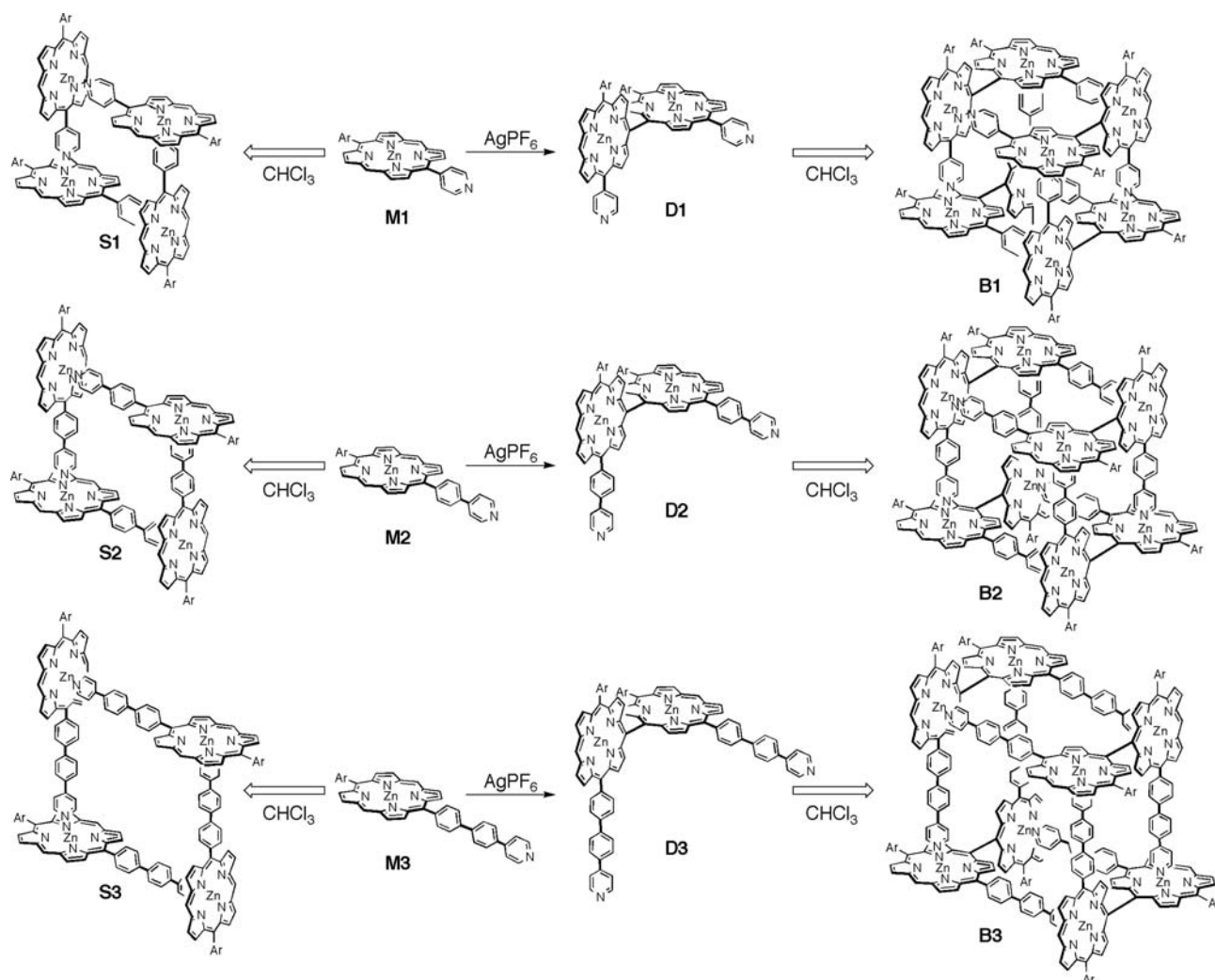
Scheme 6. Construction of self-assembled porphyrin squares **S1–S3** and porphyrin boxes **B1–B3**. Ar = 3,5-dioctyloxyphenyl.

basis of the practical concentration independence of its fluorescence spectral shape (up to 1.0×10^{-8} M), the association constant of **B1** was estimated to be at least $>10^{25}$ M^{-3} in CHCl$_3$. Formation of porphyrin boxes **B2** and **B3** from **D2** and **D3** was similarly indicated by ^{1}H NMR spectra in CDCl$_3$.

The three-dimensional zinc(II) porphyrin boxes **B1–B3** are well-defined discrete molecular entities that are pertinent for the investigations of excitonic interactions and excitation energy migration processes. Actually, optically pure enantiomers of **B1** and **B2** display strong Cotton effects in the CD spectra depending on the length of the pyridyl arm, thus providing evidence for the exciton coupling between the non-covalent neighboring porphyrin rings.

Excitation energy migration processes within **B***n* have been investigated by steady-state and time-resolved spectroscopic methods in conjunction with polarization anisotropy measurements. Consequently, the excitation energy hopping rates between the zinc(II) diporphyrin units have been estimated for **B1** $(48 \text{ ps})^{-1}$, **B2** $(98 \pm 3 \text{ ps})^{-1}$, and **B3**

$(361 \pm 6 \text{ ps})^{-1}$. Overall, the self-assembled porphyrin boxes **B***n* serve as a well-defined three-dimensional model for the light-harvesting complex.

6. Summary

The *meso–meso* linked porphyrin arrays where constituent porphyrins are connected directly without any linkages can be promising molecular architectures for the application of molecular photonic and electronic wires, since they have well-defined rigid structures and ample electronic interactions between neighboring porphyrin pigments for efficient EET without any energy or charge sink. The directly linked cyclic porphyrin architectures were synthesized in a stepwise manner. These porphyrin ring molecules have been shown to serve as a platform to enable very efficient EET processes along the ring circuit with rates that rival those of natural cyclic photosynthetic antenna. Future work will focus on incorporation of these functional units into more elaborate model systems and exploration of larger directly linked porphyrin arrays.

Acknowledgements

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