

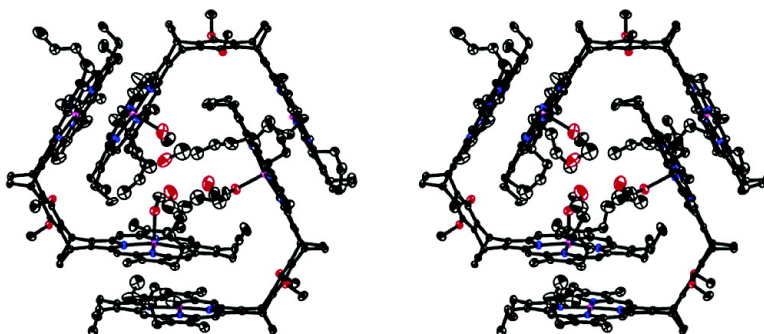
Communication

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Hexagonal Columnar Porphyrin Assembly by Unique Trimeric Complexation of a Porphyrin Dimer with π - π Stacking: Remarkable Thermal Behavior in a Solid

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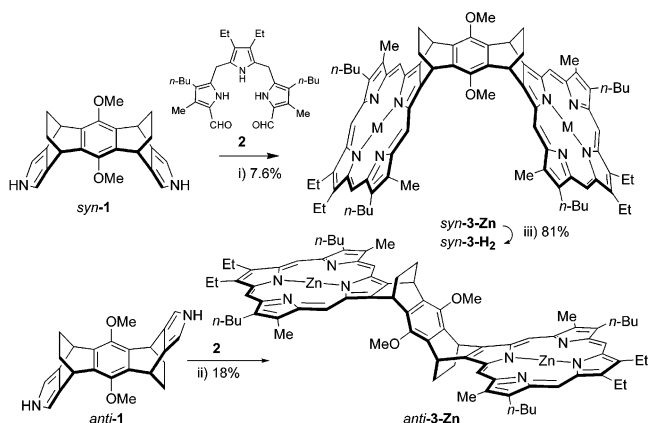
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Construction of structurally well-defined, highly ordered supramolecular systems containing porphyrinoid units is of great interest in relation to the light-harvesting system in photosynthesis¹ and application to material chemistry.² Most investigations on porphyrin assemblies toward construction of the artificial light-harvesting system have been focused on the connection of porphyrin units with strong bonds such as covalent,³ coordination,⁴ and hydrogen⁵ bonds forming oligomeric or polymeric porphyrin molecules, because the intermolecular interactions such as π - π stacking, van der Waals, and hydrophobic interactions are thought to be too weak to maintain the supramolecular motif even under slightly different conditions, although many porphyrins are known to exist as dimeric couples by the π - π stacking in crystals.⁶ During the course of our investigation on the preparation of a series of diporphyrins fused with acene units,⁷ we found a unique trimeric π - π stacking assembly of a diporphyrin intermediate. In this paper, we will show the structure of the diporphyrin intermediates and their conversion to diporphyrins fused with an anthracene derivative.

Diporphyrins were prepared starting from the known 5,8-dihydro-5,8-ethanonaphthoquinone⁸ via dipyrroles **1**. Porphyrin synthesis of reverse [3+1] protocol⁹ was applied to the preparation of diporphyrin intermediates **3**, and *syn*-**3-Zn** and *anti*-**3-Zn** were obtained in respective yields of 7.6% and 18% (Scheme 1). Conversion of *syn*-**3-Zn** to free base *syn*-**3-H₂** was achieved by treatment with TFA in 81% yield.

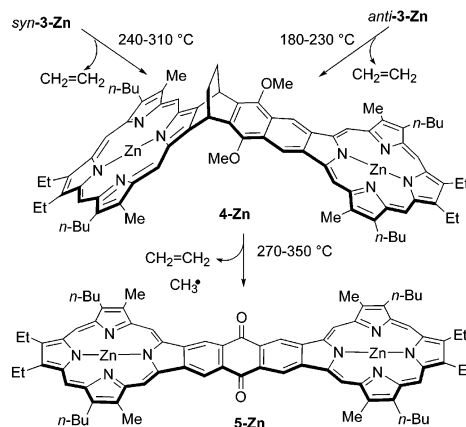
The thermal behavior of diporphyrin intermediates **3** was examined by DSC and TG-GCMS at a rate of 15 °C/min. In *syn*-**3-Zn**, extrusion of one ethylene molecule was observed from 240 to 310 °C, and another ethylene molecule came off in the range 280–350 °C. In the latter conversion, methane and C₃H₆ species (cyclopropane or propene) were simultaneously generated. The total amounts of these gases generated from one molecule of *syn*-**3-Zn** were 1.89 (ethylene), 0.96 (methane), and 0.35 (C₃H₆). The latter species can be formed by the disproportionation¹⁰ of methyl radicals to methane and a methylene carbene followed by cyclopropanation of the carbene with ethylene, or by addition of a methyl radical to ethylene followed by hydrogen abstraction with the methyl radical. To examine the conversions, we checked the remaining material (Scheme 2). When the red crystals of *syn*-**3-Zn** were heated at 270 °C for 1 h under vacuum in a glass tube oven, a green solid of porphyrin-naphthoporphyrin diad **4-Zn** was quantitatively obtained. Further heating of the solid at 340 °C in 1.5 h caused the next conversion, giving a black solid. The solubility of the black solid was very poor, and the solid was only sluggishly soluble in hot pyridine. Spectroscopic analyses of the pyridine extract revealed

Scheme 1^a



^a Reagents and conditions: (i) TFA, CHCl₃; Zn(OAc)₂·2H₂O, CHCl₃; (ii) TFA, PhCl; Zn(OAc)₂·2H₂O, PhCl; (iii) TFA.

Scheme 2. Thermal Behavior of Diporphyrins **3-Zn** in a Solid



that the obtained product was quinone **5-Zn**.¹¹ Similar but rather lower thermal conversions were observed in *syn*-**3-H₂** (240–290 °C and 260–330 °C).

Contrary to the behavior in the solid, *syn*-**3-Zn** was converted to **4-Zn** at 200 °C for 1 h in diphenyl ether, and then **4-Zn** completely changed to **5-Zn** at 260 °C for 1 h. The thermal solid-state conversions of *anti*-**3-Zn** to **4-Zn** occurred in a temperature range (180–230 °C) similar to that of the decomposition of *syn*-**3-Zn** in the solution.

The remarkably different behavior of *syn*- and *anti*-**3-Zn** prompted us to perform X-ray analyses. Single crystals of *syn*-**3-Zn** suitable for the X-ray analysis were easily obtained when a solution of *syn*-**3-Zn** in CH₂Cl₂/PhCl (2/1) was placed in a jar containing MeOH for a few days, and the structures were successfully solved

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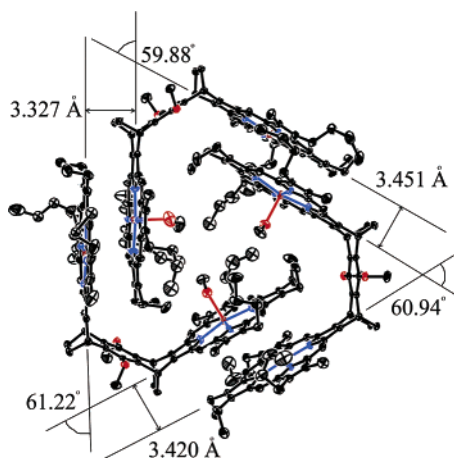


Figure 1. Asymmetric unit of the crystal structure of *syn*-3-Zn from PhCl/MeOH (vertically from the *a*–*b* plane). Solvents except for the coordinated methanol, less popular disordered atoms, and hydrogen atoms are omitted for clarity.

and refined.¹² The space group is *P*-1, and atoms without the non-coordinated solvent and disordered less-popular atoms in the asymmetric unit are shown in Figure 1.

From Figure 1, three diporphyrin molecules of *syn*-3-Zn gathered nicely as three comma-shaped figures in a circle, forming a hexagonal columnar porphyrin assembly. In this unit, the angles between the intramolecular porphyrin rings are 60.94(4)°, 61.22(4)°, and 59.88(4)°; the porphyrin rings are nicely stacked intermolecularly; and no distinctive strain seems to exist. The averaged distances of zinc and four nitrogen atoms to the facing porphyrin mean planes are calculated to be 3.451(5), 3.420(5), and 3.327(5) Å. These values are commonly observed in stacking porphyrins.⁶ In the shortest pair of stacking porphyrin rings, each zinc atom sits just on the nitrogen atom of another porphyrin to minimize the electrostatic π – π repulsive interactions.⁶ In other cases, zinc atoms are nearly above the meso carbons where the interaction is thought to be also small. In the center cavity of this trimeric motif, there are six methanol molecules which form a hydrogen bonding network, and three of them coordinate to zinc atoms. Other solvent molecules occupy the space between the trimeric units with disordered structures.

Single crystals of *anti*-3-Zn were obtained only in the presence of pyridine, and the structure was solved and refined.¹⁴ The space group is *P*-1, the *anti*-3-Zn molecule occupies one of the special positions (-1), and two pyridine molecules coordinate to the zinc atoms from the same side of the ethylene bridges. The molecules are piled along the *a* axis with an off-set angle of ca. 30°. Therefore, no stacking of the porphyrin chromophores is observed.

In conclusion, we have found the first example of a hexameric porphyrin assembly of *syn*-3-Zn which is made only by π – π stacking interactions. This structural feature of *syn*-3-Zn would be one reason for its quite different thermal behavior as compared to that of *anti*-3-Zn in a solid. This unique motif of hexameric porphyrin assembly may open a new strategy for accumulation of porphyrin chromophores in artificial photosynthesis or photodevices. We also demonstrated the efficiency of our retro-Diels–Alder strategy for the construction of large π systems even if they were labile toward oxidation with air.

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Supporting Information Available: Crystallographic information files (CIF) for *syn*-3-Zn from PhCl/MeOH and *anti*-3-Zn from pyridine/PhH, ORTEP drawings of *syn*- and *anti*-3-Zn, stacking figures of the porphyrin chromophores of *syn*-3-Zn, packing diagram of *anti*-3-Zn, TG-GCMS data of *syn*-3-Zn, preparation scheme for **1**, and spectroscopic data for *syn*-1, *anti*-1, *syn*-3-Zn, *syn*-3-H₂, *anti*-3-Zn, 4-Zn, and 5-Zn (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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