JOURNAL OF THE AMERICAN CHEMICAL SOCIETY

Communication

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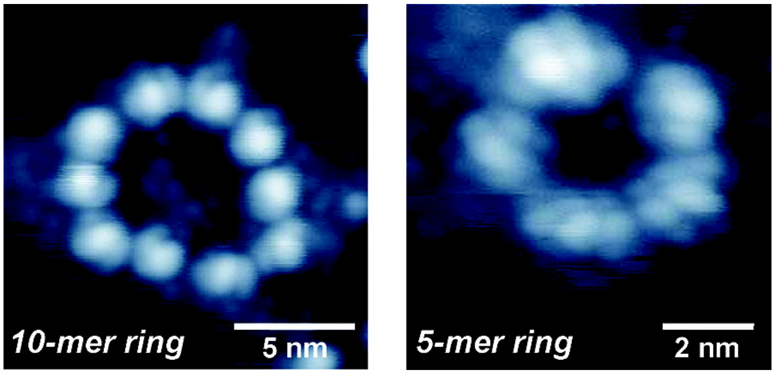
*J. Am. Chem. Soc.*, **2005**, 127 (24), 8598-8599• DOI: 10.1021/ja051344y • Publication Date (Web): 25 May 2005



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# Single Molecule Visualization of Coordination-Assembled Porphyrin Macrocycles Reinforced with Covalent Linkings

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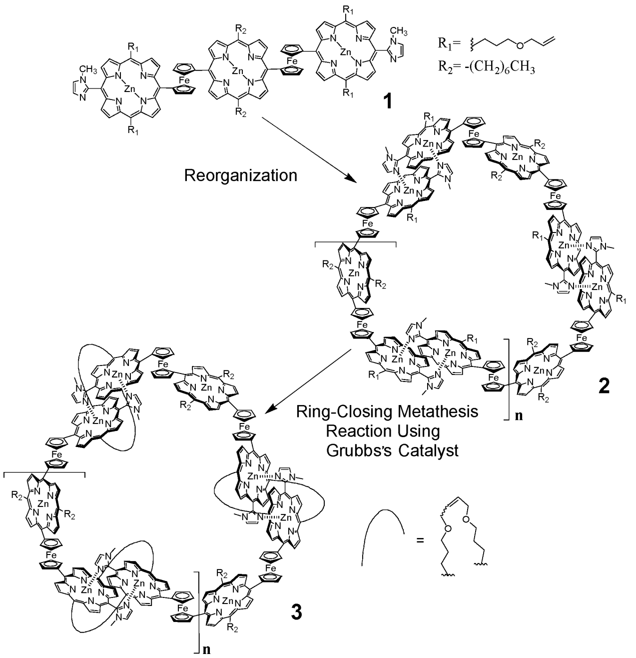
Supramolecular chemistry has emerged as a powerful strategy for construction of molecular-based devices with advanced functions and well-defined nanometer-scale structures.[1] Structural determination of supramolecular aggregates is of great importance and mainly performed by means of NMR and/or X-ray crystal analysis. One of the convincing ways to evaluate or even visualize the structure, other than those just mentioned, is scanning probe microscopy. For example, antenna complexes in photosynthetic bacteria and their aggregates have been demonstrated.[2] Scanning tunneling microscopy (STM) has received considerable attention since it provides clear images of organic molecules adsorbed on a conductive substrate with atomic resolution.[3] In STM measurements, porphyrins and phthalocyanines have been most appealing organic molecules as their extended large $\pi$ system with flat and rigid structure is suitable for adsorption on substrate and for tunneling current generation, as well. A large number of studies have been reported for STM measurements of porphyrins,[4] phthalocyanines,[5] their mixtures,[6] and covalently linked multi-porphyrins.[7] Even though multi-porphyrins assembled on metal substrates and at metal−liquid interfaces have been widely exploited and have afforded clear STM images with molecular resolution,[4] those assembled in solution, in contrast, have not yet been a target of STM observation because large adsorption energy during deposition tended to dissociate the self-assembled structures formed in solution. Recently, we have reported that ferrocene-bridged trisporphyrin (**1**) formed a series of self-assembled porphyrin rings (**2**) from dimer to decamer based on the complementary coordination of imidazolylporphyrin and confirmed their ring structures by covalent linking of the complementary coordination pairs using Grubbs's catalyst (Scheme 1).[8] The coordination-assembled large rings reinforced with covalent linking (**3**) are expected to survive during deposition onto the metal substrate and to be applicable to STM measurements. In this report, we provide the first clear single molecular STM images of the decamer ($\mathbf{3}_{(10-\mathrm{mer})}$) and the pentamer ($\mathbf{3}_{(5-\mathrm{mer})}$) rings in a series of the coordination-assembled porphyrin macrorings.

We have already established a method of pulse injection on a metal surface for observing structures of supramolecular assemblies under ultrahigh vacuum (UHV) condition at liquid nitrogen temperature.[9] An image of an almost perfect circular shape of the decamer ring ($\mathbf{3}_{(10-\mathrm{mer})}$) deposited on a Au(111) surface was observed, as shown in Figure 1a.[10] The number of bright spots in the image was consistent with the number of constitutional units along the circle. In addition, the ring size, taking an almost perfect circular shape (10.4 nm), is in good agreement with the corresponding model structure assuming the circular structure (10.5 nm, Scheme 2). In contrast, the decamer ring without covalent linking did not give clear circular images (see Supporting Information), suggesting that the complementary coordination alone is not sufficient to maintain the supramolecular structure on metal substrate despite its extremely large binding constant (more than $10^{11}\ \mathrm{M}^{-1}$ that corresponds to 62.8 kJ/mol at $T = 298.15$ K). The nonamer ring ($\mathbf{3}_{(9-\mathrm{mer})}$) image with nine bright spots was also observed, affording an image similar to that of $\mathbf{3}_{(10-\mathrm{mer})}$ (see Supporting Information).[11] The pentamer ring ($\mathbf{3}_{(5-\mathrm{mer})}$) also gave an image of five bright spots in a circle (Figure 1b), and its size, again, agreed well with the calculated model structure (Scheme 2). The bright spot must correspond to the complementary dimer unit including two ferrocene moieties because the linear oligomer,[8] which has three complementary coordination pairs and two central porphyrins, gave linear images with three bright spots (see Supporting Information). The absence of clear internal structure in the bright parts, having often been observed for porphyrin and phthalocyanine, whose planes come into contact with the substrate,[4−6] suggests that the porphyrin planes are not sitting on the substrate. The boundary parts between two bright spots may correspond to the central porphyrins in the trisporphyrins whose planes are assumed to be sitting on the surface. The center-to-center (zinc to zinc) distance of the central porphyrins calculated by molecular

***Scheme 1.*** Preparation of the Coordination-Assembled Porphyrin Rings Reinforced with Covalent Linking (**3**)[a]



[a] A series of rings (**2**) was prepared from **1**, and its covalent linking was performed by a ring-closing metathesis reaction of allyl substituents at *meso*-positions of the porphyrin using Grubbs's catalyst. Each component of **3** was separated using preparative GPC.[8]

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10.1021/ja051344y CCC: $30.25

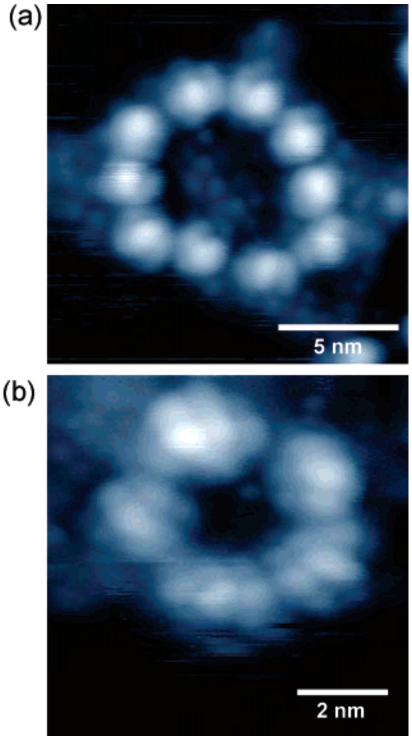
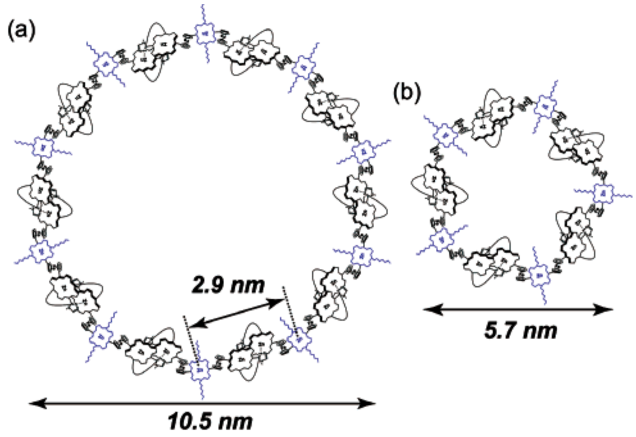


***Figure 1.*** UHV−STM images of the rings of ferrocene-bridged trisporphyrin on a Au(111) surface at liquid nitrogen temperature: (a) $\mathbf{3}_{(10-\mathrm{mer})}$, $I = 0.3$ nA, $V_s = +2.5$ V; (b) $\mathbf{3}_{(5-\mathrm{mer})}$, $I = 0.3$ nA, $V_s = +3.25$ V.

***Scheme 2.*** Schematic Representation of (a) $\mathbf{3}_{(10-\mathrm{mer})}$ and (b) $\mathbf{3}_{(5-\mathrm{mer})}$ Expressed in Perfect Ring Structures[a]



[a] The sizes of the rings are values estimated using the molecular models created using Cerius$^2$ MatSci (version 4.6) (see Supporting Information).

modeling (2.9 nm) agreed with the average distance between two boundaries across the bright spot (2.4 ± 0.3 nm) in the image of decamer ring. The geometry calculation of 5,15-bis(ferrocenyl)-porphyrinatozinc(II) using AM1[12] method indicated that the angle between the cyclopentadienyl ring of ferrocene and the porphyrin plane is about 45° due to their mutual steric repulsion (see Supporting Information). The plane of the central porphyrin in the trisporphyrin should, therefore, be almost orthogonal to that of the imidazolylporphyrinatozinc(II). The interaction of the decamer ring with the substrate may be stabilized when the plane of the central porphyrin comes into contact with the surface in which *n*-heptyl substituents at the *meso*-positions of the central porphyrin contribute to the favorable adsorption. Accordingly, the complementary dimers stand on the substrate with almost perpendicular orientation of porphyrin planes, in accord with the above observation. It is also compatible with the idea that the bulky *N*-methylimidazolyl group coordinated to zinc porphyrin is likely to avoid a close contact with the plane of the complementary coordination porphyrin to the surface.

In conclusion, we have observed single molecular STM images of the coordination-assembled porphyrin macrocycles deposited on a metal surface by the pulse injection method and succeeded in visualizing the extremely large porphyrin macroring consisting of 30 porphyrins with hollow structure. Covalent linking of the coordination pairs was effective to reinforce the supramolecular structure on a metal surface. This strategy will allow us to know the real structure of supramolecular assemblies by STM, rather than by NMR or X-ray crystal analysis. This will be applicable to a variety of supramolecular assemblies.

**Acknowledgment.** The work at Nara Institute of Science and Technology was supported by a Grant-in-Aid for Scientific Research (A) (No. 15205020) and on Priority Areas (No. 16033244), from the Ministry of Education, Culture, Sports, Science, and Technology, Japan. The work at Osaka University was supported by the Center of Excellence (COE) program supported by the Ministry of Education, Culture, Sports, Science, and Technology.

**Supporting Information Available:** Experimental Section and STM images of $\mathbf{3}_{(10-\mathrm{mer})}$ with different shapes and $\mathbf{3}_{(9-\mathrm{mer})}$, the linear oligomer, and large-scale STM images of $\mathbf{3}_{(10-\mathrm{mer})}$, $\mathbf{3}_{(9-\mathrm{mer})}$, and the noncovalently linked decamer ring. The molecular models of 5,15-bis-(ferrocenyl)porphyrinatozinc(II), $\mathbf{3}_{(10-\mathrm{mer})}$, and $\mathbf{3}_{(5-\mathrm{mer})}$. This material is available free of charge via the Internet at http://pubs.acs.org.

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(10) Reflecting the hinge-like flexibility provided by the ferrocene connector, circular images of the decamer and nonamer rings with different shapes were also observed (see Supporting Information).

(11) The decamer ring was accompanied by small amounts of $\mathbf{3}_{(9-\mathrm{mer})}$ and $\mathbf{3}_{(11-\mathrm{mer})}$, which were clearly differentiated from $\mathbf{3}_{(10-\mathrm{mer})}$ in the image observation.

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JA051344Y