

Single molecular observation of penta- and hexagonal assembly of bisporphyrin on a gold surface†

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Artificial light-harvesting antennae of coordination-organized macrocyclic porphyrin pentamer and hexamer are visualized by high resolution scanning tunneling microscopy (HRSTM) on a gold surface.

The advance of supramolecular chemistry has made available various nanometer-sized organic molecules.¹ In addition to traditional structural analysis techniques for organic compounds, such as NMR and X-ray diffraction of single crystals, direct observation of real supramolecular structures by high-resolution scanning tunneling microscopy (HRSTM) is expected to provide a new structural analysis method.²

Porphyrins and their related compounds are known to be electronically active and good photomaterials. Their well-ordered aggregates are of interest for nanometer-sized photonic and electronic devices, such as light-harvesting antennae,³ conductive wires,⁴ and non-linear optical devices.⁵

In our continuous effort to construct porphyrin-based supramolecular light-harvesting antennae,⁶ pentagonal and hexagonal macrocycles, **C-EP5** and **C-EP6**, were recently synthesized.⁷ Proton NMR analysis in solution indicated clear cyclic structures in which imidazolyl-zinc-porphyrins formed slipped-cofacial arrangements, and all of the porphyrins rotated freely along the ethyne axis. (Fig. 1)

In this report, the pentagon and the hexagon are characterized directly by HRSTM. In our previous report on STM observation of ferrocene-bridged trisporphyrin macrorings, although we were able to resolve clearly the numbers of aggregated units, submolecular resolution was not achieved.⁸ Now, the slipped-cofacial arrangement is clearly observed and assigned by comparison with the disassociated structure obtained at submolecular resolution.

Pentameric and hexameric porphyrin macrorings, **C-EP5** and **C-EP6**, and linear **C-EP2** were prepared from bis(imidazolyl-zinc-porphyrin) **Zn-EP-Zn** according to the literature.⁷ They were purified by gel permeation chromatography. A **C-EP5**-rich sample containing approximately 2% **C-EP6**⁹ was used for ultrahigh vacuum STM measurement. A chloroform solution of the sample (1–0.1 μM) was deposited on a Au(111) surface by the pulse injection technique reported previously.¹⁰ STM images obtained

under +4 V and +2 V are shown in Fig. 2. At the high sample bias voltage ($V_s = +4$ V), circles are composed of five or six large bright spots of almost even brightness, whereas at $V_s = +2$ V, the brightest spots turn to medium brightness. Thus, in the former image, all the porphyrins appear as bright spots. Each bright spot corresponds to two porphyrins separated by imidazolyl groups, and each dark node corresponds to a bisethynylphenylene moiety. (Fig. 2a and b) By contrast, the latter image represents more local information. (Fig. 2c and d) Different brightnesses in the latter images reflect mainly height differences in the object. The detailed molecular structure at submolecular resolution is obtained by STM at $V_s = +2$ V.

Careful examination of Figs. 2c and S1 reveals that some rings contain different numbers of bright spots at random. The bright spots are thought to lie at a higher position than the other ring components. In order to find the origin of the different heights in the ring, two extreme pentagonal rings are magnified in Fig. 3. One consists of five isolated spots (Fig. 3a), while the other consists of many smaller dots (Fig. 3b). Each profile along the line indicated in Figs. 3a and 3b is shown below the respective figure.¹¹ In Fig. 3a, the height of the bright spots reaches *ca.* 6 Å. By contrast, an almost flat structure is observed in Fig. 3b, except for one bright dot. The height of the flat part (*ca.* 1.5 Å) suggested a porphyrin monolayer^{2b,12} and the bright dot is higher than the flat part by approximately 1 Å. The ring size in Fig. 3a is almost consistent with a molecular model of **C-EP5**, as superimposed in Fig. 3c.¹³ The center-to-center distance (3.6 nm) between the two bright spots in the ring agrees well with that obtained from the model (3.66 nm). On the other hand, the size of the ring in Fig. 3b is apparently larger than the model and distorted from the symmetric pentagon. The flat structure suggests dissociation of the slipped-cofacial structures. When molecular models of **Zn-EP-Zn** are applied to the image,¹³ STM images obtained as submolecular resolution are assigned as shown in Fig. 3d. Characteristic points in the image are well-fitted in detail. (1) Five elbows are assigned as 1,3-bis(ethynylphenylene) moieties, as indicated by arrows in Fig. 3d. (2) Square shapes connected to the elbows are assigned as porphyrin rings. (3) Bright dots at the opposite corner to the elbows are assigned as *N*-methyl groups (white circles in Fig. 3d) of imidazoles substituting the porphyrins because they lie higher than the porphyrin plane due to their perpendicular orientation.¹⁴ (4) Dots extended from the other two corners are assigned as substituents at the *meso* position of the porphyrins. Another image of a completely disassociated hexamer was assigned in a similar manner. (Fig. S2)

STM images of acyclic **C-EP2** are also measured at $V_s = +2$ V for comparison. (Fig. S3) Similarly to the ring images, bright spots

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† Electronic supplementary information (ESI) available: Experimental section. STM images of **C-EP2**, **C-EP5** and **C-EP6**. See DOI: 10.1039/b603360a

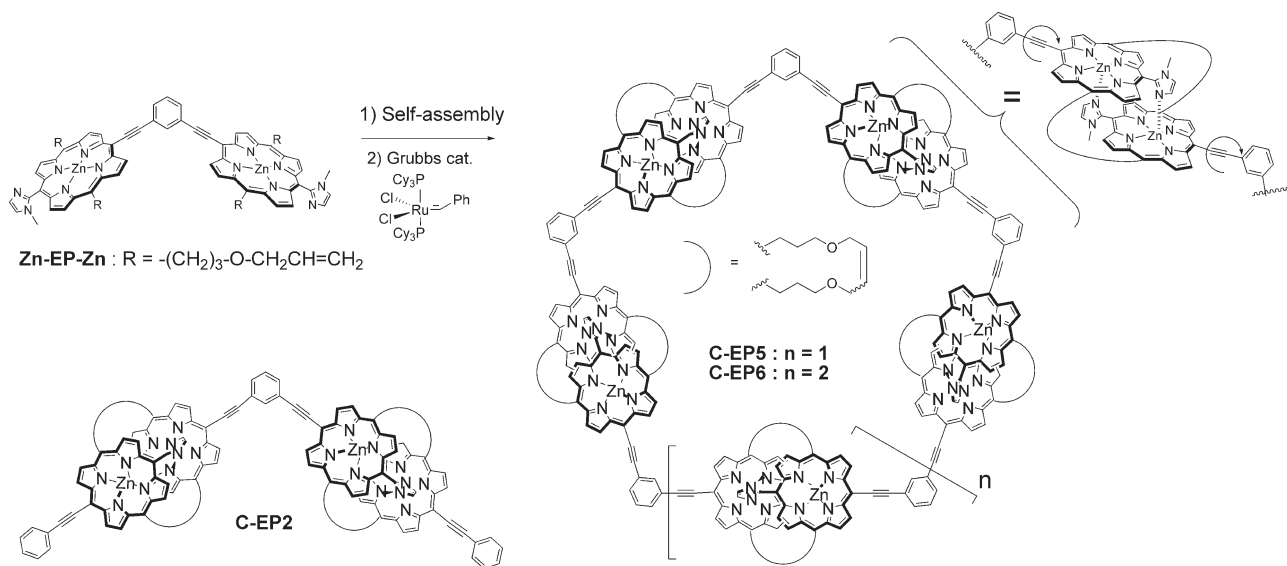


Fig. 1 Structures of Zn-EP-Zn, C-EP5, C-EP6, and C-EP2.

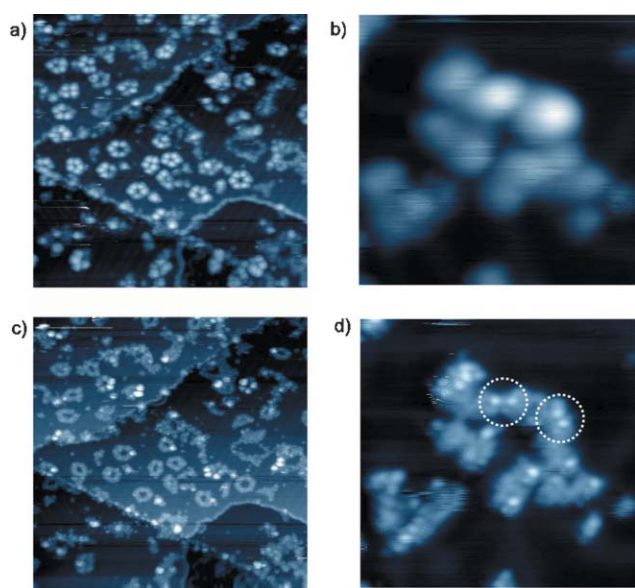


Fig. 2 HRSTM images of C-EP5 and C-EP6 on Au(111). Bias voltage: (a) and (b) +4 V, (c) and (d) +2 V. Scale: (a) and (c) X = 100 nm, (b) and (d) X = 15 nm. Data of the same area are shown in (a) and (c), and (b) and (d). White circles in (d) indicate bright parts in (b). The linear arrays, single dots and much larger rings in (c) are probably formed after deposition on gold as a result of bond breaking or due to contaminations.

corresponding to the slipped-cofacial dimer moieties are observed. The distance between two bright spots in the molecules is consistent with that obtained from the molecular model (3.6 nm). Thus, the image of the reference compound C-EP2 supports the assignment of the ring image in Fig. 3c.

To validate the assignment further, attempts were made to disassociate slipped-cofacial dimers operationally by repeated scanning. In Figs. 4a and 4b, six bright spots corresponding to six slipped-cofacial dimers were observed. One of the bright spots darkened after the eighth scanning (Fig. 4c). Another bright spot

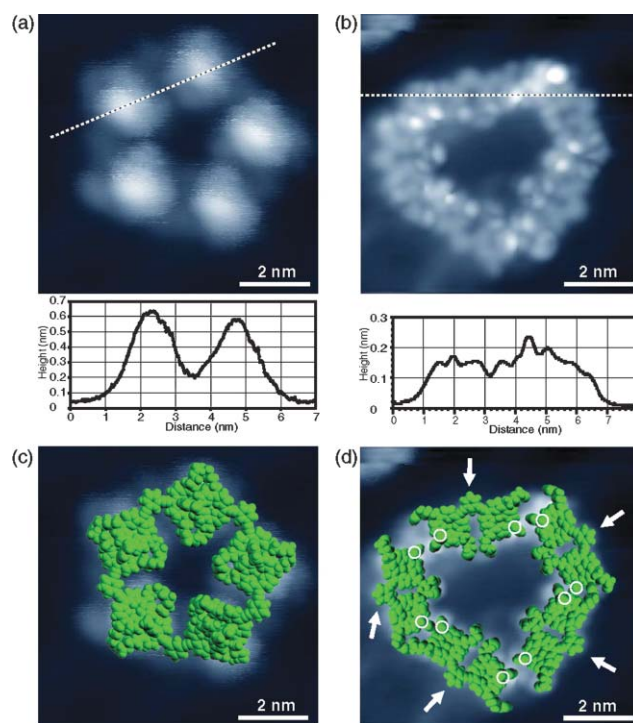


Fig. 3 Selected HRSTM images of C-EP5 on Au(111) (Bias voltage: +2 V, Scale: X = 9 nm). (a) non-disconnected pentameric ring, (b) completely disconnected pentameric ring, (c) superimposed image of molecular model C-EP5 (green) on (a), and (d) superimposed image of molecular model from five Zn-EP-Zn (green) on (b). White circles in (d) indicate N-methylimidazole parts standing orthogonally to porphyrin planes. They correspond to five pairs of bright spots in (b). White arrows in (d) indicate elbows. (See text).

darkened after the twelfth scanning (Fig. 4d). The scanning triggered disassociation of the slipped-cofacial dimer. These results clearly indicate that the disassociated structures originate from the slipped-cofacial dimers.

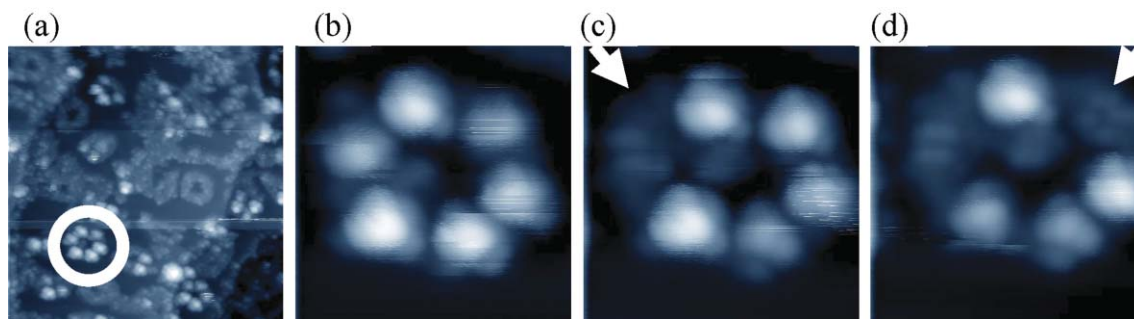


Fig. 4 Successive HRSTM images of C-EP6 on Au(111) (Bias voltage: +2 V) Scale: (a) X = 50 nm, (b), (c), and (d) X = 9 nm. (a) and (b) the initial state, (c) after 8th scans, (d) 12th scans. White arrows in (c) and (d) indicate disassociated dimers due to repeated scans.

In conclusion, the molecular pentagon C-EP5 and hexagon C-EP6 were observed by HRSTM. Each slipped-cofacial dimer part structurally defined by NMR was observed as one bright spot. The profile indicated that the slipped-cofacial dimer plane lay horizontally, not oriented vertically on the Au surface. In contrast, the disassociated structure of the slipped-cofacial dimer was observed at submolecular resolution. These results indicate that the intact (not disassociated) slipped-cofacial dimer that lay on the Au surface was observed as one spot with the height of the dimer.

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