STM images of individual porphyrin hexamers; *meso–meso* singly linked orthogonal hexamer and *meso–meso*, β–β, β–β triply-linked planar hexamer on Cu(100) surface

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Geometrical structures of chain porphyrin arrays adsorbed on Cu(100) are observed by STM: a bridge-like bent structure for *meso–meso* singly linked orthogonal hexamer, whereas a rigid planar and one-dimensionally stacked structure for *meso–meso*, β–β, β–β triply-linked hexamer.

Porphyrins have been studied in a variety of fields including artificial photosynthesis, catalysts, photodynamic therapy, sensors, light-emitting diodes, and so forth.[1] Porphyrins have been shown to be quite tunable through a variety of organic transformations, hence leading to diverse interesting functionalized monomers or oligomers.[1,2] These advances in the synthesis of discrete oligomeric porphyrin arrays have stimulated the consideration of their uses for future molecular-based electronics. Recently we have explored discrete *meso–meso* linked porphyrin arrays up to 128-mer[3] and fully conjugated porphyrin tapes up to 12-mer.[4] The former is by far the longest (*ca.* 0.1 μm) man made discrete molecule and the latter exhibits an unprecedented very small optical HOMO–LUMO gap (*ca.* 0.43 eV).[4] Understanding of the properties of these porphyrin arrays adsorbed on metal surfaces that may differ from those in solution is apparently a key requirement for the future use of these molecules as molecular wire in single molecular electronic devices. Although scanning tunneling microscopy (STM) has been often demonstrated to be useful for studies on the conformational and electronic structures of porphyrin monomers on metal surfaces,[5] covalently linked discrete porphyrin oligomers whose molecular lengths may be long enough for application in molecular electronics have been outside the STM study.

In this communication, we report the STM images of directly linked porphyrin hexamers, *meso–meso* singly-linked hexamer **A** and *meso–meso*, β–β, β–β triply-linked hexamer **B** adsorbed on a Cu(100) surface. Peripheral long side chains are necessary for rendering these long molecules soluble enough for manipulations as well as the STM molecular scale imaging feasible with avoidance of rapid diffusion of the arrays on the metal surface. As schematically shown in Fig. 1, the hexamer **A** is considered, on the basis of its symmetric ^{1}H NMR spectrum, to take an averaged linear structure consisting of six directly linked porphyrins that are held in an orthogonal conformation in solution,[3,6] whereas the hexamer **B** has a rigid tape-shaped flat structure due to the triple linkages between the constituent porphyrins that is favorable for π-conjugation, hence exhibiting a small optical HOMO–LUMO gap (0.67 eV from the absorption spectrum and 0.61 eV from the IR spectrum of KBr pellet).[4]

meso–meso Linked orthogonal porphyrin hexamer **A** was prepared by Ag[I]-promoted *meso–meso* coupling reaction,[4] and *meso–meso*, β–β, β–β triply-linked planar porphyrin hexamer **B**

was prepared by Sc[III]-catalyzed oxidation of *meso–meso* linked porphyrins.[3] Clean flat Cu(100) surfaces were obtained by Ar^{+} sputtering and annealing (550 °C) cycles for a substrate. The arrays dissolved in CH$_2$Cl$_2$ to *ca.* 10^{-5} mol L^{-1} in concentration were deposited by spraying *ca.* 0.5 μL of the solution onto the substrate in vacuum (10^{-6} mbar) using a pulse injection method,[7] which is suited for deposition of large fragile molecules while escaping the decomposition often encountered in sample deposition from the gas phase. *In-situ* STM measurements were performed at room temperature in ultra high vacuum ($< 10^{-10}$ mbar) with a laboratory-built STM by using an electrochemical etched Pt/Ir tip. All STM images were obtained in constant height mode. Vs and I indicate the sample bias voltage and tunneling current, respectively.

Figure 2a shows the image of **A** taken at $Vs = -1.0$ V and $I = 0.03$ nA. Here, it is interesting to note that the even number, 6, of the porphyrins in the array may lead to a situation where the adsorption of both end porphyrins must be unfavorable, provided the array takes the averaged orthogonal conformation as in solution. Despite this situation, Fig. 2a demonstrates that **A**
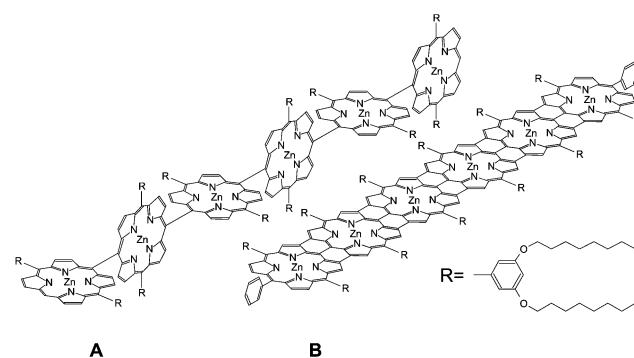

Fig. 1 Schematic representation of *meso–meso* singly-linked hexamer **A** and *meso–meso*, β–β, β–β triply-linked hexamer **B**.
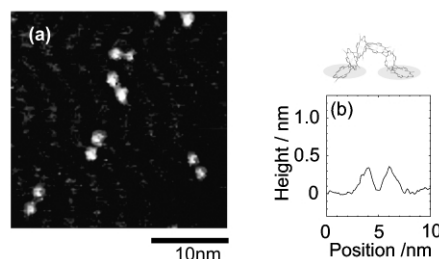

Fig. 2 (a) STM image of **A** obtained at $Vs = -1.0$ V and $I = 0.03$ nA. (b) Height profile of typical array.

is observed as a pair of images that are spaced with a nearly constant distance and aligned along the crystalline axes in six fold symmetry of the metal substrate. The statistical analysis revealed 0.30 ± 0.17 nm height and 4.30 ± 0.52 nm length for the images and 2.00 ± 1.04 nm for the spacing between the two bright images. Since bright STM images usually stem from strong adsorption of π-conjugated molecules on a metal surface,[5] the bright pair-wise images may be assigned to the adsorption of the two end porphyrins with their porphyrin planes parallel to the metal. Thus, the pair-wise bright STM images suggest a deformed, bent conformation with intervening porphyrins being somewhat detached from the metal surface as indicated above Fig. 2b.[8] This assignment may indicate considerable conformational flexibility of *meso–meso* linked porphyrin arrays depending on the circumstances. The observed image length (*ca.* 4.30 nm) is clearly shorter than the expected molecular length (*ca.* 5 nm) between the end porphyrins of the straight linear conformation of **A**, being consistent with a bent conformation. In the solution state (^{1}H NMR), the molecule **A** is considered to have rather flexible conformational freedom. It is interesting to note that the adsorption of **A** on the Cu(100) surface seems to induce the fixation of its bent conformation with the aid of the strong interaction of the end porphyrins with the metal surface.

Figure 3a shows the STM image of the porphyrin tape hexamer **B** obtained at $Vs = -1.0$ V and $I = 0.10$ nA, which indicates a dispersed rectangular shape at random directions on the metal substrate. Height and length histograms are shown in Fig. 3b and 3c, respectively. The height histogram has been fitted with Gaussian functions to be resolved as two peak heights, 0.60 ± 0.23 nm and 1.15 ± 0.20 nm. Since the latter height is almost twice the former but the image width is almost the same, this histogram has been interpreted in terms of partial formation of π-stacking along the long molecular axis. The π-stacked dimer population has been estimated to occupy *ca.* 15% of the total images on the basis of the fitting curve in Fig. 3b. In the length histogram (Fig. 3c), the gray and black bars indicate arrays whose STM image heights are lower or higher than 1 nm, which are assigned to be the single and double layer arrays, respectively. The length of single arrays is thus estimated to be 6.08 ± 0.91 nm by fitting the gray bar histogram with a Gaussian function, which is in good agreement with the expected molecular length of the porphyrin tape **B**. Thus, the arrays **B** are adsorbed as the flat structure schematically shown above Fig. 3d. In contrast, the length of the stacked arrays represented by the black bars is rather variable for each STM image. The height profiles of the arrays indicated by d, e, and f in Fig. 3a are shown in Figs. 3d, 3e, and 3f, respectively. Bars at the bottom of the profiles represent the length of the single array **B**. The height profile of the array d (Fig. 3d) is typical for the single array in terms of its height of *ca.* 0.6 nm as well as its length of *ca.* 6 nm.
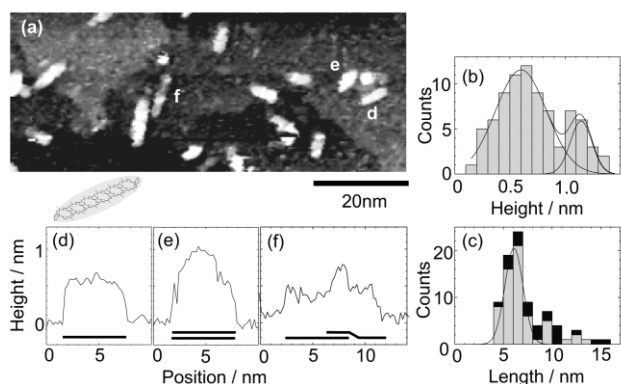
The height profile of the array e (Fig. 3e) represents a fully π–π stacked double array in terms of its height (*ca.* 1.1 ~ 1.2 nm) and length (6 nm). It is worth noting that this is, to the best of our knowledge, the first example of the STM detection of a stacked H-aggregate-type dimer. On the other hand, the height profile of the array f (Fig. 3f) indicates that this array consists of two partially piled-up molecules of **B** aligned along their long molecular axis. The array d thus may be regarded as a dimeric unit of J-aggregate. We also observed a few arrays that have triple-layer and even higher π–π stacking structures, as judged from their height profiles.

In summary, the STM images of the two porphyrin hexamers **A** and **B** adsorbed on Cu(100) substrate were observed. The *meso–meso* linked porphyrin hexamer **A** was all observed as a pair of images, which suggested that a bent bridge-like structure was forced through the interaction of the two edge porphyrins with the metal surface. In contrast, the triply-linked flat porphyrin array **B** was observed as a rectangular image with variable π–π stacking structures.

Notes and references

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Fig. 3 (a) STM image of **B** obtained at $Vs = -1.0$ V and $I = 0.10$ nA. Height (b) and length (c) histograms. Height profiles of (d) single array, (e) fully stacked arrays, and (f) partially stacked arrays.