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Molecular Devices

A Supramolecular Multiposition Rotary Device**

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In recent years, artificial molecular devices have been strongly in the focus of research.[1] Bi- or multistable molecules as well as supramolecular assemblies have been built using highly sophisticated strategies.[2] Triggered by external stimuli, electronic and conformational states of these systems can be reversibly switched.[3] While the majority of these strategies result in large thermodynamic ensembles supported within fluids or the 3D bulk, recent advances allow for the deposition of complex units onto solid surfaces.[4] Thereby, reversible conformational changes and isomerizations of single molecules can be induced with local probe techniques such as scanning tunneling microscopy (STM) or atomic force microscopy (AFM).[5] Also, systems are known in which the adsorption state or site of a whole molecule is changed; this happens either thermally[6] or can be induced by the STM tip.[7] For technological applications, however, it is highly important to place supramolecular devices in an ordered and easily accessible structure such as a two-dimensional lattice.

Herein, we show that highly complex and ordered supramolecular entities can be fabricated on solid surfaces by taking advantage of a self-organization process, which follows the self-assembly approach introduced by Lehn.[8] Specifically, self-assembly of a specially functionalized porphyrin molecule (Figure 1) leads on Cu(111) surfaces to the formation of a regular nanoporous network that hosts single porphyrin guests nested on top of the pores. This unprecedented structural arrangement allows the guest to rotate. Because it is not placed directly on the surface, as in other existing rotational systems on metals,[9] it can snap into six different positions, of which three are distinguishable by the STM technique. Ultimately, the regular arrangement leads to the possibility of independently addressing each entity by labeling its position within the network and determining its state by looking at the arrangement of the guest relative to the STM scanning direction.

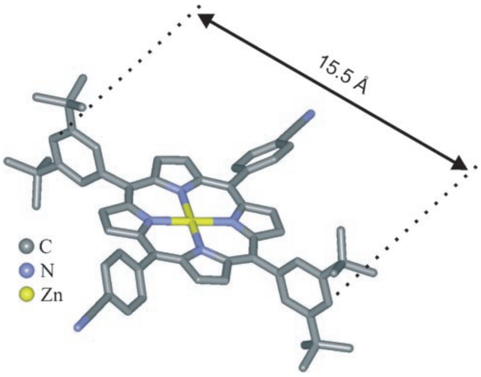

Figure 1. Optimized molecular structure of the porphyrin derivative **1**[21] used in this study, as generated by PM3 calculations implemented within Spartan.

Porphyrin **1** was vapor-deposited under ultrahigh vacuum (UHV) conditions on an atomically clean and flat Cu(111) surface. In the submonolayer regime the porphyrin molecules self-assemble into a highly ordered two-dimensional porous network (Figure 2a) with a pore–pore distance of (32 ± 1) Å and a pore diameter of (18 ± 1) Å (measured as indicated by the yellow circle in Figure 2a), as determined by the analysis of several STM images at variable temperatures (between 77 K and 298 K).[10] In the STM images each pore appears as a chiral windmill-shaped structure consisting of six wings. Each wing itself can be resolved by high-resolution imaging into two separated lobes, of which the outer one usually appears brighter. For the arrangement of the porous network, two homochiral domains are possible[11] in which the wings are organized either clockwise or counterclockwise (Figure 2b). The two lobes that form the windmill structure can be associated with the two *tert*-butyl residues contained in the 3,5-di(*tert*-butyl)phenyl substituents.[12] The less bright structures between two parallel wings (Figure 2c) can be attrib-

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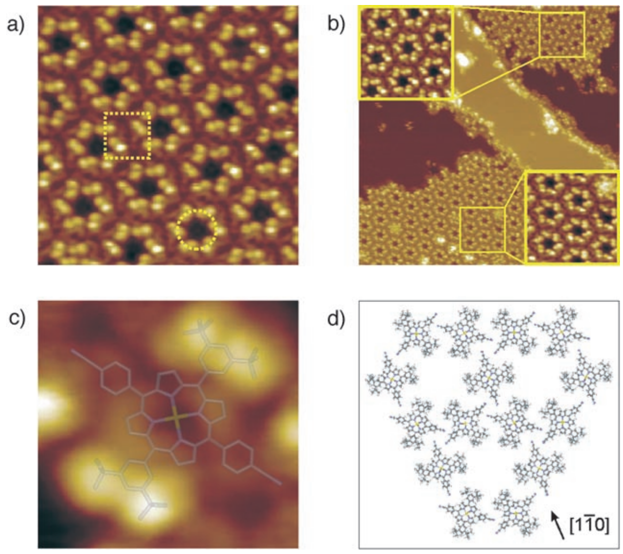

Figure 2. STM images taken with $U_{gap} = -1.5$ V, $I_{tunnel} = 20$ pA, and a sample coverage around 20%. a) STM image (scan range: 12.5×12.5 nm^2) of a self-assembled network of porphyrin **1** on an atomically clean Cu(111) surface. The dashed rectangle marks the position where the image in Figure 2c was taken. b) The network can be found in two homochiral domains (scan range: 50×50 nm^2; insets: 9.1×9.1 nm^2). c) Detailed view of a single molecule inside the porphyrin network (scan range: 2.1×2.1 nm^2). A transparent model of porphyrin **1** is embedded to show the location of the molecule and the structure–image correlation. d) Proposed pattern model of the two-dimensional porous network.

uted to the central tetrapyrrolic core and to the 4-cyanophenyl groups.[13] Therefore, a single molecule in the network can be identified as a rectangle with bright lobes on the edges and mean dimensions of 4.0 Å and 14.7 Å for the smaller and longer sides, respectively. These distances reflect very well the intramolecular distances (approximately 5.0 Å and 15.5 Å) as measured from the PM3-optimized geometry of porphyrin **1**.

On the basis of this structural correlation, we were able to develop a model of the porous network (Figure 2d; see Movie 3 in the Supporting Information). According to this proposed pattern, each nanopore is surrounded by six flat-lying porphyrins whereas each porphyrin is part of two neighboring pores. Based on the fact that in STM images each 3,5-di(*tert*-butyl)phenyl substituent appears as a brighter and a darker lobe, by comparison with previous studies of similar porphyrins deposited on Au(111) and Cu(111) surfaces,[13,14] the dihedral angle between the 3,5-di(*tert*-butyl)phenyl substituents and the porphyrin core is estimated to be about 20°. Furthermore, in the proposed model each 4-cyanophenyl group points towards the hydrogen atoms of a 4-cyanophenyl group of a neighboring porphyrin molecule. We therefore believe that the formation of the network is likely driven by weak hydrogen-bonding interactions between the phenyl rings and the cyano residues, as it has been reported for supramolecular aggregates and porous networks of similar porphyrins.[15]

Parallel to the self-assembly of the porous network, we have found that at a temperature of 77 K some of the pores are occupied by a four-lobed structure that appears much brighter in the STM images than the empty pore (Figure 3a). As we added no other types of molecules, the only explanation for this observation is self-trapping of porphyrin **1**. The lobes form a rectangle with mean dimentions of 3.4 Å and 8.1 Å for the smaller and longer sides, respectively. This structure shows a striking similarity to the appearance of a single porphyrin molecule in the network (Figure 2c), although the mean length of the longer sides is almost 45% smaller. Nevertheless, Moresco et al.[14] and also Sekiguchi et al.[16] have observed that for similar molecules the intramolecular distances can appear drastically reduced in STM images as a result of conformational changes of the 3,5-di(*tert*-butyl)phenyl substituents. We assume that a similar mechanism takes place here and therefore conclude that the lobes belong to one single porphyrin molecule nested horizontally on top of a pore (see also the Supporting Information). As the supporting pore has a hexagonal symmetry, the porphyrin guest molecule can take six different positions separated by a rotational angle of 60°. Because of the structural guest symmetry (C_{2h}), only three of these positions are distinguishable. In Figure 3a, three porphyrin guests, arranged in one of the three distinguishable positions, are shown.

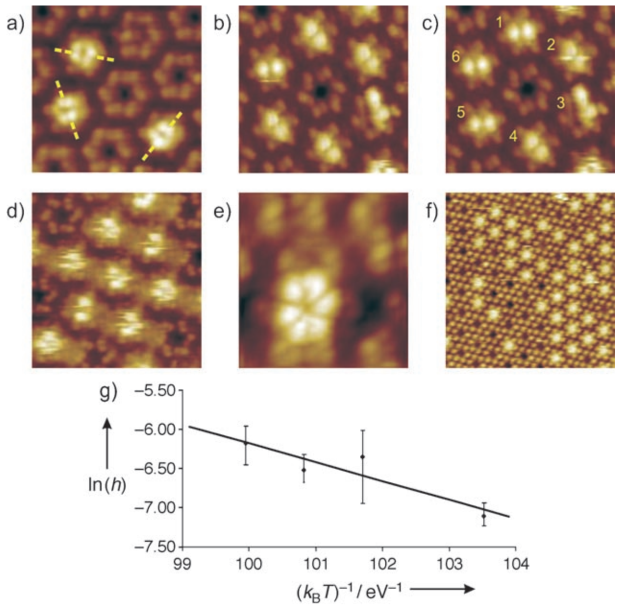

Figure 3. a–f) STM images of the porphyrin network taken with $U_{gap} = -1.5$ V, $I_{tunnel} = 20$ pA, and a sample coverage around 10% (a–c) or around 30–40% (d–f) at different temperatures (from 77 K to 298 K). Some of the pores are filled. a) At 77 K the filling of the pore can be resolved into four rectangularly arranged lobes (scan range: 10.2×10.2 nm^2). These can take three distinguishable positions, all of which occur in the imaged frame (as indicated by the dashed lines). b, c) At 112 K only two lobes are visible (scan range: 7.4×7.4 nm^2). They can switch to a different position over time (see especially structures 1 and 5). d) At 115 K the porphyrin guest appears extremely fuzzy (scan range: 8.8×8.8 nm^2). e) At 150 K all possible positions can be seen simultaneously leading to a flowerlike appearance of the pore filling (scan range: 3.0×3.0 nm^2). f) At room temperature some pores seem to be completely filled (scan range: 29.9×29.9 nm^2). g) Arrhenius plot for the determination of the activation energy needed to switch between two neighboring positions.[22]

After the sample is heated to 112 K, the guest molecules appear mostly as two opposing lobes (Figure 3 b and c). This behavior might be a result of a thermally induced shivering of the 3,5-di(*tert*-butyl)phenyl groups. Very interestingly, in STM sequences we discovered that the guest molecules can thermally switch from one stable position to another (Movie 1 in the Supporting Information). Figure 3 b and c show two subsequent STM images (148 seconds per image). One can clearly see that the porphyrin guests 1 and 5 in Figure 3 c have switched. The horizontal line in pore 2 indicates that the nested molecule switched into a new position and then back while scanning the underlying pore. A preferred rotational direction or hopping to neighboring pores[17] was never observed. Molecule 3 seems to be adsorbed onto a position which prevents the rotation. Such defects are observed only very rarely.

At a temperature of 115 K the structure of the porphyrin guest appears extremely fuzzy (Figure 3 d, see also Movie 2 in the Supporting Information), and at 150 K the fillings show a flowerlike structure consisting of six leaves (Figure 3 e). This observation can be explained by the characteristic scanning speed of the STM in the millisecond range for each imaged pixel. At elevated temperatures, the thermally induced rotation of the nested molecules is faster than the time resolution of the STM. Thus, the molecules change their position while the STM tip is scanning across them and give rise to fuzzy imaging. Above a certain rotational speed, the STM image shows a superposition of all possible positions that the guest molecule can take on a single pore, leading to the shown flowerlike structure.[18] At room temperature, even this structure disappears and owing to the very high rotational speed of the nested molecule the pores appear completely filled (Figure 3 f).

From the analysis of successive STM images taken at temperatures between 112 K and 116 K, we estimated the switching activation energy by applying a model that is commonly used to describe the diffusion of molecules on metal surfaces.[19] By counting the number of guests that did not switch in the time interval between two STM frames, we obtained the switching rate h. From the Arrhenius plots of h versus $(k_B T)^{-1}$ (Figure 3 g), we then extrapolated an activation energy of (0.24 ± 0.08) eV with a pre-exponentional constant of around $5 \times 10^7\,s^{-1}$ (standard deviation $= \pm 1 \times 10^{2.8}\,s^{-1}$). Nevertheless, owing to the characteristic scanning speed of the STM, the activation energy determined by this method is slightly underestimated.[20]

As the guest molecule is embedded into a nanoporous network, each device can be selectively addressed and switched by the STM tip. For this purpose the sample was cooled down to a temperature where no thermally induced switching occurs ($T = 77$ K). The tip was then placed above a porphyrin guest under scanning conditions ($U_{gap} = -1.5$ V, $I_{tunnel} = 10$ pA). By applying short pulses (around 1 s) with $U_{gap} = -0.7$ V and $I_{tunnel} = 150$ pA, single switching events could be triggered. Figure 4 a and b show one typical example where tip-induced switching was applied to the porphyrin guest in the right part of the image. One can clearly see that the guest switched into a different position, while the neighboring one (on the left) did not rotate. Although this method revealed to be successful in inducing a switching event, the direction of rotation (i.e., clockwise or counterclockwise) could not be preferentially induced.

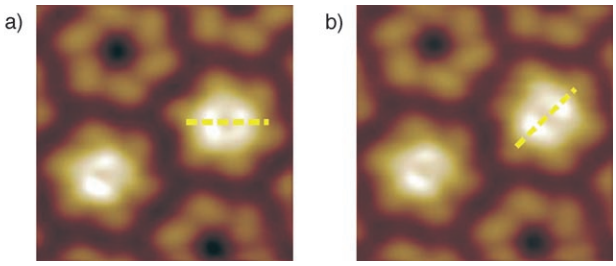

Figure 4. Controlled rotation of the nested guest molecules can be induced by the STM tip. a, b) STM images recorded with a scan range of 6.5 × 6.5 nm^2, $U_{gap} = -1.5$ V, and $I_{tunnel} = 10$ pA. The guest on the right in part (a) was switched by applying a short pulse with $I_{tunnel} = 150$ pA at $U_{gap} = -0.7$ V.

In conclusion, we have demonstrated that by skillful functionalization, organic molecules can self-assemble into complex and independently addressable supramolecular nanodevices. Future refinements of the approach presented here may provide assemblies with activation energies that are high enough for technologic applications.

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