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# The Molecular Abacus: STM Manipulation of Cyclodextrin Necklace

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Preparation of molecular devices has been one of the most attractive goals for scientists.[1−3] A number of nanostructured supramolecular assemblies have been proposed heretofore. Among them, "molecular shuttles", which travel back and forth on molecular rails, are particularly promising.[1−9] These molecular shuttles can store molecular information in terms of shuttle position. Applications to molecular machines have also been proposed. However, the following problems remain to be solved: (1) how to initiate and terminate shuttle movement at a predetermined time, (2) how to control the direction of the movement, and (3) how to read the shuttle position.

Since Eigler's pioneering research,[10,11] the scanning tunneling microscope (STM) [12] and atomic force microscope (AFM) have been recognized as two of the most powerful tools for the actuation of atoms and molecules.[13−15] The possibility of developing a molecular counting-device was demonstrated by repositioning $C_{60}$ molecules along the steps of a Cu metal surface.[16] These findings have spurred us toward STM manipulation of the molecular necklace of cyclodextrin (CyD) [17] (Figure 1) to develop a "molecular abacus" which fulfills the above-mentioned criteria, 1−3. Here, we demonstrate that the selected α-CyD molecule(s) in this polyrotaxane is reversibly shuttled using a STM. All manipulation is carried out under ambient conditions, since the α-CyD molecules are noncovalently bound to poly(ethylene glycol) (PEG).

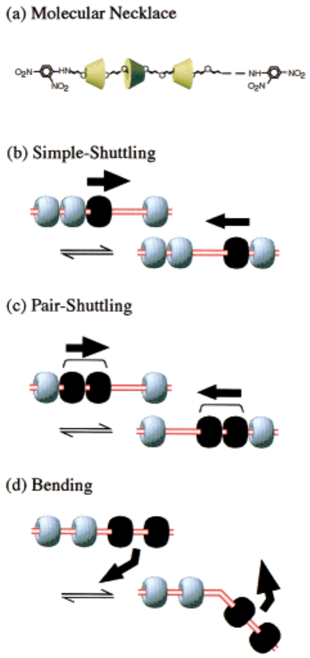

**Figure 1.** (a) Structure of the "molecular necklace", and three modes (b, c, and d) of the shuttle manipulation by STM.

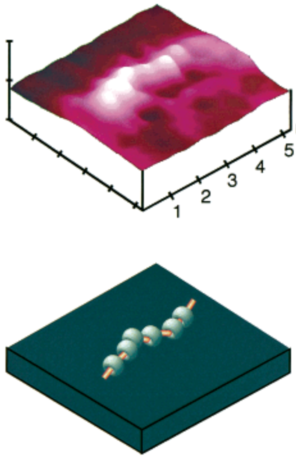

**Figure 2.** A typical STM image of the molecular necklace (a) and its schematic structure (b).

The specimens for STM were prepared by dripping aqueous solution of the 1$\mu$M molecular necklace dissolved in 0.1 N NaOH onto freshly cleaved $MoS_2$, followed by evaporating the liquid under ambient conditions. The concentration of the material was sufficiently diluted for the molecular necklace to be observed independently, and the molecular necklaces were formed following the procedure in ref 17.

Figure 2a shows a typical STM image of the molecular necklace on a $MoS_2$ substrate (sample bias voltage +200 mV, tunneling current 900 pA, and a Pt/Ir tip). Regularly aligned α-CyDs are clearly observed. As schematically shown in Figure 2b, the main chain of PEG runs along the surface of the substrate, and the α-CyDs lie with their longitudinal axis parallel to the surface. The rotaxane structure of the molecular necklace has been clearly

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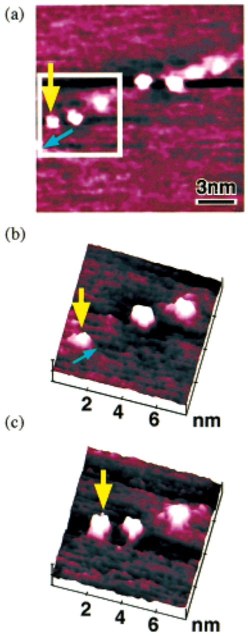

**Figure 3.** STM images of the simple-shuttling (Figure 1b).

visualized on an atomic scale. It is noteworthy that stable imaging was accomplished at room temperature in air.[18]

First, one of the α-CyDs in the molecular necklace was mechanically pushed by the STM tip along the main chain of PEG, as has been performed previously to manipulate atoms/molecules on the surface of the substrate.[10,11,13−16,19] An example of the shuttling is shown in Figure 3. The images were acquired before and after each manipulation, respectively. As designed, the target α-CyD (designated by the yellow arrow in Figure 3a) moved by the tip-sweep from right to left (compare images a and b in Figure 3). Since the PEG chain is railed diagonal in this case, the target α-CyD stably moved by 2.4 nm in the direction along the chain. This is the first observation of ring-component manipulation along the chain of an interlocked molecule. All the other α-CyDs retained their initial positions. Upon moving the tip in the reverse direction, the α-CyD retraced its path and returned to its original position (image c). Thus, the shuttling of one α-CyD could be stably repeated. There is no requirement for a specific surface structure on the substrate for guiding the shuttle in a prescribed manner.

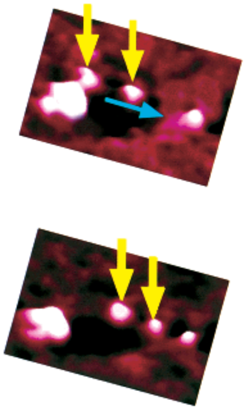

**Figure 4.** STM images of the pair-shuttling (Figure 1c).

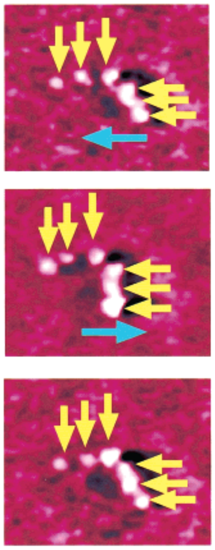

**Figure 5.** STM images of the bending (Figure 1d).

It was also possible to move a pair of α-CyDs simultaneously (Figure 4). The two α-CyDs, being adjacent to each other in the molecular necklace, were reversibly manipulated while keeping their mutual conformation intact. Furthermore, the main axis of the molecular necklace could be bent with the tip by pushing it laterally in the perpendicular direction (Figure 5). A hook-shape is shown to be formed by this synchronized repositioning of several α-CyDs. Even this drastic transformation was stably reproduceable.

In previous actuations of atoms and molecules using a STM or an AFM, strictly controlled conditions (ultrahigh vacuum, low-temperature (e.g., liquid He), or specifically structured substrates) were required. However, the present manipulation of α-CyDs is stable in air at room temperature, mainly due to the characteristic structure of the polyrotaxane. The system can be further advanced by combining the three modes of transformation and also by attaching functional groups (e.g., photoresponsive or redox-active groups) to CyDs; this is currently being attempted. The present finding will be a milestone in the development of molecular devices, which are the ultimate devices in terms of large-scale integration.

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(18) This is partially because the structure of α-CyD fairly matches with the lattice of $MoS_2$: Miyake, K.; Aiso, Y.; Komiyama, M.; Harada, A.; Kamachi, M.; Shigekawa, H. *Jpn. J. Appl. Phys.* **1994,** ***33***, 3720−3722.

(19) For the manipulation, the interaction between the STM tip and the target molecule(s) was adjusted first by changing the sample bias voltage and the tunneling current. In the cases of this paper, they were changed from the stable measurement condition (+200 mV, 900 pA) to the manipulation mode (−200 mV, 700 pA). Then, the tip was swept in the designed direction using the constant height mode, and pushed the α-CyD molecule(s).