Positioning and Switching Phthalocyanine Molecules on a Cu(100) Surface at Room Temperature

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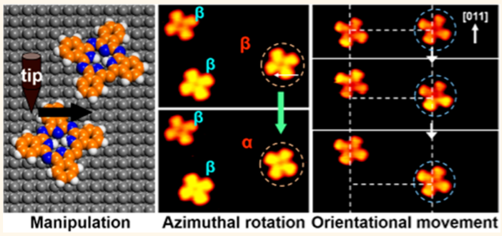
ABSTRACT Reversible molecular switches with molecular orientation as the information carrier have been achieved on individual phthalocyanine (H_2Pc) molecules adsorbed on a Cu(100) surface at room temperature. Scanning tunneling microscopy (STM) imaging directly demonstrates that H_2Pc molecules can be controlled to move along the [011] or [01$\bar{1}$] surface direction of the Cu(100) surface, and the orientation of H_2Pc molecules can also be switched between two angles of ±28° with respect to the [011] surface direction by a lateral manipulation. Owing to the highly efficient control over the adsorption site and orientation of H_2Pc adsorbed on the Cu(100) surface by lateral manipulation, a pyramidal array formed by 10 H_2Pc molecules has been constructed on the Cu surface as a prototype of binary memory, and every molecule within such a molecular array can be individually and reversibly controlled by a STM tip.



KEYWORDS: molecular switches · scanning probe microscopy · molecular orientation · manipulation

Molecular devices have attracted wide attention because they provide promising ways to miniaturize electronic devices at the nanometer scale and build new types of devices with novel functions. Since the concept on a molecular device was proposed, various prototypes of molecular devices such as switches, motors, data storage bits, and diodes have been constructed and demonstrate unique functions.[1−11] Scanning tunneling microscopy (STM) has been proven to be a powerful tool to exploit molecular devices as this technique not only provides atom-resolution images of atoms and molecules but also allows one to position individual atoms and molecules precisely at the atomic scale.[12−16] It is worth noting that most of the attempts based on STM manipulation of single molecules were carried out at low temperature (5−100 K). However, it is desirable to construct molecular devices which work at room temperature for the purpose of realistic applications.

Although manipulating a single molecule or atom at room temperature is much more challenging, many works have been devoted to overcome the limitation caused by thermal disturbance and to realize the control of a single molecule or atom. Cu-TBP-porphyrin molecules were precisely repositioned on a Cu(100) surface by a controlled lateral "pushing" action of the STM tip to form a hexagonal ring.[17] C_{60} molecules on a Si(111)-7 × 7 surface were moved by the STM tip to form a shape of the letter "S".[18] The position, bonding site, and orientation of individual C_{60} molecule on the Si(100)-2 × 1 surface were also manipulated by a STM tip.[19] $C_{59}N$ molecules were moved parallel and perpendicular to the silicon dimer rows on the Si(100)-2 × 1 surface by pushing a molecule with a STM tip.[20] Switching the molecular orientation of individual fullerene was recently achieved at room temperature by applying a bias between the molecule and a STM tip.[21]

In this study, manipulating individual H_2Pc molecules was performed on a Cu(100) surface at room temperature by pushing a molecule with a STM tip. H_2Pc molecules can be controlled to move along the [011] or [01$\bar{1}$] surface directions of the Cu(100) surface when the STM tip pushes the specific parts of a molecule. Two azimuthal orientations of a H_2Pc molecule on

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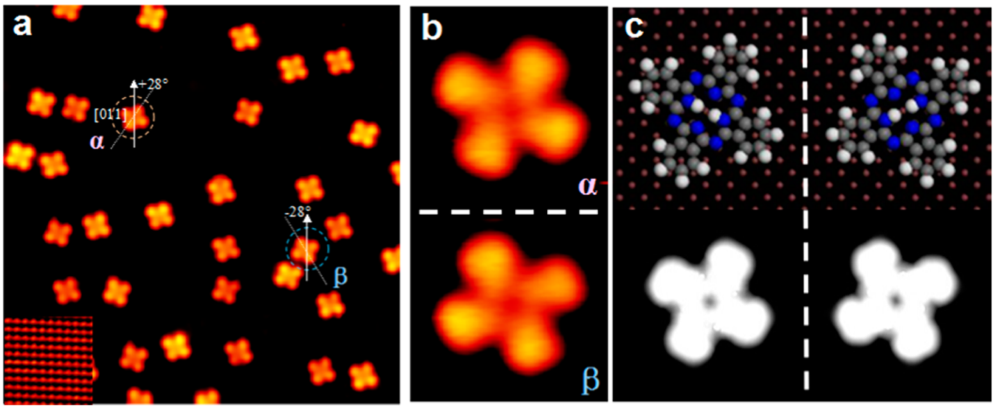

Figure 1. (a) Typical large-area STM image of H_2Pc molecules absorbed on a Cu(100) surface at room temperature: $V_b = -2.58$ V, $I_t = -0.05$ nA. (b) Image of two H_2Pc molecules with two different azimuthal orientations: $V_b = -2.58$ V, $I_t = -0.04$ nA. (c) Top view of the optimized adsorption configuration for a H_2Pc molecule on the Cu(100) surface and the corresponding simulated STM image.

Cu(100) is also switched reversibly between each other by placing a pushing force on one of the lobes of the molecule in a clockwise or counterclockwise direction. A pyramidal array formed by 10 H_2Pc molecules has been constructed on the Cu surface, and every molecule within such a molecular array can be individually and reversibly controlled by a STM tip.

RESULTS AND DISCUSSION

Figure 1a shows a typical large-area room-temperature STM image of H_2Pc molecules adsorbed on a Cu(100) surface. The [01$\bar{1}$] surface direction within the Cu(100) surface derived by an atomic resolution image of a bare copper surface (inset of Figure 1a) is parallel to the horizontal edge of the image. The H_2Pc molecules adsorb randomly and individually on the Cu(100) surface for the case where the coverage of the molecules is less than 0.35 ML. Each H_2Pc molecule lying on the surface is imaged as a four-lobe cross feature with a central depression, suggesting that the interaction between molecules and the copper surface is strong enough to inhibit thermal diffusion. The molecules have two different azimuthal orientations, similar to ZnPc molecules adsorbed on a Cu(100) surface.[22] Close inspections of individual molecules and careful measures of molecular azimuthal orientations reveal that two different azimuthal orientations rotated by $\pm 28°$ relative to the [011] surface direction. The H_2Pc molecules rotated by $+28°$ are labeled as α molecules (highlighted in yellow circles), and the molecules with the other orientation are labeled as β molecules. As shown in Figure 1b, it is clear that the four lobes within a molecule do not point straight toward the center of the molecule and they actually form a windmill-like arrangement with a counterclockwise or clockwise direction. All α molecules possess a counterclockwise direction, and all β molecules possess a clockwise direction, which is consistent with the observations for ZnPc and CuPc molecules adsorbed on a Cu(100) surface.[22] Such a windmill-like structure is caused by asymmetric charge transfer from the copper surface to the molecule, in accord with previous reports.[23,24] Figure 1c gives the optimized configuration for H_2Pc molecules adsorbed on Cu(100) where the center of the H_2Pc molecule is located at the Cu hollow site. The azimuthal orientation for the molecule in the optimized configuration forms an angle of 27° with respect to the [011] surface direction, and the molecule in the corresponding simulated STM image (the bottom plane of Figure 1c) does appear as a windmill-like feature, which is in good agreement with our STM observations.

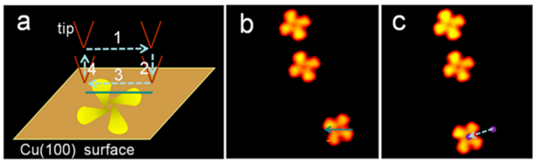

Figure 2. (a) Schematic illustration of the process used to manipulate individual molecules on the Cu(100) surface. Red arrow represents the STM tip, and the light blue arrow is the movements of the STM tip during the manipulation process. (b,c) Blue arrow in (b) is the predefined line, and the arrow indicates the moving direction of the STM tip during the backward process. STM images directly demonstrate that the H_2Pc molecule has been moved a distance after a lateral manipulation. The blue arrow in (c) shows the positional change of the target molecule after manipulation, and the purple dots represent centers of molecules. (b,c) Scanning parameters: $V_t = -2.58$ V, $I_t = -0.04$ nA. Manipulating parameters: $V_m = -0.6$ V, $I_m = -2.5$ nA.

The process to manipulate the molecules on the copper surface consists of four steps, as shown in Figure 2a. First, the STM tip is positioned at the target location and moves along a predefined line with the parameters $V_t \simeq -2.5$ V, $I_t \simeq -0.035$ nA, which are used for the normal scanning process. This action is the so-called "forward" process. The predefined line decides the track of the STM tip during the manipulation process. Second, the STM tip is suddenly lowered to an appropriate height so that the interaction between the tip and the molecule is strong enough to move or

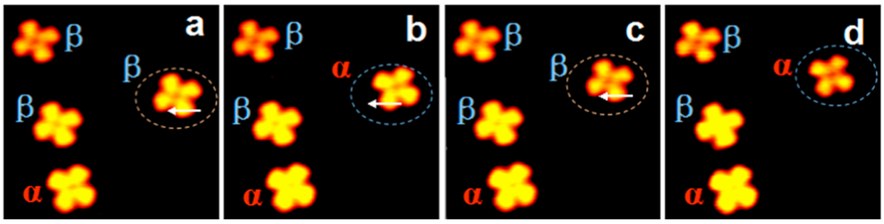

Figure 3. Molecular reversible switch between two azimuthal orientations. (a) Molecule with β orientation highlighted by a dashed circle is chosen as the target molecule, and the other three molecules on the left of the target molecule act as the indicators for the STM manipulation. The movement of the STM tip during the manipulation is parallel to the $[0\overline{1}1]$ surface direction and is shown by the white arrow. (b–d) Orientation of the targeted molecule is switched between two azimuthal orientations reversibly. (a–d) Scanning parameters: $V_t = -2.84$ V, $I_t = -0.04$ nA. Manipulating parameters: $V_m = -0.6$ V, $I_m = -2.5$ nA.

switch a molecule. In order to achieve a high success rate of operation, the STM tip is normally lowered to a certain height by reducing the voltage to $V_m \sim 0.6$ V and increasing the tunneling current to $I_m \sim 2.5$ nA. Third, the STM tip moves backward along the predefined line with the manipulation parameters, which is called a "backward" process. Lastly, the parameters are changed to the original values ($V_t \simeq -2.5$ V, $I_t \simeq -0.035$ nA), and the STM tip is retracted to its original height. Figure 2b,c shows two STM images acquired before and after a manipulation. The molecule at the bottom of the STM images is chosen as the target molecule manipulated by the STM tip. The blue arrow in Figure 2b is the predefined line indicating the moving direction of the STM tip during the backward process. Comparison between Figure 2b and Figure 2c clearly shows that the target molecule is removed from its original absorbed position to another place after the STM manipulation. The dashed blue arrow in Figure 2c shows the positional change of the target molecule with the purple dots as the centers of the molecule before and after the manipulation. The two molecules at the top of the STM images stay in the same positions before and after the manipulation, confirming that the movement of the targeted molecule is indeed caused by the manipulation rather than thermal drift.

Our studies clearly demonstrate that the H_2Pc molecules adsorbed on Cu(100) have two identical in-plane orientations; therefore, an individual H_2Pc molecule randomly takes one of these two orientations when it lands on the surface. In other words, the adsorbed H_2Pc molecule actually is at one of these bistable states, which provides the possibility for switching an individual molecule between these bistable states. Figure 3a shows four individual H_2Pc molecules adsorbed on the Cu(100) surface at room temperature before the manipulation. The molecule with β orientation highlighted by a dashed circle is chosen as the target molecule, and the other three molecules on the left of the target molecule act as the indicators for the STM manipulation. The movement of the STM tip during the manipulation is parallel to the $[0\overline{1}1]$ surface direction and is shown by the white arrow in Figure 3a. During the manipulation in this particular track, the STM tip only interacts with one lobe of the target molecule. Figure 3b gives the STM image for the molecules after the manipulation. It is evident that the target molecule is with α orientation rather than the previous orientation, while the orientations and the positions of the other three molecules remain unchanged. This observation unambiguously demonstrates that the orientation of the targeted molecule is indeed switched from β to α by this lateral manipulation. To avoid the influence of the tip's change, the second manipulation is still along the same trajectory of the tip in Figure 3b, and the results indicate that this targeted molecule can also be switched to its initial β orientation, as shown in Figure 3c. Although the threshold energies to trigger these two different switches are different, this observation still directly reveals that this switching on the molecular orientation of the H_2Pc molecule is reversible. The following manipulation on the targeted molecule switches the molecular orientation to α orientation again in Figure 3d, indicating that this switching process by the lateral manipulation is also reproducible and efficient. It is worth mentioning that the lateral manipulations with various trajectories of the STM tip, such as the movement of the tip across the center of the molecule, also can switch the in-plane orientation of an individual H_2Pc molecule between α and β, but those manipulations usually cause a large displacement of molecular position (larger than 7 Å and reaching 20 Å) when the molecular orientation is switched. In contrast, the manipulation along the track shown in Figure 3 is found to move the target molecule to the nearest neighbor site, and the symmetric manipulation along the [011] surface direction can also have the same efficiency for switching due to the symmetry structure of the Cu(100) surface. Therefore, such manipulation is a preferred way to switch a H_2Pc molecule adsorbed on a Cu(100) surface.

Lateral manipulation can induce not only molecular switching but also orientational motion of H_2Pc molecules with constant step size. In order to achieve orientational motion with constant step size, lateral manipulation with a different trajectory of the STM tip from that in Figure 3 is applied to the targeted molecules, as shown in Figure 4a. The STM tip moving along

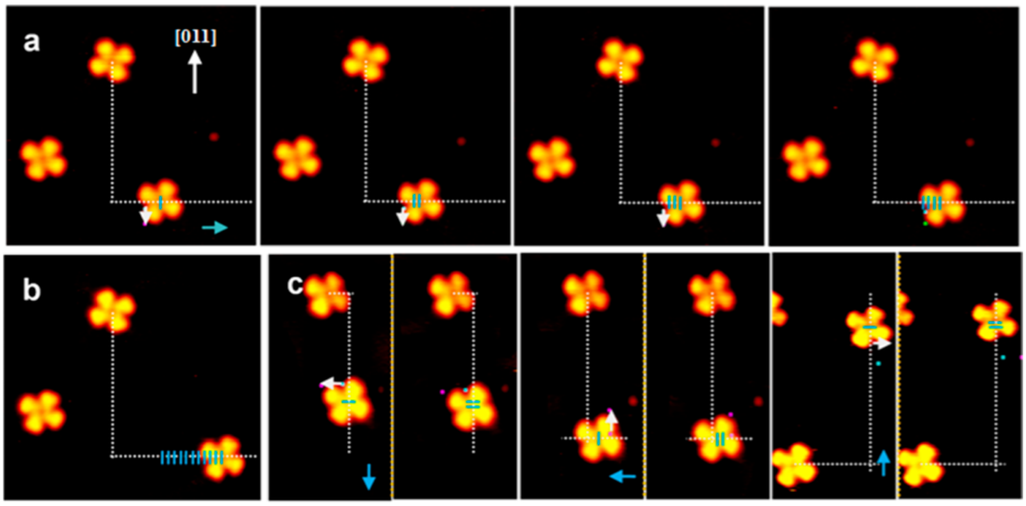

Figure 4. Orientational motion with constant step size of H_2Pc molecules along a different surface direction by lateral manipulation. (a) STM images of an α molecule moved by lateral manipulation step by step along the $[01\bar{1}]$ surface direction with a certain step size. The blue short lines in the images present the center of the target molecules, and the blue arrow indicates the movement direction of the molecules after the STM tip moves along the white arrow. (b) Trajectory of the target molecule after 11 manipulations. (c) Molecular motions with a certain step size along the $[0\bar{1}\bar{1}]$, $[0\bar{1}1]$, and [011] surface direction. (a−c) Scanning parameters: $V_t = -2.84$ V, $I_t = -0.04$ nA. Manipulating parameters: $V_m = -0.8$ V, $I_m = -2.6$ nA.

the $[0\bar{1}\bar{1}]$ surface direction passes the edge of the left lower lobe of the target molecule but does not cross the lobe during rotational manipulation. Four STM images in Figure 4a show three consecutive motions induced by three consecutive lateral manipulations. The blue short lines in the images present the centers of the target molecules and depict the track of the target molecule under manipulations clearly. The leftmost image obtained before manipulations shows the initial position of target molecule and the following image is obtained after the first manipulation. The changes in these two images show that the target molecule moves along the $[01\bar{1}]$ surface direction during manipulation, and more detailed measurements reveal that the target molecule hops over only one lattice constant and locates on the adjacent adsorption site after the manipulation. The last two images are recorded after the second and third manipulations were performed. It is obvious that the motions of the target molecule during the second and third manipulation are the same as that during the first manipulation. The observations shown in Figure 4a demonstrate that an individual H_2Pc molecule was controllably moved along the $[01\bar{1}]$ surface direction by the STM tip, and each movement is only over one constant lattice to the nearest neighbor site. Figure 4b demonstrates the trajectory of the target molecule after 11 manipulations, and the molecular displacement of 24.8 Å is equal to 10 lattice constants. In 10 of 11 manipulations, the target molecule was successfully moved in the same way as shown in Figure 4a. The success of hundreds of similar manipulations further suggests that the controllable orientational motions with a constant step size of H_2Pc are achieved reliably. We propose that the repulsive interaction between the tip and the target molecule becomes stronger gradually while the tip moves closer to the target molecule, and the motion of the target molecule is triggered once the repulsive interaction is strong enough. During the whole manipulation process, the target molecule is always forced to move away from the tip and the interaction between the molecule and the tip is suddenly reduced so that the molecule only moves one time to the nearest neighbor adsorption site during every manipulation. Considering the symmetry of the H_2Pc molecule and the Cu(100) surface, we expected that an individual H_2Pc molecule can also controllably move along the $[0\bar{1}\bar{1}]$, $[0\bar{1}1]$, and [011] surface directions under lateral manipulation. Each of the three groups of the STM images in Figure 4c includes two STM images obtained before and after a lateral manipulation. The direction of the manipulation and the molecular movement are depicted by white and blue arrows. It is found that the step size for the molecular movement during these manipulations remains to be one lattice constant. Hundreds of manipulations have been performed for both lateral movements and azimuthal rotation at the suitable parameters ($V_m = -0.6$ V, $I_m = -2.5$ nA). The statistic results indicate that the switching rates for lateral movement along certain surface directions and azimuthal rotation are 81 and 73%. Such controllable molecular motions in [011], $[0\bar{1}1]$, $[01\bar{1}]$, and $[0\bar{1}\bar{1}]$ directions with a step size of one lattice constant and azimuthal rotation make this kind of manipulation feasible to reposition any individual H_2Pc molecule at any desired position at room temperature.

Controllable movements along the specific surface directions of the copper surface can be realized on H_2Pc molecules with both α and β orientations, but the

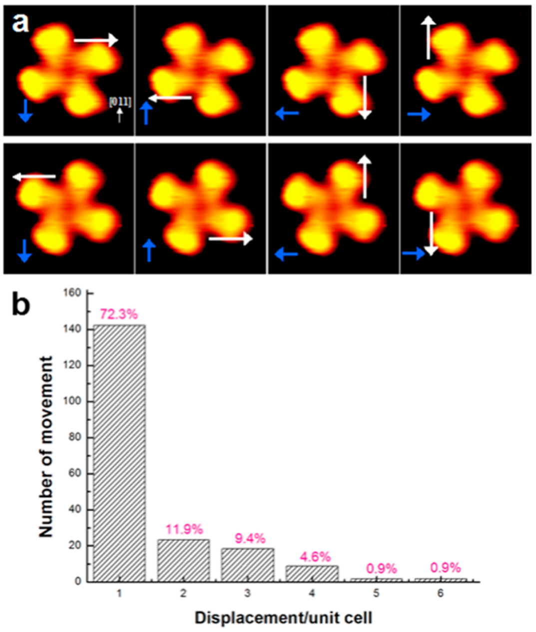

Figure 5. (a) Diagram for the directions of molecular motions (indicated by the blue arrow) induced by the trajectories of the STM tip (indicated by the white arrow) during manipulation needed for α and β molecules. (b) Histogram showing the distribution of molecular displacement in manipulations.

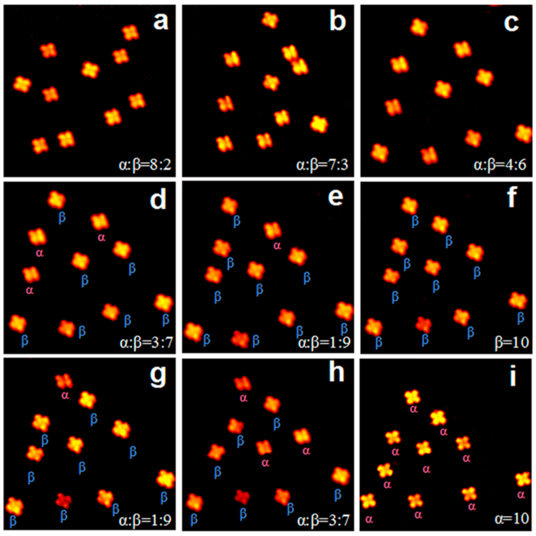

Figure 6. (a−c) Ten H_2Pc molecules adsorbed randomly were moved by lateral manipulation and assembled to form a pyramidal array. (d−f) Three molecules with α orientation in the array were switch to β orientation by manipulation, and a pyramidal array formed by 10 molecules with β orientation was constructed. (g−i) Ten molecules with β orientation in the pyramidal array were all changed to α orientation gradually. (a−i) Scanning parameters: V_t = −2.51 V, I_t = −0.04 nA. Manipulating parameters: V_m = −0.7 V, I_m = −2.8 nA.

trajectories of the STM tip during the manipulation processes are dependent on the molecular orientation in order to trigger molecular motions in different directions. As shown in the top four pictures of Figure 5a, the relationship of manipulation trajectory and the movement for H_2Pc with β orientation and the trajectories of STM tips for manipulating the molecules in certain directions are factually perpendicular to the corresponding molecular movements. In addition, these manipulation trajectories match each other by rotating integrated times of 90°, which is consistent with the geometry symmetry of H_2PC molecules, a four-fold rotation axis perpendicular to the molecular plane and across the center of the molecule. For the molecules with α orientation, the same tendency is found where the STM trajectories during the manipulation processes are perpendicular to the expected movement directions and have C4 rotation symmetry, as shown in the bottom four pictures of Figure 5a. Moreover, the comparisons between one of the top pictures and the corresponding bottom picture with the same movement direction clearly demonstrate that the STM trajectory to drive a molecule with α orientation is mirror-symmetric with respect to $[0\bar{1}1]$ or [011] surface directions to that for the molecule with β orientation. This experimental finding is in good agreement with the fact that the geometries between α-H_2PC and β-H_2PC are mirror-symmetric to each other with respect to $[0\bar{1}1]$ or [011] surface directions. Although the molecular displacement varies with different parameters applied to the STM tip and the target molecules, the larger current and smaller voltage increase the uncertainty of the molecular movements. In order to move the molecule one lattice constant per step, a parameter (V_m = −0.6 V, I_m = −2.5 nA) has been applied during orientational movement manipulation. Under these parameters, the statistic results on hundreds of manipulations in Figure 5b show that the molecular movement with one lattice constant per step is the dominant process with the probability of 72.3%, although the largest displacement is up to six lattice constants.

The efficient controls over the adsorption sites and orientations of H_2Pc molecules adsorbed on the Cu(100) surface by lateral STM manipulation make such a system feasible to act as data storage bits at room temperature. As shown in Figure 6a, 10 individual H_2Pc molecules with α or β orientation are present randomly on the copper surface at the initial stage. With the assistance of STM manipulations, the positions of these 10 molecules have been gradually readjusted to form a pyramidal array, as shown in Figure 6b,c. Assuming that the molecular orientation acts as the information carrier, the α orientation for "0" state and the β orientation for "1" state, such a pyramidal array formed by H_2Pc can act as a unit of data storage bits as the orientation of each molecule in this pyramidal array can be independently controlled by the STM tip. To demonstrate this point, the molecules with α orientation within the pyramidal array in Figure 6d at the initial stage were switched to the corresponding molecules with β orientation one after another, as shown in

Figure 6e,f. In Figure 6f, all the molecules in this pyramidal array have the same orientation of β and the all storage bits are in "1" states. Moreover, due to the reversibility of molecular orientation switching, the orientations of these molecules in the pyramidal array can further be manipulated gradually to α orientation, as shown in Figure 6g–i; as a consequence, all the storage bits in this unit are in "0" state. Such experimental observations demonstrate the feasibility of constructing binary memory using individual H_2Pc adsorbed on Cu(100) surfaces at room temperature with the high efficiency of replacing and switching H_2Pc molecules by lateral manipulation.

CONCLUSIONS

Reversible and reproducible molecular movements and the switches of molecular orientation have been achieved on individual H_2Pc molecules adsorbed on a Cu(100) surface at room temperature. Individual H_2Pc molecules on the copper surface can be controlled to move along the [011] or $[01\bar{1}]$ surface direction of a Cu(100) surface, and the orientation of H_2Pc molecules can also be switched between two angles of ±28° with respect to the [011] surface direction by a lateral manipulation. A pyramidal array formed by 10 H_2Pc molecules has been constructed on a Cu surface as a prototype of binary memory, and every molecule within such a molecular array can be individually and reversibly controlled by a STM tip. Such precise controls over molecular movement and orientation provide the possibility of constructing molecular binary memory at room temperature using individual organic molecules adsorbed on a solid surface.

METHODS

The experiments were carried out in a multichambers with an ultrahigh vacuum system housing a SPECS variable-temperature STM with a base pressure of less than 5×10^{-10} mbar. A Cu(100) single crystal with 7 mm diameter and 0.5 mm thickness was used as a substrate, and the clean Cu surface was prepared by repeated sputter and annealing cycles. H_2Pc was evaporated from a Knudsen cell at 504 K onto a precleaned Cu surface held at room temperature. All STM images were acquired in constant current mode at room temperature with a chemically etched W tip. Positive voltage indicates that the samples were biased positively with respect to the tip.

Conflict of Interest: The authors declare no competing financial interest.

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