

Tuning molecular orientation with STM at the solid/liquid interface†

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Triptycene molecular orientation has been tuned with a STM tip at a Cu(111) surface in solution from flat, to tilt, to vertical. The tuning is completely bias dependent and reversible. The study is important in the fields of nanoscience and technology.

Understanding and controlling molecule motion on a solid surface and in a molecular system is one of the most attractive issues in the fabrication of nanodevices. Muscle fibre, flagella and cilia are used to make controlled motion in biological motors.^{1–4} Koumura *et al.* constructed a monodirectional molecular rotor with two identical halves connected by a central double bond.⁵ In addition, scanning tunneling microscopy (STM) has been employed to image and manipulate molecular nanostructures in UHV and ambient environments.^{6–13} For example, molecular conformation of Cu-TDBPP on different metallic substrates was determined.⁷ “Quantum corral” was constructed by manipulating individual atoms.⁹ Six Cu-TDBPP molecules were controllably translated across atomically clean Cu(100) surfaces into a hexagonal structure by lowering the tip toward the surface and translating it.⁷ HB-DC molecular rotation in a supramolecular bearing was detected.¹² STM induced flip-flop switching of adsorbed SubPc molecular arrays.¹³ The accumulated results provide significant information for single molecule study and nanoscience. However, results on the manipulation of organic molecules at solid/liquid interface in aqueous solution are rarely reported, although the importance of such study is apparent in fundamental research and application in nanoscience and technology.

In this communication, we report the results of manipulating of triptycene molecule with a STM tip in solution. It is demonstrated that the orientation of the molecules on the Cu(111) surface depends on bias voltage between the STM tip and the substrate. Although Au(111) is widely used as substrate in electrochemical research and STM experiments, Cu single crystal is also an important electrode material. The study on Cu(111) surface will supply more valuable information to studies in, for example, surface science and electrochemistry. It is found that three orientations of parallel, tilt and vertical, could be achieved. The triptycene molecule is tuned at the solid/liquid interface as a molecular fan. The orientation is completely bias dependent. For a comparison, a planar molecule of triphenylene was investigated. It was found that the behaviour of the planar molecule is bias independent. The results demonstrate that the molecular orientation of triptycene molecules is controllable at the solid/liquid interface. Although the system is simple, the presented principle may prove relevant for a functional electronic device.

Cu(111) single-crystal disk with a diameter of 10 mm (from MaTeck Co.) was used as a working electrode. Triptycene (Aldrich Chem. Co.), triphenylene (Kanto Chemical Co., Inc.) saturated solutions and 0.1 M HClO₄ (Cica-Merck, Kanto

Chemicals) were prepared with ultrapure Millipore water. A home-made electrochemical cell contained a reversible hydrogen electrode (RHE) in 0.1 M HClO₄ and a Pt counter electrode. All electrode potentials are reported with respect to the RHE. STM experiment was carried out with a Nanoscope E (Digital Instruments, Santa Barbara, CA, USA). The electrode potential of Cu(111) was held at -0.20 V in the experiment. All STM images shown here were acquired in the constant-current mode to evaluate the corrugation heights of the adsorbed molecules. Raw images are presented without applying Fourier transform filters. The details of the experiment were described in the literature.^{14–15} HyperChem software was used to provide molecular models of triptycene and triphenylene. The molecular conformation was optimized using an AM1 method until RMS (root-mean-square) was less than 0.01 kcal Å⁻¹.

Fig. 1a is a high resolution STM image. From the image and chemical structure of the molecule, it can be concluded that the molecules form a well-defined close packed adlayer on the Cu(111) surface. On the basis of the orientation of molecular rows and the intermolecular distance, we conclude that the observed adlayer possesses a (4×4) structure. A unit cell is outlined in Fig. 1a. Each molecule appears like a three-bladed propeller. The length of each blade is measured to be 0.39 ± 0.02 nm in agreement with that of 0.38 nm from the central axis to the end of benzene ring of the molecule, indicating a parallel orientation to the Cu(111) surface. This image was recorded at a bias of 0.04 V.

It can be clearly discerned that triptycene molecules appear in three different conformations with the change of bias voltages applied between the STM tip and substrate. Fig. 1b, acquired at a bias of 0.12 V, shows a new feature. Although the adlayer structure is in a (4×4) symmetry, each molecule appears in a “V” shape indicated by “a”, “b” and “c”. The distance between “a” and “b” measures 0.65 ± 0.02 nm close to the largest

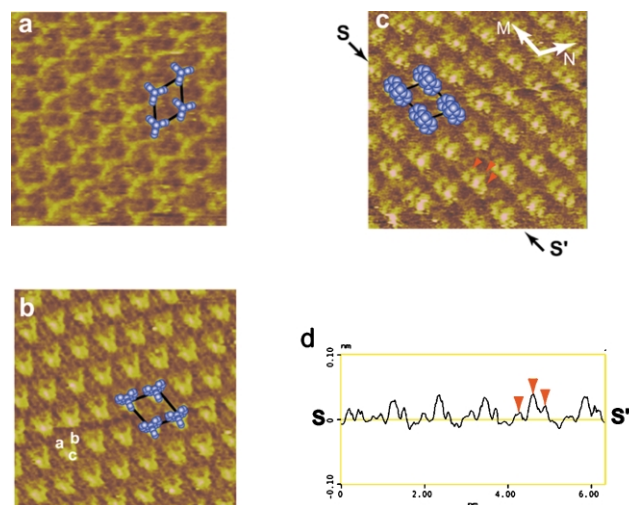


Fig. 1 (a)–(c) STM images of triptycene on Cu(111) at different bias voltages. Scanning size: 6.5 nm \times 6.5 nm. (d) Cross-sectional profile along the the SS' direction in (c).

† Electronic supplementary information (ESI) available: chemical structures of triptycene and triphenylene molecules and STM image of triphenylene molecules on Cu(111). See <http://www.rsc.org/suppdata/cc/b3/b308155a/>

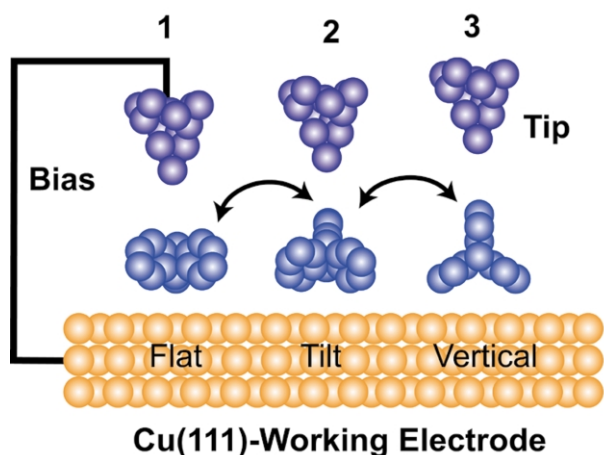


Fig. 2 Schematic illustration for the three orientations of the triptycene molecule on the Cu(111) surface.

distance of 0.656 nm between two blades of the molecule. The distance between “b” and “c” measures 0.53 ± 0.02 nm, smaller than 0.656 nm. The contrast of the spot “c” is brighter than that of the other spots “a” and “b”. This information reveals that the molecule is tilted up relative to the substrate plane. In a possible structural model for the adlayer, as shown in Fig. 1b, the obliquity of the molecules on the Cu(111) surface is illustrated schematically.

With the increase of bias to 0.2 V, a different adlayer was observed. Intriguingly, the molecules are seen in a vertical orientation. Fig. 1c is a typical STM image of the adlayer. According to the intermolecular distance and orientation of molecular rows, a (3×4) structure for the adlayer can be determined. A unit cell is outlined in Fig. 1c. Each molecule consists of three bright spots along M direction. The contrast of the center spot is brighter than that of other two. Fig. 1d shows a cross-sectional profile of the molecule along SS'. It is clearly seen that there is a difference of corrugation height in the molecule, indicating that it stands vertically on the Cu(111) surface. Two benzene “blades” of the molecule bind on the Cu(111) surface, while the third “blade” extrudes from the surface resulting in a height difference.

What controls adsorption orientation of the triptycene molecules on Cu(111) surface? In order to solve this problem, repeated experiments have been carried out. The results reveal that the orientation of the triptycene molecules on Cu(111) is independent of electrochemical potential applied to working electrode and only related to bias voltages applied between tip and working electrode. The results demonstrate the possibility of manipulating molecules at the solid/liquid interface in solution by bias. The ability of the manipulation is schematically summarized in Fig. 2. Three states of the molecule should be achieved by the procedure. The molecule can be tuned on the solid surface. On the other hand, if this ability is true, a reversible manipulation should be possible. Therefore, we have acquired a series of composite STM images to demonstrate the possibility.

Fig. 3 shows three composite STM images by stepping bias voltage under a constant set-point current. In Fig. 3a, the upper part of the image was acquired at a bias voltage of 0.061 V. The individual molecules exhibit a three-blade appearance, indicating a flat-lying orientation. When the bias voltage was stepped from 0.061 to 0.179 V in the scanning direction from top to bottom, a vertical orientation was observed. In Fig. 3b, when the bias was changed from 0.18 V to 0.098 V in the same scanning direction from top to bottom, the vertical molecules are immediately converted to tilt orientation. In Fig. 3c, the bias was changed from 0.066 V, 0.10 V to 0.189 V. With the bias changes, it is clear that the molecular orientation is sequentially varied from flat-lying, tilt and vertical. The transition from flat to vertical orientation is completely bias voltage dependent,

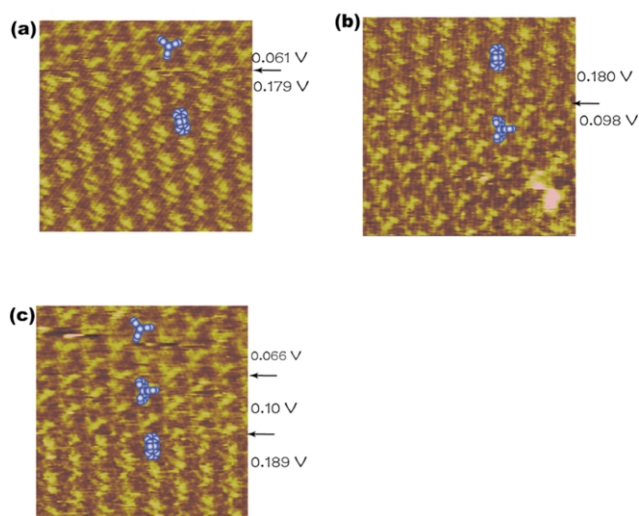


Fig. 3 Composite STM images showing the bias effect on molecular orientation. Scanning size: $8 \text{ nm} \times 8 \text{ nm}$.

reproducible and reversible. The molecule behaves like a reliable electronic element.

In order to prove orientation transition of triptycene molecules on Cu(111) to be dependent on bias voltages, we investigated a planar molecule of triphenylene. Three benzene rings surround a benzene center. The molecules form a 2D-ordered adlayer structure in (4×4) symmetry (not shown here). Each molecule consists of three bright spots corresponding to three benzene rings of the molecule. The results show a stable flat-lying orientation at a wide range of bias voltages from 0.01 to 0.5 V. A typical STM image is shown in the ESI.†

The investigations demonstrate that the triptycene molecule can be manipulated in solution by STM. The molecules rotate to different orientations on the Cu(111) surface with bias stimulation. At the constant set-points in the range from 5 to 20 nA, the molecules are tuned on Cu(111) in different orientations: flat-lying at an applied bias voltage lower than 0.066 V, tilt at 0.089 to 0.12 V, and vertical at 0.15 to 0.2 V. The results indicate the possibility of controlling molecular orientation on an electrode surface for feasible application in nanodevices.

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