Manipulation of Organic Molecules in Ambient Condition and Liquid Studied by Scanning Tunneling Microscopy

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This review describes how the manipulation of single molecules on solid state surface is available in air or at the liquid/solid interface, observed with scanning tunneling microscope (STM). First, the influences of the STM tip on the observation and manipulation of molecules are discussed. Then how the STM tip induced the ordering and how the molecular structures on the surface can be manipulated are shown. Last, the STM observations of the manipulation of molecules by changing the ambient conditions such as solvent, photon irradiation, and electrochemical potential, are shown.

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I. INTRODUCTION

Since Eigler and Schweizer at IBM Almaden demonstrated how single atoms can be manipulated with the tip of a scanning tunneling microscope (STM) [1] and Jung et al. at IBM Zurich demonstrated how single molecules can be manipulated [2], various kinds of atoms and molecules were manipulated with the STM tip [3]. The scanning tunneling microscope [4] is an instrument not only used to see individual atoms by imaging but also used to touch and take the atoms or to hear their vibration by means of manipulation, and it can be considered as the eyes, hands and ears of the researcher, connecting our macro-world to the nano-world [5].

In case of ultrahigh vacuum (UHV) and low temperatures (< 77 K), STM observation is stable and diffusion of molecules is constrained and no obstacles such as adsorbents exist so that the manipulation of a single atom/molecule is with facility [6]. In case of ambient condition, however, we have to consider not only the interaction between the single atom/molecule and the substrate but also the effect of drift, diffusion, and adsorbates [7].

The author has made progress in the manipulations of the large molecules thanks to collaborators who are expert in large-molecule synthesists. Phthalocyanine on silicon surface [8] is not suitable system for the study of single molecular manipulation due to the strong interaction between the molecule and dangling bonds of the substrate. Though changing the substrate to a noble metal can reduce the interaction, the manipulation at room temperature is not available due to the “skating” (diffusion) of the molecules on the substrate. In order to overcome the diffusion problem, the author consulted with Ken-ichi Sugiura and in 1992 we had the idea to attach four 3,5-di-tert-butylphenyl (DtBP) groups on the large molecule as legs [9]. The DtBP group has been widely used for the legs of molecules, maintaining the active part high enough from the substrate to allow manipulation with the STM tip. Moresco and Gourdon demonstrated how the DtBP group works as a leg [10].

The other famous example of the use of molecular design for the single-molecular manipulation is “nanocar” synthesized by Jim Tour’s group. The nanocar was first driven with the STM tip in UHV by Kevin Kelly’s group [11]. Recently, a motor has been added to the nanocar and it now can be driven by photons – no need to push with the STM tip [12]. The other example is “Molecular Landers”, or “Molecular Moulds”, synthesized by Andre Gourdon [13]. The DtBP groups are utilized for the legs, and the molecular landers have been manipulated with the STM tips [14].

On the other hand, in liquid, electrochemical STM is a powerful method since it is possible to use potential to control the surface structure [15]. However, the STM tip used for electrochemical STM is covered with insulator for the reduction of leakage current and the covered insulator can be an obstacle for the manipulation. This is a prac-

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FIG. 2: Schematics showing how the electric field from the STM tip puts a perturbation to the structure of observing molecule.

tical reason why manipulation with the electrochemical STM is difficult.

There are a number of review papers on the manipulation of single molecules with STM [5, 6, 16–19]. However, most of the manipulation studies have been conducted in UHV or low temperature. In this review paper, we show our work on the manipulation of organic molecules at the interface between liquid and solid state substrate and would like to answer a question “To what extent can we manipulate single molecules in the air or in liquid?”.

II. THEORY ON STM MANIPULATION

When a molecule is adsorbed on the surface with the adsorption energy $E_a$ and trapped in the well of diffusion barrier $E_{dif}$, and vibrating laterally in the well with the period $\tau_0$ (typically in the order of picoseconds), as shown in Fig. 1, the mean dwelling time of molecule on the surface, $\tau$, is estimated from the following equation (1) [20].

$$\tau = \tau_0 \exp \left( \frac{E_{dif}}{kT} \right),$$  \hspace{1cm} (1)

where $k$ is Boltzmann constant and $T$ is ca. 300 K (room temperature) in this study. The binding energies for physisorbed molecules are typically 0.25 eV or less [20]. We have to consider this interaction between the molecule and substrate during the manipulation. Hla categorized the STM manipulation as lateral manipulation and vertical manipulation [5]. In liquid, however, we can add two more categories in the STM manipulation; insertion and extraction of the molecules in the solution, since the liquid solution can be the source or drain of the molecules.

In the air, we cannot forget to treat the effect of meniscus between the tip and surface due to the existence of water. The existence of water caused the oxidation of materials in some case, which can be utilized for the nanofabrication of graphene oxides on graphene surface [21].

In liquid, on the other hand, the environment between the STM tip and sample is more well-defined than that in the air because the liquid can be chosen in such a way that STM tip surface is clean. We can also control the environment by adding different liquid such as polar solvent, as discussed in Chapter V.

III. EFFECT OF STM TIP ON OBSERVING MOLECULES

Scanning tunneling microscopy is a powerful tool for the determination of atomic structures such as the Si(111)7 × 7 structure [22, 23]. However, the electric field from the STM tip can perturb the structure of an adsorbed molecule, as shown in Fig. 2. It is possible to argue that structure determined by STM might differ from other methods such as X-ray diffraction. Considering the influence of the strong electric field from STM tip, in the order of 1 V/nm ($10^9$ V/m), deformation of the molecule under an STM tip is unavoidable. Soe et al. [24] demonstrated with their STM study that the $D_{4h}$ flat structure of copper phthalocyanine is distorted into $C_{4v}$ structure due to the adsorption on Au(111) surface [25]. Girard et al. [26] calculated the local electric field in the tip-sample gap, and field induced diffusion processes of a physisorbed atom were discussed. Moresco et al. [27, 28] observed Cu-tetrakis-di-tert-butylphenylporphyrin and the observed molecules had two-fold symmetry whereas the original molecular structure has four-fold symmetry. The author concluded that the perturbation to the observing
molecule from the STM tip should be considered for the structure analysis with STM. This kind of deformation induced by STM tip should be considered during the manipulation of single molecules. Also, scanning the STM tip in liquid can induce the ordering of the surface structure, which was pointed out from the early days of STM studies of liquid crystal, called anchoring the molecule [29]. However, the initial stage imaging with molecular resolution is usually difficult due to the initial large mechanical drift of the position between the tip and sample. The initial mechanical drift can be avoided in the following sequence. (1) Observe substrate and scan until the drift stopped. (2) Retract the STM tip slightly from the sample in the order of several ten nanometers. (3) Drop the solution on the substrate. (4) Close the STM to the sample until tunneling, and observe. In this way, we obtained the virgin scan STM image with molecular resolution as shown in Fig. 3 [30, 31]. The Y scan direction is from lower to upper in the image. The large periodic Moire pattern was observed at the initial stage, as shown in the lower domain in the image.

IV. MANIPULATION OF SINGLE MOLECULE WITH STM TIP

Initial studies of the observation of organic molecules were conducted by Shirley Chiang and co-workers [32]. The first observation of organic molecule with STM was reported by Ohtani et al. [33] on the surface of co-adsorbed benzene and carbon monoxide molecules on rhodium (111). Lippel et al. [34] reported high-resolution images of phthalocyanine on copper (100) surface. Hallmark et al. [35] observed the rotation of naphthalene on platinum (111) surface at room temperature.

Griessl et al. succeeded in playing “nanosoccer”, as shown in Fig. 4 [36]. They manipulate single Buckminster fullerene molecules with a Pt/Ir STM tip at the interface between the solvent of heptanoic acid and the template monolayer of trimellitic acid on graphite. They mentioned phenyloctane or dodecane did not work as the solvent in this study [36], which might be due to the property of heptanoic acid forming the monolayer network.

Gimzewski and co-workers manipulated molecular abacus of fullerenes at copper steps in UHV [37]. Although functioning only slowly as a calculator for demonstration purposes, the work shows that complex molecules can be manipulated with STM. Shigekawa et al. manipulated molecular abacus of rotaxane necklace with the STM tip in air [38], as shown in Fig. 5. Each bead of the abacus is a single molecule of a glucose complex of cyclodextrin. The cyclodextrin molecule is shaped like a truncated hollow cone. Each molecular bead slides along a “wire” made from polyethylene glycol.

Scudiero and Hipps [39] manipulated physisorbed self-assembled nickel octaethylporphyrin (NiOEP) monolayer on graphite. They fabricated the pattern of molecule-free regions created by removal of NiOEP molecules from the surface when the STM is operated at the tunneling resistance of about 120 MΩ or less. They showed that the removed molecules were not collecting at the boundaries of the scanned regions. Once the molecular film was damaged, the size of the uncovered area kept on growing with subsequent scans. They also observed that the triclinic and tetragonal monolayer structures formed under the same experimental conditions.

These works were conducted with the STM tip, and more sophisticated method of manipulation is necessary in order to meet practical needs. To be useful, a much faster method of manipulation is needed. Molecular manipulation without using an STM tip is shown in the next chapter.

V. MANIPULATION OF MOLECULES WITH ENVIRONMENTAL CONDITIONS

Tip manipulation can also be used to perform chemical reactions with single molecules. Laff erentz et al. [40] measured the conductance of single polymer chains with STM. In their work, polyfluorene chains were synthesized on Au(111) surfaces and the individual manipulation of these chains by the STM tip allowed the length-dependent measurement of chain conductivity [40]. The STM tip can also be used to initiate and control the growth of single-chain molecular wires. Okawa et al. [41] reported the controlled synthesis of polydiacetylene chains on graphite surfaces. They demonstrated that this technique allows construction of molecular electronics made single-chain polymer devices realize.

On the other hand, molecular manipulation with external variables, such as illumination or electrochemical potential, is possible at the nanoscale and the process can
be observed with STM. Kumar et al. manipulated the cis-trans azobenzene molecular switch with ultraviolet light [42]. Figure 6 shows that the isolated azobenzene-functionalized molecules in the matrix of dodecanethiols rendered stability, allowing the control over reversible photoswitching. Such rigid assembly can potentially be utilized in stabilizing single molecules for other switching studies in which the matrix plays a key or interfering role. The assembly of practical molecular devices may become possible with increased stability in ambient conditions and improved understanding of photoswitches.

Ye et al. manipulated a molecular shuttle with electrochemical potential [43]. Using electrochemical STM, they observed electrochemically controlled station changes of individual bistable rotaxane molecules in situ, as shown in Fig. 7. Motions of the cyclobis(paraquat-p-phenylene) rings were correlated with redox states of the tetrathiafulvalene station relative to the 1,5-dioxynaphthalene station and showed partial reversibility. The trajectories of the rings suggest that once a bistable rotaxane molecule is adsorbed on a surface, the motion of the cyclobis(paraquat-p-phenylene) ring relative to the dumbbell is affected by its local environment and the flexibility of the molecule. Bistable rotaxane molecules with rigid dumbbells should enable consistent and fully reversible motions, as well as direct visualization of the rings and the shafts of the molecules. The molecular design and synthesis of such systems are underway. Consistent and complete reversibility of switching in these bistable molecules will be required for efficient actuation of nanoelectromechanical devices and for reliable nanoelectronic device applications.

The author et al. manipulated surface structure with polar solvents [44]. Figure 8 demonstrates two-dimensional arrays of phthalocyanine derivative molecules controlled by the choice of solvent. A pseudosquare lattice array was formed using 1-bromo-4-n-octylbenzene, whereas a pseudohexagonal two-dimensional ordered array was formed using 1-bromo-8-phenyl-octane. In the parent solvent, octylbenzene, only one-dimensional ordering is observed with occasional regions of dimer row formation. Solubility and solvent-metal complexation mechanisms were ruled out as major contributors to the structural reorganization.

The author et al. also succeeded in manipulating double-decker phthalocyanine complexes with the STM tip [45]. They have controlled and manipulated phthalocyanine and the double-decker molecules with STM. Partial substitution of the double-decker monolayers with octakis(octyloxy)-phthalocyanine was accomplished by nanografting, and the substituted domains formed bilayer stacks epitaxially on graphite. Figure 9 demonstrates nanografting of double-decker phthalocyanine molecules in matrices of single layer octakis(octyloxy)-phthalocyanine. Rectangular scans with a STM tip at low bias voltage resulted in the removal of the adsorbed double-decker molecular layer and substituted bilayer-stacked octakis(octyloxy)-phthalocyanine from phenylbenzene solution. These results demonstrate compositional control through scanning probe lithography at the liquid-solid interface at room temperature. Moreover, single-molecular decomposition of heteroleptic double-decker molecules of a lutetium complex sandwiched with naphthalocyanine and octaethylporphyrin with voltage pulses applied by the STM tip was demonstrated: the top octaethylporphyrin ligand was removed, and the bottom naphthalocyanine ligand remained on the surface. A domain of the decomposed molecules was formed in the
FIG. 6: Azo-molecular switch. Upper left: schematics showing photo-induced changes in apparent height of the azobenzene-functionalized molecules in STM images due to isomerization of the azobenzene moiety between trans and cis are defined as on (apparent height ) 2.1 (0.3 Å) and off (apparent height ) 0.7 (0.2 Å) states, respectively. Right images: azobenzene-functionalized molecules switch off and switch on upon irradiation with ultraviolet (∼365 nm) and visible (∼450 nm) light, respectively. Images are recorded after irradiating (A) 0 min, (B) 10 min, (C) 35 min, (D) 60 min, and (E) 160 min with ultraviolet light and visible light irradiation for (F) 30 min. A–E show switching off of single molecules with continued UV illumination. The squares in E and F show switching on of molecules with visible illumination. The arrow in E shows switching on of a molecule with UV illumination. Lower left: fraction of azobenzene-functionalized molecules in the on state decreases as a function of time of ultraviolet irradiation (12 mW/cm²). The decay constant (τ) under these conditions is 54 minutes. From Ref. [42]. Reprinted with permission. Copyright 2008 American Chemical Society.

FIG. 7: Rotaxane shuttle controlled by electrochemical potential. (A) The tetracationic cyclobis(paraquat-p-phenylene) ring (CBPQT⁴⁺, blue) is known to move along the thread between two recognition sites (tetrathiafulvalene, TTF, green and 1,5-dioxynaphthalene, DNP, red stations) depending on the redox state of the TTF unit. (B) The protrusions are assigned as CBPQT⁴⁺ rings. (C) In its reduced state at +0.12 V, the CBPQT⁴⁺ ring prefers to encircle the TTF station. (D) Upon oxidation (+0.12 to +0.53 V) of the TTF station into a radical cation, electrostatic repulsion propels the ring to the DNP station (blue arrow). (E) Upon reduction (+0.53 to +0.12 V) of the TTF station to neutrality, the metastable state of the bistable rotaxane relaxes back to its thermodynamically favorable state, wherein the CBPQT⁴⁺ ring occupies the TTF station (red arrow). From Ref. [43]. Reprinted with permission. Copyright 2010 American Chemical Society.

double-decker molecular domains, and the boundary of the decomposed molecular domain re-formed to be rectangular via self-curing. Figure 10 demonstrated a molecular “sliding block puzzle” with the cascades of double-decker molecules. After the first image was recorded (lower left), two double-decker molecules slid to the adjacent vacancies. Moreover, after the second image was recorded (lower middle), a double-decker molecule was extracted from the layer and another double-decker molecule filled in a vacancy. In this way, room temperature manipulation of single molecules with the STM tip at the liquid-solid interface is available. Recently, Mao et al. [46] measured the lateral critical force for the manipulation of single phthalocyanine molecule on Pb(111) surface in UHV with the STM combined with non-contact atomic force microscope. The observed average value of 25 pN is typically two times larger than the molecule–substrate interaction. At the liquid–solid interface, the critical force should be increased while the desorption of manipulated molecules from the interface is suppressed by the solvent.

VI. CONCLUSION AND FUTURE DIRECTIONS

This review paper has demonstrated that the manipulation of molecules in air or in liquid is available in several cases. 1-phenyloctane is one of the best solvents for this purpose because it prevents molecules in liquid from the adsorption on STM tip. Stability of STM tip is also important in order to realize the certain manipulation without destroying the manipulated structure.

Finally, the author would like to demonstrate the perspective for the future study on nanoscale patterning with self-assembly observed with the STM.

Fabrication of Penrose patterning with local five-fold symmetry [46, 47] using five-fold symmetrical molecules such as ferrocene [48] would be interesting for the control of surface nanoscale properties. In case of metals and alloys, the fabrication of five-fold symmetric structure is available, such as quasi-crystal [49] and multiply-twinned particle [50]. Though the STM images of the quasi-crystal alloys with five-fold symmetric structure have been reported [51–53] and there are several attempts to fabricate Penrose tiling with five-fold symmetric molecules [54–56], nobody has succeeded in fabricating two-dimensional Pen-
FIG. 8: Manipulation of interface structure of copper-tetra(t-butyl)phthalocyanine at the interface of octylbenzene solvent and graphite. (Upper) Scanning tunneling microscope images of the phthalocyanine molecules before adding extra solvents. Image scale: 50 nm×50 nm (left), 20 nm×20 nm (middle), and 1.8 nm×1.8 nm with molecular resolution (right). (Lower) the STM images after adding the 0.1 ml solvent of octylbenzene with no change (left), 1-bromo-4-n-octylbenzene changed into square lattice (middle), and 1-bromo-8-phenyl-octane changed into hexagonal lattice (right). The local density of state maps of each solvent for highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) obtained from the ab initio molecular orbital calculation are shown beside the corresponding STM images. The STM images are from Ref. [44]. Reprinted with permission. Copyright 2010 American Chemical Society.

FIG. 9: Sliding block puzzle (upper left) playing with double-decker molecules. (Upper middle) Schematics of the double-decker molecules aligned on surface. (Upper right) Scanning tunneling microscope image of naphthalocyanine-lutetium-octaethylporphyrin double-decker molecules on graphite before the playing of nanoscale sliding block puzzle. Scanning tunneling microscope images of sliding blocks of naphthalocyanine-lutetium-octaethylporphyrin double-decker molecules: (lower left) before sliding, sliding molecules are indicated by arrows, (lower middle) after sliding but before extracting and filling the double-decker molecule, indicated by arrows, and (lower right) after extracting and filling. The STM images are from Ref. [45]. Reprinted with permission. Copyright 2010 American Chemical Society.

rose tiling with molecules with the bottom-up method. Various examples of Fibonacci patterning are available in nature; phyllotaxis as a dynamical self-organizing process during the ontogeny [57] or the seed pattern of helianthus annuus (sunflower) with the predominance of Fibonacci order [58]. Though one-dimensional Fibonacci superlattice has been fabricated and studied [59, 60], nobody has ever succeeded in fabricating two-dimensional Fibonacci pattern with molecules, either. These are the near-future topics of nanoscale self-assembly, which provide the novel application from organic surface science.
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Axe, Phys. Rev. Lett. 57, 1157 (1986).

[60] M. W. C. Dharma-wardana, A. H. MacDonald, D. J. Lockwood, J.-M. Baribeau, and D. C. Houghton, Phys. Rev. Lett. 58, 1761 (1987).