4-4 Fabrication and Characterization of Nanometer-size Structures Consisting of Organic Molecules

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Overlayer structures consisting of organic molecules deposited on clean metal surfaces were observed by using scanning tunneling microscope (STM), which has sub-nanometer spatial resolution. Structural isomers of the molecules, whose difference is the binding sites of substituents, can be clearly distinguished from STM images. Introducing the substituent having attractive force, to the molecules causes specific overlayer structure by self-assembly manner controlled by the substituent. We succeeded to observe a single molecular image on a metal surface with noncontact atomic force microscope (NCAFM) that can be applicable to nonconductive sample. These techniques forming the structures and obtaining highly resolved molecular images are fundamental and essential techniques to develop future information/communication devices with molecules.

Keywords
Organic molecule, Self-assembly, Scanning Tunneling Microscopy (STM), Structural isomer, Noncontact Atomic Force Microscopy (NCAFM)

1 Introduction

The devices used in telecommunications and information processing are becoming increasingly smaller and denser, and, as a result, the facilities required to produce them are rapidly becoming enormously complicated. Even with such advanced facilities, currently available lithographic micromachining technology using light or electron beams is expected to reach the lower limit (several nanometers) in terms of manufacturing techniques within 10 years. One proposed means of overcoming this micromachining limit is referred to as “self-assembly” technology, in which molecules spontaneously form nanoscale structures. This highly promising approach is expected as an indispensable fundamental technology in the future manufacture of telecommunication devices.

Self-assembly technology is among what are referred to as “bottom-up” technologies. The molecules, as the basic elements, spontaneously assemble themselves to form highly functional structures without the application of external operations [1]. This type of spontaneous behavior is ordinarily observed in living things, in the extensive functions that collectively define life. However, we have not yet succeeded in establishing the technology to reproduce this self-assembly function, and today molecule-based assembly remains but an ambitious goal. If we are to establish the fundamental techniques of self-assembly, we must first understand molecular behavior in more detail. As a first step toward this goal, we should begin by designing and synthesizing suitable organic molecules and then observing their structures and behavior, using high-resolution microscopes such as scanning probe microscopy (SPM).

The SPM technique, including scanning tunneling microscopy (STM), is currently under application in the investigation of nanotechnology. STM creates an image of surface morphology and electronic states by scanning the sample surface with a sharp tungsten probe (made by chemical etching) while monitoring the tunneling current that flows between the sample surface and the probe when the two are in very close proximity. This microscope features sub-nanometer resolution (to approximately the size of an atom), and is proving an indispensable surface observation technique in nanotechnological studies [2]. Noncontact atomic force microscope (NCAFM) obtains images by monitoring the atomic force between the sample surface and a single crystal silicon cantilever probe when the probe and surface are just short of contact. This microscope has also revealed its effectiveness in atomic-scale observation of the surface morphology of a sample on a non-conducting substrate; however, this technology has yet to mature [3].

This paper presents an overview of the results of high-resolution observations of molecular overlayer structures on metal substrates, performed as part of efforts to establish self-assembling nano-structures by molecules.

2 Outline of experimental conditions

All experiments were performed in ultra-high vacuum (UHV) chambers in which pressure was maintained below 10^{-8} Pa to avoid the contamination of impurities. Under these conditions, impurities—i.e., substances other than the target molecules—do not adsorb on the substrate or the probe; this enables observation of extremely high-resolution images. To obtain this level of vacuum, the chambers was evacuated using a combined pump system consisting of turbo molecular pumps, ion pumps, and titanium sublimation pumps. To eliminate mechanical vibrations, the ultra-high vacuum was maintained with an ion pump alone during SPM measurements.

The target molecules were evaporated onto the substrate at room temperature by resistive heating from a crucible in the ultra-high vacuum chamber. In many of the experiments, the amount of evaporated target molecules was insufficient to cover the entire surface of the substrate. Instead, the molecules were evaporated to achieve sub-monolayer coverage (30%–60%). This range was selected for its suitability in the analysis of molecular structures and superstructures by STM. The molecular evaporation temperature depended on the molecular species, but was generally from 400 K to 500 K.

The samples were observed by SPM at selected temperatures in the regions between room temperature and 63 K. At room temperature, some molecules were adsorbed on the substrate via weak forces and were very readily displaced, sometimes rendering it difficult to perform observations. At low temperatures, thermal fluctuations are suppressed, which in some cases facilitates high-resolution observations. Liquid nitrogen or nitrogen solidified through decompression is used as the coolant.

The substrate used in this study was mainly of an Au (111) surface of a single crystalline gold or a gold thin film deposited on a mica substrate. The Au (111) surface was prepared by repeated sputtering by argon ions accelerated to 600 V–1000 V and annealing at 700 K–800 K, resulting in the production of a clean surface. An Au (111) clean surface is known to show a reconstructed structure, “herringbone structure,” consisting of a combination of face-centered cubic (fcc) and hexagonal close-packed (hcp) crystalline structures. This structure can be used to verify the cleanness of the surface; additionally, as the adsorbates tend to adsorb on the “elbow” or along the stripes of the structure, this structure also proves convenient in stabilizing the molecules for observation.

3 Construction of molecular superstructures and observations

3.1 Identification of molecular structures

When analyzing a molecular sample in ordinary chemical analysis, several milligrams of sample are generally required. One milligram of a sample consisting of molecules with a molecular weight of 1,000 contains 6×10^{17} molecules. Even after reducing the sample amount to 1 microgram, the number of molecules in the sample is on the order of 10^{14}; the sample thus holds 100 trillion molecules. This means that ordinary analysis of a substance must treat an extremely large number of molecules, with measurement possible only in terms of statistical quantities. Nanotechnology, working on the nanometer level, can treat much smaller groups of molecules, enabling analysis at the level of the single molecule. Our Nanotechnology Group has succeeded in identifying structures at this single-molecule level through high-resolution, UHV-STM observations of the molecules discussed below.

The first such molecule was a subphthalocyanine derivative (chloro [tri-tert-butyl-subphthalocyaninato] boron(III), TBSubPc). This molecule is a derivative of subphthalocyanine, which has a triangular, cone-like structure, and a chlorine atom at its top. TBSubPc has three t-butyl groups around a subphthalocyanine structure. As shown in Fig. 1 (A–D), there are four possible structural isomers including enantiomers, depending on the relative positions of the t-butyl groups. As the molecule is conical and not planar, it can also adsorb on the surface in one of two ways: with the chlorine atom toward the substrate, or with the chlorine atom away from the substrate. This molecule was evaporated to the Au (111) surface in an ultra-high vacuum and observed with an STM at the temperature of liquid nitrogen (77 K). In the STM images of this molecule (Fig. 1 E and F), bright spots corresponding to the t-butyl groups were clearly identified, and three bright spots indicates a single molecule. It was also clear that the distances between these bright spots corresponded to those between the t-butyl groups in the structural isomers. When a chlorine atom was away from the substrate (Fig. 1 E), an additional bright spot corresponding to the chlorine atom appeared at the center of the three bright spots. These observations demonstrate that STM images can be used to identify the structural isomers of molecules as well as the adsorbation configuration of the molecules on the substrate [4].

The second such molecule is a porphyrin derivative with two methoxy groups (-OCH3), tertialybutyl-methoxy-phenyl-porphyrin (TBMPP). This molecule can take one of two structures: in one, the two methoxy groups face each other (Fig. 2 A); in the other, the groups are adjacent (Fig. 2 B). The yellow circles in Fig. 2 A and B indicate the methoxy groups. A sample containing both of these structures was evaporated to the Au (111) surface in ultra-high vacuum and observed with an STM at room temperature. Single molecules are indicated with white squares in the STM image (Fig. 2 C) obtained. This STM image shows that the two types of molecules (a and b), here featuring different contrast tones, formed a square lattice structure. The difference in the contrast reflects the difference in the molecular structure described above. For the molecules in bright contrast (a), the methoxy groups are assumed to bulge out at the center of the TBMPP molecule, distorting the central porphyrin ring convexly against the substrate. The molecules with darker contrast must also contain the methoxy groups, but in this case these groups are considered to cause only small distortions in the porphyrin ring [5]. As the methoxy groups are not identifiable as protrusions, and the entire central part of the molecules features bright contrast in both molecular images, the methoxy groups are considered to be positioned between the molecule and the substrate.

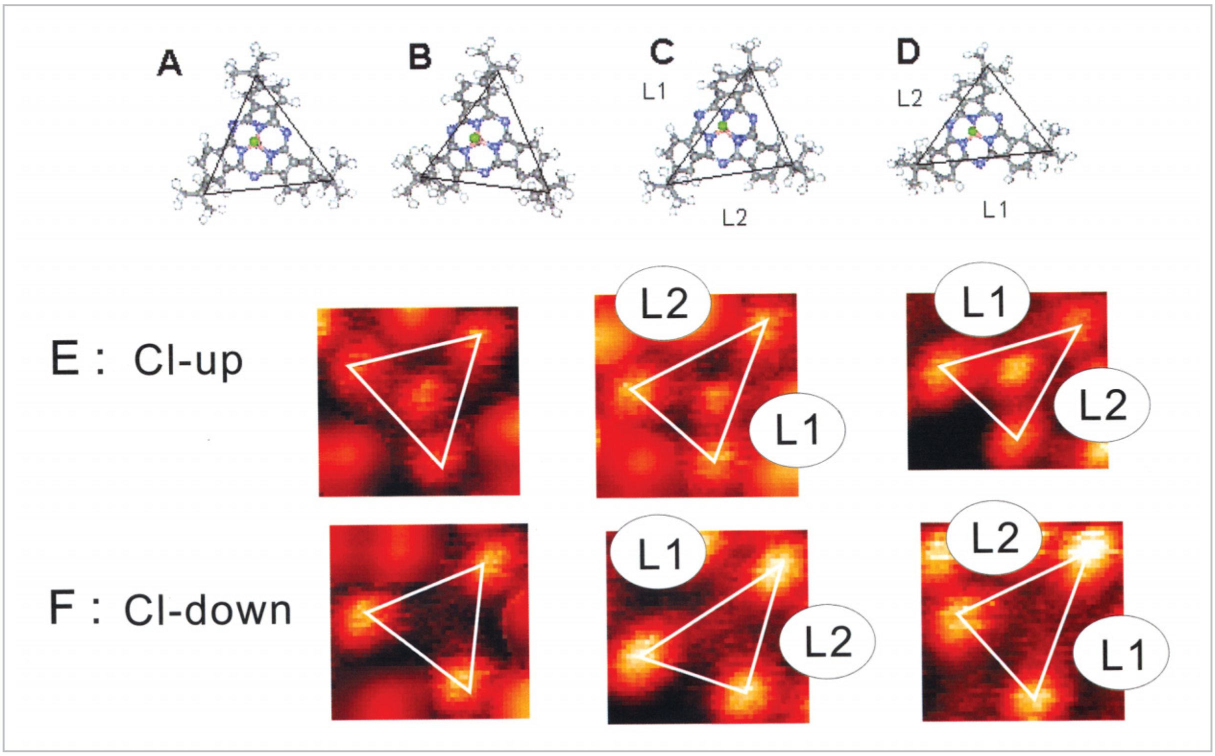

Fig. 1 4 types of structural isomers of TBSubPc molecules and corresponding STM images

This distortion induced by the methoxy groups agrees with the results of molecular structure calculated by computer simulations [6] [7].

3.2 Configuration of molecular superstructures

Molecular superstructures formed by the molecules adsorbed on the surface of substrates depend on molecule-molecule and molecule-substrate interactions. If an understanding of these interactions can reveal the principles required to control the interactions, we will be able to arrive at the self-assembly techniques that will allow molecules to spontaneously form nanometer-scale structures; this will lead to significant innovation in device manufacturing technologies. Below we discuss two examples of research conducted with these considerations in mind. The first example deals with structural formation by selective self-assembly induced by a change in the molecule-molecule interactions. The second example addresses the phase separation observed when the molecule-substrate interaction is changed through modification of a portion of the molecule contacting the substrate.

Porphyrin molecules with t-butyl phenyl groups (TBPP) have been observed to aggregate on the Au (111) surface to form a square lattice [8]. When some of the t-butyl phenyl groups in these molecules are replaced by cyano phenyl groups (cyanophenyl-di-tertiary-butyl-phenyl-porphyrin, or “cyano TBPP”), weak polarization occurs around the cyano groups. This polarization works as the attractive interaction between the molecules [9] [10]. Cyano TBPP molecules (Fig. 3 A) with cyano phenyl groups in trans positions were deposited on the Au (111) substrate and observed with an STM at a low temperature (63 K). Figure 3 B shows the results, in which the molecules are shown to align linearly [11]. This linear alignment indicates that the molecules arranged themselves with the cyano phenyl groups facing each other, as shown in Fig. 3 C. Hydrogen bonding between the nitrogen atom of the cyano group and the hydrogen atom of the phenyl group is the cause of this arrangement, as confirmed via theoretical calculations [9]. The two rows of bright spots are observed because the two t-butyl phenyl groups, bound to both sides of

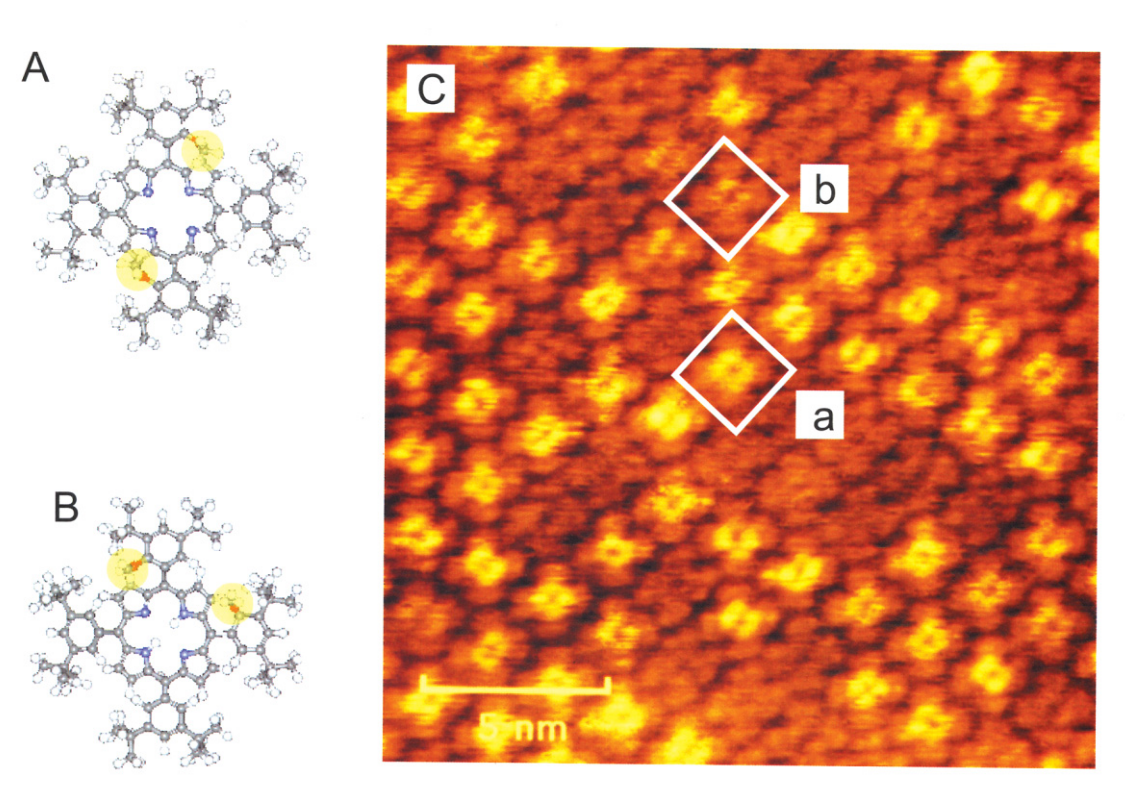

Fig.2 Structures of TBMPP molecules and corresponding STM images
The methoxy groups are indicated in yellow in both (A) and (B).

the porphyrin ring, are generated with bright contrast. For example, the section enclosed with the black rectangle consists of 13 molecules aligned in a row. This formed a wire-type structure along the elbow lines in the herringbone structure (the minute up-down structure on the Au (111) substrate surface). Branching was sometimes observed along the herringbone structure. This is because the elbows in the herringbone structure are energetically stable with respect to the adsorbed molecules. Molecules each containing a single cyano group are observed to form a trimer structure, along with the cyano groups of three molecules facing each other. The self-assembling construction of this type of linear structure at such a narrow width (approximately 2 nm, or one molecule) represents a significant step toward the construction of micro-circuit structures through molecular self-assembly.

The above example illustrates the formation of a superstructure based mainly on molecule-molecule interaction. The molecule-substrate interaction, on the other hand, can sometimes result in the formation of different structures. For example, in the case of the TBSubPc (Fig. 4 A) already discussed, approximately 80 percent of the molecules were adsorbed on the substrate surface, with its chlorine atom pointing to the substrate. The molecule featuring a phenyl group (phenyl TBSubPc, Fig. 4 B) in place of a chlorine atom at the top adsorbed on the substrate surface as well, with the phenyl group oriented toward the substrate surface. In other words, the differing characteristics of the phenyl group relative to the chlorine atom results in a different strength of interaction between the molecule and the substrate. In general, comparing the chlorine atom (halogen) and the phenyl group, the chlorine atom features a stronger polarity and thus greater affinity to metals such as silver. The TBSubPc molecules are therefore subject to strong interactions with the substrate, while the phenyl TBSubPc molecules feature weaker substrate interactions, although these two molecules have nearly identical structures.

Both types of molecules were evaporated

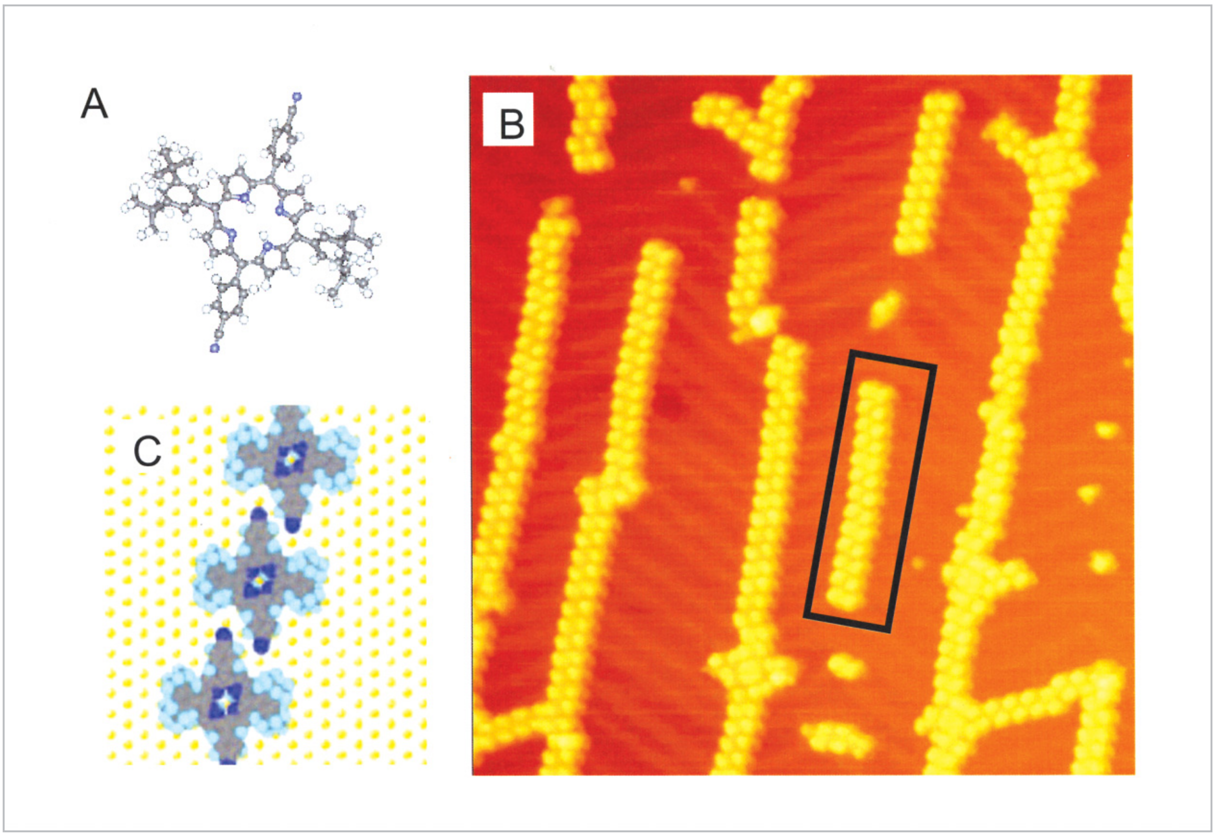

Fig.3 *Structural models of cyano TBPP molecules and corresponding STM images (70 nm × 70 nm)*

to the Au (111) substrate surface at room temperature, cooled to 77 K, and observed with STM. Figure 4 C shows the STM image obtained, revealing the presence of both molecules [12]. In this figure, the white triangles connecting the three bright spots corresponding to the t-butyl groups indicate single molecules. This figure shows two different molecular superstructures. In section (a), the molecules form a slightly distorted hexagonal structure. The cause of the distortion is as discussed in 2.1: structural isomers are present, depending on the positions of the t-butyl groups bonding sites, and these isomers intermix when forming the lattice structure. On the other hand, in section (b), distortion is also observed to some extent; however, a completely different lattice structure is seen, in a honeycomb pattern. These different lattice structures correspond to the structures obtained when TBSubPc and phenyl TBSubPc were independently evaporated to the Au (111) substrate. These results indicate that molecules with extremely similar structures do not intermix but instead form separate superstructures.

When the molecule-substrate interaction is varied, it is natural that different lattice structures will appear as a result of the effect of the substrate surface. However, the resultant phase separation of these different molecules and the formation of different structures demonstrate that the subtle differences in the molecule-molecule interaction become conspicuous due to the difference in the molecule-substrate interaction. Other reports have indicated that molecules form unexpected superstructures in mixed systems containing two or more different types of molecules, as the increase in the number of interactions renders the system more complex [13]. Systems containing many different types of molecules will undoubtedly prove indispensable in the construction of molecular devices. It will also be necessary to study further the effects of the complex combination of interactions on structural formation.

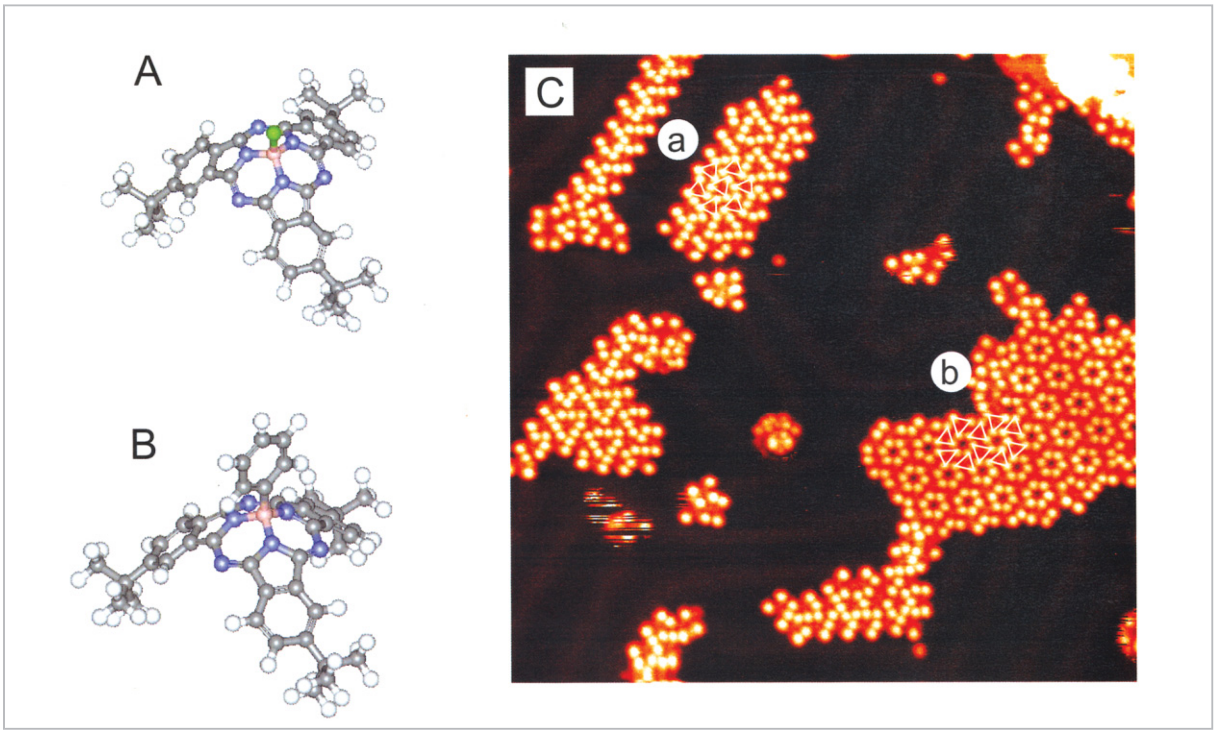

Fig.4 Molecular models of TBSubPc molecule and phenyl TBSubPc molecule and their STM images (40 nm × 40 nm)

3.3 Observation technique for molecules utilizing an atomic force microscope

The STM technique for observing molecules as discussed above is a powerful tool for surface observation, providing extremely high resolution. On the other hand, to construct so-called molecular electronics devices that make use of the electrical properties of the molecular superstructures on the substrate, these structures must be formed on insulating substrates, in order to optimize the pure electrical properties of the superstructures. However, STM measures the tunneling current between the probe and the sample surface, and this mechanism makes it difficult to measure the sample on an insulating substrate.

In light of this issue, NCAFM is expected to provide the means to observe the surface structures of such samples at high resolution. As stated earlier, NCAFM uses the atomic force between the sample and the probe for feedback, and thus in principle this technique does not depend on the conductivity of the sample. However, the NCAFM technique is still under development and is thus not as mature as the STM technique. In particular, the target molecules adsorb on the substrate surface with extremely weak forces (such as the van der Waals force) and tend to be displaced easily or to adsorb on the probe. These are among the phenomena that hinder molecular observation using NCAFM. To advance toward the construction of molecular devices on nonconductive substrates, it is important that these problems be resolved and that we establish high-resolution observation of molecular superstructures on the substrate using the NCAFM technique, as we also develop methods of manipulating these superstructures. Based on these considerations, our group has begun attempts at high-resolution observation of molecules via NCAFM.

Our group began observations using porphyrin derivatives on Au (111) substrates as samples due to our success in high-resolution observation using these substrates with STM. The molecule employed was methylthiophenyl-tris-t-buthylphenyl-porphyrin (MST-BPP). Figure 5 A shows its structure. This molecule features a methylthiophenyl group that contains a sulfur atom. In general, the sulfur atom in the thiol group (-SH group) is known to bind to gold atoms with extremely high selectivity. From this it is deduced that the sulfur atom in this methylthiophenyl group will also show strong bonding to the gold substrate, but, unlike the thiol group, the methylthiophenyl group features a bulky methyl group at its end, which is considered to result in a correspondingly weaker bond. This type of bonding is appropriate for the current purposes, fixes the highly mobile molecules on the substrate, and is expected to act as a stabilizing factor as the probe approaches.

Figure 5 B shows the results of NCAFM observation performed with this molecule evaporated to the gold substrate. The white squares indicate single molecules. The protrusions enclosed in white circles correspond to t-butyl groups. The sections enclosed with black circles correspond to a methylthiophenyl group, where no protrusions are observed. The NCAFM images in principle show contrast according to the geometrical irregularities on the surface and not according to the electrical states of the molecules. Thus, the bulky t-butyl groups appear as protrusions, whereas the relatively small methylthiophenyl groups are in dark contrast. The figure also shows that all molecules adsorbed on the substrate with the methylthiophenyl groups are oriented facing the stepped edge on the substrate. This result confirms predictions regarding the interaction between a methylthiophenyl group and gold [13] [14]. The NCAFM overview image (Fig. 5 C) shows one of the molecules adsorbed on a terrace of the substrate. A pair of large protrusions (large white circles) and a pair consisting of a small protrusion (small white circle) and no protrusion (black circle) are observed to face each other in the figure. This image is interpreted as follows: the methylthiophenyl group in the black circle bonded strongly to a gold atom on the substrate surface, convexly distorting the molecule and consequently causing the t-butyl groups (in the large white circles) to protrude, with the t-butyl group (in the small white circle) and the methylthiophenyl group oriented facing down toward the substrate. This type of distortion in molecular structures has been confirmed in theoretical calculations [7].

In this example a gold substrate surface was used for NCAFM observations of molecules on the surface, due to the success seen in

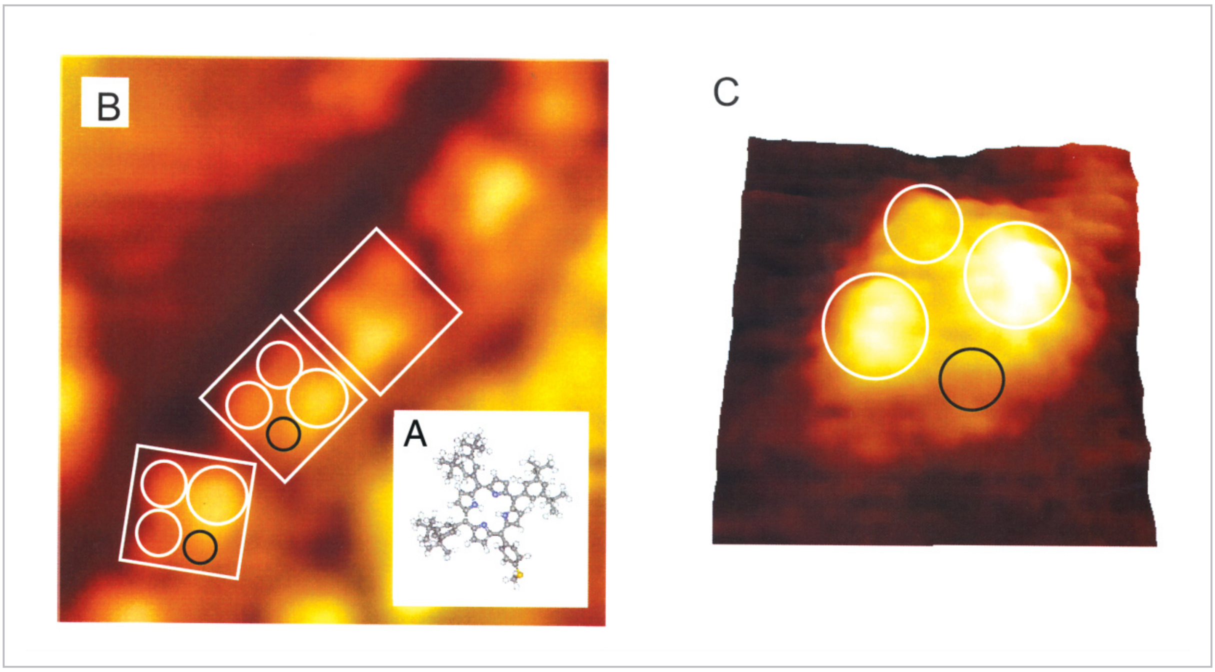

Fig.5 Structural model of an MSTBPP molecule (A), NCAFM image of MSTBPP molecules adsorbed on the stepped edge of the gold substrate (8.5 nm × 8.5 nm) (B), and an NCAFM image of the molecule adsorbed on the terrace of the substrate surface (C)

this use of this metal in STM observations. Developing this technique further will enable observation of molecules on nonconductive substrates; this technique is thus expected to become an important tool in the development of molecular electronics.

4 Conclusions

This paper presents an overview of the results of observations conducted by typical scanning probe microscopes, STM and NCAFM, designed to observe nano-scale superstructures formed by organic molecules evaporated on clean metal substrates. The achievements of these studies include the identification of molecular structures at the single-molecule level, formation of superstructures based on intermolecular interactions, and observation of a single organic molecule using an NCAFM. These series of studies have been made possible through the close integration of the scanning probe microscope, specific techniques of physical observation, and chemical synthesis in the formation of suitable molecular structures. The nano-scale structures formed by these molecules have the potential to break through the limitations of devices fabricated using current lithography techniques. These structures can be seen as the seeds for the extensive development of functions or techniques of fabrication of future telecommunication devices. However, studies involving these techniques have only just begun, and thus at present we are insufficiently capable of wielding or controlling them. Further studies are required if we are to establish a solid foundation for future telecommunications.

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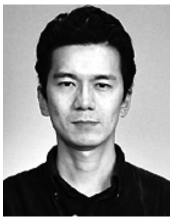

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