

Identifying Subphthalocyanine Molecule Isomers by Using a Scanning Tunneling Microscope

Hitoshi Suzuki,* Hideki Miki, Shiyoshi Yokoyama, and Shinro Mashiko

Kansai Advanced Research Center, Communications Research Laboratory, 588-2 Iwaoka, Nishi-ku, Kobe 651-2492, Japan

Received: November 12, 2002; In Final Form: January 23, 2003

Structural isomers of chloro[tri-*tert*-butyl-subphthalocyaninato]boron(III) (TBSuPc) molecules on the Au(111) surface were identified by using the scanning tunneling microscope (STM). A TBSuPc is a corn-shaped and triangular molecule with a chloride atom at the top and three *tert*-butyl groups on its periphery. The molecule has four kinds of structural isomers depending on the binding sites of the *tert*-butyl groups. It can have two different adsorbed configurations on the surface, Cl-up and Cl-down. The STM image shows three spots that correspond to the three *tert*-butyl groups and one central spot that reflects the Cl atom. Analyzing the relative distances between the spots enables us to identify the isomers and the adsorbed configurations.

1. Introduction

Most chemical measurements used for analyzing molecules, including optical spectroscopy, NMR, and mass spectroscopy, measure the average value of an ensemble of many molecules. They need a certain amount of specimens containing molecules to detect signals. This means that general analytical methods provide statistical information of a molecule ensemble. If the specimen includes certain kinds of molecules (the kind of an object with impurities), the measured signal is a mixture of these from the object and others. They can be discriminated but not always. It depends on the difference in the molecular properties, which reflect on the measured signals. These statistical characteristics of the measurements are almost the same as for surface analytical methods used in UHV.

On the other hand, scanning tunneling microscope (STM), which has become one of the most effective tools used in surface science in the past decades, has proved to be applicable enough to access signals of a single molecule. Conformational changes of the substituent's angle of a single porphyrin derivatives on a surface has been determined from STM images,¹ and furthermore, the substituent angle has been modified by applying additional force from the STM tip.² These STM measurements proved that we can recognize a single molecular image with a sub-nanometer resolution instead of the ensemble average of the molecules. This accessibility to a single molecule has enabled detecting a single molecular rotation^{3,4} and controlling a chemical reaction between two molecules.⁵ Time-resolved STM measurements have also elucidated the dynamics of the molecular diffusion and aggregation, as if for a liquid/gas interface which provides an interesting view of the relation between statistical behavior and single-molecular behavior.⁶ The high-resolution image given by the STM has enabled distinguishing two kinds of molecules; phthalocyanine molecules containing different central metals showed a clear contrast.⁷ Recently, chiral isomers have also been discriminated by analysis of their aggregating structures on a metal surface in STM images instead of a distinct molecular image that reflects their own structure.^{8–10}

Here, we report that structural isomers, including enantiomers of a subphthalocyanine derivative, and adsorbed configurations can clearly be distinguished from each other on Au(111) with the STM. The molecule, which has a triangular and corn-shaped structure, has four kinds of isomers depending on the position of substituents and different adsorption faces on the surface caused by the nonplanarity of the molecular structure. This is one clear example of chirality distinguished by one molecular identifiable image.

2. Experimentals

The molecule used in the experiments was chloro[tri-*tert*-butyl-subphthalocyaninato]boron(III) (TBSuPc) synthesized according to a previous report.¹¹ This molecule is one derivative of subphthalocyanine (SubPc), which has a characteristic triangular and corn-shaped structure with a chloride atom on top and three diiminoisoindol rings around a boron core.^{11,12} The STM image of this molecule on Ag(111) surface shows three lobes corresponding to the three isoindol groups with a central dimple, which suggests that it is adsorbed on the surface in Cl-down configuration.^{6,13} A TBSuPc has three additional *tert*-butyl groups on the periphery of the SubPc molecule (Figure 1a). This molecule can adsorb to the surface in two different configurations: Cl-up and Cl-down.

The STM image of molecules on a metal surface generally reflects a complicated convolution of molecular geometrical and electronic structures and its interpretation by calculation has been proposed.¹⁴ However, in most of the cases of large molecules with bulky substituents such as *tert*-butyl groups, the bulky substituents are dominantly observable rather than its electronic structures.^{1,15} Therefore, the configurations of TBSuPc adsorption are expected to result in two different molecular images obtained by STM. In the case of Cl-up, four bright spots should be appeared in STM images, which correspond to the central Cl-atom standing out from the semiplaner π -electron system and three *tert*-butyl groups (Figure 1b). In the case Cl-down, only the three spots of *tert*-butyl groups should be observed (Figure 1c).

In addition, this molecule has four kinds of isomers depending on the position of the *tert*-butyl groups; (1) MMM TBSuPc,

* To whom correspondence should be addressed. Fax: +81-78-969-2259. E-mail: suzuki@crl.go.jp.

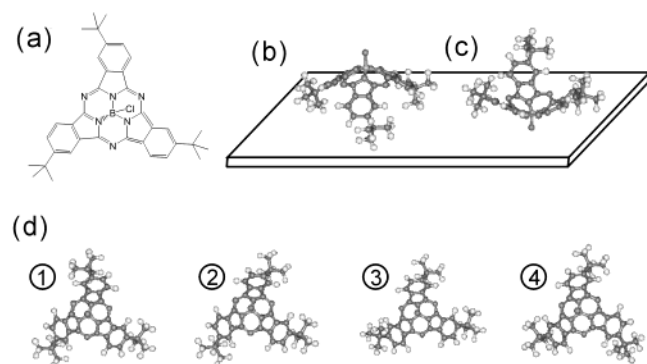


Figure 1. (a) Chemical structure of TBSuPc and (b) Cl-up and (c) Cl-down models of two adsorbed configurations on a surface. (d) Models of four kinds of isomers of the TBSuPc molecule. Top view from Cl side. (1) MMM TBSuPc, (2) MMP TBSuPc, (3) MPP TBSuPc, and (4) PPP TBSuPc according to the reported notation.¹²

(2) MMP TBSuPc, (3) MPP TBSuPc, and (4) PPP TBSuPc, according to the notation of the previous report (Figure 1d).¹² The isomers MMM and PPP belong to the same C_3 symmetry, and MMP and MPP belong to the C_1 symmetry. The three *tert*-butyl groups of MMM and PPP should form an equilateral triangle, but those of MMP and MPP should form a scalene triangle, which are supported by simply calculated models. The MMM and MMP TBSuPc are enantiomers of PPP and MPP, respectively. As a result, TBSuPc would show eight kinds of possible STM images. However, distinguishing between an STM image of an MMM isomer and one of a PPP isomer is impossible in both Cl-up and Cl-down case because the configuration of the three *tert*-butyl spots and the central Cl atom spot should be identical in both isomers. Therefore, an STM image can only provide six distinctive molecular images.

The Au(111) surface of a single crystal was used as the substrate for molecular deposition. Its clean surface was prepared by a repeated cycle of Ar sputtering (1 kV) and successive annealing (~ 800 K) in UHV according to the previously reported method.¹⁶ The STM observation showed the well-known reconstructed herringbone structure and confirmed that the Au (111) surface was atomically clean.

The TBSuPc molecule was evaporated by resistive heating and deposited on the Au surface at room temperature. The deposited amount was approximately 30% or 100% of one monolayer coverage. After the deposition, the sample was cooled to 77.5 K on the STM stage to reduce thermal fluctuation of the molecules. The STM measurements were done by LTSTM (Omicron) at 77.5 K with a chemically etched W tip. The base pressure of the STM chamber was kept below 5×10^{-9} Pa during measurements.

3. Results and Discussions

An STM image of the TBSuPc overlayer on Au (111) at low coverage, approximately 30%, is shown in Figure 2. Bright spots reflecting the protrusion of molecules are observable. These spots are thought to be *tert*-butyl groups bound to the TBSuPc's periphery, and a group of three spots, which are marked by a black triangle, can be consistently assigned to an individual TBSuPc molecule. The molecules are trapped on the valley of the herringbone structure showing quasi-hexagonal overlayer structure. The centers of molecules are likely to form hexagonal lattice, but the molecular orientation is not uniform. Furthermore, the distances between the spots belonging to some molecules are not equal, which suggests that structural isomers coexist in the same overlayer without segregation. Therefore,

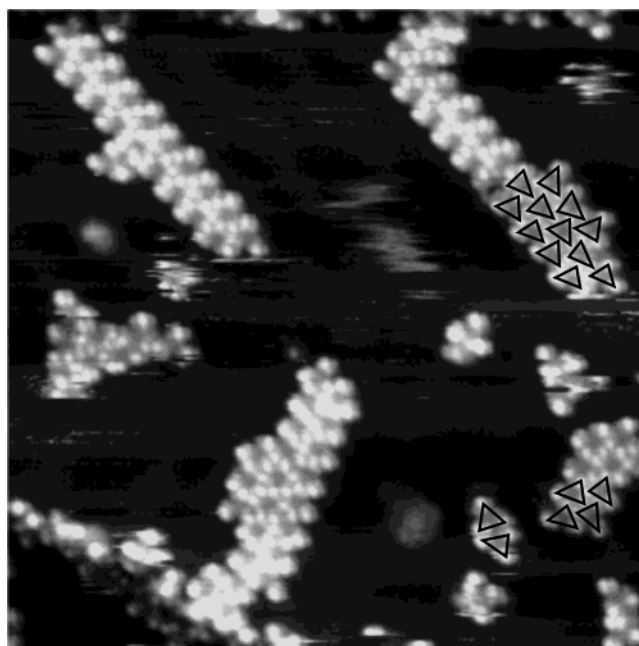


Figure 2. STM image of TBSuPc at approximately 30% coverage. Three bright spots corresponding to *tert*-butyl groups are assigned to one TBSuPc molecule. A black triangle represents an individual TBSuPc molecule. The molecules are preferentially adsorbed along the herringbone structure of Au surface. Image size is 32 nm. $I_t = 25$ pA, $V = 1.93$ V.

it is impossible to define the relative orientation of the molecular overlayer to the surface. At the low coverage, only the three spots, which can be assigned to the individual molecule, are observable. All molecules form an island consisting of more than two molecules, which shows that the intermolecular interaction stabilizes the overlayer structure.

The variety of the spot distance can be clearly observed in an STM image of the molecule at high coverage (Figure 3). Bright spots do not form a spatially periodic structure but show a vague tendency to align along the white arrow. This impression of an alignment is induced by the preferential adsorption of molecules along the substrate morphology of the Au(111), the herringbone structure. However, coexisting isomers and irregular orientation of the molecules prevent them from forming regular overlayer structure and identifying the relative orientation of the overlayer to the substrate even at the high coverage. The dark region (Figure 3a), which corresponds to an uncovered area, has small streak noise resulting from mobile molecules induced by the tip and the noisy area that may be caused by small amount of impurity also appears in Figure 3b. The bright spots near the boundaries of the uncovered area can be easily assigned to a single molecular image of the TBSuPc as well as those at low coverage (white triangles in Figure 3). The three spots forming a triangle can be also assigned to the three *tert*-butyl groups bound to the peripheries of the SubPc molecule by analogy of the low coverage STM image.

A high resolution image (Figure 4) explicitly manifests the variety of the observed seven protrusions. In Figure 4, parts a, b, and c consist of three spots; b and c are not equilaterally triangular. For example, the distances between the spots of c are 1.4, 1.2, and 1.0 nm. On the other hand, parts d, e, and f have central spots surrounded by three spots (four spots); and e and f are not equilaterally triangular. The image showing three spots and the one showing four spots suggest the two adsorbed configuration models mentioned above (Figure 1, parts b and c): Cl-down or Cl-up. Other STM images that differ in a similar

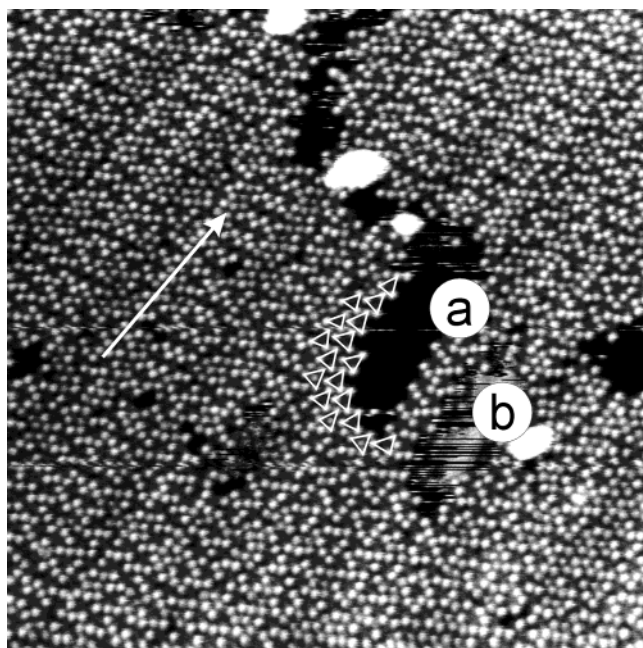


Figure 3. STM image of monolayer TBSuPc. Bright spots representing molecular protrusions show tendency of alignment along the white arrow. A white triangle represents an individual TBSuPc molecule. Uncovered area (a) with small streak noise and noisy area (b) caused by small impurity are observed. Image size is 40 nm. $I_t = 23$ pA, $V = 1.89$ V.

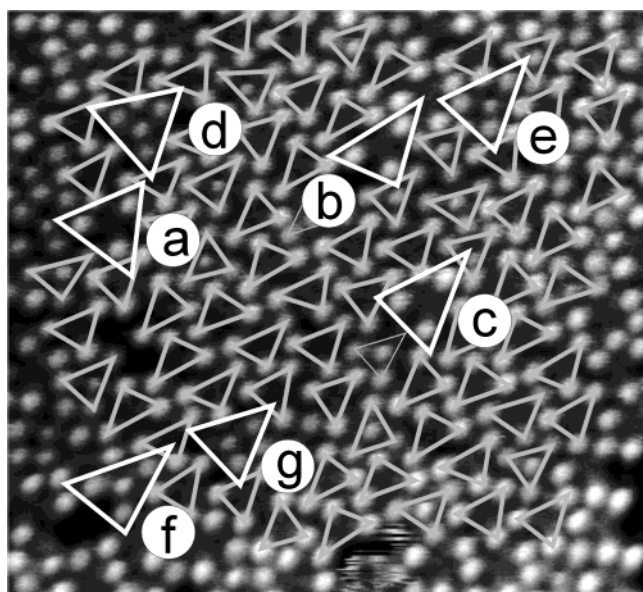


Figure 4. Magnified STM image. Seven different protrusions corresponding to a single molecule outlined by white lines are clearly identified. (a) Cl-down MMM or PPP, (b) Cl-down MMP, (c) Cl-down MPP, (d) Cl-up MMM or PPP, (e) Cl-up MMP, (f) Cl-up MPP, and (g) Cl-up with two *tert*-butyl spots. Image size is 15.4×14 nm. $I_t = 23$ pA, $V = 1.89$ V.

way because of adsorbed configurations have been reported on previously.¹⁷ The central spot in the images, parts d, e, and f, is thought to reflect a Cl atom. These observed molecular images that show different distances between two spots belonging to one molecule can be related to each structural isomer of the TBSuPc: Figure 4a corresponds to the Cl-down MMM or PPP TBSuPc, Figure 3d is the Cl-up MMM or PPP TBSuPc, and parts b and c of Figure 4 are the Cl-down MMP and the Cl-down MPP isomers, respectively. The Cl-up MMP and MPP isomers also are identified in parts e and f of Figure 4. A slight

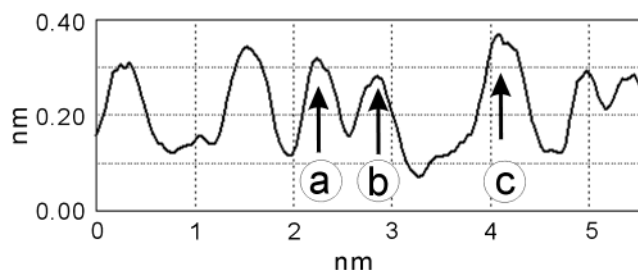
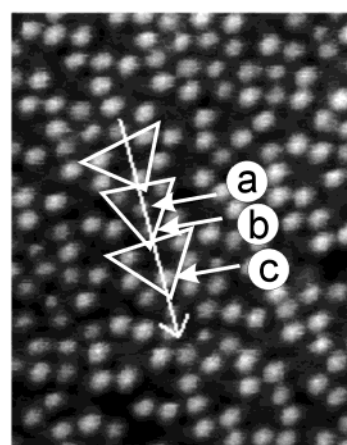


Figure 5. Cross section along white arrow. Typical profile of the contrast difference in the spots can be seen. (a) Cl spot, (b) *tert*-butyl spot of Cl-up molecule, and (c) *tert*-butyl spot of Cl-down molecule.

impurity, such as SubPc that only has two *tert*-butyl groups, is also recognizable in the STM image as three spots corresponding to the Cl spot and two *tert*-butyl groups (Figure 4g). The percentage of the MMM or PPP molecule is 37.3%, the MMP is 40.5%, and the MPP is 22.2%, which are obtained from containing 595 molecules. These ratios should not be compared to the statistical data because we did not accumulate the enough data of the molecular images from many highly resolved STM images.

Typical profile of the cross section of the STM image (Figure 5) manifests that the central spot (part a) of the Cl-up molecule is higher contrast than the surrounding three spots (part b); furthermore, the three spots around the central spot are lower than the three spots (part c) of the Cl-down molecule. This contrast difference between the central one and the other three is generally observed in most of the Cl-up molecules with a few exceptions (Figure 4e). The contrast of the STM image does not represent straightforwardly the geometrical structure because it includes electronic structures and modification by substrate. However, the difference in contrast between the spots (Figure 5, parts b and c) shows that they are not the same state, which supports the two adsorbed configuration models.

The two kinds of adsorbed configuration, Cl-up and Cl-down, can be easily added up from the STM image to estimate their ratio. The percentage of the Cl-down molecule is 80.1% and the Cl-up is 19.9%, which are obtained from two different images containing 1360 molecules. This ratio reflects the difference in interaction between the Cl and the Au substrate and that between *tert*-butyl and the substrate; that is, the Cl atom has a stronger affinity to Au than *tert*-butyl groups, which is certainly reasonable in consideration of dipole induced in B–Cl bond. This asymmetry should be inspected from the view of molecular interaction with substrate in future. However, this observation is consistent with the previous report on similar structural molecule.⁶ TBSuPc does not show a tilted Cl-down conformation which is supposed to be geometrically more stable

than the Cl-down conformation, whereas the similar configuration of another triangular molecule has been observed with STM.¹⁷ TBSuPc molecules are always observed in the form of an island composed of more than two molecules on the substrate terrace even at lower coverage. The interaction between the molecules in the island is thought to stabilize the Cl-down configuration rather than the tilted one. The number of TBSuPc molecules that only have two *tert*-butyl groups and one group is also estimated to be 3.1%. However, it does not straightforwardly represent the actual impurity amount because the evaporation rate of two *tert*-butyl molecules is not supposed to be the same as that of three *tert*-butyl molecules. Calculating the numbers of adsorbed configurations and molecule types to compare them with the statistically measured results is difficult because of lack of total number, but these results confirm that a new analytical possibility exists on a single molecular scale.

In summary, three kinds of isomers in four kinds of TBSuPc and two different adsorbed faces were each identified by comparison of the distances between *tert*-butyl spots in the STM image that elucidates the substituents positions. This is an example method for distinguishing enantiomers by using direct imaging. It also shows a new way of analyzing single molecules besides the conventional statistical analysis.

References and Notes

- (1) Jung, T. A.; Schlittler, R. R.; Gimzewski, J. K. *Nature* **1997**, 386, 696.
- (2) Moresco, F.; Meyer, G.; Rieder, K.-H.; Tang, H.; Gourdon, A.; Joachim, C. *Phys. Rev. Lett.* **2001**, 86, 672.
- (3) Stipe, B. C.; Rezaei, M. A.; Ho, W. *Science* **1998**, 279, 1907.
- (4) Gimzewski, J. K.; Joachim, C.; Schlittler, R. R.; Langlais, V.; Tang, H.; Johannsen, I. *Science* **1998**, 281, 531.
- (5) Hla, S.-W.; Bartels, L.; Meyer, G.; Rieder, K.-H. *Phys. Rev. Lett.* **2000**, 85, 2777.
- (6) Berner, S.; Brunner, M.; Ramoino, L.; Suzuki, H.; Güntherodt, H.-J.; Jung, T. A. *Chem. Phys. Lett.* **2001**, 348, 175.
- (7) Hipps, K. W.; Lu, X.; Wang, X. D.; Mazur, U. *J. Phys. Chem. B* **2000**, 104, 11899.
- (8) Böhrringer, M.; Morgenstern, K.; Schneider, W.-D.; Berndt, R.; Mauri, F.; Vita, A.; Car, R. *Phys. Rev. Lett.* **1999**, 83, 324.
- (9) Böhrringer, M.; Morgenstern, K.; Schneider, W.-D.; Berndt, R. *Angew. Chem., Int. Ed.* **1999**, 38, 821.
- (10) Kühnle, A.; Linderoth, T. R.; Hammer, B.; Besenbacher, F. *Nature* **2002**, 415, 891.
- (11) Geyer, M.; Plenzig, F.; Raushnabel, J.; Hanack, M.; del Rey, B.; Sastre, A.; Torres, T. *SYNTHESIS* **1996**, 1139.
- (12) Claessens, C. G.; G.-Rodrigues, D.; Torres, T. *Chem. Rev.* **2002**, 102, 835.
- (13) Suzuki, H.; Berner, S.; Brunner, M.; Yanagi, H.; Schlettwein, D.; Jung, T. A.; Guentherodt, H.-J. *Thin Solid Films* **2001**, 393, 325.
- (14) Sautet, P.; Joachim, C. *Chem. Phys. Lett.* **1991**, 185, 23.
- (15) Yokoyama, T.; Yokoyama, S.; Kamikado, T.; Mashiko, S. *J. Chem. Phys.* **2001**, 115, 3814–3818.
- (16) Musket, R. G.; Maclean, W.; Colmenares, C. A.; Makowiecki, D. M.; Siekhaus, W. J. *Appl. Surf. Sci.* **1982**, 10, 143–207.
- (17) Lin, R.; Braun, K.-F.; Tang, H.; Quade, U. J.; Krebs, F. C.; Meyer, G.; Joachim, C.; Rieder, K.-H.; Stokbro, K. *Surf. Sci.* **2001**, 477, 198.