

# Overlayer structure of subphthalocyanine derivative deposited on Au (111) surface by a spray-jet technique

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## Abstract

A new spray-jet technique was used to deposit subphthalocyanine derivative (chloro[tri-*tert*-butyl subphthalocyaninato]boron (TBSuPc) on Au (111) surface in an ultra-high vacuum (UHV) chamber. The deposited molecular overlayer was observed with UHV scanning tunneling microscopy (STM) at 77 K. The STM images showed that TBSuPc molecules formed a stripe pattern with regular spacing, indicating that they preferentially adsorbed along the herringbone structure of the Au (111) surface. This behavior was very similar to that of TBSuPc molecules deposited by thermal evaporation.

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## 1. Introduction

Molecular overlayer structures have been extensively studied with scanning tunneling microscopy (STM) under ultra-high vacuum (UHV) conditions because this form of observation provided highly resolved molecular images reflecting the structures and electronic properties [1–8]. UHV–STM observation of organic molecules has thus become indispensable for learning the molecular overlayer structure on a surface. In these previous studies, organic molecules were evaporated from a crucible by heating and were deposited on clean metal or on semiconductor surfaces in UHV chambers. This thermal evaporation was useful for making a molecular thin film with little contamination. However, it has been difficult to obtain good thin films from huge molecules and reactive molecules that cannot be evaporated by heating. This difficulty hampered highly resolved observation of these molecules by UHV–STM. To overcome the problem, some groups tried to deposit large molecules such as

carbon nanotubes, polymers, or DNA strands through a pulse-injection method, where a solution including the large molecule was sprayed into a vacuum chamber from a small syringe or a pulsed valve [10–15]. In these methods, both the target molecules and solvent piled up on a substrate because no purification process was applied during injection into the chamber.

To improve the quality of the deposited film, we have developed a new method that uses a spray-jet technique. In this method, the molecules dissolved in an organic solvent are made into a mist which is injected into a vacuum chamber through a pulsed valve. The mist is made into a molecular beam by two skimmers in vacuum chambers that are differentially pumped. The molecules are purified while they fly through the vacuum chambers. We have examined the quality of this molecular beam through time-of-flight mass spectroscopy (TOF-MASS) and obtained mass spectra representing the target molecules [16–18]. We were previously able to deposit a subphthalocyanine derivative using this method and successfully observed its image by STM [19].

Here, we report on the overlayer structure of the subphthalocyanine derivative deposited on a Au (111) surface by the spray-jet technique and discuss its quality in comparison with that deposited by thermal evaporation.

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## 2. Experiments

### 2.1. Spray-jet method

The deposition system using the spray-jet technique has been described in detail elsewhere [19]. The system consisted of four chambers which were differentially pumped with combinations of turbo molecular pumps (TMPs) and rotary pumps. These chambers had a pressure gradient from nearly  $1 \times 10^5$  Pa to  $10^{-7}$  Pa. A clean substrate was kept in the final-stage chamber which was pumped by a TMP and ion pump down to  $10^{-7}$  Pa. The mist including the target molecule was introduced from a small pulsed valve on the atmospheric pressure side.

This deposition system had many noise sources because of the many pumps, so it was completely separated from the STM measurement system. We transferred the sample from the deposition system to the STM chamber by using a small mobile chamber to avoid exposure of the sample to air. After the transfer, the sample was heated to approximately 470 K to remove any excess solvent from the sample.

### 2.2. Molecule and substrate

We used a subphthalocyanine derivative (Fig. 1): chloro[tri-*tert*-butyl subphthalocyaninato]boron (TBSuPc), which was also used in our previous studies [6,9]. The molecule was a derivative of subphthalocyanine (SubPc), which has a characteristic triangular and corn-shaped structure with a chloride atom on top and three diiminoindol rings around the boron core. The TBSuPc molecule has three additional *tert*-butyl groups bound to the periphery of the SubPc molecule (Fig. 1(B)). TBSuPc was dissolved in acetone for the spray-jet and made into a mist with a nebulizer.

The molecules were deposited onto a clean Au (111) surface at room temperature through the spray-jet technique. The Au (111) surface was prepared on a cleaved mica

surface and cleaned by cycles of Ar sputtering (1 kV) and annealing ( $\sim 800$  K). An STM image of the Au (111) surface showed the well-known reconstructed herringbone structure.

As the TBSuPc could also be evaporated by resistive heating, we deposited it onto the Au (111) surface by resistive heating to compare its overlayer with that deposited by the spray-jet technique. The deposition of the molecule by thermal evaporation is described elsewhere [6,9].

### 2.3. STM observation

All STM measurements were done with LTSTM (Omicron) in UHV at 77 K. The samples were cooled to 77 K on the STM stage after the deposition and appropriate annealing processes. The images were obtained in constant-current mode with an electrochemically etched W probe. The pressure in the STM chamber during the measurements was kept close to  $10^{-9}$  Pa.

## 3. Results and discussion

TBSuPc molecules deposited by the spray-jet technique are preferentially adsorbed along the herringbone structure of the Au (111) surface. An STM image (Fig. 2(A)) shows that bright spots corresponding to the *tert*-butyl groups of TBSuPc are clearly observed. TBSuPc molecules are assigned to three bright spots. Some molecules lose a *tert*-butyl group, which results in a pair of bright spots. The bright spots reflecting the positions of the molecules form a stripe pattern with regular spacing. The distance between the neighboring stripes (e.g.,  $d$  in Fig. 2(A)) is approximately 6.3 nm, which closely agrees with the periodicity of the herringbone structure. In addition, the stripes cross each other at an angle of  $60^\circ$  or  $120^\circ$ . These results support that the existing molecular regions are either fcc or hcp regions of the herringbone structure. A cross-section along the white

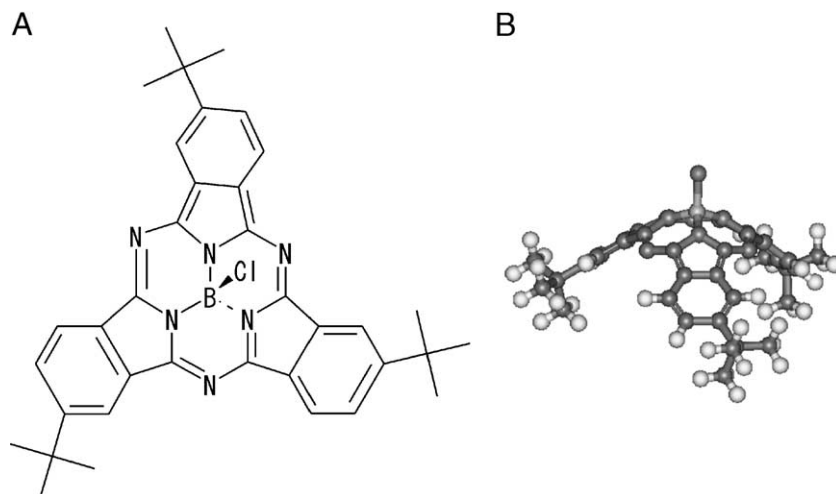


Fig. 1. Molecular structural formula (A) and molecular models of TBSuPc (B).

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