

# Adlayer Structures of Organic Molecules with Different Functional Groups on Cu(111) in Solution

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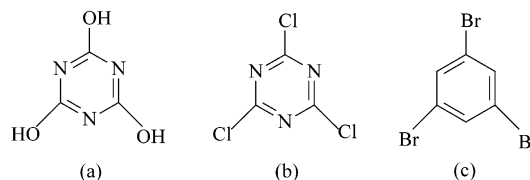
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In situ STM and cyclic voltammetry are employed to investigate the adsorption of organic molecules with different functional groups on Cu(111) in a 0.1 M HClO<sub>4</sub> solution. The molecules of cyanuric acid, cyanuric chloride, and 1,3,5-tribromo-benzene adsorb on the Cu(111) electrode surface and form well-defined adlayers with (3 × 3) structure in the double layer potential region. The STM image feature for each molecule is a set of three bright spots, suggesting a flat-lying orientation for the molecules. Structural models are proposed for the three adlayers. The results are compared with those obtained on aromatic and heterocyclic molecular adlayers.

## Introduction

The adsorption of organic molecules on electrode surfaces is of special issue in the studies such as catalysis, corrosion, self-assembly, nanoengineering, and surface coordination. In recent years, there has been an increasing interest in the investigation of organic molecular adsorption on well-defined single-crystal surfaces, and progress for this research has been made in diverse fields. As a result, it is known that the adsorption of organic molecules on a solid surface is dominated by various factors such as molecular structure and interactions between molecule and molecule and molecule and substrate. In an electrolyte solution, the nature of the liquid/solid interface plays an important role in molecular adsorption. The pioneering works were previously performed by using vibrational spectroscopic methods such as IR and Raman.<sup>1–3</sup> This research has supplied important structural information for molecular adsorption. The examples include the study of pyridine, pyrazine, and 2, 2-bipyridine on Au(111) and Ag(111) surfaces.<sup>1,4</sup> On the other hand, the well-established scanning tunneling microscopy (STM) is a powerful tool to reveal structural details of the organic molecular adlayer formed on single-crystal surfaces in real space at atomic and molecular scale.<sup>5</sup> The investigation was originally carried out in ultrahigh vacuum (UHV) and ambient.<sup>6–9</sup> The coordination of the organic molecule with the substrate lattice, adlayer structure, and phase transition was well studied. The structural models were successfully proposed from high-resolution STM images. In recent years, STM has been used in electrolyte solution to study the adsorption of organic molecules under potential control.<sup>10–15</sup> In the previous reports including the adsorption of benzene, naphthalene, and anthracene on Rh(111), Pt(111),<sup>13</sup> Cu(111),<sup>14</sup> Ag(111), Ag(100), and Ag(110),<sup>15</sup> it was found that different adlayer structures for the same molecule could be observed on different metal substrates, and the same adlayer structures for different molecules could be formed on the same metal substrate. In the previous study, we investigated the adsorption of aromatic molecules such as benzene, naphthalene, anthracene, pyrene, and perylene by using

**SCHEME 1: Chemical Structures of (a) Cyanuric Acid (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>3</sub>), (b) Cyanuric Chloride (C<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub>), and (c) 1, 3, 5-tribromo-benzene (C<sub>6</sub>H<sub>3</sub>Br<sub>3</sub>)**



electrochemical STM.<sup>12,14</sup> Recently, the adsorption of pyridine, pyrazine, and triazine on a Cu(111) electrode surface is also studied.<sup>16</sup> The three molecules have structural similarity characterized by  $\pi$  electrons and a nitrogen lone-pair orbital with an increase of nitrogen atoms from one to three in these heterocyclic molecules. STM imaging revealed the same adlayer structures for the three molecules, indicating that the intermolecule interaction seems less important than the molecule–substrate interaction in forming the adlayers, although the proposed coordination between adsorbate and Cu(111) substrate for the three molecules are different. To further explore the effect of molecular structure and various interactions on organic molecular adsorption, we are extending the previous research to the adsorption of cyanuric acid (C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>3</sub>), cyanuric chloride (C<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub>), and 1,3,5-tribromo-benzene (C<sub>6</sub>H<sub>3</sub>Br<sub>3</sub>). Scheme 1 shows the chemical structures of the three molecules. From the scheme, it can be seen that the three molecules have similar chemical structures but with different functional atoms of oxygen, chlorine, and bromine. The effort is made to know how the different functional groups affect the adlayer structures and to understand the STM image features of the three molecules on the Cu(111) surface. The bonding and coordination of the molecules with the Cu(111) lattice are deduced by high-resolution STM images. The results are compared with those on aromatic and heterocyclic molecules.

In the present paper, we report the results of the study of adsorption of cyanuric acid, cyanuric chloride, and 1,3,5-tribromo-benzene adsorbed on a well-defined Cu(111) in aqueous HClO<sub>4</sub> solution with electrochemical technique and STM. The three molecules are found to adsorb on Cu(111) and form two-dimensional well-ordered layers with (3 × 3) sym-

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metry, and the corresponding structural models of these adlayers are proposed.

### Experimental Section

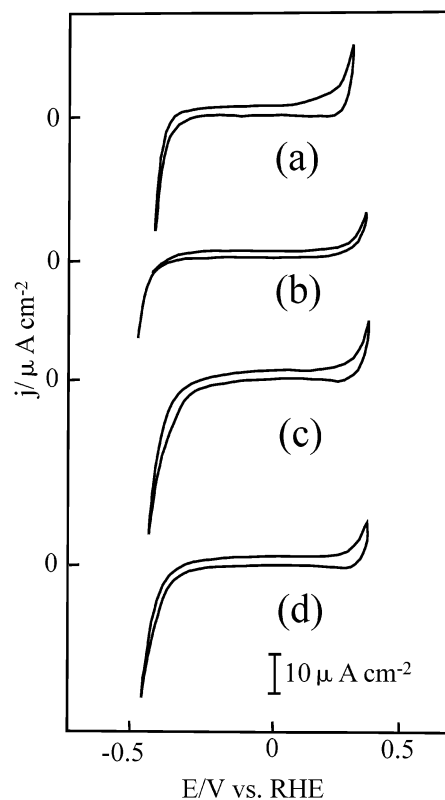
A bulk Cu(111) single-crystal disk with a diameter of 10 mm (from MaTeck) was used as a working electrode for both electrochemical measurement and in situ STM observation. A well-defined single-crystal surface was prepared as described in the previous papers.<sup>14</sup> After electropolishing, a droplet of water was left on the electrode surface to protect it from contamination. A solution of 0.1 M HClO<sub>4</sub> was prepared by diluting ultrapure HClO<sub>4</sub> (Cica-Merck, Kanto Chemicals) with ultrapure Millipore water. Reagent grade cyanuric acid, cyanuric chloride, and tribromo-benzene were from Aldrich Chemicals Co., Inc. All of the three molecules were used as received. The solutions containing these organic molecules were prepared at a specific concentration or at saturated concentration. The homemade electrochemical cell contained a reversible hydrogen electrode (RHE) in 0.1 M HClO<sub>4</sub> and a Pt counter electrode. All electrode potentials were reported with respect to the RHE. The in situ STM apparatus used was a Nanoscope E (Digital In. Strument Inc., Santa Barbara, CA). The tunneling tips were prepared by electrochemically etching a tungsten wire (0.25 mm in diameter) in 0.6 M KOH. The W tips were coated with clean nail polish to minimize the faradaic current. The details of the experiment were the same as described in the literature.<sup>14</sup> All of the STM images shown here were acquired in the constant-current mode to evaluate the corrugation heights of the Cu(111) substrate and the adsorbed molecules.

### Results and Discussion

**Cyclic Voltammetry.** Steady-state cyclic voltammograms of Cu(111) were obtained by using the so-called hanging meniscus method in the absence and presence of organic molecules in 0.1 M HClO<sub>4</sub>. The first scan of each CV was made in the negative direction from the open circuit potential (OCP, ca. 0.23 V). Figure 1a shows a CV of Cu(111) in the absence of organic molecules. A double layer region extends from -0.35 to +0.15 V. At potentials more negative than -0.35 V, hydrogen evolution occurs. At potentials more positive than 0.15 V, copper dissolution takes place with an abruptly increasing anodic current. The result is the same as that reported previously.<sup>14</sup>

The CVs obtained in the presence of cyanuric acid, cyanuric chloride, and tribromo-benzene are shown in parts b, c, and d of Figure 1. The overall shape of each CV is almost the same as that in Figure 1a obtained in the absence of organic molecules. However, the electric charge involved in the double-layer potential region becomes smaller because of the adsorption of the molecules. No obvious current peak corresponding to the phase transition is observed. The voltammograms shown in Figure 1b–d suggest that the organic molecules adsorb on Cu(111). We expect that these molecules can form a highly ordered adlayer on the Cu(111) surface in solution.

**In Situ STM. Cyanuric Acid Adlayer.** After the atomic resolution image of the Cu(111)-(1 × 1) structure was observed in 0.1 M HClO<sub>4</sub>, a small amount of cyanuric acid solution was directly injected into the electrochemical cell at -0.2 V and the average concentration of cyanuric acid was adjusted to ca. 1 mM. Completely different patterns appeared in STM images within 10 min after the injection of cyanuric acid molecules. Several well-defined domains with parallel molecular rows were observed, and the average domain size was more than 20 nm<sup>2</sup>. Figure 2a is a typical STM image of the cyanuric acid adlayer acquired at -0.2 V. The molecular rows cross each other at an

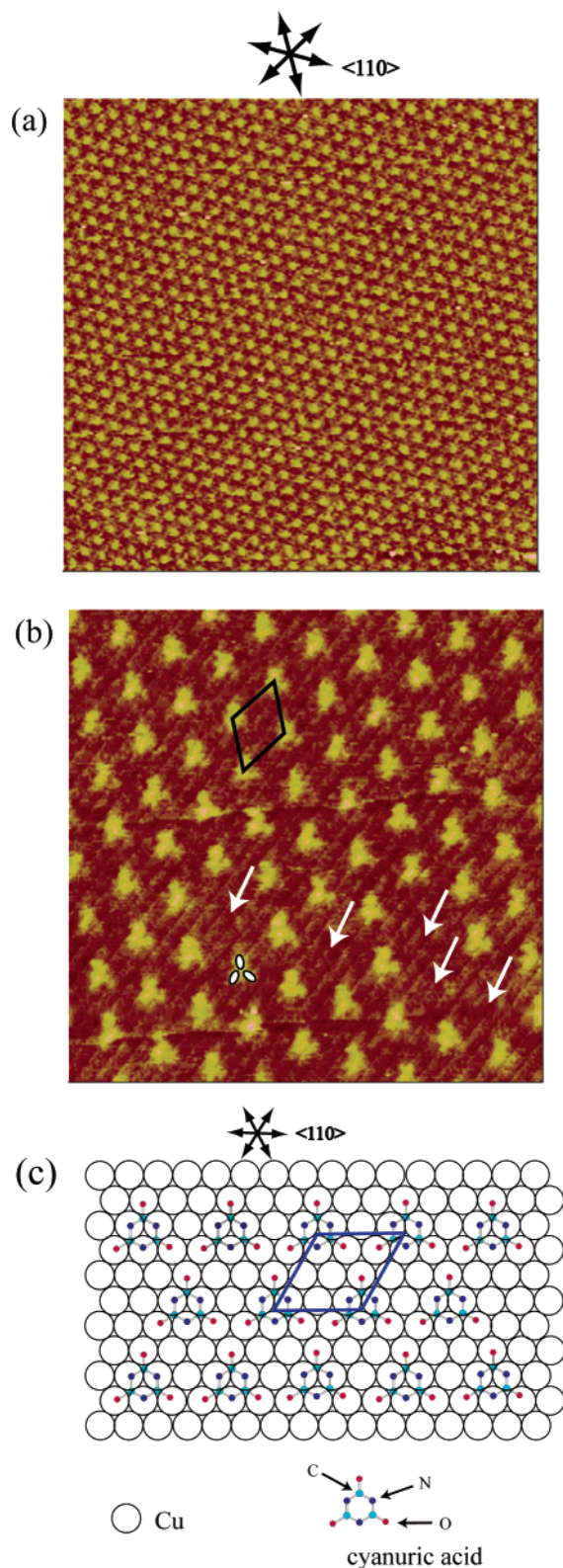


**Figure 1.** Cyclic voltammograms of Cu(111) in (a) 0.1 M HClO<sub>4</sub>, (b) 0.1 M HClO<sub>4</sub> + 1 mM cyanuric acid, (c) 0.1 M HClO<sub>4</sub> + 1 mM cyanuric chloride, and (d) 0.1 M HClO<sub>4</sub> + 1 mM tribromo-benzene. The potential scan rate was 50 mVs<sup>-1</sup>.

angle of either 60° or 120° within an experimental error ±2°. From a comparison with the crystal orientation of <110> determined by the underlying Cu(111)-(1 × 1) lattice as indicated by arrows, it can be seen that the molecular rows are aligned along the close-packed direction of the Cu(111) substrate. The cyanuric acid molecule exhibits a corrugation height of ca. 0.02–0.03 nm close to previous STM observation on aromatic molecules.<sup>14</sup>

STM images acquired with even higher resolution allowed us to determine the internal structure and orientation of each cyanuric acid molecule adsorbed on Cu(111). Figure 2b is a high-resolution STM image of the cyanuric acid adlayer. Several defects indicated with arrows correspond to the positions where the molecules are missing. Each molecule appears in a set of three bright spots outlined by three oval rings in the STM image of Figure 2b. From the molecular structure, one can assume that each molecule adsorbs on Cu(111) in a flat-lying orientation as the adsorption of benzene molecule on various substrates. The intermolecular distance along the molecular rows is measured to be ca. 0.798 nm, close to three times the lattice of Cu(111). On the basis of the intermolecular distance and orientation of molecular rows, a (3 × 3) structure for the adlayer is deduced. A unit cell is outlined in Figure 2b.

The adsorption model for aromatic molecules such as benzene has been well studied by STM and other techniques, resulting in important conclusions. In both UHV and electrolyte environments, the benzene molecule was clearly imaged with STM. The molecular appearance in STM images is completely different according to its adsorption site. For example, when the molecule adsorbs on the three-fold position with a flat-lying orientation, a set of three bright spots was seen in the STM image. In the present research, the STM image feature of the cyanuric acid molecule is almost the same as that of benzene.



**Figure 2.** (a) Large scale STM image of a Cu(111)-(3 × 3)-C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>3</sub> adlayer acquired at −0.2 V. Tunneling current was 8.00 nA. Scanning rate was 20.35 Hz (scanning area: 22.5 × 22.5 nm<sup>2</sup>). (b) High-resolution STM image of a Cu(111)-(3 × 3)-C<sub>3</sub>H<sub>3</sub>N<sub>3</sub>O<sub>3</sub> adlayer (scanning area: 8.0 × 8.0 nm<sup>2</sup>). Tunneling current was 10 nA. Scanning rate was 20.35 Hz. (c) Schematic model for cyanuric acid adlayer on the basis of STM observation and theoretical optimization.

Because the similarity of the two molecules in chemical structure, the observed result suggests the same coordination with the substrate lattice between the two molecules. A tentative

structural model is proposed in Figure 2c. In this model, the cyanuric acid molecules site at the three-fold positions with flat-lying orientation and form a (3 × 3) structure. In the study of the adsorption of the glycine molecule on Cu(110), both oxygen and nitrogen atoms were proposed to bind on top sites of the substrate.<sup>17,18</sup> There are three oxygen atoms and three nitrogen atoms in a cyanuric acid molecule. In the proposed model shown in Figure 2c, all nitrogen and oxygen atoms bind on the top sites of the Cu(111) lattice, consistent with the results of glycine on Cu(110).

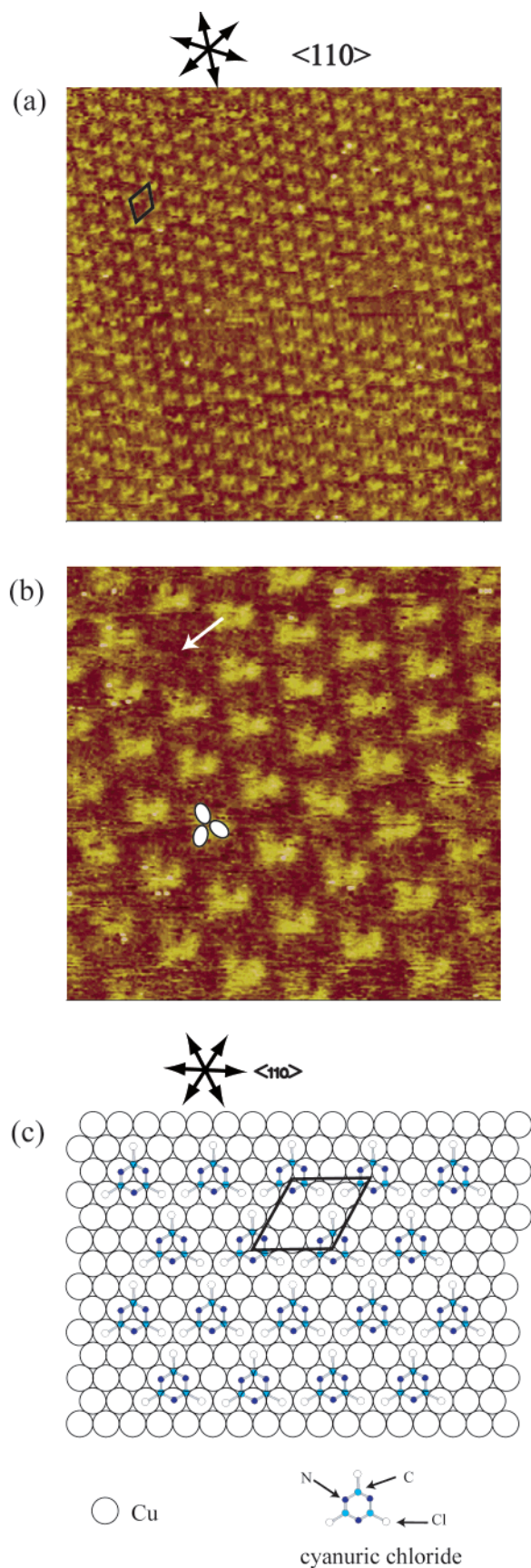
The cyanuric acid adlayer on Cu(111) was stable, and the ordered adlayer was consistently observed in the potential range from −0.35 to +0.15 V. At a potential more positive than 0.15 V, the ordered structure became unclear and produced noisy images. No clear peak corresponding to phase transition is observed in the CV of Figure 1, indicating that the charge-transfer processes may be not involved in the investigated potential region. The molecule desorption might take place with Cu surface dissolution that resulted in a noisy STM image.

**Cyanuric Chloride Adlayer.** The image features of the cyanuric chloride adlayer on Cu(111) surface are almost the same as those of the cyanuric acid adlayer. Figure 3a is a large scale STM image of the cyanuric chloride adlayer acquired at −0.2 V in 0.1 M HClO<sub>4</sub> + 1 mM cyanuric chloride. It can be seen in the image that cyanuric chloride molecules uniformly cover the Cu(111) surface. Although several molecular defects appear in Figure 3a, a well-ordered adlayer with characteristic molecular feature is extended over the wide atomically flat terrace. The molecular rows are found to be parallel to the <110> direction of the underlying Cu(111) lattice, and the molecules form a hexagonal pattern. The intermolecular distances are measured to be ca. 0.80 nm, nearly three times the lattice of Cu(111). Therefore, the adlayer of cyanuric chloride can be assigned to a (3 × 3) structure, and a unit cell is outlined in Figure 3a. In situ STM was also used to investigate the potentially dependent structures. The same molecular arrangement as that in Figure 3a was consistently observed in the potential range between −0.30 and +0.15 V when scanned the electrode potentials in both negative and positive directions in the increments of 10 mV.

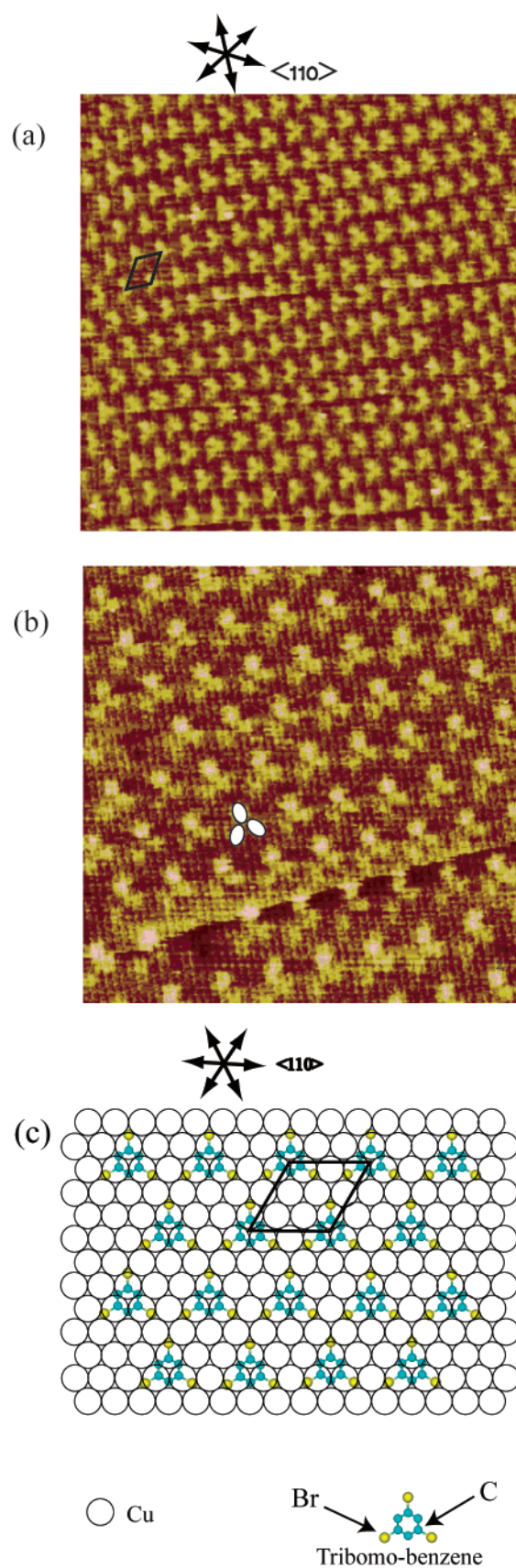
The higher resolution STM image in Figure 3b reveals the details of the packing arrangement and internal structure of the cyanuric chloride adlayer. An arrow indicates a single molecular defect in the image. The molecular feature with a set of three bright spots similar to that of benzene and cyanuric acid molecules can be clearly seen in Figure 3b. Despite the existence of thermal drift in the image, the three spots for a molecule are symmetrically arranged as illustrated by three oval rings. On the basis of previous results of aromatic molecular adsorption and the molecular structure, each cyanuric chloride molecule is assumed to bind to Cu(111) with a flat-lying orientation. A structural model for the (3 × 3)-C<sub>3</sub>N<sub>3</sub>Cl<sub>3</sub> structure is proposed in Figure 3c. In this model, the cyanuric chloride molecule is located on the three-fold hollow position and the molecular plane is parallel to Cu(111) substrate. Both nitrogen atoms and chlorine atoms in a molecule occupy the top-site positions. The molecules form a well-defined (3 × 3) structure

**Tribromo-benzene Adlayer.** The observation was continued on Cu(111) surface in a solution of 0.1 M HClO<sub>4</sub> + 1 mM tribromo-benzene. Tribromo-benzene molecules were found to adsorb on the Cu(111) surface, and a typical STM image of the tribromo-benzene adlayer acquired at −0.2 V is shown in Figure 4a. In this image, it can be seen that tribromo-benzene molecules form a long-range adlayer without the presence of





**Figure 3.** (a and b) High-resolution STM images of a  $\text{Cu}(111)$ -( $3 \times 3$ )- $\text{C}_3\text{N}_3\text{Cl}_3$  adlayer acquired at  $-0.2$  V. Tunneling current was 10 nA. Scanning rate was 20.35 Hz (Scanning area: (a)  $15.5 \times 15.5$  nm<sup>2</sup> and (b)  $5.5 \times 5.5$  nm<sup>2</sup>). (c) Schematic representation for the  $(3 \times 3)$  cyanuric acid adlayer.



**Figure 4.** (a) Large scale STM image of a  $\text{Cu}(111)$ -( $3 \times 3$ )- $\text{C}_6\text{H}_3\text{Br}_3$  adlayer acquired at  $-0.2$  V. Tunneling current was 3 nA. Scanning rate was 20.35 Hz (scanning area  $14 \times 14$  nm<sup>2</sup>). (b) High-resolution STM image of a  $\text{Cu}(111)$ -( $3 \times 3$ )- $\text{C}_6\text{H}_3\text{Br}_3$  adlayer. Tunneling current was 10 nA. Scanning rate was 24.41 Hz. (scanning area  $7.5 \times 7.5$  nm<sup>2</sup>) (c) A proposed model for the  $(3 \times 3)$ - $\text{C}_6\text{H}_3\text{Br}_3$  adlayer.

molecular defect in the scanning area. The molecular rows cross each other at an angle of 60° or 120° within experimental error. By a comparison with the underlying Cu(111) lattice, the molecular rows are found to be parallel to the close-packed Cu(111) substrate. The intermolecular distances along the  $\langle 110 \rangle$  directions are measured to be ca. 0.81 nm, as long as three times the lattice distance of Cu(111). The adlayer of tribromo-benzene can be assigned to a  $(3 \times 3)$  structure. A unit cell is outlined in Figure 4a.

The higher resolution STM image shown in Figure 4b has revealed the details of the tribromo-benzene adlayer. The features of molecule adlayers are almost the same as those in cyanuric acid and cyanuric chloride adlayers. Each molecule appears in a set of three bright spots that form a triangular configuration. The results implicate that the molecules take the same coordination with the Cu(111) lattice as cyanuric acid and cyanuric chloride molecules. A tentative structure model for the tribromo-benzene adlayer on Cu(111) is proposed in Figure 4c. In the model, tribromo-benzene molecules are located at the three-fold hollow sites with flat-lying orientation. The bromine atoms in a tribromo-benzene molecule are located on the top sites.

It is known that the molecular appearance in STM images is depended on the chemical structure of the molecule and the crystallography of the underlying substrate. The three molecules observed here have the same molecular structures despite the difference of functional atoms of oxygen, chlorine, and bromine. The functional atoms symmetrically distribute around the central benzene rings and form the similar molecular configurations. The structural similarity of these molecules implicates the similarity in their electronic states that could result in the same STM features. Therefore, the almost same image feature with three bright spots for a molecule can be seen in the three adlayers. From the image feature, the same coordination for three molecules to the Cu(111) lattice could be expected. According to the STM result of benzene on various fcc(111) substrate under UHV and solution,<sup>19,5</sup> the three molecules are proposed to bind on the three-fold position. On the other hand, the formation of the adlayer is dependent on the molecular structure and various interactions. The introduction of functional atoms such as Br and Cl will increase the interaction between molecule and substrate, resulting in an ordered and close-packed adlayer. In the experiment, although effort was made to explore whether the orientational change of the three molecules happened during potential scanning, only the flat-lying orientation in the adlayers with the  $(3 \times 3)$  structure was observed in the double layer region consistent with that of benzene on Cu(111), indicating a strong interaction between molecule and substrate. Considering the molecular size, the three molecules should form well-ordered hexagonal patterns in the same  $(3 \times 3)$  structure.

## Conclusion

In situ electrochemical STM has been employed to study the adsorption of cyanuric acid, cyanuric chloride, and tribromo-benzene molecules on a Cu(111) electrode surface in aqueous solution. High-resolution STM images reveal the packing arrangement and internal molecular structure. The three molecules form long-range ordered adlayers on Cu(111) in the same  $(3 \times 3)$  structure and show similar molecular appearance in STM images. The molecular feature for each molecule in STM images is a set of three bright spots, which indicates a special coordination of the molecules with the Cu(111) surface. Three structural models are proposed for the three adlayers. The same structure and coordination are attributed to the molecular structure and interactions between molecules as well as those of the molecule–substrate.

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