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# Ordered Adlayers of Organic Molecules on Sulfur-Modified Au(111): In Situ Scanning Tunneling Microscopy Study

Li-Jun Wan, Shuko Shundo, Junji Inukai, and Kingo Itaya\*

Department of Applied Chemistry, Graduate School of Engineering, Tohoku University,  
Aoba-yama 04, Sendai 980-8579, Japan

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In situ scanning tunneling microscopy (STM) was employed to study the structure of adlayers of crystal violet (CV) and water-soluble porphyrin formed on a sulfur-modified Au(111) electrode in perchloric acid solution. It was confirmed that a well-defined sulfur adlayer with  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure can be prepared on Au(111) under potential control. Highly ordered adlayers of the molecules were found to form on the sulfur-modified Au(111) surface. In situ STM revealed the characteristic shape, packing arrangement, and even internal structure of each molecule. It is demonstrated that the sulfur-modified Au(111) electrode can be used as a substrate suitable for the investigation of the adsorption of organic molecules in solution.

## Introduction

In situ scanning tunneling microscopy (STM) has made it possible directly to determine orientations, packing arrangements, and even internal structures of organic molecules at solid–liquid interfaces.<sup>1,2</sup> We have demonstrated that high-resolution in situ STM images allow determination of adlayer structures of simple aromatic molecules such as benzene, naphthalene, and anthracene on Pt(111), Rh(111), and Cu(111).<sup>3–5</sup> For example, benzene was found to form highly ordered adlayers on Rh(111)<sup>3</sup> and Cu(111),<sup>5</sup> whereas disordered structures were found on Pt(111) at positive potentials.<sup>3</sup> For anthracene, disordered structures were consistently observed on Pt(111) and Rh(111), but an ordered adlayer was formed on Cu(111). In general, these differences can be explained in terms of the difference in the nature of interaction between organic molecules and substrates. When the surface mobility of adsorbed molecules is low due to strong interactions between molecules and substrates, ordered adlayers are not expected to form at solid–liquid interfaces.

Relatively weak van der Waals type interaction of substrates with adsorbates seems to allow the formation of highly ordered adlayers. We previously reported that various organic molecules such as porphyrin and crystal violet (CV) form highly ordered adlayers on iodine-modified Au(111),<sup>6–8</sup> Ag(111),<sup>9</sup> and Pt(100)<sup>10</sup> electrodes. It was clearly demonstrated that the iodine adlayer plays a crucial role in the formation of the highly ordered molecular arrays.<sup>11</sup> Disordered adlayers of porphyrin were

found to form on the Au(111) surface in the absence of the iodine adlayer.<sup>8</sup>

In view of our previous results described above, we were interested in the sulfur adlayer formed on Au(111) electrode, the so-called sulfur-modified Au (S–Au) electrode. Voluminous reports describe the formation of alkanethiol monolayers mainly on Au(111), in which thiol headgroups are attached directly to Au atoms at the surface.<sup>12</sup> However, only a few reports are available on the adsorption of organic molecules on S–Au and S–Pt electrodes.<sup>13–16</sup> Clavilier et al.<sup>16</sup> reported irreversible adsorption processes of thionine and methylene blue on the S-modified electrodes, in which they proposed the formation of a chemical bond between the S adatom and the S heteroatom of these molecules.

No study has previously been carried out on the adsorption of simple organic molecules containing no S heteroatom onto a well-defined S–Au(111) in aqueous electrolyte solutions. Here we describe, for the first time, the effect of sulfur adatoms on the formation of ordered adlayers of CV and porphyrin, which have previously been well-characterized for the adsorption on iodine-modified electrodes as described above.<sup>6–11</sup>

## Experimental Section

Single-crystal beads of gold were prepared at the end of Au wires (99.99%) by the method described in a previous paper.<sup>8</sup> The (111) facet formed on the single-crystal bead in an octahedral configuration was used directly for STM experiments. Mechanically exposed (111) surfaces were prepared for electrochemical measurements. As a final treatment for exposing well-defined Au(111) surfaces, the single-crystal electrodes were annealed in an oxygen–hydrogen flame and then brought into contact with ultrapure water saturated with hydrogen. The electrode was

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transferred to an electrochemical cell with a droplet of ultrapure water to protect the surface from contamination. A well-defined sulfur adlayer was prepared in a solution of 0.05 M  $\text{HClO}_4$  containing 1 mM  $\text{Na}_2\text{S}$  under potential control.

In situ STM measurements were carried out with a Nanoscope-E (Digital Instruments) with a homemade electrochemical cell. All images were acquired in the constant-current mode by using electrochemically etched tungsten tips (0.25 mm in diameter) coated with transparent nail polish.

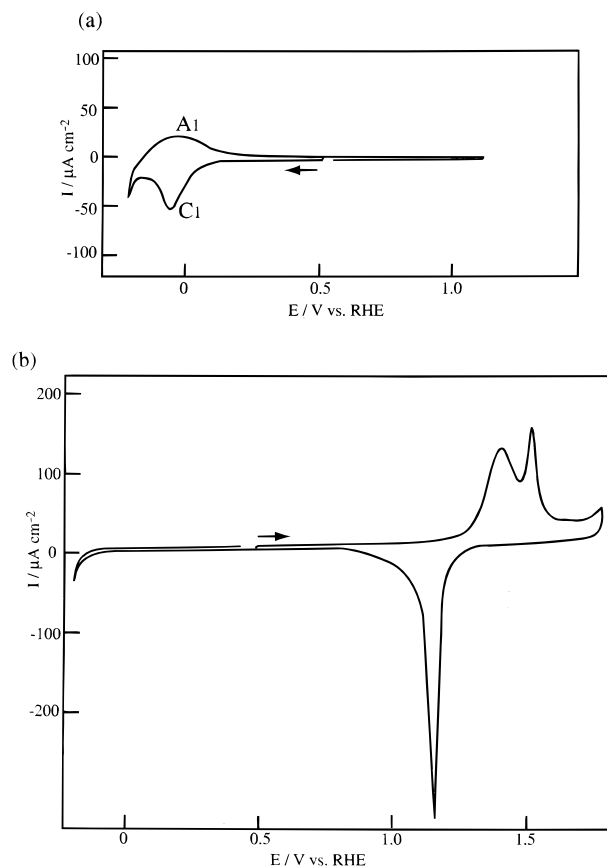
Electrolyte solutions were prepared with ultrapure  $\text{HClO}_4$  and  $\text{Na}_2\text{S}$  (Kanto Chemical Co., Japan), and ultrapure water (Millipore-Q). CV (chloride) and 5,10,15,20-tetrakis(*N*-methylpyridinium-4-yl)-21*H*,23*H*-porphine tetrakis(*p*-toluenesulfonate) (TMPyP) (from Doujin Co.) were used without further purification. All electrode potentials are reported with respect to a reversible hydrogen electrode (RHE) in 10 mM  $\text{HClO}_4$ .

## Results and Discussion

**Voltammetry of S-Modified Au(111).** Voltammetric behavior of sulfide ions has previously been investigated with polycrystalline Au electrodes.<sup>17,18</sup> To find appropriate conditions to obtain a well-ordered sulfur adlayer on Au(111), we carried out voltammetric studies in a solution of 0.05 M  $\text{HClO}_4$  containing 1 mM  $\text{Na}_2\text{S}$  with a flame-annealed Au(111) electrode. Quasireversible reduction and oxidation peaks were observed at ca.  $-0.1$  V vs RHE just before the hydrogen evolution reaction. Anodic current commenced to flow at ca. 0.15 V and reached a peak at ca. 0.5 V. The current–voltage characteristics observed on Au(111) are similar to those reported previously (see Figure 2 in ref 18). An in situ STM study carried out by Weaver's group reported a  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure at potentials more negative than the onset potential of the oxidation peak.<sup>19</sup> They also found dramatic alterations in STM images upon shifting the electrode potential in the positive direction, demonstrating that the formation of polysulfide adlayers took place at positive potentials.<sup>19</sup> Indeed, we reiterated their in situ STM study, and observed the same structural change from  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  to a well-ordered adlayer consisting of  $\text{S}_8$  rings at potentials more positive than 0.15 V.

On the basis of the result described above, we prepared a sulfur adlayer having the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure on Au(111) under potential control without the formation of  $\text{S}_8$  rings. The flame-annealed Au(111) electrode was immersed into 1 mM  $\text{Na}_2\text{S}$  + 0.05 M  $\text{HClO}_4$  at the specific potential of 0.1 V for a few minutes and then rinsed thoroughly with 0.05 M  $\text{HClO}_4$ . The electrode was then transferred into an electrochemical cell containing 0.01 M  $\text{HClO}_4$ . Figure 1a shows a voltammogram obtained on a S–Au(111) in the  $\text{HClO}_4$  solution. As described previously,<sup>18</sup> the cathodic and anodic peaks marked  $\text{C}_1$  and  $\text{A}_1$  appear even in the absence of sulfide ions in solution. These peaks have been attributed to a surface redox reaction involving two electrons between adsorbed  $(\text{SH})^-$  and  $\text{S}$ .<sup>17,18</sup> A cyclic coulometric curve showed ca.  $120\text{--}140 \mu\text{C}/\text{cm}^2$  to be the charge consumed for these peaks.

When the anodic potential scan was limited within the double-layer region and reversed at a potential below 1.1 V, the peaks,  $\text{C}_1$  and  $\text{A}_1$ , were essentially unchanged, indicating that no desorption of S adatoms occurred. However, the  $\text{C}_1$  and  $\text{A}_1$  peaks disappeared almost completely when the potential scan was extended to 1.75 V as shown in Figure 1b. The two oxidation peaks appearing at potentials more positive than 1.3 V are



**Figure 1.** Cyclic voltammograms of sulfur-modified Au(111) in 0.01 M  $\text{HClO}_4$ . The potential scan was initiated at 0.5 V. The electrode potentials were reversed at 1.1 V (a) and 1.75 V (b), respectively. The scan rate of the electrode potential was 50 mV/s. A reversible hydrogen electrode (RHE) in the 0.01 M  $\text{HClO}_4$  solution was used as a reference electrode.

thought to be due to the oxidation of the sulfur adlayer<sup>20</sup> and that of the Au(111) substrate.<sup>21</sup> The height of the peaks  $\text{C}_1$  and  $\text{A}_1$  also decreased gradually when the electrode potential was set at  $-0.15$  V, the onset potential of the hydrogen evolution reaction. This result is consistent with that of the previous work.<sup>18</sup>

**Structure of Sulfur Adlayer on Au(111).** Large-scale STM images of the S–Au(111) electrode consistently showed atomically flat terrace-step structures in the potential range between 0.2 and 1.1 V. Atomically flat terraces usually extended over 100 nm, indicating that the present procedure was appropriate to form the S-monolayer on Au(111). Figure 2 shows a typical high-resolution STM image acquired at 0.2 V in 0.01 M  $\text{HClO}_4$  in the absence of sulfide ions. A hexagonal structure with an interatomic distance of 0.5 nm ( $\sqrt{3}a_{\text{Au}}$ ) can be clearly seen in this image. The orientation of the atomic rows is along  $(121)$  ( $\sqrt{3}$  direction) of the underlying Au(111) lattice. The STM image indicates that the sulfur adlayer has a  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure, which is consistent with the previous study carried out in an acidic solution containing  $\text{Na}_2\text{S}$ .<sup>19</sup> However, it is important to note that the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure was exclusively observed in the potential range between 0.2 and 1.1 V. Other structures such as  $\text{S}_8$  rings were not observed even at the positive potential of 1.1 V, indicating that no structural change occurred in the sulfur adlayer in the  $\text{HClO}_4$  solution in

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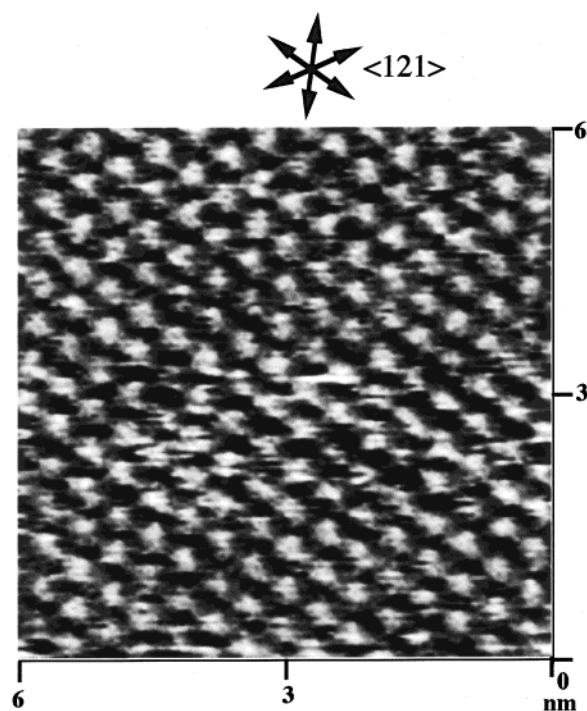
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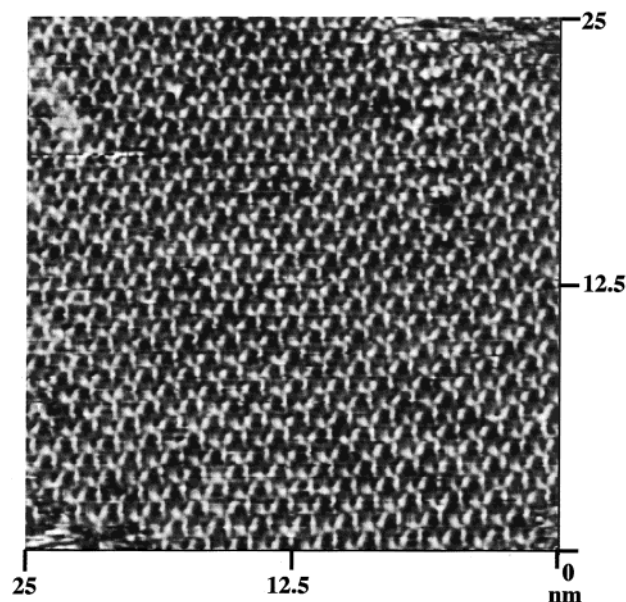
**Figure 2.** Unfiltered high-resolution STM image of S-Au(111) electrode acquired at 0.2 V in 0.01 M HClO<sub>4</sub>. The tip potential was held at 0.3 V. The tunneling current was 6 nA. Scan rate was 27.13 Hz. The arrows show the  $\sqrt{3}$  directions determined by the crystallographic orientation of the electrode.

the absence of sulfide ions. STM imaging was also conducted at potentials more negative than the peak C<sub>1</sub>, where "reduced" sulfur adatoms (SH<sup>-</sup>)<sup>18</sup> were expected to form as described above. However, no structural change was observed at the negative potential of -0.1 V. At potentials more negative than -0.1 V, the atomic image shown in Figure 2 became unclear, because of the reductive desorption of sulfur adatoms as described for Figure 1.

The number of atoms in an ideal Au(111)-(1 × 1) surface is  $1.39 \times 10^{15}/\text{cm}^2$ , which corresponds to  $148 \mu\text{C}/\text{cm}^2$ , assuming that the sulfur monolayer forms at the atomic ratio of S to Au equal to 1:3 with a transfer of two electrons per S atom. The observed values (ca.  $120\text{--}140 \mu\text{C}/\text{cm}^2$  described above) are nearly equal to the expected value. Note that a Coulombic charge of  $200 \mu\text{C}/\text{cm}^2$  was reported for the peaks C<sub>1</sub> and A<sub>1</sub> obtained with an electrochemically roughened Au electrode,<sup>18</sup> for which the roughness factor was not reported. The appearance of the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure in the STM image obtained at -0.1 V suggests that STM cannot distinguish between the adsorbed SH<sup>-</sup> and S. More detailed investigations are needed for further discussion of the peaks C<sub>1</sub> and A<sub>1</sub>.

**Structure of CV on S-Au(111).** After achieving atomic resolution as shown in Figure 2, an aqueous solution of CV was injected into the STM cell. The average concentration of CV was typically  $10^{-6}\text{--}10^{-5}$  M. Usually within the first 5–10 min after addition of CV, no significant changes were observed with only the sulfur adlayer being resolved. However, after 1 h the atomically flat terraces of the S-Au(111) surface were almost completely covered by a highly ordered adlayer of CV.

A typical STM image of an area of  $25 \times 25 \text{ nm}^2$  is shown in Figure 3. This image was acquired at 0.3 V, which is in the double-layer potential region. It is seen that the molecules form a highly ordered adlayer. The molecular array is extended over the wide atomically flat terrace of the sulfur-modified Au(111) substrate. The  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$



**Figure 3.** Typical STM image of crystal violet (CV) adlayer formed on S-Au(111) surface in 0.01 M HClO<sub>4</sub> containing  $10^{-6}$  M CV. The image was obtained at 0.3 V. The tip potential was 0.35 V. The tunneling current was 1 nA. Scan rate was 13.56 Hz.

sulfur adlayer is completely covered with CV molecules. It is clearly seen that each molecule has a distinctly characteristic, propeller-shaped feature, which is identical to that found previously for CV on the iodine-modified Au(111).<sup>7,11</sup> It is also clearly seen that all molecules in each molecular row are oriented in the same direction. Although the image shown in Figure 3 demonstrates that ordered domains are extended over a large area, the image includes distortion due to thermal drift.

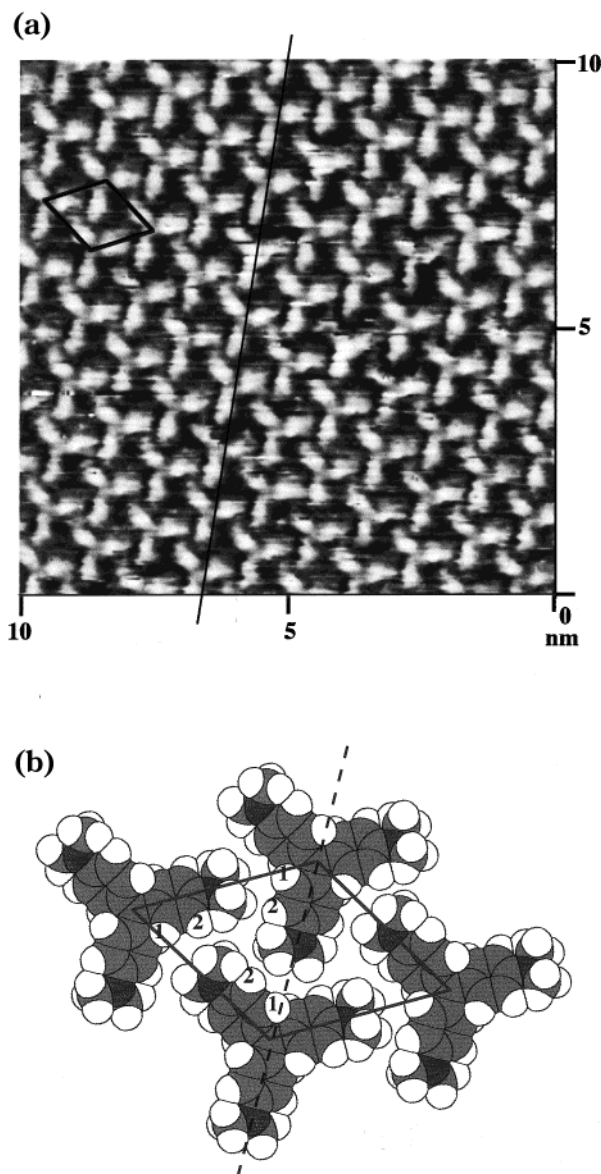
Further details of the adlayer are revealed in Figure 4a, which is an atomic-resolution STM image acquired specifically under conditions with minimal thermal drift in the *x* and *y* directions in order to determine the unit cell of the adlayer as accurately as possible. It can be seen that the molecular rows cross each other at an angle of either  $60^\circ$  or  $120^\circ$  with an experimental error of  $\pm 2^\circ$ , showing a 3-fold symmetry. It is also clearly seen that molecular planes of CV are parallel to the S-Au(111) surface. The image of each molecule consists of three bright elongated spots, which correspond to three benzene rings in the CV molecule. The three bright elongated spots form a propeller shape with 3-fold symmetry. A distorted unit cell has previously been reported for the CV adlayer formed on the I-Au(111),<sup>7</sup> which reflects the fact that the iodine adlayer has an incommensurate centered  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  phase.<sup>22–24</sup> The 3-fold symmetry observed for the CV adlayer on the S-Au(111) is expected to result from the fact that the sulfur adlayer forms a 3-fold symmetric  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure. It is also noteworthy that an additional spot was seen at the position of the central carbon atom of CV in the STM image reported previously.<sup>7</sup> The center spot could be attributed to incorporated anions such as chloride or iodide that might have existed in the solution.<sup>25</sup> However, no such spots are seen in the image taken in the pure HClO<sub>4</sub> solution as shown in Figure 4a. Because the CV molecule has a positive charge, the

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**Figure 4.** High-resolution STM image (a) and model structure (b) of CV adlayer formed on S-Au(111). The image was acquired in an area of  $10 \times 10 \text{ nm}^2$  at 0.3 V. The tip potential was 0.4 V. The tunneling current was 1.1 nA. Scan rate was 11.63 Hz.

repulsive interaction between CV molecules must be compensated by the perchlorate anions existing on the solution side of the interface. The absence of the center spot suggests that the perchlorate anion is not fixed at the center of each molecule and is mobile on the adlayer of CV.

The length of each bright elongated spot is measured to be  $\text{ca. } 0.7 \pm 0.05 \text{ nm}$ , which is close to the length of a benzene ring in the CV molecule. The intermolecular distance is measured to be  $\text{ca. } 1.2 \pm 0.05 \text{ nm}$ . On the basis of the molecular orientation and intermolecular distances, a unit cell for the CV adlayer is outlined in the STM image of Figure 4a.

A schematic depiction of the unit cell for the molecular arrangement is shown in Figure 4b with a space-filling model. The model is drawn based on the size of CV molecule and the intermolecular distance measured from the STM image shown in Figure 4a. The space-filling model of CV was drawn with the assumption that each *N,N*-dimethy-

laniline ring is tilted by  $30^\circ$  with respect to the surface plane of Au(111) due to the hindered rotation of benzene moieties.

It is also important to note in Figure 4a that the bright elongated spots located at the same relative position of the CV molecules are not exactly in the same orientation with respect to the line drawn across the centers of those CV molecules. This misalignment was initially thought to be due to a slight rotation of CV molecules with respect to the direction of molecular rows. However, it seems more reasonable to assume that the CV molecules are close-packed, and the axis drawn across the centers of benzene rings forms a straight line as shown by the dashed line in Figure 4b. This model assumes that the protruded parts result from the positions numbered 1 and 2 in the unit cell as shown in Figure 4b. These positions are higher in elevation than those on the opposite side of the benzene ring because of the nonplanar configuration of CV. Note that the relation between the CV and sulfur adlayer structures was not fully understood in the present work.

Nevertheless, it is concluded that S-Au(111) is an appropriate substrate for the investigation of the adsorption of organic molecules in solution. The result shown in Figures 3 and 4a strongly encouraged us to investigate the adlayer structure of much larger molecules such as TMPyP.

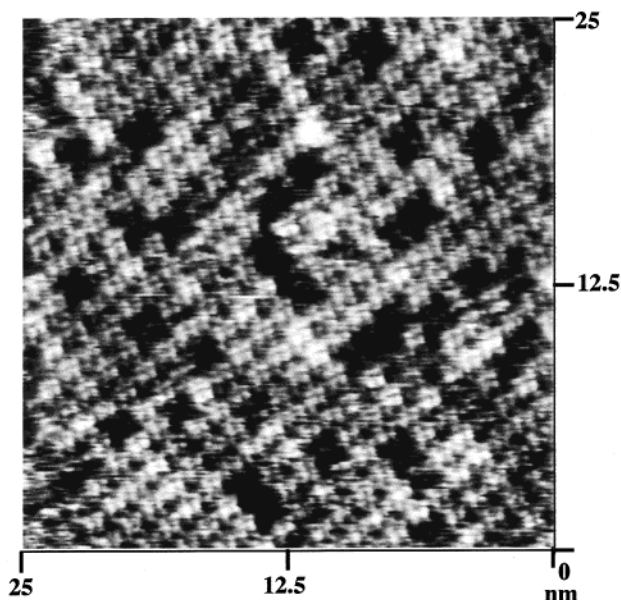
**Structure of TMPyP on S-Au(111).** It was shown in our previous paper<sup>8</sup> that reversible voltammetric peaks were observed for adsorbed TMPyP on the I-Au(111), which were attributed to the surface redox reaction of TMPyP molecules. In the present study, we found very similar peaks at 0.32 V in a 0.01 M  $\text{HClO}_4$  solution containing TMPyP, suggesting that TMPyP molecules are irreversibly adsorbed on S-Au(111), similarly to those adsorbed on I-Au(111).

The experimental procedure used was the same as that for CV described above. After observation of the S adlayer, a few drops of TMPyP solution was added to 0.01 M  $\text{HClO}_4$ . The average concentration was  $\text{ca. } 5 \times 10^{-7} \text{ M}$ . Approximately 5–10 min after the TMPyP solution was added, small ordered domains with a square shape were found over atomically flat terraces. The ordered domain increased in size with increasing immersion time.

Figure 5 shows an STM image acquired at 30 min in an area of  $25 \times 25 \text{ nm}^2$ . It can be seen that the S-Au(111) surface is almost covered by a highly ordered TMPyP adlayer. Although several defects of the molecular size are seen in the image, the surface was almost completely covered with flat-lying TMPyP molecules after 1 h. The surface mobility of the adsorbed TMPyP molecules seemed to be relatively slow compared with those on the I-Au(111)<sup>8</sup> and I-Ag(111) surfaces.<sup>9</sup> Molecular defects as seen in the image of Figure 5 were rarely observed in the previous work.<sup>8,9</sup>

Figure 6a shows a high-resolution STM image acquired after 1 h in a small area of an ordered domain, which was used to determine the packing arrangement and even the internal molecular structure. In this image each flat-lying TMPyP molecule can be recognized as a square with four additional bright spots. The feature observed in this image clearly corresponds to the chemical structure of the TMPyP molecule. The characteristic four bright spots seen for each molecule correspond to the pyridinium units of TMPyP. It is clear that all molecules show almost the same orientation. The unit cell is almost a square with each side measuring  $\text{ca. } 1.7 \pm 0.1 \text{ nm}$  as shown in Figure 6a. The angle between two crossing molecular rows is  $90^\circ \pm 2^\circ$ . The structural model for the TMPyP lattice is illustrated in Figure 6b. However, the relation between





**Figure 5.** STM image acquired in a relatively large area ( $25 \times 25 \text{ nm}^2$ ) of a TMPyP adlayer on S-Au(111) surface in 0.01 M  $\text{HClO}_4$  containing  $5 \times 10^{-7}$  M TMPyP. The image was obtained at 0.5 V. The tip potential was 0.65 V. Tunneling current was 1 nA. Scan rate was 16.28 Hz.

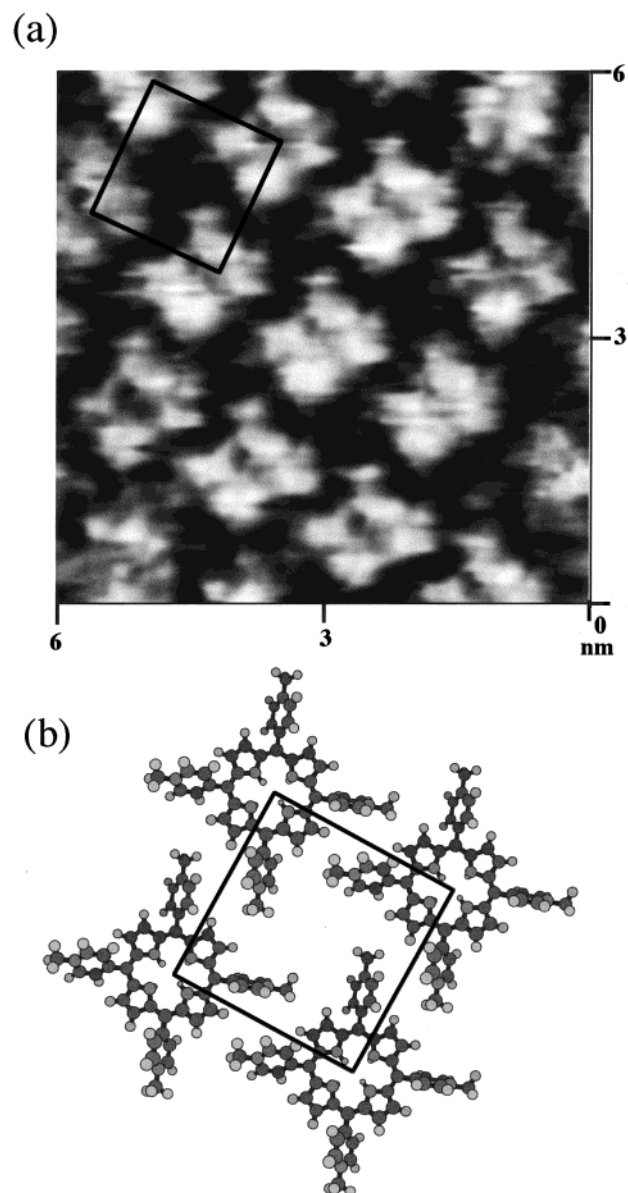
the TMPyP and sulfur adlayer could not be determined in this work.

We previously investigated the adlayer structures of TMPyP on I-Au(111),<sup>6-8</sup> I-Ag(111),<sup>9</sup> I-Pt(100),<sup>10</sup> and I-Pt(111)<sup>11</sup> surfaces and reported that the adlayer structure of TMPyP on I-Pt(100) is totally different from those observed on I-Au(111) or I-Ag(111).<sup>10</sup> This difference was explained by different atomic arrangements of iodine adatoms on different metals.<sup>10</sup> The adlayer structure of TMPyP on S-Au(111) is also totally different from that observed on I-Au(111). Several phases appeared on I-Au(111) before formation of the thermodynamically most stable phase.<sup>8</sup> The structure shown in Figure 6b was not found on I-Au(111) in the self-ordering process.<sup>8</sup> However, it is an interesting fact that a similar structure was found on I-Ag(111), even though ordered domains were rather narrow on that surface.<sup>9</sup> In general, many factors such as the interaction between the sulfur adatoms and the molecule and that between the molecules are involved in the formation of ordered molecular adlayers.

Nevertheless, the present study demonstrates that sulfur-modified electrodes can be used as the substrate for the formation of ordered adlayers of various organic molecules. The relatively weak van der Waals type interaction between CV and TMPyP molecules and the sulfur adlayer on the Au(111) substrate can reasonably be expected to result in the formation of an ordered molecular array. Other S-modified electrodes such as S-Pt(111) are of special interest to us.

### Conclusions

The sulfur adlayer with the  $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$  structure formed on Au(111) was found to be stable in pure  $\text{HClO}_4$  solutions over a wide potential range. Highly ordered CV and TMPyP adlayers formed on the sulfur-modified Au(111) electrode in solution. The sulfur adlayer on Au(111) played an important role in the formation of the highly



**Figure 6.** High-resolution STM image (a) and model structure (b) of a TMPyP molecular array. The image was acquired in an area of  $6 \times 6 \text{ nm}^2$  at 0.5 V. The tip potential was 0.55 V. Tunneling current was 0.5 nA. Scan rate was 20.35 Hz.

ordered adlayers. Similar effects have previously been found for iodine adlayers on various substrates. The molecular structures and the packing arrangements of both molecular adlayers were determined by high-resolution STM imaging. The CV and TMPyP adlayers have 3-fold and 4-fold symmetries, respectively. The results shown here strongly suggest that sulfur-modified electrodes can be used as an ideal substrate for studying the adsorption of various organic molecules.

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