

## LETTERS

### STM Study of Two-Dimensional Assemblies of Tricarboxylic Acid Derivatives on Au(111)

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Two-dimensional assemblies of tricarboxylic acid derivatives, 1,3,5-tris(carboxymethoxy)benzene (TCMB,  $C_6H_3(OCH_2COOH)_3$ ) and 1,3,5-tris(3-carboxypropoxy)benzene (TCPB,  $C_6H_3(OCH_2CH_2CH_2COOH)_3$ ), have been investigated on an Au(111) surface by electrochemical scanning tunneling microscopy in  $HClO_4$  solution. TCMB molecules are self-organized into a hexagonal network. Each molecule appears in a propeller shape, consistent with its chemical structure. The adlayer structure of TCPB molecules is significantly different from that of TCMB. Compared with their chemical structures, the difference can be attributed to the increase of the length of alkyl chains. In addition, the molecule–substrate interaction plays an important role in the formation of H-bonding in the two adlayers.

#### Introduction

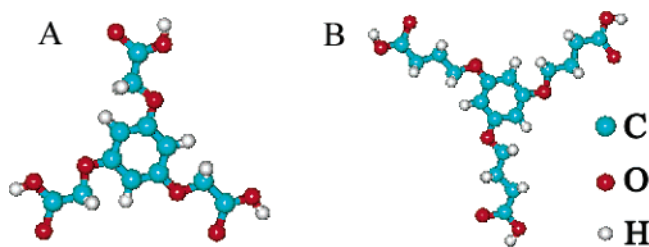
Two-dimensional (2D) assemblies of functionalized organic molecules on a solid surface have been intensively investigated. The self-assembly of the functional molecules provides a promising class of candidates for potential applications such as crystal engineering, heterogenic catalysis, molecular electronics devices, organic network templates, biosensors, and supramolecular structures.<sup>1–12</sup> Understanding the arrangement of the molecules in the monolayers is a key step in the construction of molecular devices.<sup>13</sup> Therefore, investigating the detailed structure of organic molecules on solid surface is of great value for clarifying their role in the applications. In general, the structure of organic monolayers on solid surfaces strongly depends on the size and symmetry of the molecule and the lattice of the underlying substrate.<sup>4</sup> Scanning tunneling microscopy (STM) technology provides a powerful tool for addressing the adlayer structure of organic molecules on a solid surface with atomic or submolecular resolution. Various adlayer structures

on different solid surfaces, such as Au and HOPG, are revealed with STM.<sup>4–8,12–18</sup>

1,3,5-Benzenetricarboxylic acid (TMA,  $C_6H_3(COOH)_3$ ) and its derivatives are important organic molecules with three-fold symmetry for supramolecular chemistry. The 2D network of TMA was previously investigated on a single-crystal graphite surface by STM under ultra-high-vacuum (UHV) conditions.<sup>4</sup> One of the two coexisting structures of TMA molecules shown in that paper is composed of a six-fold ring of TMA molecules with a perfect arrangement of intermolecular hydrogen bonds. This structure is consistent with the intralayer arrangement in the three-dimensional (3D) crystal.<sup>4</sup> It is interesting that the structure of a six-fold ring can act as a host network to accept single TMA guest molecules in its hexagonal vacancies, which embodies the concept of a host–guest system in supramolecular chemistry.<sup>4,16</sup> Dmitriev et al.<sup>6</sup> reported that TMA molecules form a hydrogen-bonded honeycomb structure on a Cu(100) surface at low temperature (<280 K) in UHV. This honeycomb structure was transformed to a striped array at room temperature (300 K). It is believed that the planar adsorption geometry of TMA molecules in honeycomb networks transforms to an upright geometry due to carboxylate formation in the striped structure. Kunitake et al. found that TMA also can form 2D

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**Figure 1.** Chemical structures of the two molecules: (A) TCMB and (B) TCPB.

networks on an Au(111) surface in  $\text{HClO}_4$  solution. At more positive potential, the 2D network was found to transform into close-packed arrays.<sup>17</sup> Recently, we found that a TMA adlayer was transferred in several different phases with potential shifting.<sup>18</sup> Furthermore, the adsorption of citric acid, which is also a tricarboxylic acid, has been investigated by Nichols et al. through the subtractively normalized interfacial Fourier transform infrared spectroscopy (SNIFTIRS) technique.<sup>19,20</sup> They found the three carboxylic acid groups of citric acid all deprotonated and coordinated with the Au(111) surface.

To extend the tricarboxylic acid study and understand the formation of molecular adlayer structure, a series of tricarboxylic acid derivatives of 1,3,5-trihydroxybenzene such as 1,3,5-tris(carboxymethoxy)benzene (TCMB,  $\text{C}_6\text{H}_3(\text{OCH}_2\text{COOH})_3$ ) and 1,3,5-tris(3-carboxypropoxy)benzene (TCPB,  $\text{C}_6\text{H}_3(\text{OCH}_2\text{CH}_2\text{CH}_2\text{COOH})_3$ ), were synthesized as described elsewhere.<sup>5,21</sup> The chemical structures of two molecules are shown in Figure 1, with a phenyl ring and three carboxyl groups like a propeller with three blades. The molecular adlayers were explored on a HOPG surface by STM.<sup>5</sup> As a result, it is seen that TCMB molecules form hexagonal networks by the formation of intermolecular H-bonds with carboxyl groups,<sup>5</sup> while TCPB molecules construct column-like networks.<sup>21</sup> To elucidate the substrate–molecule and molecule–molecule interactions on a metal surface, in the present study we investigate the adlayer structures of the two molecules on an Au(111) surface in  $\text{HClO}_4$  solution by electrochemical scanning tunneling microscopy (ECSTM). It is found that TCMB molecules form stable hexagonal networks. TCPB molecules organize themselves into close-packed arrays on an Au(111) surface. Two models for the monolayers are proposed on the basis of the obtained STM images.

## Experimental Section

TCMB and TCPB molecules were synthesized as described previously.<sup>5,21</sup> The solution containing the molecules (ca. 1 mM) was prepared with ethanol (Acros Organics, USA). The electrolyte solutions were prepared by diluting ultrapure  $\text{HClO}_4$  (Acros Organics, USA) with Milli-Q water.

The (111) facets on an Au single-crystal bead, prepared by melting an Au wire (99.999%), were used for STM experiments. The molecular adlayers were prepared by immersing the single-crystal Au bead into the ethanol solution containing sample molecules. After the formation of molecular adlayers, the Au bead was rinsed with Milli-Q water to remove the remnant sample molecules and then was mounted onto the STM electrochemical cell. The observation by STM was performed in  $\text{HClO}_4$  solution under potential control. The potentials used were positioned at the double-layer region.

The in situ STM apparatus was a Nanoscope E microscope (Digital Instruments, CA). The tunneling tips were prepared by electrochemically etching a tungsten wire (0.25 mm in diameter) in 0.6 M KOH. The ac voltage of 12–15 V was applied until

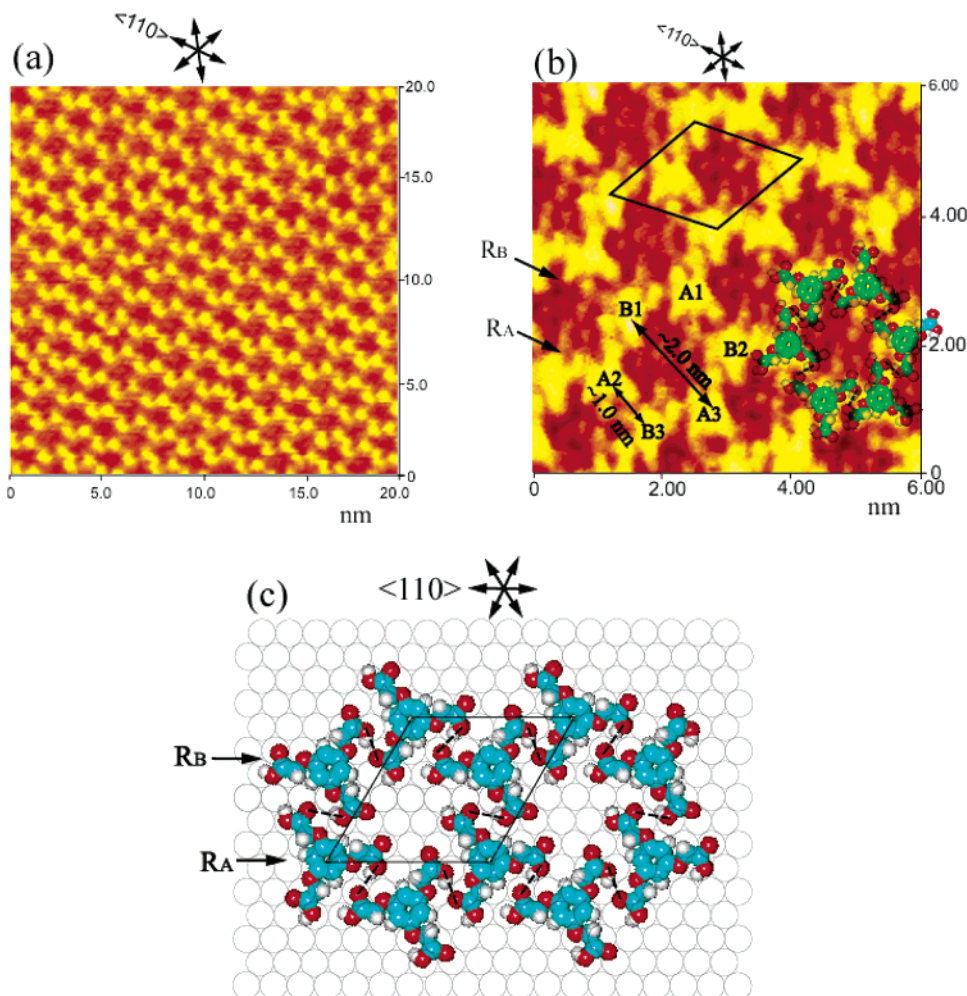
the etching process stopped. The W tips were then coated with clear nail polish to minimize the faradic current. The STM images shown here were obtained in the constant-current mode to evaluate corrugation heights of adsorbed molecules. A platinum wire and a reversible hydrogen electrode (RHE) were used as the counter electrode and the reference electrode. All potentials are reported with respect to the RHE.

## Results and Discussion

**TCMB Adlayer.** A well-ordered adlayer of TCMB molecules was observed on the wide, atomically flat terrace of reconstructed Au(111) surface. Figure 2a is a large-scale STM image acquired at 0.63 V. Each bright spot corresponds to one TCMB molecule. It can be clearly seen that TCMB molecules are self-organized into a 2D honeycomb networks showing six-fold rings with a hexagonal cavity in the center of each ring, similar to the structures of TMA and TCMB molecules on a graphite surface.<sup>4,5</sup> The adlayer of TCMB molecules on an Au(111) surface may also act as a host system to accept other guest molecules. More details of the orientation of individual TCMB molecules in the honeycomb networks are revealed with the higher resolution image. Figure 2b is a typical higher resolution STM image obtained at 0.52 V. The bright spots in the honeycomb networks in Figure 2a now appear as a propeller with three blades, consistent with the chemical structure of individual TCMB molecules. This feature suggests that TCMB molecules adopt a flat-lying geometry on Au(111).<sup>14,22</sup> Apparently, the three blades of each propeller should be attributed to the three carboxymethoxyl groups of TCMB molecules. It can be distinguished from Figure 2b that the three blades of individual molecules in each six-fold ring adopt two different orientations: three molecules labeled A1, A2, and A3 have the same orientation; the other three molecules labeled B1, B2, and B3 adsorb at another orientation. From a comparison with the orientation of the underlying Au(111) lattice, determined from the atomic STM image and indicated by arrows, it is found that molecular rows  $R_A$  (along A2 and A3) and  $R_B$  (along B1 and B2) are almost perfectly parallel to the close-packed direction of the underlying Au(111) surface. All the molecular rows of  $R_A$  (or  $R_B$ ) cross each other at an angle of either  $60^\circ$  or  $120^\circ$  within an experimental error of  $\pm 2^\circ$ . The distance between neighboring molecules with the same orientation is  $1.7 \pm 0.1$  nm, about 6 times the lattice parameter of Au(111). A  $6 \times 6$  structure for the molecular adlayer can be concluded on the basis of intermolecular distances and orientation of molecular rows. A unit cell is superimposed in Figure 2b. Each unit cell includes two molecules. The corresponding surface coverage is estimated to be 1/18.

A careful observation reveals the intermolecular arrangement in the two-dimensional assembly. The distance through the hexagonal cavities center of  $B_1$ – $A_3$  is  $2.0 \pm 0.1$  nm. The distance between two adjacent TCMB molecules in each six-fold ring of  $A_2$ – $B_3$  is  $1.0 \pm 0.1$  nm, as illustrated by arrows in Figure 2b. The distance is so small that the adjacent TCMB molecules cannot arrange with a head-to-head geometry but in an interdigitation geometry. The STM image in Figure 2b demonstrates the interdigitation of carboxymethoxyl groups of TCMB molecules.

A tentative model in Figure 2c is proposed for the hexagonal networks of TCMB molecules on an Au(111) surface. The phenyl rings of TCMB molecules are proposed to be located on the three-fold sites of the Au(111) substrate. The carboxymethoxyl groups are parallel to the  $\langle 110 \rangle$  direction due to the preferred adsorption geometry of alkyl chains.<sup>13</sup> The



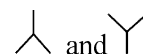
**Figure 2.** (a) Large-scale STM image of TCMB molecules on an Au(111) surface.  $E_{\text{Au}}$  (Au(111) substrate potential) = 0.63 V,  $I = 1$  nA. (b) Higher resolution STM image of TCMB molecules.  $E_{\text{Au}} = 0.52$  V,  $I = 900$  pA. (c) Tentative model for the monolayer of TCMB molecules.

hydrogen atom in carboxyl groups can revolve toward the oxygen atom of another carboxyl group to form H-bonding, as illustrated by the dashed lines in Figure 2c. This model is in good agreement with the results of STM images.

**TCPB Adlayer.** TCPB molecules also form large and uniform molecular arrays with domain sizes more than 100 nm. Figure 3a is a typical STM image of a TCPB monolayer on an Au(111) surface with a large scale of  $60 \times 60$  nm<sup>2</sup>. It is clear that the structure of the TCPB adlayer is different from that of the TCMB honeycomb networks. TCPB molecules construct close-packed arrays. Two domains in Figure 3a extend over an atomically flat Au(111) surface with an angle of  $120^\circ$ . Previous results have shown that the reconstructed line of Au(111) substrate is along the orientation of  $\langle 121 \rangle$  and that the  $\langle 110 \rangle$  orientation is perpendicular to the  $\langle 121 \rangle$ .<sup>13</sup> According to the results, the orientation of TCPB molecular rows can be easily decided.

The submolecular structure of an individual TCPB molecule can be clearly resolved from the higher resolution STM image shown in Figure 3b. Each bright spot in Figure 3a can be seen as one big bright spot surrounded by three small bright spots, just like a propeller with three blades. Because the  $\pi$ -conjugated systems can cause high contrast in STM images, the big bright spots are attributed to the phenyl rings of TCPB molecules with a flat-lying orientation on a Au(111) substrate. Naturally, the three small bright spots with the size of  $0.60 \pm 0.02$  nm to the phenyl core could be ascribed to three carboxypropoxyl groups connected with the phenyl ring of TCPB molecules. Three

carboxypropoxyl groups are oriented to the  $\langle 110 \rangle$  direction. Moreover, along the  $\langle 121 \rangle$  direction, it can be recognized that the TCPB molecules in neighboring molecular rows adopt antiparallel orientations,

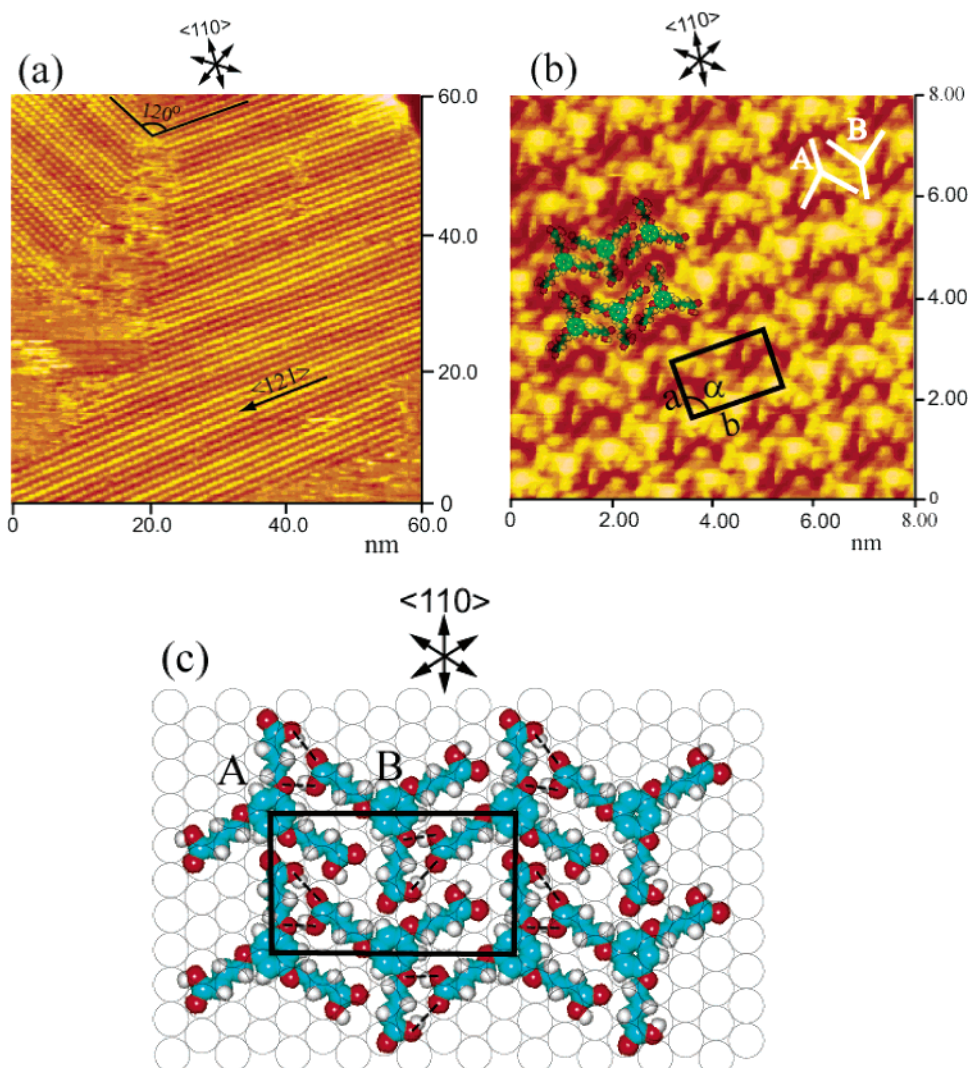


which are indicated with **A** and **B** in Figure 3b. Based on the above analysis, a rectangular unit cell is outlined in Figure 3b. The unit cell parameters are  $a = 1.15 \pm 0.02$  nm,  $b = 2.00 \pm 0.02$  nm, and  $\alpha = 90 \pm 2^\circ$ . A  $4 \times 4\sqrt{3}$  structure can be identified for the unit cell. Each unit cell includes two molecules.

A structural model for the monolayers of TCPB molecules is proposed in Figure 3c. The phenyl motifs of TCPB molecules are located on the three-fold sites of the Au(111) substrate. Three carboxypropoxyl groups are parallel to the  $\langle 110 \rangle$  direction. The formation of H-bonding is the same as that of the TCMB adlayer, as illustrated by dashed lines in Figure 3c. Note that H-bonding could also be formed between the carboxyl groups and the oxygen atom directly connected with the phenyl rings. This model is consistent with the STM image in Figure 3b.

It can be seen that TCMB and TCPB molecules form two different adlayers on an Au(111) surface. Compared with their chemical structures, it is clear that the structural difference should be attributed to the increasing length of the alkyl chains bonded to carboxyl groups. Similar structure variation has been reported for other organic molecules,<sup>23–25</sup> such as columnar





**Figure 3.** (a) Large-scale STM image of TCPB molecules.  $E_{\text{Au}} = 0.63$  V,  $I = 0.42$  nA. (b) Higher resolution STM image of TCPB molecules.  $E_{\text{Au}} = 0.67$  V,  $I = 1$  nA. (c) Tentative model for the monolayer of TCPB molecules.

liquid crystal molecules, a series of alkyl-substituted triphenylenes with disklike polyaromatic cores symmetrically surrounded by flexible alkyl chains.<sup>23,24</sup> Our previous studies show that long alkyl moieties can enhance the steric hindrance of molecules, hinder the molecules from freely revolving, and result in a highly (anti)parallel arrangement regardless of molecular symmetries.<sup>24</sup> In the present study, the hexagonal networks of TCMB have three-fold symmetry, in accordance with the chemical structure of TCMB molecules. However, TCPB forms a close-packed adlayer with antiparallel oriented arrangement regardless of the symmetry of the TCPB molecule itself.

In addition, the intermolecular H-bonding in the two adlayers on an Au(111) surface cannot be formed with the head-to-head geometry of intermolecular carboxyl groups, different from that of TCMB and TMA on a graphite surface.<sup>4,5</sup> This may be due to the strong molecule–substrate interactions. The structure of organic monolayers on solid surfaces mainly depends on the molecule–molecule and the molecule–substrate interactions. The molecule–molecule interactions dominate the structure of organic adlayers on a graphite surface since there is a weak interaction between molecules and the graphite substrate. Therefore, intermolecular H-bonding can be freely formed between carboxyl groups due to the high mobility of organic molecules on a graphite substrate. In contrast, there is a strong interaction between molecules and gold substrate,<sup>26</sup> resulting

in the low surface mobility of molecules and the formation of intermolecular H-bonding. The observed results in the present study demonstrate that the molecule–substrate interactions play an important role in the adlayer structures of TCMB and TCPB molecules. Certainly, it is clear that more techniques such as IR and theoretical calculation are needed to clarify the formation of intermolecular H-bonding. Furthermore, the variation of the two adlayers with electrode potentials should be investigated. The detailed study is in progress.

## Conclusion

Two tricarboxylic acids derivatives, TCMB and TCPB molecules, form self-assembled monolayers with different patterns on an Au(111) surface. TCMB molecules form honeycomb networks with hexagonal cavities on an Au(111) surface, which will be of great value for the host–guest system in crystal engineering and other technological applications. TCPB molecules are self-organized into close-packed patterns on a gold surface. The variation of the length of alkyl moieties in the two derivatives may be responsible for the structural difference between two adlayers. Hence, modulation of alkyl chain lengths should be an efficient way to control the 2D arrangement of functionalized molecules on metallic surfaces such as Au(111).

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