

# Formation and Structure of Ordered Pentachlorobenzenethiol Self-Assembled Monolayers on Au(111) Studied by Scanning Tunneling Microscopy

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Molecular-scale surface structures of self-assembled monolayers (SAMs) prepared by the adsorption of pentafluorobenzenethiols (PFBT) and pentachlorobenzenethiols (PCBT) on Au(111) were investigated by scanning tunneling microscopy (STM). High-resolution STM imaging revealed that PFBT SAMs on Au(111) have long-range ordered domains with a row structure at room temperature, whereas PCBT SAMs have small ordered domains, with disordered domains as the main phase. This may reflect the larger diffusion barriers of PCBT molecules on Au(111) surfaces compared to PFBT molecules during SAM formation. The structural transitions of PCBT SAMs from the mixed phase containing disordered and ordered domains to the uniform ordered domains were observed at 50 °C depending on immersion time. The ordered packing structure of PCBT SAMs is an incommensurate ( $\sqrt{3} \times \sqrt{10}$ )R45° structure, which differs from that of PFBT SAMs with a ( $2 \times 5\sqrt{13}$ )R30° structure. We found that a small modification in the chemical structures of aromatic rings using a halo-substituent strongly affects the self-assembly mechanism and packing structure of aromatic thiol SAMs on Au(111). Moreover, we demonstrated that highly ordered PCBT SAMs can be obtained at a solution temperature of 50 °C after immersion for 60 min.

**Keywords:** Self-Assembled Monolayers, Pentachlorobenzenethiol, Surface Structure, Scanning Tunneling Microscopy, X-Ray Photoelectron Spectroscopy.

## 1. INTRODUCTION

The spontaneous adsorption of organic thiols on metal surfaces creates self-assembled monolayers (SAMs) with high degrees of structural order and chemical stability. The physical and chemical properties of metal surfaces can be easily tuned by forming SAMs using  $\omega$ -functionalized thiols. Due to these advantages, organic thiols have been applied for a variety of technological applications in sensors, biointerfaces, nanopatterning, and molecular electronics.<sup>1–3</sup>

In particular, SAMs of aromatic thiols are often used for the fabrication of functional molecular electronic

devices.<sup>4,5</sup> SAMs formed by thiols containing strong electron-withdrawing groups offer a facile method to control the work functions of metal electrodes, resulting in enhancements of device performance.<sup>6–8</sup> The charge transport properties of devices are markedly influenced by the adsorption orientation, packing density, and structural order of SAMs.<sup>9</sup> Hence, it is essential to understand the surface structures and self-assembled phenomena of halo-substituted aromatic thiol SAMs for the development of high performance electronic devices.

High-resolution scanning tunneling microscopy (STM) observations show that the adsorption of aromatic thiols with *p*-bromo, chloro, and fluoro substituents on Cu(111)<sup>10,11</sup> yields different packing structures, which

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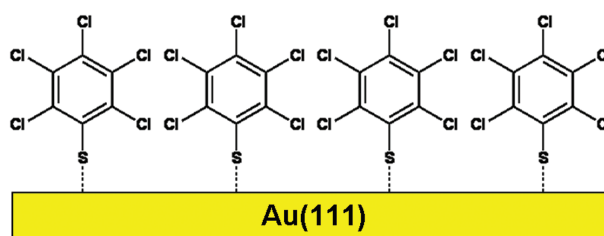
implies that the 2D structures of aromatic SAMs depends on the nature of the halogen substituent. For instance, *p*-chlorinated benzenethiol SAMs on Cu(111) showed totally different surface structures compared to *p*-fluorinated SAMs due to the different size and electronegativity of the substituent.<sup>10,11</sup> Pentafluorobenzenethiol (PFBT) is one of the most popular molecules for modifying metal electrodes because PFBT SAM-covered metal electrodes show a low contact resistance and high carrier mobility. STM studies revealed that PFBT SAMs on Cu(111) have a randomly oriented molecular phase,<sup>10,11</sup> whereas, at 75 °C they form domains with long-range order.<sup>12,13</sup> In addition, PFBT SAMs prepared by liquid-phase deposition have  $(2 \times 5\sqrt{13})R30^\circ$  structure,<sup>12</sup> but those prepared by vapor-phase deposition have  $c(2 \times \sqrt{3})$  structure.<sup>13</sup>

Unlike PFBT SAMs, there have been no studies on the formation and structures of pentachlorobenzenethiol (PCBT) on Au(111) surfaces. To extend the applications of halo-substituted aromatic thiol SAMs, it is essential to develop and characterize PCBT SAM systems. We also need to understand how the self-assembly mechanism and surface structure of the SAMs depend on the nature of the halo-substituent. In this study, the formation and structures of PCBT SAMs were examined as a function of immersion time using STM. We report herein the first molecular-scale STM results demonstrating the incommensurate  $(\sqrt{3} \times \sqrt{10})R45^\circ$  packing structures of PCBT SAMs.

## 2. EXPERIMENTAL DETAILS

### 2.1. Materials, Au(111) Substrates, SAMs Preparation

All PFBT and PCBT were purchased from Aldrich and used without further purification. Au(111) substrates were prepared by thermal evaporation of gold onto freshly cleaved mica sheets pre-baked at 330 °C for 2 h under a vacuum pressure of  $10^{-7}$ – $10^{-8}$  Torr for molecular-scale STM observation. Prior to SAM preparation, the substrates were annealed in a furnace at 420 °C for 2 h in order to obtain atomically flat large terraces.<sup>14</sup> To compare the formation and structure of PFBT and PCBT SAMs, these SAMs were prepared by immersing the Au(111) substrates in freshly prepared 1 mM ethanol solutions of the corresponding thiols at room temperature for 24 h. This is a standard procedure that represents typical experimental conditions for the preparation of SAMs with closely packed structure. In addition, well-ordered PCBT SAMs were obtained by dipping the Au(111) substrates in a freshly prepared 0.01 mM ethanol solution of PCBT at 50 °C as function of immersion time: for 20, 40, and 60 min. After the SAM samples were removed from the solution, they were carefully rinsed with copious amounts of pure ethanol, and dried in a stream of nitrogen gas. The schematic in Figure 1 shows the formation and structure of SAMs prepared by the adsorption of PCBT molecules on Au(111) surfaces.



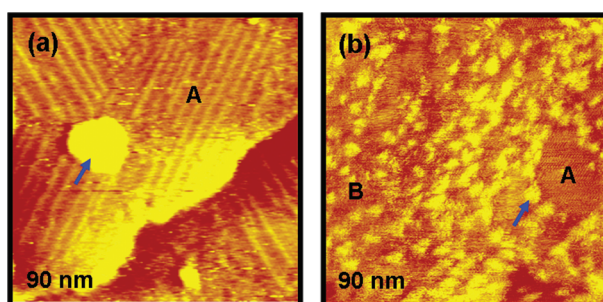
**Figure 1.** Schematic showing the formation of SAMs by the spontaneous adsorption of PCBT molecules on Au(111).

### 2.2. Scanning Tunneling Microscopy Measurements

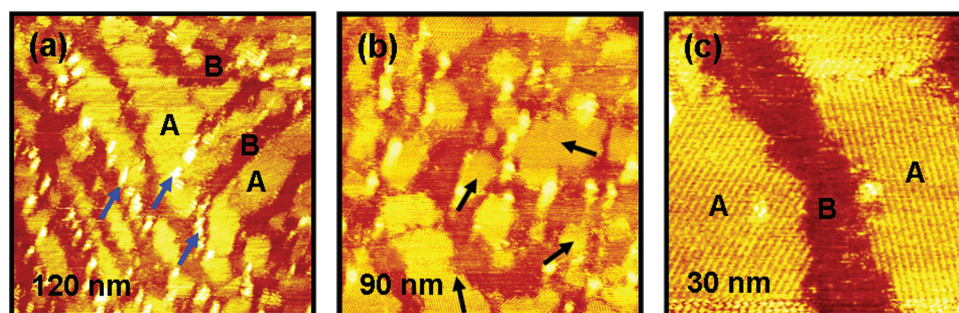
STM measurements were performed with a NanoScope E (Veeco, Santa Barbara, CA, USA) and a commercially available Pt/Ir tip. All STM images were acquired in ambient conditions using constant current mode at room temperature. A tunneling current ( $I_t$ ) of 0.30–0.60 nA and a bias voltage ( $V_b$ ) of 300–500 mV between the tip and the samples (sample positive) were used for STM imaging.

## 3. RESULTS AND DISCUSSION

The STM images in Figure 2 show the typical surface morphologies of PFBT and PCBT SAMs on Au(111) formed after 24 h immersion of the gold substrates in a 1 mM ethanol solution at room temperature. The surface structures of PFBT SAMs differ considerably from those of PCBT SAMs, as shown in Figure 2. The PFBT SAMs shown in Figure 2(a) were composed of large ordered domains with a row structure (region A) and gold adatom islands (blue arrow). We discussed the structural details of PFBT SAMs in a previous study.<sup>12</sup> The bright domains protruding from the surface with heights of approximately 2.3 Å are identified as gold adatom islands, which have previously been observed for SAMs of aromatic thiols with phenyl groups directly attached to the sulfur atom.<sup>12,13,15,16</sup> These islands may be kinetically trapped due to the low mobility of SAM-covered gold adatoms emerging from the chemisorption of aromatic thiol molecules on Au(111) surfaces.<sup>16</sup> Contrary to PFBT SAMs, PCBT SAMs had ordered (Region A) and



**Figure 2.** STM images showing the structural differences between (a) PFBT and (b) PCBT SAMs on Au(111) formed after 24 h immersion in a 1 mM ethanol solution of each compound at room temperature ( $I_t$ : 300 pA,  $V_b$ : 500 mV, and scan rate: 5 Hz).



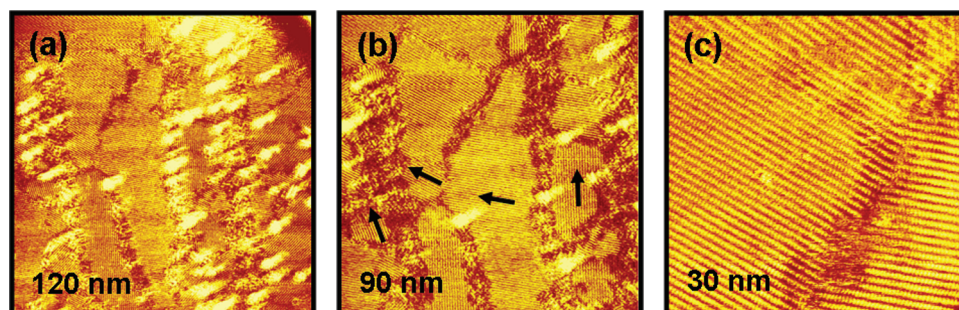
**Figure 3.** STM images showing the surface structures of PCBT SAMs on Au(111) formed after 20 min immersion in a 0.01 mM ethanol solution at 50 °C ( $I_s$ : 350 pA,  $V_b$ : 450 mV, and scan rate: 7 Hz).

disordered (Region B) domains and many adatom islands (Fig. 2(b)). The sizes of ordered domains and adatom islands were much smaller for PCBT SAMs compared to PFBT SAMs, which implies that PCBT molecules have a larger diffusion barrier than PFBT molecules. The molecular size of PCBT with pentachlorinated atoms is actually larger than that of PFBT with pentafluorinated atoms, so PCBT molecules can induce strong interactions with gold substrates in the initial SAM growth stage because the molecular backbones (phenyl groups) are lying flat on the surface at this stage. This is supported by the fact that individual *p*-fluorinated benzenethiol on Cu(111) at 15 K in a lying-down molecular orientation is smaller than *p*-chlorinated benzenethiol, as revealed by molecular-scale STM observations.<sup>1</sup>

We prepared PCBT SAM samples on Au(111) in a slightly diluted solution at a high temperature on Au(111) to increase the diffusion barriers of PCBT molecules during self-assembly and reduce molecular aggregation. Figure 3 shows the surface structures of PCBT SAMs on Au(111) formed in a 0.01 mM ethanol solution at 50 °C for 20 min. PCBT SAMs in Figure 3(a) were composed of ordered (region A) and disordered (region B) domains and gold adatom islands (blue arrows). We found that the structural order of PCBT SAMs at 50 °C was enhanced compared to that of the SAMs at room temperature (Fig. 2(b)). The ordered domains were mainly surrounded by disordered phases and gold adatom islands, and had row structure with inter-row spacing of  $9.0 \pm 0.2$  Å (Fig. 5). On the other hand, we did not observe any structural order

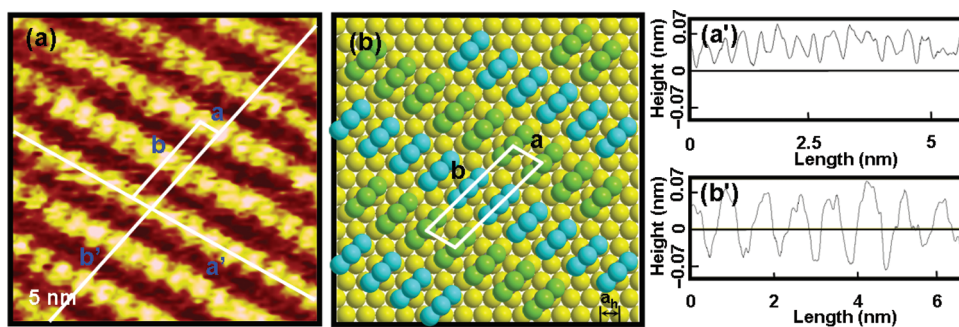
in region B, which was identified as a liquid-like disordered phase due to low surface coverage. Region B did not include the vacancy islands (VIs) that have been observed for conventional alkanethiol SAMs,<sup>1, 14, 16, 17</sup> because the height difference between regions A and B was measured to be about 1 Å, which differs from the monatomic height of 2.5 Å. On the other hand, alkanethiol SAMs usually have a commensurate  $(\sqrt{3} \times \sqrt{3})R30^\circ$  or  $c(4 \times 2)$  structure with three domain orientations. The angles between each domain were measured 60° or 120°, suggesting that the growth of alkanethiol SAMs is strongly affected by three-fold Au(111) symmetry. This indicates that the formation of alkanethiol SAMs is mainly driven by strong interactions between the sulfur atoms and gold substrates. However, PCBT SAMs have four different domain orientations with various domain angles, including 18°, 30°, 50°, 58°, and 78°. Based on the domain formation, we suggest that PCBT SAMs tend to have incommensurate packing structure and that the main driving force for the formation of SAMs results from lateral interactions between pentachlorinated phenyl groups. A similar incommensurate structure was observed for arenethiol SAMs.<sup>18</sup>

To enhance the structural order of PCBT SAMs on Au(111), SAM samples were prepared after a longer immersion for 40 min at 50 °C. STM images in Figure 4 clearly show the structural changes of PCBT SAMs on Au(111). The disordered regions (A) were significantly decreased after 40 min immersion, resulting in the formation of larger ordered regions (B), as shown in Figure 4(a). We also found that the gold adatom islands



**Figure 4.** STM images showing the surface structures of PCBT SAMs on Au(111) formed after 40 min immersion in a 0.01 mM ethanol solution at 50 °C ( $I_s$ : 350 pA,  $V_b$ : 450 mV, and scan rate: 7 Hz).





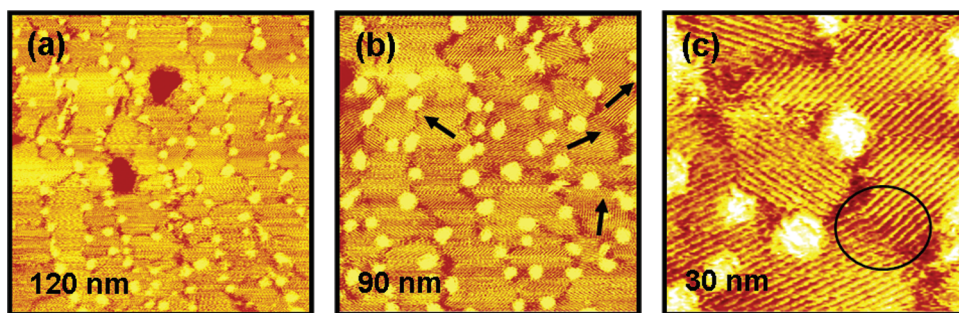
**Figure 5.** (a) STM image (5 nm  $\times$  5 nm) and (b) proposed structural model of PCBT SAMs formed after 40 min immersion in a 0.01 mM ethanol solution at 50  $^{\circ}$ C ( $I_t$ : 400 pA,  $V_b$ : 400 mV, and scan rate: 8 Hz).

were mainly located around ordered domain boundaries. Therefore, we hypothesize that the growth of ordered domains markedly affected the movement and distribution of the gold adatom islands on Au(111) surfaces. This kind of structural behavior may energetically be much more favorable than when the islands exist inside ordered domains, because the lateral interactions between aromatic backbones may be optimized when uniform ordered domains are formed. The STM image in Figure 4(b) shows four different domain orientations with various domain angles, including 16 $^{\circ}$ , 45 $^{\circ}$ , 62 $^{\circ}$ , 64 $^{\circ}$ , and 80 $^{\circ}$ , which means that PCBT SAMs formed after 40 min immersion have incommensurate structure, as do SAM samples formed after 20 min immersion (Fig. 3(b)). The high-resolution STM image shown in Figure 4(c) shows ordered domains with row structure and domain boundaries.

The STM image (5 nm  $\times$  5 nm) shown in Figure 5(a) clearly shows highly ordered packing structure of PCBT SAMs formed after immersion for 40 min at 50  $^{\circ}$ C at a molecular level of resolution. The line profiles taken along lines (a') and (b') on the STM image shown in Figure 5 illustrates the periodicities in the packing structure of PCBT SAMs (Figs. 5(a') and (b')). Based on these high-resolution STM observations, we draw the lattice constants of the oblique unit cell that contained two molecules:  $a = 4.9 \pm 0.2 \text{ \AA} = \sqrt{3}a_h$ ,  $b = 9.0 \pm 0.2 \text{ \AA} = \sqrt{10}a_h$ , and  $\alpha = 45^{\circ}$ , where  $a_h = 2.89 \text{ \AA}$  corresponds to the interatomic distance of the

Au(111) lattice. Figure 5(b) shows a schematic structural model of PCBT SAMs on Au(111). The molecular packing structures of PCBT SAMs can be described as incommensurate ( $\sqrt{3} \times \sqrt{10}$ ) $R45^{\circ}$  adlayer structures, which differs markedly from those of simple benzenethiol SAMs<sup>15,17</sup> or PFBT SAMs.<sup>12,15</sup> The STM study revealed that PCBT SAMs have ( $\sqrt{3} \times \sqrt{10}$ ) $R45^{\circ}$  adlayer structure, whereas PFBT SAMs have ( $2 \times 5\sqrt{13}$ ) $R30^{\circ}$  structure. Following this adsorption model, we also hypothesized that all sulfur atoms occupied the bridge sites of the Au(111) surfaces. Thus, the self-assembled mechanisms and packing structures of aromatic thiol SAMs are significantly influenced by small modifications in the chemical structures of aromatic rings using halo-substituents, which alter sulfur atom-gold substrate interactions and molecule-molecule interactions.

As confirmed by the STM images shown in Figure 4, an immersion time of 40 min is not sufficient to form fully ordered PCBT SAMs. After a longer immersion time of 60 min, the surface structures of PCBT SAMs were dramatically changed compared to those formed after immersion for 20 min or 40 min, as shown in Figure 6. The disordered phases largely disappeared, and were replaced by fully covered ordered phases (Figs. 6(a) and (b)). Domain boundaries were clearly present, as in alkanethiol SAMs.<sup>1,19,20</sup> Most of the round gold adatom islands were located around domain boundaries. This observation supports the hypothesis that the movement and distribution of



**Figure 6.** STM images showing the surface structure of PCBT SAMs on Au(111) formed after 60 min immersion in a 0.01 mM ethanol at 50  $^{\circ}$ C ( $I_t$ : 350 pA,  $V_b$ : 450 mV, and scan rate: 7 Hz).



the gold adatom islands on Au(111) surfaces were limited by the growth of ordered domains. The STM image shown in Figure 6(b) demonstrates four domain orientations with various domain angles for PCBT SAMs that appeared after immersion for 20 min or 40 min. Figure 6(c) shows ordered domains with row structure, which is the same as those observed for samples formed after a shorter immersion. Interestingly, we observed that there are no domain boundaries between the two domains when the domain angle is about  $16^\circ$ , as indicated by the circle. We observed that well-ordered PCBT SAMs on Au(111) have incommensurate  $(\sqrt{3} \times \sqrt{10})R45^\circ$  structure regardless of immersion time.

#### 4. CONCLUSION

High-resolution STM observation indicated that PFBT SAMs formed on Au(111) at room temperature had long-range ordered domains with row structure, whereas PCBT SAMs had small ordered domains and disordered domains as the main phase. Thus, PCBT molecules have a larger diffusion barrier on Au(111) surfaces than PFBT molecules during SAM formation. We also observed structural changes of PCBT SAMs, from the mixed phase containing disordered and ordered domains to the uniform ordered domains depending the immersion time at  $50^\circ\text{C}$ . The ordered packing structures of PCBT SAMs can be identified as  $(\sqrt{3} \times \sqrt{10})R45^\circ$  structures, which are different from those of PFBT SAMs, which have  $(2 \times 5\sqrt{13})R30^\circ$  structure. Based on the domain formation of PCBT SAMs with multiple domain orientations, we hypothesize that PCBT SAMs prefer incommensurate packing structure, primarily due to lateral interactions between the pentachlorinated phenyl groups, rather than sulfur atom-Au(111) substrate interactions. In addition, we found that most of the gold adatom islands were located near ordered domain boundaries. Hence, we suggest that the growth of ordered domains affects the movement and distribution of gold adatom islands on Au(111) surfaces. In this study, we demonstrated that the self-assembly mechanisms and packing structures of aromatic thiol SAMs on Au(111) are significantly influenced by small modifications in the chemical structures of aromatic

rings using halo-substituents, which alter sulfur atom-gold substrate interactions and molecule-molecule interactions.

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