

## Comparative Study of Tetrahydrothiophene and Thiophene Self-Assembled Monolayers on Au(111): Structure and Molecular Orientation

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Surface structure and molecular orientation of self-assembled monolayers (SAMs) formed by the spontaneous adsorption of tetrahydrothiophene (THT) and thiophene (TP) on Au(111) were investigated by means of scanning tunneling microscopy (STM) and carbon K-edge near edge X-ray absorption fine structure (NEXAFS) spectroscopy. STM imaging revealed that THT SAMs have a commensurate ( $3 \times 2\sqrt{3}$ ) structure containing structural defects in ordered domains, whereas TP SAMs are composed of randomly adsorbed domains and paired molecular row domains that can be described as an incommensurate packing structure. The NEXAFS spectroscopy study showed that the average tilt angle of the aliphatic THT ring and  $\pi$ -conjugated TP ring in the SAMs were calculated to be about  $30^\circ$  and  $40^\circ$ , respectively, from the surface normal. It was also observed that the  $\pi^*$  transition peak in the NEXAFS spectrum of the TP SAMs is very weak, suggesting that a strong interaction between  $\pi$ -electrons and the Au surface arises during the self-assembly of TP molecules. In this study, we have clearly demonstrated that the surface structure and adsorption orientation of organic SAMs on Au(111) are strongly influenced by whether the cyclic ring is saturated or unsaturated.

**Key Words:** Near-edge X-ray absorption fine structure, Self-assembled monolayer, Thiophene, Tetrahydrothiophene, Molecular orientation

### Introduction

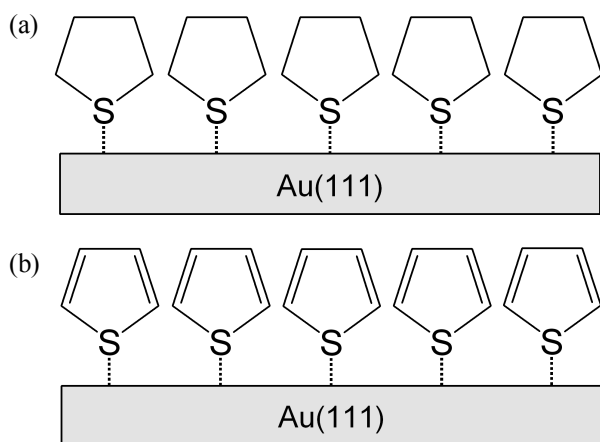
Self-assembled monolayers (SAMs) of organosulfur compounds adsorbed on metal surfaces have attracted a considerable amount of attention because of the uniformity and easy preparation of well-ordered monolayer films.<sup>1-3</sup> It is generally believed that well-ordered SAMs can be utilized for the fabrication of organic molecular devices or the modification of the surface properties of a metal electrode. Adsorption states, molecular structures, growth processes, and electronic structures of alkanethiol (AT) SAMs on gold have been extensively investigated using various surface characterization techniques.<sup>4-9</sup> The introduction of functional groups to the tail of the sulfur headgroup may be useful in future applications to organic electronic devices. For example, the use of a  $\pi$ -conjugated tail group is very simple and convenient method for obtaining functionality in organic electronics. The surface structure and adsorption states of  $\pi$ -conjugated organic molecules such as tolanes, thiophene (TP), and oligothiophenes have been studied, using scanning tunneling microscopy (STM), X-ray photoelectron spectroscopy (XPS), and surface-enhanced Raman spectroscopy.<sup>10-14</sup>

Several XPS and NEXAFS studies have focused on TP monolayers on a gold surface deposited under an ultra-high vacuum (UHV) condition. Recently, it was found<sup>14,15</sup> that the positions of the S2p peaks in the TP SAMs are different from those of UHV-prepared TP monolayer film.<sup>15-17</sup> This means that the adsorption states of the TP monolayers prepared in solution and UHV conditions are different, probably due to

the growth process of SAMs. Sako *et al.*<sup>15</sup> examined the electronic structure of the TP SAM by near-edge X-ray absorption fine structure (NEXAFS) spectroscopy in C K-edge, and proposed that the TP ring decomposed. However, the molecular-scale STM observation in our study revealed that TP molecules on Au(111) in an ethanol solution can form low coverage<sup>12</sup> or high coverage<sup>13</sup> ordered SAMs, depending on the experimental conditions.

The reaction and adsorption of tetrahydrothiophene (THT) with an aliphatic cyclic ring (heterocyclic compound) on a Pt(111) surface from gas phase have been investigated to elucidate the catalytic desulfurization.<sup>18,19</sup> Recently, we found that the adsorption of THT molecules on Au(111) in an ethanol solution led to the formation of ordered SAMs via the chemical reaction between the sulfur headgroup and the gold surface.<sup>20</sup>

Our previous XPS studies showed that the S atoms both in the THT and TP SAMs were chemically bound to the Au(111) surface,<sup>13,14,20</sup> since the observed peak positions were almost the same as those of the alkanethiol SAMs.<sup>21,22</sup> This means that the THT and TP molecules were bound to the Au(111) surface through the S-Au chemical bond, as shown in Figure 1. Although both TP and THT molecules have a five-membered heterocyclic ring, TP has a  $\pi$ -conjugated ring and THT has an aliphatic cyclic ring without a  $\pi$ -conjugated system. This may lead to different intermolecular interactions or different growth processes in these SAMs. Therefore, the surface structure and adsorption orientation of THT and TP SAMs on Au(111) should be compared directly.



**Figure 1.** Self-assembled monolayers formed by the spontaneous adsorption of (a) tetrahydrothiophene (THT) and (b) thiophene (TP) on Au(111).

In this study, the surface structure and molecular orientation of THT and TP SAMs on Au(111) formed in an ethanol solution were examined by means of STM and NEXAFS spectroscopy. NEXAFS spectroscopy is useful for investigating the structure and orientation of an organic monolayer film. So far, molecular orientations of various SAMs have been determined using the polarization dependence of the NEXAFS spectra.<sup>23–27</sup> In addition, the C K-edge NEXAFS can provide information about the local unoccupied orbital structure of the carbon-containing group in a molecule. This means that the change of the electronic structure of the five-membered ring resulting from adsorption on the metal can be examined by NEXAFS spectroscopy. From this study, we can provide a clear answer as to how the  $\pi$ -conjugated system of the molecular backbone affects the formation and structure of organic SAMs on Au(111).

### Experimental Section

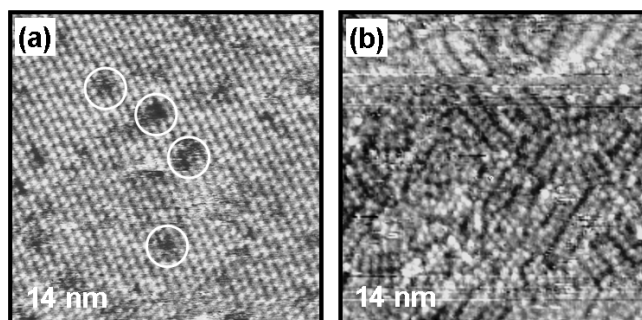
The THT and TP sample materials were purchased from Tokyo Chemical Industry (Tokyo, Japan) and used without further purification. Au(111) substrates were prepared by the vacuum deposition of gold onto cleaved mica plates and prebaked at 573 K under a vacuum pressure of  $\sim 10^{-5}$  Pa. After the deposition of gold, the substrate was annealed at 593 K in the same vacuum chamber for 2 h. It was confirmed by STM observation that the substrates contain large and flat terraces with herringbone reconstruction structures of a clean Au(111) surface. SAMs were formed by dipping the gold substrates into freshly prepared 1 mM ethanol solutions, at room temperature (RT) for 24 h. Figure 1 shows the schematic view of SAM formation by (a) THT and (b) TP molecules on Au(111). After the SAM samples were taken out of the solution, they were carefully rinsed with pure ethanol to remove multilayers that were weakly adsorbed onto the surface.

STM measurements were carried out using NanoScope E (Veeco, Santa Barbara, CA) with a commercial Pt/Ir (80/20) tip. All STM images were obtained in constant current mode, under ambient conditions at room temperature. For STM

imaging, a bias voltage ranging from 300 to 500 mV and a tunneling current ( $I_t$ ) ranging from 0.30 to 0.60 nA were applied between the tip and the sample. NEXAFS measurements were performed at the soft X-ray beamline 7A of the Photon Factory in the High Energy Accelerator Research Organization (KEK-PF, Japan). The C K-edge spectra at different incident angles of soft X-rays were recorded in partial electron yield mode with a retarding bias of  $-245$  V. Photon flux was monitored by measuring the photocurrent from a gold evaporated mesh inserted in the optical path. The signal was detected by a channeltron with the method described in a previous study.<sup>28</sup> The energy calibration was performed with a spectrum of hexatriacontane ( $n\text{-C}_{36}\text{H}_{74}$ ), where the main peak assigned to the  $\sigma^*(\text{C-H})$  transition is located at 287.8 eV.<sup>29</sup> In order to estimate the tilt angle of molecules, we measured spectra at 5 or 3 different angles for THT and TP SAMs, respectively.

### Results and Discussion

STM images in Figure 2 show the surface structures of THT and TP SAMs on Au(111) formed after immersion of the Au(111) substrates in a 1 mM ethanol solution at RT for 24 h. STM imaging with molecular-level resolution reveals that the adsorption of THT and TP molecules on Au(111) leads to the formation of well-ordered SAMs with unique domain structures, as shown in Figure 2. THT SAMs have large ordered domains containing several structural defects, as indicated in Figure 2a by white circles around the small dark areas that appeared inside ordered domains. Similar structural defects inside ordered domains were observed in dioctadecyl sulfide (DOS) SAMs.<sup>30</sup> Both THT and DOS molecules can be classified as monosulfide systems with nearly identical structural behaviors, such as the formation of ordered domains and vacancy islands. Therefore we propose that these unique structures are regarded as one of the intrinsic characteristics of organic monosulfide SAMs on Au(111). The origin of structural defects in ordered domains may be due to the structural strain of an aliphatic ring or two alkyl groups attached to the sulfur atom. Molecular packing arrangements of THT SAMs can be described as a commensurate ( $3 \times 2\sqrt{3}$ ) structure. Interestingly, SAMs of TP with a  $\pi$ -conjugated ring had a completely different domain structure, as shown in Figure 2b. TP SAMs were



**Figure 2.** High-resolution STM images of (a) THT and (b) TP SAMs on Au(111), formed after immersion of the Au(111) substrates in a 1 mM ethanol solution at RT for 24 h.

composed of two molecular domains: the randomly adsorbed domains and the small-size ordered domains with paired molecular rows. The distance between paired rows was measured to be 3.9 Å, and the intermolecular distance was measured to be 4.4 Å. From the STM image resolved at the molecular level, we revealed that TP SAMs have an incommensurate packing structure, contrary to THT SAMs. The structural details and a proposed model of THT and TP SAMs on Au(111) were described in our previous paper.<sup>13,20</sup> The comparative STM study for THT and TP SAMs clearly demonstrated that the  $\pi$ -conjugated systems of the molecular backbone strongly affect the formation and structure of SAMs during the molecular self-assembly of organic thiol molecules. On the other hand, the phase transitions of TP SAMs from a flat-lying orientation with a  $(3 \times 3)$  structure, to a vertical orientation with a  $(\sqrt{3} \times \sqrt{3})R30^\circ$  structure, were observed at 0.3 and 0.6 V in 0.1 M HClO<sub>4</sub> solution.<sup>31</sup> TP SAMs on Au(111) have various adlayer structures that depend on the experimental conditions of the SAM preparation,<sup>12,13,31</sup> which may be due to the relatively weak van der Waals interaction between the TP rings.

We examined the electronic structure changes that result from changing the molecular backbone of THT and TP on Au(111) by comparing them with the spectra of these SAM molecules in the gas phase. From the polarization dependence of the spectra, the average orientation of these molecules was also estimated.

The carbon K-edge NEXAFS spectra of the THT SAMs in Figure 3a do not show  $\pi^*$  resonances resulting from the lack of an unsaturated bond. The spectrum is very similar to the gas-phase spectrum,<sup>18</sup> suggesting that the electronic structure of the hydrocarbon moiety is not changed by adsorption. The lowest energy feature, at around 287.5 eV, has a few shoulders, suggesting the presence of several transitions. In Ref. 18, it was reported that this feature was assigned to the  $\pi^*(\text{CH}_2)$  and  $\sigma^*(\text{C-S})$  transitions. The direction of the transition moment for the  $\pi^*(\text{CH}_2)$  orbitals is considered to be perpendicular to the plane of the five-membered ring. Thus, the transition

moment of the  $\sigma^*(\text{C-S})$  orbital is in the same direction as that of the  $\sigma^*(\text{C-C})$  transition, while the  $\pi^*(\text{CH}_2)$  orbital is perpendicular to them. The feature at higher energy, 292 eV, which is strongly observed at the normal incidence, is assigned to the transitions of the  $\sigma^*(\text{C-C})$  orbitals. The feature A shows opposite polarization dependence from the  $\sigma^*(\text{C-C})$  transition, while the transition peak B has the same polarization dependence as the  $\sigma^*(\text{C-C})$  transition. We assign feature A to  $\pi^*(\text{CH}_2)$  and the shoulder (B) to the  $\sigma^*(\text{C-S})$  transition. In the following qualitative analysis of the orientation, we focus on peaks A and B, which showed opposite polarization dependence.

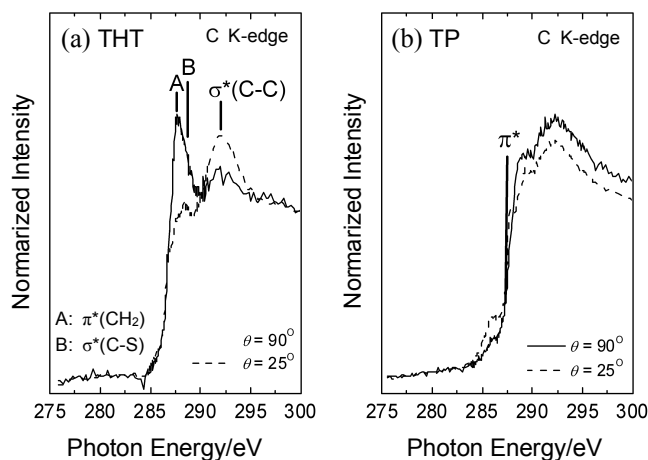
Since the intensity depends on the incident angle of the X-ray, the average tilt angle of the THT ring could be determined with the following equation,<sup>32</sup> assuming random azimuthal orientation:

$$I(\theta) \propto P \cos^2 \theta \cdot (1 - \frac{3}{2} \sin^2 \alpha) + \frac{1}{2} \sin^2 \alpha \quad (1)$$

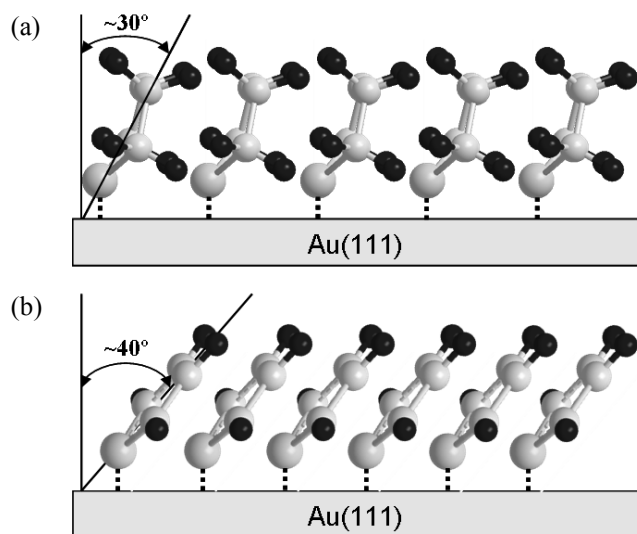
where  $I$  is the transition intensity into a  $\pi^*$  orbital,  $P$  is the degree of polarization of soft X-ray,  $\theta$  is the incident angle, and  $\alpha$  is the average tilt angle of the  $2p_z$  atomic orbitals forming the  $\pi^*$  orbitals. For intensity analysis, we assumed  $P = 0.85$ , since the intensity curve of the  $\sigma^*(\text{C-H})$  transition in the spectrum of the alkanethiol SAM fits well with this value. Using the above equation for the polarization dependence of the  $\pi^*(\text{CH}_2)$  transition peak, the average tilt angle of the molecular plane was estimated to be about  $30^\circ$ . This means that THT molecules have “standing up” adsorption geometry on Au(111).

On the contrary, TP SAMs had a change of spectral shape with adsorption on the Au(111) surface. The TP molecule has  $\pi$ -electrons, and the NEXAFS spectrum of the TP molecule in the gas phase and multilayer film shows a strong  $\pi^*$  transition peak at 285.8 eV.<sup>18,33,34</sup> However, the spectrum of the TP SAMs shown in Figure 3b shows a much weaker peak at this energy. This means that the  $\pi$ -electron system of TP molecules is significantly modified on the Au(111) surface, indicating strong interaction between the  $\pi$ orbital and the Au surface. The results of thermal desorption spectroscopy showed decomposition of the TP molecules by heating, indicating again the strong interaction of TP SAMs with the Au surface.<sup>14</sup> The weakness of the  $\pi^*$  transition peak was already reported by Sako *et al.*,<sup>15</sup> and they concluded that the thiophene ring opened to form thiolates. They also measured S2p XPS, and assigned the peaks at 162.0 eV and 163.2 eV to the thiolate S atoms bound to the Au surface.

However, we suggest that the TP rings were not broken by adsorption, since we observed well-ordered structures by molecular-scale STM observation of the TP monolayers, as shown in Figure 2b. If the TP molecules decompose during self-assembly, we could not observe the ordered TP SAMs. In addition, the S2p peaks in the THT SAM,<sup>20</sup> in which the molecules were not decomposed on the Au surface, appeared at a similar peak position to those of the TP SAM,<sup>13</sup> suggesting that the peak position of the S atoms in the five-membered ring chemically bound on the Au surface is the same as that of the thiolate on the Au surface.



**Figure 3.** C K-edge NEXAFS spectra of (a) THT and (b) TP SAMs on Au(111), formed after immersion of the Au(111) substrates in a 1 mM ethanol solution at RT for 24 h. Note that the solid line was measured at normal incidence and the dotted line was measured at grazing incidence.



**Figure 4.** A schematic describing the adsorption orientation of THT and TP molecules adsorbed on Au(111).

Although we can not make a clear explanation about the weak  $\pi^*$  peak in the TP SAM, we assumed that the S-Au bond formation induces a significant change in the electronic structure of the S atom, probably leading to the modification of the  $\pi$  electron configuration of the TP molecule. Another possibility would be that effective interaction between the  $\pi$  orbitals and the Au surface occurs if the thiophene rings are lying in a tilted orientation with respect to the substrate. Although the weak intensity of the  $\pi^*$  transition prevented the precise determination of the molecular orientation, the tilt angle of the thiophene ring could be estimated to be about  $40^\circ$  from the surface normal using equation (1) with the peak intensities measured at three different detection angles ( $20^\circ$ ,  $55^\circ$ , and  $90^\circ$ ). The obtained angle is the averaged value. This suggests that the molecules are significantly tilted on the Au surface, although we did not take into account of distribution of the orientation. In this tilted orientation, direct interaction between the  $\pi$  electrons of the TP molecule with the Au surface is unlikely. Thus we conclude that the S-Au bond formation causes a change in the  $\pi$  electronic system. Figure 4 shows a schematic describing the adsorption orientation of THT and TP molecules adsorbed on Au(111), which were deduced from our NEXAFS study.

The electronic structure and intermolecular interactions of THT molecules are different from those of  $\pi$ -conjugated TP molecules, leading to different film growth and adsorption states. In particular, the NEXAFS features are sensitive to the differences in the electronic structure. We can determine the difference in the adsorption states and molecular orientation among these molecules based on the spectral shape of the C K-edge NEXAFS spectra, as discussed above. Understanding the relationship between the growth process and the electronic structure of an organic SAM is very important for the fabrication of organic electronic devices. From the STM and NEXAFS results, we demonstrated that the formation of two-dimensional ordered THT or TP SAMs is mainly driven by both the van der Waals interactions between the five-membered

cyclic rings and the interactions between the sulfur atoms and gold surfaces.

## Conclusions

From STM and NEXAFS spectroscopy studies, we revealed the surface structure and adsorption geometry of THT and TP SAMs on an Au(111) surface. STM imaging revealed that the surface structures of THT SAMs are quite different from those of TP SAMs: THT SAMs have a commensurate ( $3 \times 2\sqrt{3}$ ) structure containing structural defects in ordered domains, whereas TP SAMs are composed of randomly adsorbed domains and ordered domains with paired molecular rows, which are described as an incommensurate packing structure. The C K-edge NEXAFS spectra of THT SAMs are very similar to the spectra of the gas phase, indicating that the electronic structure of the aliphatic cyclic ring does not change after SAM formation on an Au(111) surface. We also show that the average tilt angle for the molecular plane of THT was about  $30^\circ$  from the surface normal, which means that THT molecules in the SAMs have a “standing up” adsorption configuration on the Au(111) surface. On the other hand, the  $\pi^*$  transition peak in the NEXAFS spectrum of the TP SAM became very weak with adsorption, which suggests that the  $\pi$ -electron system of the TP molecules was significantly modified after adsorption on the Au(111) surface. This means that the strong interaction between  $\pi$ -electrons and the Au surface arises during the self-assembly process of TP molecules. The tilt angle of the molecular plane of TP was about  $40^\circ$  from the surface normal, suggesting that the molecules are significantly tilted. Our study revealed that the  $\pi$ -conjugated system of the TP ring strongly affects the formation and 2D final structure of SAMs on Au(111) surfaces.

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