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Hierarchical Chiral Framework Based on a Rigid Adamantane Tripod on Au(111)

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Abstract: We have investigated the tripod-shaped bromo adamantane trithiol (BATT) molecule on Au(111) using scanning tunneling microscopy (STM) at 4.7 K. Adsorption of BATT leads to formation of highly ordered self-assembled monolayers (SAMs) with three-point contacts on Au(111). The structure of these SAMs has been found to have a two-tiered hierarchical chiral organization. The self-assembly of achiral monomers produces chiral trimers, which then act as the building blocks for chiral hexagonal supermolecules. SAMs begin to form from the racemic mixture of assembled molecules in ribbon-shaped islands, followed by the transformation to enantiomeric domains when SAM layers develop two-dimensionally across hcp domains. Such a chiral phase transition at the two-dimensional domain can arise from a subtle balance between molecule−substrate and intermolecular interactions. Two structural factors, the S atom (stabilization) and the methylene groups (chirality) located just above the S atom, induce the chiral ordering of BATT on Au(111).

Introduction

Two-dimensional ordering of molecules on metal surfaces has received much attention in relation to the development of molecular electronic devices.[1] Well-ordered molecular layers are expected to play a prominent role in novel technologies beyond Si-based electronics, owing to their versatility in controlling physical and chemical properties by selecting appropriate molecular precursors.[2] Recently, tripod- (or caltrop)-shaped molecules have drawn considerable interest[3−11] because such tapered molecules ensure the development of upright functional chains due to sufficient bonding at surfaces at multiple contact points.

As previously reported,[12] Kitagawa et al. have successfully synthesized a tripod-shaped trithiol based on the adamantane cage (bromo adamantane trithiol, or BATT), containing CH_2-SH groups at three of the bridgehead positions of the adamantane cage and a bromine at the fourth, as shown in Figure 1a. The bromine atom can be readily replaced with other functional groups, i.e., an iodophenyl group, through organic synthesis.[12]

Each S atom in the three CH_2SH feet of BATT facilitates chemical bonding to the metal surface, by replacing the S−H bonds with S-metal bonds. Similarly, the multipoint contact of BATT is expected to offer substantially stronger adsorption to metal surfaces, compared to the single-point contact of adamantane-cage monothiols.[13−15] Self-assembled monolayers (SAMs) of BATT molecules prepared on the Au(111) surface were characterized using infrared reflection absorption spectroscopy (IRAS), scanning tunneling microscopy (STM), and cyclic voltammetry (CV).[12] It was demonstrated that BATT is strongly adsorbed on the gold surface through the three S atoms. However, previous STM measurements were performed under liquid at atmospheric pressure, which did not allow measurement performed under controlled surface conditions.

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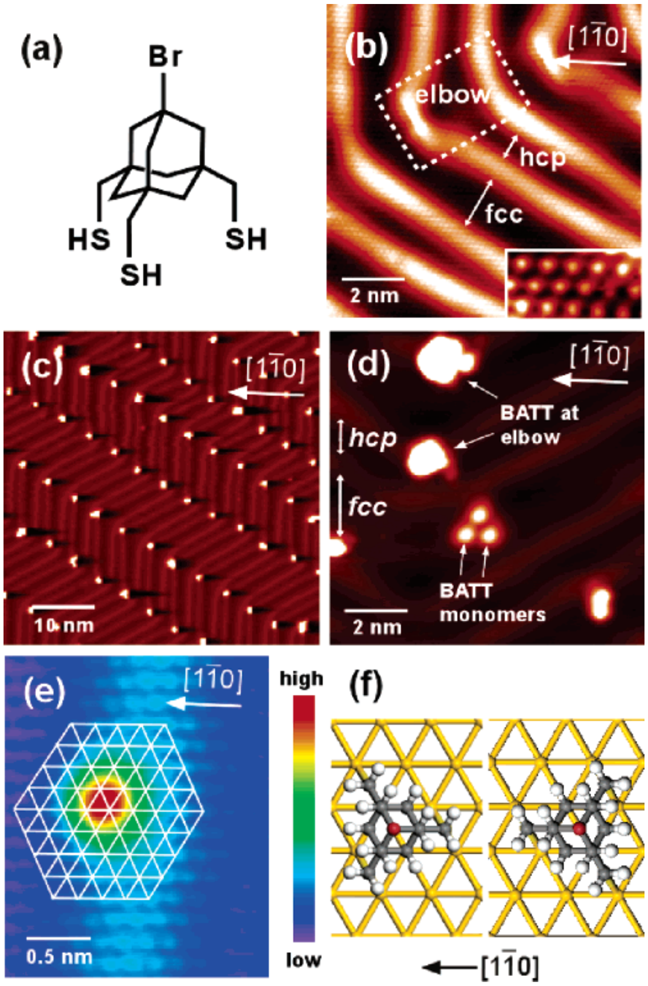

Figure 1. (a) Schematic model of bromo adamantane trithiol (BATT). (b) STM image of clean Au(111) ($V_s = 0.08$ V, $I_t = 25$ nA). (Inset) Magnified image, showing the close-packed structure of Au (1.0 nm × 0.5 nm). (c) STM image of BATT adsorbed on Au(111) at low coverage (0.002 ML) ($V_s = -0.5$ V, $I_t = 0.5$ nA). The high-resolution image is shown in (d) ($V_s = -0.5$ V, $I_t = 0.3$ nA). (e) STM image of BATT monomer adsorbed on Au(111) with atomic resolution of the Au substrate ($V_s = -0.7$ V, $I_t = 1.0$ nA). The Au lattice is indicated by the grid lines. (f) The top view model of BATT monomer adsorbed on Au(111).

In this study, we made STM measurements under ultrahigh vacuum (UHV) conditions to establish a plausible model for the adsorption structure of BATT on the Au(111) surface. Moreover, we have found growth of BATT SAMs to be characterized by a two-tiered hierarchy, i.e., formation of hexagonal units consisting of BATT trimer subunits. Of further interest is the fact that these SAMs exhibit a chirality inherited from their hierarchical subunits. We note that the chirality of these subunits shifts from racemic to enantiomorphic phases when SAMs layers develop two-dimensionally. Here, we present the mechanism of self-assembly of BATT and discuss how chirality can arise from the achiral monomer and then be transferred from trimers to hexagonal arrangements and SAMs.

Experimental Section

All experiments were performed using a low-temperature STM (LT-STM, Omicron GmbH) with an electrochemically etched tungsten tip in a UHV chamber (base pressure: 3×10^{-11} Torr). The Au(111) surface was cleaned by repeated cycles of Ar^+ sputtering and annealing to 800 K. Atomic-resolution STM imaging was used for confirming the clean Au surface. The 1-bromo-3,5,7-tris(mercaptomethyl)adamantane (bromo adamantane trithiol, or BATT) shown in Figure 1a was synthesized by the method reported previously.[12] The purity of the synthesized BATT is 98%, as checked by nuclear magnetic resonance (NMR) spectroscopy. The BATT was further purified by vacuum sublimation at 300 K prior to use. The BATT was evaporated onto the clean Au(111) surface at 298 K by resistive heating under UHV conditions. The evaporation temperature was estimated to be 325−332 K as monitored by a K-type alumel−chromel thermocouple. All STM images were acquired at 4.7 K with the constant current mode except for the image shown in Figure 1c (the constant height mode).

Results and Discussion

Figure 1b shows an STM image of the clean Au(111) surface. The observed periodic pattern, which appears here as a corrugation, is the well-known $23 \times \sqrt{3}$ herringbone reconstructed structure.[16] The surface consists of periodic domains of face-centered cubic (fcc) and hexagonal close-packed (hcp) stacking regions. The domain boundaries appear as ridges and exhibit discommensuration, indicating the transition between fcc and hcp regions.[17] The bended boundaries are generally referred to as elbow sites.[16]

Shown in Figure 1c is an STM image obtained after small amounts of BATT (Figure 1a) were dosed on Au(111) at room temperature. The coverage is 0.002 monolayer (ML; 1 ML corresponds to the number of metal atoms on the bulk metal surface). The BATT molecules appear as protrusions and preferentially occupy the Au monatomic step and elbow sites at low coverages. The periodic arrays formed at elbow sites continue growing as the coverage increases. Defect sites such as steps and elbows are less coordinated than sites in the close-packed regions, and metals and molecules usually preferentially adsorb at these defect sites.[16−22]

The high-resolution image reveals that BATT can adsorb at fcc regions as a monomer (Figure 1d). The STM images show that BATT molecules adsorbed at elbow sites protrude considerably (1.8 Å) more than when adsorbed at fcc terrace sites (0.6 Å).

The STM image of a monomer with the atomically resolved Au surface is presented in Figure 1e. Superimposing a drawn Au lattice on the molecule reveals that the center of the protrusion is located at the bridge site of Au(111). The proposed adsorption model of BATT on Au(111) is illustrated in Figure 1f. The previous IR study on Au(111)[12] and the previous X-ray photoelectron spectroscopy (XPS) study on a Au polycrystalline surface[3] indicated that BATT forms a three-point contact on the gold surface through the S atoms, following cleavage of the S−H bonds. Thus, consistent with the structure of BATT, the molecular center should be positioned at a bridge site. If the molecular frame is not obviously distorted upon adsorption, it follows that the three S atoms would be located at bridge sites (Figure 1f), because other configurations result in an

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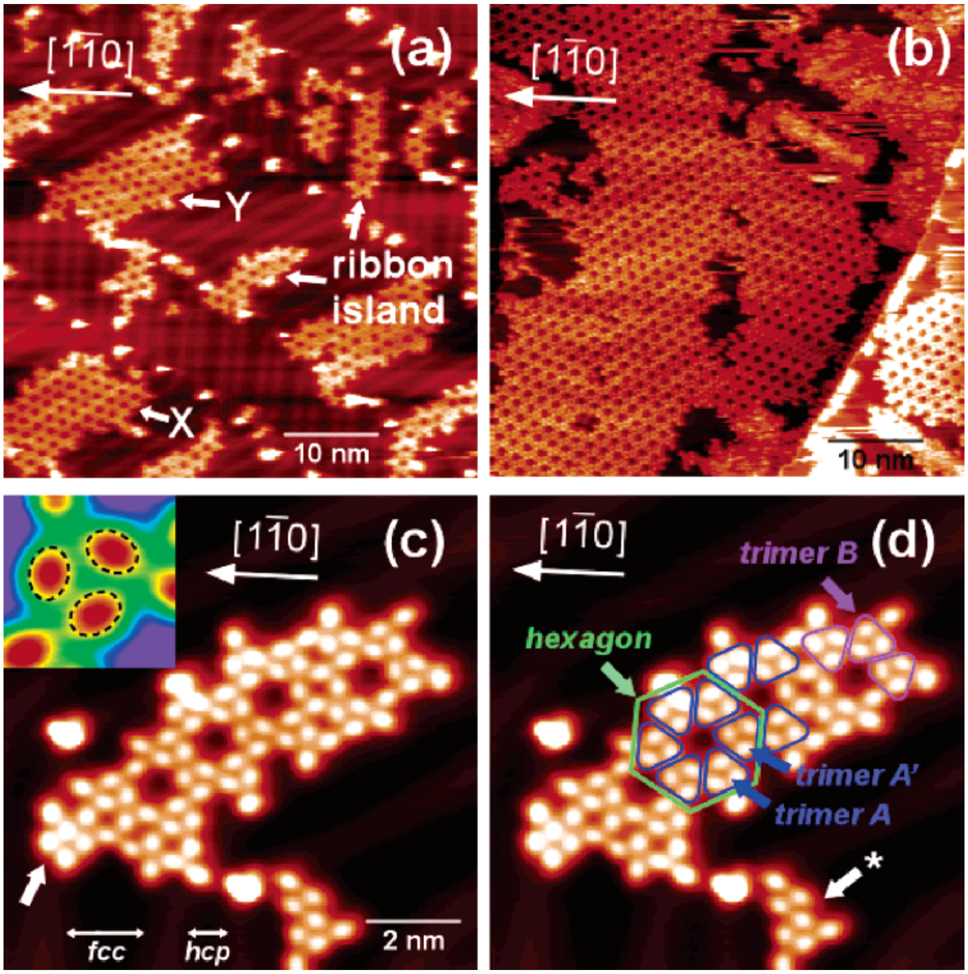

Figure 2. (a) and (b) STM images of BATT on Au(111) with increasing BATT coverages ((a) 0.023 ML, (b) 0.062 ML). X and Y denote the chiral domains ($V_s = -0.8$ V, $I_t = 0.3$ nA) (see details in Figure 4). (c) STM image of a ribbon-shaped BATT island (0.021 ML) formed in the fcc domain ($V_s = -0.5$ V, $I_t = 0.5$ nA). (Inset) Magnified image of a trimer. Trimer and hexagon units are indicated in (d).

inequivalent adsorption for each S atom. The adsorption of S atoms at bridge sites is consistent with previous high-resolution electron energy loss spectroscopy (HREELS) studies[23] and density functional theory (DFT) calculations[24] of methane thiolate adsorbed on Au(111).

BATT forms more complex self-assembled structures when the coverage increases. The STM images of BATT SAMs on Au(111) at higher coverages are shown in a (0.023 ML) and b (0.062 ML) of Figure 2. Figure 2a shows ribbon-shaped islands beginning to develop from elbow sites. Each grows unidirectionally along an fcc domain and ends at the next elbow site. Meanwhile, the hcp domains are occupied when neighboring fcc domains are filled with SAMs, as indicated by X and Y in Figure 2a. This reveals that the growth of SAMs at hcp domains proceeds by lateral intermolecular interactions with the BATT SAMs at fcc domains. Continuous exposure of the surface to BATT results in the two-dimensional development of SAMs (Figure 2b).

The observed complex structure can be explained by its hierarchical organization. STM images c and d of Figure 2 show high-resolution images of a ribbon-shaped island. We found that three BATT molecules assemble into trimer subunits (trimer A), which then act as the building blocks for constructing a hexagonal unit (hexagon). The hexagon is composed of two types of trimers (trimer A and A′) with rotational symmetry with respect to an axis at the center of a trimer. The molecules adsorbed at the fcc domain at the bottom right of Figure 2d (indicated by *) represent the nascent stage of SAMs growth. They assemble to form trimers, the basis for further hierarchical construction.

A careful look at the STM images reveals that the shapes of individual BATT molecules alter when they form a trimer. Isolated monomers appear round in the STM images (Figure 1 d and e), while individual molecules in a trimer are distorted and appear as symmetric ellipsoids in the STM images in Figure 2. We confirmed that this alteration in shape does not arise from a tip-induced effect because, as shown in Figure 2c, molecules not forming trimers (indicated by the arrow in Figure 2c) and located at the edge of ribbon-shaped islands appear as round protrusions and coexist in the same image with the ellipsoidal protrusions in the trimer domains. We believe that this shape change in BATT is a result of a substantial intermolecular interaction as discussed below. The major axes of ellipsoidal protrusions of each BATT molecule in a trimer cross at an angle of 120°. Note that in Figure 2d the orientation of trimer B is

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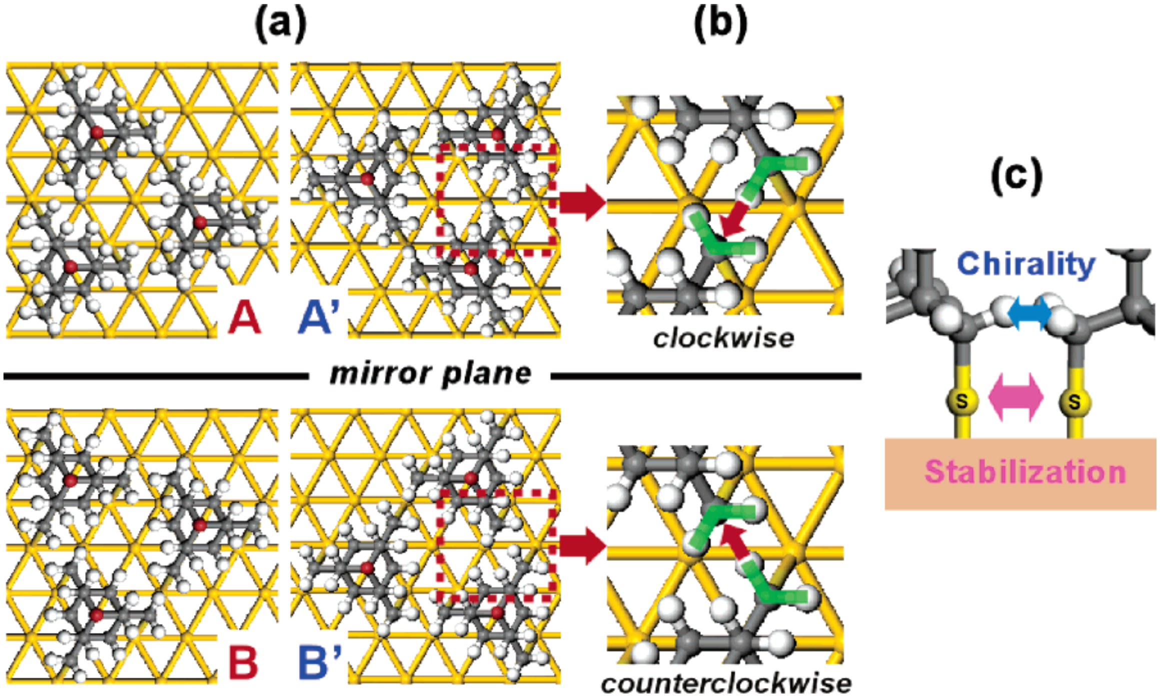

Figure 3. (a) Schematic adsorption models of BATT trimers. B (B′) is the enantiomer of A (A′), whose mirror plane is aligned parallel to the [1$\bar{1}$0] direction. 180°-rotated configuration of A (B) is presented as A′ (B′). (b) Expanded model of (a). The chirality for the assembled layers is caused by meshing of methylene between adjacent molecules. (c) Side view of (b), showing two structural factors driving the chiral ordering. The S atom is associated with stabilization of the molecular assembly. The methylene is associated with formation of the chiral configuration.

not identical to that of A: rather, the trimer frames are slightly rotated in relation to each other. Furthermore, the same kinds of trimers build their own hexagonal superstructures. This is most clearly seen on the two-dimensional SAMs indicated as X and Y in Figure 2a. These SAM structures differ from each other in ways that cannot be explained merely by the surface symmetry.

These observed features of the SAMs are explained by their chiral assembly, which is inherited from their hierarchical organization. The proposed models of the BATT layer are shown in Figure 3 for the trimer units, where the adjacent protrusions are about 7.4 Å apart, and in Figure 4 for the hexagons and the SAMs. On the basis of STM images of the trimers, the structure of trimer A (B) in Figure 2d can be illustrated as A or A′ (B or B′) in Figure 3a, respectively. In the model, the center of each BATT molecule is located at a bridge site. Here, the S atoms are only one lattice constant (2.88 Å) apart from the S atom of nearby molecules, indicating that substantial interaction occurs between the molecules via the S atoms.[25] This interpretation is supported by the observation of deformation of a single BATT into an ellipsoidal protrusion when it is included in a trimer (inset of Figure 2c). Another intermolecular interaction may explain the observed structure: the geometric configuration of the methylene (CH_2) included in the CH_2S legs (Figure 3b). The CH_2 groups, indicated by chevrons in the expanded picture shown in Figure 3b, mesh with each other to form clockwise pinwheels in the trimers of A and A′. Trimers of B and B′, meanwhile, form counterclockwise pinwheels. It is important to note that A (A′) is the enantiomer of B (B′), whose mirror plane is parallel to the [1$\bar{1}$0] direction.

Indeed, the chirality of each trimer is passed on to the hexagons, and then to the SAMs. Shown in Figure 4 are proposed models of hexagonal and two-dimensional SAM structures. A hexagon is composed of six trimers with the same chirality (Figure 4a), i.e. a clockwise pinwheel of A and A′ (or a counterclockwise pinwheel of B and B′). The subsequent buildup of hexagons then forms the chiral SAMs (Figure 4b). The STM images (Figure 4c) coincide well with the models. The enantiomeric SAMs have unit cells as indicated in b and c of Figure 4, have their periodicities represented as

$$\begin{pmatrix} 10 & 4 \\ 6 & 10 \end{pmatrix}$$

for A and

$$\begin{pmatrix} 10 & 6 \\ 4 & 10 \end{pmatrix}$$

for B, and have a coverage estimated to be 0.079 ML. The calculated monolayer coverage from the STM image is slightly less than that from the model. This is mostly due to the imperfect ordering by the presence of mono-atomic Au step and defects. The centers of the hexagons always remain vacant, although they have enough space for an additional adsorbate. This is probably due to a modification of the binding energy at the cavity[26,27] caused by the stabilization of the trimers via the S−S interaction and/or electronic modification by the surrounding molecules. Growth of the ribbon-shaped islands is accompanied by the development of chirality in the trimers as well as in the hexagons. The initial step in SAM formation includes a racemic mixture of hexagons as observed in the ribbon-shaped islands in a and c of Figure 2. Such unidirectional growth is associated

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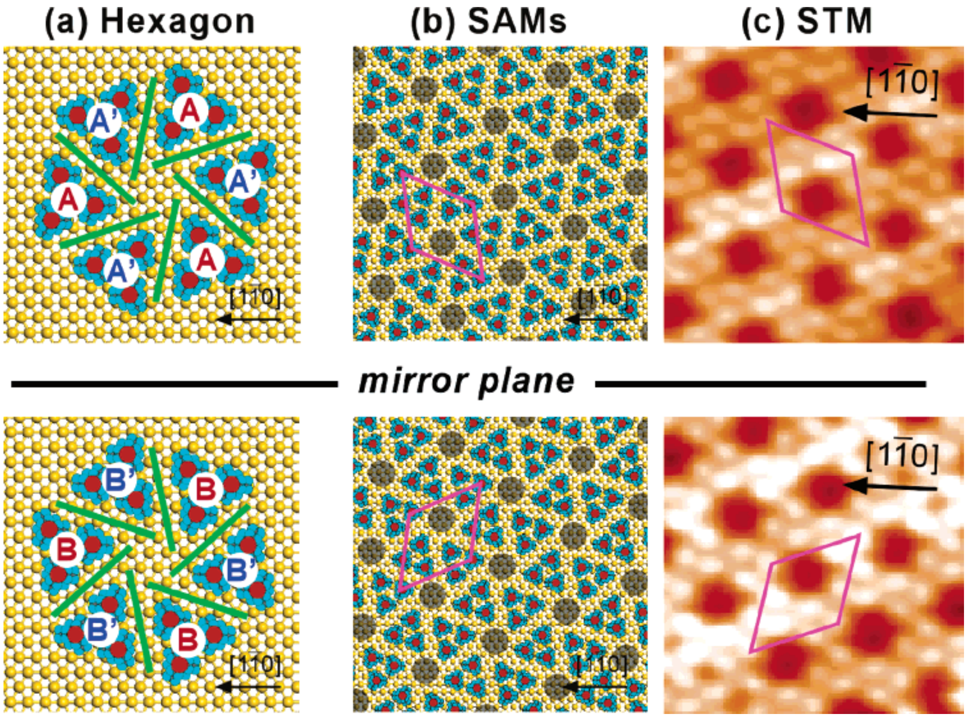

Figure 4. Schematic self-assembly models of (a) hexagon and (b) SAMs of BATT on Au(111). The chiral components of the trimers are indicated as A, A′, B, and B′. The hierarchical assembly is passed from trimer to hexagon and then to SAMs. Each enantiomeric hexagon is composed of the same chiral trimers as shown in (a). The unit cell of the SAMs are indicated in (b), whose periodicities are represented as $\begin{pmatrix} 10 & 4 \\ 6 & 10 \end{pmatrix}$ and $\begin{pmatrix} 10 & 6 \\ 4 & 10 \end{pmatrix}$. (c) Corresponding STM images of monolayer SAMs (0.079 ML) ($V_s = -0.8$ V, $I_t = 0.3$ nA).

with the preferential adsorption of BATT at fcc domains and thus suggests that the substrate–molecule interaction dominates the self-assembly of BATT at low coverage. Furthermore, this racemic mixture changes to one enantiomeric domain as the SAM layer develops two-dimensionally across hcp domains. The observed chiral transformation is evidence that the growth of the SAMs at high coverages proceeds by lateral intermolecular interactions. As the adsorbed BATT monomer is achiral, the chiral development of trimers takes place by a thermally activated diffusion process. Here, molecular chiral self-assembly at surfaces is governed by the balance between intermolecular and molecule–substrate interactions.

Two possible structural factors driving chiral ordering of BATT on Au(111) are the S atoms and methylene groups in the molecular frame (Figure 3c). The former affects stabilization of the molecular assembly, and the latter is associated with chiral recognition. In this system, we note that the two components function independently. This is due to the structure of BATT: methylene is located just above each S atom. There have been several reports related to the chiral interaction and recognition of adsorbed molecules on metal surfaces.[28–32] However, most of the reported systems have used planar molecules, which inhibits multifunctional interaction. The chirality of such planar molecules can be driven by unidirectional chemical bonding. Our results suggest that controlling intermolecular interactions derived from three-dimensional molecular configurations is key to the construction of nanomolecular systems.

Conclusion

We investigated the tripod-shaped bromo adamantane trithiol (BATT) molecule on Au(111) using STM at 4.7 K. Adsorption of BATT leads to formation of highly ordered SAMs with three-point contact on Au(111). The structure of these SAMs has been found to have a two-tiered hierarchical chiral organization. The self-assembly of achiral monomers produces chiral trimers, which then act as the building blocks for chiral hexagonal supermolecules. SAMs begin to form from the racemic mixture of assembled molecules in ribbon-shaped islands, followed by the transformation to an enantiomeric domain when SAM layers develop two-dimensionally across hcp domains. Such a chiral phase transition at the two-dimensional domain can arise from a subtle balance between molecule–substrate and intermolecular interactions. Two structural factors, the S atom (stabilization) and the methylene groups (chirality) located just above the S atom, induce the chiral ordering of BATT on Au(111).

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