

Two-Dimensional Chirality: Self-Assembled Monolayer of an Atropisomeric Compound Covalently Bound to a Gold Surface

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Stereoselective syntheses or sensing of chiral organic compounds is one of the most important and attractive areas of chemistry. Chiral discrimination should be the key step in these processes. The use of the surface of a solid, e.g., catalyst^{1,2} or electrode,^{3,4} modified with chiral components has provided a feasible approach for discrimination which is applicable to industrial processes. Such discrimination, however, may arise from interaction between the surface-bound compound and the reaction substrate, i.e., the modified surface may be a simple assembly of host–guest complexes without any two-dimensional orders. Several reports^{5–9} have claimed that the attachment of chiral molecules forms a surface consisting of “chiral structure” which is different from that with racemic molecules, but its two-dimensional order has not yet been detected. We are aiming at a feasible preparation of a stable chiral surface consisting not of a simple random assembly of chiral compounds but of a two-dimensionally ordered arrangement of molecules. Here, we show the first example of the preparation and direct STM observation of two-dimensional chirality induced by an atropisomeric compound anchored covalently on a gold surface. Although recent studies have succeeded in direct STM or AFM detection of the two-dimensional chirality of physisorbed monolayer films of enantiomers of chiral organic molecules,^{10–15} such observations are quite natural and easily expected since they were assembled chiral molecules similar to the surface of their molecular crystals. Our strategy has been to use self-assembling and covalent binding on metal surfaces of compounds having thiol group(s) to fabricate a monolayer film of chiral organic compounds. The stability and potential ability as a functionalized surface of a self-assembled monolayer have already been well-documented.¹⁶ For the chiral component, we used two enantiomers of an atropisomeric compound, (*R*)- and (*S*)-1,1'-binaphthalene-2,2'-dithiol¹⁷ (BNSH,

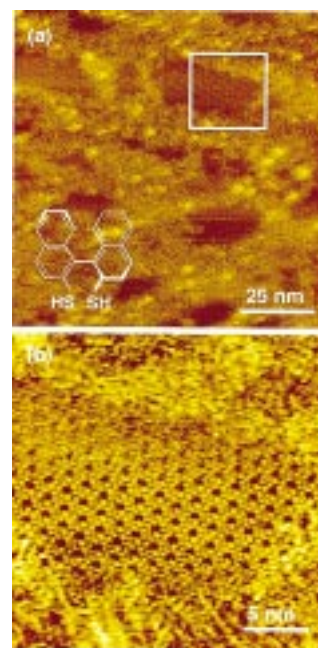


Figure 1. Unenhanced STM images of a spontaneously formed (111) facet on a gold substrate modified with (*R*)-BNSH, the molecular structure of which is superimposed, in the size of (a) 100 nm and (b) 25 nm square. The gold substrate was prepared by following a method developed by Clavilier,²⁰ and it was dipped in an ethanolic solution of (*R*)-BNSH¹⁷ (1 $\mu\text{mol dm}^{-3}$) and potassium hydroxide²¹ (10 mmol dm^{-3}) for 10 min and then rinsed several times with ethanol. STM observation was performed in air using a probe unit (Molecular Imaging PicoSPM) controlled by Digital Instruments Nanoscope E. Representative conditions for the STM measurement were bias voltage of 200–600 mV and tip (platinum–iridium alloy) current of 500–800 pA.

Figure 1), and they are attached to a gold (111) surface. The use of an atropisomeric compound having two twisted aryl groups enabled us to detect the shape of the molecule in STM observations even without atomic resolution.

Figure 1a shows a representative unenhanced (i.e., obtained without any data processing) STM image of the facet of a gold substrate dipped in an ethanolic solution of (*R*)-BNSH. The image was categorized into a honeycomb-like ordered part (Figure 1b) and a disordered part. The former layer was thinner than the latter. The fact that repeated rinsing of the treated surface with ethanol expanded the ordered part suggests the formation of an ordered monolayer and disordered multilayer structure. The high-resolution images in Figure 2 show that the ordered surface structure consists of a combination of balls (yellow, the size of which roughly corresponds to one naphthalene moiety) and holes (red-brown). A unit cell of this two-dimensional structure was rhombus for both (*R*) and (*S*) isomers. It should be noted that these two unit cells were of reflected images by considering the disposition of, e.g., the balls; that is to say, modification of the surface with BNSH induces two-dimensional chirality. To distinguish these two surface structures clearly, we paid attention to the assembly of balls surrounding the hole. As shown in Figure 2, three triangles composed of six balls (colored white) surround a hole, and the rotating direction differed according to the stereo structure. In this report, we call the rotating directions, for convenience, counterclockwise (a) and clockwise (b). In our STM measurements, (*R*)- and (*S*)-BNSH gave only counterclockwise and clockwise arrangements, respectively; no exceptions were seen.

In STM images (not shown) of the gold substrate modified with a racemic mixture of the two enantiomers, domains of the

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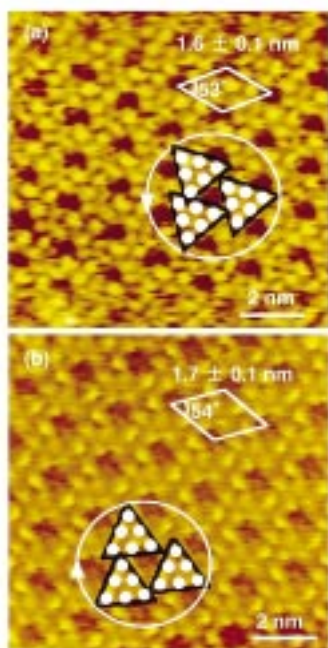


Figure 2. Unenhanced high-resolution STM image of the ordered part of a gold (111) surface modified with (a) (*R*)- and (b) (*S*)-BNSH. The size of a white ball-like image corresponds to one naphthalene moiety in BNSH. The pattern of arrangements were apparently independent of the bias and tip current.

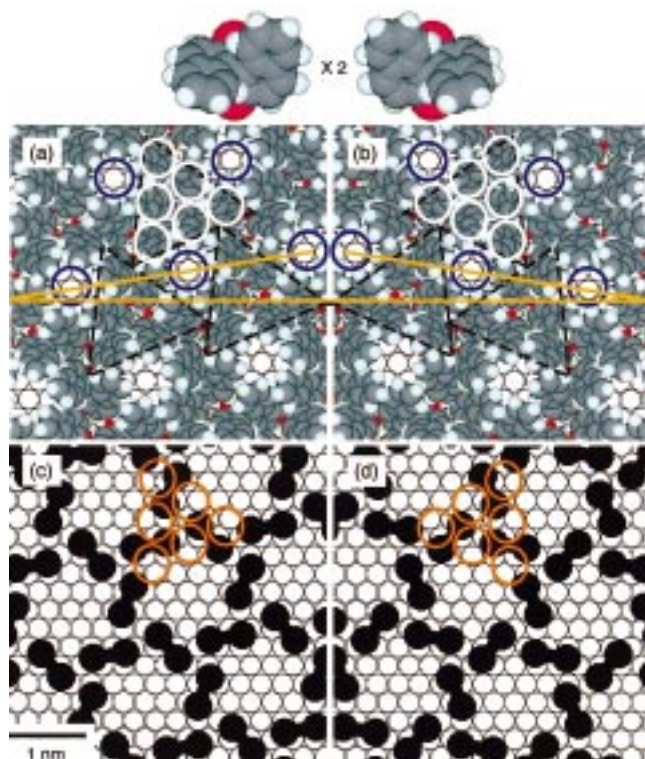


Figure 3. Proposed structure of two-dimensionally chiral surfaces induced by (a) (*R*)- and (b) (*S*)-BNSH. Naphthalene moiety (white circle) and hole (blue circle) are shown. Arrangement of naphthalene moiety (orange circle) and sulfur atoms (dumbbell) bound at a 3-fold hollow site of surface gold atoms (circle) are shown in (c) and (d).

ordered structure were also seen, but their proportion to the whole surface was a little smaller than that with each pure enantiomer. Detailed investigation showed that each ordered domain was one of the above-mentioned counterclockwise or clockwise structures. These patterns enable us to distinguish the domains consisting

of one of the enantiomers, (*R*) or (*S*). These STM images also provided information on the azimuthal angle of the ordered structure; it can be concluded that each enantiomer makes the ordered-structure domains on the same crystal terrace with the same direction, and linear lines connecting the neighboring holes in the counterclockwise and clockwise structures cross at ca. 20°. These facts are a strong indication that the chiral surface is commensurate with the structure of an underlying gold (111) surface. This is also supported by the observation that the angles of step lines to the hole-connecting-lines were ca. 10 and -10° for the cases of (*R*)- and (*S*)-domains, respectively.

Electrochemical measurements confirmed chemical bonding of BNSH with the gold surface, as cathodic current peaks at ca. 700 mV due to reductive desorption of thiols self-assembled on the gold surface ($\text{RS-Au} + \text{e}^- = \text{RS}^- + \text{Au}$)¹⁸ were observed. Consistent with the STM observations, both enantiomers showed almost the same desorption behavior, while their racemic mixture tended to desorb at the negative potential. Since the electric charge of these desorption peaks should be proportional to the number of cleaved Au–S bonds, comparison of the relative peak area of these two desorption peaks with the ratio of ordered and disordered areas in STM images leads to a hypothesis that the positive and negative peaks are attributed to the ordered and disordered areas, respectively. In all cases, the total electric charge was 32–35 $\mu\text{C cm}^{-2}$, i.e., $(1.0\text{--}1.1) \times 10^{14}$ molecules cm^{-2} , corresponding to the close packing of BNSH molecules of cross section of 1 nm^2 bound via two S–Au bonds. This fact is reasonable if we assume that the disordered part consists of ordered underlying layer covered with physisorbed, i.e., electrochemically inert, upper layer.

The proposed surface structure which is consistent with all of the above results is shown in Figure 3a, b. We assumed the binding of a thiol group at the 3-fold hollow site of surface gold atoms.¹⁶ The distance between neighboring sulfur binding sites is almost the same as that of two thiol groups in BNSH (0.40–0.45 nm) if the angle between two naphthyl groups in BNSH is assumed to be 94° , a little larger than that of unsubstituted binaphthyl (68°).¹⁹ The distribution of BNSH molecules shown in Figure 3a, b makes the hole-connecting line cross with the (111) step at ca. 10° . An oblique unit cell with sides of 1.62 nm contains three BNSH molecules, giving a surface density of ca. 1.3×10^{14} molecules cm^{-2} . As shown in Figure 3c, d, the arrangement of the surface-bound sulfur atoms of (*R*) and (*S*)-BNSH also forms reflected images, i.e., the chiral molecular structure made a two-dimensional chiral arrangement of attached molecules. Although the reason the holes are made in this surface structure is not clear at present, such a chiral structure in supermolecular size should be preferable for catching and discriminating guest organic molecules.

In conclusion, we demonstrated the preparation of a two-dimensional chiral structure via self-assembling and covalent binding of atropisomeric molecules onto gold. Modification of BNSH with various functional groups and application of this chiral surface to stereoselective catalytic and electrochemical reactions are now in progress.

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