Communication

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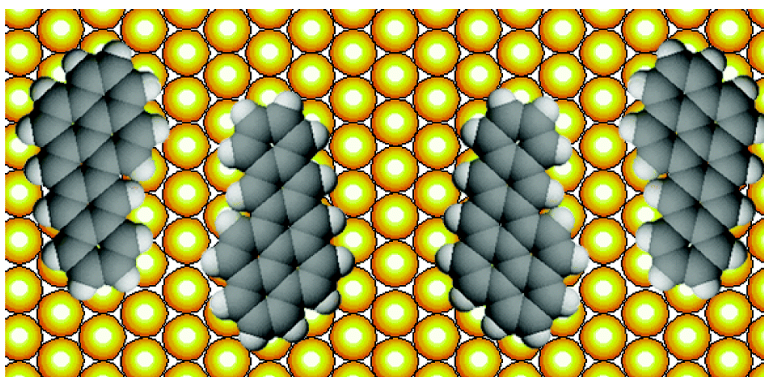
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Chiral structures are present in nature in the form of minerals, biological structures, and biomolecules. Stereospecific chemistry is particularly important in the preparation of enantiopure drugs. A chiral surface will be of great utility for enantioselective catalysis and sensing. One method of producing chiral substrates is to generate high index chiral metal surfaces;[1] another is the adsorption of chiral molecules.[2,3] Scanning tunneling microscopy (STM) has been used to show that chrial adsorbates segregate into domains of pure enantiomers at the liquid/solid interface.[4] DL-Cysteine has been observed to form racemic domains of homochiral pairs on Au in a vacuum environment.[5] Two-dimensionally chiral molecules can also be used to produce chiral domains. While these molecules are not chiral in three dimensions, adsorption results in loss of mirror plane symmetry producing two nonsuperimposable forms of the molecule on the surface. Recent studies investigating the adsorption of two-dimensionally chiral molecules have utilized covalently bound adsorbates,[6] metal−organic complexes,[7] organic acids with long alkane tails,[8] and hydrogen bonding adsorbates.[9] The polar 2D chiral molecule 1-nitronaphthalene has been observed to form a racemic structure on reconstructed Au(111).[10] While numerous morphological studies have been performed on adsorbed symmetric aromatic molecules,[11−16] to our knowledge, this report is the first direct observation of phase segregation of two-dimensional enantiomers in a simple aromatic system.

A gold film was deposited on a mica surface to produce a flat predominantly (111) surface. The Au(111) film was cleaned under ultrahigh vacuum (UHV) conditions utilizing argon ion sputtering and annealing to 300 °C. The sample was determined to be clean by X-ray photoelectron spectroscopy (XPS) and by the presence of the characteristic $23 \times \sqrt{3}$ reconstruction in STM images.[17] Naphtho[2,3-a]pyrene (NP) (Figure 1) was evaporated onto the cleaned Au(111) surface from a Knudson cell after measurement and stabilization of the deposition rate using a quartz crystal microbalance (QCM). The substrate was maintained at room temperature, while the sublimation temperature of the organic molecule was around 100 °C. After deposition of the organic film, the sample was immediately transferred in situ for analysis with a variable temperature STM. All STM images presented in this report were obtained at room temperature.
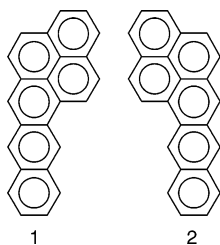

Figure 1. Molecular structure of naphtho[2,3-a]pyrene. When this molecule is restricted to a surface, it loses its mirror plane symmetry and has nonsuperimposable forms, labeled enantiomer 1 and 2.

The molecular structure of the naphtho[2,3-a]pyrene (NP) molecule showing the two 2D surface enantiomers is presented in
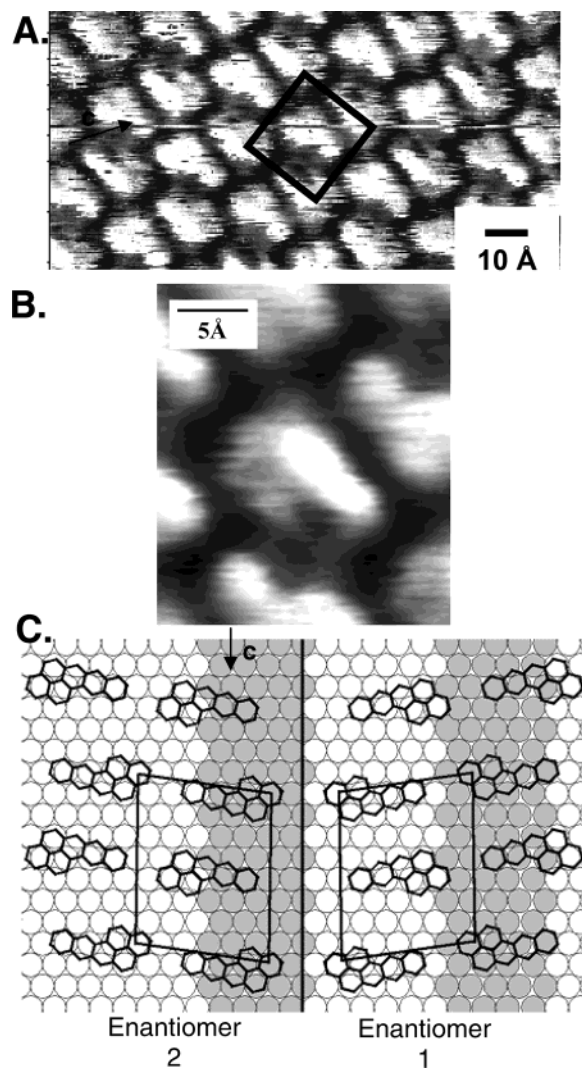

Figure 2. (A) An STM image of 2D chiral packing of NP molecules. (B) Magnified image of the chiral unit cell. (C) A model of the reconstructed Au(111) surface (dark substrate atoms) and the intersection of two chiral domains of NP molecules (separated by the black line across the model). Enantiomer 2 is the chiral form that is imaged in Figure 2A and B. (To align the model and STM images, rotate enantiomer 2 clockwise by ~23°.)

Figure 1. Deposition of these molecules will result in equal numbers of the 2D enantiomers on the surface. There are then two possibilities for the formation of ordered structures: unit cells containing racemic pairs or segregation of homochiral molecules into domains with chiral unit cells.

STM images with intramolecular resolution, obtained after deposition of a 4 Å NP film on Au(111), revealed that the ordered molecular domains contained only one 2D enantiomer. An STM image of a portion of a chiral domain showing the backward "P" shape of the molecules is shown if Figure 2A. A black box drawn in the figure shows the 2D unit cell that contains two NP molecules.

A higher magnification image is shown in Figure 2B where the "P" shape of the molecules is again apparent. The chiral nature of the domain is unambiguously observed because all of the molecules are superimposable by simple rotation of the molecules within the plane of the Au(111) surface. Unit cell parameters were determined from averaging values obtained from numerous line scans from multiple images as well as an FT averaging algorithm contained in Scanning Probe Image Processing software (Image Metrology Aps.). The average a cell distance, along the direction where the NP molecules have an end-to-end nearest neighbor interaction, was 16.3 Å with a standard deviation of ±0.4 Å ($a = 16.3 ± 0.4$ Å). The average b unit cell distance was 19.4 Å with a standard deviation of ±1.0 Å ($b = 19.4 ± 1.0$ Å). The unit cell angle measured between a and b is $50 ± 3°$. The Au(111) reconstruction was not lifted upon adsorption of the NP molecule. While not seen in Figure 2, the angle between the direction of the reconstruction [11$\bar{2}$] and the a unit cell direction on other images was measured to be $86 ± 2°$. The distance between molecules making up a "row" (labeled c in Figure 2A and C corresponding with the long axis of the side by side molecules) provided an additional distance that was utilized in modeling the unit cell. This c distance was $11.4 ± 0.6$ Å. The dark atoms of the substrate represent the $23 × \sqrt{3}$ elevated Au(111) reconstruction that traverses the surface in the [11$\bar{2}$] direction. The NP molecules in the model are divided into two chiral domains by the solid black line, labeled enantiomer 1 and 2. The 2D enantiomers pack with molecular rows having the large end of the molecule pointing in one direction instead of with alternating rows having the large end of the molecule rotated 180°.

A proposed model for the chiral domains and unit cells is presented in Figure 2C. The model unit cell contains two molecules and is representative of the chiral plane group p2. The domain is modeled with the terminal rings of the molecules located on atop sites of the gold surface; although we have not directly observed this level of detail, the orientation of the molecules with respect to the reconstruction is consistent. Our previous studies with similar large aromatic molecules, as well as other investigations, suggest this is the probable overlayer interaction with the gold atoms.[11–14,18] The modeled unit cell parameters are compared with the experimental measurements in Table 1. Furthermore, the model predicts that the chiral domains should intersect at an angle of 162° (between adjacent a unit cell vectors) that was also observed in STM images. All modeled parameters are in good agreement with the experimentally measured distances and angles.

In summary, we have demonstrated the formation of chiral domains from simple low symmetry aromatic molecules on a highly symmetric, hexagonal, low index metal surface. We have observed these chiral domains with high-resolution STM and imaged the intramolecular structure. A proposed structural model agrees with the experimental observations and measurements. The chiral

Table 1. Experimentally Measured and Modeled Parameters for the Chiral Domains Formed by Naphtho[2,3-*a*]pyrene Molecules on Au(111)

parameter	experimental	modeled
a	16.3 ± 0.4 Å	16.1 Å
b	19.4 ± 1.0 Å	19.9 Å
α	50 ± 3°	50.2°
c	11.4 ± 0.6 Å	11.5 Å
$\angle a$, reconstruction	86 ± 2°	81°
$\angle$ enantiomeric domains	163 ± 5°	162°

domains formed spontaneously without strong interactions between molecules such as hydrogen bonding moieties or large dipoles and without chemical bonds with the substrate such as gold−thiol interactions. The dynamics of chiral domain formation via surface diffusion of enantiomers or molecules "flipping" between enantiomeric forms is currently under study. Note that the spaces between the molecules form "chiral pockets" that may be selective for adsorption of a specific enantiomer of a 3D chiral molecule to the particular 2D chiral domain. Such chiral recognition may be important for future studies of sensors for optically active molecules or enantioselective catalysis.

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