

Scanning Tunneling Microscopy Investigation of a Supramolecular Self-Assembled Three-Dimensional Chiral Prism on a Au(111) Surface

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Chirality is an important and widespread phenomenon in nature, and its importance in applications such as catalysis, stereoselective syntheses, and medical/pharmaceutical sensing has been well documented.^{1–3} While numerous studies continue to elucidate the details of the preparation of and interactions between chiral molecules in solution, considerably less is known about chirality on surfaces.^{4,5} The reduced inherent symmetry of two-dimensional (2D) surfaces makes the study of chirality on surfaces especially interesting. The development of scanning tunneling microscopy (STM)^{4–6} allows for the details of chiral surface assemblies to be viewed at atomic resolution, a level of detail not available to solution-phase studies.

Chiral surfaces have been fabricated artificially by a variety of methods: employing high-index chiral metal surfaces,⁴ depositing chiral molecules on nonchiral surfaces,^{4,7,8} and depositing achiral molecules on nonchiral substrates.^{4,9,10} STM and synchrotron grazing incidence X-ray diffraction have also been used^{11,12} to study chiral assemblies formed at the air–water interface. Recently, a number of theoretical investigations^{13,14} have helped elucidate the details of how chirality is expressed on surfaces and how symmetry-breaking of macroscopically racemic mixtures can occur. It has generally been found,^{5,13,14} that substrate–adsorbate interactions dictate the conformation(s) adopted by isolated molecules as they adsorb onto a surface, and the subsequent adsorption of additional molecules is heavily influenced by the conformation(s) of prior adsorbates. Each enantiomer of a chiral compound tends to self-assemble into individual domains on the surfaces. It is difficult, however, to predict *a priori* the extent to which domain separation will occur. A particularly surprising example of this uncertainty involves the deposition of a chiral diacetylene isophthalic acid derivative on highly oriented pyrolytic graphite (HOPG), which resulted in a completely achiral surface.¹⁵

Over the past few years, a variety of highly symmetric and complex structures have been synthesized by dynamic self-assembly.¹⁶ More recently, the higher-order self-assembly of these supramolecular complexes on 2D surfaces and their resultant structures have received considerable attention^{17–19} because of their functionalities and the variety of unique patterns that can be formed, likely to be of use in heterogeneous stereoselective syntheses and catalysis. Our groups have reported the STM images of self-assembled supramolecular cages, triangles, and rectangles on HOPG and Au(111) surfaces.¹⁷ We have also used a molecular template to promote the monodispersion of a well-ordered array of supramolecular rectangles that otherwise form disordered adlayers on HOPG.¹⁸ Schalley and co-workers have reported a chiral adlayer of metallacyclic rhomboids at a chloride-modified Cu(100) surface.¹⁹ These studies have demonstrated the facile formation of well-defined, uniquely patterned arrays of supramolecular metallacages and metallacycles on various surfaces and have also shown domain separation^{17b} in some mixed monolayers. A natural extension of such studies is to investigate the possibility of chiral

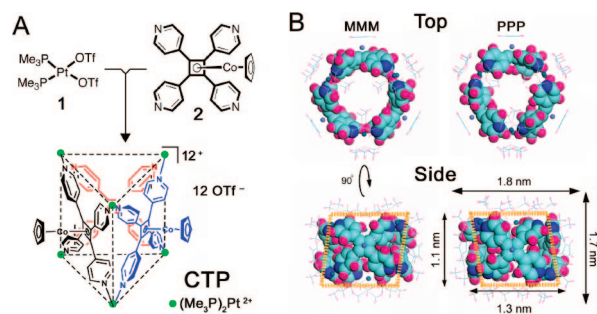


Figure 1. (A) Chemical structure of a chiral 3D trigonal prism (CTP). (B) Space-filling models of the MMM and PPP enantiomers.

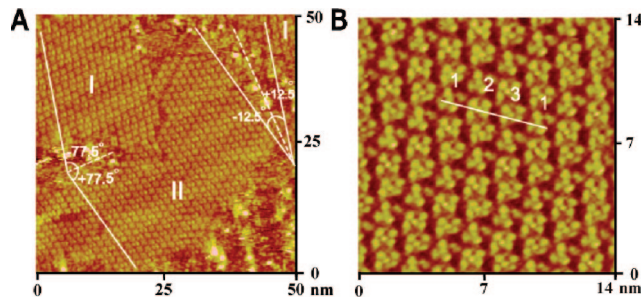


Figure 2. (A) Large-scale STM image ($E = 550$ mV, $E_{\text{tip}} = 373$ mV, $I_{\text{tip}} = 919.1$ pA) of the racemic mixture adsorbed on a Au(111) surface. (B) High-resolution STM image ($E = 514$ mV, $E_{\text{tip}} = 393$ mV, $I_{\text{tip}} = 1.046$ nA) of the molecule on a Au(111) surface.

resolution upon the adsorption of chiral supramolecular metallacages on surfaces. In the present Communication, we describe an STM study of previously reported²⁰ chiral supramolecular trigonal prisms (Figure 1A) on a Au(111) surface.

Details of the self-assembly of supramolecular chiral trigonal prisms (CTP, Figure 1A) from 6 equiv of 90° Pt(II) acceptor **1** and 3 equiv of tetrapyrrolyl “star” connector **2** have been reported elsewhere.²⁰ Molecular space-filling models of CTP’s two helical enantiomers—MMM and PPP—are shown in Figure 1B. When viewed from the top, the molecules appear as a trigonal prism, while when viewed from the side, they look like parallelograms. For clarity, the parallelograms are represented by dashed lines in the space-filling models.

Experimental details of the surface deposition of supramolecular complexes have been described previously.^{17,18} Self-assembled monolayers of the supramolecular trigonal prisms were prepared by immersing a gold bead for 1 min in a racemic mixture of CTP in EtOH (10 μ M). STM images were recorded with a Nanoscope E STM instrument in 0.1 M HClO₄. The potentials applied to the Au(111) surfaces were set at the double-layer region, and all STM images were recorded in the constant-current mode without further processing.

Figure 2A is a representative large-scale STM image of the adlayer. Upon adsorption of the racemic mixture on Au(111), each enantiomer forms separate, well-ordered, locally chiral domains, denoted as I and

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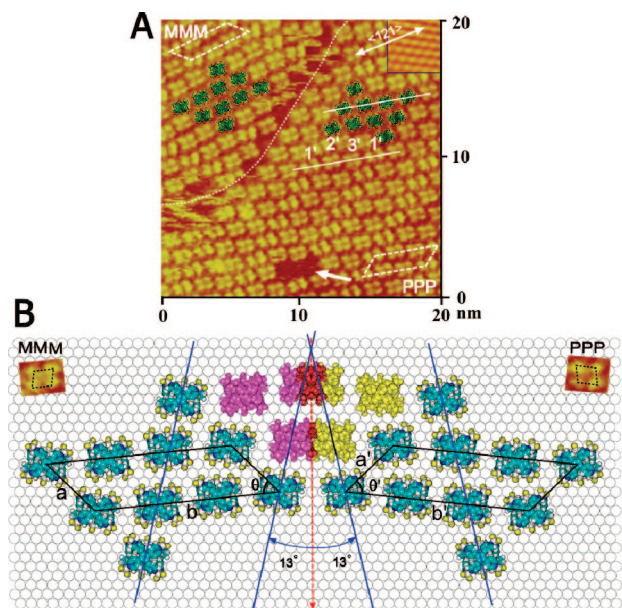


Figure 3. (A) High-resolution STM image ($E = 550$ mV, $E_{\text{tip}} = 446$ mV, $I_{\text{tip}} = 919.1$ pA) of the molecular adlayer. The underlying Au(111)-(1 \times 1) lattice is inserted in the upper right corner. (B) Structural model for the adlayer. Images of the two enantiomers are shown in the upper left and upper right corners.

II in Figure 2A. The boundaries between domains I and II cross, forming an angle of $25 \pm 2^\circ$. Figure 2B is a high-resolution STM image of domain I showing the structural details of the adlayer. Each molecule appears as a four-petal parallelogram with a bright spot in the middle (pistil), indicating that the molecules lie edge-down on the Au(111) surface while projecting their flat face upward, consistent with the side-view model presented in Figure 1B. The dimensions of each parallelogram are $1.5 \times 1.4 \pm 0.2$ nm, which agrees very well with the molecular size calculated from molecular modeling data. The “pistil” corresponds to the Cp–Co groups, while the dark regions around the parallelogram are attributed to the methyl groups. Only a single shape can be seen in the image, implying that adsorption of the racemic mixture on the Au(111) surface results in spontaneous symmetry-breaking and the formation of chiral domains. However, molecules within a molecular row do not form perfectly straight lines but, rather, ordered repeating units of three molecules each, such as those marked 1, 2, and 3 in Figure 2B (see Supporting Information for details).

Detailed information about the enantiomeric adlayer, including symmetry and molecular orientation, is provided by the high-resolution STM image shown in Figure 3A. Two domains are observed in the image and are separated by a dotted white line. Because the exact enantiomer cannot be determined from the STM images alone, we have arbitrarily assigned the left domain as being composed of MMM enantiomers and the right domain as PPP enantiomers. The molecules in each domain are very similar, with the major difference being the position of the ordered rows within the adlayer with respect to the underlying Au(111) surface. Presumably this difference results from the different “twist” of the enantiomers. Molecular defects do appear; an example is indicated in the PPP domain by the white arrow where two molecules are missing.

Though the individual molecules in the MMM and PPP domains appear to have the same parallelogram shape, their molecular orientations are different. Enlarged STM images of single molecules from the two domains in Figure 3A are shown in the upper corners of Figure 3B. The mirror image relationship between these two images suggests that they are different enantiomers of the same molecule.

A structural model for the adlayer is shown in Figure 3B. In constructing this model, molecules from the STM image were transposed onto a simulated Au(111) surface, preserving the molecular orientation of the two domains. In this model, the molecules at the junction of the domains are shaded in purple (MMM) and yellow (PPP) to emphasize the different orientation of each chiral domain. The Cp–Co and the methyl groups have been omitted for clarity. The two enantiomeric domains are separated by the θ direction of the substrate, and the molecular rows cross, forming an angle of 26° . On the basis of the adlayer symmetry and the intermolecular distances, unit cells were determined to be the same in both domains, with $a = 1.8 \pm 0.2$ nm, $b = 2.5 \pm 0.2$ nm, and $\theta = 50 \pm 2^\circ$, corresponding to a $\sqrt{39} \times \sqrt{73}$ structure. Isolation of either pure MMM or pure PPP enantiomers of CTP will allow for straightforward determination of the absolute configuration of each chiral domain.

In conclusion, we have observed the formation of well-ordered chiral domains upon deposition of a racemic mixture of a chiral supramolecular trigonal prism on a Au(111) surface. This report sheds light on chiral surface fabrication and has potential applications in stereo-selective synthesis and chiral sensing. The results provide a facile method for fabricating 2D chiral structures on a bare, nonchiral metal surface using nanoscale 3D self-assembled supramolecular metallacages.

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Supporting Information Available: Details of adlayer preparation and the adlayer conformation. This material is available free of charge via the Internet at <http://pubs.acs.org>.

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