Probing molecular-level organizational structure and electronic decoupling of tartaric acid domains supported on Ag(111)

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Probing molecular-level organizational structure and electronic decoupling of tartaric acid domains supported on Ag(111)

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Abstract. Mechanisms of adsorption and organization of organic molecules on metallic surfaces play a significant role in the growth of chemically and electronically tuned monolayer thin films. Intercommunication between functional groups for individual adsorbates can serve as the primary driving force for monolayer crystallinity as well as electronic structure, especially in the limit of weak interaction between the adsorbate and substrate. In this article we discuss the submonolayer ordering of a chiral molecule, tartaric acid (C₄H₆O₆), weakly bound to an achiral metal surface, Ag(111), as studied with low temperature scanning tunneling microscopy (STM) and differential conductance imaging. Molecularly resolved images of enantiomerically pure (R,R)- and (S,S)-tartaric acid domains on Ag(111) are presented and the role of intermolecular hydrogen bonding in stereospecific domain and superlattice formation is addressed. Additionally, we consider films formed from the deposition of a racemic mixture of tartaric acid enantiomers. Lastly we present differential conductance mapping of tartaric acid molecular domains that highlights an intrinsic decoupling of molecular film electronic states with respect to the metallic lattice. While the chiral expression that drives the formation of enantiomeric domains does not induce stereospecific conductance, we demonstrate electronic differentiation of submonolayer organic domains from the Ag(111) surface.

1. Introduction

Tartaric acid (C₄H₆O₆) is a chiral molecule whose stereochemistry was first reported by Pasteur in 1848 [1]. It has been shown experimentally that highly organized networks of tartaric acid form upon chemisorption of enantiopure forms of the tartrate on the (111) and (110) crystal planes of Cu and Ni surfaces [2]. Interestingly, though enantiomers of the molecule have the same structural arrangement, the inherent differences in spatial location of internal hydroxyl groups is expressed in the formation of extended two-dimensional chiral domains. In other words, films composed of pure (S,S)- or (R,R)-tartaric acid represent non-superimposable mirror images of each other, just as the enantiomerically pure solids. Considering that the constituents that are attached to the chiral centers are not involved in bonding to the surface, global film chirality is then controlled by intermolecular hydrogen bonding at chiral centers.

We have chosen to study the adsorption of tartaric acid enantiomers onto Ag(111), a surface to which the molecule is only physisorbed, in contrast to the chemistry for tartaric acid adsorbed to Cu...
and Ni surfaces. The interaction of (S,S)-, (R,R)-, and DL-tartaric acid with Ag(111) has been studied with low energy electron diffraction (LEED), scanning tunneling microscopy (STM), and differential conductance imaging. These experiments have yielded structural information that gives evidence to a weakly bound adsorbate film that exhibits extended two-dimensional surface chirality. Results concerning enantiomerically pure films are considered first, followed by similar results regarding binary films. Spectroscopic measurements, which further suggest a physisorbate whose unique electronic structure remains decoupled from that of the metallic surface to which it is anchored, will be discussed in detail in the final section.

2. Experimental details
All experiments were performed in a custom-built ultra-high vacuum (UHV) chamber (base pressure $7.5 \times 10^{-11}$ Torr) using a home-built low and variable temperature scanning tunneling microscope (STM), both of which have been described previously [3]. Briefly, the chamber is equipped with a high energy ion gun and an e-beam heater for sample preparation, along with low energy electron diffraction (LEED) optics for sample characterization. The Ag(111) crystal (MaTeck, GmBH) was first cleaned by argon ion bombardment (1 keV Ar$^+$ ions) and then annealed at 800 K. STM and LEED confirmed that this method routinely produced a clean, well ordered Ag(111) surface with terraces on the order of several hundred nanometers wide. Solid (R,R)-, (S,S)-, or DL-tartaric acid (enantiomerically pure: Fluka, racemic: Aldrich) was dosed onto a room temperature surface from differentially pumped glass vials that were heated to approximately 385 K and degassed at that temperature for several hours prior to dosing. STM imaging and spectroscopic measurements were carried out at $T_{\text{sample}}=300\,\text{K}$, 83 K, or 17 K with a mechanically cut Pt/Ir (90:10) tip prepared in situ by field emission or voltage pulses. Imaging conditions (i.e., sample bias and tunneling current) are data specific and included in the figure captions. Spectroscopic measurements, obtained simultaneously with topographic images, were recorded using a lock-in-amplifier by modulating the sample bias with a small $V_{\text{AC}}$ (1 kHz, 10 mV), allowing for phase sensitive detection of the first harmonic of the input tunneling current signal. The magnitude of the first derivative of the current with respect to voltage, $dI/dV$, is plotted as a function of spatial position at a fixed $V_{\text{sample}}$ and is roughly proportional to the local density of states (LDOS). The data is displayed as spatially resolved conductance maps of the surface region of interest. All conductance images reported here were taken using these settings.

3. Structure of enantiomerically pure and racemic tartaric acid/Ag(111) films
Both LEED and STM data confirm two hypotheses: first that the internal molecular chirality controls the organization of the film at the global level, and second that the tartaric acid is weakly bound to the Ag(111) surface. LEED data of the stereospecific domains shows that the two enantiomers, when adsorbed on Ag(111) in their pure forms, produce chiral films [4]. Global organizational chirality is also readily resolvable from low temperature STM experiments. Large scale images of tartaric acid films obtained at cryogenic temperatures show periodic long range undulations in the film, most likely a result of a structural energy minimization, that are used as a chirality metric [4]. Confirmation of the second hypothesis, namely that the molecule is physisorbed to the surface, is made by relatively unstable LEED patterns that are sensitive to the electron beam. In addition, room temperature STM imaging in the submonolayer coverage regime also support this assertion by revealing that the island edges are easily perturbed by repeated rastering of the STM tip.

Figure 1 shows two molecularly resolved low temperature STM images of pure films of (S,S)-tartaric acid (left) and (R,R)-tartaric acid (right). We attribute each bright feature to a single tartaric acid molecule. The dimensions of the corresponding eight molecule unit cell are corroborated by LEED measurements [4]. As is evident from the images, the molecules appear to adopt one of two orientations and this is shown with molecular models overlaid on the image features for both enantiomers. We hypothesize that the molecules physisorb to the Ag(111) surface in a “sawhorse” confirmation, characterized by a weak van der Waals attraction between oxygen atoms in the terminal carboxylic acid groups and the underlying silver substrate. It is plausible that this physisorption
geometry is stabilized by the image charge that is induced by the negatively charged oxygen atoms that lie in close proximity to the surface. The internal chiral centers and corresponding hydroxyl groups are then elevated from the surface with respect to the end groups, forming the sawhorse structure. The position of these hydroxyl groups lends to intermolecular hydrogen bonding if neighboring molecules are oriented such that their chiral centers lie within several Ångstroms of one another. There is a small difference in the length of the long axis of the unit cells between the two structures shown in Figure 1. We attribute this effect to local variations in molecular packing density that are possible due to the weak adsorbate-metal interaction as well as the range over which hydrogen bonding can occur.

Coadsorption of (S,S)- and (R,R)-tartaric acid was also studied with low temperature STM. Dual component films were grown by first exposing the clean silver surface to the pure (S,S) enantiomer, and then to an equivalent dose of the pure (R,R) enantiomer [4]. It is apparent that phase separation is observed upon serial exposure to a room temperature substrate and subsequent imaging at low temperature. Not only does the binary film serve as an internal calibration, but also demonstrates the relative robustness of the chiral domains that are formed independently by each enantiomer. As an extension of this work, we chose to also study the formation of binary films from a racemic (50:50) mixture, DL-tartaric acid, of the two isomers (supplementary data). For concurrent adsorption of both enantiomers onto Ag(111), as compared to serial deposition on the same surface, we report that though long range periodic undulations are present, but they do not appear with comparable regularity as those used to characterize the chiral nature of the enantiomerically pure films. Furthermore, the racemic films do not exhibit the same long range structural order as the pure films. Multiple domains emanate from step edges and domain boundaries and multiple vacancy sites are present within the films. High resolution images (supplementary data) show molecular resolution for a film that was grown by sublimation of the racemic mixture. At this length scale, it becomes more obvious that the structure does not correspond to that observed after deposition of the pure enantiomer. Instead, the films are characterized by what we hypothesize to be enantiomeric pairs of molecules where each bright feature corresponds to an (S,S)/(R,R)-tartaric acid doublet.

4. Electronic properties of tartaric acid domains
The molecular films adsorbed to the Ag(111) surface exhibit striking electronic features that are readily resolvable with STM. Most notably, the topography of the racemic films is elevated (Δh~2 Å) with respect to the clean Ag(111) surface, a result that is the opposite of that observed for the enantiomerically pure films. This highlights a difference in electronic properties and/or a possible
distinction in the adsorption geometry to the metal lattice between enantiospecific and racemic domains. Secondly, differential conductance maps at sub-monolayer coverages for both the enantiopure and racemic films reveal a clear distinction between molecular domains and bare Ag terraces (Figure 2). The center panel displays a topographic STM image of (R,R)-tartaric acid/Ag(111) recorded at V sample=+50 mV (image at V sample=-50 mV is identical). The left and right panels show resolution of tartaric acid domains through differential conductance imaging (dI/dV) recorded concurrently with topography. Different areas of the surface have different relative conductances as a function of junction bias. For V sample=+50 mV (right panel) the conductance of the clean silver terraces is higher (bright regions) than the conductance of the adsorbed film (dark regions). The standing wave pattern that is associated with surface state electron scattering from the step edges is readily accessible at this energy and is used to distinguish clean silver regions. Imaging at V sample = -50 mV (left panel) reveals that the conductance of the clean metallic regions are lower than that of the physisorbed film. We likewise considered the differential conductance associated with racemic films, which appears to show an inflection point for conductance that is associated with the surface state band edge of Ag(111) at -65 mV [5].

5. Conclusions
The interaction of tartaric acid enantiomers with Ag(111) has been studied with high resolution STM and differential conductance imaging in order to understand the role of hydrogen bonding in the expression of chirality at inert surfaces. Weak binding for tartaric acid adsorbed to Ag(111) allows for multiple hydrogen bonding interactions and molecularly driven structures. Electronic measurements for the molecular films reveal distinct features that can be resolved relative to the underlying metallic lattice through differential conductance.

Acknowledgments
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Supplementary data-Figure 1.

**Left panel:** Low temperature STM image of a binary (S,S)/(R,R)-tartaric acid film (2300 Å × 2300 Å, \(I_t=100\) pA, \(V_{\text{sample}}=700\) mV, \(T_{\text{sample}}=83\) K). This structure was generated by exposing the clean Ag(111) surface first to (S,S)-tartaric acid and then to an equivalent dose of (R,R)-tartaric acid. The total exposure resulted in a monolayer film. The high resolution insets were recorded from areas within the larger scale image (115 Å × 115 Å, \(I_t=100\) pA, \(V_{\text{sample}}=635\) mV, \(T_{\text{sample}}=83\) K), and the Ag(111) inset demarks the alignment of the Ag lattice as verified by microscopy (15 Å × 35 Å, \(I_t=100\) pA, \(V_{\text{sample}}=25\) mV, \(T_{\text{sample}}=83\) K). The dashed blue and red lines are aligned with the direction of the modulation rows in the enantiospecific domains. The black arrows denote Ag(111) lattice directions. This dual-component monolayer was grown to assess the robustness of the chiral structure as well as for use as an internal calibration and verification of mirror image structures.

**Right panel:** Submonolayer binary film grown from a racemic (50% (S,S)/50% (R,R)) mixture of tartaric acid (1700 Å × 1700 Å, \(I_t=100\) pA, \(V_{\text{sample}}=50\) mV, \(T=83\) K). Tartaric acid domains grown from concurrent deposition of both enantiomers contain distinct domain boundaries and ordering at the local level that is distinctly different from the film grown by serial deposition.
Supplementary data-Figure 2. Pairing interaction between enantiomers as a result of the adsorption of equal amounts of each enantiomer from a racemic source. Top left image shows boundaries between ordered rotational domains (350 Å × 350 Å, $I_t=100$ pA, $V_{sample}=50$ mV, $T_{sample}=83$ K) and higher resolution images highlight the appearance of distinct lobes within each feature (bottom left: 115 Å × 115 Å, $I_t=100$ pA, $V_{sample}=50$ mV, $T_{sample}=83$ K; right: 95 Å × 95 Å, $I_t=100$ pA, $V_{sample}=50$ mV, $T_{sample}=83$ K). Smaller features are present at domain edges and support the enantiomeric pair hypothesis.