

Mesoscopic chiral reshaping of the Ag(110) surface induced by the organic molecule PVBA

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We report scanning tunneling microscopy observations on the restructuring of a Ag(110) surface induced by the molecule 4-[*trans*-2-(pyrid-4-yl-vinyl)]benzoic acid (PVBA). Our data reveal that the surface undergoes a mesoscopic step faceting following exposure to submonolayer coverages and thermal activation. A sawtooth arrangement evolves implying long-range mass transport of substrate atoms and forming a regular arrangement of kink sites. Its formation is associated with the molecules' functional headgroups forming carboxylates with {100} Ag microfacets at step edges, and eventually operating to reshape the surface morphology. Interestingly, the resulting microfacets act as chiral templates for the growth of supramolecular PVBA structures. Theoretical modeling based on *ab initio* results indicates that chiral recognition processes discriminating between the two enantiomers of adsorbed PVBA molecules occur in this process. © 2004 American Institute of Physics. [DOI: 10.1063/1.1763836]

I. INTRODUCTION

Chiral surfaces play an important role in enantioselective heterogeneous catalysis, identification of enantiomers and crystal growth.¹⁻⁵ In recent investigations it was pointed out that single crystal surfaces are chiral when they expose kinked step edges, i.e., discontinuities at a step edge where neighboring atomic planes come together.^{6,7} When deliberately miscut crystals are employed, this property can be exploited for fabrication of enantioselective surfaces.⁸⁻¹¹ On the other hand, it was found that homochiral facets may be fabricated by adsorption of the chiral molecule L-lysine on a Cu(100) surface.¹² In a recent scanning tunneling microscopy (STM) study it was moreover demonstrated that or-

ganic adsorbates may even bestow chirality to atomically flat terraces by inducing local surface reconstruction.¹³ There, the employed organic species locally displaces substrate Cu atoms to increase molecule-substrate interactions¹⁴ whereby chiral kink sites in the substrate are introduced.

In the present STM study we discuss the formation and mesoscopic ordering of chiral regular steps on a Ag(110) surface which are mediated by lateral molecule-step interactions due to the functionality of a molecular endgroup. We employed the rigid and rodlike molecule 4-[*trans*-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA).¹⁵⁻¹⁷ The new stepped surface evolves towards the formation of mesoscopic facets in conjunction with nucleation and growth of PVBA domains, which present a characteristic structure reflecting the chiral fingerprint and the symmetry properties of the metal template.

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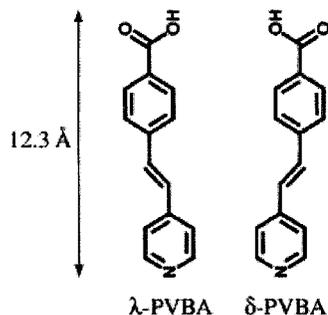


FIG. 1. The molecule 4-[*trans*-2-(pyrid-4-yl-vinyl)] benzoic acid (PVBA). Upon confinement to a surface 2-D chiral species exist, which are labeled λ and δ . For free molecules the projection of the distance of the extremal N and H atoms on the symmetry axis of the pyridine moiety amounts to 12.3 Å.

II. EXPERIMENTAL SECTION

Sample preparation and characterization have been conducted under ultra-high vacuum (UHV) providing well-defined conditions on the atomically clean Ag(110) single crystal surface. An UHV system equipped with a home-built 4-K scanning tunneling microscope¹⁸ as well as standard facilities for sample preparation and characterization was employed. The surface was prepared by cycles of argon ion sputtering (500–1000 eV, $\sim 9 \mu\text{A}/\text{cm}^2$) and subsequent annealing (~ 800 K) resulting in large defect-free terraces.

In Fig. 1 the PVBA structure formula is reproduced with its extrema given by a carboxylic acid ('head') and a pyridyl moiety ('tail'). Upon 2-D confinement the angled molecular structure of PVBA imposes chirality that is not present in the gas phase. Thus two chiral species exist on a surface, which are labeled λ and δ PVBA, respectively. The molecules were deposited in UHV by using a conventional Knudsen-cell at background pressures of $\approx 3 \times 10^{-9}$ mbar with the Ag crystal held at 300 K. All STM data were obtained at $T=4$ K.

III. RESULTS AND DISCUSSION

Following room temperature deposition of small amounts of PVBA on Ag(110), the molecules cluster in islands stabilized by intermolecular lateral attractive interactions. The islands frequently decorate substrate steps and detailed STM observations reveal that the magnitude of the lateral interactions is insufficient to stabilize regular H-bonded supramolecular arrangements, such as those observed upon PVBA deposition on the Ag(111) substrate under identical conditions.^{19–21} This is associated with the increased surface corrugation of the anisotropic (110) surface. However, upon tempering the PVBA covered Ag(110) surface at $T \sim 430$ K, a dramatic restructuring of the surface is encountered, resulting in a characteristic sawtooth pattern which prevails on large portions of the surface, as illustrated by large-scale STM images shown in Fig. 2(a). The pattern is composed of regular $\{5\bar{5}4\}$ steps zigzagging with side lengths reaching several hundred Angstroms. Interestingly, the new steps group in bunches evolving towards the formation of mesoscopic facets. These newly created steps have a predominant angle of 30° with respect the $[1\bar{1}0]$ crystallographic orientation of the substrate, which is a symmetry

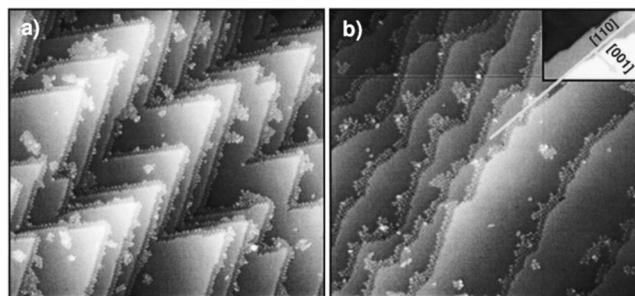


FIG. 2. Mesoscopic "sawtooth" morphology of Ag(110) induced by PVBA following thermal activation. The large-scale STM images were obtained upon PVBA deposition at room temperature and tempering at ~ 430 K for 10 min [(a) $V_s=0.97$ V, $I=0.25$ nA, image size: 110×110 nm², (b) $V_s=0.3$ V, $I=1$ nA, image size: 90×90 nm²]. The inset (11×7 nm²) shows the typical structure of the clean Ag(110) substrate.

axis of individual 60° sawtooths. $\{5\bar{5}4\}$ oriented steps consist of a (2×5) regular arrangement of kinks sites, each defined by intersection of $[1\bar{1}0]$ and $[001]$ steps, where a single PVBA molecule can be accommodated. Occasional deviations from this (2×5) regular kink arrangement can be detected as 70° (i.e., 2×4) and 50° (i.e., 2×6) sawtooths or mixtures of them. Additionally, in those surface regions with characteristic bunches of straight $[001]$ steps, the new $\{5\bar{5}4\}$ steps reproduce a wider zig-zag pattern around the $[001]$ surface direction with average angle consequently supplementary to 30° [Fig. 2(b)].

In every case, the mesoscopic arrangement involves appreciable surface mass transport [cf. for comparison, the morphology of the pristine surface shown in the inset in Fig. 2(b)]. It is important to note that under the preparation conditions of the PVBA layer, the substrate steps are fluctuating whereby Ag atoms continuously evaporate from step edges and condense. This accounts in particular for the presence of a 2-D lattice gas of Ag adatoms at the surface.²² With the present system, the reactivity of these adatoms is not sufficient to drive the formation of complexes within the terraces, albeit Ag-carboxylates are well documented.²³ This is in marked contrast to results obtained with other carboxylic acids on Cu surfaces, where following deprotonation of the carboxyl moiety Cu adatoms may be incorporated in distinct carboxylate complexes stabilized by metal-ligand interactions.^{24–27} The particular orientation of the facets observed here must be closely related to the specific geometry and reactivity of PVBA. While surface faceting induced by organic adsorbates has been reported in earlier studies,^{12,28–30} the presently encountered formation of regular mesoscopic sawtooth patterns is a novel phenomenon.

The chirality of the PVBA-induced kink sites is visualized by the 3-D atomistic model reproduced in Fig. 3. For the designation of the kink chirality we follow the nomenclature proposed by Ahmadi *et al.*⁸ The surface is viewed from above and the orientation of the crystallographic planes defining the kink sites is identified. The $R(S)$ configuration corresponds to a clockwise (anticlockwise) sequence $(111) \rightarrow (100) \rightarrow (110)$ (following crystal planes with decreasing density; coined in analogy with the common Cahn–Ingold–Prelog sequencing rules employed for optically active compounds³¹).

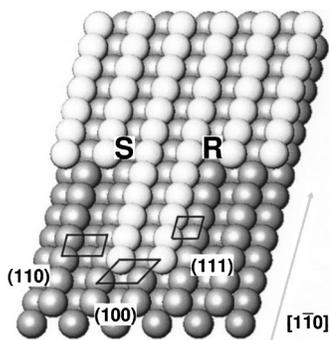


FIG. 3. 3-D representation of the chiral kink sites labeled *S* and *R*. The crystallographic (110), (111), and (100) orientations are indicated.

The chiral new microfacets evolve in conjunction with an ordered molecular assembly. The STM image in Fig. 2 shows that the created steps are decorated by a ~ 30 Å wide zone covered with PVBA. In contrast to larger PVBA islands, where molecules assemble barely in parquetlike patterns, the narrow PVBA domains present a characteristic regular structure. A high-resolution STM image of these domains around a single sawtooth is reproduced in Fig. 4(a). It reveals that every kink forming part of a regular $\{5\bar{5}4\}$ step accommodates a PVBA molecule with a functional endgroup coupling to step edge atoms. The axis of these molecules is nearly oriented parallel to the sawtooth symmetry axis (i.e., the $[1\bar{1}0]$ direction), thus pointing to a local (100) micro-

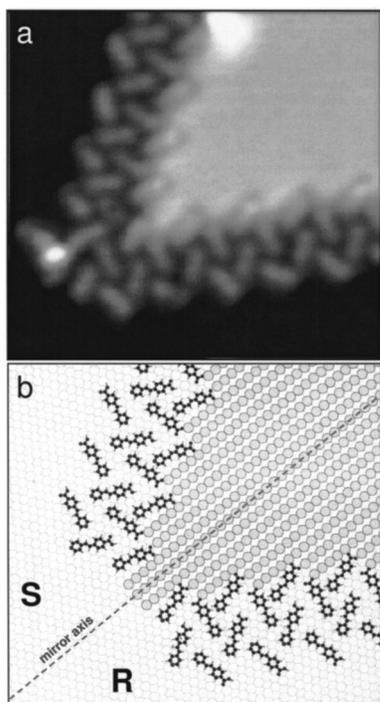


FIG. 4. (a) STM image of a PVBA-induced “sawtooth blade” in a restructured Ag(110) surface terrace ($V_s = 20$ mV, $I = 0.5$ nA, image size: 10×10 nm 2). (b) Structural model of the chiral kink arrangements induced by lateral interaction of molecular carboxylate endgroups with Ag (100) microfacets. The orientation of the adsorbed PVBA is proposed on the basis of theoretical modeling, and occupying all PVBA aromatic rings the high-symmetry substrate sites. Chirality of adsorbed PVBA is proposed following arguments given in the text. The mirror axis of the sawtooth is marked.

facet. The preference of the endgroups’ lateral coupling to the (100) microfacet as opposed to the similarly available (111) microfacet fits well to the general trend that more open surfaces exhibit a higher chemical reactivity. In view of the well-known tendency of carboxylic acids to form carboxylates with Ag,²³ we presume that, as a result of the high temperature annealing, the PVBA heads are deprotonated so that the carboxylic group binds directly to the Ag step atoms. Thus, metal-ligand interactions are associated with the driving force underlying the surface reshaping. This is an action which can be regarded as complementary to the recently reported “nano-molding” of toothlike metal structures with a width of two atomic rows induced by so-called “lander” species on a Cu(110) surface.³² The present observations underline that such effects are highly face-specific and depend strongly on the chemical nature of the employed substrate material: mesoscopic sawtooth restructuring and chiral kink formation under the influence of PVBA was neither found on close-packed (111) surfaces of Ag, Au or Cu nor on the Pd(110) surface. Keeping this delicate restriction in mind, the application of functional groups to connect molecular units and metallic electrodes seems a promising endeavor.³³

A model³⁴ for the PVBA arrangement at the kink sites and the attachment of neighboring molecules is represented in Fig. 4(b). The model is constructed by imposing a constrained geometry to the two topmost molecular chains, i.e., those directly decorating the step edge—consistent with the observed 2×5 arrangement and with the orientation of the benzene rings as revealed by the STM images. The position of the PVBA molecules belonging to the remaining two molecular rows is determined as the structural energy minimum associated to a force field specifically constructed to model the intermolecular interactions in adsorbed PVBA systems, and based on *ab initio* results.²⁰ The structure found is consistent with the benzoic rings preferentially sitting close to high symmetry sites of the Ag(110) surface (ontop or hollow sites³⁵). However it cannot be understood simply in terms of occupation of high-symmetry substrate sites of all aromatic rings, as is the case for PVBA molecules adsorbed in terraces of other metal surfaces.^{19,21,36,37} Considering the structure in Fig. 4(b), we note that while the optimal orientation of PVBA molecules in the third molecular row is determined by electrostatic and steric interactions to be approximately midway between the orientation of its neighboring molecules of the first two rows, the orientation of the molecules in the fourth (lowermost) molecular row is approximately orthogonal to this and misaligned by as much as 30° with the orientation of the row itself. This is consistent with the operation of weak attractive forces between the N tail atoms and H atoms covalently bound to aromatic carbons, as seen in the figure. This linkage structure is significantly different from the optimal bonding structures found in PVBA aggregates on close packed terraces,²⁰ which invariably involve hydrogen bonding of N atoms to acid carboxylic groups, and where the misalignment between molecules and row orientation is at most a few degrees.^{20,21} This suggests that the fourth molecular row in the present system does not provide an optimal template for further aggregation. In particular the formation of further molecular rows on the terrace may be

inhibited, in strong agreement with the experimental observation that regular step decoration is in general limited to four assembled rows.

It is interesting to note that the quadruple chain structure described above possesses supramolecular chirality, i.e., takes two possible configurations related by mirror symmetry, in compliance with the chiral fingerprint of the metal facets acting as template. These are visible, e.g., on the two opposite edges of every single “tooth” in the reconstruction shown in Fig. 2(a), and in Fig. 4(a) showing how the two edges connect seamlessly at sharp angle into a tidily decorated “tooth tip.” Since the (1 $\bar{1}$ 0) plane is a symmetry plane also for the Ag(110) surface, the two configurations have the same formation energy.

The exact chirality of individual PVBA molecules in the structures described is elusive in topographic STM imaging. While we did not attempt to model all the possible quadruple chain arrangements obtainable by mixing molecules of the two chiral species, test calculations indicate that the observed regular patterns can only be produced if a fixed four-molecule PVBA enantiomer sequence is periodically repeated to construct the quadruple chains. For a general analysis of the main features, the enantiomer sequence in the model of Fig. 4(b) has been constructed specifically to match one kind of coordination of the C=C moiety connecting the molecules' aromatic rings with substrate atoms. Together with the chirality of the substrate steps this supports the view that chiral recognition processes are operative during nucleation and assembly of the supramolecular structures, yielding structures with a relatively small amount of chiral defects. It is, therefore, reasonable to suppose that the supramolecular chirality of the sawtooth structure may be related to the 2-D chirality of adsorbed PVBA. Earlier investigations employing PVBA on Ag(111) and Au(111) surfaces demonstrated that chiral recognition is operative in the self-assembly of supramolecular chiral nanostructures.^{20,21} In particular, the different shape of the two chiral molecular species is reflected in small, but decisive energy differences in assemblies stabilized by hydrogen bonds and can account for remarkable effects such as mesoscopic chiral resolution. Besides determining the relative stability of different intermolecular bonding geometries, in the present system chirality-dependent energy differences are expected to be associated to the interaction of chiral adsorbates and kink sites, in analogy with related systems.^{8–10,12} In summary, since the chirality signature of the metal facets of the surface reflect the supramolecular chirality of the ordered patterns at the two sides of the sawtooth, it appears reasonable that chiral recognition mechanisms may actually mediate the minimization of the overall domain energy during surface reshaping and growth of molecular assemblies. In this scenario, the observed symmetric step decoration patterns are the optimal substrate response to the adsorption of a molecular species which comes in two chiral enantiomers and thus can form superstructures with distinct supramolecular chirality.

IV. CONCLUSIONS

A novel type of mesoscopic surface reordering induced by prochiral organic molecules was found. The carboxylic

acid species PVBA reshapes Ag(110) step edges by virtue of a functional group, thus producing a periodic structure of kink sites to accommodate molecules which acts as template for 2D molecular assemblies. This distinct surface rearrangement is mediated by lateral metal-ligand interactions between Ag atoms at (100) microfacets and the PVBA carboxylate moiety. The microfacets exhibit a well defined chiral signature, similarly reflected in the structure of the molecular domains, which we characterize by theoretical modeling. Our results suggest that chiral recognition is operative in both molecular step reshaping and assembly.

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