Adsorption of Enantiomeric and Racemic Tyrosine on Cu(111): A Scanning Tunneling Microscopy Study

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The adsorption of enantiomers and a racemic mixture of tyrosine (tyr) on Cu(111) has been investigated by cyclic voltammetry and electrochemical scanning tunneling microscopy. D-tyr and L-tyr molecules adsorb on Cu(111) and show a (4 × 4) structure. The mirror symmetry between two adlayers is demonstrated by high-resolution scanning tunneling microscope images. The spontaneous separation of racemate into homochiral domains is observed. The result presented here is hoped to supply direct evidence for the chiral adlayer ordering at the solid/liquid interface.

Introduction

Chirality at the surface or interface is of increasing interest both in fundamental study and industrial application. Obtaining enantiopure compounds by enantioselective heterogeneous catalysts is a long-time subject in synthesis chemistry and commonly used in modern pharmaceutical and chemical industries.[1,2] On the other hand, chirality in biology and life may stem from chirality at surfaces. For example, homochiral oligopeptides can be obtained from self-assembled amino acid derivatives at the water/air interface.[3] The unique power of scanning tunneling microscopy (STM) in the study of chirality at the surface has been demonstrated by a number of instances including identifying the absolute chirality of adsorbates,[4,5] observing the chiral faceting and reconstruction of an achiral metal surface induced by chiral adsorbates,[6,7] constructing chiral "channels" from self-assembled chiral molecules,[8] or addressing the enantiomorphous nature of 2-D enantiomer and racemate crystals.[9–11] Compared with the above-mentioned progress, chirality at electrode surfaces seems poorly addressed, despite its obvious importance. The different electrochemical behavior of electrodes modified by enantiopure compounds and the racemate was demonstrated by cyclic voltammetry.[12,13] It is proposed that different adlayer orderings exist at enantiomer- and racemate-modified

electrodes. Recently, Attard et al. studied the electrochemical behavior of chiral adsorbates on different Pt single-crystal metal surfaces.[14] The enantioselectivity of the chiral metal surface was demonstrated by the different electrooxidation of D-glucose and L-glucose. In contrast, similar electrochemical behavior was found on an achiral single-crystal surface. This result is consistent with the thermodynamics study of enantiospecific desorption of chiral compounds from chiral and achiral surfaces.[15] However, there is a lack of direct evidence on the microscopic structure of chiral adlayers at electrode surfaces. It is necessary to conduct in situ and real-space electrochemical scanning tunneling microscopy (ECSTM) studies to elucidate the chiral adlayer orderings of enantiomer and racemate at the electrode/electrolyte interface.

In the present study, the adsorption of tyrosine (tyr), an amino acid, on a Cu(111) electrode was studied by in situ STM and cyclic voltammetry. Another stimulation encouraging us to study the adsorption of amino acids on surfaces is that it represents a model system for understanding the interactions of peptides and proteins with surfaces, a key element of many advanced and emergent applications, such as biosensors, aspects of biocompatibility of artificial biomaterials, and the electron transfer between proteins and surfaces.[16–19] With the high resolution of ECSTM, the adlayer orderings of enantiomeric and racemic tyr on a Cu(111) electrode were revealed. The mirror symmetry between the adlayer of D-tyr and L-tyr is demonstrated by high-resolution STM images, although they all show the same (4 × 4) structures. The spontaneous enantiomeric separation of racemate into homochiral domains was found on the DL-tyr adlayer.

Experimental Section

A commercial Cu(111) single-crystal disk with a diameter of 10 mm (from MaTeck) was used as the working electrode for

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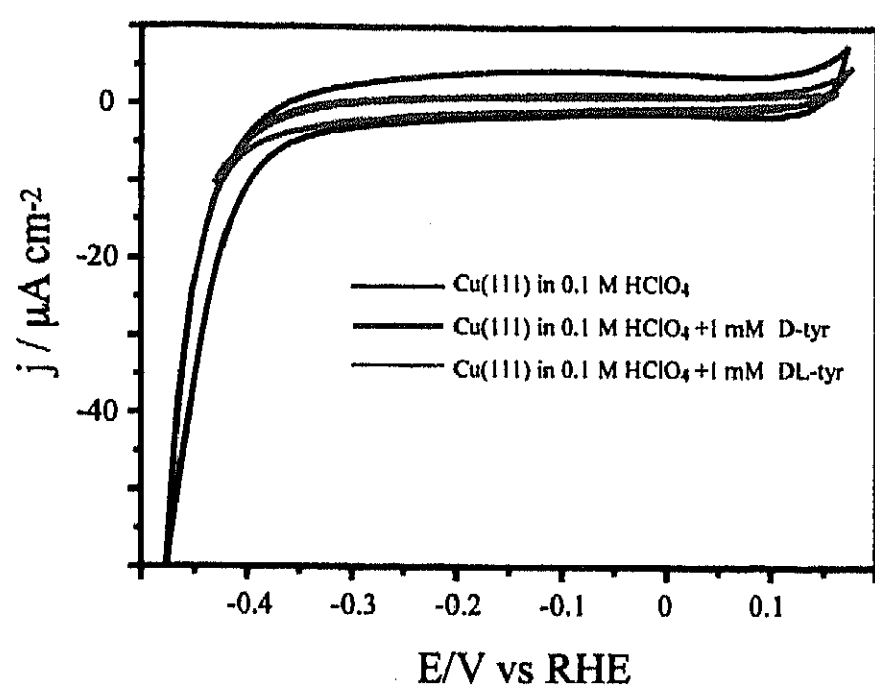
Figure 1. Cyclic voltammograms of the Cu(111) electrode in 0.1 M HClO$_4$ with (green line) and without (black line) the presence of 1 mM D-tyr. Similar CVs were obtained on the L-tyr (not shown here) and DL-tyr (orange line) adlayers. The scan rate was 50 mV/s.

both electrochemical measurement and in situ STM observation. The well-defined single-crystal Cu(111) surfaces were prepared by electrochemical polishing. All solutions were prepared by diluting ultrapure HClO$_4$ and reagent grade D-tyr, L-tyr, and DL-tyr (Cica-Merck, Kanto Chemicals) with Millipore water. A homemade electrochemical cell with a reversible hydrogen electrode (RHE) in 0.1 M HClO$_4$ and a Pt counter electrode was employed for electrochemical measurement. The in situ STM apparatus used was a Nanoscope E (Digital Instruments Inc.). W tips were electrochemically etched in 0.6 M KOH. All electrode potentials were reported with respect to the RHE. The details of the experiment were the same as those described in our previous paper.[20]

Results and Discussion

Electrochemical Measurement. First, cyclic voltammetry was performed to study the electrochemical behavior of enantiomer- and racemate-modified Cu(111) electrodes. The green line in Figure 1 shows the cyclic voltammogram (CV) of Cu(111) in 0.1 M HClO$_4$ + 1 mM D-tyr solution. For comparison, the CV of Cu(111) in 0.1 M HClO$_4$ is also shown by the black line. The featureless CV obtained after the addition of D-tyr indicates no electrochemical reaction involving in the double layer potential region, although the electric charge involved in the double layer becomes smaller due to the molecular adsorption. Similar CVs were observed in the electrolyte containing 1 mM L-tyr (not shown). According to the electrochemical results by Attard, the low Miller index or, in another words, high-symmetry single-crystal surface has no enantioselectivity toward chiral molecules.[14] Thus a similar CV was obtained on the adlayer of enantiomers. It is interesting that the similar CV is also obtained upon DL-tyr adsorption (orange line). The result here significantly differs from that reported by Muskal and Inose,[12,13] indicating that a similar adlayer structure may exist in the enantiomer and racemate adlayers.

STM Measurement. D-*tyr Adlayer*. To understand the adlayer orderings of tyr on the Cu(111) surface, the in situ STM study was performed. The atomic image of a Cu(111)-(1 × 1) structure was routinely discerned on the atomically flat Cu(111) surface in the absence of the molecules for the ease of determining the registry of the molecular adlayers to the underlying Cu(111) lattice. After the examination of the bare Cu(111) surface, a droplet of D-tyr molecules was directly injected into the STM

electrochemical cell. The average concentration of D-tyr in 0.1 M HClO$_4$ was ca. 1 mM. A few minutes later, the uniform adlayer of D-tyr was clearly resolved in the widely extended flat terrace. Figure 2a shows a typical STM image of the D-tyr adlayer acquired at −0.2 V in a relatively large area. A well-ordered defect-free molecular array is seen to extend over the atomically flat terrace. The molecular rows cross each other at an angle of either 60° or 120° within experimental error of ±2°. From a comparison with the Cu(111)-(1 × 1) atomic image, it is found that all molecular rows run parallel to the ⟨110⟩ orientation of the underlying Cu(111) lattice. The intermolecular distance along the ⟨110⟩ orientation is measured to be ca. 1.0 nm, about 4 times the lattice distance of Cu-(111). On the basis of the orientation of molecular rows and the intermolecular distance, we conclude that the observed structure of the D-tyr adlayer is (4 × 4) as shown in Figure 2a by the superimposed drawn unit cell.

More details of the molecular adlayer were revealed by the higher resolution STM image shown in Figure 2b. It is clear that each spot in Figure 2a now appears as an elongated spot with a tail at the end of it. The feature of the molecules is outlined by a visualized symbol ⌐. Binding of amino acids on metal surfaces is important for understanding the interaction between adsorbates and substrates and has a dramatic effect on the adlayer structure. The most common feature of the adsorption geometries proposed for the superstructures of the amino acid/Cu-(110) and Cu(001) systems studied so far is that two oxygen atoms of the carboxyl group bind on the atop sites directly.[21] On the other hand, the phenol groups are hoped to adsorb on the Cu(111) with a flat-lying conformation to maximize the interaction between π electrons and substrate.[20] The recent in situ Fourier transform infrared studies indicate that the adsorption of tyr and phe on Au and Pt electrodes involves the interactions of the carboxyl and π electrons of these two molecules with the substrate.[22,23] Based on the above results and the obtained STM images, a tentatively proposed model for the adlayer of D-tyr on Cu(111) was depicted in Figure 2c. The elongated part is thought to correspond to the p-hydroxylbenzyl, while the tail is ascribed to the carboxyl groups binding on atop sites of the Cu(111) substrate.

The ordered (4 × 4) structure was consistently observed in the potential range from −0.35 to 0 V. At potentials more positive than 0 V, the well-ordered adlayer became disordered. This result is consistent with the CV measurement.

L-*tyr Adlayer*. With a similar procedure, the L-tyr adlayer was prepared on Cu(111). A well-defined adlayer similar to that of D-tyr shown is observed. The same (4 × 4) adlayer structure was obtained by analyzing the registry of the adlayer to the substrate. To get the details of the molecular chirality, a higher resolution STM image as shown in Figure 3a is acquired. A unit cell with (4 × 4) symmetry was superimposed for comparison with that of D-tyr. Although several defects corresponding to the missing molecules were disclosed in the STM image, the adlayer structure was not affected by them, indicating the special stability of the adlayer. It is surprising that each molecule is also composed of an elongated ellipse and a tail.

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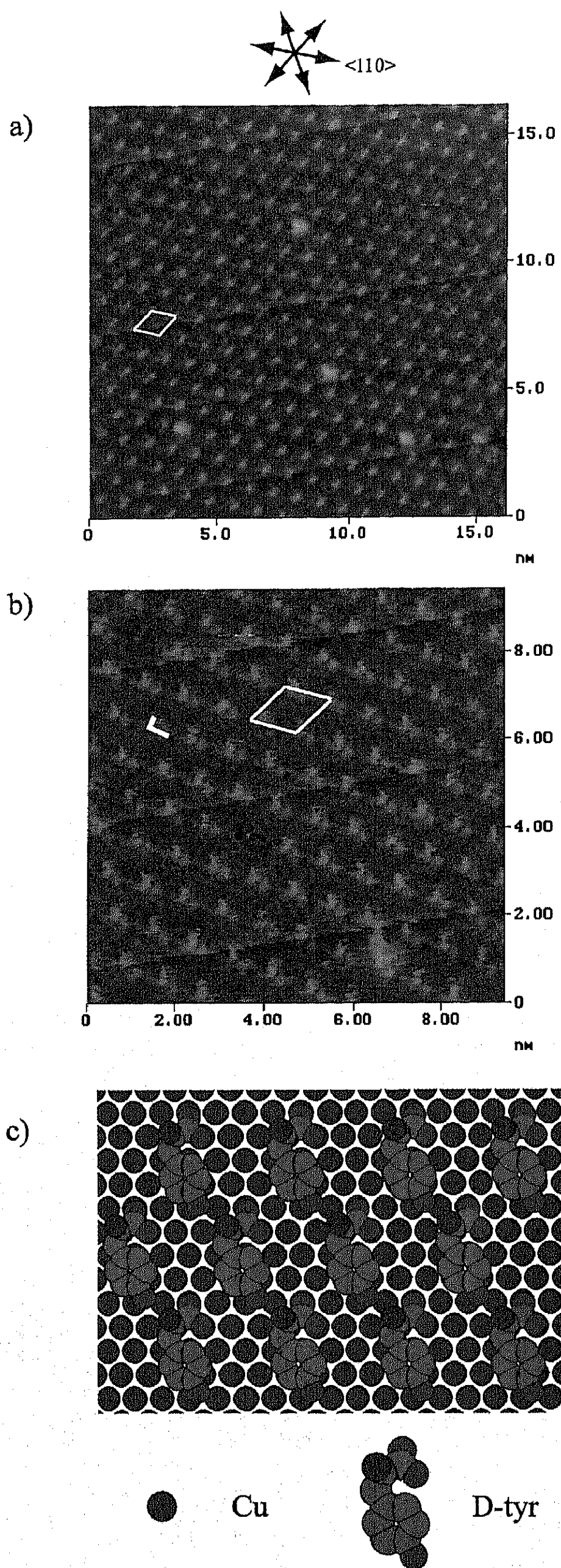
Figure 2. (a) STM top view of the D-tyr adlayer on Cu(111) in 0.1 M HClO₄ + 1 mM D-tyr at −0.2 V. The tunneling current was 10 nA. The scanning rate was 13 Hz. (b) High-resolution STM image of the D-tyr adlayer. The tunneling current was 10 nA. The scanning rate was 13 Hz. (c) A schematic representation of the (4 × 4)-D-tyr structure.
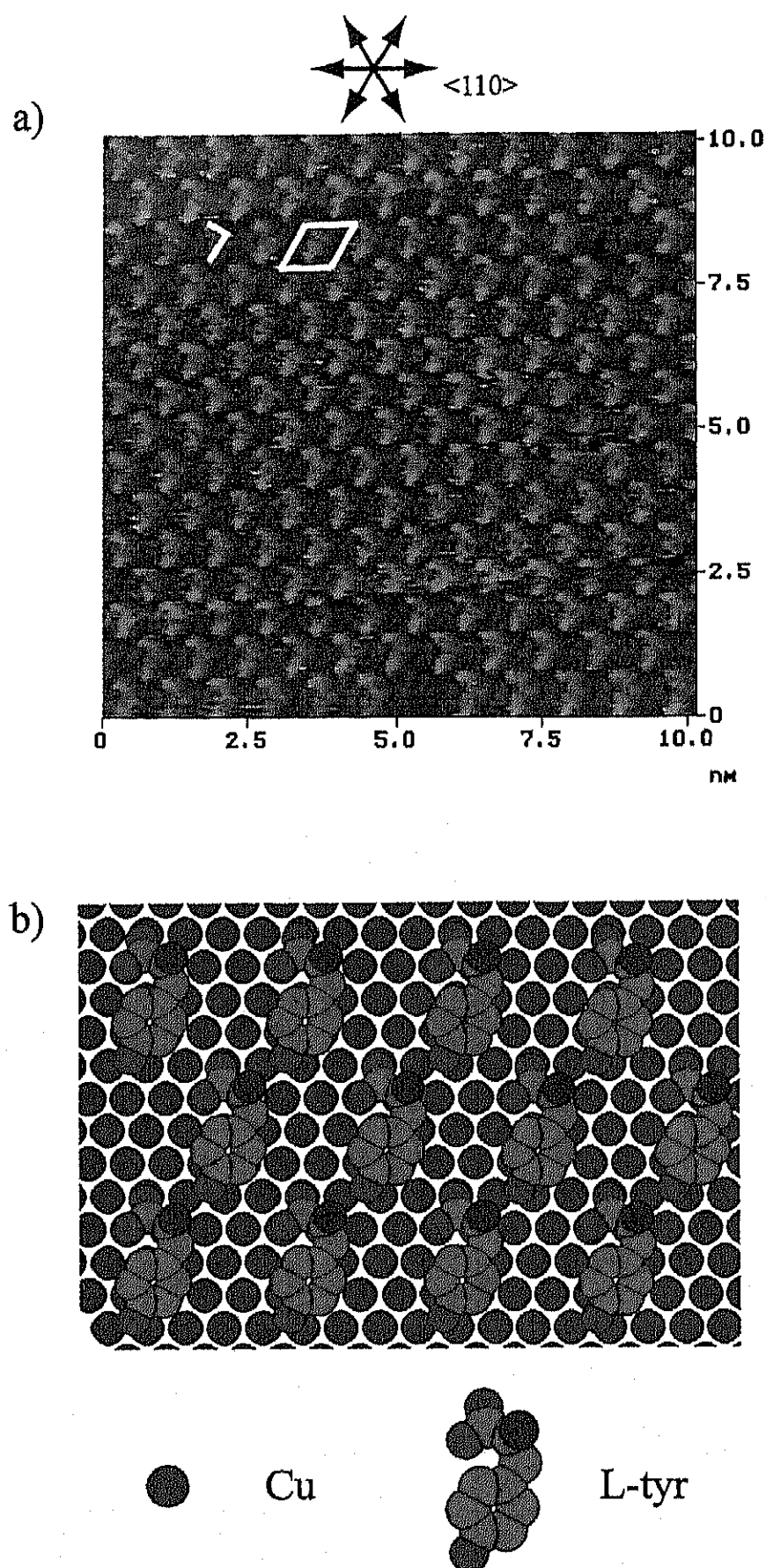

Figure 3. (a) STM top view of the L-tyr adlayer on Cu(111) in 0.1 M HClO₄ + 1 mM L-tyr at −0.2 V. The tunneling current was 10 nA. The scanning rate was 15 Hz. (b) A schematic representation of the (4 × 4)-L-tyr structure.

Similarly, we use the symbol ⌐ to depict the observed STM image. Figure 4a,b shows the magnified images of Figure 2b and Figure 3a. The rotation manipulation was applied on the two images to give a sharp contrast of the similarity of the two adlayers. It is obvious that the two images cannot be superimposed no matter what surface symmetry manipulation is employed. In fact, the two adlayers can be related only by mirror symmetry manipulation. That is, the chiral adlayer of enantiomer with similar structure was obtained on the achiral Cu(111) surface. On the basis of the above-mentioned results, it is natural to propose the model for the adlayer of L-tyr on Cu(111) as shown in Figure 3b. There exists a mirror symmetry between the adsorption geometries of D-tyr and L-tyr. The chirality of the adlayer clearly stems from the chiral adsorption geometries of D-tyr and L-tyr.

The ordered (4 × 4) structure was consistently observed in the potential range from −0.35 to 0 V. At potentials more positive than 0 V, the well-ordered adlayer became disordered. The similar electrochemical thermodynamics
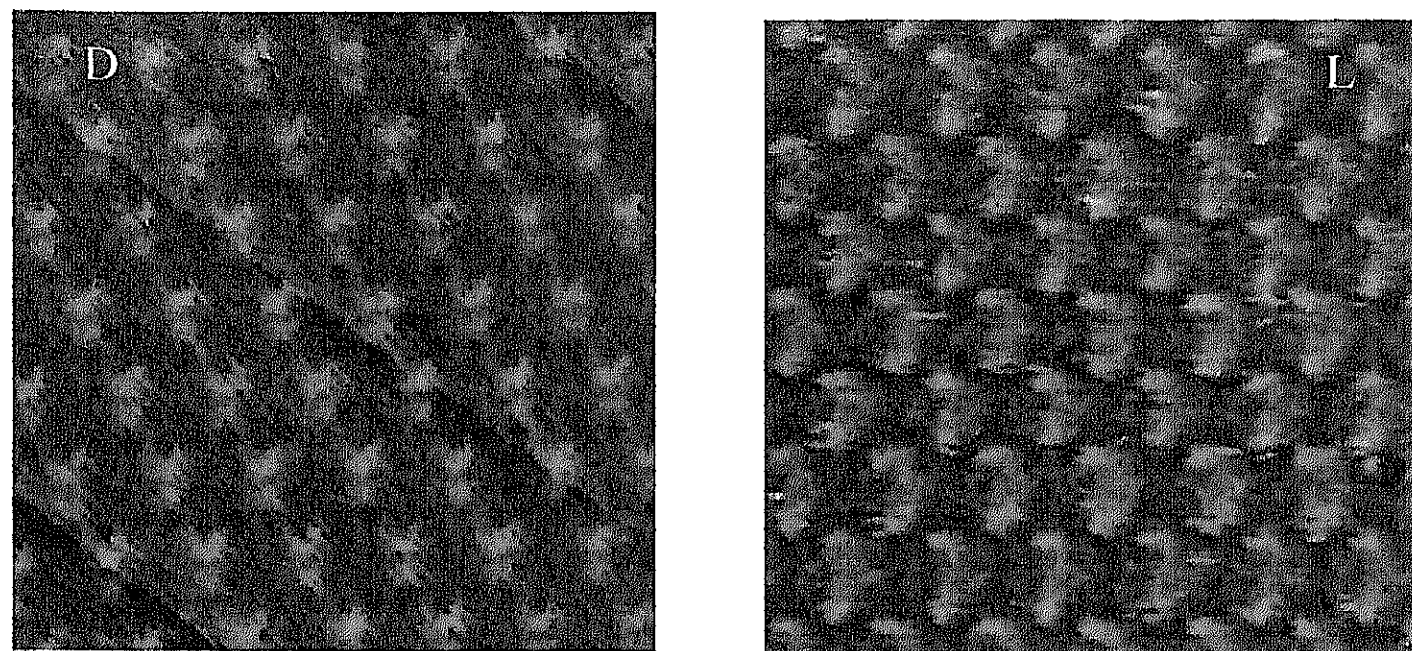
Figure 4. Magnified STM images of D-tyr and L-tyr adlayers in the same scale (6.5 nm × 6.5 nm) to show the mirror symmetry relationship between them.
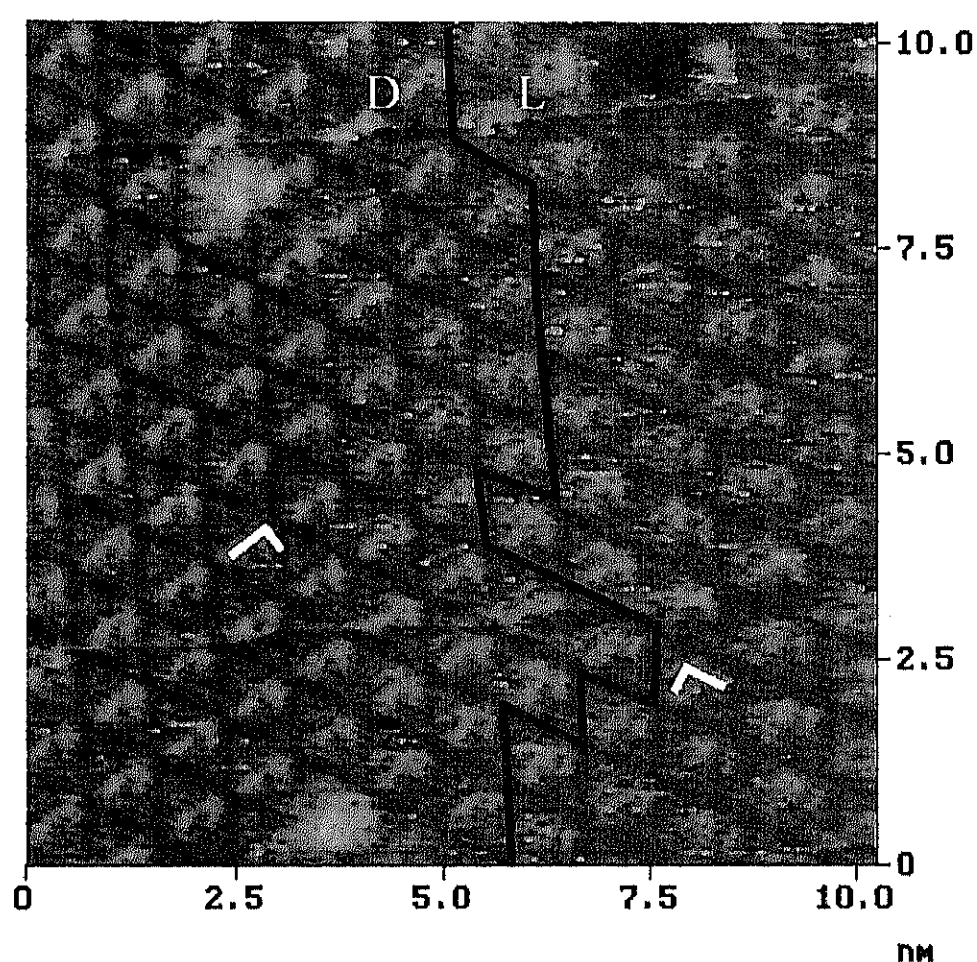

Figure 5. (a) STM top view of the DL-tyr adlayer on Cu(111) in 0.1 M HClO$_4$ + 1 mM DL-tyr at −0.2 V. The tunneling current was 10 nA. The scanning rate was 15 Hz. A domain boundary is indicated by the solid lines.

behavior of D-tyr and L-tyr adlayers indicates the same adsorption energy of enantiomers on the achiral surface.

DL-tyr Adlayer. The observation of chiral adlayers of D-tyr and L-tyr, respectively, on the Cu(111) surface encourages us to explore of the adsorption of the racemic mixture DL-tyr. A few minutes after injecting DL-tyr solution into the STM cell, a uniform adlayer of DL-tyr was formed on the Cu(111) surface. The high-resolution STM images reveal that the adlayer consists of D-tyr and L-tyr domains. The molecular chirality in different domains can be identified by comparing the STM image with the previously obtained images in Figure 4. The domain boundary between D and L chiral domains is shown in Figure 5. The boundary is outlined with a solid line to guide the eye. Intriguingly, the adlayer structure is not affected by the chirality difference at the two sides of the boundary. However, the STM image seems blurry at the two sides, indicating the high mobility of adsorbates at the boundary.

After obtaining the homochiral domains of DL-tyr, the potential was scanned negatively by steps of 10 mV to observe the electrochemical desorption of DL-tyr. At the

potential of −0.4 V, the STM image became unclear, indicating either the desorption or another electrode process occurs. No special stability of one enantiomer over the other one was found in the whole potential range. The result also indicates the equal adsorption energy of the enantiomers on the achiral electrode surface.[11−12,24]

The achiral surface has no enantioselectivity toward chiral molecules. The formation of chiral adlayers of individual enantiomers can be understood because the mirror symmetry of the achiral surface was completely destroyed upon adsorption of chiral molecules, which internally have no mirror symmetry. The chirality of the adlayer stems from the mirror adsorption geometry of the enantiomers. Thus, it is natural to expect that two enantiomers form chiral adlayers with mirror symmetry, because the enantiomers have equal adsorption energy when adopting the mirror adsorption geometry. However, the adlayer structure of racemate adsorbates is a little more complex. The intermolecular interaction is of special importance in determining the formation of homochiral or heterochiral domains when the racemic mixture adsorbs on the surface. The chiral recognition of cysteine on Au-(110) was related with the hydrogen bondings between two cysteines with the same chirality.[25] Other than hydrogen bondings, even weaker coupling between adsorbates may produce a measurable orientational preference and affect the adlayer orderings. For example, the chirality of an 8CB molecule monolayer in molecule corrals was related with that at the terraces.[26] In the present case, the weak coupling between adsorbates with the same chirality determines the formation of the homochiral domains. As the domain grows, the two enantiomers have an equal possibility to approach and attach to the domain edge because the concentration of enantiomers in the solution is the same and the enantiomers can take mirror adsorption geometry with equal adsorption energy upon adsorption. However, in the present case, the coupling between the molecules with the same chirality is preferred to that between enantiomers with different chirality. The molecules with the same chirality as the preadsorbed molecules attach to the domain, and the homochiral domains form.

In summary, the adsorption of enantiomeric and racemic tyr on Cu(111) electrodes was studied by cyclic voltam-

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metry and ECSTM. The similar CV features of Cu(111) in 0.1 M HClO$_4$ with the presence D-tyr and L-tyr indicated that the achiral surface has no enantioselectivity toward enantiomers. With the high-resolution STM image, the chirality of D-tyr and L-tyr was clearly discriminated at the Cu(111) electrode. The two adlayers both have (4 × 4) symmetry. The chirality of enantiopure adlayers is attributed to the mirror adsorption geometry of the two enantiomers on the surface. The difference between racemic and enantiomeric adlayers on the surface is an interesting topic. The different electrochemical behavior of enantiomeric and racemic adlayers has been demonstrated by some previous studies.[12,13] However, no significant difference has been observed between the CV of Cu(111) in the presence of DL-tyr and D-tyr (L-tyr). This result indicates that there exist homochiral domains in the DL-tyr adlayer. In fact, the spontaneous separation of the racemic mixture into homochiral domains was ob-

served by ECSTM. The formation of homochiral domains is not the only result of racemate adsorption. Heterochiral domains of racemic mixture on the achiral surface have been observed in ultrahigh vacuum and ambient environments.[27,28] The heterochiral adlayers of racemate modifiers will be another interesting aspect for future investigation.

LA026821U

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