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A metal surface with chiral memory

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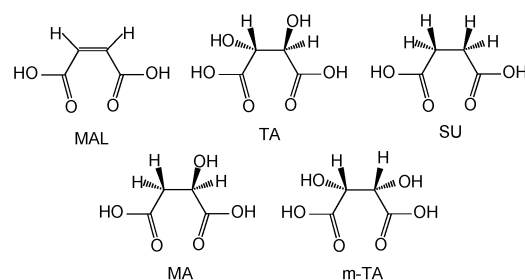
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Adsorption of maleic acid onto the copper(110) surface in ultrahigh vacuum induces a restructuring of the surface such that locally its original mirror symmetry becomes broken. Scanning tunnelling microscopy performed on areas, which contain no molecules after annealing, reveals that Cu adatoms are still lined up on the surface in a chiral fashion.

When a prochiral molecule is adsorbed onto a surface it turns chiral due to mirror-symmetry breaking alignment as adsorbate.¹ Because of equal probability to engage in a left- or right-handed adsorbate motif, formation of both enantiomers is expected. Close packing restrictions or enantioselective interactions, however, may favour local homochirality. In such case a two-dimensional (2D) conglomerate will form.^{2,3} Chiral molecules may also induce restructuring of the metal surface and create chiral facets or pits.⁴⁻⁷ The reconstruction of the topmost atomic metal surface layer by molecules can be considered as initial step of such faceting. Reconstructions have previously been discussed in particular for tartaric acid (TA) and succinic acid (SU) on Cu(110)⁸⁻¹⁰ For TA on Ni(110) reconstruction of the metal surface underneath a tartrate molecule was concluded from density functional theory (DFT).^{11,12} The chiral restructuring of Cu(110) by chiral malic acid has been directly observed by Roth et al. by using scanning tunnelling microscopy (STM).^{13,14} Cu adatoms, placed in a chiral fashion on the surface, were either observed between islands of molecules or between molecular rows. Gellman and Sykes reported recently a chiral metal surface after thermal treatment of a TA/Cu(110) surface system.^{15,16} Prochiral molecules may also show chiral structural effects at step edges.¹⁷

Here we report chiral restructuring of a metal surface by a prochiral molecule, as directly observed by STM. Maleic acid (MAL, Fig. 1) restructures the flat Cu(110) terraces such that they are rendered chiral. After removing the molecules by gentle prolonged annealing, the bare Cu surface is locally still chiral, but globally both enantiomorphs are observed. Hence, the chiral reconstruction induced by the molecules remains intact, even without the origin causing it!

The motivation for studying MAL was based on the chiral zigzag footprint that C4 dicarboxylic acids impose to the Cu(110) metal surface.^{18,19} All carbon atoms of MAL are sp² hybridised, so a higher barrier for a zigzag deformation of the molecular backbone with its double bond, and therefore for a chiral footprint, was expected. Moreover, MAL is not necessarily prochiral. Adsorbed in a planar geometry it still possesses mirror symmetry, and if this mirror plane becomes aligned parallel with a mirror plane of the substrate, the surface system remains achiral. However, judged on low-energy electron diffraction (LEED) studies, MAL forms actually identical superstructures as SU on Cu(110), suggesting a similar adsorbate structure.



Scheme 1. Structural formulas for the C4 dicarboxylic acids maleic acid (MAL), tartaric acid (TA), succinic acid (SU), malic acid (MA) and meso-tartaric acid (*m*-TA).

Preparation of the copper surface *in vacuo* has been described in detail previously.²⁰ Cleanliness and crystallographic quality were evaluated with X-ray photoelectron spectroscopy (XPS) and LEED. The freshly prepared surface (held at room temperature) was exposed to MAL vapour, sublimed from a home-made evaporator held at 50 °C. Coverage calibration has been performed with XPS and by means of a c(2×4) structure observed in LEED at saturation of the monolayer after gentle annealing. This structure has an absolute coverage of $\theta=0.25$, i.e., one molecule per four Cu surface atoms. Integrity of the molecule on the surface was tested by reflection-absorption infrared spectroscopy (RAIRS) and by thermal desorption spectroscopy (TDS). STM images were taken with a

variable-temperature instrument (Aarhus 150, SPECS) in constant current mode. Negative voltages describe tunnelling into unoccupied states of the molecules and the surface. Where mentioned, STM images were filtered after fast Fourier transformation (FFT) with a first order low pass Butterworth filter to remove the higher frequency noise followed by inverse FFT.

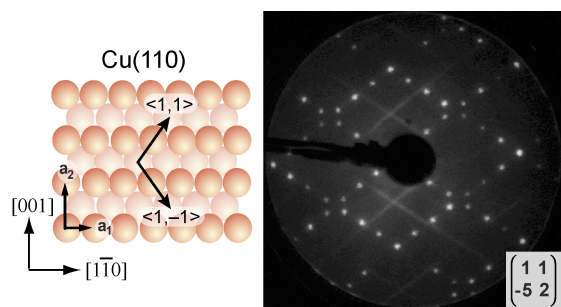


Figure 1. The LEED pattern of the (1 1, -5 2) structure of maleic acid on Cu(110) ($E_p = 55\text{eV}$, $T = 28\text{ }^\circ\text{C}$) is comprised of two enantiomorphous domains. The shown surface model is aligned to the LEED pattern.

At a coverage of 65% of the complete monolayer and after prolonged gentle annealing (30 minutes at $150\text{ }^\circ\text{C}$) a (1 1, -5 2)[†] LEED diffraction pattern with sharp spots was obtained (Figure 1). Its diamond-shaped sectors show also weak stripes that indicate in addition a double periodicity, i.e., (2, 2) periodicity, superimposed on a (1, 1) periodicity of stronger or better-ordered scatterers. Although this pattern has overall C_{2v} symmetry, it is actually a superposition of two mirror domains. That is, the electron beam probes two laterally separated chiral structures with domain sizes that are smaller than the size of the electron beam ($\varnothing \approx 200\text{ }\mu\text{m}$). In one mirror domain an adsorbate lattice vector points into the $\langle 1, 1 \rangle$ direction in the surface plane, in the other mirror domain into the $\langle 1, -1 \rangle$ direction (Fig. 1, for definition see Supplementary Information Fig. 1). Whether the single domains are homochiral, i.e., the molecules in a single domain occupy the same absolute handedness upon adsorption, remains unclear. Both enantiomers within the unit cell could also be aligned in a mirror symmetry-breaking motif.^{13,21}

The chemistry of MAL on Cu(110) is also quite similar to TA and SU at this coverage and treatment. RAIR spectra strongly suggest that MAL is bound in the (1 1, -5 2) structure with both carboxylates to the surface after double deprotonation. Under our preparation conditions the hydrogen would then desorb as H_2 after recombination.²²

For the (1 1, -5 2) structure basically two structural motifs are observed in STM. Fig. 2a shows a (1 -1, 4 3) domain, which constitutes the opposite mirror domain of the (1 1, -5 2) domain. The molecules appear as bright lobes and are aligned in zigzag rows along the $\langle 1, 1 \rangle$ direction. In a few cases complete rows of molecules are missing and the surface shows rows of Cu atoms in those gaps, which are aligned exactly along the same direction as the molecules. The coexistence of Cu adatom and molecular rows has previously been reported for racemic malic acid on Cu(110).¹³ At higher magnification it is clearly seen that the molecular rows have a periodicity with twice the distance in $\langle 1, -1 \rangle$ than observed for Cu atoms (Fig. 2b). Exactly this discrepancy in periodicity between LEED and STM has been discussed for SU/Cu(110). The (1, ± 1) periodicity has been observed in LEED for a (1 1, -6 3)[‡] structure, but STM showed only (2, ± 2) periodicity for the molecules without identifying any Cu adatoms.⁸ This leads to the conclusion that the LEED pattern here is dominated by the arrangement of the Cu atoms, which are much stronger electron scatterers than carbon and oxygen atoms. The weak streaky feature in the LEED pattern reflects

the (2, ± 2) periodicity of the molecular adlattice. This feature disappears upon prolonged electron exposure, but reappears after the beam is turned off and on again, which shows that the molecules do not desorb under the electron beam.

At some places of the surface, patches that do not show any molecules, but still the metal surface reconstruction, can be observed in STM (Fig. 2c). Here, the true (1 1, -5 2) periodicity as established by the Cu adatoms is observed. Weak darker features are also observable between the rows. These are either decomposition products of the molecules or pits, i.e., the original location of the adatoms in the rows. The annealing temperature used for preparation is far below the decomposition temperature, as determined by TDS. However, MAL decomposes in an autocatalytic “surface explosion” reaction which is highly coverage dependent and shows induction far below the temperature determined in TDS.^{16,23} The prolonged annealing may therefore induce at some places already this decomposition step, leading to empty surface areas. We can only speculate about the mechanism of stabilizing the chiral metal surface. The annealing temperature seems to be too low for restructuring the Cu(110) surface back into its original shape. Carbon is usually detected after complete decomposition, so there might be additional meta-stabilizing factors, like debris between the Cu rows. The chiral copper metal islands are relatively small and still surrounded by molecules (Supplementary Information Figure 2), which may also have a stabilizing influence.

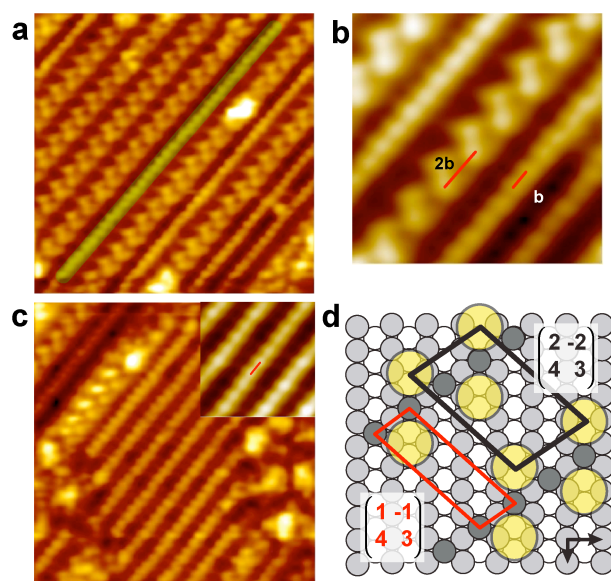


Figure 2. STM images and tentative model for the (1 1, -5 2) structure. (a) STM image of the (1 -1, 4 3) domain [= mirror domain of (1 1, -5 2)]. A zigzag row of molecules is the basic motif. The green semi-transparent line marks a row of Cu adatoms ($17\text{ nm} \times 17\text{ nm}$, $I = 680\text{ pA}$, $U = 464\text{ mV}$). (b) STM image highlighting the doubled periodicity of the molecular unit cell with respect to the adatom row periodicity ($4.8\text{ nm} \times 4.8\text{ nm}$, $I = 780\text{ pA}$, $U = 464\text{ mV}$, filtered). (c) STM image of chiral metal area without molecules ($17\text{ nm} \times 17\text{ nm}$, $I = 780\text{ pA}$, $U = 464\text{ mV}$, inset: $4.8\text{ nm} \times 4.8\text{ nm}$, filtered). (d) Tentative model for a reconstructed Cu(110) surface with Cu adatom rows stabilized by MAL molecules. The molecular adlattice unit cell and the adatom lattice unit cell are indicated.

For the complete intact adsorbate structure, the adatom rows are decorated with molecules. The distance between two bright lobes in molecular zigzag motif is too large in order to be parts of the same molecule.²⁴ This leads to the conclusion that the (2 2, -5 2) and (2 -2, 4 3) domains contain two molecules per unit cell, whereas the surface (1 1, -5 2) and (1 -1, 4 3) cells contain only one molecule

(Fig. 2d). It is assumed that the molecules are bound with their carboxylate groups to the adatoms, thus stabilizing them on the surface. That carboxylates stabilize Cu adatoms has been observed before on Cu(100).²⁵ As source for adatoms serve very likely step edges, similar to the “added-row” mechanism identified for the Cu(110)-(2x1)O reconstruction.²⁶

Our results also shine new light onto the chiral amplification mechanism via the so-called Sergeants-and-Soldiers principle, as observed for SU and *m*-TA with TA as chiral dopant on Cu(110).^{27,28} If Cu adatom rows are present in the “soldier” phases of SU and *m*-TA as well, the chiral “sergeant” gives the adatom alignment a bias either in favour of the $\langle 1, 1 \rangle$ or $\langle 1, -1 \rangle$ alignment. That TA forms Cu adatoms underneath the molecular structure has not been proven yet. However, the $(1\ 2, -8, 2)$ [¶] structure of MA on Cu(110), which has been observed for TA as well,^{29,30} shows exactly adatom rows along the $\langle 1, \pm 2 \rangle$ direction.¹⁴

In conclusion, after gentle prolonged annealing of maleic acid adsorbed on the Cu(110) surface a reconstructed surface structure is formed, in which in part molecules are removed from areas without lifting the surface reconstruction. Such preparation provides a direct “view” by STM onto the reconstructed surface that would have been inaccessible with the molecules still in place.

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Notes and references

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† The (2×2) transformation matrix, linking the adsorbate lattice vectors (b_1, b_2) to the substrate lattice vectors (a_1, a_2) via $b_1 = m^{11}a_1 + m^{12}a_2$ and $b_2 = m^{21}a_1 + m^{22}a_2$, is written here in the form $(m^{11} \ m^{12}, m^{21} \ m^{22})$. The $(1\ 1, -5\ 2)$ structure has previously been described by us as $(7\ 0, \pm 1\ 1)$.²⁷ A more consistent definition for surface unit cells, in particular for chiral domains, is used here now.³¹ That includes the master matrix convention: The structure as whole is named after the one of all the mirror and rotational domains that has a highest priority. Here: $(1\ 1, -5\ 2)$ structure. Its mirror domain is actually $(1\ -1, 4\ 3)$.

‡ Named $(9\ 0, \pm 1\ 1)$ in the original paper.

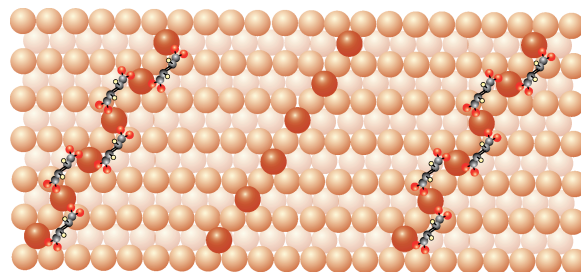
¶ Named $(9\ 0, \pm 1\ 2)$ in the original papers.

Electronic Supplementary Information (ESI) available: Long-range STM image and definition of surface directions. See DOI: 10.1039/c000000x/

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Prochiral molecules induce locally a chiral restructuring of the Cu(110) surface that persists after removal of the molecules.