

Self-assembly and chiral recognition of butanedioic acids on Cu(110)

Christian Roth¹, Daniele Passerone², Davide Ferri³, Manfred Parschau¹, Karl-Heinz Ernst¹

¹Nanoscale Materials Science, Empa-Swiss Federal Laboratories for Materials Research, Dübendorf, Switzerland

²nanotech @ surfaces, Empa- Swiss Federal Laboratories for Materials Research, Dübendorf, Switzerland

³Laboratory for Solid State Chemistry and Catalysis, Empa- Swiss Federal Laboratories for Materials Research, Dübendorf, Switzerland

The enantiomeric purity of a chiral compound in pharmaceutical products or fragrances is of paramount importance. Thus, enantioselective synthesis became very important, as reflected by the 2001 Nobelprize in chemistry awarded to scientists working in that field. In particular enantioselective heterogeneous catalysis, in which a chiral modifier at the metal surface guides a reaction towards a single enantiomer, is a sustainable approach. However, neither the transfer of chirality from a single modifier molecule into extended 2D crystals nor the nature of the stereochemical control between modifier and reactant is clear.

We studied the adsorption and two-dimensional self assembly of enantiopure and racemic malic acid (MA, Fig. 1a) as well as chiral recognition between tartaric acid (TA, Fig. 1b) and MA on Cu(110) by means of temperature programmed desorption (TPD), reflection adsorption infrared spectroscopy (RAIRS), UV- and X-ray photoelectron spectroscopy (UPS, XPS), low energy electron diffraction (LEED), as well as scanning tunneling microscopy (STM).

Depending on the coverage and the deposition conditions, a family of different enantiopure and racemic MA structures has been observed via LEED and STM. Via STM reconstruction of the underlying Cu surface has been observed for different structures. This suggests a pronounced chirality transfer via the substrate, rather than by intermolecular hydrogen bonding.

In the cross-contamination experiments of TA with MA a suppression effect can be observed: The mixture of left and right handed TA (*rac.*-TA) shows a superposition of the two homochiral enantiomorphs in LEED. Adding one enantiomer of MA to the mixture suppresses formation of one of the two enantiomorphs. (*R*)-MA allows thereby only the formation of the structure known for pure (*R,R*)-TA, while (*S*)-MA leads to the (*S,S*)-enantiomorph. STM investigations and density functional theory (DFT) calculations suggest energy minimization as driving force. This includes the formation of heterochiral, pseudo-racemic triplets of molecules in a low-ordered region by strong intramolecular hydrogen bonds.

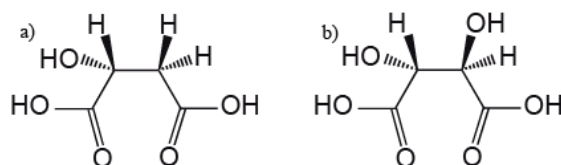


Figure 1: Structural formula of butanedioic acids.
a) (*R*)-MA, b) (*R,R*)-TA.