"TUNING THE EXPRESSION OF SUPRAMOLECULAR CHIRALITY BY MOLECULAR FOOTPRINT ENGINEERING ON METAL SURFACES"

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The emergence of homochirality in biomolecular systems is one of the most intriguing open questions of Nature. The self-assembly and amplification of chiral subunits into higher-order species is crucial in understanding the development of homochirality in biological function. On the other hand, a practical perspective of molecular chirality arises from the fact that the two mirror images of a chiral molecule can have vastly different physiological impacts when ingested by living organisms [1]. As a consequence, there is a strong industrial need to produce and separate single enantiomers (i.e., *Chirotechnology*).

Unraveling the basics mechanisms of chiral recognition, templation and enantioselectivity is then crucial for the development of more effective separation methods and reactions used to achieve enantiopurity. Amino acids and peptides appear as good candidates for the creation of enantioselective surfaces, since they present a variety of functional groups that can be chosen to achieve specific reactions.

Although the enantioselectivity of metal surfaces templated with organic modifiers has been demonstrated by a couple of experiments over the past years [2], the requirements for the design of enantioselective surfaces are not yet clear. In particular, local characterization of the supramolecular structures formed by the chiral modifiers and systematic studies on the effects of specific molecular adsorption and 'chiral footprints' [1] of the same molecule on the templating effect are very rarely found in literature [3]. One proposition is that for a surface to show enantioselectivity, the template molecule should be rigidly bonded to the surface in order to prevent azimuthal rotation of the chiral center [4]. This lack of freedom would allow the adsorption mode of the chirally modified organic reactant to be more strictly controlled, enabling the enantioselective response to survive under a variety of conditions [5]. More recent studies on amino acids seem to support this hypothesis, suggesting that two anchoring adsorption points are needed for chiral templating to work [3].

To get an insight into the basic requirements for bestowing chirality to achiral metal surfaces, we have studied the chiral templation of the amino acid L-Phe (Figure1.1a, 1.2) on the Cu (110) substrate. As a first step, information on the local level was obtained by Scanning Tunneling Microscopy (STM). Reflection-Absorption Infrared Spectroscopy (RAIRS) and Temperature Programmed Desorption (TPD) have been combined to determine the chemical states, orientations, molecular arrangements and bonding interactions of the molecules at the Cu surface. The interpretation of the adsorption geometries was aided by molecular dynamics simulations. The studies show that L-Phe is present on different chemical states going from acidic to zwitterionic to anionic depending on the adsorption temperature in the 85 K-400 K range. We concentrate on the phase at 400 K to discuss the interplay of inherent molecular chirality and the expression of chiral motifs induced by the preferential adsorption geometry of two anchoring points to the surface in terms of conformational flexibility and optimized molecule-surface interactions (*footprint chirality*).

[1] the adsorption geometry determined by the preferential interaction of specific functional groups in close proximity to the surface

Moreover, we study the effect of a third anchoring point molecule-surface by comparative adsorption of different isomers of L-Tyr (Figure 1.1b, 1.3) on Cu(110). Our results show that preventing the conformational flexibility for rotation of the functional groups around the chiral center is crucial for the expression of only one chiral footprint on the surface. This is likely to play an important role for potential enantioselective reaction paths on the templated surface.

We have recently demonstrated that chiral recognition of adsorbed dipeptides takes place via an induced-fit mechanism [6,7]. Moreover, we can now show that conformational rigidity is a key parameter for the expression of footprint homochirality on metal surfaces and that this parameter can be tuned by the appropriate choice of the amino acid residue [8].

References:

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Figures:

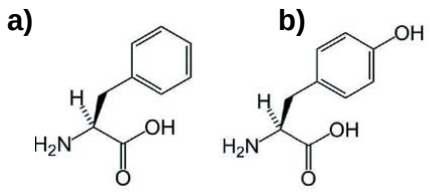

Figure 1.1 a) squematic drawing of L-Phe .b) squematic drawing of L-Tyr

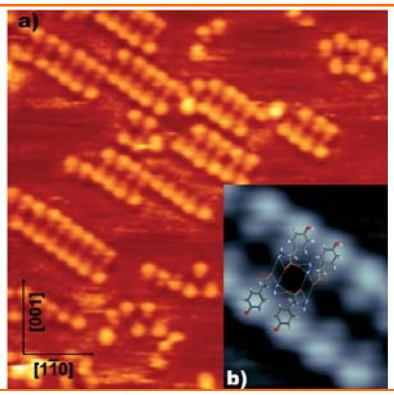

Figure 1.3
a) Supramolecular chains of L-Tyr on Cu(110).b) HR STM image

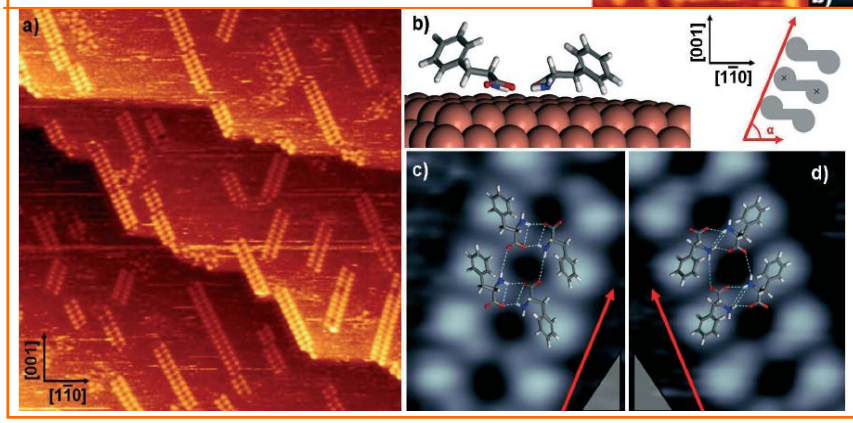

Figure 1.2 Supramolecular chains of L-Phe on Cu(110) . a) STM image c),d) HR STM (4x3 nm) of the different adsorption motifs and superimposed schematic model. b) lateral view of the model proposed in c). The triangles indicate mirror-imaged footprints.