Surface Science xxx (2014) xxx–xxx

Contents lists available at ScienceDirect

Surface Science

journal homepage: www.elsevier.com/locate/susc

Organizational chirality expression as a function of the chirality measure of simple amino alcohols on Cu(100)

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ARTICLE INFO

Available online xxxx

Keywords:
Chirality measure
Amino alcohols
Cu(100)
Ethanolamine
Alaninol
Butanolamine

ABSTRACT

Chiral self-assembled molecular networks (SAMNs) are important for technological and fundamental reasons. In spite of the large number of works in this field, the mechanism of chirality transfer from single molecules to large-scale two-dimensional (2D) networks is not fully understood yet. This work reports on the self-assembly of simple amino alcohols with different chirality measures on Cu(100). Ethanolamine (2-amino-1-ethanol), alaninol (2-amino-1-propanol) and butanolamine (2-amino-1-butanol) adsorbed on Cu(100) have been investigated with scanning tunneling microscopy (STM), low-energy electron diffraction (LEED), photoelectron spectroscopy (PES) and density functional theory (DFT) calculations. This study addresses the role of the single-molecule handedness in the global chirality expression, showing how the chirality measure of the precursors plays an important role in the formation of globally chiral superstructures.

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1. Introduction

Chiral SAMNs are important in a large number of applications where enantioselectivity is required, such as in the synthesis of pharmaceutical compounds and in heterogeneous catalysis [1–4]. Chirality at surfaces can manifest at different scales, with local or global character [5–7]. The handedness at the single-molecule level is a crucial parameter in determining the self-assembling symmetry upon adsorption on surfaces. Intrinsically achiral molecules may assemble on surfaces in 2D networks with local organizational chirality but with no global handedness, due to the degeneracy of mirror enantiomorphs [6]. On the other hand, adsorption of chiral precursors typically leads to chiral superstructures that break the substrate mirror symmetry, although 2D lattices with no handedness may form as well [8,9].

In 2D self-assembled nanostructures the complex interplay between molecule–substrate and intermolecular interactions dictates the order and the stability of the system [10]. Molecules are laterally bonded through weak forces such as Van der Waals (VdW) [11,12], π–π stacking [13,14], hydrogen bonding [15,16], halogen bonding [17,18] and organometallic interactions [19,20], which in turn also allow for long-range order and self-healing of defects [21]. If the building blocks of a SAMN are chiral, molecular recognition events can lead to chirality transfer from the single molecule to the extended 2D lattice. Research in this field is in progress but a detailed explanation for the chirality-transfer process is still lacking.

A quantitative approach to the concept of the chirality of an object is a challenging task. Several attempts have been made to provide a chirality measure [22–27] and many difficulties have been pointed out by the various authors. One of the mostly used methods for developing a chirality metrics suitable to molecules is based on the concept of the

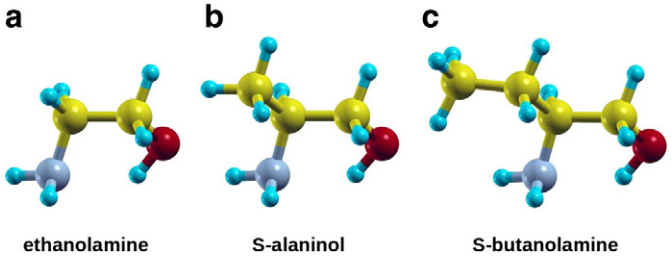

Fig. 1. Molecular structure of (a) 2-amino-1-ethanol (ethanolamine), (b) (S)-2-amino-1-propanol (alaninol) and (c) (S)-2-amino-1-butanol (butanolamine). Oxygen is displayed in red, nitrogen in blue, carbon in yellow and hydrogen in cyan. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Abbreviations: Scanning tunneling microscopy, STM; Low-energy electron diffraction, LEED; Photoelectron spectroscopy, PES; Density functional theory, DFT.

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http://dx.doi.org/10.1016/j.susc.2014.02.006

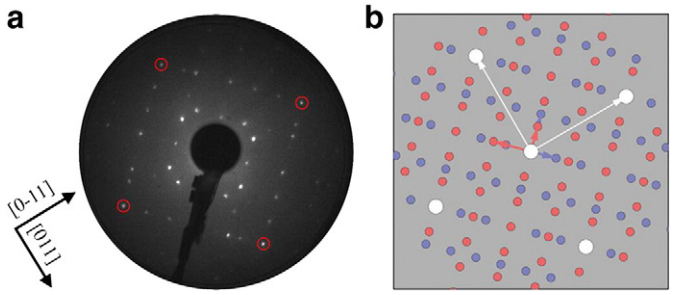

Fig. 2. (a) Experimental achiral LEED pattern of S-alaninol on Cu(100) at RT ($E_p = 67$ eV); red circles indicate the Cu(100) 1×1 spots. (b) Simulated pattern, obtained by merging two superstructures described by the matrices $(3\ 3, 2\ -2)$ (blue spots) and $(2\ 2, 3\ -3)$ (red spots); the two unit cells are identical, except for a 90° rotation. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

Hausdorff distance between sets (Hausdorff chirality measure) [23]. Starting from this concept, we studied how the chirality expression in the molecular adlayer obtained by the adsorption of simple amino alcohols on Cu(100) varies as a function of the chirality measure of the precursors. In this work we report on the self-assembly on Cu(100) of three amino-alcohols with different lengths of the aliphatic chain: the achiral 2-amino-1-ethanol (ethanolamine), the chiral (S)-2-amino-1-propanol (S-alaninol) and the chiral (S)-2-amino-1-butanol (S-butanolamine) (Fig. 1). The chirality measure, referred to its own enantiomer, increases for the investigated molecules as a function of the length of the aliphatic chain (0, 0.33 and 0.42, respectively) [23].

In a previous study on the organizational chirality of R- and S-alaninol on Cu(100), we have already shown that the two enantiomers self-assemble in a chiral single-phase domain, composed of molecular tetramers [7,28–32]. Further investigations on this system, reported in this paper, show the possibility of obtaining a globally achiral molecular superstructure. This dual behavior observed for S-alaninol has been compared with the one of ethanolamine and S-butanolamine on Cu(100) by means of scanning tunneling microscopy (STM), low-energy electron diffraction (LEED) and photoelectron spectroscopy (PES) techniques, supported by density functional theory (DFT) calculations.

2. Experimental and theoretical methods

The experiments were carried out in different ultra-high vacuum (UHV) apparatuses with a base pressure below 10^{-8} Pa. STM analyses were performed with an Omicron LT-STM. STM images were collected at room temperature (RT) using a tungsten tip cleaned by electron bombardment, with an applied bias voltage (V_s) referred to the sample; data were analyzed with the program WSxM [33].

Photoelectron data were obtained using an X-ray laboratory source (Al Kα) for core state X-ray photoelectron spectroscopy (XPS) and synchrotron radiation (SR) for valence state ultraviolet photoelectron spectroscopy (UPS). SR experiments were carried out at the Circular Polarization (CiPo) beamline (Elettra, Trieste, Italy), equipped with grazing or normal incidence monochromator and using an Omicron 125 hemispherical electron energy analyzer. The binding energy (BE) scale was calibrated using the Cu 3p core line and the Fermi level. Experimental data are reported after a Shirley background subtraction [34]. All molecular depositions and spectroscopic analyses, except where differently specified, have been performed at RT. The Cu(100) surface was cleaned by repeated cycles of Ar^+ sputtering (with a pressure of 5×10^{-4} Pa and energy ranging from 600 to 1000 eV) and annealing at about 800 K. Ethanolamine, S-alaninol and S-butanolamine (Sigma-Aldrich), liquid at RT, have been purged by repeated freeze–pump–thaw cycles before introduction into the UHV system through a leak valve. The overall pressure in the preparation chamber was kept in the low 10^{-7} Pa range, while controlling the molecular purity during deposition by means of a mass spectrometer. The substrate exposure to the molecular vapor is expressed in Langmuir ($1\ L = 1.33 \times 10^{-4}$ Pa × s).

The adsorption of the three aminoalcohols on Cu(100) was modeled by DFT using the plane-wave pseudopotential code Quantum Espresso [35]. The employed ultrasoft pseudopotentials use a semilocal Perdew–Burke–Ernzerhof treatment of exchange and correlation energy [36]. A kinetic energy cutoff of 25 Ry was used in the plane-wave expansion. The system was represented in a repeated slab approach, with the Cu(100) surface composed by three atomic layers separated by 1.68 nm of vacuum. The model describes the adsorption of an isolated molecule using a 4×4 Cu(100) surface cell, that provides enough separation between the periodic replicas of the adsorbed molecule. The surface Brillouin zone was sampled by a 4×4 Monkhorst–Pack mesh of *k*-points [37]. The systems were relaxed using the Broyden–Fletcher–Goldfarb–Shanno algorithm [38–41] until the forces on each ion were reduced below 10^{-3} a.u. Semiempirical dispersion corrections to the forces were applied to better describe weak physical interactions, such as van der Waals interactions or non-covalent bonds [42,43]. Core level BE shifts for N 1s and C 1s were calculated, in the framework of pseudopotential DFT, as total energy differences between ionized and neutral states in the same geometry; relative BEs are obtained as differences with respect to a reference configuration [44]. Constant-density STM images, that can be compared to experimental constant-current

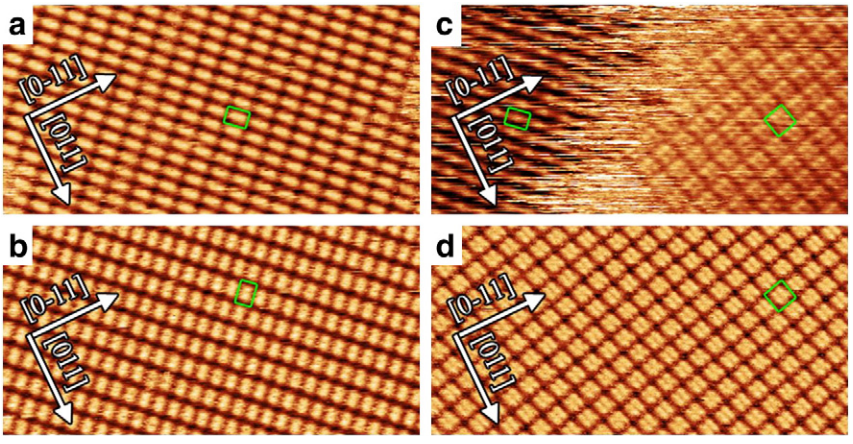

Fig. 3. 20×10 nm^2 constant-current STM images of (a), (b) the two achiral overlayers of S-alaninol on Cu(100) ($V_S = 1.0$ V, $I_t = 2$ nA), (c) the coexisting achiral (left) and chiral (right) domains of S-alaninol on Cu(100) ($V_s = 1.0$ V, $I_t = 2$ nA) and (d) chiral overlayer of S-alaninol on Cu(100) ($V_s = 0.1$ V, $I_t = 0.1$ nA).

Please cite this article as: F. Ronci, et al., Organizational chirality expression as a function of the chirality measure of simple amino alcohols on Cu(100), Surf. Sci. (2014), http://dx.doi.org/10.1016/j.susc.2014.02.006

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