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Christophe Méthivier, Hervé Cruguel, Dominique Costa, Claire-Marie Pradier, Vincent Humblot. Tuning Surface Chirality of Adsorbed Gly-Pro Dipeptide/Cu(110) by Changing its Chemical Form via Electrospray Deposition.. *Langmuir*, 2016, 32 (51), pp.13759-13763. 10.1021/acs.langmuir.6b03553 . hal-01401619

HAL Id: hal-01401619

<https://hal.sorbonne-universite.fr/hal-01401619>

Submitted on 23 Nov 2016

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Tuning Surface Chirality of Adsorbed Gly-Pro Dipeptide/Cu(110) by Changing its Chemical Form *via* Electrospray Deposition.

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KEYWORDS: *Surface Chirality, Gly-Pro dipeptide, Sublimation, electrospray ionisation, Scanning Tunnelling Microscopy.*

ABSTRACT: By changing the Ultra High Vacuum (UHV) deposition method, classical sublimation versus electrospray ionization, one can tune the chemistry of a chiral dipeptide molecule (Gly-Pro, GP), when adsorbed on a Cu(110) surface, from anionic to zwitterionic, respectively. This chemical shift will influence the adsorption mode of the dipeptide; either in a three-point fashion in the case of anionic GP molecules with a strong interaction between the copper surface, both O atoms of the carboxylate moiety and the nitrogen atoms, while in the case of zwitterions GP, the adsorption mode relies on the sole interaction of 1 carboxylate oxygen atom. These different anchoring modes strongly modify the expression of surface 2D chirality and the supramolecular assemblies with two very distinct unit cells.

Introduction

Adsorption of biomolecules such as amino acids and peptides on surfaces is of the highest importance in the understanding of biointerfacial phenomena¹, e.g. for the mystery of origin of Life, in the fields of biocompatibility and chiral recognition², to cite a few. Chiral recognition is particularly intriguing having in mind the omnipresence of homochirality in biological systems; note also the well-known and remarkable chiral-sensitivity of the human body, displaying physiological answers so different depending of the biomolecule enantiomeric form³.

Although chirality is now better understood at the molecular level, fundamental questions remain concerning the transfer of the chirality from one molecule to a molecule-solid interface, or from one reactant to a product. As an example, for an asymmetric synthesis reaction to occur, the enantioselectivity must be brought on by the initial presence, during the reaction, of a chiral compound (initiator)⁴. In biology, the majority of biomolecules are of one same chiral form, homochirality being apparently critical for life as we know it, but how did it appear in the first place?

Homochiral macro-molecules (and Life) have evolved, because, once, there must have been a mechanism which could discriminate between the molecular sub-

units from their mirror images, and construct the macromolecules from the sub-units of dictated chirality. In all cases, one key parameter in this mechanism is molecular recognition, where the chiral factor seems to be determining. Chiral recognition at an interface depends on specific and defined arrangement of units in complementary structures interacting together *via* short range interactions, likely multiple weak forces such as hydrogen bonds⁵. Another factor that can imprint surface chirality lies on the structure of the chiral molecule which needs to have the right size. For instance by adding 1 of 2 carbons to a given molecule (*ca.* 2-amino-1-ethanol, -propanol or -butanol) the expression of surface chirality on Cu(100) will change drastically⁶. Over the last 15 years, adsorption of amino acids and small peptides on metal surfaces have been studied extensively, with the objective of unravelling their chemistry, adsorption modes, as well as their 2D (chiral) supramolecular assemblies⁷. No doubt that understanding, at the fundamental level, the various types of existing biomolecule-metallic surface interactions is a clue to explain, maybe predict, the surface arrangement and reactivity⁷⁻¹⁰. It is, in particular, clear that chiral supramolecular structures are driven by intermolecular chiral recognition processes¹¹. In the other hand, surface chirality and chiral recognition enable to

1 design new 2D patterns and in certain extend to
2 choose to express only one preferred surface-chirality.
3 This last point was explored over 10 years ago first by
4 Parschau *et al.* by LEED¹², thus by STM by Raval and
5 co-workers¹³ *via* the “soldier-sergeant” effect where
6 only a small amount of chiral tartaric acid (TA) forced
7 non-chiral succinic acid arrays(SU) into only one sur-
8 face-chirality while both enantiomorphous SU domains
9 were present without any TA molecules. A second ex-
10 ample of surface-chirality tuning was reported when a
11 small surface-enantiomeric excess of (*R,R*)-tartaric acid
12 over the (*S,S*)-enantiomer, imbalances the racemic
13 SS/RR surface into predominant (*R,R*)-TA islands with
14 smaller (*S,S*)-TA islands (together with some disor-
15 dered areas).¹⁴ The same phenomenon was also ob-
16 served by Fasel *et al.* using achiral molecules forming
17 chiral surface assemblies; M- and P-enantiomers of
18 heptahelicenes are equivalently present on Cu(111)
19 surface when dosed from a racemic mixture, evidenced
20 by the simultaneous presence of λ and ρ domains.
21 However, when a small enantiomeric excess, as little
22 as 0.08 % of M-enantiomer, is implemented in the mix-
23 ture, the surface assembly are thus doped into one ρ
24 domain of 2D superassembly¹⁵.

26 However, in these examples, the change of surface
27 chirality is a consequence of the addition of a chiral
28 “sergeants” in the case of achiral “soldiers” or the dop-
29 ing of racemic mixtures by one enantiomer. Surface
30 chirality changes have also been observed upon cov-
31 erage increase^{16, 17} surface adlayers annealing^{18, 19} or
32 due to some other parameters such as relaxation time
33 after adsorption/annealing²⁰ or sublimation flux²¹. Sev-
34 eral examples are summarised in two reviews by Bar-
35 low and Raval⁷ and by Ernst²².

36 However, it is only very rarely reported in the literature,
37 if never, that investigations on surface chirality have
38 been carried out on the influence of the chemistry of
39 the molecular beam prior to the adsorption of a mole-
40 cule on a surface. Therefore, in this paper, our objec-
41 tive was to willingly tune, or at least vary the chemical
42 form of a given adsorbed peptide, in order to investi-
43 gate the consequences on its binding mode and 2D-
44 arrangement on a well-defined copper surface. The
45 Cu(110) surface was chosen for its known ability to
46 create chiral domains upon adsorption of amino acids
47 and peptides^{7, 23}. To vary the chemical form of peptides
48 when landing on a surface, two very different deposi-
49 tion methods were applied under Ultra High Vacuum
50 (UHV). The first method is conventional deposition from
51 sublimation (using a Knüdsen cell or a crucible) into the
52 gas phase, while the second one relies on the use of
53 an electrospray ionisation or electron beam device
54 allowing the deposition of molecular ions from the liquid
55 phase. When using the first method, the chemistry of
56 the molecule in the gas phase is fixed by its confor-
57 mation in the crystalline phase (most often neutral for
58 amino acids) only the reactivity of the metal surface
59

onto which it is adsorbed will influence the chemistry of
the admolecule. For instance, methionine (neutral in
the gas phase, will be adsorbed as zwitterionions on
Au(111) or Ag(111)^{24, 25} while it will be as anions on Cu
surfaces^{26, 27}. However, the use of electrospray ionisa-
tion devices offers an alternative quite seducing to the
classical sublimation method. First of all, it allows
evaporating under UHV conditions fragile and heavy
molecules such as proteins, without breaking or dam-
aging the molecules^{28, 29}. Furthermore, as the mole-
cules to be adsorbed are in solution, it is easy to
change their protonation state by varying the pH of the
solution, or by changing the high voltage (HV) applied
during the electrospray beam³⁰.

Thus in these experiments, we have decided to use
positive HV when dosing GP molecules to obtain a flux
of positively charged molecules (COOH/NH₃⁺) and to
compare it with the classical method where the mole-
cules are neutral in the gas flux (COOH/NH₂).The so-
obtained surfaces were fully characterized by X-ray
photoelectron spectroscopy (XPS), Polarization Modu-
lation Reflection Absorption Infrared Spectroscopy
(PM-RAIRS), Low Energy Electron Diffraction (LEED)
and Scanning Tunelling Microscopy (STM); in addition,
periodic DFT-D2 geometry optimizations were per-
formed, see Supp Info section for more details.

Results and Discussion

The present study is focused on the surface chemistry
and arrangement of the Gly-Pro di-peptide at an inter-
mediate coverage, ~1/3 of a monolayer, based on stud-
ied carried out as a function of increasing GP cov-
erage³¹. Figure S1 of the Supplementary Information
section shows the O1s and N1s XPS spectra taken on
the surface after either Gly-Pro sublimation or ioniza-
tion on Cu(110). The O1s regions show, in both cases,
a single contribution at 532.1 eV after sublimation and
531.5 eV, after ionization; these narrow peaks are both
assigned to oxygen in carboxylate moieties. One
should note that the O1s peak is shifted towards higher
binding energies by about 0.5 eV and accompanied by
an enlargement of the *fwhm* (*full width at half-
maximum*) in the case of ESI deposition. This phenom-
enon can be explained by the anchoring mode of the
GP molecules, where in the case of ESI, only 1 O atom
is in close vicinity to the surface, while after sublima-
tion, the two O atoms interact, or atlas are very close to
the Cu(110) surface. In addition, the change in the
global charge of the molecule (-1 in the case of subli-
mation, 0 for ESI) may also influence the BE of O at-
oms. The N1s region, following adsorption by sublima-
tion, exhibits two main contributions at 400.3 eV and
398.6 eV; the former one is assigned to N in NH_{amide} or
NH₂ groups, while the latter is usually observed when a
nitrogen atom is in strong interaction with a metallic
surface³². One can notice the non equivalence in

weight of the two N1s contributions, which suggests 2 different anchoring mode of the GP molecules on the copper surface. This point will be explored in the following sections, mainly in the DFT part.

After adsorption by electrospray, the two N1s contribution, at 400.4 eV and 401.1 eV are rather attributed to N in NH or NH₂ and in protonated NH₃⁺ group, respectively. Again, here, one can notice the non equivalence of all N1s contributions, suggesting that some of the molecules are in a different chemical form. It has been calculated from the low BE contributions that less than 10 % of the GP adsorbed molecules are present as anionic admolecules, likely interacting via the N atom thus explaining the low BE contribution.

These data enable to identify the chemical form of the adsorbed Gly-Pro molecules: after sublimation, Gly-Pro is mainly adsorbed under its anionic chemical form («A», NH₂/COO⁻) with the NH₂ terminal group being in interaction with the Cu(110) surface³¹. Conversely, after electrospray deposition, most of the Gly-Pro molecules are adsorbed at the Cu(110) surface under their zwitterionic form («Z», NH₃⁺/COO⁻).

When looking at the PM-RAIRS data obtained after deposition by sublimation or electrospray, Figure S2, one can see very different IR profiles indicating a change in the chemical form and/or orientation of the Gly-Pro molecules at the Cu(110) surface. Indeed, the anchoring modes of the molecules, and consequently their orientation can be deduced from the IR spectra^{7, 33}. In the present case, after deposition by sublimation one principal IR peak arises at 1428 cm⁻¹, assigned to the symmetric stretch of the COO⁻ group, accompanied with a much smaller contribution for the asymmetric contribution at 1610 cm⁻¹, suggesting an anchoring mode via both oxygen atoms of the carboxylate group¹⁹. In opposition, when Gly-Pro is deposited via electrospray ionisation, one observes an inversion of the respective intensities of the asymmetric and symmetric contributions, at 1610 and 1400 cm⁻¹ respectively. This dominating asymmetric contribution indicates a change in the orientation of the molecule with respect to the surface, with the GP molecule being now anchored to the surface via only one oxygen atom of the carboxylate moiety³⁴. Looking now at the 2-dimensional arrangements, different adsorption geometries seems to propagate and dictate the peptide supramolecular assemblies. Figure 1 (a) and (c) shows the LEED data obtained for the Gly-Pro adsorbed as zwitterionic and anionic molecules, respectively. Two different unit cells are observed: after electrospray evaporation (left side of Figure 1), the LEED unit cell is depicted as a (2 0, 1 3) chiral unit cell, while the gas phase deposition surface leads to a larger (2 -1, 2 5) chiral unit cell (Figure 1 right side). The unit cell are reproduced on the adsorption model of Figure 1 (b) and (d); in (b) the chiral unit cell bears around half the size of the one exposed in (d), showing, in addition, different alignments with respect to the crystallographic axes.

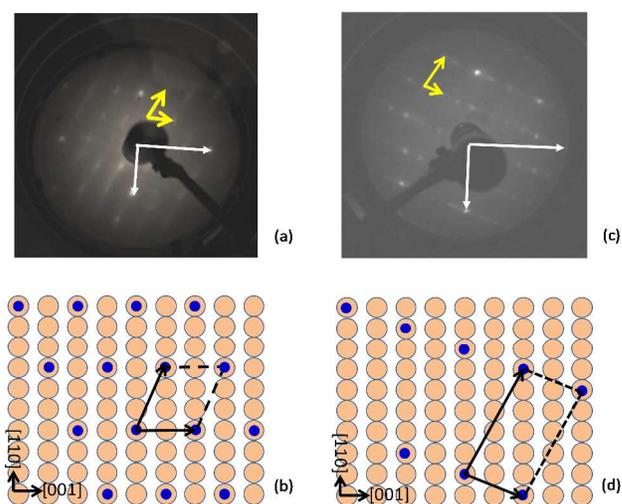


Figure 1. 2-Dimensional data of zwitterionic adsorbed Gly-Pro on Cu(110) (after electrospray) (a) and (b), and anionic (after sublimation) (c) and (d). (a) and (c) LEED data showing the chiral units cells (yellow lines), (20,13) and (2-1,25) for zwitterionic and anionic molecules, respectively. The white lines represent the Cu unit cells. (b) and (d) show the 2D adsorption model with the chiral unit cells joining blue dots. For details on the description of the LEED pattern see Ref. ³¹.

These differences are even more visible on the STM images presented on Figures 2 (a) and (c). One can recognize the chiral unit cells depicted by the yellow lines, but the shapes of the 2D arrays are totally different. In the case of the anionic molecules, Figure 2 (c), the molecules are aligned, forming rows of dimers, while in the case of zwitterionic molecules, Figure 2 (a), the 2D arrays are forming islands of close-packed molecules. Using the STM images to draw profiles and calculate intermolecular distances, one can locate the molecules within the unit cells deduced from LEED diagrams; molecules are represented as diamonds and triangles in Figure 2 (b) and (d).

Finally, it is worth noting that ESI experiments with negative HV have also been carried out; the molecular beam was thus anionic (COO⁻/NH₂) and the adsorbed Gly-Pro molecules were also anions. When performing the STM analyses, we ended up with the same 2D arrays as those formed upon sublimation from the gas phase.

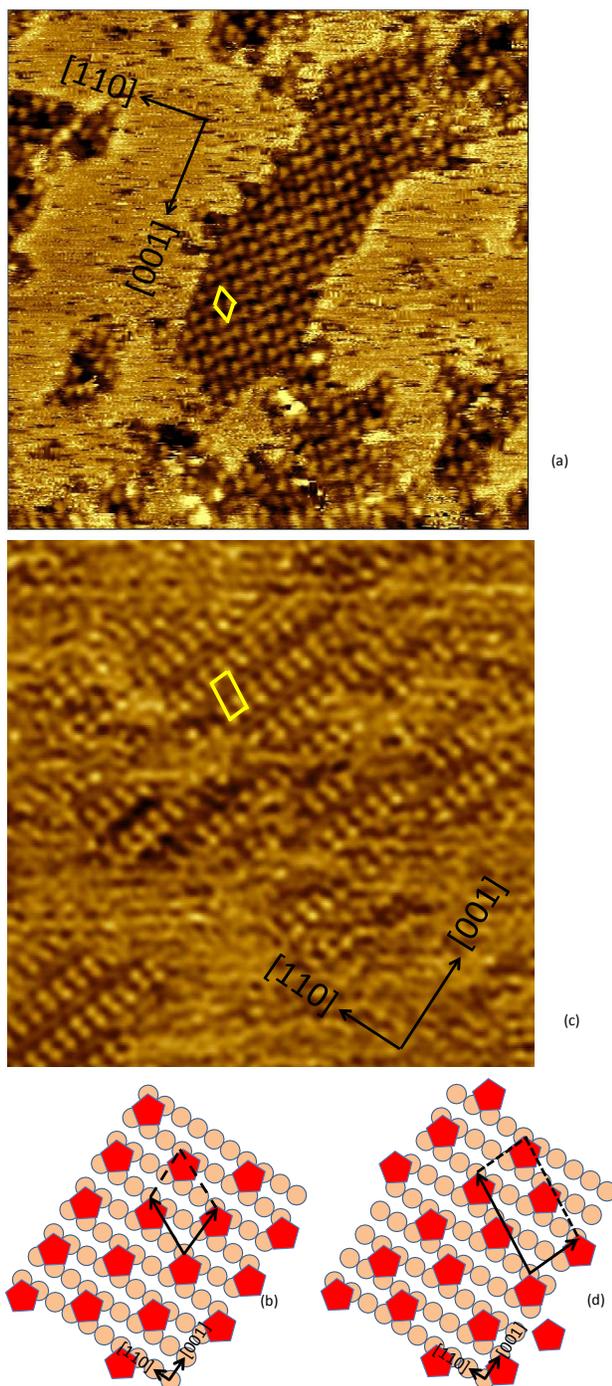


Figure 2. STM images of (a) zwitterionic Gly-Pro molecules (Z) and (c) anionic Gly-Pro molecules (A) adsorbed at low coverage on Cu(110). The yellow lines show the chiral units, (20,13) and (2-1,25) for zwitterionic (Z) and anionic (A) surstructures, respectively. Images: 25 nm x 25 nm. (b) and (d) are the deduced adsorption models obtained from STM profiles measurements. Arbitrary schematic representation of GP molecules as pentagones. More details on the description of the STM data of anionic GP can be found on Ref. ³¹.

These geometrical arrangements are obviously related to different intermolecular interactions. To visualize the adsorbed molecules and address the issue of intermo-

lecular interactions, we performed DFT calculations for both identified super-structures. They are reported in Figure 3 (a-b) for the zwitterionic structure, “Z”, and (c-d) for the anionic structure, A. Starting from the known structures and the molecule chemical states deduced from spectroscopic data, different possible adsorption modes were explored. The Z structure is composed of rows of interacting zwitterions adsorbed through the carboxylate moiety. The carboxylate can interact with Cu in a mono (one O of COO is adsorbed on Cu) or a bidentate (both carboxylate O interact with Cu) configuration. We found that the mode of adsorption of the carboxylate has a direct impact on the lateral interactions and therefore monitors the stabilization of the NH_3^+ moiety. Indeed, in a bidentate adsorption where both carboxyl O are involved in a covalent bond with Cu, an H-bond is formed between NH_3^+ and the neighbour peptide O (see figure S3 in Supp Infos). This configuration is less stable by 0.7 eV than the unidentate COO^- adsorption shown in Figure 3a-b. In the latter case, one carboxylate O accepts an H-bond from the NH_3^+ moiety of a neighbouring molecule). The Cu rows where adsorption occurs are separated by two empty Cu rows, which are distorted, evidencing a stressed surface. The energy of adsorption per Z molecule is 3.3 eV, which is composed of 2.35 eV of cohesion in the layer and 0.95 eV of layer-surface interaction. The A structure is more complex; the cell is larger, and contains dimers of anions. A preliminary study of adsorption of the isolated anions evidences a tridentate adsorption mode with both carboxylate O and the NH_2 moiety in interaction with Cu (Figure 3c).

In this configuration, rows of adsorbed anions are formed (Figure 3c), with an adsorption energy of the anion of 4.8 eV. Then a neighbouring molecule can adsorb either in the same configuration, without H-bonds to the previous molecule, or form a dimer, with H-bond between the NH_2 moiety and one carboxylate O of the neighbour molecule, (Figure 3d). In the dimer the energy of adsorption is 5.1 eV/anion, thus by 0.6 eV more stable than the tridentate adsorption of two anions. Indeed, lateral interactions in the dimer are 1.05 eV, whereas the dimer-surface interaction accounts for 4.05 eV per anion. In other words, there is a competition between molecule-molecule and molecule-surface interactions.

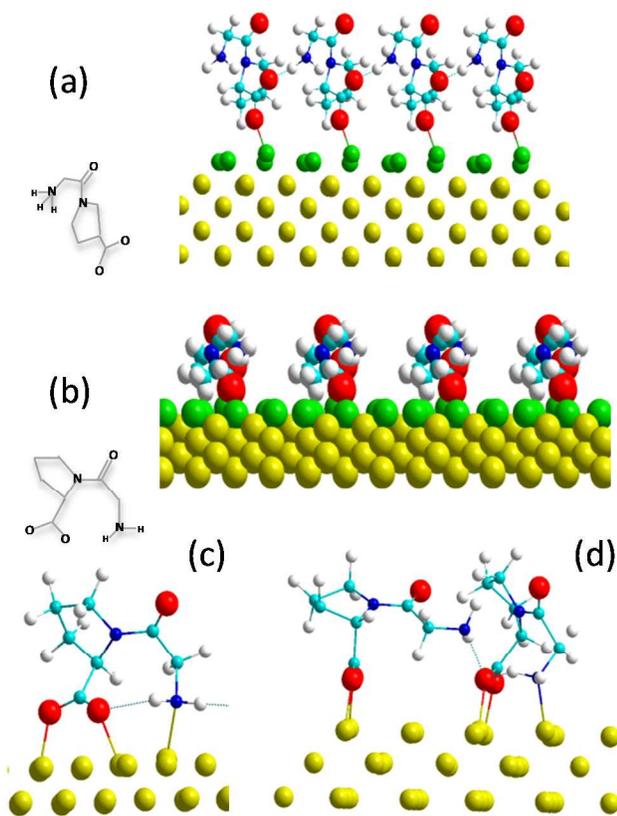


Figure 3. DFT obtained structures a), b) Zwitterionic structure, a) intermolecular interactions in one row, b) side view of different rows, c, d) Anionic structure; snapshot on c) the tridentate molecule, d) the dimer adsorbed. Inserts are showing flat 2D sketches of the molecules drawn from their 3D model.

Finally, in both Z and A surstructures, (see the modelled surstructures in SI Figure S4) we find that the lateral interactions impact the geometry of adsorption, and that the formation of an ordered array induces a partial detachment from the surface, from bidentate to unidentate for Z structure, and from tridentate to bidentate for the A structure, in order to reinforce cohesion in the molecular layer. Note also that, as expected, the Z layer is much more cohesive than the A dimers, but A dimers interact most with the surface.

Conclusions

By changing the mode of admission of a Gly-Pro peptide in UHV, we were able to adsorb either anionic or zwitterionic molecules on a Cu(110) surface. These two forms interact with the surface in different modes and form different surface chiral arrangements. By combining PM-RAIRS data and DFT calculations, we propose the formation of either rows of dimers, stabilized by the underlying surface, or aggregates of molecules resulting from possible intermolecular interactions. Limited intermolecular interactions (when all reactive groups

interact with the surface) prove to let molecule-surface interactions dictate the surface arrangement. These findings prove that it is possible to influence, change and even choose the 2D chirality of a surface by making the right choice of the chemical form of adsorbed molecules. We demonstrated that playing around with the admission mode enables it. This, by the way, shows the potential of sending (macro)molecules under UHV by an electrospray device. The resulting surface assemblies are profoundly different, related to the nature and strength of intermolecular forces. One may anticipate significant consequences upon the further reactivity of both types of surfaces.

ASSOCIATED CONTENT

Supporting Information for this article is given via a link at the end of the document PM-RAIRS and XPS data are presented as well as experimental details. Details of DFT calculations are also presented.

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Author Contributions

The manuscript was written through contributions of all authors. / All authors have given approval to the final version of the manuscript.

ABBREVIATIONS

UHV, Ultra High Vacuum; GP, Gly-Pro; .LEED, Low Electron Energy Diffraction; STM, Scanning Tunneling Microscopy; TA, Tartaric Acid; SU, Succinic Acid; HV, high Voltage; XPS, X-ray Photoelectron Spectroscopy; PM-RAIRS, Polarization Modulation Reflection Absorption Infrared Spectroscopy; DFT, Density functional Theory; fwhm, full width at half maximum.

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