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UHV Deposition of the Gly-Pro Dipeptide on Cu(110) by Sublimation or Electrospray Ionization

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ABSTRACT

While most of the peptide adsorption studies, in vacuum, are achieved by sublimation, we demonstrate here the possible use of electrospray ionization (ESI) to deposit entire peptides, possibly surrounded by solvated ions, on a surface in ultra high vacuum (UHV) conditions. This paper is then focused on the possible differences, depending on the way the peptide is sent onto the surface, sublimation or electrodeposition, in the resulting adsorption chemical state and geometry.

As a matter of fact, both the chemical state of the molecule, and its anchoring points with the surface, significantly change: from sublimation, the Gly-Pro molecules are adsorbed under an anionic form (COO^-/NH_2) and bound to the copper surface *via* both COO^- and NH_2 groups; whereas, after deposition by ESI under positive voltage, the adsorbed peptides are under their zwitterionic form ($\text{COO}^-/\text{NH}_3^+$); and only interact with the surface *via* one oxygen atom of the carboxylate groups. These changes modify both the geometry of the adsorbed molecules but also the growth of further layers.

Introduction

Amino acids and peptides interactions with well defined metal surfaces have been investigated, most often in UHV conditions, in order to determine both the chemical form and the conformation of the molecule once adsorbed¹. Though bringing clues to understand the important role of a metal upon the behavior of model biomolecules, in such studies, the molecules of interest are deposited onto the surface by thermal evaporation, therefore with some risk of chemical and conformation changes compared to their state in the crystalline phase. In contrast, the electrospray ionization process, which is capable of creating intact molecular ions

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3 from a solution into a gas phase ², allows small or large molecules to be deposited on a surface in
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5 a state very close to their in solution. ESI was first developed to preserve molecule conformation
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7 and interactions (even non covalent) that exist in solution ³, and analyze these molecular
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9 complexes by mass spectrometry. Recently, Carlton et al. review the results obtained thanks to
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11 ESI-MS (mass spectrometry) to investigate peptide-metal interactions, measure the stoichiometry
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13 of metal-peptide complexes as well as the binding site location⁴.
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18 Another related interest of such a ionization-deposition process is that it can generate either
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20 positive or negative molecular ions, depending on the isoelectric point of the peptide, on the
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22 solution pH as well as on the voltage polarity; it may also enable deposit peptides, protonated or
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24 deprotonated, just as they are in the pristine solution. When studying the interaction of peptides
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26 with solid surfaces, droplets can be ejected from a needle, thus leading to solvated ions which
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28 then form a gas phase ions and interact with the desired surface, instead of being directed
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30 towards the mass analyzer. This method has proven to enable molecular deposition of long
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32 oligothiophene wires ⁵, and also of more complex and fragile molecules like ruthenium dyes on
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34 Au(111) surfaces⁶. Thontasen *et al.* used ESI for the soft landing of host-guest complexes, that
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36 are very fragile macromolecules; they also varied the central cations, simply by tuning the nature
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38 of the salt in the source solution ⁷.
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45 Having a good knowledge of peptides interaction with model metal surfaces⁸⁻¹³, and willing to
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47 investigate the influence of the sublimation onto the real peptide-metal interactions, we chose a
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49 model di-peptide, Gly-Pro, and deposited it on Cu (110) surface by either sublimation from a
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51 Knüdsen cell, or by electrospray ionization, both in ultrahigh vacuum (base pressure 10⁻¹⁰ Torr);
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53 adsorbed molecules were then characterized by *in situ* PM-IRRAS and X-ray photoelectron
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55 spectroscopy (XPS).
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3 Special attention was put on the chemical form of the peptide molecules as well as on their
4 binding point with the copper surface. We will show how the chemical form of the adsorbed
5 proteins may influence the formation of multilayers.
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10 11 12 **Experimental Section**

13 14 *Materials*

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18 Gly-Pro (GP) from Bachem, was used as received. For sublimation evaporation, the peptide was
19 deposited in a small glass tube and resistively heated with a W/Th wire wrapped around the
20 crucible. The evaporator was initially separated from the main chamber by a gate valve and
21 differentially pumped by a turbomolecular pump. Before sublimation, the Gly-Pro powder was
22 outgassed at 390 K. It was then heated to 400 K and introduced in the chamber, where the glass
23 tube was placed in front of the gold crystal. The dosing pressure was maintained around 2×10^{-9}
24 Torr during the deposition of the adlayer.
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32 Electro spray deposition system from Molecular Spray Ltd (UK) was used for the deposition of Gly-
33 Pro from a solution. The Gly-Pro solution at 1 mM in a ethanoic/water 75:25 ratio was put in a
34 syringe. The ions of molecules were produced by applying a voltage of 2 kV to a flow of 1 $\mu\text{l}/\text{mn}$ of
35 solution in the needle of the syringe. At the tip of the needle, the produced charge droplets were
36 introduced in a first vacuum chamber through a capillary (250 μm inner diameter). The charged
37 droplets are guided towards the surface via three differential pumping stages where the solvent
38 evaporates leading to the Gly-Pro ion beam. During the electro spray deposition the partial pressure
39 in the main chamber was around 10^{-7} Torr.
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46 The copper Cu(110) crystal (12 mm diameter, 2 mm thick) was provided by Surface Preparation
47 Laboratory (The Netherlands) with a purity of 99.99% (4N), and alignment accuracies of 0.1° .
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50 51 *PM-RAIRS and XPS experiments*

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53 The Cu(110) single crystal was mounted in a multi-technique Ultra High Vacuum UHV
54 chamber, base pressure 1×10^{-10} Torr, with PM-RAIRS, LEED, and XPS facilities¹². The copper
55 crystal was cleaned by cycles of Ar^+ ion sputtering ($P_{\text{Ar}} = 5 \times 10^{-5}$ Torr, 3 kV, during 5 minutes),
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3 flashing, and annealing to 850 K for 10 minutes. The surface structure and cleanliness were
4 monitored by LEED and XPS before and after adsorption experiments.
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8 Adsorption of Gly-Pro was monitored *in-situ* by PM-IRRAS; a Nicolet 5700 spectrometer was
9 interfaced with the UHV chamber, together with a liquid nitrogen-cooled MCT detector. All
10 spectra were recorded *in-situ*, after stopping the dosing of Gly-Pro by closing a gate valve
11 between the UHV chamber and Knüdsen cell or the ESI device. All spectra were recorded at 8 cm⁻¹
12 resolution by co-addition of 1024 scans (time of acquisition: 10 min). The modulating
13 frequency was set for a maximal sensitivity at 1500 cm⁻¹.
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20 The sample was analyzed by X-ray photoemission spectroscopy using a SPECS GmbH (Berlin,
21 Germany) Phoibos 100-1D delay line detector hemispherical analyzer and a monochromatized
22 AlK α X-Ray Source (1486.6 eV). After recording a broad range spectrum (pass energy 100 eV),
23 high resolution spectra were recorded for the N 1s, C 1s and O 1s core levels (pass energy 20
24 eV). High-resolution XPS conditions have been fixed:” Fixed Analyser Transmission” analysis
25 mode, a 7 x 20 mm entrance slit; leading to a resolution of 0.1 eV for the spectrometer, and an
26 electron beam power of 150 W (15 kV and 10 mA). The spectra were fitted using Casa XPS
27 v.2.3.17 Software [Casa Software Ltd., UK] and applying a Gaussian/Lorentzian ratio G/L equal
28 to 70/30.
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43 **Results and Discussion**

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46 Figure 1 presents the XPS data obtained after dosing Gly-Pro by means of sublimation (blue
47 spectra, top part) or ESI (red spectra, bottom part) for both the N1s and O1s regions. Note that
48 the coverage was deduced from calculations of the average layer thickness based on XPS copper
49 peak attenuation (see SI). Spectra shown in Fig. 1 correspond to similar coverage values, namely
50 *ca.* 1 monolayer (ML) of Gly-Pro.
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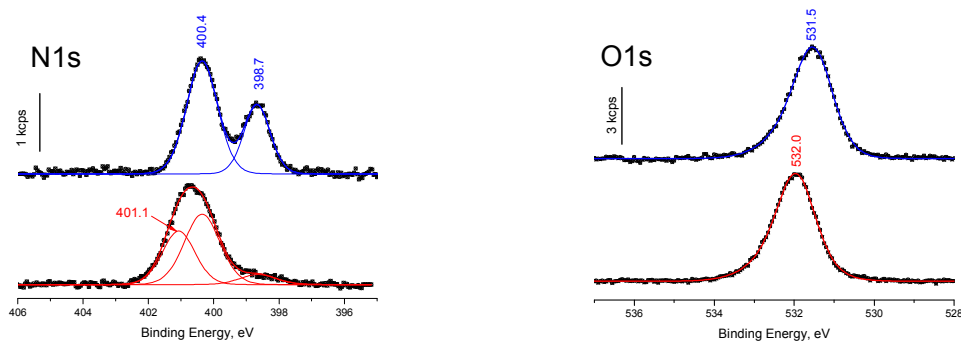


Figure 1. N1s (left) and O1s (right) XPS peaks recorded on the Cu(110) surface after deposition of Gly-Pro by sublimation (blue spectra, top part) and by ESI (red spectra, bottom part). The corresponding C 1s peaks are given in Supplementary Information.

After sublimation of Gly-Pro, the N1s peak shows two contributions, one at a binding energy (BE) of 400.4 ± 0.1 eV, assigned to nitrogen atoms in amide NH and/or amine NH_2 groups^{12,14}, while the second one, at lower BE, 398.7 ± 0.1 eV, can be reasonably attributed to N atoms in strong interaction with the metal surface $\text{NH}\dots\text{Cu}$ ^{8,11,15}. In parallel, the O1s peak (Fig. 1, top right part), centered at 531.5 ± 0.1 eV (fwhm = 1.5 eV), may be attributed to the contribution of the two equivalent oxygen atoms in COO^- groups in a bidentate configuration, in addition to that in the C=O amide bond^{8,12,16}. XPS Data thus indicate that, after dosing GlyPro on a Cu(110) surface by sublimation, the molecules are adsorbed in their anionic form, NH_2/COO^- .

After deposition of Gly-Pro molecules on Cu(110) by ESI, the main difference in the XPS data lies in the N 1s peak, the low BE contribution is hardly detectable while that ~ 400 eV is now broader and could be decomposed into two peaks, at 400.4 ± 0.1 eV and 401.1 ± 0.1 eV, the former can be attributed to nitrogen atoms in NH/ NH_2 group, while the latter is assigned to N atoms originating from NH_3^+ groups^{17,18}.

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3 The O1s peak is slightly shifted towards higher BE by *ca.* 0.5 eV (Figure 1, bottom right part)
4 and slightly broader than the previous one. This peak is again due to oxygen in the amide group
5 and from the COO⁻ groups; attributions of these O1s and N1s contributions are similar to those
6 and from the COO⁻ groups; attributions of these O1s and N1s contributions are similar to those
7 done by many authors¹⁹. We think that the shift to higher BE of the latter may be explained by a
8 weaker interaction of the COO⁻ groups with the copper surface, or by an interaction via only one
9 of the two COO⁻ oxygen atoms. Note that Feyer *et al.*, when studying the adsorption of an amino
10 acid on Cu(110) in a zwitterionic form, made clear a downshift of the O 1s peak of 0.3 eV when
11 passing from multilayers to one monolayer of molecules bound via the COO⁻ groups²⁰. In
12 addition, the absence of any contribution at 533-534 eV leads us to exclude the presence of
13 protonated COOH^{12,16}. After dosing Gly-Pro molecules on the Cu(110) surface using ESI, the
14 surface is mainly covered with zwitterionic molecules, NH₃⁺/COO⁻. Moreover, according to the
15 ratio between both N1s contributions (401.1 vs 400.4 eV) on Figure 2, one can estimate that
16 around 15% of the molecules are adsorbed under their anionic chemical form (NH₂/COO⁻), thus
17 explaining the presence of a small, but still present, contribution at lower BE (398 eV). Important
18 to notice that the oxygen over nitrogen XPS intensity ratio is equal to the atomic ratio in the
19 molecule indicating that neither water molecule nor OH groups are adsorbed together with the
20 molecule, even via the ESI process; such a result indicates that residual solvent molecules (water
21 + ethanol), surrounding the peptide molecule during the ionization process, evaporate either in
22 the vacuum phase or immediately after hitting the surface.
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49 The C 1s peaks, recorded after sublimation or ESI deposition, show no significant differences
50 (see SI), except a small shift towards high binding energy in the former case, likely due to the
51 additional positive charge on the molecules.
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3 Finally, it is worth noting that whatever the dosing process, molecules initially bear COOH
4 groups, NH_2/COOH and $\text{NH}_3^+/\text{COOH}$ in the case of sublimation and ESI respectively;
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8 carboxylic acid groups then deprotonate once adsorbed on the Cu surfaces²¹ leading to COO^-
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10 groups, accompanied by recombinative H_2 desorption²². Amine groups behave differently: they
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12 mainly keep their protonation state when using sublimation or ESI.
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19 PM-IRRAS analyses of the surface, after sublimation, or ESI deposition of Gly-Pro, lead to the
20 spectra reported in Figure 2. In the former case (Figure 2 upper spectrum), the dominating
21 absorption band at 1427 cm^{-1} , together with that at 1611 cm^{-1} , assigned respectively to the
22 symmetric and asymmetric stretching of carboxylate groups (νCOO^-) confirm that Gly-Pro is
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29 deprotonated and likely binds to the surface via one of the two oxygen atoms of the COO^- group,
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31 the O-C-O plane being normal or slightly tilted towards the surface^{23,24}; a proposed adsorption
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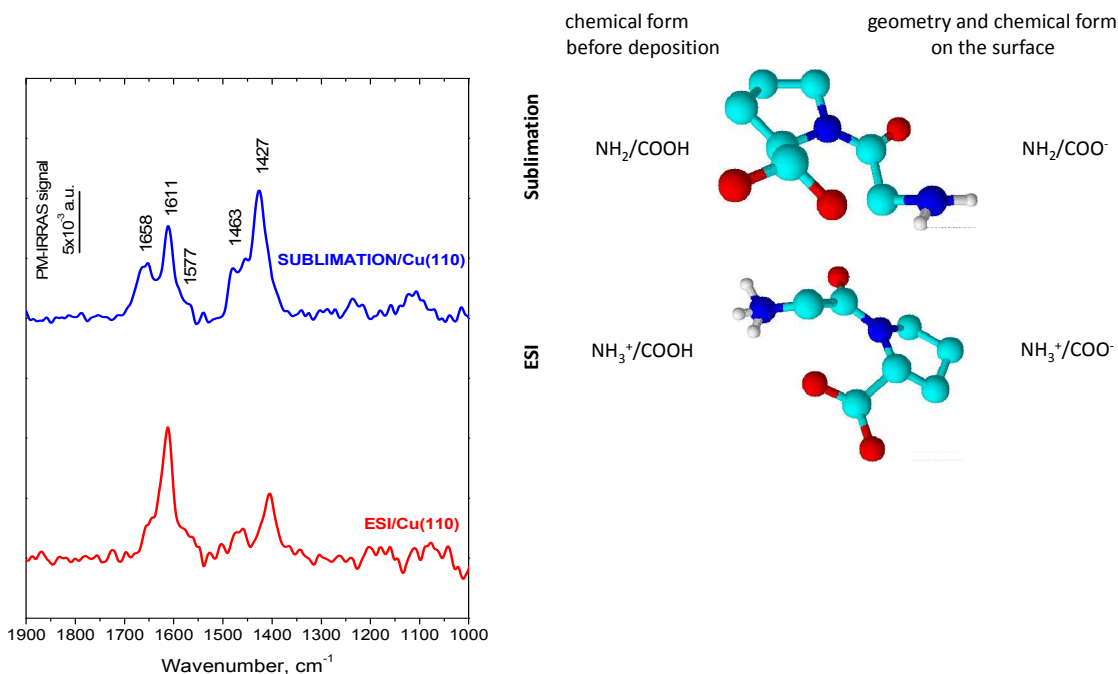


Figure 2. Left panel: PM-RAIRS spectra recorded after Cu(110) exposure under a flux of Gly-Pro in gas phase condition (sublimation, top blue spectrum) and from solution (electrospray, bottom red spectrum). Right panel: Schematic representation of the chemical forms of the molecule before and after deposition, as well as a model for the geometry on the surface. These are only schemes to help the reader; they show the most likely binding points of the molecules, consistent with the spectroscopic data, but do not result from any optimization calculation.

After deposition of Gly-Pro by ESI, one notes an inversion of the symmetric/anti-symmetric COO^- band intensities (1410 and 1611 cm^{-1}) and a decrease of the amide I band (1658 cm^{-1}), a strong indication of a change in the orientation of the molecule, the axis between the two oxygens of the COO^- groups being now almost parallel to the surface plane (very weak COO^- symmetric band). This, together with the broadening and shift towards higher BE of the COO^- XPS oxygen peak, proves a change in the geometry of the molecule on the surface (Figure 2 right panel). Note also a slight shift of the $\nu_{\text{sym}} \text{COO}^-$ band (from 1427 to 1410 cm^{-1}) which confirms the change in its interaction with the metal. These IR assignments and interpretation are strongly inspired from Barlow's review¹.

The growth profile of GlyPro adlayers, also appears to be very much dosing process-dependent (Figure 3). Adsorption *via* sublimation rapidly (after *ca.* 5 minutes) leads to a saturated monolayer, as measured from the XPS C, N and Cu intensities (see calculation in SI); in contrast, adsorption *via* ESI enables to grow multilayers (an average coverage of 2 monolayers after 30 mins). We ascribe this phenomenon to the chemical form and conformation of the molecules on the surface, and propose the following mechanism:

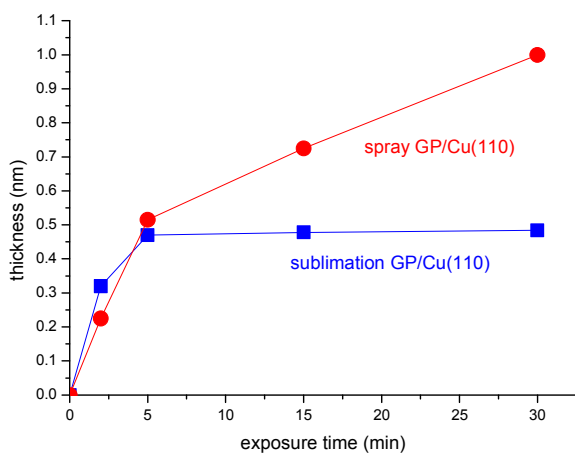


Figure 3. Thickness of the GP layer as a function of increasing dosing time on Cu(110) under a flux of Gly-Pro in gas phase condition (sublimation, bottom blue spectrum) and from solution (electrospray, top red spectrum).

After sublimation, Gly-Pro adsorbs in an anionic (COO^-/NH_2) form, and interacts with the surface *via* the N and both oxygen atoms of the carboxylate groups; in such a configuration, most of the reactive groups of the molecules are involved in the molecule-surface binding process, leaving only the C+O of the amide bond free to interact with potential incoming molecules. In opposition, after adsorption by ESI, the molecule is in its zwitterionic form on the surface ($\text{COO}^- / \text{NH}_3^+$), and interacts with the surface only via one oxygen of its carboxylate group; such a geometry leaves groups accessible for further interactions with the COO^- groups of incoming molecules thus explaining the possible building of multilayers.

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3 To summarize these results, adsorption of molecules is strongly dependent on the way they are
4 introduced in UHV ; one can modulate the chemistry of the molecules in the dosing stream and
5 thus modify their reactivity. In the case of GlyPro/Cu(110), COOH is always deprotonated on the
6 surface; however, while adsorption from sublimation facilitates interaction via oxygen and
7 nitrogen atoms of the NH₂ groups, adsorption via an ESI process (chemical form in the stream:
8 NH₃⁺/COOH), preserves NH₃⁺ groups which then do not interact with the surface. We suggest
9 the two geometries on Figure 2 which also explain the presence/absence of possible
10 intermolecular H-bonds, and thus the possibility to create or not multilayer.
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23 As a conclusion, taking the Gly-Pro peptide as a first example, adsorption under UHV conditions
24 *via* ESI, compared to classical sublimation, reveals that the former technique is a unique way of,
25 not only avoiding fragmentation of fragile (macro)molecules, but also of tuning the chemical
26 form a macromolecule once adsorbed. It is of particular importance since these chemical changes
27 have a direct consequence on the binding mode and geometry of the adsorbed peptides. These
28 changes (chemical and conformational) will also change the accessibility of incoming molecules
29 and the possibility to create a molecular film composed of mono- or multilayers. In a more
30 general point of view, tuning the chemistry of a molecules by using ESI enables the possibility or
31 not for specific molecular recognition at the multilayer scale, opening new routes towards
32 surface functionalization by immobilization of complex molecules.
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47 ASSOCIATED CONTENT

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51 The Supporting Information is available free of charge on the ACS Publications website at DOI:
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53 Details of of C, N and Cu XPS data are presented as well as the thickness calculation method.
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6 The authors declare no competing financial interests.
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TOC GRAPHICS

