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# Comparative Study of the Adsorption of Thiols and Selenols on Au (111) and Au (100)

*Nicolás Arisnabarreta,<sup>1,\*</sup> Gustavo D. Ruano,<sup>2</sup> Magalí Lingenfelder,<sup>3</sup> E. Martín Patrito,<sup>1</sup> Fernando P. Cometto,<sup>1,3\*</sup>*

1. Departamento de Fisicoquímica, Instituto de Investigaciones en Fisicoquímica de Córdoba (INFIQC), Facultad de Ciencias Químicas, Universidad Nacional de Córdoba, Córdoba, Argentina.

2. Instituto de Física del Litoral (IFIS), Santa Fe, Argentina.

3. Max Planck-EPFL Laboratory for Molecular Nanoscience, EPFL, Lausanne, Switzerland.

KEYWORDS. Thiols, selenols, self-assembly, Au (100), electrochemical stability.

## ABSTRACT

The effect of the Au crystalline plane on the adsorption of different thiols and selenols is studied via reductive desorption (RD) and X-Ray Photoelectron Spectroscopy (XPS) measurements. SAMs using aliphatic (ATs) and aromatic thiols (ArTs) on both Au (111) and Au (100) were prepared. The electrochemical stability of these SAMs on both surfaces is evaluated by comparing the position of the RD peaks. The longer the AT's chain the more stable the SAM on Au (100) when compared to Au (111). By means of XPS measurements, we determine that the binding energy (BE) of the S 2p signal corresponding to the S atoms in the thiol/Au interface, commonly assigned at 162.0 eV, shifts 0.2 eV from Au (111) to Au (100) for SAMs prepared using thiols with the C\* (C atom bonded to S) in  $sp^3$  hybridization; such as ATs. However, when the thiol presents the C\* with a  $sp^2$  hybridization, such as in the case of ArTs, the BE remains at 162.0 eV regardless the surface plane. Selenol-based SAMs were characterized comparatively on both Au (100) and Au (111). Our results show that selenol SAMs become even more electrochemically stable on Au (100) with respect to Au (111) than the analog sulphur-based SAM. According to our results, we suggest that the electronic distribution around  $Au-S/Se$  bond, could be responsible for the different structural arrangements reported in literature (gold adatoms, etc.), which should be dependent on the crystalline face ( $Au(hkl) - S$ ) and the chemical nature of the environment of the adsorbates ( $sp^3-C^*$  vs.  $sp^2-C^*$  and  $Au - SR$  vs.  $Au - SeR$ ).

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3 INTRODUCTION  
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6 In the last decades, self-assembled monolayers (SAMs) composed by thiolated molecules on  
7 different metals have been extensively studied.<sup>1,2,3</sup> In comparison to Au (111), much less is  
8 known about SAMs on the Au (100) crystalline face.<sup>4,5,6,7,8,9,10</sup> It is commonly known that both  
9 Au (111) and Au (100) are the most stable crystalline faces in Au nanoparticles (NPs) and their  
10 percentage and distribution is highly dependent on the NPs size.<sup>11</sup> Therefore, a deep  
11 understanding of thiol adsorption on the different crystalline faces is a crucial requirement in the  
12 design of functionalized Au NPs and other applications.  
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23 The surface Au atoms extraction mechanism during the self-assembly process of alkanethiols  
24 (AT) on Au (111), generating Au adatoms ( $\text{Au}_{\text{Ad}}$ ) and RS- $\text{Au}_{\text{Ad}}$ -SR moieties as well as Au  
25 vacancy formation is highly accepted nowadays.<sup>12,13,14,15</sup> However, early investigations of  
26 ethanethiol and butanethiol adsorption on Au (100) showed no surface vacancy island suggesting  
27 no RS- $\text{Au}_{\text{Ad}}$ -SR complexes formation.<sup>16</sup> Moreover, a recent study of the adsorption of aromatic  
28 thiols (6-mercaptopurine) on Au (100) suggested a more stable adsorption in an ordered adatom-  
29 free configuration rather than RS- $\text{Au}_{\text{Ad}}$ -SR formation.<sup>17</sup>  
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40 On the other hand, selenol based SAMs hold promise for future applications in the field of  
41 molecular electronics due to their remarkable optical and electronic transport features.<sup>18</sup>  
42 Nevertheless, only a few contributions scattered along the past decades have been made  
43 regarding the fundamental understanding of these adlayers.<sup>19,20,21,22,23,24,25,26,27</sup>  
44 In an earlier study, we have demonstrated that despite selenol and thiol SAMs present many  
45 similar properties, thermal stability is noticeably different.<sup>28</sup> To the best of our knowledge, the  
46 adsorption of molecules containing a selenium head-group on Au (100) has not been reported  
47 before.  
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3 In the present work, the effect of the Au surface plane on the self-assembly of thiols and  
4 selenols is investigated by means of electrochemical stability and XPS measurements. In order to  
5 obtain specific comparative trends, we used a wide variety of molecules with a sulfur group,  
6 such as *n*-alkanethiols, aromatic thiols, dialkyl disulfides, and functionalized aromatic thiols. In  
7 comparing both surfaces, a higher increase in the electrochemical stability of ATs on Au (100) is  
8 observed when the chain length is increased. However, the electrochemical stability of aromatic  
9 thiols seems not to be affected by different functionalization, length, etc. with the difference in  
10 the desorption potential depending mainly on the characteristic potential of zero charge of the  
11 bare surfaces. Moreover, the binding energy (BE) of the S 2p signal for the thiol/Au interface,  
12 shifts 0.2 eV from Au (111) to Au (100) for ATs; whereas it remains constant for aromatic thiols.  
13 On the other hand, selenol-based SAMs present a higher electrochemical stabilization than the  
14 analog sulphur-based-SAM when the Au surface plane is changed from Au (111) to Au (100).  
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## 32 EXPERIMENTAL METHODS

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34 *Gold Substrates.* We used two types of Au substrates. For all the electrochemical  
35 measurements we used 100 and 111 monocrystals (4 mm in diameter, oriented better than 1°  
36 towards the face and polished down to 0.03 μm) from MaTeck, Jülich, Germany. Before the  
37 assembly process, both crystals were annealed in a hydrogen flame for two minutes, cooled  
38 under constant N<sub>2</sub> flux, and put in contact with water after one minute. For the XPS  
39 measurements on preferred oriented (111) substrates we used Au films evaporated on  
40 borosilicate glass (250 nm thick, Arrandee) and for (100) substrate, we used a monocrystal (10  
41 mm in diameter, MaTeck). Before the assembly process the Au films were immersed in a hot  
42 piranha solution (H<sub>2</sub>SO<sub>4</sub>:H<sub>2</sub>O<sub>2</sub>, 70:30) during 30 seconds and then copiously washed with Milli-  
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3 Q water. Finally, they were annealed in a butane flame for two minutes and then cooled down to  
4 room temperature under constant N<sub>2</sub> flux.  
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7 *Preparation of SAMs.* Precursors were purchased from Sigma-Aldrich: *n*-alkanethiols (C<sub>*n*</sub>T,  
8 where *n* = 2, 3, 5, 6, 8, 9, 11, 12 and 16), 3-mercaptopropionic acid (MPA), 4-methylthiophenol  
9 (MT), benzenethiol (BT), 4-mercaptobenzoic acid (MBA), 2-mercaptocotinic acid (MNA).  
10 Benzeneselenolates (BSe) and benzylselenolates (Benzyl-Se) adlayers were prepared from  
11 diphenyl diselenide and dibenzyl diselenide (Aldrich). Pure ethanol (Baker) or 0.1 NaOH  
12 aqueous solutions (for MNA and MBA) were used as solvents. Chemicals were used as received  
13 without further purification. The samples were immersed in 0.2 mM deoxygenated solutions at  
14 room temperature by different periods of time. After the monolayers were formed the substrates  
15 were rinsed copiously with ethanol and Milli-Q water and blown dry with N<sub>2</sub>.  
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29 *Cyclic voltamperometry.* Cyclic Voltammograms (CV) measurements were performed with a  
30 Solartron 1260 electrochemical interface and a 3-electrode cell with separate compartments for  
31 reference (Ag/AgCl (NaCl 3M)) and a counter electrode (Pt wire). The 0.1 M KOH electrolyte  
32 was thoroughly deoxygenated by bubbling with N<sub>2</sub> prior to each experiment. Measurements were  
33 made at a sweep rate of 50 mV/s.  
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41 *Photoelectron Spectroscopy.* X-ray photoemission spectroscopy (XPS) measurements were  
42 carried out in a commercial SPECS spectrometer exciting with the monochromatized light of a  
43 standard aluminum source (*K*<sub>α</sub> line at 1486.6 eV). A hemispherical (*r* = 15 cm) Phoibos analyzer  
44 was employed, at a constant pass energy of 10 eV, to detect the photoelectrons in the energy  
45 regions corresponding to the S2p and Au 4f photoemission peaks. The fitting of these spectra  
46 where performed using the standard Doniach-Sjunic algorithm assuming a reference binding  
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3 energy of 84.0 eV for the Au 4f 7/2 peak. Lorentzian contributions to the signals were set in 0.2  
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5 eV and 0.15 for Au 4f and S 2p doublets respectively as in previous works.<sup>29</sup>  
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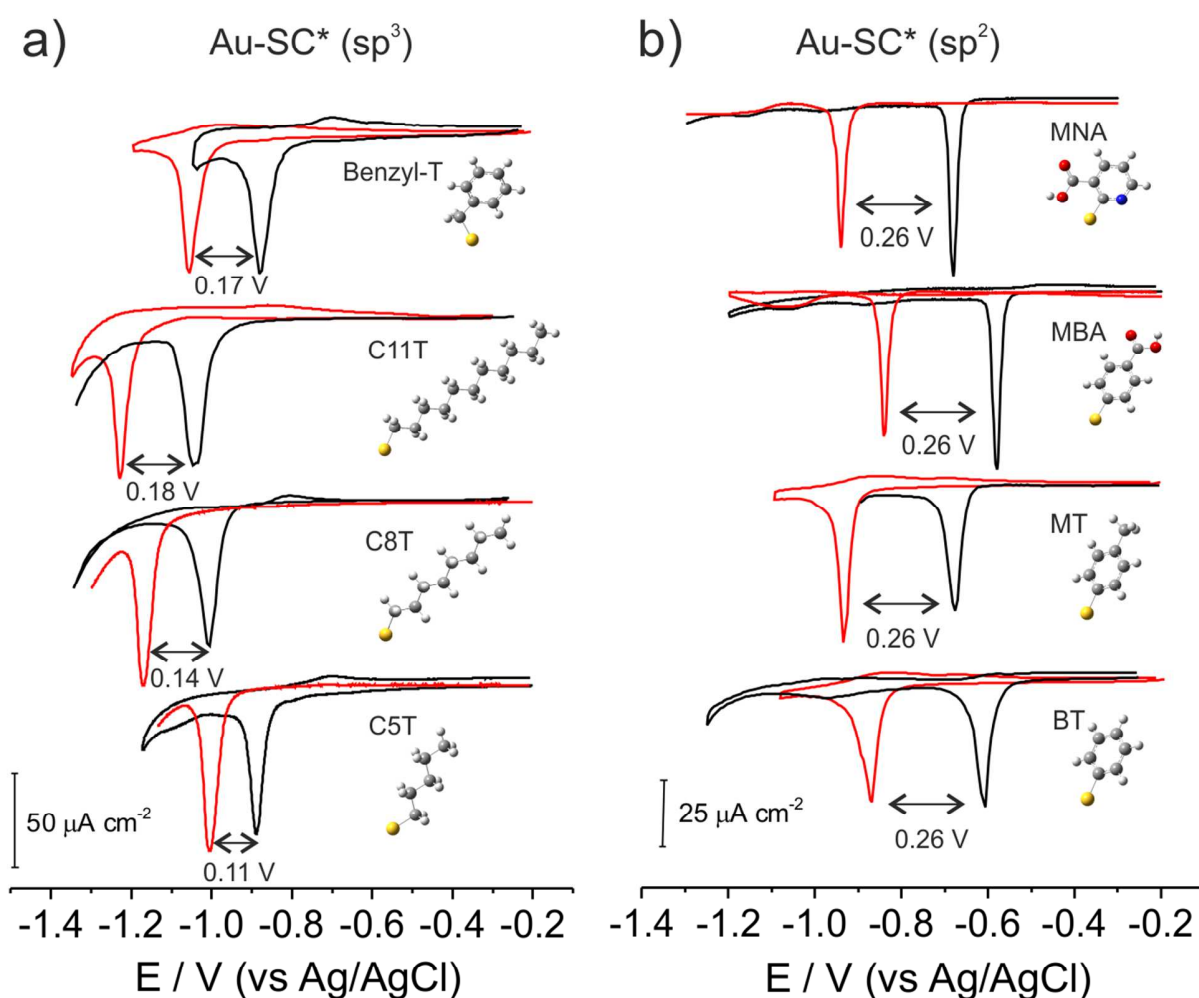
## 8 RESULTS

### 9 10 a) *RD of Aliphatic and Aromatic Thiols on Au (111) and Au (100).*

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12 In this section, the reductive desorption (RD) characterization of the adsorption of different  
13 types of *n*-alkanethiols (ATs) and aromatic thiols (ArTs) is presented. In the case of aliphatic  
14 thiols, ATs with different chain length (*C<sub>n</sub>T*, *n* = 2, 3, 5, 6, 8, 9, 11, 12 and 16) were adsorbed  
15 from 0.2 mM ethanolic solutions on Au (111) and Au (100) surface. On the other hand, BT, MT,  
16 MNA and MBA were used as representative ArTs, in which the aromatic group presents  
17 different functionalization, conferring different kinds of adlayer's structures.<sup>30</sup> In the case of ATs,  
18 the C\* (the C atom directly bonded to S atom) presents an *sp*<sup>3</sup> hybridization while in the ArTs,  
19 the C\* presents an *sp*<sup>2</sup> hybridization. The influence of the C\* hybridization on the binding energy  
20 of the AT vs ArT on both surfaces will be discussed later in this work. In order to gain insight on  
21 the role of the electronic configuration of the C\* atom, we used Benzyl-T, which is an aromatic  
22 thiol with an *sp*<sup>3</sup>-C\* hybridization. Figure 1 shows representative RD profiles of ATs and ArTs  
23 adsorbed on both Au (111) (black lines) and Au (100) (red lines). Large peaks at around -0.89 V,  
24 -0.99 V and -1.05 V are obtained for the RD of C5T, C8T and C11T on Au (111), respectively;  
25 following the expected chain length dependence for these SAMs (Figure 1.a).<sup>31</sup> The same trend  
26 is observed when ATs are adsorbed on Au (100), but RD peaks turn out to be shifted towards  
27 more negative potentials (-1.01 V, -1.14 V and -1.23 V for C5T, C8T and C11T, respectively).  
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50 For ArTs, where the C\* presents now a *sp*<sup>2</sup> hybridization, the same trend was also found  
51 (Figure 1.b). The RD of BT, MT, MNA and MBA on Au (111) and Au (100) exhibit single sharp  
52 peaks; even though these ArTs present different molecule structure/functionalization that could  
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alter the homogeneity of the SAM; e.g. in the MNA case a N atom may also bond to the surface.<sup>32</sup> Surprisingly, the cathodic shift value (from Au (111) to Au (100)) is constant (0.26 V), irrespectively of the terminal group and functionalization. The special case of Benzyl-T, which is an ArT but with  $sp^3$ -C\* hybridization, exhibits single peaks separated by only 0.17 V in a clear contrast with the shift observed for the rest of the essayed ArTs (0.26 V). This result, strongly implies that the C\* atoms play an important role in the configuration of the SAMs.



**Figure 1.** Reductive desorption (RD) profiles of SAMs prepared from 0.2 mM solutions of thiols containing **a)**  $sp^3$ -C\*, C5T, C8T, C11T, Benzyl-T and **b)**  $sp^2$ -C\* BT, MT, MBA and MNA

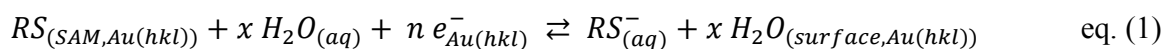


on both Au (111) (black line) and Au (100) (red line). Electrolyte: 0.1 M KOH. Scan rate: 50 mV/s.

*b) Effect of the chain length and C\* hybridization on the SAM stability on Au (111) and Au (100)*

In order to study the dependence in the electrochemical stability of the SAMs adsorbed on Au (111) and Au (100), the cathodic shift, namely  $|\Delta E_p(100 - 111)|$  (in general  $|\Delta E_p(hkl)|$ ), was analyzed. Figure 2 shows the  $|\Delta E_p(100 - 111)|$  vs chain length profile. In addition,  $|\Delta E_p(100 - 111)|$  for the RD of the ArTs is also showed in Figure 2. A high  $|\Delta E_p(100 - 111)|$  suggests a preferential adsorption of the SAM on the Au (100); i.e. the SAM is more stable on this surface rather than on the Au (111), resulting in a more negative  $E_p$ . In contrast, low  $|\Delta E_p(100 - 111)|$  would suggest similar stability on both surfaces.

From each one of the experiments, we can evaluate the electrochemical stability of the SAM. The position of the RD peak, i.e. the magnitude of RD potential that must be supplied to accomplish the reduction of the SAM, translates into the net change of the free energy experienced by the surface. Doneux *et al.*<sup>33</sup> proposed a general description for the reductive desorption process:



Matching this description, the energetic contributions that should be considered are the following: for the initial state (left term in the eq. 1); 1) substrate–adsorbate interactions, 2) lateral interactions (vdW, H–bonding, dipole–dipole, etc.), 3) substrate/SAM–solvent interactions. Whereas for the final state (described in the right term in the eq.) involves 4) desorbed surfactant–solvent and 5) substrate–solvent interactions.

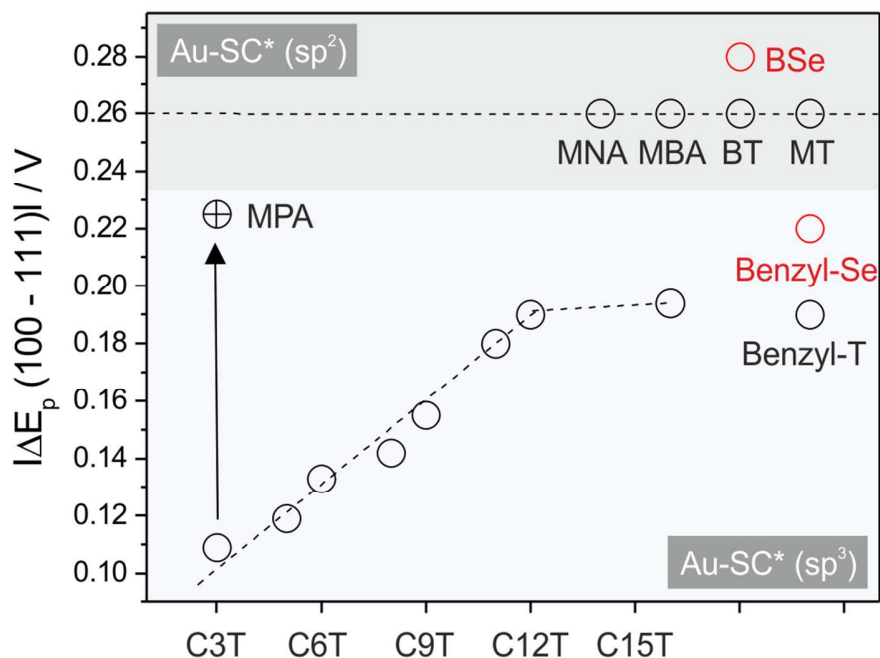
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3 Substrate–adsorbate interaction ( $Au(hkl) - S$ ) is mainly determined by the energy of the S–Au  
4 bond. The dependence of this magnitude on the crystallinity, for the model system  $Au(hkl) -$   
5  $SCH_3$ , was theoretically predicted<sup>34</sup> finding higher bond energies for the more open surfaces. It is  
6 interesting, at this point, to mention that the difference in the bond energy is linked to a shift in  
7 the core energy levels of both Au and S atoms. Thus, by performing XPS measurements in the  
8 binding energy (BE) region of the S 2p photoelectrons we can infer the change in the strength of  
9 the  $Au(hkl) - S$  bond. The lateral interactions, mainly attractive vdW forces in the case of ATs  
10 ( $C_nT/vdW_{Au(hkl)}$ ), contribute to stabilize the monolayer, shifting the RD potential towards more  
11 negative values.<sup>35,36</sup> Thiol–solvent interactions in the adsorbed state can affect the inner spatial  
12 regularity in the topology of the adsorbed moieties and stability of the monolayer–substrate  
13 system. Thus, the third energetic contribution, mainly depends on the potential of zero charge  
14 ( $pzc$ ) of the complex substrate/SAM in specific solvents ( $pzc_{CnT-Au(hkl)}$ ). Previous studies on  
15 thiol SAMs on Au (111)<sup>37</sup> showed an inverse dependence of the  $pzc$  with the AT's chain length  
16 ( $n$ ) associated to an increment of the perpendicular dipolar moment  $\mu_{perp}$  at longer chain lengths.  
17 A similar effect with  $n$  is also expected for SAMs on Au (100); however, the proportionality ( $n$   
18 to  $pzc$ ) is not the same as in Au (111) mainly due to the differential adsorption angle, i.e.  
19 different  $\mu_{perp}$ . In the final state, when ATs were desorbed from the surface, AT's solvation  
20 energy ( $C_nT - solvent$ ) in aqueous solutions changes with the chain length. Also, in the  
21 desorbed state, gold surface is in contact with the aqueous solution (solvent). Thus, this energetic  
22 contribution is directly dependent on the difference in the  $pzc$  of the bare gold surface  
23 ( $pzc_{bare Au(hkl)}$ ).<sup>33</sup>

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25 Accordingly, the cathodic shift of the RD potential observed for a given SAM formed on  
26 different surfaces ( $|\Delta E_p(hkl)|$ ), depends on the  $\Delta(Au(hkl) - S)$ ,  $\Delta(C_nT/vdW_{Au(hkl)})$ ,  
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3  $\Delta(pzC_{CnT-Au(hkl)})$  and  $\Delta(pzC_{bare Au(hkl)})$ ; since the  $C_nT - solvent$  interaction is equal  
4 regardless of the surface used. For this reason, RD shifts should not be misinterpreted as a direct  
5 measure of the change in the adsorption energy of specific adsorbates without considering every  
6 energetic contribution; i. e. the shift of the RD peak towards more negative values, does not  
7 necessary imply a higher energy of the bond  $Au(hkl) - S$ . The effect of the surface on the  
8  $Au(hkl) - S$  bond of ATs and ArTs SAMs will be discussed later in the light of the XPS results.  
9 Therefore,  $\Delta|\Delta E_p(hkl)|$ , i. e. the variation of  $|\Delta E_p(100 - 111)|$  when the AT's chain length is  
10 changed, only depends on the  $\Delta(C_nT/vdW_{Au(hkl)})$  and  $\Delta(pzC_{CnT-Au(hkl)})$ , since  
11  $\Delta(pzC_{bare Au(hkl)})$  and  $\Delta(Au(hkl) - S)$  contributions should be constant regardless of the length  
12 of the ATs.  
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28 Figure 2 shows that an increase of the AT's chain length results in an increase of the  
29  $|\Delta E_p(100 - 111)|$ ; suggesting a greater stabilization on Au (100) in comparison with Au (111).  
30 This effect could be caused by either a strong increment of the  $C_nT/vdW_{Au(100)}$  or to a stronger  
31 decrease of  $pzC_{CnT-Au(100)}$  (or both). Since  $\Delta(pzC_{CnT-Au(hkl)}) \propto -\Delta\mu_{perp}$ , the variation of the  
32  $\Delta\mu_{perp}(100 - 111)$  vs chain length profile is shown in Figure SI\_1 to provide insight on the  
33 behavior of that contribution. To obtain  $\mu_{perp}$ , we performed DFT calculations (Gaussian 09,<sup>38</sup>  
34 B3LYP) for every AT on both surfaces. An increase of the chain length produces a higher  
35 increase of the AT's  $\mu_{perp}$  adsorbed on Au (100) (decreasing the  $pzC_{CnT-Au(100)}$ ). Thus,  $E_p$   
36 shifts towards more negative values (increasing the  $|\Delta E_p(100 - 111)|$ ). However, this effect is  
37 more pronounced for short ATs, where the  $\mu_{perp}$  changes considerably with the AT chain length.  
38 For longer ATs, the  $\mu_{perp}$  reaches a long-chain limiting value and the  $|\Delta E_p(100 - 111)|$  rises  
39 because of the more effective  $C_nT/vdW_{Au(100)}$  interactions. This explains how the linear  
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dependence of  $E_p$  with  $n$  (up to  $n = 12$ ) is kept beyond the stagnation on the  $\Delta(pzC_{nT}-Au(nkl))$  quantity.



**Figure 2.** The modulus of the cathodic shift  $|\Delta E_p(100 - 111)|$  obtained for the RD of different ATs and ArTs. In the upper (bottom) part, the cathodic shifts of species with C\* that present  $sp^2$  ( $sp^3$ ) hybridization are presented.

As an additional experiment to show the validity of our description in Fig. 2, we studied the stability of the SAM formed on both surfaces using a thiol with polar terminal group. When a  $-COOH$  group is replaced as a terminal group in C3T (MPA molecule), the comparative stability on Au (100) is highly increased since the  $|\Delta E_p(100 - 111)|$  rises from 0.11 to 0.23 V (crossed open symbol in Fig. 2). This shift in the  $E_p$  supports our hypothesis; modification of the  $\mu_{perp}$  induced by the polar terminal, even in this short molecule ( $n = 3$ ) drives the increase in the preferential stability of the SAM on the (100) face. This result suggests the potential tailoring of

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3 functionalized gold nanoparticles by stirring the preferential adsorption/desorption on a given  
4 phase with the addition of suitable terminal groups. In this way, patterned multi-molecular  
5 coatings, i.e. patches, rows, stripes etc., could be obtained by controlling both the crystalline face  
6 and the after mentioned prosthetic groups.  
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12 SAMs of aromatic thiols (ArTs) are known to be quite disordered and thus, presenting lower  
13 coverages (0.2 – 0.25).<sup>28,39,40,41</sup> Therefore, lateral interactions should be less effective than those  
14 observed for ATs on both surfaces. This suggests that  $|\Delta E_p(100 - 111)|$  strongly depends on  
15 the difference in the *pzc* of the bare surfaces  $\Delta(pzc_{bare\ Au(hkl)})$ , since the difference in lateral  
16 interactions, as well as the rest of the energies considered, should be negligible for aromatic  
17 SAMs and that explains the fact that the  $|\Delta E_p(100 - 111)|$  is constant and equal to 0.26 V for  
18 ArTs.  
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31 It is to point out that, in this case, no effect is observed when substituting a non-polar methyl  
32 group (MT) by a highly polar one like a carboxylic group (MBA). This may be due to the  
33 aromatic delocalization of the electrons in the moieties that quenches the difference in the  
34 molecular  $\mu_{perp}$ . As an indicative, the work function difference between the unreconstructed  
35 surfaces is 0.16 eV<sup>42</sup> ( $\phi_{100} - \phi_{111}$ ) which, although not accounting for the solvation nor the  
36 reconstruction upon the SAMs desorption, points in the same direction that our experimental  
37 results.  
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### 49 *c) XPS characterization of AT and ArT on Au (111) and Au (100)*

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52 In order to gain further insight into the nature of the  $Au(hkl) - S$  interactions of aliphatic and  
53 aromatic thiols on both surfaces, XPS measurements were performed. Figure 3 shows the S 2p  
54 XPS for C8T, Benzyl-T, MNA and MBA on both Au (111) and Au (100). In general, three  
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3 different doublets can be obtained. The first feature, a signal at 162.1 eV (S1-orange), is assigned  
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5 to the S atoms in the thiol–Au interface.<sup>43</sup> This signal confirms the adsorption on the surface  
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7 with a thiolate-Au bond. The second one, a signal centered at 163.8 eV (S2-yellow) is attributed  
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9 to the S atoms in either free terminal –SH groups or in S–S bonds formed in the links between  
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11 layers in a multilayer configuration. Finally, a doublet centered at 161.2 eV (S3- blue) arises  
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13 from contamination with chemisorbed S atoms. The XPS of SAMs formed using C8T and  
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15 Benzyl-T adsorbed on Au (111) are composed mainly of the S1 signal, centered at 162.1 eV, as  
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17 expected. The contaminating S3 signal is detected on the XPS for Benzyl-T/SAM. When the  
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19 surface is changed to Au (100) a notable difference takes place; S1 doublet shows a 0.2 eV core  
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21 level shift to higher BE since it is centered at 161.8 eV for both Benzyl-T and C8T. This effect is  
22  
23 attributed to a difference in the charge transfer on the *Au – S* interface probably originated from  
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25 the difference in the adsorption sites on both surfaces. However, when repeating these studies  
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27 using thiols with the C\* in  $sp^2$  hybridization, a remarkable contrast is observed (Figure 3.b).  
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29 Unlike the results obtained using the thiols with C\*– $sp^3$ , the S1 signal for ArTs (corresponding to  
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31 the S atoms in the thiol/Au interface) is centered at 162.1 eV regardless of the surface plane  
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33 (SAMs formed by MBA also present the S2 doublet probably arising from free –SH groups).  
34  
35 Also, as discussed in the EC section, the  $|\Delta E_p(100 - 111)|$  changes for ATs according to the  
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37 chain length; whereas it remains constant for ArTs. These interesting results suggest that the  
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39 *Au – S* surface bonding for aromatic thiols (with a  $sp^2$  C\*) is chemically similar on both  
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41 surfaces.  
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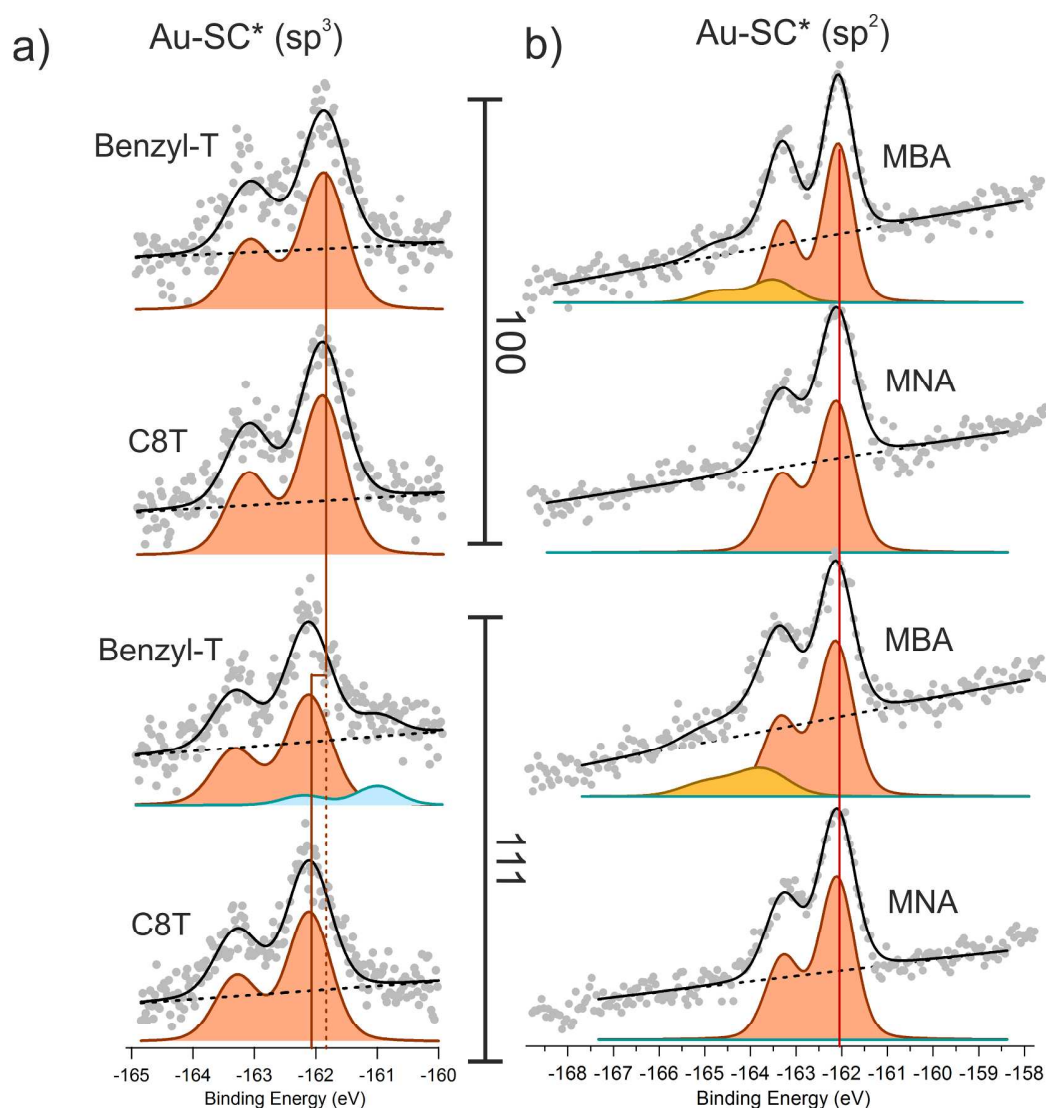
51 The binding energy of the photoelectron S 2p is associated to the electronic configuration of  
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53 the S atom in the thiol. Thus, the changes introduced by the environment of the *S – C\** and  
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55 *Au – S* bonds may affect the electronic screening of the S 2p orbital. As an example, in Fig. 3  
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4 for the undesired atomic S contamination (lower BE signal for Benzyl-T (S3-blue) in panel a)  
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6 when the S atom is only bonded to Au, the minimum BE is achieved since the electron transfer  
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8 from the substrate should be maximum. On the other hand, larger BE are obtained for the S-S  
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10 bonds (163.8 eV as shown by the yellow doublets in Fig. 3b) and even higher ones result from a  
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12 drainage in local electronic density when the S atom is bonded to a more electronegative atom  
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14 such as O (168 eV).<sup>44</sup> Thus, by comparing the S 2p BE resulting from  $Au(hkl) - S$  and  
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16  $Au(hkl) - S - C_{sp^3}^*H_2 - C_{n-1}H_{2(n-1)+1}$  we can infer that the alkyl chain reduces the S local  
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18 electron density rather than increasing it (otherwise the BE would be larger than the  $Au - S$   
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20 case).  
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25 This charge transfer takes place within the molecule regardless of the  $Au(hkl) - S$  bond, so if  
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27 we assume it does not change with the  $Au(hkl) - S$  formation we must conclude that the  
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29 decrease in the BE when comparing  $Au(111) - S - C_{sp^3}^*H_2 - C_{n-1}H_{2(n-1)+1}$  and  $Au(100) -$   
30  
31  $S - C_{sp^3}^*H_2 - C_{n-1}H_{2(n-1)+1}$  is associated to a larger charge transfer from the atoms in the Au  
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33 (100) surface. This is consistent with the report of a stronger  $Au(hkl) - S$  bond for the adsorption  
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35 of thiols on more open crystalline planes.<sup>34</sup> Going further into the analysis, we do not see the  
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37 same effect when an aromatic thiol (with C\* in  $sp^2$  hybridization) is adsorbed. In this case, the S  
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39 2p BE remains unaltered for both situations and we attribute this effect to a charge compensation  
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41 of the S atom by the delocalized electrons in the phenyl ring. In this way, the  $sp^2$ -C\* atom would  
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43 behave as a gauge allowing the charge compensation and precluding the local electron density to  
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45 build-up on the S atom (lowering the BE as in the other case). This effect vanishes when a  $sp^3$ -  
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47 C\* atom is intercalated in between the conjugated system and the S atom as seen in the  
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49 comparison between the SAM of Benzyl-T and those of any other of the ArT measured. The  
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51 reason may reside in the interruption of the aromatic  $e^-$  delocalization avoiding the injection of  
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the extra charge (imposed by the 100 surface to the S atom) to empty extended states in the aromatic part of the molecule.

According to this, we can infer that the electronic distributions around the surface bond should be responsible of the different structural arrangement on the surface, which should be dependent on the crystalline face and the chemical nature of the environment of the adsorbates.

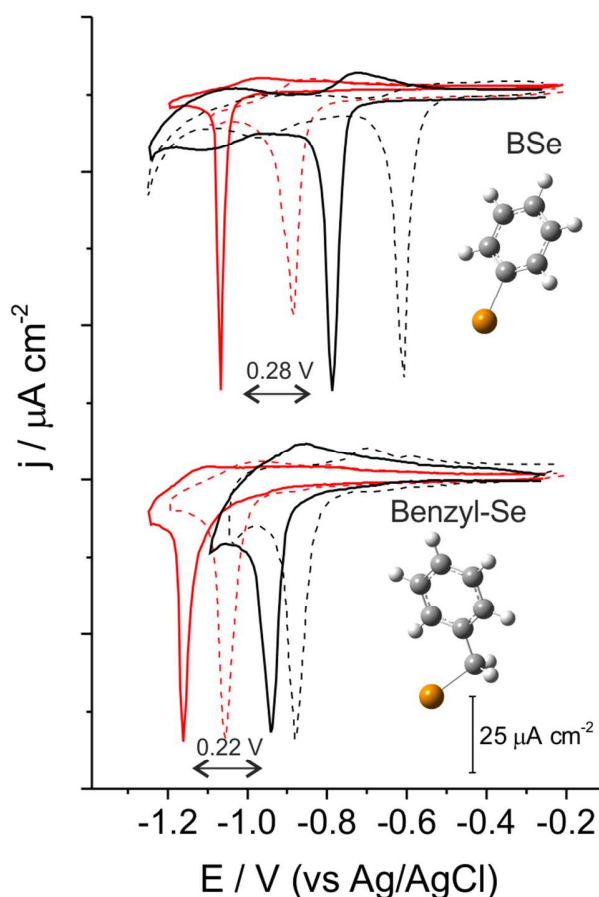


**Figure 3.** Photoemission spectra showing the S 2p region for SAM preparing from a) C8T and Benzyl-T; and b) MNA and MBA; formed on Au (111) and Au (100).



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4 *d) Adsorption of selenols on Au (111) and Au (100)*

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6 In this section, the characterization of SAMs composed by selenols (where a Se atom working  
7 as the head group is bonded to the gold surface) adsorbed on Au (100) and Au (111) is discussed.  
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9 To the best of our knowledge, this is the first work that analyzes the adsorption of selenols on Au  
10 (100). Figure 4 presents the reductive desorption voltammograms of 2 different selenol-based  
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12 species; Benzyl-Se (prepared by the immersion of clean substrates in 0.2 mM dibenzyl diselenide  
13 solution) and BSe (prepared from diphenyl diselenide). These molecules were chosen as  
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15 representative selenol-based SAMs containing a  $sp^3$ -C\* (Benzyl-Se) and a  $sp^2$ -C\* (BSe). The RD  
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17 profiles of these molecules present single and prominent sharp peaks. For comparison, the analog  
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19 sulfur-based SAMs were added in Figure 4. In agreement with previous works,<sup>23,28,27</sup> RD  
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21 potential is shifted to more negative values for Se-based SAMs than that obtained for thiolated  
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23 SAMs from Au (111) (from -0.61 V to -0.79 V for BT to BSe and from -0.88 V to -0.94 V for  
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25 Benzyl-T to Benzyl-Se). This effect is also found for the desorption from Au (100) since RD  
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27 varies from -0.88 V to -1.07 V for BT to BSe and from -1.06 V to -1.16 V for Benzyl-T to  
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29 Benzyl-Se. The RD shifts  $|\Delta E_p(100 - 111)|$  are 0.22 V and 0.28 V for Benzyl-Se and BSe,  
30  
31 respectively (red circles in Figure 2). Therefore, according to our EC data Se-based SAMs are  
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33 electrochemically more stable than the analog thiols and the  $|\Delta E_p(100 - 111)|$  for selenols are  
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35 both higher than that for the analog thiols (Figure 2, 0.22 V vs 0.17 V and 0.28 V vs 0.26 V for  
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37 Benzyl and Benzene spacer groups, respectively). These results suggest that the Au (100)  
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39 crystalline face stabilizes more the Se-based SAMs than S-based SAMs on the Au (111) surface.  
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**Figure 4.** Reductive desorption (RD) profiles of SAMs prepared from 0.2 mM solutions of BSe and Benzyl-Se on Au (111) (black lines) and Au (100) (red lines). For comparison, the RD profiles of the similar thiolated molecules, are presented in discontinuous lines. Electrolyte: 0.1 M KOH. Scan rate: 50 mV/s.

The characterization of selenols on Au (100) and on Au (111) by means of XPS, for the same SAMs characterized by RD technique, has been performed. The Se 3d photoemission spectra shown in Figure 2\_SI shows one doublet at around 54.2 eV (assigned to R-Se molecules adsorbed on gold surfaces);<sup>25</sup> regardless the molecules and substrate used. Thus, in contrast to the core level shift shown for aliphatic thiols, no changes in the binding energy were found for different type of selenols adsorbed on different crystalline facets. These data are not completely

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4 conclusive due to the difficulty in the fitting procedure; Se 3d component is superimposed with  
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6 another broad feature at around 57 eV attributed to photoelectrons from Au 5p<sub>3/2</sub> (Figure SI\_2).  
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8 Further investigations on this topic should be performed to clarify this issue.  
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11 Summarizing, the hybridization of the C\* atom on the electrochemical stability and chemical  
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13 characteristics of the Au(*hkl*) – S bonds is determinant for thiols SAMs. For sp<sup>3</sup>-C\* SAMs, the  
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15 core level shift observed for Au (100) surfaces, suggests different chemical environments;  
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17 whereas from EC results, a chain length dependence of the stability of the SAM is observed. In  
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19 contrast, for sp<sup>2</sup>-C\* SAMs there is no core level shift and the  $|\Delta E_p(100 - 111)|$  is constant  
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21 regardless the functionalization of the species, suggesting that are chemically similar on both  
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23 surfaces. For Se-based SAMs, an even higher stabilization was found for Au (100) surfaces.  
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## 31 CONCLUSIONS

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34 In this paper, we have analyzed the effect of the Au crystalline face, Au(111) and Au(100) on  
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36 the electrochemical stability of sulfur and selenol based-SAMs. The chemical strength of the  
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38 Au(*hkl*) – S and Au(*hkl*) – Se bonds in these SAMs was studied via X-Ray Photoelectron  
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40 Spectroscopy measurements. A relevant role of the C\* (C atom bonded to S) hybridization in the  
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42 configuration of the SAMs was found. Thus, the effect of the C\* hybridization on the EC  
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44 stability as well as the Au(*hkl*) – S bond strength was discussed. In this context an interesting  
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46 increment of the EC stability of AT- based SAMs (thiols that presents the C\* in sp<sup>3</sup>  
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48 hybridization) on Au (100) with the increase of the chain length was found. It was shown that for  
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50 short AT, this higher EC stabilization on Au (100) is due to the rise of the surface normal dipole  
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52 moment and thus, a decrease of the potential of zero charge. For longer ATs, lateral interactions  
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3 between the spacer groups become more significant. The effect of the modification of the AT  
4 terminal group (-CH<sub>3</sub>) on the EC stability was also presented. On the other hand, a constant EC  
5 cathodic shift was found when forming a sulfur based SAM with thiols with the C\* in a  $sp^2$   
6 hybridization. Finally, a 0.2 eV core level shift, from Au (111) to Au (100), of the S 2p signal  
7 corresponding to the S atoms in the thiol/Au interface was found only for SAMs formed with  
8 thiols with C\* with a  $sp^3$  hybridization (ATs). In contrast, for thiols that present the C\* atom  
9 with a  $sp^2$  hybridization, such as ArT, the BE remains constant (162.0 eV) regardless of the  
10 surface plane, indicating a similar chemical nature of the head-group and the surface. Also, Se-  
11 based systems were characterized on both Au (100) and Au (111), showing a higher EC  
12 stabilization than the analog S-based-SAMs when modifying the Au surface plane from Au (111)  
13 to Au (100).  
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## 31 ASSOCIATED CONTENT

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34 **Supporting Information.** Perpendicular dipole moment of *n*-alkanethiols and XPS spectra for  
35 selenols.  
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## 38 AUTHOR INFORMATION

### 39 Corresponding Authors

40 Dr. Fernando P. Cometto, e-mail: [fcometto@fcq.unc.edu.ar](mailto:fcometto@fcq.unc.edu.ar).

### 41 Author Contributions

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