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The role of the crystalline face in the ordering of 6-mercaptopurine self-assembled monolayers on gold

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Well-ordered molecular films play an important role in nanotechnology, from device fabrication to surface patterning. Self-assembled monolayers (SAMs) of 6-mercaptopurine (6MP) on the Au(100)-(1 × 1) and Au(111)-(1 × 1) have been used to understand the interplay of molecule–substrate interactions for heterocyclic thiols capable of binding to the surface by two anchors, which spontaneously form a highly disordered film on Au(111). Our results reveal that for the same surface coverage the simple change of the substrate from Au(111)-(1 × 1) to Au(100)-(1 × 1) eliminates molecular disorder and yields well-ordered SAMs. We discuss these findings in terms of differences in the surface mobility of 6MP species on these surfaces, the energetics of the adsorption sites, and the number of degrees of freedom of these substrates for a molecule with reduced surface mobility resulting from its two surface anchors. These results reveal the presence of subtle molecule–substrate interactions involving the heteroatom that drastically alter SAM properties and therefore strongly impact on our ability to control physical properties and to build devices at the nanoscale.

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1. Introduction

Thiol self-assembled monolayers (SAMs) on gold were discovered in the early 80s and since then have attracted the interest of both the surface science and nanotechnology communities.^{1,2} These monolayers are robust and easy to prepare and represent fundamental building blocks for creating complex structures for a wide variety of nanotechnological applications, as they are a simple means to link inorganic, organic, and biological materials to both planar and nanostructured gold surfaces.³

Thiol SAMs on gold are particularly attractive as key elements for the fabrication of molecular electronic devices, as functional units or building blocks for the development of new sensors and biosensors, and as inks for writing in the nanoscale by different types of lithography, among many others.^{3,4} Moreover, thiols are routinely used as capping agents in the synthesis of monodisperse gold nanoparticles (AuNPs).

The presence of defects, either of the substrate (in some cases induced by thiol adsorption, such as vacancy islands) or

of the adsorbed molecules (among them molecular disorder, domain boundaries, and pinholes), and the thiol mobility on the gold surface⁵ all have a strong impact on our ability to perform surface engineering at the nanoscale, and thus ultimately determine the fate of many of the applications of the SAMs.

Thiol SAMs on Au(111) are by far the most studied^{6–8} although some aspects concerning their surface chemistry still remain a matter of controversy.⁹ In contrast, thiol SAMs on Au(100) have been much less studied even if, for instance, {100} planes account for ≈30% of the surface area in gold nanoparticles ≈15 nm in size, which are those mostly employed for biomedical applications.¹⁰ Indeed there are only a few studies on the Au(100) substrates that have been limited to alkanethiol SAMs on the (hex) and (1 × 1) surfaces, where they form well-ordered SAMs without the formation of vacancy islands.^{11–13} On the other hand, to the best of our knowledge, there are no studies concerning the surface structure and chemistry of aromatic thiols on Au(100) surfaces.

In this work we have investigated 6-mercaptopurine (6MP) adsorption on Au(100)-(1 × 1).¹⁴ This N containing heterocyclic thiol (Fig. 1) of synthetic origin, which has medical relevance because of its use in the treatment of leukemia and some autoimmune diseases, has interesting features when self-assembled on the Au(111)-(1 × 1) surface. In fact, 6MP adsorbs on the Au(111)-(1 × 1) surface forming a thiolate bond but also interacts with the gold surface through the N(7) atom, *i.e.* the molecule exhibits a double anchor to the substrate that could limit molecule mobility on the Au surface. Also, 6MP reaches a

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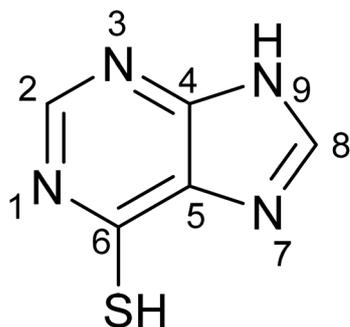


Fig. 1 Chemical structure of the 6-mercaptopurine (6MP) molecule.

maximum thiol surface coverage ≈ 0.25 and does not induce vacancy island formation^{14,15} in a similar manner to other aromatic thiols, such as benzenethiol¹⁶ and 4-mercaptobenzoic acid.¹⁷ However, it is unable to form ordered molecular domains, and thus there are no domain boundaries at room temperature, unlike the case of the aforementioned aromatic thiols.¹⁴ This seems to be a general behavior of heterocyclic thiols that can form double anchors with the Au(111) surface. In fact, it has been found that they spontaneously form very disordered molecular structures containing islands of agglomerated molecules, as in the case of 2-mercaptoimidazole, 2-mercaptobenzothiazole and mercaptobenzoxazole on Au(111).¹⁸ Only when molecules are partially desorbed can ordered molecular patterns be observed.

The results for the self-assembly of 6MP on the Au(100)-(1 × 1) surface presented in this work show that by simply changing the substrate from (111) to (100) it is possible to eliminate molecular disorder in heterocyclic thiols, and to obtain large crystalline molecular domains. These results reveal the presence of subtle molecule–substrate interactions involving the heteroatom that drastically alter SAM properties and therefore strongly impact on our ability to control physical properties and to build devices at the nanoscale.

2. Experimental methods

Sample preparation

Au(100) and Au(111) single-crystal substrates (MaTeck) were cleaned by repeated cycles of sputtering with Ar⁺ ions and annealing at 825 K. The cleanliness of the samples was checked with an STM operating in UHV. The Au(100)-(1 × 1) surfaces were electrochemically generated¹² by starting from the Au(100)-hex substrate and then lifting the reconstruction in 0.05 M H₂SO₄ solution by applying a potential $E = 1$ V (vs. Ag/AgCl 3 M) for 3200 s, as already reported.¹³

SAMs of 6-mercaptopurine (6MP) (Aldrich, 98%) were prepared by immersion in 100 μM 6MP ethanolic solutions (BASF 99%) for 30 min. Then, the samples were removed from the solution, rinsed with ethanol and dried under Ar.

STM imaging

Samples were imaged using a home-made UHV STM operating at room temperature. W tips were used with 100–600 mV tunneling voltages and 100–350 nA tunneling currents. The STM was calibrated in *x*, *y* and *z* directions using the stripes of the well-known Au(100)-(5 × 20) (“hex”) surface reconstruction. WsXM software was used for image analysis.¹⁹

Electrochemical experiments

A home-built sample transfer system between UHV and the electrochemical environment was used. After UHV sample preparation or characterization the sample was brought to the transfer chamber and an argon atmosphere ($P = 1$ bar) was established.

Cyclic voltammetry was performed with an Autolab PGSTAT30 potentiostat and a three-electrode conventional electrochemical cell. A large area Pt coil was used as the counter electrode and a silver/silver chloride (3 M KCl) electrode was employed as reference (RE). All the potentials in the text are referred to that reference electrode. Aqueous 0.1 M NaOH solutions were prepared by using NaOH pellets (Sigma-Aldrich; 99.99% trace metals basis) and ultrapure water with 18.2 MΩ cm resistivity (Millipore Products, Bedford). Argon gas was 5.0 purity grade.

Thiol reductive electrodesorption curves were performed at room temperature by scanning the potential from -0.3 to -1.4 at 0.05 V s⁻¹ in the 0.1 M NaOH solution. In each case the charge density (*q*) involved in the reductive peak desorption was obtained by integration of the peak area. The geometrical area of the single crystal electrode (0.196 cm²) was used to calculate the current densities. This figure was taken as an indication of the surface coverage by the thiol SAM.

XPS measurements

Photoemission experiments for 6MP SAMs on Au(100)-(1 × 1) and Au(111)-(1 × 1) surfaces were carried out in a commercial ultrahigh vacuum chamber with a double anode X-ray source and a 150 mm hemispherical electron energy analyzer (SPECS Phoibos 150). The base pressure was in the range of low 10^{-10} mbar. Spectra were collected after exciting the sample with monochromatized Al K α radiation at 1486.7 eV. The binding energy (BE) scales for the SAMs on Au surfaces were calibrated by setting the Au 4f_{7/2} BE to 84.0 eV with respect to the Fermi level. High-resolution S 2p and Au 4f_{7/2} spectra were acquired using the fixed analyzer transmission (FAT) mode with the analyzer pass energy of 20 eV.

Quantitative analysis was performed with CasaXPS v 2.3.14 software. The atomic concentrations were calculated with the corresponding relative sensitivity factors (RSF). High resolution spectra were fitted with XPS Peak v 4.1 software. Shirley type backgrounds were used during the fitting procedure and peaks that are a combination of Lorentzian and Gaussian functions were employed for all regions. In the case of the S 2p signal, the spin–orbit doublet separation was fixed at 1.18 eV and an intensity ratio of 2 : 1 was used.

Computational methods

Density functional calculations have been performed with the periodic plane-wave basis set code VASP 5.2.12.^{20–22} We have followed the scheme of non-local functional proposed by Dion *et al.*²³ vdW-DF, and the optimized Becke88 exchange functional optB88-vdW²⁴ were used to take into account van der Waals (vdW) interactions. The projector augmented plane wave (PAW) method has been used to represent the atomic cores²⁵ with PBE potential. The electronic wave functions were expanded in a plane-wave basis set with a 420 eV cutoff energy. Optimal grids of Monkhorst-Pack²⁶ k -points $5 \times 5 \times 1$ and $3 \times 5 \times 1$ have been used for numerical integration in the reciprocal space of the $(3 \times \sqrt{10})$ and $(3\sqrt{2} \times \sqrt{5})R45^\circ$ unit cells, respectively. The Au(100)-(1 × 1) substrates were represented by a five atomic layer and a vacuum of ~ 17 Å that separates two successive slabs. Surface relaxation is allowed in the three uppermost Au layers of the slab, as well as the atomic coordinates of the adsorbed species were allowed to relax without further constraints. The atomic positions were relaxed until the force on the unconstrained atoms was less than 0.03 eV \AA^{-1} . The adsorbates are placed on just one side of the slab and all calculations include a dipole correction. Radical 6MP species was optimized in an asymmetric box of $20 \text{ \AA} \times 20 \text{ \AA} \times 40 \text{ \AA}$. The calculated Au lattice constant is 4.16 \AA , which compares reasonably well with the experimental value (4.078 \AA).²⁴ The average binding energy per adsorbed 6MP species on Au(100)-(1 × 1) surfaces, E_b , is defined in eqn (1):

$$E_b = \frac{1}{N_{\text{thiol}}} [E^{\text{thiol/Au}} - E^{\text{Au}} - N_{\text{thiol}}E^{\text{thiol}}] \quad (1)$$

where $E^{\text{thiol/Au}}$, E^{Au} and E^{thiol} stand for the total energy of the adsorbate–substrate system, the total energy of the Au slab, and the energy of the 6MP radical, respectively, whereas N_{thiol} is the number of 6MP radicals in the surface unit cell. A negative number indicates that the adsorption is exothermic with respect to the separate clean surface and 6MP radical. The Gibbs free energy of adsorption of each surface structure (γ) was approximated through the total energy from DFT calculations by using eqn (2):

$$\gamma = \frac{N_{\text{thiol}}E_b}{A} \quad (2)$$

where A is the unit cell area. Considering that we are concerned with free energy differences, it is reasonable to assume that the contributions coming from the configurational entropy, the vibrations and the work term pV can be neglected.^{27,28}

The change in the work function, ΔW , caused by SAM formation with respect to the clean Au(100) surface is defined as

$$\Delta W = W_{\text{SAM}} - W_{\text{clean metal}} \quad (3)$$

Changes in the vertical component of the surface dipole due to the adsorption of the SAM, $\Delta\mu_\perp$,²⁹ are related to ΔW values by

$$\Delta W = \frac{N\Delta\mu_\perp e}{\epsilon_0} \quad (4)$$

where N represents the molecular density of the SAM, e the elementary charge and ϵ_0 the permittivity of vacuum. The change in the surface dipole $\Delta\mu_\perp$ involves two components. The first component is μ_{SAM} , the molecular dipole moment of the SAM along the normal direction that represents the dipole moment along the surface normal of adsorbates embedded in a free-standing SAM (without the substrate). The second one is μ_{CHEM} , the change in the surface dipole resulting from the charge transfer between the adsorbate and the gold surface. We have calculated μ_{SAM} by using

$$\mu_{\text{SAM}} = \frac{[V_{\text{SAM}}(\infty) - V_{\text{SAM}}(-\infty)] \epsilon_0}{e N} \quad (5)$$

where $V_{\text{SAM}}(\infty)$ and $V_{\text{SAM}}(-\infty)$ are the asymptotic electrostatic potential on both sides of the SAM. Thus, μ_{CHEM} can be obtained from $\Delta\mu_\perp$ and μ_{SAM} values.

3. Results and discussion

Experimental results

STM images of the Au(100)-(1 × 1) surface after 6MP adsorption (Fig. 2a) show atomically smooth terraces separated by steps of monoatomic height (blue arrow and inset in Fig. 2a), and some isolated Au islands (green arrow in Fig. 2a) that are produced during the electrochemical lifting of the hex surface prior to 6MP adsorption. Also, no evidence of vacancy island

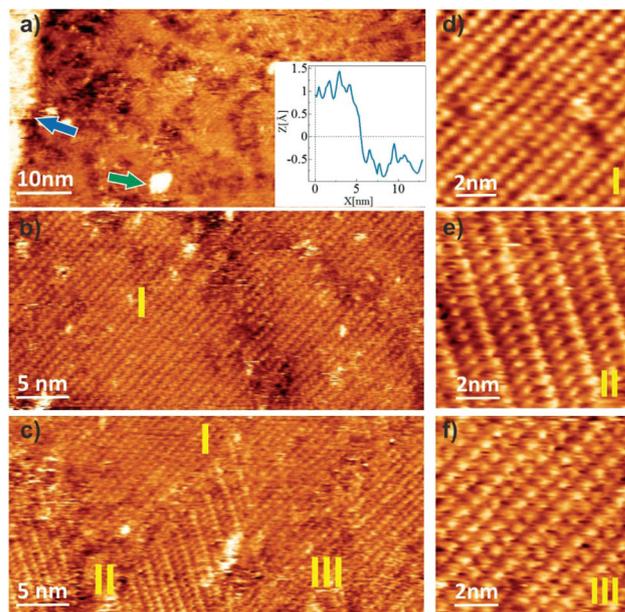


Fig. 2 (a–f) STM images (raw data) of a 6MP-covered Au(100)-(1 × 1) surface. (a) Flat terrace showing Au islands (green arrow), and steps of monoatomic height (blue arrow and inset). (b) Ordered surface structure of 6MP molecules arranged in the most frequently observed pattern (type I). (c) Type I domains coexisting with domains of type II and III surface structures. (d) 6MP molecules forming rectangular patterns (type I). (e) 6MP molecules forming the type II surface structure. (f) 6MP molecules forming the type III surface structure.

formation on the terraces was detected in the STM images, as the black regions shown in the images correspond to pinholes (depth < 0.2 nm). At higher resolution the images (Fig. 2b) reveal that the terraces are covered by ordered rows of molecules (type I structure).

This surface structure, by far the most frequently observed on this substrate, consists of rectangular structures $0.5 \pm 0.03 \text{ nm} \times 0.7 \pm 0.03 \text{ nm}$ in size (Fig. 2d). In some cases we were able to image domains with other structures (that we will call type II and type III surface structures) coexisting with type I domains (Fig. 1c). Type II domains are the least frequently observed and consist of molecular patterns with a bright spot and a dark spot forming rectangles $0.50 \pm 0.03 \text{ nm} \times 0.8 \pm 0.03 \text{ nm}$ in size (Fig. 2e). Thus, these domains appear as stripes with the bright spots separated by $\approx 1.6 \text{ nm}$. On the other hand, domains of type III surface structures consist of nearly squared molecular arrangements $0.65 \pm 0.03 \text{ nm} \times 0.6 \pm 0.03 \text{ nm}$ in size (Fig. 2f). Each rectangle is formed by two bright and two dark spots that form alternating rows separated by 1.3 nm. Finally, we have estimated the fractional area covered by domains I, II, and III from the analysis of 10 STM images with molecular resolution taken on different regions of the 6MP covered SAMs. Results over $20\,000 \text{ nm}^2$ of total area imaged yield 70%, 10% and 20% covered by domains of type I, II and III, respectively.

From these measurements, and taking into account the 6MP molecular area in these surface structures, the surface coverage by 6MP molecules is $\theta \approx 0.22$. Note that we should discard significant contributions from π - π stacking in these molecular structures, as they are not significant for intermolecular distances larger than 0.4 nm.^{30,31}

It is interesting to compare the STM data shown in Fig. 2 with those obtained for the same molecule on the Au(111)-(1 × 1) surface (Fig. 3). Although previous STM data were obtained on preferred oriented Au(111) and the images taken

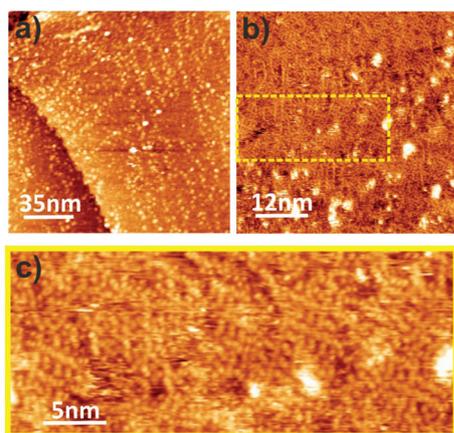


Fig. 3 STM images (raw data) of a 6MP-covered Au(111)-(1 × 1) surface. (a) Flat terraces showing molecular aggregates. (b) Molecular aggregates and 6MP molecules in disordered arrangement. (c) Zoom corresponding to the yellow region in (b) where rectangles, chain-like and isolated 6MP molecules are observed.

in air,¹⁴ present data using Au(111) single crystals and imaged in UHV confirm all the features already reported for this system. Indeed, the images clearly show that no extensive vacancy island formation takes place on Au(111)-(1 × 1) terraces (Fig. 3a and b), in agreement with what has been observed on the Au(100)-(1 × 1) surface (Fig. 2). Also in this case the black regions observed in these images correspond to pinholes, as revealed by the cross-section analysis (not shown). Moreover the molecular aggregates¹⁴ imaged for 6MP on Au(111)-(1 × 1) (Fig. 3a) are absent on the Au(100)-(1 × 1) surface where only a few, randomly distributed, islands/aggregates are imaged (Fig. 2b).

It should be noted that 6MP on the Au(111)-(1 × 1) surface exhibits much more complex molecular patterns. While some rectangular molecular structures $0.75 \times 0.6 \text{ nm}^2$ in size, which have been modeled as a $(2 \times 3\sqrt{3})$ lattice ($\theta = 0.17$),¹⁴ are evident, the image also shows a variety of other molecular structures such as long chains, trimers, dimers of closely packed molecules (intermolecular distances 0.4–0.45 nm) in a disordered arrangement (Fig. 3b). Thus, in contrast to that observed for this molecule on the Au(100)-(1 × 1) surface, neither domains nor domain boundaries can be observed in the images. Similar results are obtained by increasing the immersion time to 12 h, *i.e.* the order is not time dependent. Therefore, it is evident that the 6MP lattice exhibits a shorter range order on the Au(111)-(1 × 1) surface compared to those found on the Au(100)-(1 × 1) surface (Fig. 2b). Finally, we do not have any experimental evidence for substrate reconstruction leading to the formation of 6MP–Au adatom complexes on the terraces of both crystal faces as no vacancy islands are observed there. However, the serrated step edges in the STM images indicate that their presence cannot be completely excluded.

High resolution S 2p XPS spectra for 6MP SAMs on the Au(100)-(1 × 1) surface (Fig. 4(a)) reveal the presence of a single doublet corresponding to thiolate species with a S 2p_{3/2} binding energy (BE) at 162.2 eV, very similar to the value measured for 6MP on Au(111)-(1 × 1) (162.3 eV).¹⁴ The absence in our spectra of non-bonded 6MP (163.5 eV), sulfide species (161.3 eV) and oxidized products of the molecule (like sulfonates) at BE >166 eV is in agreement with previous data on the Au(111) surface.¹⁴

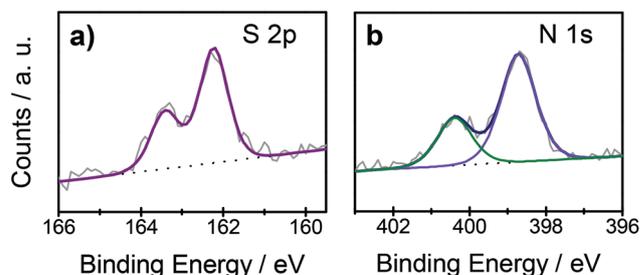


Fig. 4 High resolution XPS spectra of 6MP on Au(100)-(1 × 1): (a) S 2p and (b) N 1s.

N 1s XPS spectra (Fig. 4(b)) exhibit two components, N1 and N2, at binding energies 398.7 eV and 400.4 eV, respectively, as found in previous results for SAMs of 6MP and related molecules.^{32,33} The peak at higher BE can be attributed to protonated nitrogen atoms^{32,34} (either N(9) or N(7)), while the other one, of higher intensity, can be assigned to N atoms involved in the N=C bonds of the fused pyrimidine and imidazole rings.³⁵ The fact that the peak area ratio N1/N2 is not 3 could be attributed to partial deprotonation caused by interaction with the gold substrate, as already suggested.³²

From the quantitative analysis we have found a thiol coverage of ≈ 0.23 , in good agreement with the lattices obtained from STM imaging ($\theta \approx 0.22$). However, the measured atomic concentration ratio N/S = 7 is larger than that expected from the stoichiometry N/S = 4, which could result from the attenuation of the S signal due to the inelastic scattering³⁶ produced by the thiol ring. In addition, N/S ratios >2 has been obtained for relatively short amino-terminated thiols, such as 6-amine-1-hexanethiol, for which the expected ratio is 1.³⁷ Indeed, even for shorter amine-terminated thiols, like cysteamine, the N/S ratio in SAMs is >1.³⁸

Typical reductive desorption curves for the 6MP on the Au(100)-(1 × 1) surface show a main sharp peak located at a peak potential $E_p = -0.82$ V and a very small hump at ≈ -0.6 V (Fig. 5, full black line). The small hump appears at the same potential of the main desorption peak of 6MP on the Au(111)-(1 × 1) surface (Fig. 5, dashed gray line) suggesting that it can be assigned to 6MP desorption from (111) steps. Previous works have assigned the peaks at -0.6 V and -0.82 V to desorption of the 6MP molecules from the (111) and (100) gold single crystal facets, respectively.^{15,39} Interestingly, while the FWHM of the desorption peaks are very similar, in the case of 6MP on Au(111)-(1 × 1) there is an additional broad component that extends from -0.63 to -0.68 V, typical of a disordered adlayer.

The charge density (q) involved in the peak for the Au(100)-(1 × 1) surface is $q = 45 \pm 7 \mu\text{C cm}^{-2}$. Taking into account that the reductive desorption of thiols involves a one electron transfer, and considering the surface density of gold atoms on the

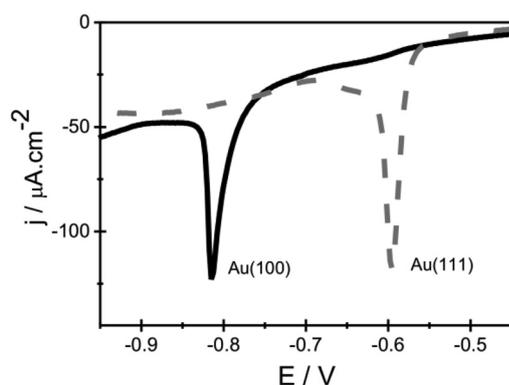


Fig. 5 Electrodesorption curves recorded in 0.1 M NaOH at 0.05 V s^{-1} for 6MP from the Au(100)-(1 × 1) (solid line) and Au(111)-(1 × 1) surfaces (dashed line).

Au(100)-(1 × 1) surface, a thiol coverage $\theta = 0.23$ is obtained, in good agreement with STM and XPS results. Also, this figure is close to that estimated on the Au(111) surface from XPS and cyclic voltammetry ($\theta = 0.25$).¹⁴

The large difference in E_p for a similar surface coverage indicates that the electrochemical stability of the 6MP molecules is larger on the Au(100)-(1 × 1) than on the Au(111)-(1 × 1) surfaces, in agreement with previous data for mercaptobenzoic (MBA) acid and cysteine⁴⁰ and also for hexanethiol,¹³ thus suggesting a general trend that should be explained.

DFT results

We have modeled the most frequently observed surface structures, type I and type III, as $(3 \times \sqrt{10})$ and $(3\sqrt{2} \times \sqrt{5})R45^\circ$ lattices, respectively, both with two 6MP moieties in the unit cell and $\theta = 0.22$. The optimized models are shown in Fig. 6a and 7a (top view) and 6b and 7b (side view). On the other hand, the positions of the S-heads are indicated in Fig. 6c and 7c. The surface structure of the $(3 \times \sqrt{10})$ consists of 6MP molecules forming rows of rectangles $0.53 \times 0.73 \text{ nm}^2$ in size rotated $\approx 45^\circ$ with respect to the substrate unit cell (Fig. 6c). Molecules are bonded through the S atoms which are placed at bridge and on top sites of the Au surface and by N(7) atoms at top sites.⁴¹ The tilt angle of the molecular plane with respect to the surface normal is $\alpha \approx 40^\circ$ (Fig. 6b).

On the other hand, the surface structure of the $(3\sqrt{2} \times \sqrt{5})R45^\circ$ lattice consists of rectangles slightly deformed into rhombohedra $0.62 \times 0.66 \text{ nm}^2$ in size with $\theta = 0.22$ (Fig. 7a). In this lattice one 6MP binds to the surface through the S and N7

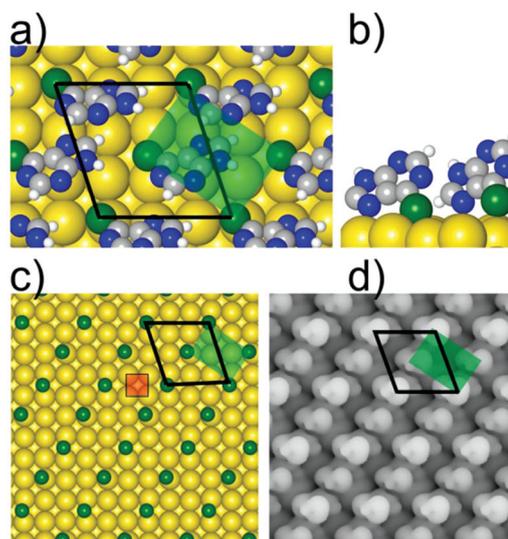


Fig. 6 Optimized $(3 \times \sqrt{10})$ surface model for 6MP on Au(100)-(1 × 1). (a) Top view scheme where the 6MP molecules are indicated. (b) Side view of the 6MP moieties on the substrate. (c) Top view where only the S heads of the 6MP are shown. Key: yellow, Au atoms; green, S atoms; grey, C atoms; blue, N atoms; white, H atoms. The rectangular motif (green) and the unit cell of surface structure (black) are indicated. The Au(100)-(1 × 1) unit cell is indicated by the red square. (d) Simulated constant current STM images for 6MP on the $(3 \times \sqrt{10})$ surface model.

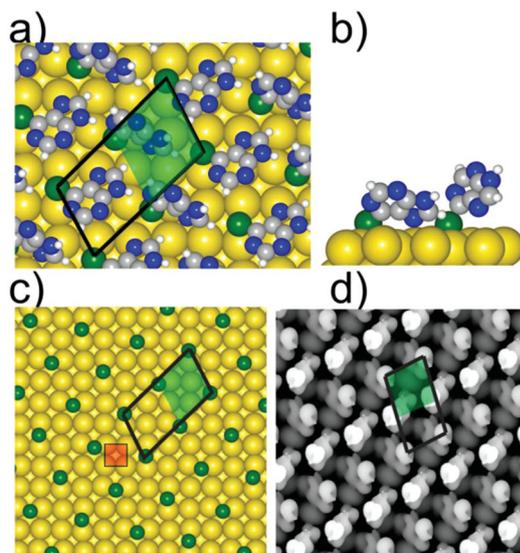


Fig. 7 Optimized $(3\sqrt{2} \times \sqrt{5})R45^\circ$ surface model for 6MP on Au(100)-(1 \times 1). (a) Top view scheme where the 6MP molecules are indicated. (b) Side view of the 6MP moieties on the substrate. (c) Top view where only the S heads of the 6MP are shown. Key: yellow, Au atoms; green, S atoms; grey, C atoms; blue, N atoms; white, H atoms. The rhombohedral motif (green) and the unit cell (black) are indicated. The Au(100)-(1 \times 1) unit cell is indicated by the red square. (d) Simulated constant current STM images for 6MP on the $(3\sqrt{2} \times \sqrt{5})R45^\circ$ surface model.

atoms at the bridge and top sites of the Au(100)-(1 \times 1) surface, respectively, while another 6MP binds to the substrate only through the S atom at a bridge position (Fig. 7b). In the former configuration the 6MP molecules adopt $\alpha \approx 55^\circ$ while in the second one (*i.e.*, only bonded by the S atom) $\alpha \approx 25^\circ$. Note that in both cases the simulated STM images of our models (Fig. 6d and 7d) reasonably agree with the experimental STM images shown in Fig. 2b and e. The marked difference in contrast between rows of molecules observed in the $(3\sqrt{2} \times \sqrt{5})R45^\circ$ lattice corresponds to 6MP molecules with different tilt angles. Interestingly, the $(3 \times \sqrt{10})$ lattice exhibits a slightly better binding energy (E_b) and thermodynamic stability (γ) than the $(3\sqrt{2} \times \sqrt{5})R45^\circ$ (Table 1), thus explaining the coexistence of these surface structures on the Au(100)-(1 \times 1) substrate.

Also, both surface structures show better energetic and stability parameters than the 6MP $(2 \times 3\sqrt{3})$ lattice already proposed to model this molecule on the Au(111)-(1 \times 1) surface (Table 1). This is not surprising, as it is known that molecules adsorb more strongly on open Au surfaces than on the compact Au(111) surface.⁴² We have also analyzed the $\Delta\mu_\perp$ values for the 6MP models on both crystal surfaces (Table 1). This quantity depends on μ_{CHEM} and μ_{SAM} (eqn (5)) and the tilt angle α . The results (Table 1) show similar $\Delta\mu_\perp$ values for the ordered 6MP lattices irrespective of the substrate. Interestingly, μ_{CHEM} has an opposite sign in 6MP (+) than that found for alkanethiols (-) because of the influence of the charge transfer reordering induced by the N-Au interactions (Table 1).

Table 1 Energetic, structural and Bader charge data for 6MP surface structure on Au(100)-(1 \times 1) and Au(111)-(1 \times 1) planes

Substrate	Au(100)-(1 \times 1)		Au(111)-(1 \times 1)
Surface lattice	$(3 \times \sqrt{10})$	$(3\sqrt{2} \times \sqrt{5})R45^\circ$	$(2 \times 3\sqrt{3})$
θ	0.22	0.22	0.17
E_b/eV	-3.24	-3.21	-2.93
$\gamma/\text{meV } \text{\AA}^{-2}$	-83.3	-82.5	-65.2
$Z(\text{S-Au}_{\text{surf}})/\text{\AA}$	2.46/1.93	1.98/1.72	2.45/2.19
$Z(\text{N-Au}_{\text{surf}})/\text{\AA}$	2.33/2.32	2.34	2.46/2.39
$d(\text{S-Au})/\text{\AA}$	2.40/2.46-2.50	2.48-2.50/2.45/2.51	2.44/2.46-2.79
$d(\text{N-Au})/\text{\AA}$	2.34/2.32	2.34	2.38/2.45
$\alpha/^\circ$	46.1/38.7	55.4/25.1	55.8/62.6
$\Delta W/eV$	-0.74	-1.03	-0.69
$\Delta\mu_\perp/D$	-0.78	-1.08	-0.83
μ_{CHEM}/D	+0.27	+0.02	+0.35
μ_{SAM}/D	-1.05	-1.1	-1.18
Bader charge/e			
S(Au _S)	6MP ₁ : -0.11(+0.07)	6MP ₁ : -0.11(+0.06)	-0.12(+0.06)
	6MP ₂ : -0.11(+0.04)	6MP ₂ : -0.11(+0.05)	
N(Au _N)	6MP ₁ : -2.75(+0.15)	6MP ₁ : -2.76(+0.12)	-2.77(+0.12)
	6MP ₂ : -2.70(+0.13)		

We have made single point calculations for each moiety in the optimized geometry to gain insight into its bonding to the substrate. Results show that the S-Au bond in the bridge position is 0.5 eV more stable than in the on-top position. Comparison of 6MP adsorption in the bridge position with the N atom bonded to gold ($(3 \times \sqrt{10})$ lattice) and without the N-Au bond ($(3\sqrt{2} \times \sqrt{5})R45^\circ$ lattice) (Fig. 7) reveals that the N-Au bond energy is ≈ -0.65 eV, close to the value found for the N-Au bond on the Au(111) surface (-0.52 eV). Charge density difference isosurfaces (Fig. 8) show that the electronic charge is accumulated between Au and S atoms in the Au-S bond and in the N atom in the Au-N bond. This behavior shows the stronger and more covalent character of the S-Au bond compared to the N-Au bond. Also, the isosurfaces reveal that the electronic charge is nearly twice for the S atom at the bridge site (Fig. 8a, c and d) than that found for the S atom at the on top site (Fig. 8b).

Because the 6MP geometry with the S atom in the bridge position and the N(7) atom interacting with the gold substrate is the energetically most favored configuration, one would expect that all molecules should be adsorbed in this configuration. However, this arrangement implies a large tilt (Fig. 8a and c) and therefore a smaller surface coverage than that obtained with less tilted configurations. This can be achieved either with the S atom at the bridge site but with a non-bonded N atom (Fig. 8d) or with the S atom at the top site (Fig. 8b). In both cases E_b is lower but the γ value of the unit cell increases due to the higher surface coverage. Note that the N(7) atom bonding to the gold surface has a strong impact in $\Delta\mu_\perp$, and accordingly in ΔW . In fact, ΔW is ≈ -0.3 eV smaller for the $(3 \times \sqrt{10})$ model (all N(7) atoms bonded) than that estimated for the $(3\sqrt{2} \times \sqrt{5})R45^\circ$ model (half of N(7) atom bonded), thus reflecting the impact of molecule configuration on the electronic properties of SAMs.

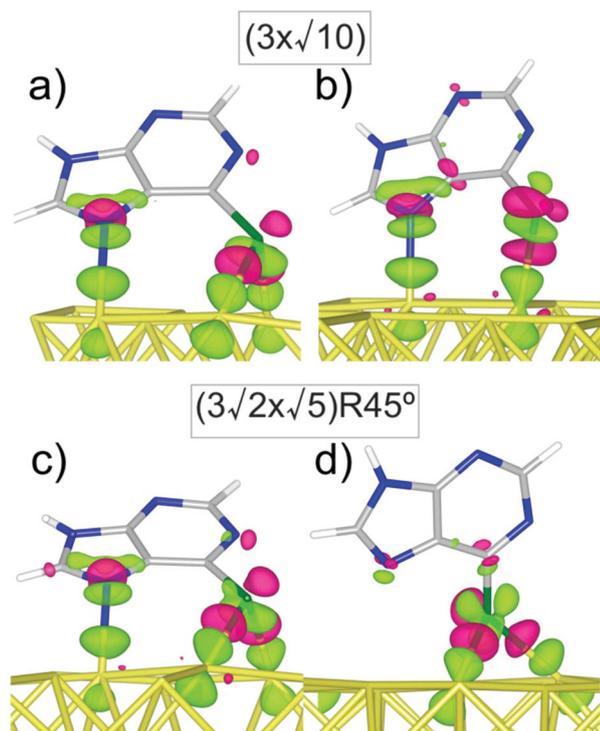


Fig. 8 Charge density difference isosurfaces for the surface models 6MP on Au(100)-(1 × 1). (a, b) $(3 \times \sqrt{10})$ lattice and (c, d) $(3\sqrt{2} \times \sqrt{5})R45^\circ$ lattice. Pink colour shows electronic charge accumulation and green depletion.

The Bader charge analysis of the Au–S and Au–N bonds of the 6MP molecules indicates that the S and N atoms are negatively charged while Au atoms are positively charged (Table 1). However, the charge at the N and Au atoms is much larger compared to that found from the Au to the S atoms. These results are similar to those found for the 6MP molecules on the Au(111) surface, as shown in Table 1.

DFT calculations reveal very interesting features about the interaction of 6MP with both crystal faces. While results from the $(2 \times 3\sqrt{3})$ model for 6MP on the Au(111)-(1 × 1) substrate should be taken with care, as the ordered lattice model for the 6MP on the Au(111) surface is valid only in small regions of the surface due to the short range order observed in this system (Fig. 3), it is evident that in the best configuration most of the 6MP molecules bind the Au substrates through the S and N(7) atoms and that the surface dipoles are of the same sign and magnitude. This information is relevant in order to understand surface order and electrochemical stability as shown below.

4. Discussion

The present results from STM imaging lead to an interesting question: why do 6MP molecules either yield ordered or disordered molecular surface structures with a similar coverage, depending on the single crystal face? This is particularly intriguing, as alkanethiols form well-ordered lattices on both substrates.^{13,43}

First, the formation of ordered domains of the adsorbate depends on the feasibility of diffusion of the molecules on the surface along a low energy barrier path.^{44,45} This diffusion can be hindered because of the structure and chemical characteristics of the molecule, including the shape and type and number of groups that are anchored to the substrate surface. In fact, it has been shown that the shape of the molecule has an important role in the diffusion process.⁴⁶ 6MP is an ellipsoidal molecule, and, as such, its displacement along the surface involves some sort of rotational movement, thus making diffusion more difficult than in the case of non-elongated species.⁴⁶ Moreover, 6MP is mainly fixed to the surface by two anchors (S and N7 atoms), therefore hindering surface mobility at room temperature, as has been observed in the case of aromatic dithiols that bind to the Au(111) surface through two S bonds.⁴⁴ This is also consistent with the large molecular disorder observed for other heterocyclic thiols, like 2-mercaptoimidazole, 2-mercaptobenzothiazole and mercapto-benzoxazole, which not only form the typical thiolate bonds but also interact with the Au(111) by the N, S or O, respectively.¹⁸ Also in this case the molecules spontaneously form very disordered molecular arrangements and ordered molecular patterns can be observed only when they are partially desorbed. Thus, the restricted surface mobility induced by the formation of two molecule–substrate bonds is a key point, as it should hinder the formation of ordered molecular domains. In fact, it should be noted that in contrast to 6MP, 4-mercaptobenzoic acid (MBA) molecules, which are anchored to the Au(111)-(1 × 1) surface only by the S atom, can form well-ordered SAMs with a similar surface coverage at room temperature.¹⁷

There are several other reasons that can contribute to the larger molecular order on the Au(100)-(1 × 1) substrate. When comparing 6MP adsorption on the Au(100)-(1 × 1) and Au(111)-(1 × 1) surfaces, it should be mentioned that in the former case the monolayer can evolve to a longer range order due to the lower number of $\langle 110 \rangle$ directions in $\{100\}$ planes compared to $\{111\}$ planes (4 vs. 6), as the preferred adsorption site lies along this symmetry direction.⁴⁷ Thus, the adsorbed molecule has fewer options (lesser degrees of freedom) to find a “correct” position in the case of the Au(100) surface and larger ordered molecular domains can be achieved.

Also, DFT calculations exploring the energetic of the (111) and (100) surfaces for 6MP adsorption on different sites show differences between adsorption sites of ≈ 0.2 eV and ≈ 0.5 eV for the (111) and (100) surfaces, respectively, although this energy strongly depends on the 6MP molecule orientation. Therefore, one could speculate that the small difference in adsorption energy exhibited by (111) surface sites at high coverage⁴⁸ also contributes to anchor the molecules with a higher degree of disorder, *i.e.* the driving force for diffusion of the 6MP molecule to a energetically more favored adsorption site so as to decrease the surface free energy is smaller on the Au(111) surface.

Another contribution could be possible to explain why the 6MP molecule is more mobile on the Au(100)-(1 × 1) than on the Au(111)-(1 × 1). It is known that the binding energy of S to Au for arenethiols is ≈ 0.2 eV smaller than that found for alka-

nethiols, and that can lead to less mobility of arenethiolate–Au complexes in the SAMs.^{49,50} In our case the E_b value of 6MP on the Au(100)-(1 × 1) is ≈ 0.2 eV greater than that estimated for the Au(111)-(1 × 1) surface that could result in the formation of more mobile 6MP–Au adatom species. Although vacancy islands are not observed upon 6MP adsorption these species could be formed from step and gold island edges and could contribute to form ordered molecular patterns on the Au(100)-(1 × 1) surface. Although the models proposed for the 6MP on the Au(100)-(1 × 1) surface are not compatible with the geometry of the well known RS–Au_{ad}–SR complexes proposed for thiols on the Au(111)-(1 × 1), another gold–thiolate complex stoichiometry could be possible. This aspect is out of the scope of the present paper and deserves further research.

But, is this difference in SAM ordering related to the larger electrochemical stability of 6MP on the Au(100)-(1 × 1) compared to the Au(111)-(1 × 1) surface (0.2 V difference in E_p)? First, one should mention that similar differences have been reported for SAMs of other thiol molecules self-assembled on both crystal faces.^{13,40} In order to assess this behavior one should first consider the values of the zero charge potentials (E_{zcp}) of the different crystal faces in electrolyte solutions,⁵¹ as E_p can be expressed as

$$E_p = E_{zcp} + \eta \quad (6)$$

η being the overpotential needed to remove a thiol molecule from the SAM–Au interface. The latter depends on the binding energy of the adsorbates (E_b), the energy to solvate the desorbed species and on the nature of the metal surface. Therefore, E_p values measured in both gold faces should be referred to the corresponding E_{zcp} , which, in turn, depends on many factors, such as temperature, pH, and, more important, on the presence of adsorbed species (such as thiol molecules).⁵² Values of $E_{zcp} = 0.23$ V and $E_{zcp} = 0.08$ V (vs. SCE) have been reported for the (111)-(1 × 1) and (100)-(1 × 1), respectively, in acid media and in the absence of specifically adsorbed anions.⁵³ In addition, it is well established that E_{zcp} is proportional to the work function (W),⁵⁴ and that thiol adsorption markedly modifies the work function of clean metal surfaces.⁵⁵ From eqn (4) it can be seen that ΔW depends on N and $\Delta\mu_{\perp}$. Considering that the experimental θ values, which reflect N for both the crystal faces are similar, the most notable difference between the two 6MP surface structures is the long range and short range order present on the Au(100)-(1 × 1) and Au(111)-(1 × 1) surfaces, respectively. We suggest that in this case, molecular disorder in the SAMs decreases the magnitude of the effective dipole moment^{56,57} with respect to that present in the ordered 6MP SAMs (Table 1), thus resulting in a smaller ΔW and more positive E_{zcp} values for the disordered 6MP SAMs on the Au(111)-(1 × 1). Also the E_b contribution to η in eqn (6) is smaller for 6MP on the Au(111)-(1 × 1) surface despite the fact that our E_b value (Table 1) is probably overestimated since it is calculated for 6MP molecules adopting the best configuration at the best adsorption site in relation to those available in the real disordered layer. Thus,

both the differences in W and E_b explain the reduced electrochemical stability range compared to the same molecule on the Au(100)-(1 × 1) surface.

5. Conclusions

We have made a detailed experimental and theoretical study of the surface structure and chemistry of an aromatic thiol, 6MP, on the Au(100)-(1 × 1) and their results are compared to those found on the Au(111)-(1 × 1) surface. The 6MP molecule binds to the Au(100)-(1 × 1) surface through the S and N(7) atoms to form SAMs with a surface coverage of 0.25, as already reported for 6MP on the Au(111)-(1 × 1) surface. However, this thiol exhibits short range order and low electrochemical stability on the Au(111)-(1 × 1) surface compared to the Au(100)-(1 × 1) surface. These results can be explained in terms of the smaller number of degrees of freedom, the larger difference in energy among sites for adsorption, and the presence of more mobile species on the Au(100)-(1 × 1) compared to the Au(111)-(1 × 1) surface. All these factors can contribute to a better organization on the Au(100)-(1 × 1) surface for a molecule such as 6MP, which has reduced mobility resulting from its elongated shape and the existence of two anchors (S and N atoms). The lower electrochemical stability on the Au(111)-(1 × 1) surface may reflect the smaller decrease in the work function due to the smaller effective dipole moment induced by the greater disorder of the adlayer and a lower binding energy of the 6MP on this crystal face. In summary, the adsorption of 6MP on different gold surfaces reveals the interplay of both the nature of the adsorbate and of the substrate in the self-assembly process that can explain the intriguing behavior of other heterocyclic thiols on Au(111). It is clear that molecular order/disorder, defects and mobility in thiol SAMs can be tuned by an adequate selection of molecule type and shape and the substrate according to the desired applications.

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