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Self-assembly of zwitterionic molecules on a Au(23 23 21) surface at low temperature

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ABSTRACT

The adsorption of zwitterionic (*E*) 4-methoxy-4'-(3-*n*-sulfonatopropyl)stilbazolium (MSPS) molecules on the stepped vicinal Au(23 23 21) surface was studied by scanning tunneling microscopy (STM) at low temperature as a function of the molecular coverage. At the sub-half monolayer, a supramolecular network based on MSPS is preferentially adsorbed onto face-centered cubic stacking regions. At the monolayer, a complete periodic supramolecular film is obtained.

1. Introduction

The investigation of molecular adsorption on surfaces is of great industrial and fundamental scientific interest. One important motivation for exploring the surface chemistry is to tune with precision the electronic properties of organic/inorganic interfaces [1]. In this context, molecular and supramolecular ordering, which are key steps in the development of complex architectures, are controlled by a balance between the intermolecular forces and the molecule–substrate interactions [2–4]. In this field, the most interesting results are obtained on metals or HOPG because in these cases, the molecules/surface interactions are often weaker than the molecules/molecules interactions [2]. Therefore, the growth of large-scale self-assemblies was successfully achieved, thanks to noncovalent interactions (hydrogen bonding, metal coordination, van der Waals interactions, π – π interactions) [5–10] or more recently to covalent bonding [11–18]. Scanning tunneling microscopy (STM) has emerged as a powerful tool to investigate the orientations and the conformations of organic molecules onto surfaces [19]. Zwitterionic molecules are a class of neutral molecules including at least a pair of opposed and covalently linked charges. Adsorbates based on zwitterions were reported on semiconductor surfaces [20–22]. In this paper, the adsorption of a zwitterionic molecule, (*E*) 4-methoxy-4'-(3-*n*-sulfonatopropyl)stilbazolium (named MSPS), onto the Au(23 23 21) surface is investigated by

low-temperature STM (LT-STM) experiments. The formation of a complete self-assembled adlayer of MSPS is achieved and is explained by electrostatic interactions.

2. Experimental

The measurements were carried out in an ultra-high vacuum chamber (UHV, pressure lower than 10^{-10} mbar) with a low temperature Omicron microscope (LT-STM) operating at 77 K. Tips were made from PtIr wires mechanically cut and were prepared in UHV by field emission in STM on a metallic surface until stable and low noise junction was obtained.

The samples were cleaned by several cycles of Ar⁺ etching and annealing at 770 K and were characterized by STM. MSPS molecules were evaporated from a Knudsen cell to the substrate previously cooled at 130 K. Then, the sample was cooled down to 77 K and STM images were acquired in constant-current mode. MSPS were synthesized according to our method [20].

3. Results and discussions

MSPS molecules were chosen as a model of organic zwitterionic molecules. They are neutral but they carry positive and negative charges on different atoms. A sulfonato group (SO₃⁻) possessing a negative charge is linked to a positive charge carried by a nitrogen atom (i.e. pyridinium ring). The total length of the molecule is 1.3 nm for a Debye length of 16.8 D (Fig. 1). The highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular

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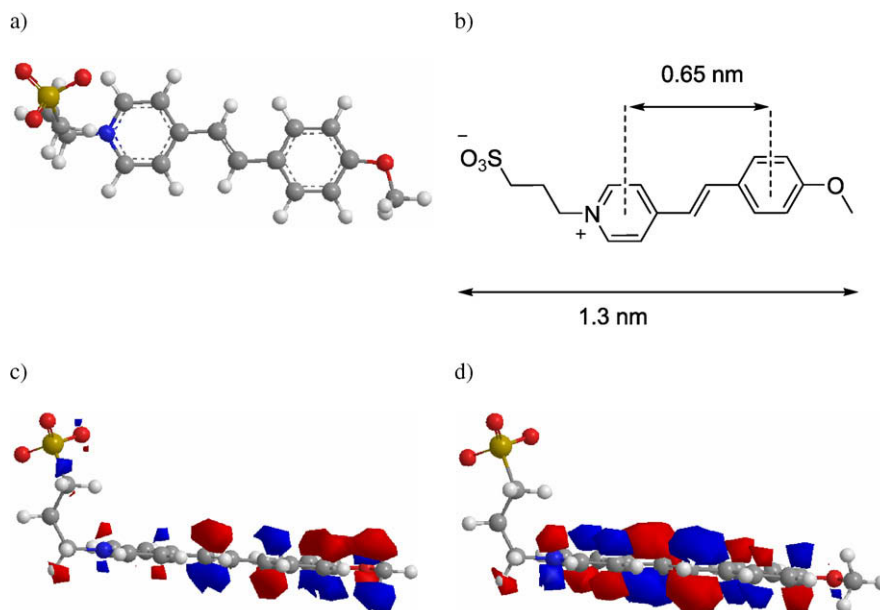


Fig. 1. (a) Corey–Pauling–Koltum model, (b) chemical structure of the MSPS molecule, (c) HOMO of MSPS molecule calculated in the vacuum, and (d) LUMO of MSPS calculated in the vacuum.

orbital (LUMO) of a MSPS molecule were calculated in the vacuum by using MMFF94 semi-empirical method (Fig. 1c and d). The main contribution in these states comes from the π -skeleton of the molecule.

A STM image of a Au(23 23 21) surface is depicted in Fig. 2a. Three adjacent terraces are observed descending along the $[-2\ 1\ 1]$ direction while the step-edges run along $[0\ 1\ -1]$. Both face-centered cubic (fcc) and hexagonal-close packed (hcp) stacking domains are observed on the substrate. They are separated by discommensuration lines which derive from the $22 \times \sqrt{3}$ reconstruction of the Au(1 1 1) (dashed lines, Fig. 2b) [23]. This nano textured vicinal surface was used as a template for the deposition metallic atoms, like Ag or Co [24,25].

In the STM images corresponding to adsorption of 0.1 MSPS monolayer (Fig. 3), bright stripes oriented along the $[-2\ 1\ 1]$ direction (perpendicular to steps) are observed on the larger terraces. These terraces can appear during the substrate annealing due to the pinning of step edges by chemical impurities. Note that the given mean coverage (0.1 ML) has been estimated from several large-scale STM images and does not correspond systematically

to the local coverage shown in Fig. 3. On the regular narrow terraces such stripes do not appear. The distance between stripes is 6.9 nm in agreement with the periodicity of the fcc (hcp) domains on the genuine surface. Moreover the stripes are aligned between adjacent terraces (see Fig. 3b). That suggests for this low coverage molecules preferentially adsorb in one type of the domains that we have identified as the fcc one. This behaviour was reported in the literature, for example adsorption of C_{60} on Au(7 8 8) [26], on Au(1 1 1) [27] or on Au(11 12 12) [28]. This phenomenon is justified by the higher reactivity of fcc than of hcp domains [29–31].

One has to note that the width of the stripes can be modified between two consecutive STM images (10 nm in Fig. 3a and 3.5 nm in Fig. 3b) and that striae appear on images along the scan direction (shown by a white arrow). This leads to the conclusion that even at 77 K, the molecules are only weakly bound to the surface, quite mobile and can be dragged by the tip. Fig. 3b also shows that molecules decorate step edges whatever the size of terraces.

For a larger exposition time to MSPS flux, a dense and highly ordered self-assembled monolayer network covers the Au(23 23 21) surface and is shown on Fig. 4a.

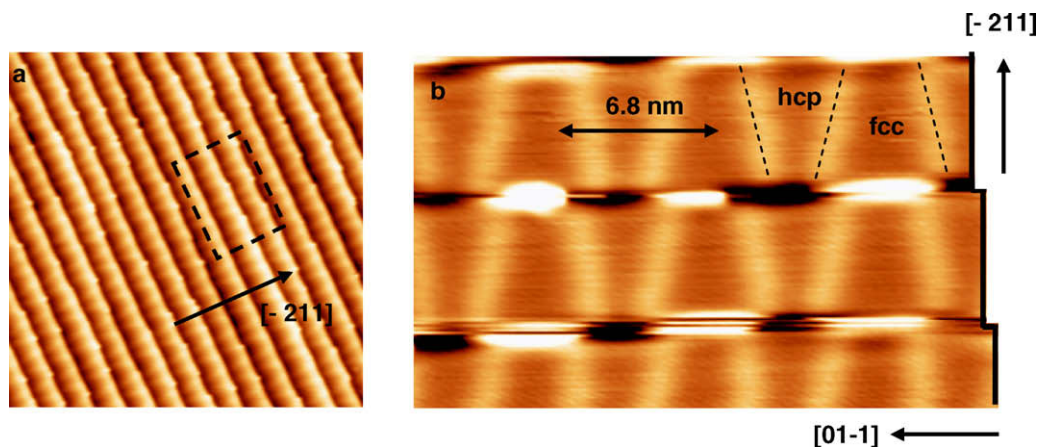


Fig. 2. (a) STM image ($70 \times 70\text{ nm}^2$) of Au (23 23 21) showing its regular array of steps separated by 5.6 nm, (b) Close up ($23 \times 14\text{ nm}^2$) on three terraces with the fcc/hcp reconstruction. The dotted lines show the discommensuration lines between fcc and hcp domains.

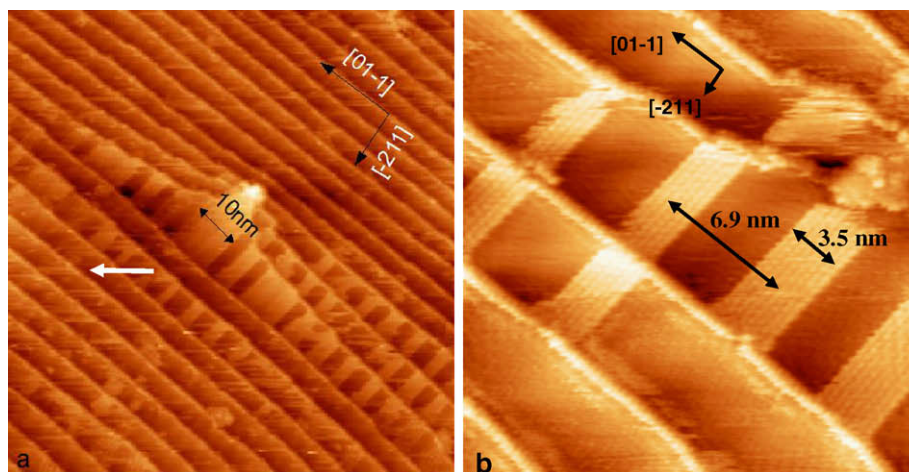


Fig. 3. (a) Large-scale STM image ($100 \times 100 \text{ nm}^2$, $V_s = -1 \text{ V}$, $I = 0.6 \text{ nA}$) obtained after MSPS deposition (0.1 ML) on Au (23 23 21), (b) Zoom in of (a) ($24 \times 24 \text{ nm}^2$, $V_s = -1.3 \text{ V}$, $I = 0.19 \text{ nA}$).

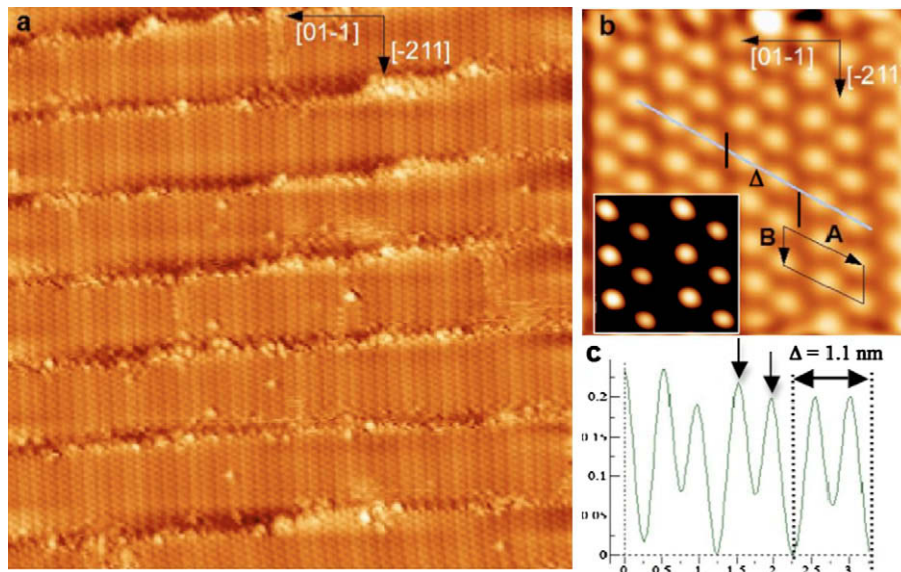


Fig. 4. (a) Large-scale STM image ($36 \times 36 \text{ nm}^2$, $V_s = -0.28 \text{ V}$, $I = 0.17 \text{ nA}$) showing the 2D supramolecular MSPS network (measured at 77 K), (b) Zoom in ($4 \times 4 \text{ nm}^2$) of (a) the high contrast insert highlights the asymmetry of the molecule), (c) Line profile showing the size and regular arrangement of molecules.

The elemental building blocks of the nanolines are constituted by two paired asymmetric protrusions (one being slightly smaller than the other). This asymmetry can be observed by increasing the STM image contrast (see insert Fig. 4b) and on the profile line, where the top of the protrusions are not equivalent (see vertical arrows Fig. 4c) whereas the curve down to zero on each side. The total length of the paired protrusions is $1.1 \pm 0.1 \text{ nm}$. The unit cell of the molecular network is therefore a parallelogram with a size $A \times B = 1.1 \times 0.5 \text{ nm}^2$ (Fig. 4b). A weak periodic modulation, close to 10 pm and running along $[0\ 1\ -1]$, is also visible on STM images (Fig. 4a). This is the reminiscence of the fcc/hcp reconstruction which is preserved with the same periodicity (6.9 nm) under the molecular layer. Only the shape of the discommensuration lines (DL's) is slightly modified being now perfectly perpendicular to the step edges. As the shape of DL's results from the elastic interaction between stacking faults and step edges [32], molecules adsorbed on step edges can be responsible for this change without the need of a strong interaction (bonding) between terraces and MSPS.

In high resolution STM images, the elemental building blocks of the nanolines constituted by the two paired spots are attributed to the π -skeleton of one molecule ($\Delta = 1.1 \text{ nm}$). Therefore, the aliphatic part of MSPS is not visible by STM [33,34]. Based on these results, a model of adsorption can be proposed in which MSPS are adsorbed in a "scorpion shape" with their π -skeleton parallel to the surface and the aliphatic chain pointing out of the plane, as described in Fig. 5.

π -Skeleton/metal interactions are weak but sufficient to allow the adsorption of the molecules on a metal surface at low temperature [2,4,6,8]. The weakness of this interaction allows isolated molecules to diffuse on the surface even at low temperature (77 K) (see striae on Fig. 3a, shown by the white arrow) and is consistent with the negligible influence on the fcc/hcp reconstruction after adsorption of MSPS.

STM investigations versus exposition time to MSPS flux show that molecular chains can be stabilized only by increasing the molecule density at the surface. This suggests that intermolecular interactions are necessary to form the molecular nanolines. The

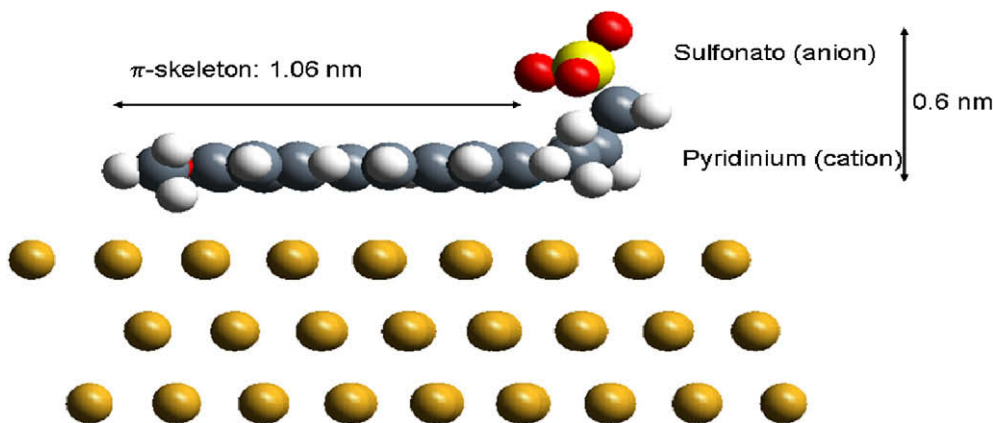


Fig. 5. Adsorption model of MSPS on Au(23 23 21) surface in a "scorpion" shape.

MSPS molecules being zwitterionic, the origin of molecules–molecules interactions could be explained by the electrostatic interactions which are strong and which work at long distance. While increasing molecular coverage, MSPS molecules arrange on the surface to achieve the growth of a complete, well ordered and stable supramolecular network at monolayer coverage.

On the basis of STM measurements, a structural model for the system can be proposed (Fig. 6). The supramolecular adlayer is based on a nanoline network of MSPS molecules. Therefore, from electrostatic point of view, the adlayer can be considered as two planes, which are parallel to the Au(23 23 21) surface. The first one is cationic and contains the pyridinium ring of MSPS, whereas the second is anionic and includes the sulfonate group of MSPS. The distance between these two planes is 0.6 nm (see Fig. 5). This organization is very stable and it is efficiently used for the development of large scale supramolecular networks by electrostatic self-assembly [35,36].

Adsorption of MSPS molecules were previously investigated on a Si(1 1 1)-7 × 7 surface [20,21]. Three MSPS molecules are adsorbed onto a half-cell in a chiral star-shape compelled by the surface template effect. The key-role of the molecule/surface interaction is highlighted by these results. On a semiconductor surface, MSPS adsorption is guided by the strong molecule/surface interactions with room temperature stability whereas on a metal

surface, a large scale supramolecular network is achieved thanks to the molecule/molecule interactions but with poor thermal stability. At room temperature, only the initial Au(23 23 21) reconstruction is observed.

4. Conclusion

To sum up, a large-scale self-assembly supramolecular network was achieved at low temperature on a Au(23 23 21) surface by adsorption of zwitterions. The supramolecular network is constituted by parallel nanolines. The growth of the adlayer seems to be explained by electrostatic self-assembly.

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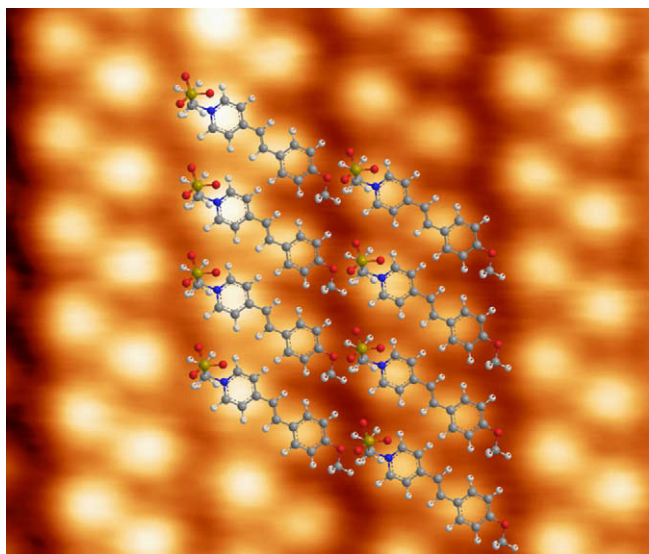


Fig. 6. Molecular network superimposed on STM image.

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