Adsorption of 2-thiophene curcuminoid molecules on a Au(111) surface

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ABSTRACT

We provide a systematic ab initio study on the adsorption of 2-thiophene curcuminoid (2-thphCCM) molecules on a Au(111) surface. In this work we present the determination of the optimal configuration of a single molecule on the surface as well as a detailed study of the energetics of the different arrangements of two molecules considering their intermolecular interactions. We simulate the STM measurements associated with the optimal configuration and compare it with the experimental data.

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1. Introduction

The physical properties and hence the potential applications of nano-devices can be modified dramatically by exploiting its interplay with suitable designed and synthesized molecules [1–4]. This idea has grown into a leading research theme, namely molecular electronics, that involves extensive collaboration between different disciplines such as organic chemistry, material sciences and condensed matter physics [5–8]. Recently, self-assembled monolayers (SAMs) have received wide attention both from experimental measurements and theoretical calculations [9–11]. Special interest has been devoted to thiolate and thiophene derivative molecules over gold surfaces [9,12–15]. This interest stems from potential applications in areas ranging from lubrication control to electronic applications [16].

Proper understanding of the binding mechanisms in the interaction between noble metals and organic molecules is of the utmost importance in molecular electronics, specially in self-assembled structures, whose specific spectroscopic and transport properties can be tuned through the competition between molecule-substrate and intermolecular interactions.

The creation of SAMs of π-conjugated aromatic compounds, such as thiophene derivatives, have received a great deal of attention due their potential in optoelectronic devices [17] that stems

from their peculiar optical and electrical properties [18]. However, the issue of the chemical state and interaction of thiophene derivatives and gold surfaces is far from being settled. More importantly, the comparison between the different electronic structure of thiophenes derivatives and alkanethiols, both well studied with respect to SAM formation, points out toward a novel binding mechanism that is interesting on its own. While both examples display unpaired electrons that can bind to the gold surface, there is an important difference. In thiophene and its derivatives the sulfur atom belongs to a conjugated aromatic ring, making the entire π-system an active participant of the bonding. This induces a strong dependence of the binding energy on the orientation of the ring with respect to the surface.

In this work, we study the morphological properties of a self-assembled monolayer of 2-thphCCM molecules onto a (111) surface of Au both from the experimental as from the theoretical viewpoints. From the experimental side we performed STM measurements to determine the topography of the surface and surface quality (terrace formation and large at atomic areas), and to identify the surface reconstruction if it corresponds. From the theoretical point of view, by performing Quantum Molecular Dynamics calculations (Car–Parrinello algorithm implemented in QUANTUM ESPRESSO package [19]), we obtained the adsorption energies for 2-thphCCM molecules over Au(111) surface. Since the interactions involved in these system based upon organic-inorganic structures are associated with short range chemical bonding on one side (molecule-Au), and long-range interactions on the other (molecule-molecule), it is crucial to handle accurately both contributions.

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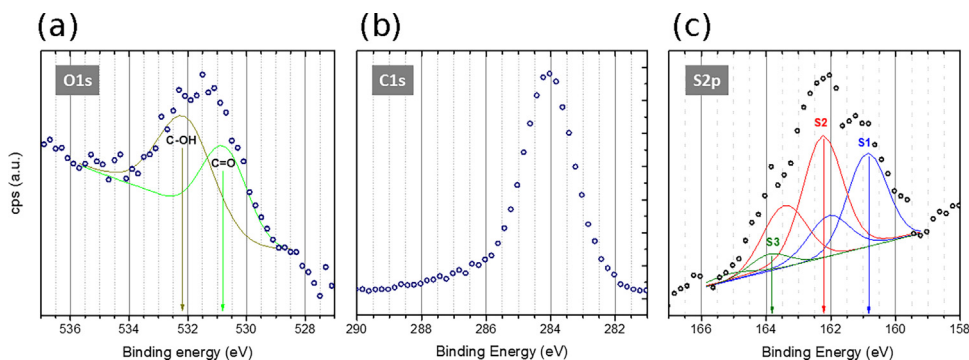eduardo.cisternas@ufrontera.cl (E. Cisternas).

Fig. 1. HRXPS of the principal signals from the 2-thphCCM/Au(111) corresponding to (a) oxygen, (b) carbon and (c) sulfur species.

The organization of this work is as follows. In Section 2 we address the experimental aspects of this research involving sample preparation to obtain the molecular capped surfaces, the compositional and topographic characterizations based upon HRXPS and STM measurements. In Section 3 we described the theoretical assessment of the system using the software QUANTUM ESPRESSO for several configurations of the molecules on gold surface, and the image simulation by Tersoff–Hamann approximation [20]. We provide some concluding remarks in Section 4.

2. Experimental details

2.1. Sample preparation

Gold films of high purity (99.99) were deposited on freshly exfoliated mica Muscovite by sputtering method. A quartz balance located close to the sample monitored the thickness of the deposited film. Depositions were performed in a high vacuum system (10^{-4} Pa); keeping the substrate temperature at 300 °C and the evaporation rate used were 3 nm/min. The resulting polycrystalline Au(111) film thickness is close to 50 nm. Synthesis of the 2-thiophene curcuminoid molecules is described in Ref. [21]. Au(111) surface were immersed in 1 mM solution of 2thphCCM in methanol for 4 h. Thereafter, the sample was washed with methanol and dried under a flow of N_2.

The adsorption of the molecules onto the gold surface were evidenced by X-ray photoelectron spectroscopy (XPS). The HRXPS measurements of the signals associated with the molecule are included in Fig. 1. The binding energy was calibrated with the Au4f$_{7/2}$ signal at 84.0 eV. The signal O1s was fitted by two peaks attributed to the oxygen species in the molecule, the C=O and C—OH bonding centered at binding energy of 530.9 eV and 532.3 eV,

respectively. In the case of the C1s signal, the peak is centered around 284.1 eV, which is attributed, in the literature, to the molecules in a configuration "lying down" onto metallic surfaces [22]. Finally, the signal S2p provide more qualitative information about the configuration of the molecules on the surface. We identified three doublet peaks, which one can be linked with the flat-lying bound, labeled S1 at 160.9 eV, upright bound, labeled S2 at 162.2 eV, and unbounded, labeled S3 at 163.8 eV [21]. From this fit, the ratio between this peaks is 7:6:1.

2.2. Topography of the surface

STM-topographic images were acquired in an Omicron UHV AFM/STM operating at room temperature in high vacuum conditions. STM measurements were performed in constant current mode with mechanically formed Pt–Ir tips. The images were processed using WSxM [23].

The STM images were recorded for bias voltage of 500 mV and tunnel current of 100 pA. On this conditions the surfaces are stable. Typically the surface show a distributions of grain in the scale of the 500×500 nm^2 (not included here). But for higher magnifications on the top of the grains we can identify the atomic flat areas where it is possible recognize patterns not attributed to the gold surface and resembling SAMs. Those domains are highlighted in Fig. 2(a) by blue arrows. The thickest arrow indicate a interesting domain were the corrugation is lower than 0.25 nm. On this area we draw out a line profile, depicted in Fig. 2(b), that can be related to the position of the molecule on the surface. The position of the maximum can be, in principle, linked to specific atoms species of the molecule. But, the precise relation of the maxima with the atomic positions is clarified by a detailed ab initio calculations in the following section.
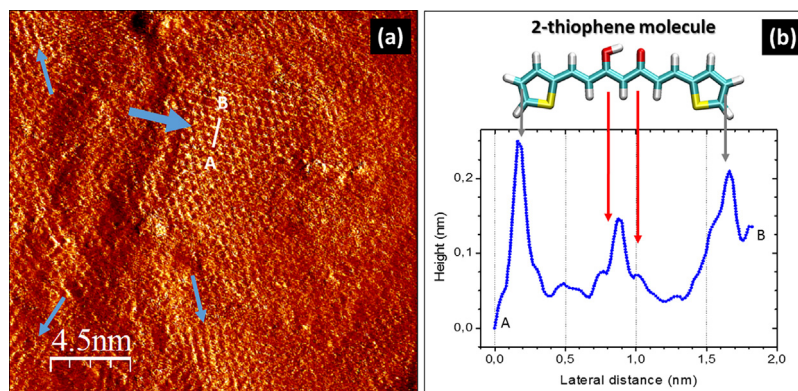

Fig. 2. Topographic image of 2-thiopheneCCM molecules on the Au(111) surface (a) and line profile onto a individual 2-thphCCM molecule (b). (For interpretation of the references to color in this figure citation, the reader is referred to the web version of this article.)
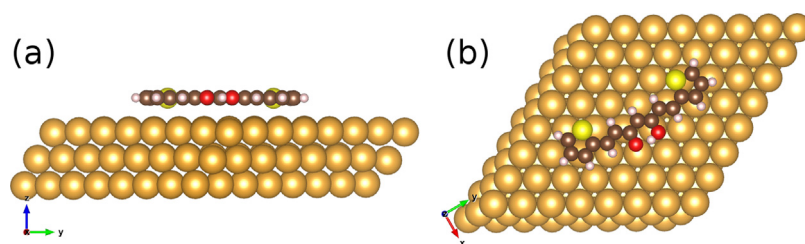
Fig. 3. Side view (a) and top view (b) of the adsorption configuration of a single 2-thiophene curcuminoid molecule on the Au(111) surface.

3. Theoretical calculations

3.1. System model

The Au(111) surface was modeled by a slab of three layers of gold atoms (64 atoms in each layer) for which we performed density functional theory (DFT) calculations using the QUANTUM ESPRESSO package [19]. The gold atoms from the topmost and middle layers were allowed to move until the atomic forces were smaller than 0.05 eV/Å, while the atoms from the bottom layer were fixed according the lattice parameter obtained after a previous DFT calculation for the bulk: 4.1932 Å (2% larger than the experimental value). An ultrasoft Perdew–Burke–Ernzerhof pseudopotenital [24] was employed for relaxation of the gold surface.

An energy cut-off of 405 eV was employed for planewave expansion and the First Brillouin Zone was sampled using a Monkhorst–Pack mesh of $8 \times 8 \times 1$. After this preliminar calculation the Au(111) surface has not showed reconstruction.

3.2. Adsorption energy

Preliminary Docking calculations [21,25] have provided the most probable position for a single 2-thphCCM adsorbed on the Au(111) surface: the molecule orients its longitudinal axis parallel to the surface, anchoring both sulfur ends to the interstices left among three superficial gold atoms. Starting from this initial configuration we performed quantum molecular dynamics (QMD) under the Car–Parrinelo approach [26] implemented in QUANTUM ESPRESSO distribution [27]. Such MD calculations indicates that the thphCCM molecule essentially conserves the position described before minimizing the total energy. Displacements of gold atoms from their equilibrium positions are negligible (less than 3% per-
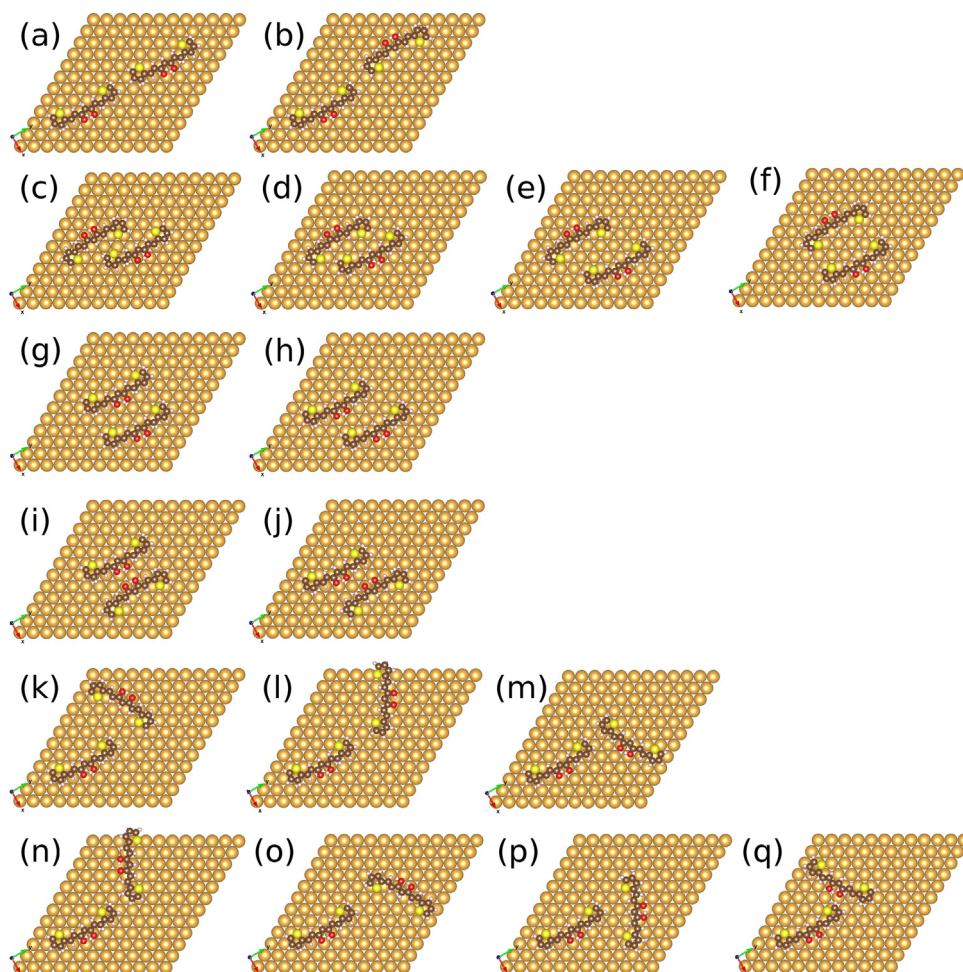

Fig. 4. Seventeen possible relative orientations for two 2-thphCCM molecules adsorbed on the Au(111) surface.

Table 1
Interaction energy in eV for relative orientations shown in Fig. 4.

Configuration		E_{int}		E_{int}		E_{int}		E_{int}
In line	(a)	4.51	(b)	5.50				
Front–front	(c)	4.57	(d)	4.69	(e)	6.32	(f)	8.22
Front–back	(g)	4.79	(h)	4.94				
Back–back	(i)	5.97	(j)	7.11				
In angle front	(k)	4.71	(l)	5.34	(m)	6.36		
In angle back	(n)	5.50	(o)	6.05	(p)	6.05	(q)	6.32

pendicular to the surface). This means that the Au(111) surface remains essentially unchanged (see Fig. 3) in accordance with previous theoretical calculations for other adsorbates [9,28–31].

To obtain the adsorption energy we have calculated separately the total energies of the surface (E_{surf}) and of a single 2-thphCCM molecule (E_{mol}). These results allow us to obtain the adsorption energy $E_{ads} = -5.98$ eV according to Eq. (1):

$$E_{ads} = E_{sm/Au} - E_{surf} - E_{mol}. \tag{1}$$

3.3. Interaction energy between molecules

Intermolecular interactions such van der Waals (vdW) forces are addressed by means of the non-local exchange-correlation functional vdW-DF [32,33]. The initial position of each molecule is according to the adsorption configuration obtained for a single molecule, i.e. by anchoring their sulfur heads to the interstices left by Au atoms. The triangular symmetry of the Au(111) surface conduces to different relative orientations, thus for a fixed density of adsorbed molecules (one per 515 Å^2), a set of sixteen representative relative orientations are shown in Fig. 4. These configurations aim to emulate the arrangement from self-assembled molecules on the metal surface to a more disordered system, for which we have performed QMD to obtain the interaction energy according to Eq. (2):

$$E_{int} = E_{sys} - E_{surf*} - 2(E_{mol} + E_{ads}), \tag{2}$$

where E_{sys} corresponds to the energy of the system composed by two molecules adsorbed on the Au(111) surface and E_{surf*} corresponds to the energy of the pristine surface. E_{ads} and E_{mol} are the adsorption energy and the total energy of a single molecule (both obtained previously). The results of the interaction energy for each relative orientation is displayed in Table 1.

Respect to the configurations showed and their energies, we observe:

- In the cases when the molecules have their oxygen pairs oriented in the same direction (a) they present less energy than if they are oriented in otherwise (b).
- On the other hand whenever, the molecules facing each other (f), the energy immediately rises with respect to the in-line configuration, but decreases by moving them slightly in the direction of the axis of the molecule (c,d,e).
- In contrast, if the molecules are in the front, but with the oxygen pairs oriented in the same direction (g), the energy goes up even more than the previous configuration, even if one moves the molecules slightly in the direction of the axis itself (h).
- If the molecules are with the opposing oxygen pairs, this is favoring bridges like hydrogen bonds (i), the energy goes up much more, even if they move in the direction of the axis of the molecule (j).
- When the system is arranged in a "disordered" form with the molecules arranged at different angles to them, the energy rises (k–m, n–q). There is still a configuration with a very low energy (k), but from this configuration it is not possible to fill the surface without going through the other higher energy configurations. Because this form of disposition of the molecules in surfaces is the least energetically favorable.

In resume, with this simple argument the surface can be covered with arranged arrays in domains like those shown in the topographic image, Fig. 2(a). The most favorable orientation from the energy point of view is reached when molecules are aligned (a). However, the arrangement of a second row of molecules should be front and slightly displaced (c), which is energetically more favorable than facing the sulfur atoms in the same direction (f). For this reason we have decided to perform the simulation of the topographic image in the configuration (c), which results the most favorable energetically (4.57 eV) for the conformation of ordered arrays emulating the topography shown in Fig. 2(a).

3.4. Scanning tunneling image simulation

Theoretical scanning tunneling microscopy images were obtained using the *PostProc* (post-processing) v6.1 code [19] included in Quantum Espresso package. *PostProc* generates STM images under the Tersoff–Hamann approximation [20]: the local density of states is evaluated in a plane parallel to the surface while the electronic states contributing to the tunneling current lie in the energy window [$E_{Fermi} - eV_{bias}, E_{Fermi}$]. In this work we considered
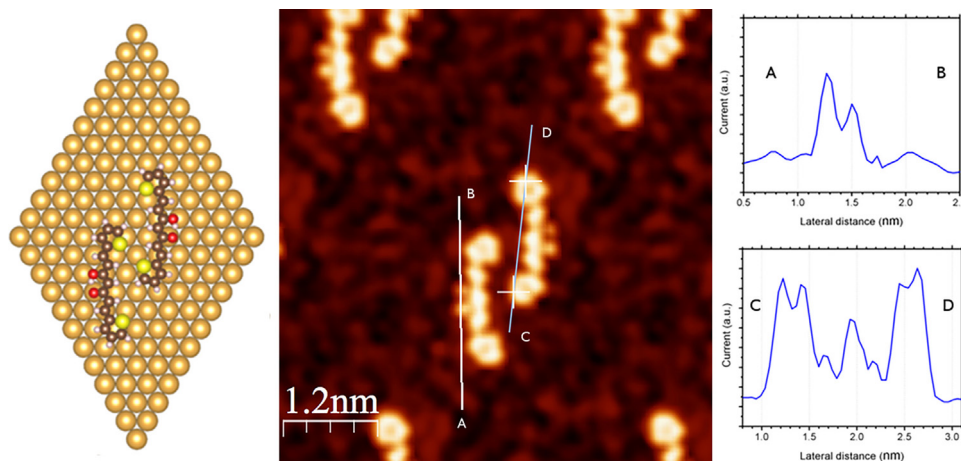

Fig. 5. Left: Relative orientation of two 2-thiophene curcuminoid molecules adsorbed on the Au(111) surface presenting an interaction energy of 4.57 eV (Relative orientation shown in Fig. 4(c).) Center: Simulated STM image for relative orientation showed on the left panel ($V_{bias} = 500$ meV and 1.0 Å as tip-surface distance). Right: Profiles along the highlighted lines AB (top) and CD (bottom). (For interpretation of the references to color in this figure citation, the reader is referred to the web version of this article.)

a bias voltage $V_{bias} = 500\,\text{mV}$, and a plane parallel to the Au(111) surface which is located 1 Å above the 2-thiophene curcuminoid molecule. Data analysis and visualization was performed by using the WSxM 8.2 freeware [23], whereas a Gaussian smoothing was applied to obtain the final simulated STM images.

Fig. 5 shows a simulated STM image (central panel) of the chosen configuration (left panel). In this image the molecules appear clearly defined, while the Au surface present modulations which are induced by the adsorption. Even is not possible to get atomic resolution, it is interesting to note that the oxygen atoms (colored red) do not present a symmetric tunneling current: the hydrogen bind darks the corresponding oxygen atom. This is better observed from the tunneling current profile AB through the oxygen atoms (right panel of Fig. 5).

Due to this it is possible clearly identify the extension of the molecule we can draw a tunneling current profile CD performed along the line closer to the carbon atoms in the STM image including the thiophene extremes. This profile reveals a local maximum between the molecule ends and the lower intensity corresponding to the carbon atoms in the backbone. The most notorious feature in the increased intensity corresponding to the carbon atom between the C=O and C—OH bonds. This is in agreement with our experimental observations, showed in Fig. 2(b).

This simulated STM-image and their profiles support the concept of self assembled molecular monolayer on top of the gold surface, within the choose configuration, correspond to the domain mainly observed in the experimental STM-image showed in Fig. 2(a).

4. Conclusions

In this paper we have pursued a systematic study of gold surfaces functionalized with 2-thiophene curcuminoid molecules. Our work has been based upon a HRXPS and STM characterization of the molecules arrangements as well as a theoretical analysis. Our results show a remarkable agreement between those studies. Our study rest heavily on previous analysis of similar system that were performed by means of molecular dynamics. Nevertheless our study goes further ahead and, by means of an ab initio analysis, undertaken under the Quantum Espresso machinery, we have studied the energetics of a single molecule adsorbed on the gold surface, determining its optimal geometrical configuration. Complementary, we have studied different situations containing two molecules finding their energetically optimal arrangement. Finally, for the optimal configuration we have simulated, within the Tersoff–Hamann approximation, the STM measurements for different settings. There is an unquestionable agreement between these results and the actual experimental data. This agreement points to a sound understanding, both theoretical and experimental, of the essential phenomenology of the system which can be the starting point of further prediction and control over the intricacies of this, and related, systems.

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