Theor Chem Acc (2009) 124:217–223
DOI 10.1007/s00214-009-0602-4

REGULAR ARTICLE

Energetic of molecular interface at metal-organic heterojunction: the case of thiophenethiolate chemisorbed on Au(111)

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Received: 4 March 2009 / Accepted: 18 June 2009 / Published online: 4 July 2009

Abstract Structural and electronic properties of thiophenethiolate chemisorbed and thiophene physisorbed on Au(111) layer have been studied by model rooted in the density functional theory. In particular, the changes in workfunction and ionization potential upon chemisorption or physisorption have been evaluated by chemical anchoring the thiol S atom above different sites and rationalized in terms of the surface dipole of the self assembled monolayer and charge reorganization. The most stable adsorption site is in the bridge configuration and the general rule stating that large variation of the tilt angle gives small shift in work function with respect to the clean Au(111) surface is confirmed. However, the work function shift is strongly dependent on the site of chemical bonding, either bridge or top site. The co-facial interaction in the thiophenethiolate systems that comes into play when the molecule is very tilted on the surface has also been investigated within a conformational study. Afterward, the bond interaction between the sulfur atom of the ring and the gold surface gives rise to a fast decrease of the workfunction.

Keywords DFT · Organic semiconductors · Interface

1 Introduction

The recent advances in organic electronics have created a large interest in the metal-organic interface [1]. The interface plays a critical role since it determines, to a large extent, the properties and performances of devices [2]. In fact the transport of charge carriers across the interface between metal electrodes and the organic materials is often responsible for the performance of a device. Once understood in detail the energetic of metal/molecular film interfaces (metal work function, ionization potential and electronic affinities), it is possible to develop a model to control their behavior and to suggest the chemical modification of organic molecules required to lower the energy barrier for charge injection and increase the device performances [3].

The shift of metal workfunction (WF) is directly correlated to the change of the surface electrical dipole caused by adsorption of molecular layer. Molecules that are physisorbed on metal usually decrease the WF. On the other hand, chemisorption can give an increase or decrease depending on nature of chemical bonding, magnitude of the charge transfer, as well as the morphological matching of molecules on metal [4].

In general, various self assembled monolayers (SAMs) formed by oligo- and poly-thiophenes are widely used as organic semiconductor since they have shown advantageous physical properties for organic field effect transistor (OFET) applications [5, 6]. Among the numerous organic SAMs exploited in applications, we have chosen to evaluate the interaction between a simple thiophene unit chemisorbed (by thiol derivate) or physisorbed on Au(111)

Electronic supplementary material The online version of this article (doi:10.1007/s00214-009-0602-4) contains supplementary material, which is available to authorized users.

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layer and to monitor the shift of WF associated to adsorption process.

The surface dipole arises from two major contributions: (1) the permanent dipoles of the molecules within the SAM and (2) the charge reorganization associated with the formation of chemical bond between metal surface and adsorbed molecules [7].

In this paper, we will explore, using density functional theory (DFT), the role played by different contributions to the surface dipole of thiophene and thiophenethiolate on gold.

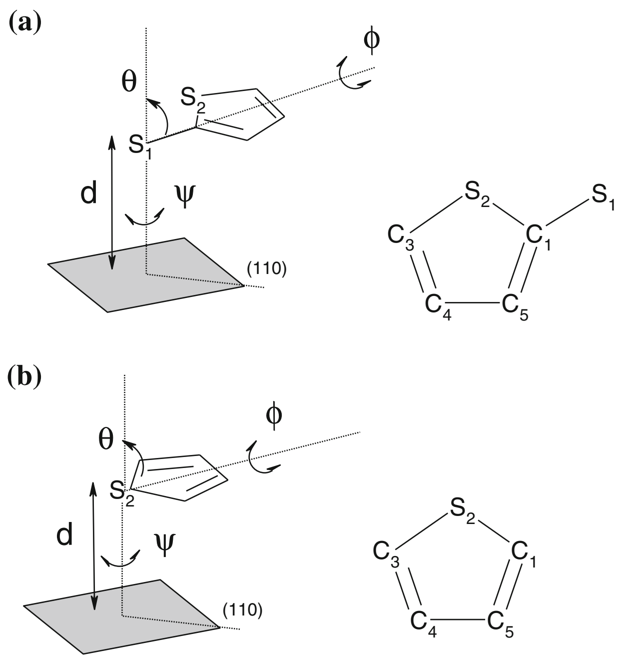
More specifically, thiophene on the Au(111) surface have attracted the attention of both experimental and theoretical research [8–12]. Extensive experimental investigations of adsorption and desorption process of different chain lengths of thiol on several gold surface have been performed [13–15]. Although several studies are reported for the interaction of alkane thiols on the Au(111) surface, few papers are available where the interaction occurs with a π-conjugated system.

Theoretical evaluation of adsorption of thiophenethiolate on Au(111) surface have been performed both on Au nanocluster model and Au(111) slab model. These studies were focused on the structural investigations of the anchoring sites and evaluated the more stable sites to provide fundamental understanding of the chemisorptions.

Recently, Heimel et al. [16] have developed a computational strategy based on first-principles calculations to evaluate the interface energetic and level alignment in biphenyl thiol derivatives on gold. In an analog way, Rusu et al. [17] focused their studies on the two contributions of surface dipole, intrinsic and adsorbed dipole of SAM, and evaluated the effects on energetic level shift at interface. These papers are very promising because they have provided a clear vision of intrinsic molecular effects that play a key role in increasing the device performance.

The nature of morphological arrangements of thiophene physisorbed on gold has been largely debated between two opposite currents [18]: the ones supporting that the sulfur atom of the thiophene ring does not interact with gold and the others sustaining the opposite. Recently, thanks to the help of scanning tunneling microscopy in the ordered phase [18], the adsorption of the sulfur head on gold was observed. In this case, the co-facial interactions between thiophene molecules play an important role in determining the morphological and surface arrangements of thiophene rings.

In summary, two types of interactions are involved in the formation of interface between thiophene thiolate molecules and the Au surface: (1) the chemical bonding between the S_1 (thiol atom) and the Au surface, (2) a dispersion interaction between S_2 (thiophene S atom) and Au (see Scheme 1). Several experiments [12, 18] have shown that thiophene thiol form a self assembled monolayer (SAM) on the Au surface via S_1 atom and chemisorption occurs. On the other hand, a stable SAM of thiophene on the Au surface is obtained thanks to the weak interaction between S_2 and Au surface. The chemical bond interaction between the S_1 and Au layer is about ten times stronger than the S_2–Au interaction. This suggests that the S_1 can bind more favorably on the Au surface than S_2 atoms.



Scheme 1 The atom labeling (*right panel*) and the parameters to characterize the adsorption geometries (*left panel*) of the chemisorbed (**a**) thiophenethiolate and physisorbed (**b**) thiophene

We have calculated the optimized geometries for the case of chemisorbed systems where the S atom in the starting configuration was constrained to lie above 4 sites that have been chosen to be representative chemical anchoring. These sites were the on-top, bridge, fcc-hollow (S directly above a threefold hollow site with no atom in the second layer just below the site) and hcp-hollow (S directly above a threefold hollow site with an atom in the second layer just below the site). We have found that not all of these sites are stable for anchoring and in particular we will see that the hollow sites are moved toward the bridge site.

Unfortunately GGA functionals fail to reproduce Van der Waals forces [19, 20] (in particular dispersion forces), where the binding is due to dipole–dipole interactions between two separated fragments that are inherently non-local interactions. In spite of the limitations of DFT calculations in describing dispersion forces, we have explored also two configurations of thiophene physisorbed on gold.

The paper is organized in the following way: a brief theoretical section is introduced before results and discussion, where the geometrical structures and the energetic at interface are discussed in details.

2 Theoretical section

The computational scheme is based on a pseudopotential planewave method using PWSCF code as implemented in the QUANTUM-ESPRESSO package [21]. All calculations have been performed using the generalized gradient approximation (GGA) with the Perdew, Burke and Ernzerhof (PBE) correlation functional [22]. The pseudopotential plane-wave calculations were performed using Vanderbilt ultrasoft pseudopotentials [23], including the scalar relativistic effects. The convergence of the total energy has been checked by varying cut-offs and grid of *k*-points to reach a good compromise between accuracy and computational times. The cut-off for the wave functions of 30 Ryd and the cut-off for the charge density of 150 Ryd allow a convergence of the total energy below 0.015 Ry. The geometry optimization was done on a $3 \times 3 \times 1$ Monkhorst-Pack grid by relaxing all the atoms in the structure with a convergence threshold of 0.001 Ryd/Å on the interatomic forces. The self-consistent calculations for electronic properties were executed on a $8 \times 8 \times 1$ grid of *k*-points granting a convergence below 0.001 Ry.

The Au(111) surface has been modeled by the repeated slab geometry with the in-plane 3×3 unit cell, which contains five Au atomic layers. We have placed one molecule per unit cell, so that the resulting covering density is 1.3×10^{14} molecules/cm^2. The vacuum gap between the topmost molecular atom and the next slab has been set to 15 Å and is large enough so that two successive metal layers do not interact significantly. Indeed by increasing vacuum thickness we found a negligible change of the total energy. The molecular structures and the top three gold layers have been fully relaxed.

3 Results and discussion

3.1 Geometrical parameters and binding energies

The geometrical parameters chosen to characterize the adsorption site, for both chemisorption and physisorption, are shown in Scheme 1. The four main parameters are defined in the following way: (a) *d* is the minimum distance between the first Au layer and thiol atom (the sulfur atom of thiophene moiety) for chemisorption (physisorption); (b) the tilt angle θ between the Au surface normal and the S–C bond (thiophene molecular axis) for chemisorption (physisorption); (c) ψ rotation angle of molecular axis, passing thought the S–C bond, around the 110 axis of the gold layer; (d) rotation angle ϕ of the tail molecule with respect to the S–C bond.

The adsorption energy for each system is defined as the difference between the total energy of the metal + molecule complex and the sum of the total energies of the free substrate and adsorbate molecule $\left(E_{\mathrm{ad}} = E_{\mathrm{complex}} - E_{\mathrm{molecule}} - E_{\mathrm{layer}}\right)$.

The thiophenethiolate when chemisorbed in the bridge site has adsorption energy of −1.40 eV. The geometrical structures collected in Table 1 show that the S_1 atom is bonded to two Au atoms of the first layer with a bond length of about 2.58 Å. The geometry of thiophene molecule following adsorption on gold does not exhibit relevant changes (see supplementary tables). The Au interatomic distances in proximity of thiophene ring are expanded until to 3.03 versus 2.88 Å for the clean Au surface.

The top site, in which the S_1 atom is located over Au atom, is 0.26 eV less stable than the bridge site. The Au–S_1 bond length of 2.432 Å is the shortest one of all of the anchor configurations, and the Au surface expansion is negligible. The molecular axis passing through the S_1–C bond is tilted of 8.9° with respect to (110) direction, with the angle θ 10° less than the bridge conformation (74.1 vs. 63.7°, for top and bridge, respectively). The data collected in Table 1 show that the preferential bond length (Au–S_1) is between 2.40 and 2.58 Å, and the bond angle (θ) in the range 60–74°.

The geometries starting in the hcp- and fcc-hollow sites are not stable and after optimization of the coordinates converge toward two bridge configurations as stable as the bridge site we have given above, that will be named here as the bridge-2 and bridge-3 sites, respectively. The bridge, bridge-2 and bridge-3 sites have different geometrical parameters, in particular, they have dissimilar tilting angle θ, as reported in the Table 1.

Table 1 Main geometrical parameters (distance in Å, angle in degrees) and adsorption energies (eV) of the thiophenethiolate chemisorbed and thiophene physisorbed on Au(111) layer for several anchor sites

	Chemisorptions				Physisorptions	
	Top	Bridge-2	Bridge-3	Bridge	Bridge	Top
d	2.432	1.967	1.959	2.029	3.095	3.024
θ	74.1	68.4	60.0	63.7	39.9	74.2
ψ	8.871	4.76	4.07	4.85	−41.02	0.0
ϕ	111.1	93.56	96.42	96.42	88.2	92.1
Au–S_1	2.432	2.508	2.510	2.576	–	–
Au–S_2	3.025	3.307	3.664	3.497	3.095	3.024
ΔE_{ads}	−1.140	−1.395	−1.404	−1.401	−0.125	−0.159

All the sites are tilted along the (110) direction with a deviation of few degrees of the ψ angle from 8.8 to 4.8° passing from the top to the bridge sites. We point out that our top and bridge geometries are close to the sites reported by Higai et al. [8], whereas the fcc-bridge and the fcc-hollow minima discussed by Higai are not stable in our calculations. The different findings can be explained with the fact that our simulation was performed with an energy cut-off for the wave functions larger and a grid of *k*-point denser than in the research of Hagai.

Other stable geometries can be found by orienting the molecule in the opposite direction (-1, -1, 0). We had a bridge configuration less stable of 0.01 eV and a top configuration more stable of 0.04 eV than the respective geometries in the (110) direction. We did not find relevant changes in the geometrical parameters when compared between the two directions. The hollow sites aligned along (-1, -1, 0) axes are not stable again.

In the case of physisorption, the most stable structure shows the S_2 atom located above the top site with the molecule tilted about 74° due to steric interaction between the ring and the surface layer. Although, a large atomic distance between the S_2 and Au atoms of about 3.1 Å is observed, a weak interaction between them has been deduced from the charge redistribution related to the adsorption. In Table 1 we report also a structure where the S_2 atom is located between two Au atoms (bridge structure).

These results are confident with the experimental observations made by Noh et al. [17] by means of XPS and STM analysis that pointed out a chemical interaction between sulfur and Au surface.

The minimum energies discussed in the present paper could be considered a not exhaustive conformational investigation of the anchoring sites. In fact, the different conformational sites of thiophenethiolate and thiophene SAM on Au(111) are very close in energy [23]. The barrier to the movement of the sulfur group between anchoring sites is lower than few kcal/mol, i.e., of order of kT at room temperature. Of course a complete simulation of the anchoring potential energy surface would require a molecular dynamics simulation. This activity overcomes the real interest of present paper, which is addressed to explore the effect of surface dipole on WF and energetic at the interface between molecule and metal electrode.

3.2 Energetics at the interface

The plane-averaged electrostatic energies of all of the systems we have investigated have been determined using the dipole correction to solve the problems relative to the artificial electric field associated to the periodic boundary conditions.

The energetic levels of interest are shown in Fig. 1 for the top site, where $\mathrm{WF}_{\mathrm{Au(111)}}$ denotes the energy associated to the WF of the clean metal layer, $\mathrm{WF}_{\mathrm{Au(111)\text{-}SAM}}$ is its shifted value upon SAM formation, E_F is the Fermi energy level. The IP is the ionization energy of the organic layer assembled on the Au(111), defined as the energy difference between the HOMO and vacuum level energy. Finally, ΔE is the energy separation between E_F and the closest molecular level (typically the highest occupied molecular orbital, HOMO). The HOMO energy in the molecular layer has been taken to be the highest-energy peak in the respective projected density of states (PDOS).

The calculated WF, the molecular gap calculated from the PDOS, the ionization potential of the adsorbed SAM and the HOMO energy relative to E_F (ΔE) for different chemisorption or physisorption sites are collected in Table 2. The WF's are lower than the clean gold value (5.2 eV). In particular, the WF of the top physisorption is very close to that of bridge, bridge-2 and bridge-3 chemisorptions and it is 0.6–0.7 eV lower than the WF of clean Au slab, whereas the WF of the top site is lowered of 0.4 eV. The molecular electronic levels are affected by the influence of the metal substrate and intermolecular interactions depend on the adsorption site. Indeed the ΔE listed in Table 2 suggests that the charge injection is favored in the top chemisorption case, where the separation between HOMO level and Fermi energy is very much lower than in all of the other sites. For the same reason, the ionization potential is the lowest for the top chemisorption (with IP = 5.76 eV), and it has the largest value in the bridge site with 6.42 eV. The ionization potential of the physisorption in the top site takes an intermediate value of 6.07 eV.

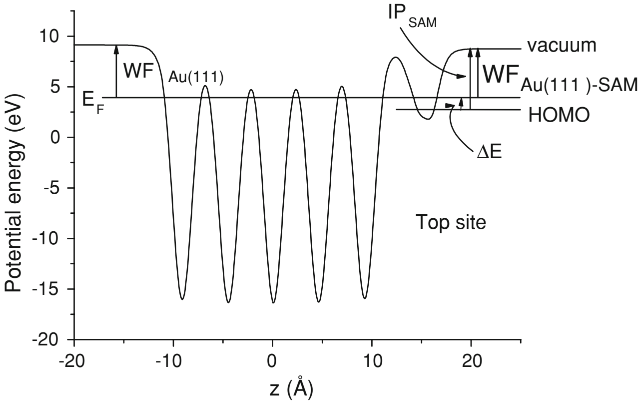


Fig. 1 The plane-averaged electrostatic energy of the Au(111) slab terminated with chemisorbed thiophenethiolate. The metal Fermi energy E_F, its workfunction $\mathrm{WF}_{\mathrm{Au(111)\text{-}SAM}}$, the workfunction $\mathrm{WF}_{\mathrm{Au(111)}}$ of the clean Au(111) slab, the vacuum and the molecular HOMO levels as well as the molecular ionization potentials (IP) are indicated

Table 2 Calculated work function (WF) of surface covered by SAM, shift with respect to clean (111) surface (ΔW), ionization potential of the adsorbed SAM (IP), HOMO energy relative to Fermi level (ΔE), HOMO–LUMO gap, dipole μ_{mol} of the isolated molecule in the SAM along z axis, ΔE_{SAM} step energy relative to dipole μ_{mol}, ΔE_{chem} step energy relative to dipole μ_{chem} (see the text for details)

System[c]	WF[a]	ΔW[a]	IP[a]	ΔE[a]	Gap[a]	$\mu_{\mathrm{mol},z}$[b]	ΔE_{SAM}[a]	ΔE_{chem}[a]
Phys. top	4.55	0.68	6.07	1.55	4.41	0.022	0.051	0.629
Phys. bridge	4.50	0.73	5.92	1.42	4.52	0.109	0.210	0.521
Chem. top	4.84	0.39	5.76	0.93	4.01	0.372	0.584	−0.194
Chem. bridge-2	4.58	0.65	6.36	1.78	3.70	0.494	0.758	−0.108
Chem. bridge	4.59	0.64	6.42	1.83	3.73	0.579	0.874	−0.234
Chem. bridge-3	4.55	0.68	6.27	1.72	3.72	0.679	1.003	−0.323

[a] Energy is measured in eV

[b] Dipole in atomic units (1 au = 2.5405 D)

[c] *Phys.* physisorption, *Chem.* chemisorption

3.3 Surface dipoles

Following the arguments presented by Rusu et al. [16], the behavior of the WF can be partly correlated to θ angles. A large tilt angle gives a small normal molecular dipole component and small shift of WF with respect to the clean Au(111). In addition, the nature of the bonding between the molecules and the surface, that is different for the several adsorption sites, contributes to the WF shift. Indeed, it is easy to show that the change of the WF, ΔW (given by the difference between the WF of the clean gold and that of the gold monolayer-terminated), is related to the difference between the dipoles formed on the gold monolayer-terminated surface and the clean gold surface, $\mu_{\text{Au-SAM}}$ and μ_{Au}, respectively, by means of the relation (in atomic units):

$$\Delta \mathrm{W} = \frac{4\pi}{A}\left(\mu_{\mathrm{Au-SAM},z} - \mu_{\mathrm{Au},z}\right) \tag{1}$$

where μ_z is the projection of μ in the z direction and A is the gold surface area in the unit cell.

In the same way we can write the relation connecting the energy step ΔE_{SAM} along the z direction, perpendicular to the metal slab, to the dipole μ_{mol} of the isolated molecule in the SAM (we removed the gold atoms):

$$\Delta E_{\mathrm{SAM}} = \frac{4\pi}{A}\mu_{\mathrm{mol},z} \tag{2}$$

where $\mu_{\mathrm{mol},z}$ is given by:

$$\mu_{\mathrm{mol},z} = \mu_{\mathrm{mol}} \cdot \cos\theta \tag{3}$$

with θ tilting angle.

If we set $\boldsymbol{\Delta\mu} = \boldsymbol{\mu}_{\text{Au-SAM}} - \boldsymbol{\mu}_{\mathrm{Au}}$, we can define the following dipole:

$$\boldsymbol{\mu}_{\mathrm{chem}} = \boldsymbol{\Delta\mu} - \boldsymbol{\mu}_{\mathrm{mol}} \tag{4}$$

and exploiting the proportionality relations (1) and (2) we can write also

$$\Delta E_{\mathrm{chem}} = \Delta W - \Delta E_{\mathrm{SAM}}. \tag{5}$$

The dipole μ_{chem} and the corresponding energy step ΔE_{chem} can be interpreted as the dipole and the energy step associated to the charge reorganization due to the formation of chemical bonds between the metal surface and the adsorbate molecule.

In Table 2, we collected the results for the WF shift ΔW, ΔE_{SAM}, ΔE_{chem} and $\mu_{\mathrm{mol},z}$. ΔE_{chem} for physisorption is opposite to chemisorption, because of the different charge rearrangement in the inter-atomic region. Unfortunately, the limitations of the DFT do not allow an accurate evaluation of the long range interactions involved in physisorption, and we limit ourself to a qualitative analysis. Moreover, in the case of physisorption the compression of the metal electronic tail due to the presence of adsorbed molecules gives rise to a potential drop at the interface. This charge rearrangement, termed “pillow” effect, has the effect of reducing the metal work function [24]. The pillow effect can be evaluated within a localized orbitals approach. Our electronic description based on DFT and pseudopotential planewave method is not able to take it into account.

Considering chemisorption only, the tilting angle decreases in the following order: top site (74.1°), bridge-2 site (68.4°), bridge site (63.7°) and bridge-3 site (60.0°), and from the Eq. 3 $\mu_{\mathrm{mol},z}$ increases in the same order. The molecular dipole resides in the plane of the molecule along the S_1–Au bond with a same module for all chemisorption sites. Although ΔW has small variations in the bridge configurations, we recognize the general trend of the WF to increase by widening tilting angle, from the bridge-3 site (where the z component of the molecular dipole is the largest one) to the top site (where the z component of the molecular dipole is the smallest). We found that ΔE_{chem} increases by increasing the molecular dipole. However, the top site has a different nature with respect to the bridge configurations, and the ΔE_{chem} is near that of the bridge site.

The energy gap of the isolated thiophenethiol and thiophene are 3.79 and 4.43 eV, respectively. In the bridge sites the energy gaps are very close to the molecular gap, as reported in Table 2. On the other hand, for the top site a bonding interaction between gold and S_1 stabilizes the molecular HOMO level with respect to the value of the isolated molecule. Indeed the molecular energy gaps are 4.01 and 3.79 eV for the top site and isolated molecule, respectively.

3.4 Dependence of the workfunction on the tilting angle

In order to explore the electronic-structural relationship, we have calculated the WF for selected values of the angle θ for ψ and ϕ frozen at their optimized values. In Fig. 2, we plot the calculated WF as a function of the angle θ. For $\theta = 0°$ we have the maximum value of the z component of the molecular dipole that induces the biggest reduction of the WF with respect to the clean gold (4.35 vs. 5.2 eV). As soon as the θ angle is widened, the z component of the molecular dipole decreases and the WF shows an increasing behavior. The maximum is reached for $\theta = 64°$, corresponding to the minimum of the total energy.

The increase of the WF up to the maximum by increasing the molecular tilting angle could be correlated to specific interaction between the S_1 atom and gold surface. However, when the thiophenethiolate is near to be fully tilted and parallel to the gold surface, a bond with the sulfur in the thiophene ring arises and causes a large decrease of the WF. The latter conformation is not an energy minimum because the destabilization effects due to the steric interactions between the ring and surface are stronger than the bond interaction described above.

We have evaluated a strong charge transfer from the sulfur to the gold atoms in the first layer connected to the formation of the bonding orbital HOMO-2 as reported in Fig. 3.

We have also calculated the dependence of the WF on the tilting of the molecule in the top site, not reported here, and we have found a similar behavior. For 74.1° tilting angle we have the minimum of the total energy and the maximum of the WF. In the range 45–75° the total energy changes of 0.31 eV and the largest WF modification is of 0.21 eV; therefore, here a stronger dependence on the molecule tilt than in the bridge site is established.

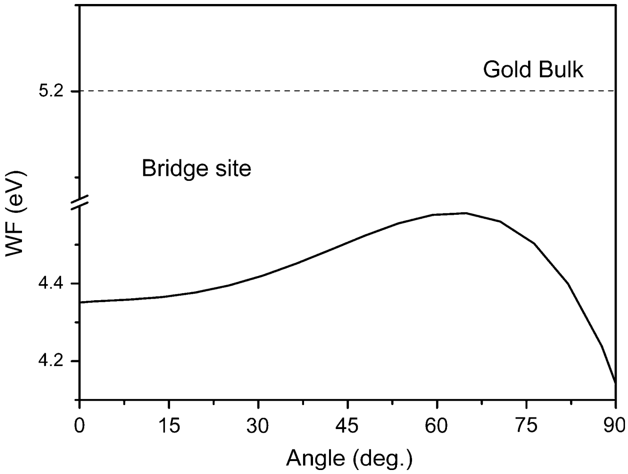


Fig. 2 The workfunction dependence on the tilting angle θ of the molecule chemisorbed in the bridge site. The *dashed line* is the calculated bulk value for gold of the workfunction

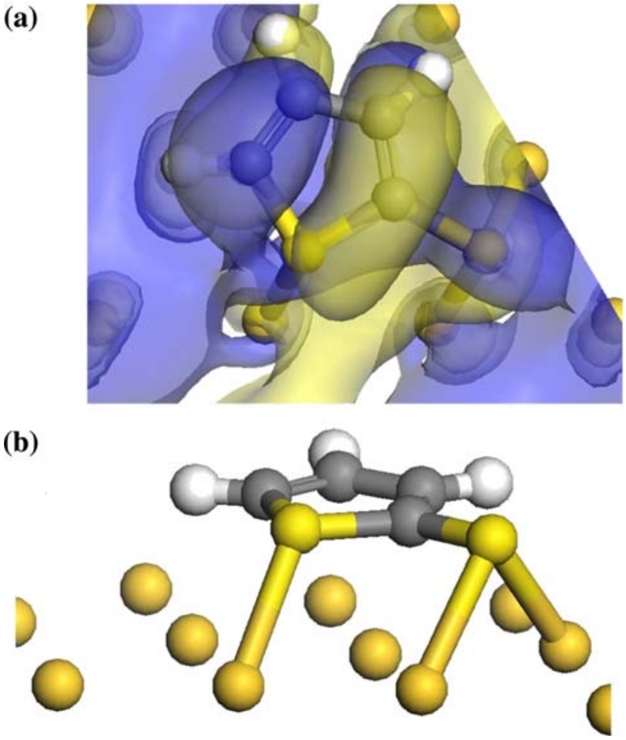


Fig. 3 **a** *Top view* of the molecular orbital involved in the specific interaction between thiophenethiolate and Au(111) surface at 0° tilt angle. **b** *Side view* of the 0° tilted geometry. For sake of clarity, only the thiophenethiolate and the first layer of the gold slab are shown

4 Conclusions

In this paper, we have investigated the morphological arrangement and the energetic at interface between thiophenethiolate chemisorbed and thiophene physisorbed on Au(111).

We have found that the most stable adsorption is in bridge sites with different tilting angle of the molecule, with adsorption energy of 1.4 eV.

The energetic results discussed in the present paper have pointed out that the general rule stating that large variation of the tilt angle gives small shift in work function with respect to the clean Au(111) surface holds also in the case of the interaction between Au(111) surface and thiophenethiolate. On the other hand, the work function shift is strongly dependent on the site of chemical bonding and is larger in the bridge configurations than in the top site. We have shown that the molecular dipole plays a key role in determining the work function and the charge reorganization at the interface.

In the conformational study we have shown that when the molecule is very tilted on the surface in the π-conjugated thiophenethiolate systems the co-facial interaction comes into play, and a bond interaction between sulfur atom of the ring and Au surface arises. Consequently an extra charge reordering gives a substantial dipole with a not negligible variation of ΔE_{chem} and a diminution of the WF. This effect is completely absent in the case of alkyl thiols and π-conjugated thiols, where specific interactions between molecule and surface, beyond the single gold-sulfur bond, do not occur.

Acknowledgments This study was supported by Po.Di. Me project DM 24439 of the MIUR Italy and the EU Integrated Project NAIMO (Project No. NMP4-CT-2004-500355).

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