

Full Length Article

Induced electronic changes at the fluorinated polyphenylthiols on nanostructured Au(1 1 1) interfaces

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ABSTRACT

A detailed analysis of fluorinated polyphenylthiols adsorbed on a nanostructured Au(1 1 1) is performed on the basis of first principle calculations to understand the interface at the atomic level. Our analysis is focused on the energetics, the density of states projected onto different atoms, the charge rearrangements induced by the presence of the adlayer as well as the modifications in the electrostatic potential to gain a deeper insight into the involved processes.

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1. Introduction

Organic electronic devices such as transistors, light-emitting diodes (LED) and photovoltaic cells have attracted a lot of attention due to their possible application in mechanically flexible and large-area devices [1,2]. In this kind of devices, the interface between the organic semiconductor layer and an electrode material plays a crucial role in its performance. The use of metal electrodes modified with polar molecules have been shown to improve the injection of the charge carrier in transistors and organic LEDs [3–5]. The main goal of this surface modification is based on the possibility of fine-tuning the work function of the pristine material with different types of adlayers. From a theoretical viewpoint, the work of Zojer [6–9] explained the factors that influence the adsorption and their consequences on the adlayer-metal interfaces.

In addition, it is well known that the study of the thiol/gold interface has revealed the complexity of the system throughout the investigation of the last decades. From the early years after the first description of thiol/Au SAMs [10,11] it was thought that the Au surface did not alter significantly upon thiol adsorption. Nevertheless, in the 2000s new molecular models were resented and experimental evidence was found that proved the contrary [12–17] and references therein. SAM models having adatoms started to be generally accepted. Although, in parallel models

with unreconstructed or only slightly modified surfaces have been used continuously in studies characterizing SAM systems. Only recently, studies showed that the reconstruction of the Au surface might depend on the type of the thiol adsorbed [18,19]. In other words, the presence of adatoms or not is expected to be dependent on the type of the thiol chain. Different types of thiols are considered, which can be alkyl chains, but also organic chains containing heteroatoms, or phenyl groups, among others. The chemical nature of the thiol chain affects the chemistry and the stability of the total SAM. In a recent study on phenyl thiol SAMs, it was shown that the Au-S bond was not influenced by the thiol chain, but only by the hybridization of the carbon atom bonded to the S atom [19,20]. The electronic structure was not studied and neither the influence of substituents on the phenyl rings, which might be used in the tailoring of the electronic properties of the SAM systems.

In this context, the present work explores the modification of the electronic properties of the substrate induced by the adsorption of fluorinated polyphenylthiols. The analysis is limited to a Self-Assembled Monolayer (SAM) of two types of polyphenylthiols (named F-mpt and F-dpt) on a nanostructured Au(1 1 1) surface; and focus on the energetics, density of states projected onto the sulfur atoms bonded to the gold surface, the charge density rearrangements at the interface as well as the modifications in the electrostatic potential are shown to provide a consistent picture and a deeper insight into the factor governing the adsorption process of these kind of compounds.

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2. Methods

2.1. First-principles calculations and modeling

Periodic DFT calculations were performed using VASP code [21–23]. The core electrons were kept frozen and replaced by pseudopotentials generated by the plane augmented wave method (PAW) [24–27]. A plane-wave basis set was used to describe the valence electrons with a cutoff of 500 eV. The correlation and exchange functionals were described within the generalized gradient approximation (GGA) in the Perdew, Burke and Ernzerhof (PBE) version [28]. The evaluation of this functional on bulk Au resulted in a theoretical lattice parameter of $a_0^{\text{Au}} = 4.18 \text{ \AA}$. Within the typical margin of error, the value is in accordance with the experimental one ($a_0 = 4.08 \text{ \AA}$). [29]. Special care was taken for the parametrization of the k-points sampling of the Brillouin zone based on the Monkhorst-Pack grid [30]. The parameters were increased systematically until the change in the absolute energy was less than 10 meV. A grid of $(5 \times 5 \times 1)$ k-points was used. Spin polarizations were considered for the isolated radicals, whereas for the adsorbed systems no spin polarization was found. In order to take into account van der Waals interactions in the SAM (Self-Assembled Monolayer) system, the DFT-D3 [31] approach of Grimme [32] was used, which consists of adding a semiempirical dispersion potential to the conventional Kohn-Sham DFT energy.

To study the thiol adsorption process a nanostructured Au(1 1 1) surface was considered, which was represented by two gold adatoms adsorbed on Au(1 1 1), identified as $\text{Au}_{\text{ad}}\text{-Au}(1\ 1\ 1)$. The substrate was modeled using a $(2\sqrt{3} \times 2\sqrt{3})$ supercell with four metal layers plus the gold adatoms, for details see Fig. 1 (left plot). The behavior of four different polyphenylthiols was evaluated: benzenethiol (mpt); 4-fluorobenzene-1-thiol (F-mpt); 1,1'-biphenyl-4-thiol (dpt) and 4'-fluoro-[1,1'-biphenyl]-4-thiol (F-dpt). Fig. 1 (right plot) shows the investigated thiols in their radical forms in gas phase. In all the calculations a vacuum corresponding to $>25 \text{ \AA}$ was considered. For all the systems, the two bottom layers were fixed at the next-neighbor distance corresponding to bulk, and all the other layers plus the thiols were allowed to fully relax. The relaxations were performed within conjugate gradient minimization scheme, and the convergence criterion was achieved if the total forces were less than 0.02 eV/\AA .

To study the adsorption process of the self-assembled monolayer, the thiols were adsorbed on a gold adatom in pairs, with a pattern where the phenyl chains were parallel and perpendicular with respect to each other as shown in Fig. 1. We opted for the T-shaped adatom configuration, according to previous STM observations [33].

3. Results and discussion

3.1. Adsorption of fluorinated polyphenylthiols on Au(1 1 1)

To begin with, non-fluorinated mono- and bi-phenylthiols adsorbed on a nanostructured Au(1 1 1) have been considered as reference systems. To evaluate the effect of an electron acceptor group the corresponding fluorinated phenylthiols have also been analyzed. The adsorption energy ($\Delta E_{\text{ads}}^{\text{disp}}$) per thiol chain has been calculated using the following expression (Eq. (1)):

$$\Delta E_{\text{ads}}^{\text{disp}} = \Delta E_{\text{ads}}^{\text{PBE}} + E_{\text{disp}} \quad (1)$$

where $\Delta E_{\text{ads}}^{\text{PBE}}$ is the adsorption energy calculated by DFT-PBE without considering dispersion, and it has been obtained according to Eq. (2):

$$\Delta E_{\text{ads}}^{\text{PBE}} = \frac{1}{n} (E_{\text{thiol}/\text{Au}_{\text{ad}}\text{-Au}(1\ 1\ 1)}^{\text{tot}} - E_{\text{Au}_{\text{ad}}\text{-Au}(1\ 1\ 1)}^{\text{tot}} - nE_{\text{thiol}}^{\text{tot}}) \quad (2)$$

The first term corresponds to the total electronic energy of the relaxed system $- E_{\text{thiol}/\text{Au}_{\text{ad}}\text{-Au}(1\ 1\ 1)}^{\text{tot}}$ with the thiol at the adsorption equilibrium position on the surface, the second term corresponds to the total electronic energy of the relaxed $- E_{\text{Au}_{\text{ad}}\text{-Au}(1\ 1\ 1)}$ surface without the thiol; the third term is the total electronic energy of the thiol in its radical form in gas phase $- E_{\text{thiol}}^{\text{tot}}$ and, n is the number of thiols in the unit cell. The dispersion interaction energy (E_{disp}) was evaluated by means of the DFT-D3 approach [31]. Thus, the adsorption energy of one thiol chain in a perfectly ordered SAM is $\Delta E_{\text{ads}}^{\text{disp}}$, as shown in Eq. (1). The Au-S binding energy $\Delta E_{\text{S-Au}}$ was also calculated with or without dispersion forces according to Eq. (3):

$$\Delta E_{\text{S-Au}} = \frac{1}{n} (E_{\text{thiol}/\text{Au}_{\text{ad}}\text{-Au}(1\ 1\ 1)}^{\text{tot}} - E_{\text{Au}_{\text{ad}}\text{-Au}(1\ 1\ 1)}^{\text{tot}} - E_{\text{thiol.SAM}}^{\text{tot}}) \quad (3)$$

where $E_{\text{thiol.SAM}}^{\text{tot}}$ is the total electronic energy of the SAM frozen at the adsorbed position without the presence of the surface. Finally, the inter-chain energy $\Delta E_{\text{inter-chain}}$ was obtained as follows (Eq. (4)):

$$\Delta E_{\text{inter-chain}} = \Delta E_{\text{ads}} - \Delta E_{\text{S-Au}} \quad (4)$$

Calculated energy values for the most favorable configuration for each system are shown in Table 1.

The energetics of alkylthiols on metal surfaces is largely reported and known in the literature; and although phenylthiols are also important, those studies are rather scarce. In this regard, we have investigated the adsorption of fluorinated polyphenylthiols, named F-mpt (Fig. 1, b) and F-dpt (Fig. 1, d), on nanostructured Au(1 1 1) surfaces to understand the effect of an electron acceptor

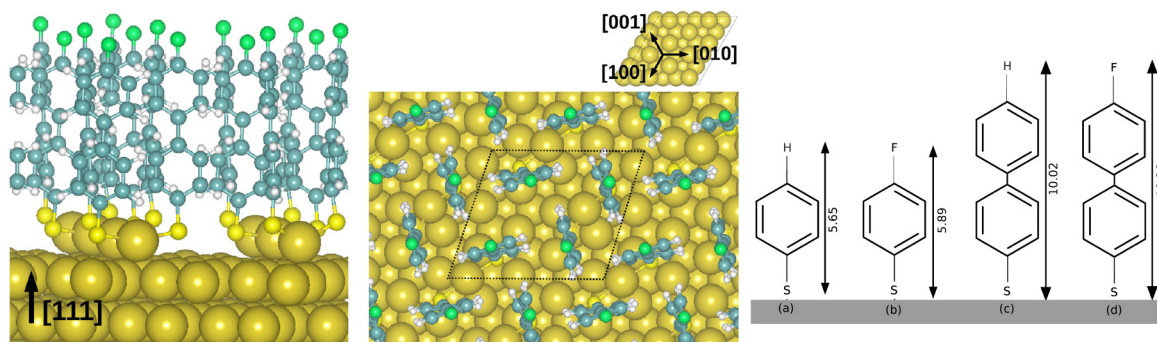


Fig. 1. Left side: nanostructured Au(1 1 1) surface used for the thiols adsorption study. Lateral and top views. The unit cell is represented by solid lines. Right side: thiols analyzed: (a) mpt, (b) F-mpt, (c) dpt, and (d) F-dpt. The length of the thiols is given in Å. Three parts can be identified in the fluorinated phenylthiols: S- is the anchoring group, phenyl group is the backbone and F- is the tail group.

Table 1Adsorption, Binding, and Inter-chain energies for thiols (mpt, F-mpt, dpt and F-dpt) on a Au_{ad}-Au(1 1 1) surface.

energy/eV	mpt[20]		F-mpt		dpt[20]		F-dpt	
	PBE	PBE-D3	PBE	PBE-D3	PBE	PBE-D3	PBE	PBE-D3
ΔE_{ads}	-1.34	-2.27	-1.25	-2.43	-1.20	-2.55	-1.20	-2.83
$\Delta E_{\text{S-Au}}$	-1.63	-2.20	-0.88	-1.98	-1.46	-1.99	-0.85	-1.44
$\Delta E_{\text{inter-chain}}$	0.29	-0.07	-0.37	-0.45	0.26	-0.49	-0.35	-1.39

such as F on the electronic properties of the SAM and its implication on the energetics and charge modification at the interface. For comparison, the corresponding non-fluorinated phenylthiols (Fig. 1, a and c) have also been evaluated. Calculated energy values at both, pure PBE and DFT-D3 levels are shown in Table 1.

An analysis of our results indicates that the replacement of a H atom by a F atom in the para position of the aromatic ring (see Fig. 1) leads to a more stable systems, with the corresponding increase in the adsorption energy according to: $\Delta E_{\text{ads}}^{\text{mpt}}$ ($|-2.27|$) < $\Delta E_{\text{ads}}^{\text{F-mpt}}$ ($|-2.43|$) and $\Delta E_{\text{ads}}^{\text{dpt}}$ ($|-2.55|$) < $\Delta E_{\text{ads}}^{\text{F-dpt}}$ ($|-2.83|$). Clearly, the decoupling of the total adsorption energy in the different contributions (Eqs. (3) and (4)) shows that the main change is due to an increase in the length of the backbone (number of phenyl groups) as reported by two of us in a previous contribution [20]. When dispersion forces are considered, the attractive intermolecular interactions increase monotonously with the number of phenyl groups in the backbone for both systems, non- ($|\Delta E_{\text{inter-chain}}^{\text{mpt}}| < |\Delta E_{\text{inter-chain}}^{\text{dpt}}|$) and fluorinated ($|\Delta E_{\text{inter-chain}}^{\text{F-mpt}}| < |\Delta E_{\text{inter-chain}}^{\text{F-dpt}}|$) ones, as expected from C-H/ π interactions [34,35]. Thus, at DFT-D3 level, the stability follows the order: mpt < F-mpt < dpt < F-dpt, Table 1.

At pure PBE level, the interchain interactions were repulsive (Table 1) for the non-fluorinated species due to the lack of van der Waals forces at this calculation level. In the case of the fluorinated phenylthiols the presence of the halogen modifies the charge density distribution (electron withdrawing effect) in the thiol and the interaction forces become attractive and constant (Table 1). The scenario changes when the DFT-D3 approach is used for correction. The intermolecular interactions between the aromatic and C-H groups (C-H/ π) are now stabilized by dispersion forces, which become attractive in all the cases (Table 1). This contribution ($\Delta E_{\text{inter-chain}}$) to the total adsorption energy (ΔE_{ads}) depends mainly on the number of phenyl groups and on the presence of the fluorine: mpt ($|-0.07|$ eV) < F-mpt ($|-0.45|$ eV) and dpt ($|-0.49|$ eV) < F-dpt ($|-1.39|$ eV). It is well-known that the existence of halide groups in a molecule causes two effects that generally compete. On the one hand, their high electronegativity, which causes an electron withdrawing effect (negative inductive effect, known as I⁻). Thus, leading to a larger electron density in the proximity of the halide region. On the other hand, the presence of lone electron pairs leads to an important electron-donating ability to the conjugated π - π system. These contributions benefit the stabilization in a T-shaped configuration of the aromatic chains (an optimal intermolecular distance) due to a compensatory effect between the dispersion forces and the decrease of the repulsive interactions between the chains, which is caused by the distorted electron density generated by the fluorine.

The adsorption energy can be separated into two energy contributions as follows from Eq. (4): interchain interactions ($\Delta E_{\text{inter-chain}}$) and the binding energy ($\Delta E_{\text{S-Au}}$). The S-Au binding energy ($\Delta E_{\text{S-Au}}$) remains almost unchanged for the non-fluorinated thiol series: -2.20 eV for mpt and -1.99 eV for dpt; the S-Au binding energy is nearly the same and around 2.00 eV, meaning that the adsorption energy is mainly determined by the nature of backbone and the intermolecular interaction forces that exist between those chains. The situation changes for fluorinated thiols with S-Au bond energies of -1.98 eV for F-mpt and -1.44

eV for F-dpt, evidencing the withdrawing effect of F and its influence on the conjugated π - π system, which increases with the number of aromatic rings and contributes to a slightly destabilization of the S-Au bond that is clearly compensated by the high attractive interchain forces that exist between the thiols, leading to a high stable adsorbed monolayer.

3.2. Electronic changes at the fluorinated polyphenylthiols/Au(1 1 1) interfaces

Understanding the electronic interactions between adsorbed species and substrate is crucial to develop new materials. Thus, our goal is to analyze the modification of the electronic structure of gold when a self-assembled monolayer of fluorinated phenylthiols (F-mpt and F-dpt) is adsorbed on a nanostructured Au(1 1 1) surface. Two effects cause the electronic modifications at the surface, according to [6–8]. On the one hand, the dipole of the molecules before adsorption; and on the other hand, an interfacial dipole, which results from a change of the intrinsic surface dipole and the charge redistribution due to bond formation between the thiol and the metal substrate upon adsorption.

In order to evaluate the contribution of the different components of the interface, we shall firstly investigate the isolated SAM of F-mpt and F-dpt in their radical forms. Each SAM was evaluated in its optimized geometry upon adsorption. It should be mentioned that the alignment of the dipole moments in this 2D layer is different from that corresponding to the single species. An analysis of the plane average potential (not shown) of these isolated SAMs -F-mpt and F-dpt- let us identify two different regions, each corresponding to different values of the electrostatic potential in the vacuum. The difference (ΔE_{vac}) between the right and left side of each zone is -0.90 eV for F-mpt and -1.00 eV for F-dpt. According to the Helmholtz equation,¹ in principle if we do not consider mutual depolarization of the species, this step can be related to the projection of the molecular dipole moment onto the surface normal μ_{\perp} .

Then, we have analyzed the behavior of the combined system: a monolayer of phenylthiols (F-mpt and F-dpt) adsorbed on a nanostructured Au(1 1 1) surface. It is generally accepted for most of thiols that the adsorption on a Au(1 1 1) surface induces a reconstruction phenomenon, involving the formation of thiol - Au_{ad} - thiol moieties [36–40]. In order to do this, the thiols should extract a gold atom from the surface and organize in a T-shaped configuration. This phenomenon in the case of mpt and dpt is under discussion nowadays, but some progress has been made for molecules as the methylthiol/Au(1 1 1) [16,36,41,42]. In this context, we shall consider that the adsorption process induces a reconstruction and hence, the behavior of the interface will be discussed and analyzed with respect to a flat gold surface (for clarification of the geometry see Fig. 2, where one side of the surface remains unreconstructed). Fig. 2 shows the plane average potential in the z-coordinate (perpendicular to the surface) for both systems: F - mpt/Au_{ad} - Au(1 1 1) (left panel) and F - dpt/Au_{ad} - Au(1 1 1) (right panel).

¹ $\Delta E_{\text{vac}} = -\frac{\mu}{\epsilon_0 A}$, where A is the area of the unit cell and ϵ_0 is the vacuum permittivity.

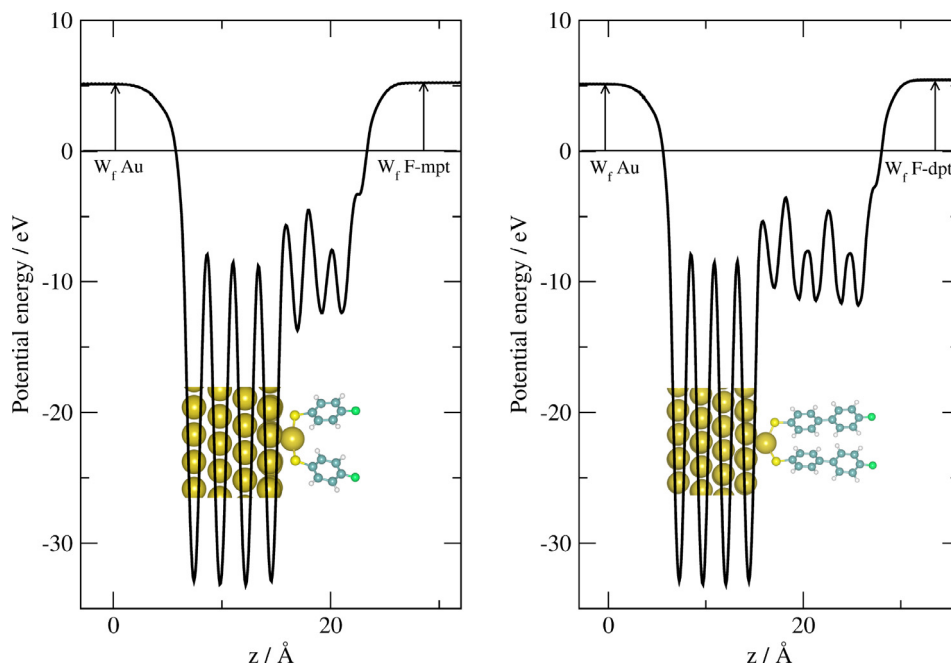


Fig. 2. Potential energy profiles of the combined systems (left side: F-mpt on a nanostructured Au(1 1 1), right side: F-dpt on nanostructured Au(1 1 1)) are displayed. The work functions are also indicated. The calculated values are reported in eV: $W_f^{\text{Au}} = 5.10$, $W_f^{\text{F-mpt}} = 5.23$, $W_f^{\text{F-dpt}} = 5.45$.

The presence of the adsorbed SAM induces a modification of the Au work function ($\Delta W_f = W_f^{\text{right}} - W_f^{\text{left}}$) of about 0.10 eV (F-mpt) and 0.30 eV (F-dpt). According to [9], the tail group (F in this case) changes the potential energy only on its side of the adlayer. The presence of F increases the work function of the pure surface from 5.10 eV to 5.23 eV (F-mpt) and to 5.45 eV (F-dpt). These changes are produced by the dipole of the adlayer and the consequent redistribution of charges at the interface [37]. The F in the thiol acts as an electron acceptor, thus it is expected that some electron density flows from the Au atoms towards the adlayer.

To evaluate the influence of the backbone length and the halogen, both variables can be decoupled by a direct comparison with the corresponding non-fluorinated species. As expected, non-fluorinated phenylthiols decrease the work function with respect to a pure Au(1 1 1) surface. This change was found to be of about -1.01 eV for mpt and -1.20 eV for dpt. Interestingly, the change in the work function caused by the addition of an aromatic ring remains almost unchanged (≈ 0.2 eV for both, non-fluorinated and fluorinated thiols), indicating that the main influence in the tuning of the work function is due to the selection of the type of the tail group. It can be observed that the changes in the work function caused by the fluorine are rather small, which can be explained by the moderate effect of this substituent group. Much stronger impact on the work function can be found with CN-, which exhibits higher ability of electron withdrawing [9].

Clearly, from a technological viewpoint, a smart selection of these groups can modify the work function of a specific system on-demand. An excellent overview on this topic can be found in the seminal work of Zojer (as a guideline see [6–9] and references therein). To the best of our knowledge, there are no studies reported about the adsorption of fluorinated polyphenylthiols on nanostructured Au(1 1 1) surfaces. However, our results are in line with the general trend found in experiments [43–45] as well as in theoretical modeling [9,46–48] for several fluorinated thiols adsorbed on a Au(1 1 1).

The corresponding rearrangement of electronic charge $\Delta\rho$ upon the formation of the adsorbed layer can be obtained by subtracting the charge densities of the non-interacting systems, isolated Au

nanostructured surface $\rho_{\text{Au}_{\text{ad}}/\text{Au}(1\ 1\ 1)}$, and isolated thiol adlayer ρ_{thiols} , both frozen at their optimized structure upon adsorption from those where the assembly of thiols interact with the nanostructured Au(1 1 1) surface, according to Eq. (5):

$$\Delta\rho = \rho_{\text{thiols-Au}_{\text{ad}}/\text{Au}(1\ 1\ 1)} - \rho_{\text{thiols}} - \rho_{\text{Au}_{\text{ad}}/\text{Au}(1\ 1\ 1)} \quad (5)$$

Fig. 3 shows the plane averaged induced charge density as a function of the position perpendicular to the surface for the F-dpt. For simplicity, since F-mpt exhibits a comparable behavior

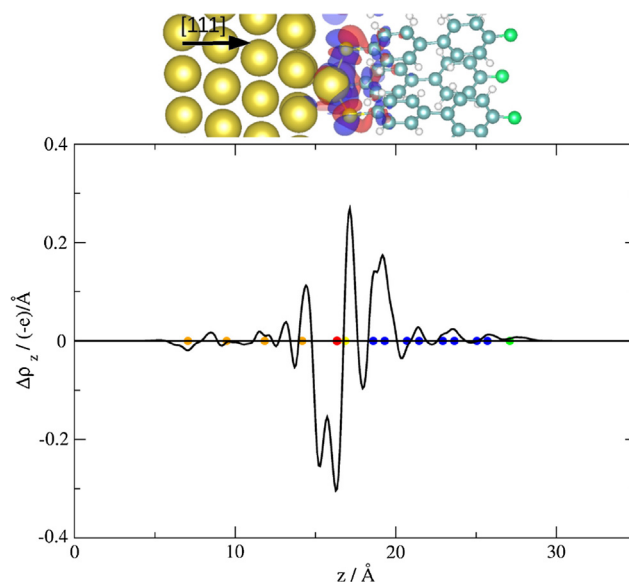


Fig. 3. Bottom part: the plane averaged induced charge density. The induced charge density gives rise to a dipole at the interface. Color dots symbolize the different z-positions of the each atom layers: orange (Au), red (Au adatom), yellow (S), blue (C) and green (F). Upper part: volumetric charge density difference of the fluorinated biphenylthiols (F-dpt) adsorbed on $\text{Au}_{\text{ad}} - \text{Au}(1\ 1\ 1)$. Red and blue indicate charge accumulation and depletion, respectively. (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

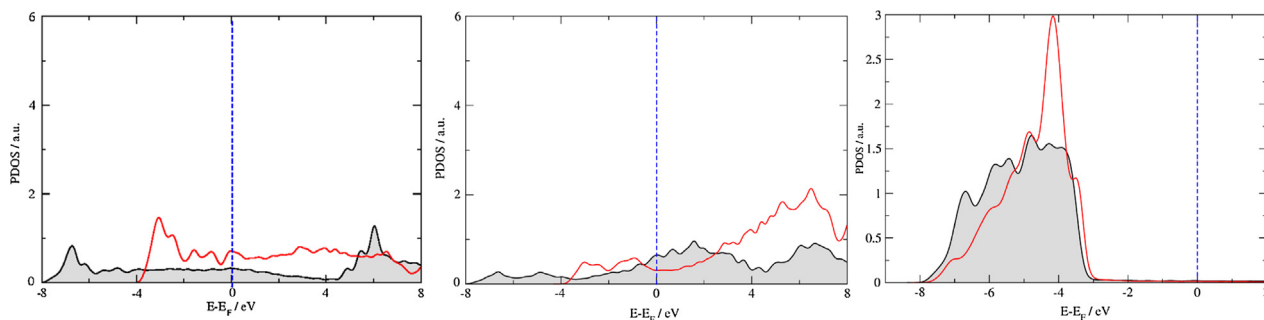


Fig. 4. Projected density of states (PDOS) of the pure flat Au(1 1 1) (black line, grey area) and the pure Au_{ad} – Au(1 1 1) (red line) surfaces. From left to right: s, p and d band profiles.

to F-dpt, we limit ourselves to show the analysis of the latter. Additionally, the volumetric charge density difference is displayed as well. Clearly, the main charge redistribution takes place between the adatom (red dot), the sulfur atom (yellow dot) and the carbon atoms closest to the sulfur. Surface electronic charge flows from Au atoms to the region close to the sulfur and the nearest carbon atoms. We can identify an electron accumulation on the sulfur atom, leading to a negative charge, which was confirmed by the Bader Method [49,50] giving a value of about $-0.1 e$; and immediately below, there is an electron depletion density between the

thiol and the gold adatom bonded to it, suggesting a rather discrete/localized states, which is expected as shown by the s, p and d band profiles of the nanostructured surface in comparison with a flat one, Fig. 4, where changes in the electronic properties are expected due to alterations in the metal structure. An obvious shift to more positive energy values is detected. Furthermore, in the nanostructured surfaces the d band profiles exhibit a typical narrowing, which indicate stronger electron localization and enhance the surface reactivity.

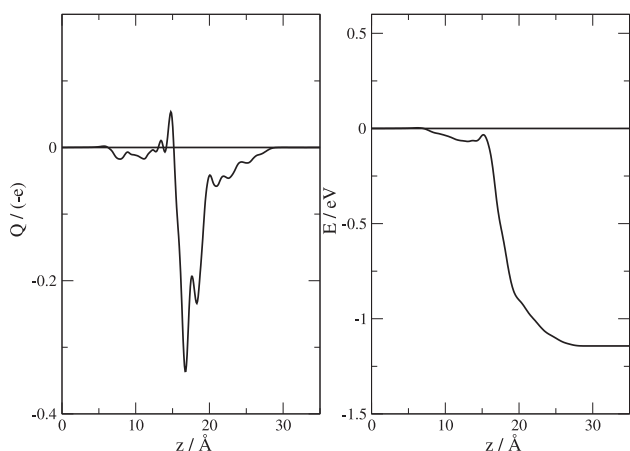


Fig. 5. Charge transfer of the F-dpt adlayer Q calculated by integration of the charge density difference over z (left side). Potential energy for the bond formation (right side).

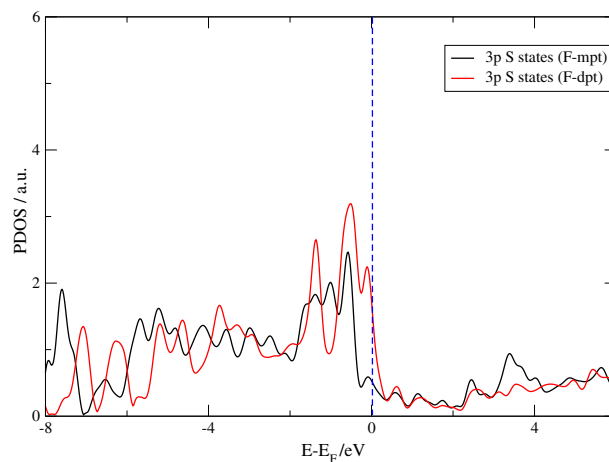


Fig. 7. Projected density of states of the fluorinated phenylthiols adsorbed on Au_{ad} – Au(1 1 1) surfaces. S 3p states of F-mpt (black line) and S 3p states of F-dpt (red line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

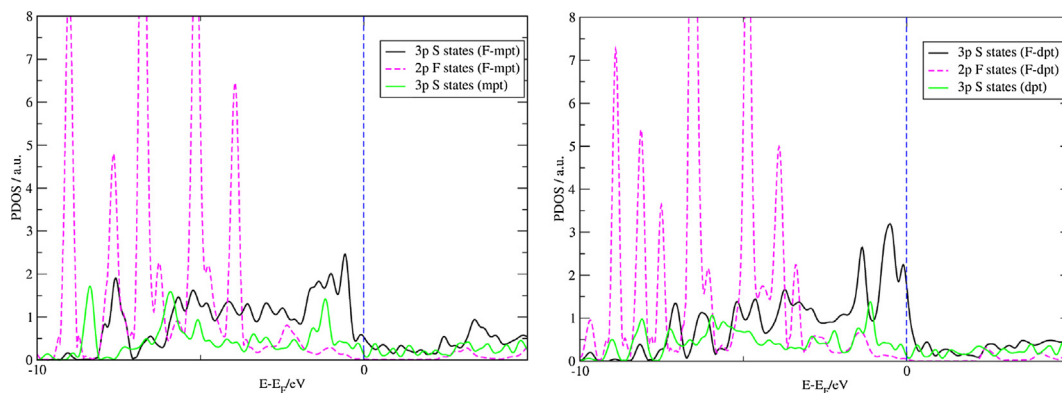


Fig. 6. Projected density of states for the non- and fluorinated phenylthiols adsorbed on Au_{ad} – Au(1 1 1) surfaces. Left side: S 3p states of F-mpt (black line), S 3p states of mpt (green line) and F 2p states of F-mpt (magenta dash line). Right side: S 3p states of F-dpt (black line), S 3p states of dpt (green line) and F 2p states of F-dpt (magenta dash line). (For interpretation of the references to color in this figure legend, the reader is referred to the web version of this article.)

A net charge transfer from Au to the thiol adlayer is found by integration of the charge density difference over z , see Fig. 5. Due to the fact that at long distances the charge approaches zero, the net charge of the total system remains unchanged. In agreement with [7], the molecular dipole moments, related to ΔE_{vac} , and the bond dipole cause the variation of the work function. We have calculated the bond dipole by a subtraction of the work function difference and the vacuum levels obtaining a value of about -1.22 eV; and by integration of Q over z by solving the Poisson equation² (see Fig. 5) with a similar estimated value (~ 1.20 eV).

Finally, we have analyzed the projected density of states of the corresponding adsorbed fluorinated SAMs. A similar behavior between both species - F-mpt and F-dpt- is found. Fig. 6 displays the PDOS profiles for the 3p states of S and 2p states of F for each fluorinated phenylthiols, respectively. As expected, its contribution appears at more negative energies and corresponds to the 2p C – 2p F bonding (not shown). The presence of F show no significant influence in the nature of the S–Au, see Fig. 6 the black and green lines, which correspond to the 3p states of the sulfur atom bonded to the gold adatom. The main feature is a small upshift of the PDOS profiles for the sulfur 3p states of the F-dpt compared to F-mpt, which is in agreement with the energetics of the S–Au bond and which might be associated with the withdrawing effect of the fluorine, see Fig. 7.

4. Conclusions

In this paper the effect of the presence of a Fluor atom in the para-position of the phenyl ring is studied in mpt and dpt adsorbed in monolayers in Au(1 1 1). Several electronic and energetic properties were calculated and investigated. The binding energy of Au-S was found to be affected by the F-substitution, indicating that the inductive effect (I- effect) of F has influenced the Au-S bond. This effect is larger compared with the difference caused by the addition of a phenyl group (mpt to dpt). The latter is expected to influence in a lesser extend the hybridization of the C atom bonded to the S atom in the thiol, which play the role of a charge sluice. The inter-chain interaction energy is also increased upon F-substitution.

The effect of surface reconstruction, especially the formation of adatoms in the case of mpt and dpt, has been studied by means of the system's work function and potential above the SAM. Almost no significant change in the work function was calculated by the addition of an aromatic ring, or after fluorination, indicating that the main influence on the work function is due to the selection of the type of the tail group, which is in line with former experimental results. The main charge redistribution is found to take place between the adatom and the sulfur atom (the binding to the surface) and the carbon atoms closest to the sulfur. The first carbon atom next to the sulfur atom in the thiol, although playing a secondary role here, is expected to play the key role in the bonding to the Au surface, via its hybridization state. The analyzed projected density of states of the corresponding adsorbed fluorinated SAMs showed no significant influence in the nature of the S–Au.

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