

See discussions, stats, and author profiles for this publication at: <https://www.researchgate.net/publication/235631918>

Lying Down to Standing Up Transitions in Self Assembly of Butanedithiol Monolayers on Gold and Substitutional Assembly by Octanethiols

ARTICLE in THE JOURNAL OF PHYSICAL CHEMISTRY C · FEBRUARY 2013

Impact Factor: 4.77 · DOI: 10.1021/jp3115786

CITATIONS

8

READS

14

6 AUTHORS, INCLUDING:



Subhrangsu Mukherjee

North Carolina State University

22 PUBLICATIONS 148 CITATIONS

SEE PROFILE



Hicham Hamoudi

37 PUBLICATIONS 426 CITATIONS

SEE PROFILE



Luca Pasquali

Università degli Studi di Modena e Reggio Emilia

101 PUBLICATIONS 1,056 CITATIONS

SEE PROFILE



Vladimir Esaulov

French National Centre for Scientific Research

206 PUBLICATIONS 1,858 CITATIONS

SEE PROFILE

Lying-Down to Standing-Up Transitions in Self Assembly of Butanedithiol Monolayers on Gold and Substitutional Assembly by Octanethiols

Juanjuan Jia,^{†,‡} Subhrangsu Mukherjee,^{§,||} Hicham Hamoudi,[⊥] Stefano Nannarone,^{||,#} Luca Pasquali,^{||,#} and Vladimir A. Esaulov^{*,†,‡}

[†]Institut des Sciences Moléculaires d'Orsay, Université-Paris Sud, Institut des Sciences Moléculaires d'Orsay, Orsay, France

[‡]CNRS, UMR 8214, Institut des Sciences Moléculaires d'Orsay, Bâtiment 351, Université Paris Sud, 91405 Orsay, France

[§]Abdus Salam International Centre for Theoretical Physics, Strada Costiera 11, 34151 Trieste, Italy

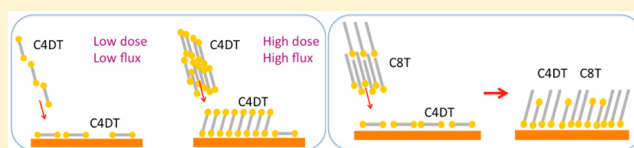
^{||}CNR-IOM, s.s.14, km 163.5 in Area Science Park, 34012 Trieste, Italy

[⊥]National Institute for Materials Science (NIMS), International Center for Materials Nanoarchitectonics (MANA), Tsukuba, Ibaraki 3050044, Japan

[#]Dipartimento di Ingegneria 'Enzo Ferrari', Università di Modena e Reggio Emilia, Via Vignolese 905, 41125 Modena, Italy

Supporting Information

ABSTRACT: Self-assembly of butanedithiol (C4DT) monolayers (SAMs) on gold and substitutional assembly by octanethiols from a lying-down doubly tethered phase of butane dithiol, were investigated in a vacuum evaporation experiment by high-resolution photoemission. The intent was to address the question of transitions from a lying-down to a standing-up phase in dithiol self-assembly and whether a standing-up phase of short chain dithiol can be formed. The lying-down doubly tethered dithiol phase, with both sulfur atoms attached to gold, was formed by evaporation and then exposed to octanethiol molecules. A mixed SAM composed of standing-up octanethiol and dithiol molecules is found to be formed. The degree of dithiol replacement, as evidenced by the increasing thickness of the SAM, is found to augment slowly with increasing exposure to octanethiol. A standing-up C4DT phase was found to be formed upon rapid very large exposure to C4DT vapors. Differences in valence band photoemission between the standing-up and lying-down phases were noted and accounted for theoretically. In all cases, measurements indicate more than one possible adsorption configuration as evidenced by different sulfur binding energies.



INTRODUCTION

Self-assembly of dithiol molecules has been the object of much interest because of the possibility to link the two thiol ends to different metallic entities. This has been used for instance to measure molecular conductance. Interest in self-assembly of these molecules on surfaces has similarly been spurred by their use in making diode structures and in superlattices involving multiple layers of dithiol molecules attached to metal nanoparticles.^{1,2} However, numerous problems have been encountered related to formation of multilayered dithiol structures by molecular interlinking with formation of disulfide bonds, photooxidation processes, and formation of lying-down phases with both sulfur ends attached to the substrate, on which the SAM assembly was attempted.^{3–17} The latter observation has led to interrogations about the possibility of at all forming a standing phase if first a lying-down doubly tethered phase is formed. However, work, by some of us^{12–17} for some dithiol molecules, shows that quite well ordered SAMs of standing-up molecules with free –SH groups can be produced.^{12,14} It was also noted that some amount of lying-down phase persisted. In the case of butanedithiol (SH-

(CH₂)₄SH or C4DT), for instance, this fraction of lying-down phase was very large in the assembly conditions used and led to the conclusion that, with increasing chain length, van der Waals forces helped in attaining the standing-up phase.¹²

More recently, we investigated¹⁸ this aspect in liquid phase assembly by first forming a lying-down phase of dithiol molecules and then substituting them with alkanethiols, disulfide, and diselenide molecules. In all cases, there was clear evidence of substitution, though in the case of substitution by thiols (dodecanethiol, CH₃(CH₂)₁₁SH, or C12T), the kinetics appeared to be very slow. This investigation was performed by cyclic voltammetry and infrared spectroscopy. The investigation by cyclic voltammetry was based on following the peak position in reductive desorption, which is distinctly different for C4DT and C12T. Cyclic voltammetry for C12T substitution showed desorption peaks appearing at intermediate values, suggesting the formation of some kind of intermediate

Received: November 24, 2012

Revised: January 14, 2013

Published: February 15, 2013



conformation of the molecular layer, i.e., there were no distinct separate domains corresponding to C4DT and C12T. Concentration effects were noted: higher C12T concentration led to faster substitution. Along this line, it was also noted that the fact that the substitution process was much faster for disulfides ($\text{CH}_3(\text{CH}_2)_9\text{--S--S--CH}_3(\text{CH}_2)_9\text{SH}$) and similar diselenides suggested that the simultaneous presence of, e.g., two S atoms in the substituting molecule accelerated the process. Of course the reaction pathways in substitution processes involving different molecules are different and the reaction kinetics would be different.

In this context, a complex and very interesting question concerns the nature of the reaction leading to substitutional assembly. For the case of substitution by C12T, it was suggested that this involved a hydrogen exchange reaction, previously proposed for upright dithiol SAM formation. For dithiols, this involves the interaction of a dithiol molecule (HSRSH) with a lying-down chemisorbed molecule on gold (AuSRSAu), with a surface mediated exchange of an H atom between the two sulfur atoms near the Au surface, belonging to the chemisorbed dithiol and incoming dithiol:



This would lead to liberation of one end of the chemisorbed molecule and adsorption of the initially free molecule, with one S attached to gold. In the case of upright dithiol SAM formation, this would allow the appearance of a free-SH end as observed in experiments.¹⁴ For the case of substitution by the disulfide and diselenide molecules, the substitution reaction would obviously involve the --S--S-- (or --Se--Se--) molecular groups instead of the --SH group in the case of C12T. Theoretical investigations of the latter surface mediated reactions have not been performed as of yet.

In this work, we extend these experiments to vapor phase assembly of C4DT and substitution to investigate its possibility in the absence of solvents. Vapor phase assembly is interesting in the context of preparing dithiol SAMs on reactive substrates that are difficult to use in ambient conditions. We base ourselves on information of the formation of self-assembled monolayers from vapor phase and its adsorption and desorption kinetics studied previously for some alkanethiols (ref 19 and references therein). In this work, it has been shown that, at low exposure doses, a lying-down phase is formed, whereas at high doses, a standing-up SAM is formed that desorbs at fairly high temperatures close to 150 °C, indicating interactions in the SAM layer and a stronger binding with substrate than for physisorbed layers, for which desorption starts below room temperature. Similar results have been obtained for 1,4-benzenedimethanethiol (1,4-BDMT).¹⁵

As in the previous study performed in liquid phase, our strategy involves first the formation of a lying-down phase of C4DT. Here, we use an evaporative assembly of C4DT, which, at moderate dosings, provides an *unambiguous* case to investigate this exchange process, and we first ascertain by XPS that we indeed start with a lying-down phase with both S atoms attached to Au. In this article, we report the investigation of substitution using an octanethiol $\text{CH}_3(\text{CH}_2)_7\text{SH}$ (or C8T).

The results of this investigation, performed using synchrotron radiation, clearly demonstrate that substitution does in fact proceed leading to production of standing-up C4DT molecules with inclusion of C8T in the SAM. These results further clearly demonstrate that the existence of a lying-down dithiol SAM, doubly tethered by sulfur ends, should not be an impediment

for producing a standing-up dithiol SAM. We also show, for comparison, that at very large C4DT high flux dosing of the pristine Au surface we can produce directly a standing-up C4DT SAM, as this had previously been demonstrated by some of us for vapor phase adsorption of BDMT.¹⁵

■ EXPERIMENTAL SECTION

Sample Preparation and Adsorption Procedures.

Butanedithiol and octanethiol were purchased from Alfa Aesar and Sigma and used as supplied. A gold Au(111) single crystal was used as a substrate. This was cleaned by sputtering and annealing cycles and its cleanliness ascertained by XPS and characteristics of valence band emission.

The thiols were inserted into a vacuum sealed glass tube connected to the vacuum chamber through a leak valve. Several freeze–pump–thaw cycles were used to pump out and degas the liquids before exposing the clean Au surface to the thiol vapors. The walls of the vacuum chamber used for exposure were preliminarily saturated with the organic molecules. The glass tube containing the thiol molecules was kept at a constant temperature of about 60 °C during exposure to increase the vapor pressure. The sample was kept at room temperature during exposure.

Photoemission Experiments. Experiments were performed at the BEAR beamline (Elettra synchrotron radiation laboratory, Trieste, Italy).^{20,21} Photoemission spectra were acquired with a hemispherical deflection analyzer, with an overall energy resolution of <200 meV (analyzer and beamline, using constant pass energy). Spectra were recorded at normal emission, with the light impinging at 45° with respect to the surface normal. The spectral intensities were normalized to the ring current. We used $h\nu = 184$ eV for Au 4f, $h\nu = 385$ eV for C 1s, and $h\nu = 260$ eV for S 2p levels to maximize the surface sensitivity, measuring photoelectrons with kinetic energies corresponding to the minimum of the inelastic mean free path ($\Lambda \approx 6$ Å).

The emission lines from Au 4f levels were acquired at each photon energy and were taken as an energy reference for the alignment of the spectra on the binding energy scale (Au 4f_{7/2} = 84.0 eV). The valence band of the system was also measured at normal emission at 60 eV photon energy.

Theoretical Methods. Standing-up and lying-down geometries for C4DT were determined by molecular mechanics using a universal force field.²² Our intent here was to delineate differences in the density of states (DOS) related to different geometries. Initial adsorption sites were based on earlier works.^{23,24} Molecular states and DOS were determined using the StoBe DFT code.²⁵

For the calculation of the DOS, an Au cluster was used (Figure S a,b). A gradient corrected RPBE exchange/correlation functional was applied,^{26,27} using all-electron triple-valence plus polarization (TZVP) atomic Gaussian basis sets for sulfur and carbon centers, while a (311/1)-type basis set was chosen for the hydrogen sites.²⁸ Effective core potentials were used for the Au cluster atoms, describing the core and the appropriate valence basis.

■ RESULTS

In the experiments, we first form a lying-down phase of the C4DT SAM. The kinetics of adsorption of thiols^{19,29} and some dithiols¹⁵ in gas phase has been studied previously, and in preparing the C4DT lying-down phase, we based ourselves on

the results of these studies that show that, in general, one can expect to find a lying-down phase for exposures typically in the 1 kL to 50 kL range. This was then verified here by XPS as described below. The sample was then exposed to increasing doses of C8T.

The XPS spectrum corresponding to the clean and thiol-exposed Au substrate showing peaks due to the Au 4f levels is given in Figure 1a. The clean substrate spectrum displays a

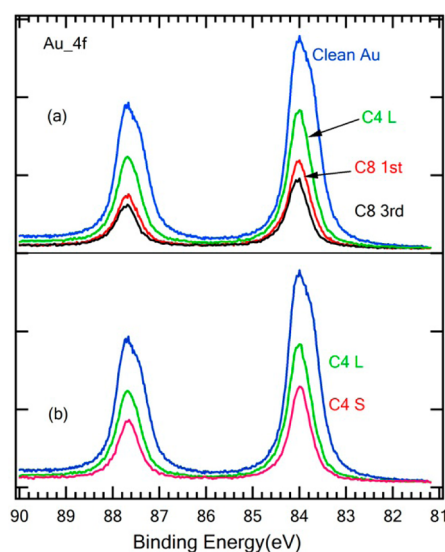


Figure 1. (a) XPS spectra in the Au 4f region for clean Au, exposed to an initial small dose of C4DT (labeled C4L; 1×10^4 L) and subsequent increasing doses of C8T (1×10^5 L, 1st, and 1×10^9 L, 3rd, see text). (b) XPS spectra of the clean Au surface and after exposure to the small dose of C4DT and a rapid large dose of C4DT (1×10^6 L; C4S).

shoulder at the lower binding energies that is associated with the reconstruction of surface atoms of the Au surface. Upon exposure to C4DT vapors, this shoulder disappears, and in general, the intensity of the Au peak decreases. The decrease of the Au peak intensity is associated with the formation of a dithiol layer leading to secondary electron scattering and attenuation of the signal.

The XPS spectrum in the S 2p region after the first C4DT exposure of 1×10^4 L is shown in Figure 2a. The spectrum is composed of two prominent structures located at about 162.1 eV and 163.3 eV and a small structure at about 164.5 eV. As is known from the literature, adsorption of thiols and dithiols on a Au surface leads to appearance of doublet structures corresponding to the $2p_{3/2}$ and $2p_{1/2}$ levels with a 1.2 eV splitting and a branching ratio of 0.5 eV. The spectrum in Figure 2a has been fitted with two Voigt doublets with a 1.2 eV separation and a branching ratio of 0.5 after a Shirley background subtraction. The peaks within each doublet were assumed to have the same width. The doublet with the $2p_{3/2}$ peak at about 162.1 eV is assigned to thiolate-type sulphurs bound to Au (S_B), whereas the 163.3 eV structure is assignable to unbound sulfur (S_U). The unbound sulfur here is attributable to the $-SH$ group of standing-up C4DT. An alternative attribution sometimes mentioned in the literature would be to $-S-S-$ groups. However, the binding energy for this case has been found to be 163.5 eV from accurate measurements³⁰ on bulk-like films of dihexadecanedisulfide ($(CH_3(CH_2)_{15}SS-(CH_2)_{15}CH_3)$).

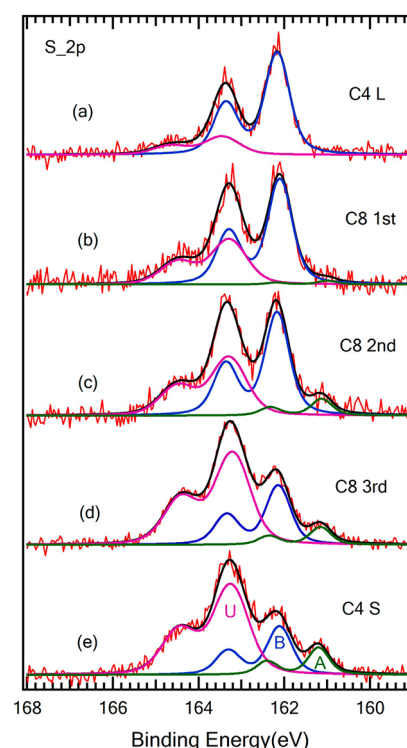


Figure 2. S 2p spectra for C4DT SAMs formed after (a) the initial C4DT exposure, (b–d) subsequent increasing C8T exposures (1×10^5 , 3×10^6 , and 1×10^9 L), and (e) after a large exposure of C4DT (1×10^6 L) as explained in the text.

The small shoulder at higher binding energy is thus assigned to the existence of a small fraction of unbound S in the layer, due to a small fraction of standing-up C4DT molecules. However, as may be seen, the spectrum is dominated by S corresponding to lying-down C4DT with both ends tethered to gold.

When the lying C4DT layer is exposed to about 1×10^5 L of C8T, one can see a strong increase in the spectrum of the component corresponding to unbound S. As may be seen in Figure 1, this also corresponds to a further decrease in the intensity of the Au peak. With increasing C8T dosage (the second and third (several hour) exposure doses correspond to about 3×10^6 and 5×10^9 L), the unbound S component increases further, and a further attenuation of the Au peak is observed.

It may be seen that, upon increasing C8T dose and growth of the standing-up C4DT component, an extra structure at about 161 eV (labeled S_A) appears. The existence of this peak is known from a number of earlier studies. It has been shown that this could arise from atomic sulfur,^{32,33} but there are also clear indications that this may be due to alternative binding sites for the alkanethiol molecules. Thus, such a feature was observed for low density or disordered alkanethiol SAMs.^{34,35} It was reported to disappear at higher coverages,³⁴ which ruled out the presence of atomic sulfur. It has also been observed, e.g., in different studies on C6T adsorption on Au where structurally well ordered films were observed,^{36,37} where the authors also privilege alternative binding sites. We shall return to this later. The spectral fits take this into account by inclusion of a third doublet with the S $2p_{3/2}$ peak at 161 eV.

Finally, in Figure 3, we show the spectrum corresponding to C1s, which gives a measure of the increase in carbon

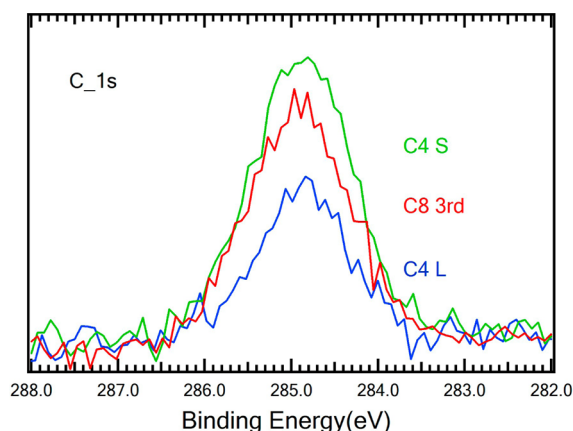


Figure 3. C 1s spectra taken after the first C4DT absorption (C4L), the third C8T exposure, and a direct rapid large exposure of clean Au to C4DT (C4S).

composition. The spectra show a single C 1s peak at 284.8 eV. This value is characteristic for undamaged aliphatic chains with thiolate headgroups bonded to the substrate.³¹ The intensity of the C signal increases significantly after exposure to C8T.

The general trend of the data in Figures 1–3 shows clearly that the lying-down C4DT phase is modified and that adsorption of C8T leads to a transition from the lying-down to standing-up phase of C4DT and incorporation of C8T thiol into the layer. We rule out physisorbed layers on the basis of earlier studies on vapor phase adsorption^{19,29} in similar room temperature conditions, and also, the appearance of the S_A structure indicates interaction with gold.

Following the usual procedure from the attenuation of the Au 4f spectra, it is possible to derive information on the effective film thickness, neglecting the optical adsorption of the film and reflectivity effects and assuming that the film is uniform in thickness and homogeneous. This method of thickness derivation was used by us previously for other alkane and aromatic dithiol SAMs and agreed well with results obtained by spectroscopic ellipsometry.^{13,14} Considering an inelastic mean free path $\Lambda = 6$ Å for the Au photoelectrons (at the measured kinetic energy of about 100 eV) in the organic film matrix,³⁸ we obtain an effective thickness value $d = 2.5$ Å for the initial C4DT film. Thereafter, an increase up to an effective thickness of 6.4 Å was observed upon successive exposure to C8T.

From Figure 2, it is clear that a complete substitution of C4DT has not yet occurred for the exposures we used. This follows the trend of our earlier substitution study in liquid, which showed a rather slow kinetics of replacement. From the spectra, we note a fast increase in the beginning and a slower increase once a sizable fraction of C4DT is standing. This would suggest that the freeing of one of the chemisorbed S ends is faster when a large number of molecules are still lying-down. This seems reasonable since in this situation it is easier for the incoming C8T to interact with the more exposed C4DT sulfur end and the Au surface.

In the case of full substitution, we would of course expect to see a complete disappearance of the unbound S peak. In the intermediate phase, we obtain a mixed SAM of C4DT and C8T. Because of this, we speak of an effective thickness of the SAM.

These XPS spectra allow us to comment on the results of the study of C4DT substitution by C12T studied by RAIRS and

electrochemistry in solution,¹⁸ in which RAIRS showed appearance of C12T related structures, but the resulting SAM in electrochemistry showed a behavior intermediate between that of the C4DT and C12T SAMs, and there was no information on the nature of the layer thus formed. Although the assembly conditions are different, in the light of the above spectra it is plausible that this is due to existence of mixed domains corresponding to a mixture of C4DT and C12T, in which the C12T fraction was slowly increasing with incubation times.

It was also interesting to investigate the characteristics of the SAM formed directly by high C4DT exposure. We exposed the clean Au surface to a very large (1×10^6 L) dose of C4DT, by opening rapidly the leak valve completely. This rapid large dosage leads to formation of a standing-up SAM as evidenced by the dominance of the unbound component in the spectrum of Figure 2e (labeled C4S), where the surface was exposed to 5×10^5 L. From the attenuation of the Au signal, we deduce a SAM thickness of about 4.9 Å. Given the length of the C4DT molecule of about 6.89 Å,^{23,24} this suggests the formation of a standing-up SAM with an inclination of about 36° from the normal, which is compatible with the 40° inclination given by theoretical investigations.²⁴ This thickness is less than that of the SAM with C8T inclusion as may be expected.

The C(1s) spectra for this case are shown in Figure 3, curve C4S. The characteristics are similar to the case of the C8T substitution. An increase in the C 1s intensity is observed in the formation of the standing-up layer. The interpretation of the relative C signal intensity increase for different cases in this figure is complicated by the fact that one needs to include different effective attenuations depending upon chain lengths, an assumption about the molecular structure of the layer, and the arrangement of the molecules on the surface, especially in case of the mixed SAM. This was not attempted here.

As in the case of C8T substitution, the C4DT spectrum in Figure 2 shows the existence of a sizable fraction of the alternative S_A component at 161 eV. A careful examination of X-ray beam damage effects was performed by scanning different areas of the sample but did not show significant variations. Also repeated measurements for newly formed layers showed similar spectra. It was seen above that, in the C4DT/C8T replacement case, the S_A component appeared when the standing-up phase of C4DT appeared. As pointed out above, this S_A feature is known from a number of previous studies.^{34–37} It is quite possible that in forming the mixed SAM and the C4DT high-coverage SAM there could exist different thiol bonding configurations leading to existence of the S_A peaks. Theoretical studies of C4DT in lying-down and standing-up phases have been performed^{23,24} and do show existence of different bonding configurations and rather different binding energies on reconstructed (with adatoms) and unreconstructed Au surfaces.

Finally, the evolution of the valence band structure of the layers was studied to see possible differences between lying-down and standing-up phases of C4DT. Figure 4 shows a comparison of the lying-down and standing-up phases of C4DT (from the large exposure experiment of C4DT in Figure 2). Clear differences in the spectra can be noticed between 0 and 4 eV and at about 8–9 eV of binding energy. In particular, we see a higher intensity of the feature labeled “a” in the spectrum for the standing-up SAM, just above the 5d Au band. In the region between 4 and 2 eV, a sizable intensity reduction is observed for the standing-up C4DT phase with respect to the flat lying case.

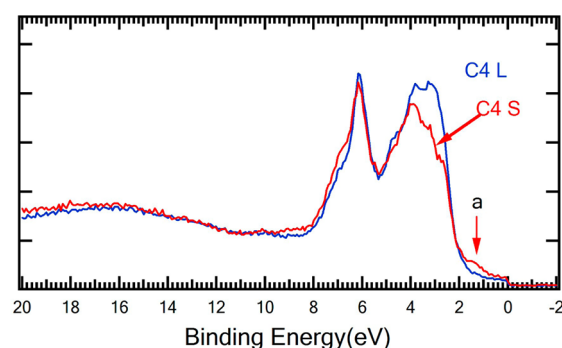


Figure 4. Comparison of the valence band spectra for the lying-down (C4L) and standing-up (C4S) phase of C4DT.

In order to understand these differences, we performed calculations of the DOS of the C4DT lying-down and standing-up phases on a Au(111) surface. A portion of the Au(111) surface was simulated here by using a gold atom cluster.³⁹

The calculated DOS are presented in Figure 5, together with a sketch of the geometries in the two configurations. To

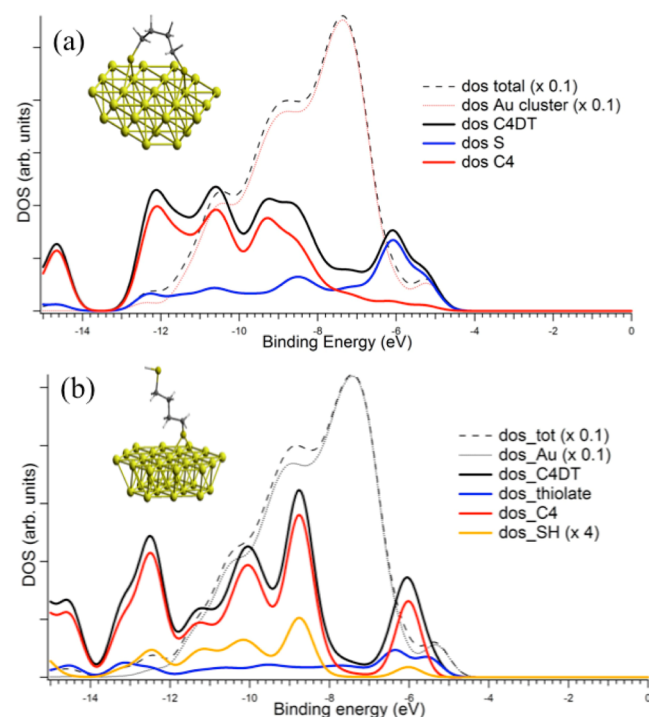


Figure 5. Calculated DOS, together with a sketch of the geometries in the (a) lying-down and (b) standing-up configurations. Total DOS and projected DOS on specific molecular groups are shown.

properly compare with the experimental valence bands, the calculated DOS should be energy shifted by about 4 eV to lower binding energy values.

The DOS in both cases are dominated by the Au 5d states of Au cluster atoms. It should be stressed that the Au 5d band refers to a cluster calculation; therefore, it should not be compared directly with the full Au 5d band obtained for full-solid-surface calculations. Instead, the contribution of the molecules are addressed in this work. The s–p Au band and adsorbate states contribute in the region between 6 and 4 eV.

In the lying-down phase (Figure 5a), major contributions due to the adsorbate in this region are spread between 6 and 4

eV with a double-peaked structure, which is assigned to bonding molecular states localized on the S terminals. The carbon chain contributes mainly below 6 eV.

In the standing phase (Figure 5b), a pronounced peaked feature is present at 6 eV, which is due to the unbound sulfur and to the C4 chain. The overall bonding sulfur contribution is shifted toward higher binding energies with respect to the lying-down phase. These effects can be nicely correlated with the feature labeled A observed in the valence band spectrum. In this frame, feature A could be considered as a signature of the standing-up molecules.

It can be also noticed that, in the region at around 7 eV in the calculation, the standing-up configuration shows negligible contributions, with respect to the lying-down phase in the same region. This could also explain the differences in the experimental valence bands, with weaker contributions in the region between 4 and 2 eV for the spectrum of the standing-up molecular configuration. Finally, the structure at about 8–9 eV in the same standing-up spectrum can be also explained in terms of the calculation, with molecular orbitals localized on the carbon C4 chain, giving sizable contributions at about 13 eV in Figure 5d.

CONCLUSIONS

Self-assembly of butanedithiol SAMs from vapor phase were investigated along with aspects of substitutional assembly starting from a lying-down phase by the addition of C8T. We clearly show using XPS that a doubly tethered dithiol phase, with both sulfur atoms attached to gold, was formed by evaporation. After exposure to C8T molecules, a mixed SAM composed of both molecules is found to be formed, with standing-up C4DT molecules. The degree of dithiol replacement, as evidenced by the increasing thickness of the SAM and the XPS peak corresponding to unbound sulfur, is found to increase slowly with increasing exposure to octanethiol, but in the exposure range to C8T used, a full replacement was not attained.

It was also shown that a standing-up C4DT phase is formed directly upon rapid large exposure to C4DT vapors of the Au(111) surface. The C4DT molecules have an inclination of about 36° to the surface normal, as deduced from the attenuation of the Au 4f peak intensity, in agreement with some recent calculations.²⁴

These results again show that the lying-down phase of dithiols can be transformed to a standing-up phase: here in the absence of any solvents. In all cases, we observe the existence of different sulfur binding energies on Au that indicate more than one possible adsorption configuration, as this has also been observed in other experiments.^{34,36} This is also compatible with the existence of differently bonded S atoms in standing C4DT SAMs as shown by calculations.^{23,24} A comparison of the valence band spectra for the lying-down and standing-up phases of C4DT reveals differences that can be accounted for theoretically.

ASSOCIATED CONTENT

Supporting Information

Complete ref list. This material is available free of charge via the Internet at <http://pubs.acs.org>.

■ AUTHOR INFORMATION

Corresponding Author

*E-mail: vladimir.esaulov@u-psud.fr. Tel: +33169157680. Fax: +33169157671.

Notes

The authors declare no competing financial interest.

■ ACKNOWLEDGMENTS

J.J. is grateful to the China Scholarship Council for supporting her to do Ph.D. in France. S.M. acknowledges support by the Abdus Salam International Centre for Theoretical Physics, Trieste, Italy, under the ICTP-TRIL fellowship scheme.

■ REFERENCES

- (1) Sarathy, K. V.; Thomas, P. J.; Kulkarni, G. U.; Rao, C. N. R. Superlattices of Metal and Metal–Semiconductor Quantum Dots Obtained by Layer-by-Layer Deposition of Nanoparticle Arrays. *J. Phys. Chem. B* **1999**, *103*, 399–401.
- (2) Ohgi, T.; Sheng, H. Y.; Nejoh, H. Au Particle Deposition onto Self-Assembled Monolayers of Thiol and Dithiol Molecules. *Appl. Surf. Sci.* **1998**, *130–132*, 919–924.
- (3) Liang, J.; Rosa, L. G.; Scoles, G. Nanostructuring, Imaging and Molecular Manipulation of Dithiol Monolayers on Au(111) Surfaces by Atomic Force Microscopy. *J. Phys. Chem. C* **2007**, *111*, 17275–17284.
- (4) Tai, Y.; Shaporenko, A.; Rong, H. T.; Buck, M.; Eck, W.; Grunze, M.; Zharnikov, M. Fabrication of Thiol-Terminated Surfaces. Using Aromatic Self-Assembled Monolayers. *J. Phys. Chem. B* **2004**, *108*, 16806–16810.
- (5) Niklewski, A.; Azzam, W.; Strunskus, T.; Fischer, R. A.; Wöll, C. Fabrication of Self-Assembled Monolayers Exhibiting a Thiol Terminated Surface. *Langmuir* **2004**, *20*, 8620–8624.
- (6) Yang, Y. C.; Lee, Y. L.; Yang, L. Y. O.; Yau, S. L. In Situ Scanning Tunneling Microscopy of 1,6-Hexanedithiol, 1,9-Nonanedithiol, 1,2-Benzenedithiol, and 1,3-Benzenedithiol Adsorbed on Pt(111) Electrodes. *Langmuir* **2006**, *22*, 5189–5195.
- (7) Pasquali, L.; Terzi, F.; Zanardi, C.; Pigani, L.; Seeber, R.; Paolicelli, G.; Sutturin, S. M.; Mahne, N.; Nannarone, S. Structure and Properties of 1,4-Benzenedimethanethiol Films Grown from Solution on Au(111): An XPS and NEXAFS study. *Surf. Sci.* **2007**, *601*, 1419–1427.
- (8) Pasquali, L.; Terzi, F.; Zanardi, C.; Seeber, R.; Paolicelli, G.; Mahne, N.; Nannarone, S. Bonding and Orientation of 1,4-Benzenedimethanethiol on Au(111) Prepared from Solution and from Gas Phase. *J. Phys.: Condens. Matter* **2007**, *19*, 305020.
- (9) Kohli, P.; Taylor, K. K.; Harris, J. J.; Blanchard, G. J. Assembly of Covalently-Coupled Disulfide Multilayers on Gold. *J. Am. Chem. Soc.* **1998**, *120*, 11962–11968.
- (10) Qu, D.; Kim, B. C.; Lee, C. W. J.; Uosaki, K. 1,*n*-Alkanedithiol (*n* = 2, 4, 6, 8, 10) Self-Assembled Monolayers on Au(111): Electrochemical and Theoretical Approach. *Bull. Korean Chem. Soc.* **2009**, *30*, 2549–2554.
- (11) Pasquali, L.; Terzi, F.; Seeber, R.; Doyle, B. P.; Nannarone, S. Adsorption Geometry Variation of 1,4-Benzenedimethanethiol Self-Assembled Monolayers on Au(111) Grown from the Vapor Phase. *J. Chem. Phys.* **2008**, *128*, 134711–134721.
- (12) Millone, M. A. D.; Hamoudi, H.; Rodríguez, L. M.; Rubert, A.; Benitez, G. A.; Vela, M. E.; Salvarezza, R. C.; Gayone, J. E.; Sánchez, E. A.; Grizzi, O.; et al. Self-Assembly of Alkanedithiols on Au(111) from Solution: Effect of Chain Length and Self-Assembly Conditions. *Langmuir* **2009**, *25*, 12945–12953.
- (13) Hamoudi, H.; Prato, M.; Dablemont, C.; Cavalleri, O.; Canepa, M.; Esaulov, V. A. Self-Assembly of 1,4-Benzenedimethanethiol Self-Assembled Monolayers on Gold. *Langmuir* **2010**, *26*, 7242–7247.
- (14) Hamoudi, H.; Guo, Z. A.; Prato, M.; Dablemont, C.; Zheng, W. Q.; Bourguignon, B.; Canepa, M.; Esaulov, V. A. On the Self Assembly of Short Chain Alkanedithiols. *Phys. Chem. Chem. Phys.* **2008**, *10*, 6836–6841.
- (15) Alarcon, L. S.; Chen, L.; Esaulov, V. A.; Gayone, J. E.; Sanchez, E. A.; Grizzi, O. Thiol Terminated 1,4-Benzenedimethanethiol Self-Assembled Monolayers on Au(111) and InP(110) from Vapor Phase. *J. Phys. Chem. C* **2010**, *114*, 19993–19999.
- (16) Hamoudi, H.; Dablemont, C.; Esaulov, V. A. Disorder, Solvent Effects and Substitutional Self-Assembly of Alkane Dithiols from Alkane Thiol SAMs. *Surf. Sci.* **2011**, *605*, 116–120.
- (17) Pasquali, L.; Terzi, F.; Seeber, R.; Nannarone, S.; Datta, D.; Dablemont, C.; Hamoudi, H.; Canepa, M.; Esaulov, V. A. UPS, XPS, and NEXAFS Study of Self-Assembly of Standing 1,4-Benzenedimethanethiol SAMs on Gold. *Langmuir* **2011**, *27*, 4713–4720.
- (18) Chaudhari, V.; Harish, M. N. K.; Sampath, S.; Esaulov, V. A. Substitutional Self-Assembly of Alkanethiol and Selenol SAMs from a Lying-Down Doubly Tethered Butanedithiol SAM on Gold. *J. Phys. Chem. C* **2011**, *115*, 16518–16523.
- (19) Rodriguez, L. M.; Gayone, J. E.; Sanchez, E. A.; Grizzi, O.; Blum, B.; Salvarezza, R. C. Room-Temperature Kinetics of Short-Chain Alkanethiol Film Growth on Ag(111) from the Vapor Phase. *J. Phys. Chem. B* **2006**, *110*, 7095–7097.
- (20) Pasquali, L.; DeLuisa, A.; Nannarone, S. The UHV Experimental Chamber For Optical Measurements (Reflectivity and Absorption) and Angle Resolved Photoemission of the BEAR Beamline at ELETTRA. *AIP Conf. Proc.* **2004**, *705*, 1142.
- (21) Nannarone, S.; Borgatti, F.; DeLuisa, A.; Doyle, B. P.; Gazzadi, G. C.; Giglia, A.; Finetti, P.; Mahne, N.; Pasquali, L.; Pedio, M.; et al. The BEAR Beamline at Elettra. *AIP Conf. Proc.* **2004**, *705*, 450.
- (22) Rappe, A. K.; Casewit, C. J.; Colwell, K. S.; Goddard, W. A., III; Skiff, W. M. UFF, a Full Periodic Table Force Field for Molecular Mechanics and Molecular Dynamics Simulations. *J. Am. Chem. Soc.* **1992**, *114*, 10024–10035.
- (23) Franke, A.; Pehlke, E. First-Principles Study of 1,4-Butanedithiol Molecules and Radicals Adsorbed on Unreconstructed Au(111) and Au(100). *Phys. Rev. B* **2010**, *81*, 075409.
- (24) Carro, P.; Hernandez Creus, A.; Munoz, A.; Salvarezza, R. C. On the Thermodynamic Stability of α,ω -Alkanedithiols Self-Assembled Monolayers on Unreconstructed and Reconstructed Au(111). *Langmuir* **2010**, *26*, 9589–9595.
- (25) Hermann, K.; Pettersson, L. G. M.; Casida, M. E.; Daul, C.; Goursoat, A.; Koester, A.; Proynov, E.; St-Amant, A.; Salahub, D. R.; Contributing authors: Carravetta, V.; Duarte, H.; Friedrich, C.; Godbout, N.; Guan, J.; Jamorski, C.; Leboeuf, M.; Leetmaa, M.; Nyberg, M.; Patchkovskii, S.; et al. *StoBe-deMon*, version 3.0; Fritz-Haber-Institut: Berlin, Germany, 2007.
- (26) Hammer, B.; Hansen, L. B.; Nørskov, J. K. Improved Adsorption Energetics within Density-Functional Theory Using Revised Perdew–Burke–Ernzerhof Functionals. *Phys. Rev. B* **1999**, *59*, 7413.
- (27) Perdew, J. P.; Burke, K.; Ernzerhof, M. Generalized Gradient Approximation Made Simple. *Phys. Rev. Lett.* **1996**, *77*, 3865.
- (28) Godbout, N.; Salahub, D. R.; Andzelm, J.; Wimmer, E. Optimization of Gaussian-Type Basis Sets for Local Spin Density Functional Calculations. Part I. Boron through Neon, Optimization Technique and Validation. *Can. J. Chem.* **1992**, *70*, 560.
- (29) Rodriguez, L. M.; Gayone, J. E.; Sanchez, E. A.; Grizzi, O.; Blum, B.; Salvarezza, R. C.; Xi, L.; Lau, W. M. Gas Phase Formation of Dense Alkanethiol Layers on GaAs(110). *J. Am. Chem. Soc.* **2007**, *129*, 7811.
- (30) Heister, K.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O.; Ulman, A. Characterization of X-ray Induced Damage in Alkanethiolate Monolayers by High-Resolution Photoelectron Spectroscopy. *Langmuir* **2001**, *17*, 8–11.
- (31) Heister, K.; Johansson, L. S. O.; Grunze, M.; Zharnikov, M. A Detailed Analysis of the C 1s Photoemission of *n*-Alkanethiolate Films on Noble Metal Substrates. *Surf. Sci.* **2003**, *529*, 36.
- (32) Shaporenko, A.; Terfort, A.; Grunze, M.; Zharnikov, M. A Detailed Analysis of the Photoemission Spectra of Basic Thioaromatic

Monolayers on Noble Metal Substrates. *J. Electron Spectrosc. Relat. Phenom.* **2006**, *151*, 45–51.

(33) Weidner, T.; Krämer, A.; Bruhn, C.; Zharnikov, M.; Shaporenko, A.; Siemeling, U.; Träger, F. Novel Tripod Ligands for Prickly Self-Assembled Monolayers. *Dalton Trans.* **2006**, 2767–2777.

(34) Ishida, T.; Hara, M.; Kojima, I.; Tsuneda, S.; Nishida, N.; Sasabe, H.; Knoll, W. High Resolution X-ray Photoelectron Spectroscopy Measurements of Octadecanethiol Self-Assembled Monolayers on Au(111). *Langmuir* **1998**, *14*, 2092–2096.

(35) Ito, E.; Kang, H.; Lee, D.; Park, J. B.; Hara, M.; Noh, J. Spontaneous Desorption and Phase Transitions of Self-Assembled Alkanethiol and Alicyclic Thiol Monolayers Chemisorbed on Au(111) in Ultrahigh Vacuum at Room Temperature. *J. Colloid Interface Sci.* **2013**, *394*, 522–529.

(36) Hamoudi, H.; Chesneau, F.; Patze, C.; Zharnikov, M. Chain-Length-Dependent Branching of Irradiation-Induced Processes in Alkanethiolate Self-Assembled Monolayers. *J. Phys. Chem. C* **2011**, *115*, 534–541.

(37) Chesneau, F.; Zhao, J.; Shen, C.; Buck, M.; Zharnikov, M. Adsorption of Long-Chain Alkanethiols on Au(111): A Look from the Substrate by High Resolution X-ray Photoelectron Spectroscopy. *J. Phys. Chem. C* **2010**, *114*, 7112–7119.

(38) Lamont, C. L. A.; Wilkes, J. Attenuation Length of Electrons in Self-Assembled Monolayers of *n*-Alkanethiols on Gold. *Langmuir* **1999**, *15*, 2037–2042.

(39) Öström, H.; Triguero, L.; Weiss, K.; Ogasawara, H.; Garnier, M. G.; Nordlund, D.; Nyberg, M.; Pettersson, L. G. M.; Nilsson, A. Orbital Rehybridization in *n*-Octane Adsorbed on Cu(110). *J. Chem. Phys.* **2003**, *118*, 3782.