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The Role of Tris(2-carboxyethyl)phosphine Reducing Agent in the Controlled Formation of α,ω-Alkanedithiols Monolayers on Au(111) with Monocoordinated and Bicoordinated Configurations

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KEYWORDS. Alkanedithiols, TCEP, Au (111), Reductive Desorption, DFT.

ABSTRACT

The addition of the reducing agent tris(2-carboxyethyl) phosphine (TCEP) during the formation of α,ω-alkanedithiols monolayers on Au(111) using the immersion method produces the assembly of monolayers with bicoordinated molecules (both S-terminal groups bound to the surface) that have a reductive desorption potential that is more positive than for monolayers with monocoordinated molecules in a standing up configuration. We show that the use of TCEP either during formation of the monolayer or as a post treatment procedure allows the controlled formation of monolayers with bicoordinated or monocoordinated configurations. Density Functional Theory (DFT) calculations were performed to elucidate the role of TCEP in the formation of the bicoordinated configuration. We investigated the TCEP-dithiol interaction in ethanol solvent as well as the coadsorption of trimethylphosphine with 1,2-ethanedithiol on Au(111). The Brønsted base character of the phosphine facilitates the H exchange from the −SH groups of the dithiol to the phosphorous atom of TCEP with very low activation energy barriers, thus allowing the thiolate groups to bind to the Au(111) surface, thus yielding the bicoordinated configuration. Dithiol lifting mechanisms such as H exchange between S atoms and the formation of intra/inter layer disulfide bonds have much higher energy barriers.

INTRODUCTION

Self-assembled monolayers (SAMs) on solid surfaces are widely studied due to their potential applications in several areas such as corrosion inhibition, molecular recognition, nanoelectronics, biosensing, etc.[1-3]

A SAM is built up of molecules made of three different parts: a head-group bonded to the surface, a spacer group responsible for intermolecular interactions and a terminal group that confers a new chemical identity to the modified surface. The most popular type of SAMs are those composed of alkanethiolates adsorbed upright on Au(111) surfaces; these SAMs can be prepared from either alkanethiols ($CH_3{-}(CH_2)_n{-}SH$) that deprotonate upon adsorption, or disulfides ($(CH_3{-}(CH_2)_n{-}S)_2$) which dissociate into two thiolates during adsorption.

Another interesting type of SAMs are those made of α,ω−alkanedithiols (DTs), i.e. carbon chains terminated with thiol groups in both ends ($HS\text{-}(CH_2)_n\text{-}SH$). DTs molecules may be adsorbed in a standing up (SU, mono-coordinated)[4-6] or a lying-down (LD) configuration (bi-coordinated)[7,8] depending on the preparation method. Bi-coordinated adsorption exposes the alkyl chain to the environment; whereas the mono-coordinated one only exposes, in principle, the –SH group. The synthesis of SH-terminated surfaces is of great interest because they have the potential ability of binding to two metallic entities, and serve, therefore, to connect nanoparticles or to bind them to a surface.[9]

The preparation procedure has an important influence on the surface structure and chemistry of SAMs of DTs on Au(111) as recently reviewed by Hamoudi et al.[10] Ordered standing up monolayers exposing the –SH group were formed in n-hexane solution in the absence of light.[11-14] The acetyl protection of one thiol end also allowed the formation of an –SH terminated surface.[15] The formation of SU dithiols has also been reported to occur from vapor phase.[16]

However, a small amount of LD phase[12] as well as bicoordinated dithiols in a U-loop configuration[17] may also coexist with the SU phase. Short immersion times of a few seconds produce LD structures of 1,5-pentanedithiol whereas at long immersion times the SU structure is obtained.[18] Under low flux and low dose conditions in adsorption experiments from vapor, LD phases have been observed for and 1,4-benzenedimethanethiol[16] and 1,4-butanedithiol.[19] LD phases of 1,4-butanedithiol were also observed from liquid phase assembly using millimolar solutions of ethanol and hexane at room temperature (RT) on gold substrates.[20] DFT calculations show that the LD → SU phase transition under vacuum conditions is favored as the hydrocarbon chain length of DTs is increased.[21] The parameters that control the thermodynamic stability of the different phases are the binding energy of the adsorbates and the number of adsorbed species per unit of substrate area.[21]

The presence of disulfide bonds has a profound influence on the structure of DT layers. Interlayer S–S bonds are responsible for the formation of SU-multilayer structures whereas intralayer S–S bonds may be present in a dithiol monolayer.[5,6,22] Small chain DTs are more reactive towards the formation of multilayers in the presence of O_2 by oxidation of −SH groups to disulfides. This complicates the reproducible and controlled formation of DT monolayers.

Disulfide reducing agents may be employed to shave the multilayers leaving only a single monolayer or they may be introduced in the forming solution containing the DT.[22-26]

XPS is a very powerful technique to elucidate the structure of dithiol layers as the S2p binding energy has different values for the –SH terminal group, the disulfide S–S bond and the surface S–Au bond.[10,19,26] In a previous investigation using high resolution photoelectron spectroscopy we found that tris(2-carboxyethyl) phosphine added to the forming solution leads to the reproducible formation of lying down structures of α,ω-alkanedithiols irrespective of the chain

length and without the need of deoxygenating the forming solution.[26] This implies that the phosphine not only inhibits the formation of disulfide bonds but also blocks the possible mechanisms responsible for the LD → SU phase transition.

In the present work we investigated the mechanisms involved in the formation of lying-down phases in the presence of TCEP. We considered 1,2-ethanedithiol (C2DT), 1,6-hexanedithiol (C6DT), 1,8-octanedithiol (C8DT) and 1,9-nonanedithiol (C9DT). The theoretical calculations were performed with C2DT. In the first part we use cyclic voltammetry as the potential of reductive desorption current peaks is very sensitive to the monolayer structure. In the second part we use density functional theory to investigate the TCEP-induced formation of a C2DT lying-down structure by considering the a) the TCEP-C2DT interaction in the ethanolic forming solution b) the energetics involved in the LD→SU transitions of C2DT molecules on Au(111) and c) the coadsorption of trimethylphosphine with C2DT on Au(111).

EXPERIMENTAL SECTION

Chemicals. Dipping solutions were prepared using C2DT, C6DT, C8DT, C9DT, tris(2-carboxyethyl)phosphine (TCEP) (Sigma-Aldrich) and absolute ethanol or *n*-hexane (Baker) as solvents.

Gold Substrates. An Au crystal, 4 mm in diameter, oriented better than 1º towards the (111)-face and polished down to 0.03 μm (MaTeck, Jülich, Germany) was used as a working electrode for cyclic voltammetry. The cleaning of this substrate involved repeated cycles of annealing on a H_2 flame and cooling in a N_2 atmosphere. Au films (500 nm thick) evaporated on heat resistive glasses were employed as substrates for the photoemission experiments. These substrates were annealed several times in a butane flame for two minutes and cooled down to room temperature in a stream of nitrogen.

SAM preparation. The self-assembled adlayers were prepared by immersing the gold substrates into 0.2 mM solutions of dithiol in ethanol without deoxygenating. In one experiment, the formation of the adlayer was also performed in an *n*-hexane solvent. The post deposition treatment consisted in the immersion of the sample in a concentrated solution (20%:80%, H_2O:ethanol) of TCEP during 10 minutes. When the reducing agent was added to the formation bath, monolayers were formed by immersing the substrates into 0.2 mM of the corresponding dithiol and 4.0 mM of TCEP ethanolic solutions for 24 h. After the adlayers were formed, the substrates were washed several times with pure ethanol and Milli-Q water in order to remove physisorbed species.

Electrochemical Measurements. Cyclic Voltammograms (CV) were performed with a Solartron 1260 electrochemical interface and a conventional electrochemical three electrode cell with separate compartments for reference (Ag/AgCl (NaCl 3M)) and counter electrode (Pt wire). Electrical contact with the working electrode was made by means of a meniscus on the surface of the electrolytic solution. The electrolyte was thoroughly deoxygenated by bubbling with nitrogen prior to each experiment. Reductive desorption experiments were performed in 0.1 M KOH solutions.

THEORETICAL METHODS

The first-principles periodic calculations within the framework of density functional theory (DFT) were performed with the SIESTA code.[27] Valence electrons were described with a set of double-z polarized bases. The number of *k*-points in the *x*-*y* plane was increased to obtain convergence in the system energy better than 0.002 eV/atom, resulting a sample of 3x3x1 *k*-points finally. The separation in the *z* direction between the neighboring metal slabs (made of 4 layers (111) on a 3×3 unit cell) was ca. 20 Å to ensure convergence in the system energy. The

exchange and correlation effects were described using the generalized gradient approximation GGA in the functional Perdew-Burke-Ernzerhof.[28] The energy shift used to confine the electrons in the pseudoatomic orbitals was 0.02 eV.

We studied the minimum energy reaction paths connecting an optimized initial configuration to the desired final structure by using the nudged elastic band (NEB) method.[29,30] The progress along the reaction pathway is represented by the so called reaction coordinate which is a dimensionless quantity varying from 0 (reactants) to 1 (products).

The TCEP-dithiol interaction was investigated using the Gaussian 09 package.[31] The solution-phase geometry optimizations were performed using the PBE functional for both exchange and correlation and 6-311++G(d,p) basis set.[28] The polarizable continuum model (PCM) was used to describe solvent effects.[32] Ethanol was used as the solvent.

RESULTS AND DISCUSSION

Electrochemical Characterization

Figure 1 shows cathodic sweep responses corresponding to C2DT gold modified samples prepared by different procedures. As it can be seen, the electrochemical response is very sensitive to the preparation method used.

The reductive desorption profile of a C2DT layer prepared after immersion for 24 hours in an ethanolic C2DT (0.2 mM) solution (Figure 1a, black line) shows a main desorption peak at –913 mV with a pronounced broad shoulder shifted to more negative potential values. The second scan (dashed line) presents two peaks, one close to the potential of the main peak and another one at nearly the same potential as that of the shoulder of the first scan. The integrated area of the first scan (colored in the Figure 1 a)) gives a desorption charge of around 200 μC cm^{-2} which

represents more than twice the charge expected for the desorption of an ideal SU dithiolate monolayer (75 μC cm^{-2}).

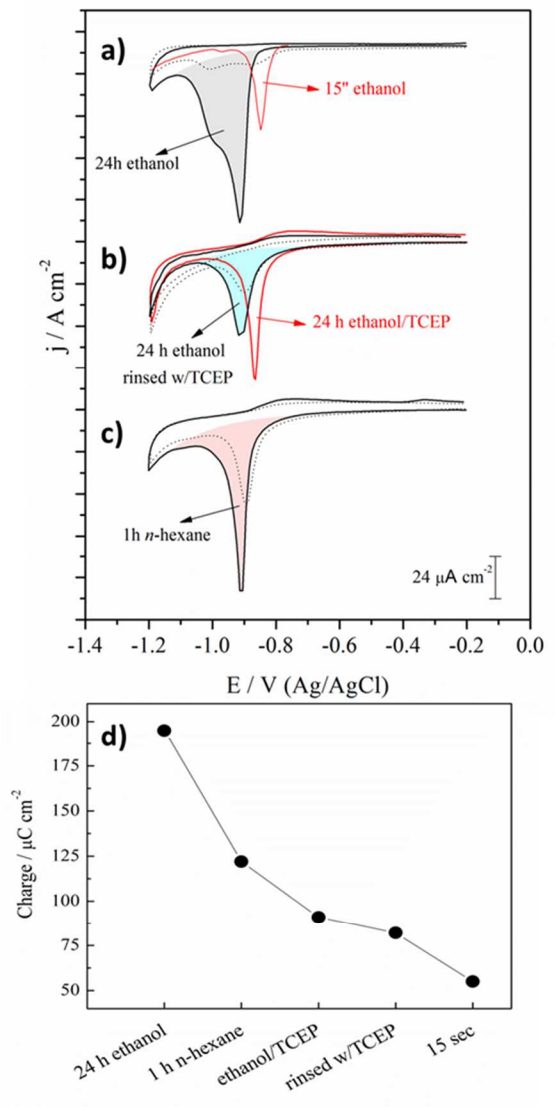

Figure 1. Reductive desorption profiles obtained for DTs-layers on Au(111) substrates prepared by different procedures. The solid curves correspond to the first potential scan and the dotted curves to the second potential scan. a) immersion for 15 sec (red curve) and 24 h (black curve) in ethanolic solutions; b) immersion for 24 h in ethanolic solution and post treatment with TCEP (black curve), and immersion for 24 h in ethanolic solution with TCEP in the forming solution (red curve); c) immersion for 1 h in a *n*-hexane solution; d) reductive desorption charge for the different preparation procedures. Electrolyte: KOH 0.1M. Scan rate: 50 mV/s.

Previous impedance[25] and XPS[26] measurements showed that after the immersion for 24h in a 0.2 mM C2DT-ethanol solution, a multilayer structure is formed, therefore the charge excess can be attributed to the additional charge necessary to reduce inter/intralayer S–S bonds. The breakage of S–S bonds and S-Au bonds seems to occur at similar potential values, a feature that prevents the separate study of these reduction processes. The presence of a shoulder in the CV profile at more negative potentials is consistent with the desorption of species with a lower solubility than that of C2DT molecules, such as remaining C2DT-dimers formed by interlayer S–S bonds not reduced in the main peak.

Haiss et al.[18] showed by means of photoemission spectra that both S atoms of a DT molecule are bonded to the gold surface when the formation procedure involves short immersion times. In order to obtain an electrochemical reference of a low coverage LD structure, we investigated different samples prepared by short immersion times. Figure 1 a) (red line) shows the cathodic sweep of a gold sample modified by the immersion during 15 seconds in a diluted C2DT-solution. This desorption profile exhibits a main desorption peak at –848 mV and a small hump at more negative values. The charge involved in the desorption process (55 μC cm^{-2}) is lower than that expected for an ideal SU monolayer (75 μC cm^{-2}) indicating a lower coverage of C2DT. The shift of the desorption potential to a more positive value indicates weaker interactions among the alkyl chains which is consistent with a low density LD structure. We interpret the remarkable differences in the CV profiles of Figure 1 a) with the immersion time in the forming solution as the transition from a low density LD monolayer to a SU multilayer structure.

An effective method to remove undesired S–S bonds is to use reducing agents (like phosphines,[22,24,25] β-ME or DTT[23]) in some stage of the preparation procedure. In Figure 1 b), two experiments accounting for the use of the TCEP reducing agent are shown. The first case

(black full line) represents the electrochemical characterization of a sample formed by the immersion during 24 hours in a diluted C2DT-solution (as that described in Figure 1 a)) and then immersed during 10 minutes in a 20 mM aqueous/ethanolic (20:80) solution of TCEP. The CV profile obtained after the modification of the sample with this procedure exhibits a desorption profile with a single peak at almost the same value (–917 mV) at which the main peak is observed for the immersion of 24 h. Remarkably, the shoulder at more negative values disappears completely and the charge involved in the reduction process decreases to 82 μC cm^{-2}, almost the charge expected for the desorption of an ideal SU monolayer.

The reducing agent was also used *during* the formation of the adlayer. We prepared an ethanolic C2DT solution with a [TCEP]/[C2DT] concentration ratio of 20. The cathodic sweep after a 24 hour immersion time (Figure 1b, red line) shows a narrow single peak at –866 mV with a charge of 91 μC cm^{-2}. The desorption potential is very close to that obtained for the diluted monolayer prepared by the short immersion time of 15 seconds (only a 18 mV difference) indicating that both monolayers should have the same LD configuration.

The formation of disulfide bonds seems to be inhibited when *n*-hexane is used as solvent.[12] The first (continuous line) and second (dashed line) CV's scans in Figure 1c) correspond to a C2DT layer formed in *n*-hexane solution. The desorption profile of the first scan (black full line) presents a sharp peak at –902 mV and a desorption charge of 122 μC cm^{-2}. This charge is much lower than the value of 200 μC cm^{-2} obtained when the layer was formed in ethanol indicating that the formation of disulfide bonds is mostly inhibited.

Figure 1d summarizes all the reduction desorption charges obtained for the different preparation procedures. The plot demonstrates the sensitivity of the surface structure on the experimental conditions. It suggests that if the forming conditions can be appropriately controlled, the desired

surface layer structure can be obtained. This is best achieved with the use of TCEP. We note that all the experiments involving TCEP are highly reproducible either when the reducing agent is used during or after the formation of the adlayer.

The lying-down structure of alkanedithiol (C2DT, C6DT and C9DT) adlayers prepared by addition of TCEP in the forming solution were verified in a previous XPS study.[26] In this work we showed the prevalence of the 162 eV feature over the 163.3 eV and 163.5 eV components in the S2p spectra of samples incubated with TCEP in the alkanedithiol solution. The component at 162 eV is attributed to electrons emitted from thiolate-S atoms at the interface with the Au substrate;[33-36] whereas recent works attributed the components at 163.1-163.3 eV and 163.5 eV to the presence of –SH and S–S groups, respectively[10,14,19,26.] Thus, the clear prevalence of the component at 162 eV proves the lying-down configuration of alkanedithiol adlayers and this trend seems to be general as it observed for alkanedithiols with different chain length.[26]

The capability of TCEP to control the monolayer structure was confirmed for longer chain alkanedithiols as shown in Figure 2. In one set of experiments the monolayers were prepared with TCEP in the forming solution and in another set the freshly prepared monolayers were post treated with TCEP. We observed the same trend as for C2DT: the monolayers prepared with TCEP have reductive desorption current peaks at more positive potentials than the monolayers prepared without TCEP. In the first case the peak potentials are -955 mV, -960 mV and -952 mV for C6DT, C8DT and C9DT, respectively; whereas in the second case they are -1031 mV, -1056 mV and -1062 mV, respectively.

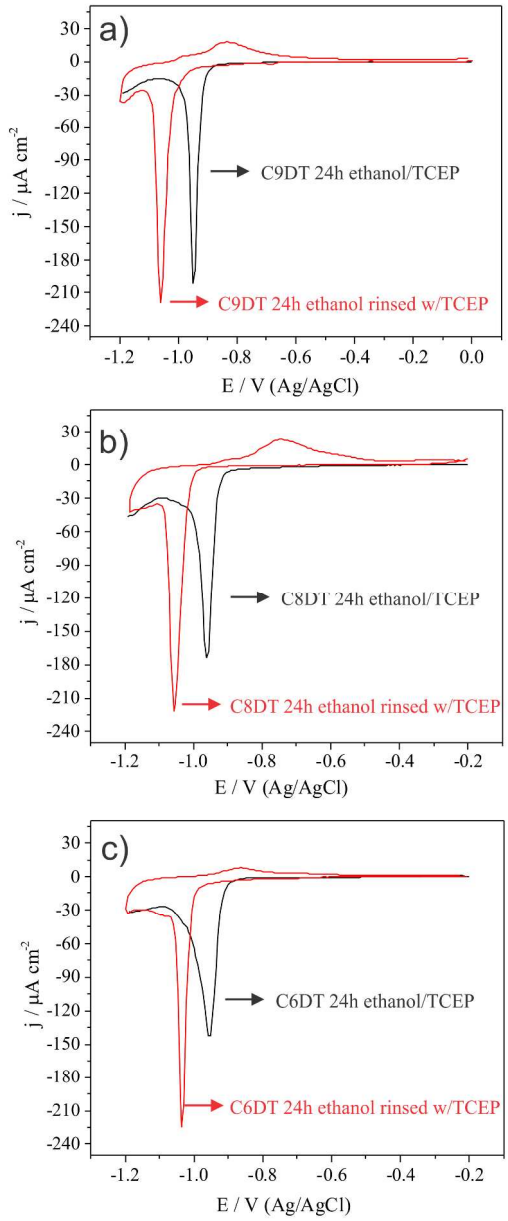

Figure 2. Reductive desorption profiles obtained for a) C9DT, b) C8DT and c) C6DT. The CV profiles in black correspond to monolayers prepared by 24 h immersion in ethanolic solution *with* TCEP. CV profiles in red correspond to monolayers prepared by 24 h immersion in ethanolic solution and post treatment with TCEP. Electrolyte: KOH 0.1M. Scan rate: 50 mV/s.

The most positive reductive desorption potential observed for the monolayers prepared with TCEP is consistent with our previous photoelectron spectroscopy study which shows that these monolayers are coordinated to the surface via both S atoms,[26] probably in a U loop configuration. On the other hand, the monolayers prepared without TCEP in the forming solution which have a standing up configuration[26] which maximized van der Waals interactions among the alkyl chains, have the most negative reductive desorption potentials. It has been reported that poor quality SAMs are obtained when the self assembly is performed in ethanol solvent.[10] The present results show that even for this challenging solvent, well ordered dithiol phases are obtained when TCEP is used in the forming solution.

Density Functional Theory Calculations

The above results motivated us to investigate the mechanism by which only LD monolayers are produced when TCEP is introduced in the forming solution. We therefore considered a) the dithiol-TCEP interaction in the ethanol solvent, b) possible lifting mechanisms of LD dithiol molecules on Au(111) and c) the phosphine-dithiol interaction when both species are coadsorbed on the Au(111) surface.

Tris(2-carboxyethyl) phosphine acts as a Brønsted base which can abstract a proton from the −SH group giving rise to thiolate-phosphonium ion pairs. Phosphorus has a relatively large polarizability and thus can stabilize charged intermediates.[37-39] Figure 3a shows the C2DT-TCEP structure before deprotonation of one of the −SH groups. The calculation was performed using the Polarizable Continuum Model with ethanol as the solvent and we also included explicitly two ethanol molecules as shown in Figure 3a. The equilibrium structure for the phosphonium cation-thiolate anion complex is shown in Figure 3b. The thiolate anion is stabilized by the hydrogen bonds (HB) of the two ethanol molecules. The HB bond length is 2.11 Å. The O atom of one of

the ethanol molecules is also involved in the HB with the protonated phosphoniun cation with a short HB bond length of 1.94 Å. The ΔE value for the deprotonation process is endothermic with 0.34 eV. An equivalent calculation with only one explicit ethanol molecule gives ΔE = 0.58 eV whereas the ΔE value in vacuum is 1.0 eV. These data show the stabilizing effect of the solvent on the charged ions. The addition of more ethanol molecules is therefore expected to further decrease the ΔE value. This shows that the deprotonation of the dithiol by TCEP is a kinetically facile process.

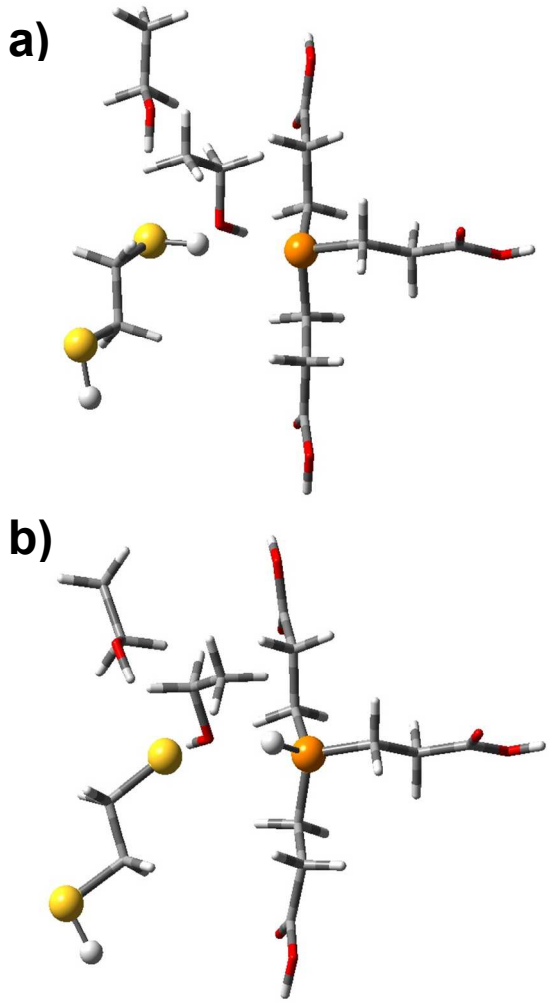

Figure 3. a) Equilibrium structure of TCEP with 1,2-ethanedithiol and two ethanol molecules in ethanol solvent. b) Equilibrium structure in ethanol solvent of the ion pair after the proton

transfer from the −SH group of the dithiol to the P atom of TCEP. The OH groups of both ethanol molecules form hydrogen bonds with the thiolate anion. For clarity, only the relevant atoms are explicitly shown.

This fact, together with the high TCEP/dithiol concentration ratio of 20, implies that a fraction of dithiols will be present in the anionic form in the ethanolic forming solution. Anions have strong electrostatic interactions with metal surfaces mainly arising from the metal polarization. In previous works we calculated the interaction of different anions with metal surfaces.[40,41] The sulfate anion (having nearly the same charge to mass ratio as the ethanedithiolate dianion), for example, has a strong interaction of 6.24 eV with the Au(111) surface. In the case of the ethanedithiolate dianion with the negative charges localized at both ends of the molecule, image-charge interactions with the metal surface are maximized when the molecule adsorbs flat on the surface. Therefore, there is a strong driving force for the ethanedithiolate anions to adsorb in a low-lying configuration on the surface.

Phosphines also interact with the gold surface via the lone electron pairs on the phosphorous atom. An STM investigation of trimethylphosphine on Au(111) showed that the interaction strong enough to lift the gold herringbone reconstruction[42] but was not so strong to eject additional atoms and create etch pits, as is the case of alkanethiols. Therefore, under a TCEP/C2DT ratio of 20 in the forming solution, the gold surface is expected to be initially covered by TCEP molecules.

Due to the large size of the TCEP molecule, we used trimethylphosphine as a model to investigate the reactivity of coadsorbed phosphine and dithiol molecules on Au(111) surface. We calculated the energy profile for the deprotonation of a −SH group (Figure 4a) of ethanedithiol interacting with trimethylphosphine on Au(111) . The corresponding structures for the reactants,

transition state and products are shown in the panels of Figure 4b. Panel I in Figure 4b shows the equilibrium structure of the phosphine-dithiol complex on Au(111). 1,2-ethanedithiol adsorbs with an S atom located on top of an Au atom whereas its H atom points towards the P atom of trimethylphosphine as a consequence of the H-bond interaction. The adsorption of this complex on the surface from vacuum is exothermic with ΔE=-0.51 eV. In the transition state (panel II in Figure 4b) the H atom has been transferred to the P atom and in the final state the phosphonium cation adsorbs on the surface (panel III) with the PH group located on a hollow site. The energy profile in Figure 4a shows that the hydrogen abstraction has a small energy barrier of 0.21 eV whereas the reaction has ΔE=0.0. Considering as a reference the energy of the phosphine-dithiol complex in vacuum, the whole reaction has ΔE=-0.506 eV.

In summary, the deprotonation of the dithiol by the phosphine molecule is favored on the surface with respect to the solution phase. For the sake of simplicity in Figure 4 we only considered the interaction of one of the −SH groups of the dithiol with a phosphine molecule, but in a solution with a phosphine concentration higher than that of the dithiol, the complex is expected to have a phosphine molecule at both ends of the dithiol thus leaving lying-down dithiolate species adsorbed on the surface.

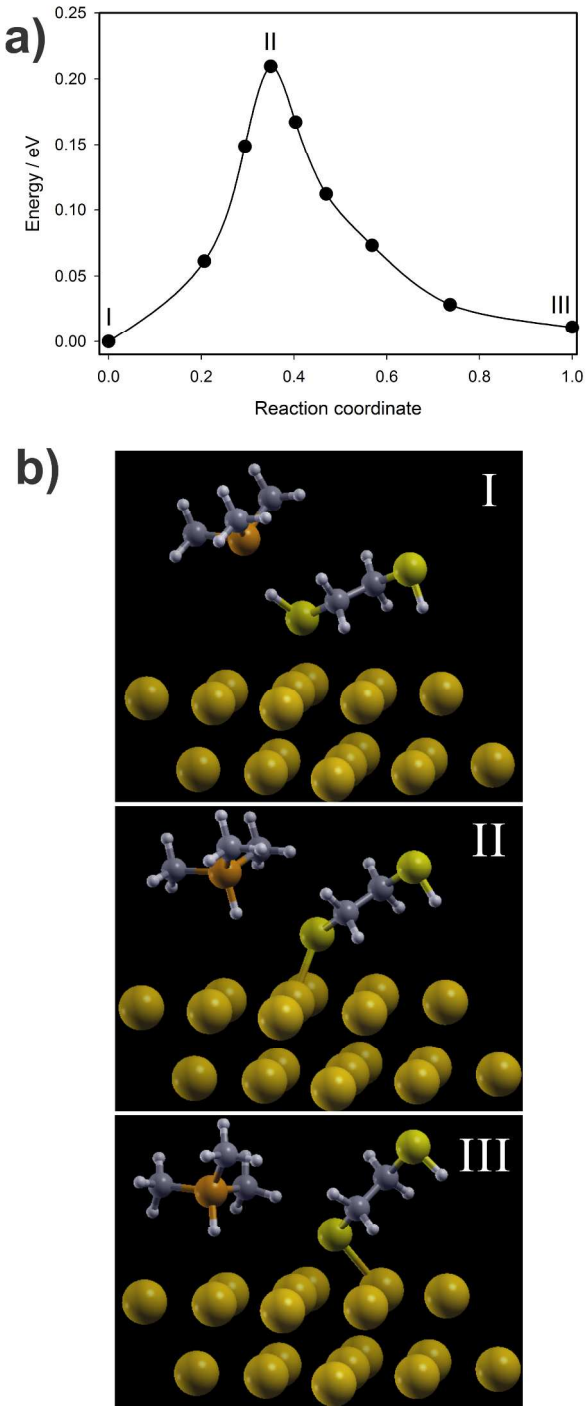

Figure 4. a) Energy profile for the H transfer from a −SH group of 1,2-ethanedithiol to the P atom of trimethylphosphine. b) Equilibrium structures of phosphine-dithiol complex (panel I), transition state (panel II) and phosphonium-thiolate complex (panel III) on Au(111).

The high stability of the LD phase in the presence of TCEP observed experimentally indicates that any mechanism involved in the LD → SU transition is inhibited by the phosphine. It has been proposed that this transition may originate from the proton transfer from the –SH group of a DT molecule approaching the surface to a DT molecule adsorbed flat on the surface. This produces both the lifting of one end of the adsorbed molecule and the adsorption of the free DT molecule through the deprotonated head-group, thus leading to two SU chemisorbed dithiol molecules. [3,12,13] We therefore addressed the energetics involved in the LD → SU transition considering three cases: the H-exchange mechanism (which we will denote with I), and two disulfide mediated mechanisms (II and III). In all cases we considered the reaction of a LD 1,2-ethyldithiolate with I) an adsorbed 1,2-ethyldithiol molecule, II) a monocoordinated SU dithiolate (with an S atom bonded to the Au surface and an –SH termination) and III) another LD 1,2-ethyldithiolate species.

Figures 5a shows the energy profiles for the three mechanisms and Figures 5b-d show the corresponding initial, transition state and final structures. Mechanism I corresponds to the following reaction:

$Au{-}SCH_2CH_2S{-}Au + HSCH_2CH_2SH_{ads} \rightarrow 2\ Au{-}SCH2CH2SH$ Mechanism I

where the bicoordinated dithiolate reacts with an adsorbed dithiol molecule to yield two standing up dithiolates. The energy profile in Figure 5a shows that this mechanism has an energy barrier of 0.68 eV. Thus, the H-exchange mechanism gives an energy barrier lower than that for the S−H bond breakage (0.8 eV)[43] during adsorption of alkanethiols on the surface. Therefore, the H-exchange seems to be a likely mechanism for the LD → SU transition of alkanedithiols. However, this mechanism cannot explain the substitution and lifting of LD dithiol molecules

mediated by dialkyl disulfide molecules[44] where there are no protons to transfer. In this case the only possibility is the formation of inter/intralayer S–S bonds.

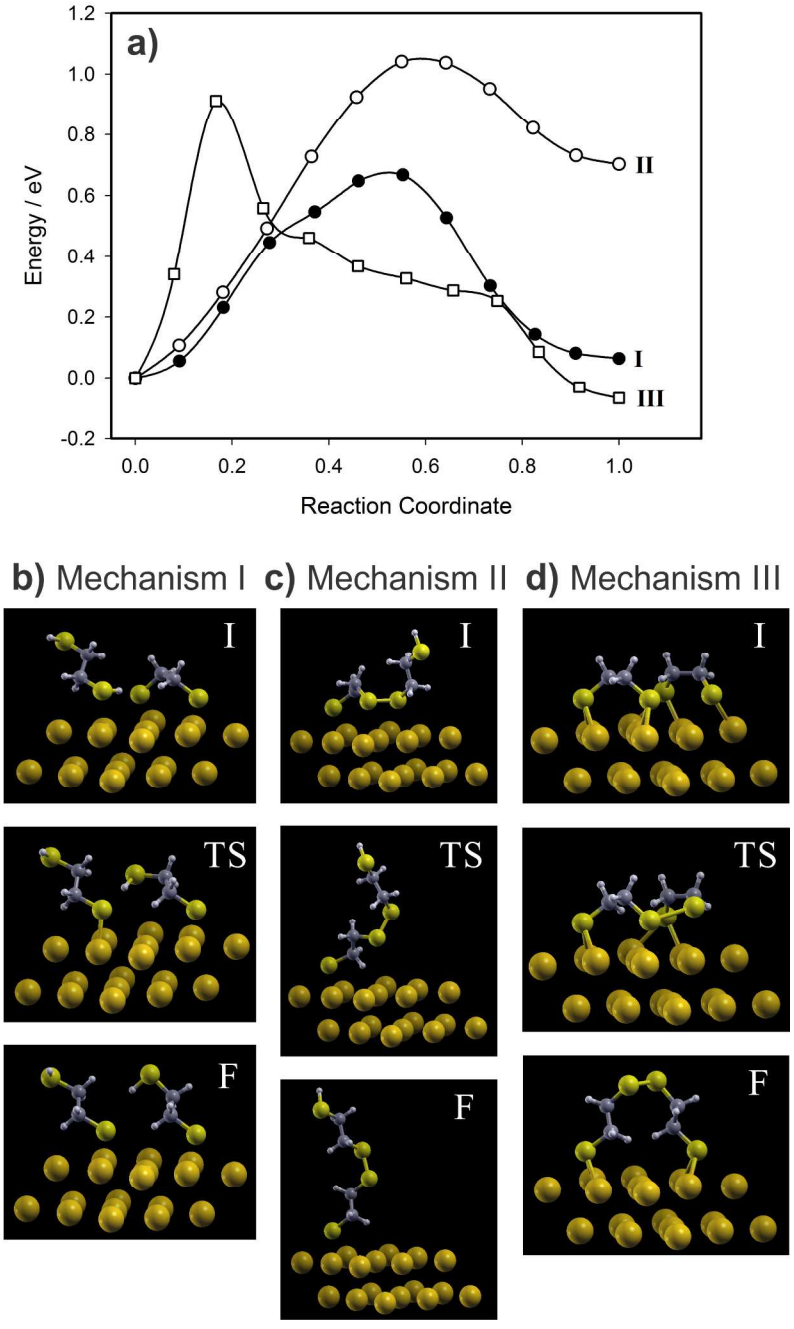

Figure 5. a) Energy profiles for 1,2-ethanedithiol lifting mechanisms (labeled I, II and III). Initial, transition state and final structures for b) H-exchange mechanism c) interlayer disulfide lifting mechanism and d) intralayer disulfide lifting mechanism.

We considered two mechanisms by which the formation of S–S bonds may be involved in the lifting of LD dithiol molecules. They lead to the formation of interlayer and intralayer disulfide bonds. In mechanism II, a surface disulfide bond is initially formed by the reaction of a SU monocoordinated dithiol with one end of a LD bicoordinated dithiol:

$Au{-}SCH_2CH_2S{-}Au + Au{-}SCH_2CH_2SH \rightarrow Au{-}SCH_2CH_2S{-}SCH_2CH_2SH$ Mechanism II

The initial state in Figure 5c shows the structure of the resulting surface disulfide thus formed. This reaction (not shown in Figure 5) has an energy barrier of 0.86 eV. In the next step, shown in Figure 5c, the disulfide moiety desorbs from the surface yielding an interlayer disulfide bond. This step has an energy barrier of 1.05 eV (Figure 5a) and involves the formation of a SU bilayer.

The third mechanism comprises the formation of a monolayer with intralayer S–S bonds.[5,6,25] It involves the reaction between two neighboring DT in a LD configuration to form a S–S bond according to:

$2\ Au{-}SCH_2CH_2S{-}Au \rightarrow Au{-}SCH_2CH_2S{-}SCH_2CH_2S{-}Au$ Mechanism III

As shown in Figure 5a, this process has an energy barrier of 0.91 eV.

The presence of intralayer S–S bonds is expected to introduce disorder in the monolayer structure and it may be responsible for the lack of structure at the nanoscale observed in STM.[5,45] The formation of surface disulfide bonds from the lifting of LD dithiols as shown in Figure 5d implies that the surface concentration of disulfide bonds should decrease with the increase of the chain length of disulfides, as saturation coverage falls progressively with the chain length. This is in agreement with our previous electrochemical measurements[5,25] which show that the surface concentration of S–S bonds effectively decreases as the alkyl chain length increases. Thus, the

mechanism represented in Figure 5d describes a situation in which intralayer S–S bonds can be formed both in vacuum and in solution phase without the need of disulfide precursors, such as O_2.

We can now address the role of TCEP in producing only lying-down structures. In the first place, mechanisms involving disulfide bonds in LD → SU transitions are inhibited as TCEP is an effective reducing agent of disulfides. In the second place, the H-exchange mechanism is not expected to be operative because the H transfer from terminal −SH groups to the P atom of phosphines has much lower energies than to the S atoms of adsorbed dithiolates. In the latter case, the energy barrier of 0.21 eV (Figure 4a) is much lower than the barrier of 0.68 eV for the H transfer between a free dithiol molecule and adsorbed thiolates (Figure 5a).

Most applications involving dithiols require a compact SU monolayer with terminal −SH groups exposed to the solution. In this context, the post treatment with TCEP assures the formation of a single monolayer as it reduces interlayer disulfide bonds. This was clearly shown for the case of the reactive C2DT which has a high tendency to form multilayers.

The alkyl chain of a dithiol may have $–NH_2$ or –OH functionalities[46] which for certain applications are required to interact with the medium. An example is the use of dithiothreitol, for which the exposure of the –OH groups in the lying-down configuration produces a biocompatible monolayer.[47] For this case, the formation of a monolayer with bicoordinated molecules may benefit from the use of TCEP during the formation of the monolayer.

Although the uncontrolled formation of lying down dithiol structures is to be avoided in most applications, the TCEP induced formation of compact bicoordinated molecules should be considered as a platform for the further development of complex nanostructures by inducing the LD to SU phase transitions using temperature or other perturbations.

It has been shown that a lying-down phase of butanedithiol (C4DT) may be removed by the immersion in a didodecyl disulfide solution in n-hexane.[44] Our calculations give some insights on the mechanisms which may be involved in the replacement of C4DT by a SU phase of dodecanethiolate (C12T), resulting from the breakage of the S–S bond of the dialkyldisulfide. In the case of dimethyldisulfide, the energy barrier for the breakage of the S–S bond on Au(111) is 0.6 eV on average[48,49] and similar values are expected for other disulfides. This implies that upon adsorption, the dialkyldisulfide may exist as an intermediate but it will finally dissociate at RT in laboratory time. The direct desorption C4DT into the n-hexane solvent is a very unlikely mechanism as it involves the breakage of two S-Au bonds of around 1.8 eV[48] whereas the energy gain due to the solvation of the molecule is small. We therefore envisage the following mechanism for the displacement of C4DT molecules by the dialkyldisulfide. First, the growth of SU domains of dodecanethiolate (originated by the dissociative adsorption of didodecyl disulfide) is expected to initiate in disordered regions between the LD domains of C4DT. Second, we think that the growth of these domains will induce the LD → SU transition of C4DT molecules, thus leaving free surface area for the formation of more S-Au bonds. The increase in the number of S-Au bonds per unit area[21] and the development of vdW interactions between the alkyl chains are the main driving forces for the growth of SAMs.

In this context, the LD → SU transition of C4DT molecules via the formation of a disulfide bond (mechanism III in Figure 5) helps to free up space and has no energetic cost as it is an exothermic reaction. If the disulfide formation reaction occurs again for the same pair of C4DT species, a cyclic dimeric disulfide is formed on the surface. The binding energy of disulfide molecules is very low (0.28 eV for dimethyldisulfide[48], for example) and therefore, an adsorbed disulfide species may readily dissolve in the n-hexane solvent. In the particular case of C4DT,

the cyclic monomeric disulfide is a very stable six-membered molecule.[50] The adsorption of dodecanethiolate molecules may also induce a transition from LD to U-looped C4DT molecules. This step is expected to have a small energy barrier as the C4DT molecules remain bicoordinated to the surface via both S-Au bonds. The next step would correspond to the breaking of the surface bonds and the formation of the cyclic six-membered disulfide which may then dissolve. For the latter reaction step we expect a similar energy barrier to that in mechanism III in Figure 5.

CONCLUSIONS

The addition of TCEP to the forming solution produces monolayers of α,ω-alkanedithiols which are coordinated to the Au surface via both S atoms in agreement with our previous high resolution photoelectron spectroscopy study.[21] The monolayers with bicoordinated dithiol molecules have reductive desorption potentials that are more positive than for monolayers with SU monocoordinated molecules. Therefore, the use of TCEP either during formation of the monolayer or as a post treatment procedure allows the precise control of the structure of alkanedithiols with high reproducibility, yielding bicoordinated or monocoordinated configurations, respectively.

DFT calculations were performed to elucidate the role of TCEP in the formation of bicoordinated dithiol structures. We investigated the mechanisms involved in the LD → SU transition of 1,2-ethanedithiol as well as the reactivity of tris(2-carboxyethyl) phosphine with 1,2-ethanedithiol in ethanol solvent and of trimethylphosphine with 1,2-ethanedithiol on the Au(111) surface.

The energy barriers for the mechanisms which may be involved in the LD to SU structural transition (H transfer between adjacent S atoms and formation of disulfide bonds) are in the

range of 0.7-1.0 eV indicating that in principle they may all be feasible, with the H transfer mechanism having the lowest barrier of 0.68 eV.

However, these mechanisms are inhibited in the presence of phosphines. The Brønsted base behavior of TCEP may deprotonate the terminal −SH groups of the dithiol with a ΔE value lower than 0.34 eV in ethanol solvent. When trimethylphosphine is coadsorbed with 1,2-ethanedithiol on Au(111), the deprotonation has an energy barrier of only 0.21 eV, indicating that this process is favored on the surface, thus leaving the molecule in a LD conformation with both thiolates bound to the gold surface.

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Author Contributions

The manuscript was written through contributions of all authors. All authors have given approval to the final version of the manuscript.

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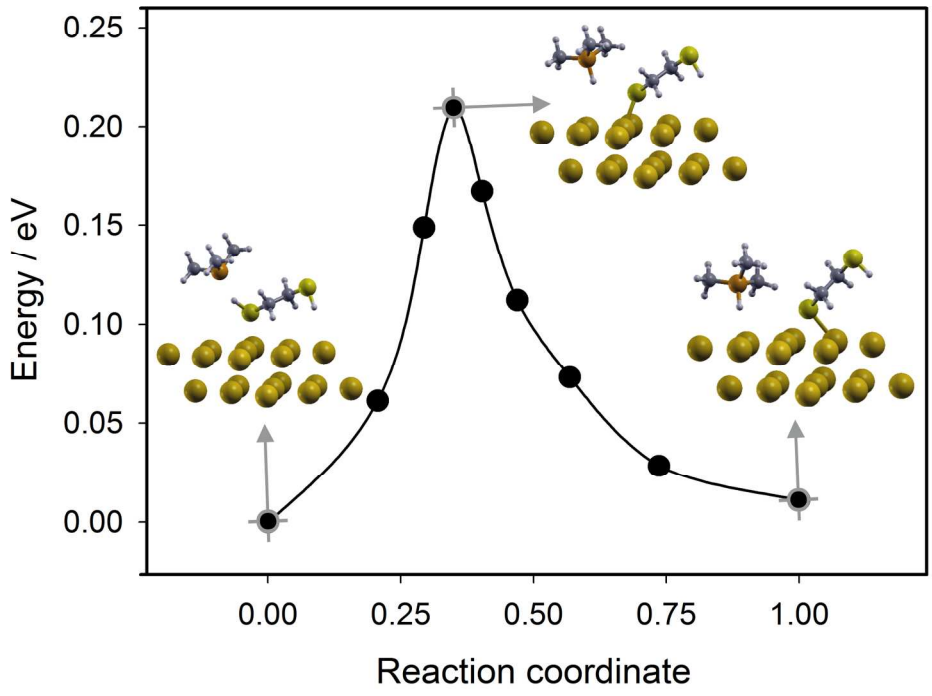
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