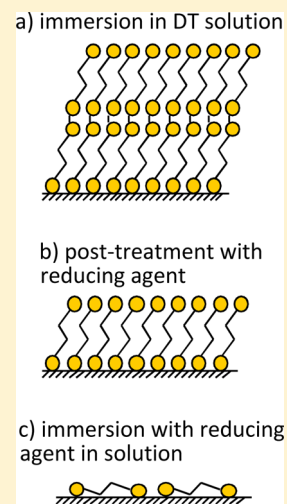


Adlayers of Alkanedithiols on Au(111): Effect of Disulfide Reducing Agent

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ABSTRACT: High-resolution photoemission spectroscopy is used to characterize adlayers of ethane-, hexane-, and nonanedithiol molecules grown on Au(111) surfaces by the immersion method. The effect of using a reducing agent during and after the immersion to inhibit or eliminate S–S bonds is investigated. Our results demonstrate that immersion 24 h in millimolar dithiol ethanolic solutions gives rise to the formation of multilayers; this effect is more pronounced in the case of ethanedithiol, the shortest molecule. A post-treatment with a disulfide reducing agent is effective to produce monolayers of standing-up molecules; this effect is again more pronounced in the case of ethanedithiol. Finally, the immersion 24 h in a solution containing dithiol and the reducing agent gives an unexpected result: most molecules remain adsorbed in the lying-down configuration; in this case, the almost complete suppression of the standing-up phase occurs equally with the three types of molecules, which suggests that the formation of S–S bonds must be important for the lifting of the molecules.



INTRODUCTION

Self-assembled monolayers (SAMs) of alkanethiol molecules grown on metallic surfaces have become popular in the past years because they can be used in a variety of applications. The special case of SAMs made of dithiol (DT) molecules (thiol groups in both ends) is particularly important for applications in nanotechnology and molecular electronics. In this type of SAMs, while one thiol group serves to bind the molecules to the surface the other can act as nucleation centers for the further growth of metal films or wires, or simply as connection to other functional units.^{1–5}

In principle, the SAMs of alkanedithiols are prepared in a similar way as the SAMs made of alkanethiols, but there are some extra difficulties that deserve special attention. One of them is the need to control the growth of multilayers through interlayer S–S bonds and the linkage between neighboring DT molecules through intralayer S–S bonds.^{6–10} The strategies to deal with this problem include optimization of the preparation procedure,^{8–11} use of protective groups at one end of the molecules,¹² and use of disulfide reducing agents either in the forming solution or in postdeposition treatments.^{11,13,14}

Another difficulty with DTs is that the self-assembly process has to overcome, in principle, a larger energy barrier than in the case of alkanethiols. For both types of SAMs, the growth is thought to proceed in two steps: first, a dilute phase of molecules adsorbed with the C chains parallel to the surface is

formed, and then this phase is replaced by a denser one with all the molecules adsorbed vertically on the surface. There is an important difference, however, in that the DT molecules in the initial phase are attached to the surface with chemical bonds at both ends. In fact, the S–Au bonds are so stable that one might arguably think that with DT molecules the transition to the upright configuration could never occur. Although this indeed occurs in some cases,^{7,9,10,15} there have also been numerous reports of successful preparation of DT SAMs with the molecules in the desired standing-up configuration.^{7–12,15–17} The mechanism that produces the lifting of the molecules remains mostly unknown. To the best of our knowledge, only one model has been proposed,⁹ involving the exchange of an H atom between an incident free dithiol and a chemisorbed lying-down dithiolate, which so far has not been tested either experimentally or theoretically.

In this paper, we report a study with high-resolution photoemission spectroscopy of ethanedithiol, hexanedithiol, and nonanedithiol adlayers grown on Au(111) by three different methods. It follows a previous work by Cometto et al.¹⁰ in which a wide variety of molecules and preparation conditions were surveyed using routine electrochemical

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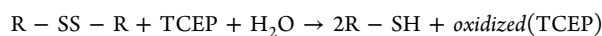
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techniques. Photoemission of the S2p core level is well-suited for this purpose because it provides clear fingerprints for the different settings at the surface.^{9,18–20} In particular, it is shown that standard overnight immersion in ethanolic solutions of the three molecules produce multilayers, and that a post-treatment with a disulfide reducing agent efficiently removes the surplus layers leaving only the first layer attached to the Au substrate. Interestingly, the best results are found with ethanedithiol, the shortest DT molecule. It is also shown that the immersion in a solution containing both DTs and the reducing agent results in the formation of a layer of lying-down molecules, a result of great significance, as it brings to the attention a new kind of mechanism for the lying-down to the standing-up transition of the adsorbed molecules.

EXPERIMENTAL DETAILS

Gold Substrates. Au films (Arrandee; 500-nm-thick) evaporated on heat resistive glass were employed as substrates. The films were immersed in a hot piranha solution (H₂SO₄:H₂O₂, 70:30) during 30 s and then washed copiously with Milli-Q water. Before the assembly process, substrates were annealed in a butane flame for two minutes and then cooled down to room temperature under constant N₂ flux.

Preparation of SAMs. 1,2-Ethanedithiol (abbreviated C2DT), 1,6-hexanedithiol (C6DT), 1,9-nonanedithiol (C9DT), and tris-carboxyethyl phosphine (TCEP) were purchased from Sigma-Aldrich. Chemicals were used as received without further purification. Pure ethanol (Baker) was used as solvent. DT adlayers were prepared by three different methods, which essentially differ in the use (or not) of the disulfide reducing agent (TCEP) after or during self-assembly. In the presence of the phosphine molecules, the S–S bonds are reduced according to the reaction:^{21,22}



The three preparation methods were as follows: (A) immersion of substrates in 0.2 mM ethanolic solutions of C_nDT (*n* = 2, 6, 9) for 24 h; (B) same method as (A) including a post treatment for 10 min in a concentrated solution of TCEP (20 mM in ethanol/water, 60:40); and (C) same as (A) but with a concentration of TCEP in the dipping solution equal to several times the concentration of C_nDT ([TCEP]/[C_nDT] = 20). After the adlayers were formed, the substrates were rinsed copiously with ethanol and Milli-Q water, blown dry with nitrogen, and quickly entered into the vacuum chamber for the photoemission experiments.

Photoelectron Spectroscopy. The photoemission experiments were carried out at the at the D08A-SGM beamline of the Brazilian Synchrotron Light Laboratory (Campinas, Brazil). The pressure in the analyzer chamber was in the low 10^{−9} Torr range. Electron energy spectra were collected with a 150 mm hemispherical analyzer with its axis placed at 90° from the light beam and in the plane of the light polarization. The samples were mounted with the surface normal lying in the horizontal plane between the photon beam and electron emission directions; most spectra were collected with the surface normal at 45° from each direction, although in two cases, we measured series of spectra varying the emission angle.

The sample cleanliness was checked with survey spectra acquired with 600 eV photons; only the characteristic peaks of Au, S, and C were observed, and in few cases a small O1s peak. The S2p core-level spectra were measured at a photon energy of 300 eV. Before and after each spectrum, we measured Au4f core-level spectra for count normalization and to calibrate the binding energies (BE) against that of the Au4f_{7/2} core level at 84.0 eV. From the Au4f peak widths, we estimate that the energy resolution was under 300 meV.

The S2p spectra were fitted with a linear background and three or four elemental 2p_{3/2}-2p_{1/2} doublets, each made of two Voigt functions separated by 1.18 eV and fixed intensity ratio 2:1. The intensities, positions, and Gaussian widths of these elemental components were varied during the fittings; the Lorentzian width was kept fixed at 0.15 eV.

RESULTS

Figures 1–3 present the S2p spectra acquired in substrates with adlayers of the three types of molecules prepared by the three

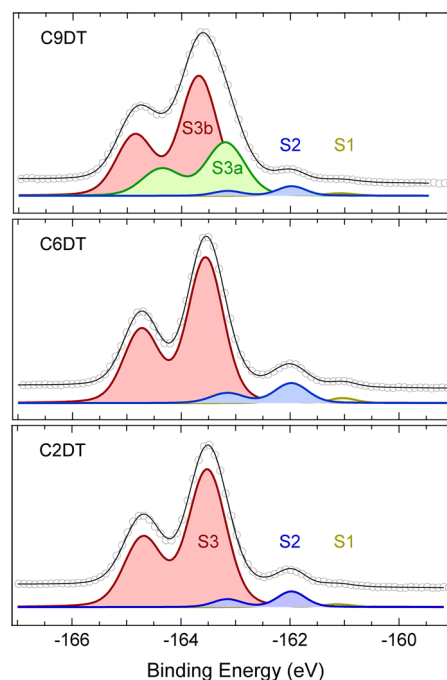


Figure 1. S2p spectra (open circles) of substrates prepared by method (A): immersion 24 h in ethanolic solutions of C2DT, C6DT, and C9DT molecules. The best fits (black lines) and the elemental components (color lines) are also shown; the latter are plotted with a vertical offset.

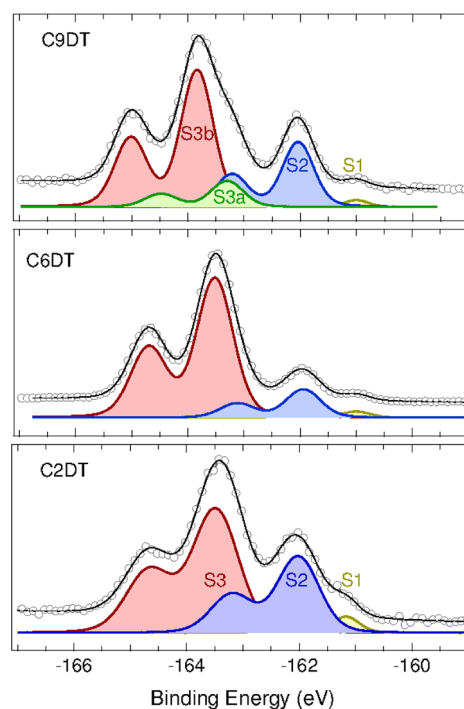


Figure 2. Same as Figure 1 for substrates prepared by method (B): immersion 24 h in ethanolic solutions of C2DT, C6DT, and C9DT molecules and then rinsed 10 min with TCEP.

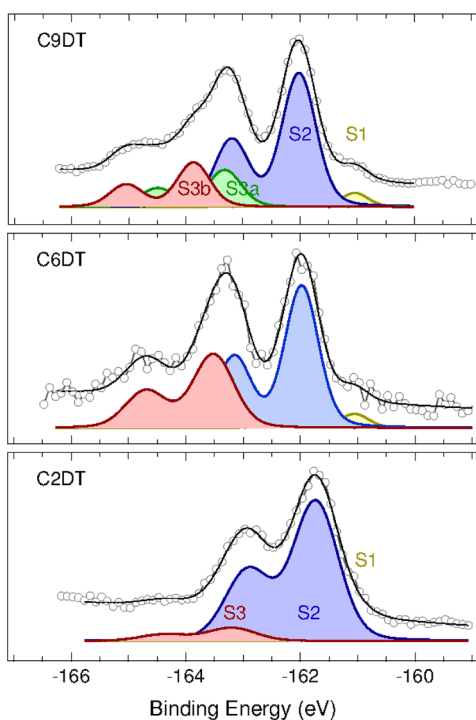


Figure 3. Same as Figure 1 for substrates prepared by method (C): immersion 24 h in ethanolic solutions of CnDT and TCEP.

methods: (A) immersion 24 h in the DT solution (Figure 1), (B) same as in (A) followed by rinsing with TCEP (Figure 2), and (C) immersion 24 h in a solution containing both DT and TCEP (Figure 3).

In general, the spectra contain two main S2p doublets with the $2p_{3/2}$ peaks located at around 162 and 163.5 eV. It can be seen in the figures that the spectra of samples prepared under the same conditions have similar features, whereas those of samples prepared under different conditions are well-differentiated. This sensitivity to the preparation conditions illustrates the power of photoemission to detect the different scenarios on the surface. The component at 162 eV is generally assigned to the S atoms in the thiol–Au interface, and that at 163.5 eV to the S atoms in either free terminal–SH groups or in S–S bonds formed between neighboring DT chains or in the links between layers.^{9,18–20}

Besides these two main components, in some spectra one can also notice a small peak at around 161 eV, which denotes a small contamination with chemisorbed S atoms.^{23–26} We also checked in all cases the region around 168 eV for the occurrence of peaks denoting the existence of oxidized S species; this search gave either negative results or detection of low-intensity signals; in these last cases, we also observed small O1s peaks in the survey spectra. In addition to low levels of contamination, the films were also well-ordered as judged by the full-width at half-maximum (fwhm) of the thiolate component at 162 eV. The fits described below yield fwhm's in the range 0.55–0.70 eV for the films prepared by methods (A) and (B), and somewhat larger for the films prepared by method (C), which are comparable with the best values reported in the literature.^{9,18–20}

During the fittings of the spectra, a difference was found between the samples prepared with C2DT and C6DT molecules and those prepared with C9DT molecules. While in the first case all the spectra could be fitted satisfactorily with

three elemental components (labeled S1, S2, and S3 in the bottom and center panels of Figures 1–3), in the case of C9DT, a fitting with only three components in general did not yield satisfactory results. This is illustrated in the top panel of Figure 4, where it is seen that the fit with three components

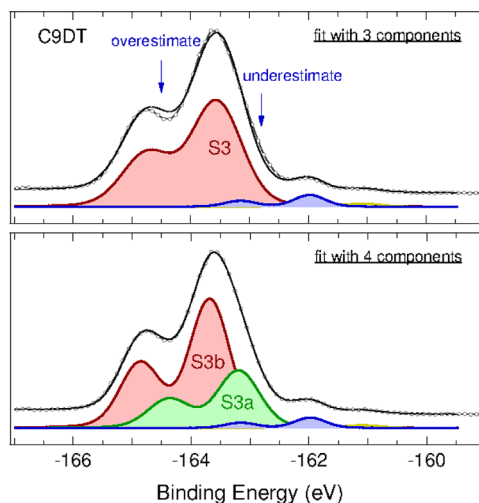


Figure 4. S2p spectrum shown in the top panel of Figure 1 fitted with 3 and 4 components.

fails to reproduce the region around the main peak. In particular, it underestimates the data in the region between 162.5 and 163 eV and overestimates the data in the region between 164 and 165 eV. This is a common situation encountered in most spectra of C9DT molecules. Clearly, the agreement cannot be improved by changing the width of the component S3, because any improvement in one side inevitably worsens the agreement in the other. To fit correctly the spectrum, one needs to use two elemental doublets in this region (labeled S3a and S3b), as it is shown in the bottom panel.

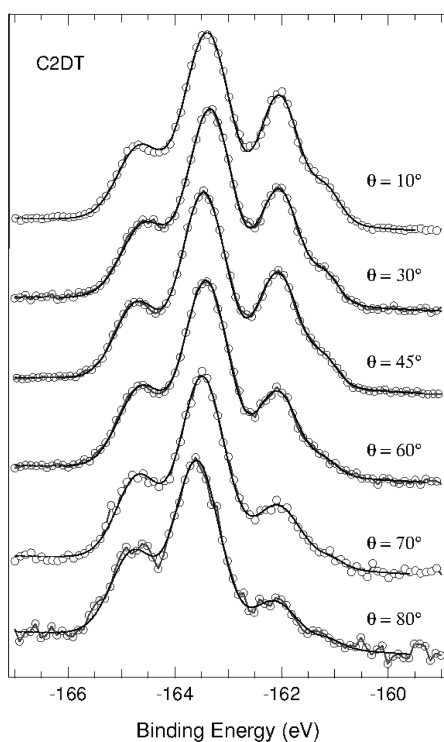
Therefore, we have fitted all the spectra of the samples prepared with C2DT and C6DT molecules with three elemental components and those of the samples prepared with C9DT molecules with four components. The positions of the elemental components obtained during the fittings of the spectra presented in the figures 1–3 are listed in Table 1. In the case of the C9DT molecules the fittings yield consistently a separation of about 0.5 eV between S3a and S3b, with the component S3a located at 1.2–1.3 eV from the component S2. The assignment of these two subcomponents is given in the next section.

Turning to the dependence of the photoemission spectra on the preparation conditions, the S2p spectra of the substrates prepared by immersion in the DT solutions, presented in Figure 1, are all dominated by the component S3 (or S3a and S3b in C9DT). The relative intensities of the component S2 are 0.09 for C2DT, 0.13 for C6DT, and 0.04 for C9DT, and it will be shown below that these low values correspond to the existence of multilayers. The effect of the post-treatment with TCEP is clearly seen in the spectra of Figure 2; it produces in all cases a noticeable increase of the component S2, assigned to the S atoms at the thiol–Au interface; the relative intensities of S2 are now 0.54 (C2DT), 0.20 (C6DT), and 0.39 (C9DT). This rise of the component at 162 eV is consistent with the assumption that the rinsing with TCEP has broken the S–S

Table 1. Positions of the Components Used in the Fittings of the S2p Spectra Shown in Figures 1–3 (all the BEs are in eV)

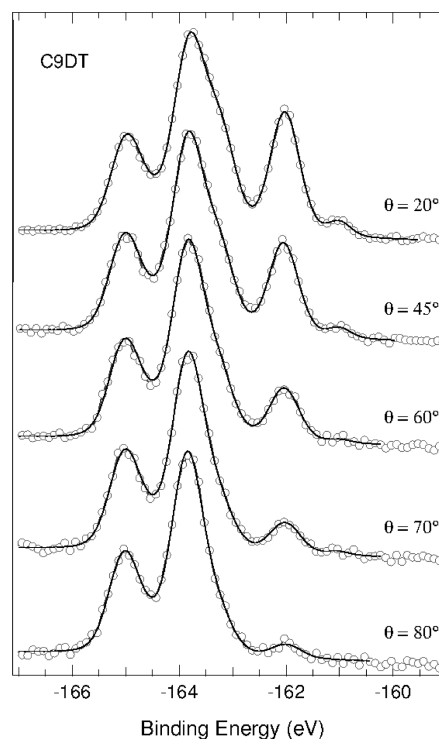
method	C2DT			C6DT			C9DT			
	S3	S2	S1	S3	S2	S1	S3b	S3a	S2	S1
A	-163.5	-162.0	-161.1	-163.5	-162.0	-161.0	-163.7	-163.2	-162.0	-161.1
B	-163.5	-162.0	-161.2	-163.5	-161.9	-161.0	-163.8	-163.3	-162.0	-161.0
C	-163.2	-161.7	-160.8	-163.5	-162.0	-161.1	-163.9	-163.3	-162.0	-161.0

links between layers, leaving only the first layer attached to the Au substrate. To confirm this further we measured two series of spectra varying the emission angle with respect to the surface normal. These are shown in Figures 5 and 6 for C2DT and C9DT, respectively.

**Figure 5.** S2p spectra of the C2DT adlayer prepared by method (B) acquired at different angles of emission with respect to the surface normal.

In both cases there is a clear decrease of the component at 162 eV when the angle increases and the emission becomes more grazing. This is the expected behavior because as the angle increases the photoelectrons emitted from the bottom travel a longer path inside the layer and are consequently more attenuated. In the next section we will show that the analysis of these angular variations is consistent with the existence of a single layer in both cases.

Finally, the spectra of Figure 3, corresponding to substrates immersed in a solution containing both DT and TCEP, show a rather unexpected result: the spectra are now dominated by the component at 162 eV, indicating a predominance of molecules adsorbed flat on the surface. This is a result with important consequences, because it implies that the presence of the disulfide reducing agent in the solution interferes with the mechanism that lifts the molecules. This point is analyzed further below.

**Figure 6.** S2p spectra of the C9DT adlayer prepared by method (B) acquired at different angles of emission with respect to the surface normal.

DISCUSSION

We have shown in the previous section that the S2p spectra of the samples prepared with the three methods exhibit important qualitative differences. In particular, the relative intensities of the two main components, namely, those at 162 eV and at around 163.5 eV, are found to vary considerably with each preparation method. Before analyzing these changes in more detail, we will address the point of the origin of the subcomponents S3a and S3b in the samples prepared with C9DT molecules. The simplest assumption is to ascribe them to S atoms in S–S and S–H bonds; on this supposition, the component at lowest BE would be assigned to the S emitters with the most electropositive neighbor, and thus S3a would correspond to S–H bonds and S3b to S–S bonds. This assignment is supported by the positions of the high-BE components reported by other authors in similar compounds. In effect, while the average position of S3a compares well with the positions reported for the high-BE component in self-assembled monolayers of benzene-dimethanethiol (163.1 eV¹⁹ and 163.3 eV²⁰) and of biphenyl- and terphenyl-dimethanethiol (163.3 eV¹⁸), where the formation of intralayer S–S bonds is unlikely, the position of S3b is higher but close to the position reported for S–S bonds in a bulk sample of dhexadecane disulfide, 163.5 eV.²⁷ Additionally, since this last BE coincides with the average position of the only high-BE component found

in our C2DT and C6DT SAMs, we also assign the component S3 in these samples to S–S bonds. The 0.3 eV difference between the positions of S3b and S3 can be attributed to differences in the screening of the photohole with metal electrons due to the different distances of the emitter to the Au substrate.²⁸

According to the above assignments, the S2p spectra show a majority of S–S moieties in all the SAMs analyzed, even after the post-treatment with TCEP. In the case of the samples prepared by method (A), both inter- and intralayer bonds are expected, but in the case of the samples prepared by method (B), we believe that the S–S bonds are mostly intralayer bonds produced by the air exposure during the transport of the samples to the analyzer chamber. It is interesting to note that only the C9DT SAMs have preserved some –SH terminations, which suggests that these SAMs would be more robust toward the formation of intralayer disulfide bonds. This difference, noted also in other studies,^{9,10} is presumably associated with the fact that the formation of disulfide bonds requires a 180° rotation of one molecule, which has a cost in van der Waals interaction that increases with the chain length.⁶

Turning to the relative intensities of the two main components, we will analyze in the first place the adlayers prepared by method (B), which are expected to be composed of a single layer of standing-up molecules. Figure 7 presents

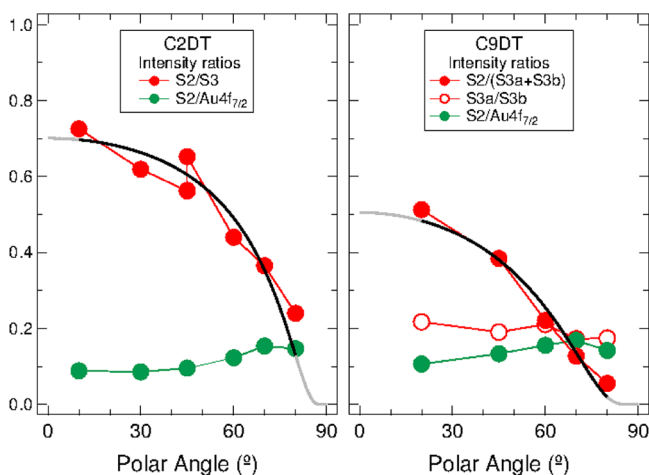


Figure 7. Intensity ratios corresponding to the spectra shown in Figures 5 and 6. The black lines are the best fits to the S2/S3 and S2/(S3a+S3b) intensity ratios.

some intensity ratios between the components in the spectra of Figures 5 and 6, plotted against the polar emission angle. Already, a qualitative analysis of these curves allows us to draw some important conclusions. First, it is seen with both molecules that the intensity ratio between the component S2 and the Au4f_{7/2} peak (green circles) is practically constant; this means that the two signals have similar angular variations, and hence the emitters are approximately at the same depth; therefore, these behaviors confirm the above assignment of the component S2 to the S atoms located at the interface with the substrate. Similarly, the observation that in both cases the intensity ratio between S2 and S3 or the sum of S3a and S3b (red circles) decreases with the emission angle, being lower for C9DT than for C2DT, confirms the assignment of the high-BE components (S3 and S3a–S3b) to the S atoms located higher up in the layer (the top S-layer if there is only one layer).

Additionally, the fact that these two intensity ratios go to zero when the angle approaches 90° (grazing emission) has an important significance: it means that all the molecules are in the upright configuration, because if there were molecules lying-down on the surface, the intensity of the component S2 would never vanish completely. It is also seen in the right panel that the intensity ratio between the subcomponents S3a and S3b (open red circles) is approximately the same at all angles, which again indicates that they are produced by emitters located at similar heights above the surface. Finally, we note that the ratios between S2 and the Au4f_{7/2} peak are similar for both molecules, meaning that the surface coverages (defined as the number of S atoms at the interface per Au surface atom) are similar in both cases.

A quantitative analysis of the intensity ratios between the component S2 and the components S3 or S3a–S3b can be performed in the following way. If one assumes that there is a single layer and that the emission from the top S-layer is not attenuated whereas that from the bottom S-layer is attenuated exponentially, the intensity ratio can be modeled with $\exp(-t/\lambda \cos \theta)$, where t is the height difference between the two S emitters, λ the attenuation length of the photoelectrons traveling inside the layer, and θ the polar emission angle. The best fit to the data points of C2DT yields $t/\lambda = 0.36$. Then, considering a distance between the S atoms equal to 4.4 Å²⁹ and the axis of the molecules tilted about 30° from the surface normal (typical for alkanethiols), we get $\lambda = 10.6$ Å, which compares well with the published values (7 Å³⁰ and 17 Å³¹). The same fit to the data points of C9DT yields a ratio $t/\lambda = 0.68$, which despite being larger than that obtained for C2DT is lower than expected considering the lengths of C2DT and C9DT molecules. In this case, using the value of λ determined above and considering a distance between the S atoms in C9DT equal to 12.8 Å²⁹ we derive a tilt angle of 55°, meaning that the C9DT molecules are not fully upright. This large tilt angle is a direct consequence of the high relative intensity of the thiolate component (S2), which for a layer of fully upright molecules should be much smaller. We remind that the high intensity of this component cannot be ascribed to the existence of lying-down molecules, because in that case the intensity would not vanish at large angles. With regards to the adlayers of C6DT molecules, it was already mentioned above that the post-treatment with TCEP did produce an increase of the thiolate component (S2), thereby confirming the removal of overlayers. Nevertheless, the intensity ratio between S2 and S3 in the spectrum of Figure 2 yields a thickness t exceeding the length of a C6DT molecule (9.1 Å²⁹), and so one must conclude that in this case the post-treatment with TCEP did not completely remove all the surplus layers.

The knowledge of the attenuation by a single layer allows the calculation of the attenuation by several layers. For N layers, one must take into account that the high-BE component will contain not only the emission from the top S-layer, but also the emissions from the $N - 1$ S-bilayers underneath, in this case, the intensity ratio of the two S2p components, can be written as

$$\frac{I_{S2}}{I_{S3}} = \frac{\exp(-Nt/\lambda \cos \theta)}{1 + 2 \exp(-t/\lambda \cos \theta) + \dots + 2 \exp(-(N-1)t/\lambda \cos \theta)}$$

where t is the thickness of a single layer. Using this expression and assuming an average tilt angle of 30° for the molecules in the multilayers, the ratios in the spectra of Figure 1 indicate the existence of 2–3 layers in the case of C2DT and between 1 and 2 layers in the cases of C6DT and C9DT, in good agreement with the results obtained in similar systems with electrochemical techniques.¹⁰

Therefore, the analysis of the relative intensities of the components shows that immersion for 24 h in ethanolic solutions followed by rinsing with TCEP is an effective method to prepare monolayers of standing-up DT molecules. The first step produces multilayers and the second step shaves all the layers except the one attached to the surface; the better results obtained with C2DT are probably due to a better access of the TCEP molecules to the sites of the disulfide bonds. This case of C2DT molecules is particularly interesting because all the attempts performed so far to prepare SAMs of such short molecules had been unsuccessful. Short DT molecules are attractive because of their higher electrical conductivity, but on the other hand, the molecular interactions are weaker than with long molecules. Our result demonstrates that the weaker molecule–molecule interactions are not an impediment for the formation of the SAM with standing-up molecules.

Another result of importance is the finding that the inclusion of TCEP molecules in the forming solution inhibits the lying-down \rightarrow standing-up transition of the DT molecules. As mentioned above, for DTs the lying-down configuration is particularly stable, because the molecules are attached to the surface with chemical bonds at both ends, and thus the passage to the standing-up configuration requires the rupture of one of these strong bonds. So far, the only model proposed to explain this transition involves the exchange of an H atom between the head-groups of an incoming DT molecule and that of a thiolate adsorbed lying-down on the surface.⁹ In principle, no important step of this mechanism would be hindered by the TCEP molecules, although one cannot totally rule out the occurrence of subtle changes at the surface that could slow or inhibit the reaction. Our result, however, can be linked with the observation in a recent experiment that a layer of lying-down C4DT molecules is chemically removed by didodecyl disulfide molecules, $\text{CH}_3(\text{CH}_2)_{11}\text{S}-\text{S}(\text{CH}_2)_{11}\text{CH}_3$, which do not contain any SH headgroup.³² This observation evidences that the rupture of the S–Au bonds can also occur via reactions other than that of H-exchange. In this respect, our results with the adlayers prepared by method (C) suggest that the formation of S–S bonds, which are kept to a minimum by the disulfide reducing agent, may also play an important role in the lifting of the molecules. Density-functional calculations indeed show that different lifting mechanisms involving the formation of S–S bonds have energy barriers comparable with that of the H-exchange mechanism.³³ We hope that these new results will motivate further work to elucidate the process by which the DT molecules lift, a crucial step in the SAM formation that has hitherto received little attention.

CONCLUSIONS

We have used high-resolution photoemission spectroscopy to characterize adlayers of C2DT, C6DT, and C9DT molecules on Au(111) prepared by three different methods. It has been shown that the standard immersion 24 h in a DT ethanolic solution leads to the formation of multilayers of standing-up molecules, and that a postdeposition treatment with a disulfide reducing agent leaves a single layer of standing-up molecules. In

this last case, however, the air exposure during the transport to the analyzer chamber produced a majority of S–S terminations. We have also found that the inclusion of the reducing agent in the dipping solution yields a single layer of lying-down molecules. The important implication of this last case for the elucidation of the mechanism that produces the lifting of the DT molecules has been stressed.

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Notes

The authors declare no competing financial interest.

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