



# Disorder, solvent effects and substitutional self-assembly of alkane dithiols from alkane thiol SAMs

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## ARTICLE INFO

### Article history:

Received 8 April 2010

Accepted 2 October 2010

Available online 8 October 2010

### Keywords:

Self-assembled monolayer

Alkane dithiol

Substitution

Nonanedithiol

Au(111)

RAIRS

Cyclic voltammetry

## ABSTRACT

Substitutional self-assembly of nonanedithiol from a hexanedithiol self-assembled monolayer and the effects of use of ethanol and *n*-hexane as solvents were investigated. It was found that presence of original solvents in the HT SAM allowed easy replacement, while dried SAMs were more resilient to substitution and much longer times are necessary for substitution to occur. In general substitution in ethanol leads to production of a disordered dithiol SAM, with existence of extra molecules bonded to the SAM. Well ordered substituted SAMs were obtained with degassed *n*-hexane solutions and in absence of ambient light.

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## 1. Introduction

In recent years SAMs of alkanedithiols [1–8] have attracted much attention because of interest in using such molecules with two thiol groups to attach to different metallic entities, such as two nanoparticles or bind nanoparticles onto dithiol SAMs on metal substrates for molecular electronic measurements, or else for creation of complex heterostructures, etc. While formation of ordered alkanethiol SAMs [9–24] is an established fact, the formation of ordered dithiol SAMs has been a highly controversial subject. Recent work, in particular by our group [25], shows that actually quite well ordered SAMs of standing-up molecules can be produced for e.g. nonanedithiol molecules, although it was also noted that some small amount of lying-down phase persisted. It was in fact found that the fraction of lying-down phase increased with decreasing chain length indicating that increasing van der Waals forces helped in attaining the standing-up phase.

Dithiol SAMs have been used as substrates to evaporate metals leading to cluster formation [26–30]. In some works, substitutional self-assembly of dithiol SAMs from alkanethiol SAMs [29,31,32] has been used to produce mixed SAMs with some dithiol “islands”. This allows to grow metal nanoparticles with variable surface densities. Another interesting aspect of use of substitutional self-assembly

could be the reduction of formation of mixed phases of lying-down and standing-up dithiol molecules. Recently use of cyclohexanedithiol SAMs has been proposed for the fabrication of nanostructures on a surface [33]. Thus substitutional self-assembly presents some appealing aspects, but has not been explored in detail for the case of dithiols.

In substitutional assembly one can ask oneself to what extent initial order in the parent SAM would affect the substitution process. Early work on substitutional assembly of alkanethiols [34–38] has discussed several aspects including chain lengths, solvent effects and kinetics. It was noted that there existed an initial fast and subsequently slow kinetics of substitution and this was discussed in terms of existence of defects and differences in substitution rates at domain boundaries and within more compact domains. A partial substitution of a dodecanethiol SAM by a biphenylthiol or by a ferrocenyl-substituted biphenylthiol has also been promoted by electron irradiation, which creates defects [39].

Our recent work has shown, that production of well ordered dithiol SAM layers depended strongly on preparation procedures and the nature of the solvent employed [25,40]. It was in particular noted that assembly in ethanol led to disordered SAMs which could have extra molecules attached at the free SAM air interface bonded to the SAM through disulfide bonds. In the ethanol case, this disulfide bond formation was tentatively assigned to photooxidation processes due to the presence of some residual oxygen (or water) in a solvent with a greater solubility for oxygen (and hygroscopic). Therefore, we decided to prepare SAMs in degassed *n*-hexane in the dark because of the lower solubility of oxygen (and water) in this solvent to avoid

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photooxidation. The SAMs grown in these conditions were found to be well-ordered. As an extension of this work and given the interest in substituted dithiol SAMs, we have studied here some aspects of substitutional self-assembly of nonanedithiol (NDT) SAMs from hexanethiol (HT) SAMs, under conditions similar to the ones employed recently in experiments involving nanoparticle growth [29]. We examine solvent effects and have used both ethanol and *n*-hexane solutions. We show that disorder in the SAMs, in particular attributable to presence of solvents, favours substitutional assembly and the quality of the final substituted SAM is strongly solvent dependent.

## 2. Experimental

### 2.1. Chemicals

1,9-nonanedithiol (NDT) 97% and 1-hexanethiol (HT) 95% was purchased from Alfa Aesar and Sigma and *n*-hexane 99% from Riedel-de Haën. All chemicals were used without further purification.

### 2.2. SAMs preparation

A crucial point in SAM preparation is related to substrate quality. SAMs were prepared on gold covered (200 nm) mica substrates purchased from Phasis. The gold area is a 6 mm wide strip on a 10 mm mica disc. The substrates were annealed in a furnace to 600 °C. The quality of these substrates has been checked elsewhere [41] by AFM and ellipsometry, showing appearance of large (111) terraces and the dielectric constant derived from spectroscopic ellipsometry gave results in excellent agreement with literature [42].

The substitutional assembly was carried out as follows. Hexanethiol SAMs were prepared by immersing the gold support into a freshly prepared 1 mM solution of HT in ethanol or *n*-hexane for 60 min at room temperature. Final rinsing was done with absolute ethanol (or *n*-hexane) and then either dried under N<sub>2</sub> (or pump dried) or else directly transferred into the dithiol solution (1 mM solution in *n*-hexane or ethanol) for variable times.

### 2.3. Electrochemical measurements

A home made three-electrode electrochemical cell was employed with a homemade operational amplifier potentiostat, driven by a computer controlled National Instruments NI6229-USB data acquisition system employing 16 bit digital to analog and analog to digital converters. We used either a Saturated Calomel Electrode (SCE) or a K<sub>2</sub>SO<sub>4</sub> saturated mercury/mercurous sulfate electrode (MSE) and a platinum wire as reference and counter electrode, respectively. All potentials in the text are referred to the SCE electrode. The base electrolyte, 0.1 M NaOH aqueous solution, was prepared with pure water and solid analytical grade NaOH. The electrolyte was degassed with nitrogen prior to the experiments. Reductive electrodesorption of thiols from the Au substrates was performed at typically 0.05 V s<sup>-1</sup> at room temperature (actual scan voltage step was of 10 mV). For electrochemical measurements a small portion (circa 2 mm of the 10 mm strip) of the gold on mica sample is immersed into the solution. The actual area in the electrodesorption measurements is referred to the Au peak.

### 2.4. Infrared spectroscopy

For RAIRS (reflection absorption infrared spectroscopy) measurements we use a Bruker Vertex 70 FT-IR spectrometer, equipped with a homemade grazing incidence reflection attachment with an incident angle of 80° to the surface normal. A deuterated triglycine sulfate (DTGS) detector was used to detect the reflected light. The spectral resolution was set to 4 cm<sup>-1</sup>. The spectrometer and sample com-

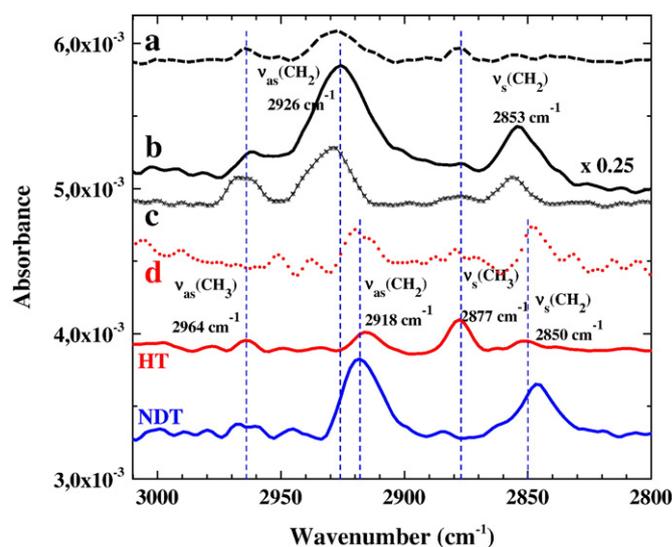
partment are first flushed with dry air and then, during measurements, by a N<sub>2</sub> flow. Prior to measurements on the SAM covered sample, reference measurements were made on the cleaned and annealed sample. PM-IRRAS has not been performed and IR light is not polarized so accurate quantitative conclusions about the orientation of the molecules based on measured peak intensities cannot be made. Only the evolution of the orientation of the molecules can be qualitatively deduced from the evolution of the relative intensities of some peaks.

## 3. Results

### 3.1. RAIRS measurements

RAIRS measurements on both HT and NDT SAMs prepared respectively in ethanol and *n*-hexane, performed by us previously, serve as a basic reference for this work. We recall for further reference (see e.g. [10,11,22,24]) that in general in well ordered alkanethiol SAMs one observes well defined quite narrow peaks at 2917 cm<sup>-1</sup> corresponding to  $\nu_{as}(\text{CH}_2)$  and 2850 cm<sup>-1</sup> for  $\nu_s(\text{CH}_2)$ . Furthermore one observes structures at 2964 cm<sup>-1</sup> due to  $\nu_{as}(\text{CH}_3)$  vibration and at 2877 cm<sup>-1</sup> due to  $\nu_s(\text{CH}_3)$ . The relative intensities of the latter two peaks changes for even-odd chain length molecules, because of final group orientation change (see e.g. [22]). More precisely, for an alkanethiol with an even number of carbon (like HT) in a standing-up configuration, the CH<sub>3</sub> symmetric stretch at 2877 cm<sup>-1</sup> dominates the CH<sub>3</sub> antisymmetric stretch at 2964 cm<sup>-1</sup>. This effect is due to the orientation of the IR dipole moments. In the gas phase the CH<sub>2</sub> related structures appear at 2926 cm<sup>-1</sup> corresponding to  $\nu_{as}(\text{CH}_2)$  and 2854 cm<sup>-1</sup> for  $\nu_s(\text{CH}_2)$  and this is also the case for disordered SAMs, where a shift from the 2917 cm<sup>-1</sup> and 2850 cm<sup>-1</sup> positions towards the gas phase positions occurs. In some cases one observes intermediate shifts and broadening of these structures related to appearance of more or less well ordered domains. This is also the case for dithiol SAMs [40].

Examples of typical RAIRS spectra for these molecules are shown in Fig. 1 (respectively red and blue bottom lines). The most notable



**Fig. 1.** RAIRS spectra of NDT substituted HT SAM and spectra of pure HT SAM on gold (red line) and pure NDT SAM (blue line) shown as reference. Substituted SAMs: (a) HT SAM is first dried and then immersed into the NDT solution for 4 h (black dashed line—procedure a), (b) HT SAM is directly transferred into the NDT ethanol solution for 4 h (black line—procedure b), (c) HT SAM is first dried and then immersed into the NDT solution for 15 h (black cross line—procedure c) and (d) HT SAM is directly transferred from the HT *n*-hexane solution into the NDT *n*-hexane solution for 4 h (red dotted curve—procedure d).

difference between the spectra is the absence of the  $2877\text{ cm}^{-1}$  peak, related to  $\nu_s(\text{CH}_3)$  vibration, for the NDT SAM and also in this case the other features are more intense. In case of NDT preparation in degassed *n*-hexane and with all preparation performed in darkness we usually obtain a quite well ordered SAM, as evidenced by the position of the peak corresponding to  $\nu_{\text{as}}(\text{CH}_2)$  at about  $2918\text{ cm}^{-1}$ , whereas in ethanol a disordered SAM is obtained with  $\nu_{\text{as}}(\text{CH}_2)$  at about  $2926\text{ cm}^{-1}$  (not shown). Note that as opposed to the HT SAM the  $\nu_{\text{as}}(\text{CH}_2)$  is prominent in the RAIRS spectrum of NDT.

Substitutional assembly was tested using different protocols as described below for both ethanol and *n*-hexane solvents.

- (a) An HT SAM was prepared in ethanol, dried and a RAIRS spectrum was acquired. The SAM sample was then (circa 2 h later) placed into a NDT ethanol solution for 4 h and then a RAIRS measurement was again performed. In this case we see some traces of substitution (line a). Some remaining HT SAM is observed as evidenced by the residual peak at  $2964\text{ cm}^{-1}$ , attributed to  $\nu_{\text{as}}(\text{CH}_3)$  vibration, and the peak at  $2917\text{ cm}^{-1}$  is now larger and appears at  $2927\text{ cm}^{-1}$ . It can be also noticed that, after this at least partial substitution, the intensities of the  $\nu_s(\text{CH}_3)$  peak at  $2877\text{ cm}^{-1}$  and of the  $\nu_{\text{as}}(\text{CH}_3)$  peak at  $2964\text{ cm}^{-1}$  are more or less the same. This may indicate a change in the orientation of the  $\text{CH}_3$  IR dipole moments and is consistent with a reorientation from the initial standing-up configuration of the remaining HT SAM.
- (b) Next an HT SAM sample was prepared and after rinsing was directly transferred into the NDT ethanol solution and kept for 4 h. It was then rinsed, dried and the resulting RAIRS spectrum taken. This is shown in Fig. 1 (line b). As may be seen in this case a very intense  $\nu_{\text{as}}(\text{CH}_2)$  peak is observed. We still see a small shoulder at  $2962\text{ cm}^{-1}$ , corresponding to some remaining HT SAM. We can see that in this case substitution of HT by NDT has very clearly occurred. It may be noted that the positions of the  $\nu_{\text{as}}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  peaks in the spectrum are respectively  $2926\text{ cm}^{-1}$  and  $2853\text{ cm}^{-1}$ , compatible with a disordered layer. A notable feature is that in this case the signal is *very intense* (note that the spectrum intensity is shown divided by 4). In our earlier study [25] we have noted that direct dithiol assembly from ethanolic solutions leads to excess dithiol presence on the SAM—linked to the terminal S by disulphide bonds. This also appears to be the case here. For this remaining HT SAM, the intensity of the  $\nu_s(\text{CH}_3)$  peak at  $2877\text{ cm}^{-1}$  is very low. This must be due to the low concentration of this component and one can also not rule out disorganisation which could lead to a change in orientation and lowering of intensity of this peak. Comparison of cases a and b shows that the dried SAM layer appears more compact and less amenable to substitution within a four-hour time span in ethanol.
- (c) We then investigated the effect of pump drying and more prolonged immersion for 15 h. In this case more intense peaks are observed (line c), than in case of four-hour immersion (case a), though still somewhat less intense than in case (b). The substitution however still appears incomplete, with persistence of the peak at  $2964\text{ cm}^{-1}$ . Again this lowered intensity may be explained by the low concentration of this component and one can also not rule out some disorganisation which could lead to a change in orientation and lowering of intensity of this peak. Again the position of RAIRS peaks indicates existence of a disordered layer.

In our previous work on dithiols it was found that well ordered SAMs, without presence of extra molecules, were obtained in *n*-hexane. It was therefore interesting to test whether substitutional self-assembly could be carried out using this solvent.

- (d) A HT SAM was prepared as above in *n*-hexane solution and was then directly transferred to a solution of *n*-hexane that had been bubbled with nitrogen. The operation was carried out in absence of light. The sample was incubated for 4 h and then after rinsing and drying analysed by RAIRS. The resulting spectrum is shown in Fig. 1 (line d). As may be seen in this case we also see substitution. A notable feature is that, as opposed to the ethanol solution (case b), in this case the intensity of the peaks is lower and is comparable to that obtained for a direct assembly of NDT from this solution. A small amount of remaining  $\text{CH}_3$  structure is observable at  $2877\text{ cm}^{-1}$  and the relative intensities of the main peaks are not the same as in the case of direct assembly, indicating that during this time full substitution did not occur. For the remaining HT SAM, the  $\nu_s(\text{CH}_3)$  peak at  $2877\text{ cm}^{-1}$  dominates the  $\nu_{\text{as}}(\text{CH}_3)$  peak at  $2964\text{ cm}^{-1}$ , as in the starting HT SAM. So, in this case, the configuration of the remaining HT SAM seems to be close to the standing-up configuration of the initial HT SAM. Most importantly, the positions of the  $\nu_{\text{as}}(\text{CH}_2)$  and  $\nu_s(\text{CH}_2)$  peaks in the spectrum are  $2918\text{ cm}^{-1}$  and  $2849\text{ cm}^{-1}$  compatible with good organisation of the substituted SAM. Thus in this case we conclude that we obtain a better quality SAM.

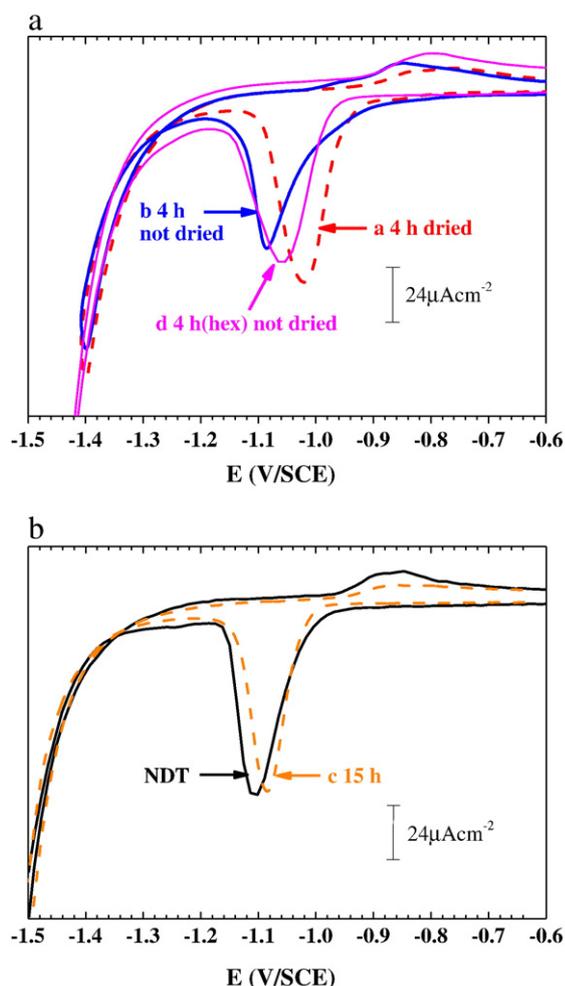
### 3.2. Electrochemistry

The SAMs after RAIRS analysis were analysed by cyclic voltammetry. Fig. 2 shows the measured cathodic current ( $j$ ) density versus potential ( $E$ ) curves for the first scan, recorded in a 0.1 M NaOH aqueous solution for the different substitutional procedures outlined above and for an NDT SAM directly grown in ethanol. The cathodic current peaks, preceding the current increase related to the hydrogen evolution reaction, are assigned to the reductive desorption of thiols or dithiols from the Au substrates. In the case of pure HT and NDT *n*-hexane grown SAMs the desorptive peak in the first scan appears at  $-0.96\text{ V/SCE}$  and  $-1.09\text{ V/SCE}$  respectively (see e.g. Ref. [25]).

In the case (a) when the HT SAM is first dried and then immersed into the NDT ethanol solution for 4 h (top part of Fig. 2 red curve) we observe a desorption peak at  $-1.02\text{ V/SCE}$  which we would assign to mainly the HT SAM. The reductive charge corresponding to the first cathodic scan, measured by integration of these current peaks referred to the real surface area, yields  $79 \pm 3\text{ }\mu\text{C/cm}^2$  (surface coverage  $1/3$ ,  $q = 75\text{ }\mu\text{C cm}^{-2}$  [43]). The same amount of thiolates is expected for the HT SAM, the NDT SAM in an upright configuration and the partial NDT substituted HT SAM. In fact, in all cases, it is possible to arrange the thiolates in a  $\sqrt{3} \times \sqrt{3}\text{ R}30^\circ$  lattice.

In the second case (b), when the HT SAM is directly transferred into the NDT ethanol solution (top part of Fig. 2 blue curve) we observe that the desorption peak is now shifted to  $-1.09\text{ V/SCE}$  and has a tail extending to  $E$  values corresponding to the position of the HT SAM peak. The difference in peak potentials observed in Fig. 2 for NDT and HT is due to the van der Waals interactions [25]. The reductive charge corresponding to the first cathodic scan is  $76 \pm 3\text{ }\mu\text{C/cm}^2$ . This value is close to the one of a NDT SAM grown in ethanol, shown in the lower panel (desorption peak at  $-1.1\text{ V/SCE}$  with a reductive charge corresponding to  $80 \pm 4\text{ }\mu\text{C/cm}^2$ ). Note that in our previous work [25], according to electrochemistry, XPS (X ray photoelectron spectroscopy), RAIRS and TOF-DRS (time of flight direct recoil spectroscopy) experiments, this NDT SAM grown in ethanol was found to present disulfide bridges between SAM molecules and some extra molecules bonded to the SAM through disulfide bonds.

For the case of the procedure (c) when the HT SAM is first pump dried and then immersed into the NDT ethanol solution for 15 h (bottom panel of Fig. 2 dashed curve), we observe the desorption at  $-1.08\text{ V/SCE}$ , which we would assign to mainly the NDT SAM. The 30 mV shift with respect to the NDT SAM grown in ethanol can be



**Fig. 2.** Cyclic voltammograms for substitution of a hexanethiol SAM by nonanedithiol for ethanol and *n*-hexane solutions. Top panel 4-hour substitution: (red line—procedure a) HT SAM is first dried in vacuum and then immersed into the NDT ethanol solution for 4 h, (blue line—procedure b) HT SAM is directly transferred into the NDT ethanol solution for 4 h and (magenta line—procedure d) HT SAM is directly transferred from the HT *n*-hexane solution into the NDT *n*-hexane solution for 4 h. Bottom panel: (black line) cyclic voltammograms of NDT SAM grown in ethanol and (orange line—procedure c) NDT substituted HT SAM when HT SAM is first dried in vacuum and then immersed into the NDT ethanol solution for 15 h.

attributed to some remaining HT domains. The reductive charge corresponding to the first cathodic scan is  $78 \pm 4 \mu\text{C}/\text{cm}^2$ .

Finally in the case (d) when the HT SAM is directly transferred into the NDT *n*-hexane solution (top panel of Fig. 2 magenta curve) we observe a desorption peak at  $-1.06 \text{ V/SCE}$ . The reductive charge corresponding to the first cathodic scan is  $72 \pm 2 \mu\text{C}/\text{cm}^2$ . The  $-1.06 \text{ V/SCE}$  value is close to the value for the ordered NDT SAM grown in degassed *n*-hexane in the dark presented in our previous work [25]. The electrochemistry, XPS, RAIRS and TOF-DRS measurements presented in that work lead to the conclusion that the NDT grown in *n*-hexane SAM is dominated by the organized standing-up phase. This result was in agreement with SFG (sum frequency generation), RAIRS and spectroscopic ellipsometry experiments [40], where ellipsometry indicated formation of a layer whose thickness was compatible with a monolayer and SFG indicated presence of free standing SH groups.

### 3.3. Discussion

The previously mentioned experiments show that substitutional self-assembly occurs much more efficiently when the thiol SAMs

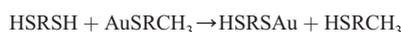
are not pre-dried. Immersion of a dried SAM into ethanol leads to appearance of some degree of substitution, which increases with duration of immersion.

In a recent work the changes in order of nonanethiol SAMs dried with He or exposed to ethanol was studied by X ray diffraction and it was found that ethanol induced disorder in a previously ordered SAM. The results of the experiments described above agree with this and indicate that disorder in ethanol exposed SAMs is an important parameter for successful substitutional self assembly [44]. In general they indicate that presence of the initial solvent is an important factor, whereas drying renders the initial HT layers much more stable against substitution.

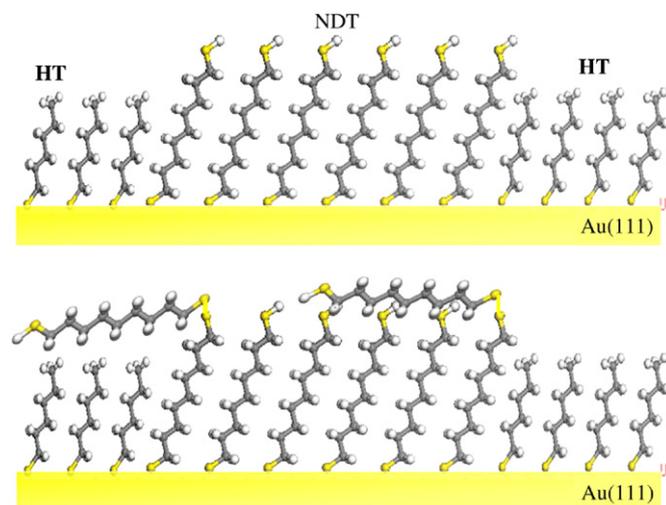
An important feature is that our RAIRS experiments reveal that dithiol substitutional assembly using ethanol leads to formation of disordered layers. This is in agreement with our earlier results for direct self-assembly in this solvent, where, as here, RAIRS spectra suggest the presence of excess dithiol molecules on the SAM [25,40]. These were ascribed to dithiol molecules linked to the dithiol SAM free SH end groups by disulphide bridges. Note that the layer thickness as deduced from spectroscopic ellipsometry in this case was still compatible with a monolayer and not with the existence of ordered multilayers as suggested in some earlier work [8]. This would indicate that the region of the dithiol domain must have an overlayer of extra linked molecules (Fig. 3). This could be a major problem for experiments involving nanoparticle deposition [28,29], when the aim is to link to the SAM dithiol SH groups.

In case of the *n*-hexane solution, we obtained much better results with RAIRS, indicating formation of an overall well ordered SAM and that the dithiol domains are well ordered and without extra bonded molecules, a situation optimal for nanoparticle deposition. In our previous work the problems related to ethanol were tentatively assigned to presence of some residual oxygen (or water) and photooxidation processes.

Finally one can ask oneself how the initially chemisorbed thiol gets free. A possible explanation could be a hydrogen substitution reaction involving interaction of a free dithiol molecule (HSRSH) with a chemisorbed thiol molecule on gold ( $\text{AuSRCH}_3$ ), with a surface mediated exchange of an H atom between the two:



This would lead to “liberation” of the thiol end of the chemisorbed molecule as  $-\text{SH}$  and adsorption of the initially free molecule, with the thiol end attached to gold.



**Fig. 3.** Schematic image of the NDT SAM substituted from HT SAM in *n*-hexane (top) and ethanol (bottom), showing some “additional” molecules on the NDT domain in case of ethanol.

We hope our results will be useful in investigation on nanoparticle growth and especially conductance measurements, where the previously mentioned problems in experiments using ethanol [28,29] would need to be assessed.

### Acknowledgements

The authors are grateful to Maurizio Canepa and Roberto C. Salvarezza for useful discussions.

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