Exploiting molecular machines on surfaces
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Chapter 5

**ACID-TERMINATED ALKANETHIOL SELF-ASSEMBLED MONOLAYERS ON Au(111)**

This chapter reports on a study of acid-terminated self-assembled monolayers of alkanethiols of different length, 11-mercaptoundecanoic acid (11-MUA) and 16-mercaptohexadecanoic acid (16-MHDA), on Au(111). STM, XPS and contact angle techniques were used for characterization and the results were compared with those obtained from n-alkanethiols of similar chain length, providing a detailed description of the two-dimensional crystalline structure. Molecular resolution STM images show that 11-MUA forms a dense-packed monolayer arranged in a ($\sqrt{3}$x$\sqrt{3}$)R30° structure with a c(2x4) superlattice, where the simple hexagonal phase, the c(2x4) superlattice and non-ordered areas coexist. 16-MHDA assembles in a uniform monolayer with similar morphology than 11-MUA but molecular resolution could not be reached by STM due to both the hydrophilicity of the acid groups and the poor conductivity of the thick monolayer. Nevertheless, the monolayer thicknesses estimated by XPS and the low water contact angle are consistent with 16-MHDA molecules forming a compact monolayer on the Au(111) substrate with fully extended alkyl chains and acid groups pointing away from the surface. The results obtained for 16-MHDA were reproducible under different preparation conditions such as the addition or omission of acetic acid to the ethanolic solution. Contrary to other reports, we demonstrate that ordered acid-terminated self-assembled monolayers are obtained with the same preparation conditions than methyl-terminated ones, without any additional treatment.
5.1 Introduction

In the last years, self-assembled monolayers (SAMs) of alkanethiols on metal substrates have attracted the attention of many scientists in physics and chemistry due to their ability to form ordered organic films with well-defined composition and thickness. They are potentially versatile building blocks for the development of advanced materials: a proper selection of head groups allows the chemical derivatization of a surface and for this reason SAMs have been employed as a link path to graft molecules onto metal substrates, with the aim of modifying the surface properties. In particular, acid-terminated alkanethiols are interesting due to their capability to react and/or strongly interact with many other chemical groups, leading to the functionalization of a surface with different molecules.

Figure 5.1. Left: schematic representation of the $\sqrt{3} \times \sqrt{3}$R30° lattice of alkanethiols on the Au(111) surface. The small gray circles represent Au atoms, the black and dark-gray circles represent the thiol molecules. Black circles indicate a (3x2√3) primitive unit mesh (---), which can also be described as a c(4x2) superlattice in terms of the $\sqrt{3} \times \sqrt{3}$R30° lattice (—). The sulfur atoms are assumed to interact exclusively with fcc 3-fold hollow sites on the Au(111) surface. Right: scheme of the lateral view of decanethiol on Au(111); alkyl chains are tilted by 30°.

Several analytical techniques such as spectroscopies, contact angle, ellipsometry and electrochemistry have been used to study SAMs. As a result, there was a general agreement that long (n > 6) methyl-terminated alkanethiols on Au(111) form densely packed monolayers, with a chain tilt of ~ 30° respect to the surface normal that maximizes the van der Waals interactions between alkyl chains, and a structure with a $\sqrt{3} \times \sqrt{3}$R30° lattice. Later helium diffraction and STM studies demonstrated the presence of a c(4x2) superlattice of the basic $\sqrt{3} \times \sqrt{3}$R30° structure (see schematic representation in Figure 5.1). However,
other authors claimed that replacing the methyl-termination by other functions does not always lead to the same organization and crystalline patterns and variations in head groups, chain length and preparation conditions can give rise to different favoured packing structures.\textsuperscript{13 – 17}

The two-dimensional characteristics of acid-terminated alkanethiol SAMs have not yet been accurately described through STM studies. Furthermore, there is no clear agreement in the literature about what are the proper preparation conditions to obtain highly ordered acid-terminated monolayers. Nuzzo et al.\textsuperscript{18} observed well-packed mercaptohexadecanoic acid monolayers by infrared spectroscopy when using ethanol as a solvent for the SAM preparation. This was confirmed by the STM data of Ito et al.\textsuperscript{19} and Gorman et al.\textsuperscript{20} for the case of mercaptoundecanoic acid. However, other studies\textsuperscript{21, 22} demonstrated a high degree of disorder in mercaptoundecanoic acid samples prepared only with ethanolic solutions and suggested that the quality of the surfaces can be improved with the addition of acetic acid to the solvent. In addition, Willey et al.\textsuperscript{23} also claimed that well-ordered carboxylic-terminated SAMs of mercaptohexadecanoic acid can be formed by adding acetic acid and they showed that rinsing in KOH causes the carboxylic group to be oriented much more upright. Finally, Wang et al.\textsuperscript{24} argued that carboxylic-terminated SAMs are harder to control than methyl-terminated ones and they proposed that addition of CF\textsubscript{3}COOH to the ethanol followed by a rinse with NH\textsubscript{4}OH improves the sample quality.

\begin{figure}[h]
\centering
\includegraphics[width=0.8\textwidth]{figure5.2.png}
\caption{Chemical structure of the four alkanethiols investigated in this chapter.}
\end{figure}
This chapter focuses on the crystalline structure of acid-terminated SAMs and compares them with methyl-terminated SAMs of similar length. For this purpose, four molecules have been selected: decanethiol (C10), hexadecanethiol (C16), mercaptoundecanoic acid (11-MUA) and mercaptohexadecanoic acid (16-MHDA). Their chemical structures are shown in Figure 5.2. SAMs were characterized by XPS, cyclic voltammetry (CV), electrochemical impedance spectroscopy (EIS), contact angle and STM techniques. Since methyl-terminated SAMs on Au(111) have been extensively studied, they have been chosen as the benchmark for comparison with carboxylic acid-terminated ones in our discussion.

By combining the above-mentioned experimental techniques, we are able to determine if carboxylic acid-terminated SAMs have equivalent chemical composition, thickness and roughness than their methyl-terminated counterparts.

5.2 The crystalline structure of SAMs as seen by STM

Figure 5.3 presents high resolution STM images of a C10 monolayer. Figure 5.3a shows a molecularly resolved area where the molecules arrange in a hexagonal structure corresponding to the \( (\sqrt{3} \times \sqrt{3})R30^\circ \) lattice. A \( c(4x2) \) superlattice with respect to the fundamental hexagonal pattern is also visible due to variations in spot brightness and the unit mesh is outlined to guide the eye. The cross section plot of the line superimposed in the image (Figure 5.3b) indicates that the brighter spots appear \( \sim 0.1 \) Å higher than the rest.\(^{12, 15}\) Figure 5.3c presents a \( 20 \times 20 \) nm\(^2\) image showing domains of molecules in which every domain has one of the three possible symmetry-equivalent orientations arising from the \( c(4x2) \) superlattice.\(^{11, 17}\) The darker areas are single-atom-deep etch pits in the gold terrace. These pits are vacancy islands of monoatomic depth on the gold substrate and are induced by the dynamic self-assembly process that takes place during the formation of the monolayer in solution.\(^4\)

Figure 5.4 shows STM images of 11-MUA, where molecular resolution was also achieved. Figure 5.4a displays a \( 27 \times 27 \) nm\(^2\) image with different morphologies. We can clearly recognize simple hexagonal domains like “A”. There are also ordered arrays of molecules forming domains “B” similar to the ones found on C10 (Figure 5.3c), which are a fingerprint of the \( c(4x2) \) superlattice. Other regions of type “C” are less defined and probably not ordered. Single-atom-deep etch pits in the gold terrace\(^4\) are visible as well. Previous STM measurements
Acid-terminated Alkanethiol SAMs on Au(111)

Figure 5.3. STM images of C10: a) 3.8 x 3.8 nm$^2$ image showing the ($\sqrt{3}\times\sqrt{3}$)R30° and c(4x2) lattices ($V_{\text{bias}}= 650$ mV, $I_{\text{set}}= 5$ pA). The c(4x2) unit mesh is outlined to guide the eye; b) cross section plot of the line superimposed in the image; c) 20 x 20 nm$^2$ image depicting domains of C10 and single-atom-deep etch pits ($V_{\text{bias}}= 500$ mV, $I_{\text{set}}= 20$ pA).

Figure 5.4. STM images of 11-MUA: a) 27 x 27 nm$^2$ image showing domains of molecules: A- simple hexagonal packing, B- c(4x2) arrangement, C- non-ordered region ($V_{\text{bias}}= 800$ mV, $I_{\text{set}}= 5$ pA); b) 4.1 x 4.1 nm$^2$ image showing the ($\sqrt{3}\times\sqrt{3}$)R30° structure ($V_{\text{bias}}= 800$ mV, $I_{\text{set}}= 5$ pA); inset: 1.5x1.5 nm$^2$ section of the same image filtered by Fourier transformation showing the hexagonal lattice.
carried out under nitrogen revealed a double-row structure in the 11-MUA SAM\(^{20}\) that was not observed in the present study. We believe that this double row arrangement corresponds to a non-resolved c(4x2) structure. A higher magnification image (Figure 5.4b) reveals that 11-MUA orders in a $$(\sqrt{3}\times\sqrt{3})R30^\circ$$ packing with an average molecular distance of 5 Å. The hexagonal packing is clearly seen in the FFT-filtered image included as inset. 11-MUA has a crystalline structure very similar to C10. However, while C10 presents large uniform areas with the same arrangement, 11-MUA forms a compact monolayer with a mixture of diverse morphologies and smaller ordered domains, which is a clear difference between acid and methyl-terminated alkanethiols. Note that a poorer image resolution is achieved for 11-MUA than for C10 measurements, probably due to the presence of environmental contamination – such as water – adsorbed by the acid groups that interfere with the tip, changing its shape and perturbing the scanning process.

**Figure 5.5.** STM images of C16: a) 30 x 30 nm\(^2\) image showing domains of molecules ($V_{bias}=700$, $I_{set}=5$ pA); b) 4 x 4 nm\(^2\) image showing the $$(\sqrt{3}\times\sqrt{3})R30^\circ$$ structure ($V_{bias}=550$ mV, $I_{set}=10$ pA). Inset: part of the same image filtered by Fourier transformation showing the hexagonal lattice.

Figure 5.5 presents STM images of C16. Figure 5.5a shows a 30 x 30 nm\(^2\) surface where ordered arrays of C16 and single-atom-deep etch pits in the Au terrace are seen. The distance between brighter spots of the ordered arrays suggests the presence of the c(4x2) reconstruction.\(^{12, 15}\) A higher resolution image (4 x 4 nm\(^2\)) shown in Figure 5.5b displays a highly ordered $$(\sqrt{3}\times\sqrt{3})R30^\circ$$ arrangement with an average molecular separation of 5 Å, as for C10. The inset is part of the
Acid-terminated Alkanethiol SAMs on Au(111)

same image filtered by Fourier transformation, which emphasizes the hexagonal lattice. These are the first STM images of C16 acquired with molecular resolution. To reach such a resolution it was necessary to work with a set point current not higher than 10 pA and bias voltage higher than 500 mV. Notice that SAMs with long alkyl-chain (n > 14) present a very poor conductivity. Bumm et al. reported that a tunneling current lower than 1 pA should be used to obtain molecular resolution STM images of C16, which is not possible with current standard STMs. We observed that higher tunneling currents can be used to successfully observe the molecular structure of C16 if working with the proper bias voltage and tip shape. A few scans over the same area under the above mentioned conditions were reproducible but the quality of the image gradually decreased, probably due to damage of the monolayer and/or changes in the tip shape. A consequence of the low set current is a rather high noise level, which does not allow to observe a c(4x2) superlattice in clear detail.

![Image](image_url)

**Figure 5.6.** 190 x 190 nm² STM image of 16-MHDA showing gold terraces covered by the SAM. Single-atom-deep etch pits are clearly seen. (Vbias= 600 mV, Iset = 10 pA).

Finally, STM results on 16-MHDA are shown in Figure 5.6. A 190 x 190 nm² scanned area reveals gold terraces covered by a uniform alkanethiol monolayer with single-atom-deep etch pits. Contrarily to the systems described above, it was impossible to achieve molecular resolution in this case. The difficulty to image the 16-MHDA SAM arises from the poor conductivity of the thick organic film and the hydrophilic nature of the acid groups that favour environmental contamination of the surface. Many samples were investigated and they always presented the
same characteristics everywhere, suggesting therefore that the monolayers are compact and uniform. As mentioned in the introduction, previous studies reported that the addition of acetic acid to the preparation of 16-MHDA and a final rinse with KOH improve the monolayer order.\textsuperscript{23} Samples prepared by this method were checked by STM (not shown) and the results were similar to those described in Figure 5.6 but some regions presented evidence of contamination, probably due to difficulties in removing acetic acid molecules adsorbed on the surface. Thus, our observations do not support the conclusions of reference 23.

5.3 Qualitative analysis and thickness estimation

Figure 5.7 presents the C $1s$ core level region of the photoemission spectra of C10, 11-MUA, C16 and 16-MHDA as well as the fit of the experimental lines. In the case of C10 and C16, at least two components are needed to mathematically reconstruct the experimental data. They occur at binding energies of 284.7 and 285.6 eV and are unambiguously attributed to aliphatic carbon and carbon bound to sulphur, respectively.\textsuperscript{29, 30} The same features are found for 11-MUA and 16-MHA, where the peak at 285.6 eV is not only due to carbon bound to sulphur, but also to aliphatic carbon atom next to the carboxylic group. There is a third peak at 289.2 eV arising from carboxylic carbons. Peak positions, area ratios and FWHM of the components are compatible with the stoichiometry of the alkanethiol molecules.

Samples of 16-MHDA prepared with solution of acetic acid/ethanol and rinsed in KOH were investigated by XPS and the C $1s$ region is also included in Figure 5.7 (16-MHDA acid+KOH). Peak positions and FWHM of the C $1s$ aliphatic components (at 284.7 eV and 285.6 eV binding energy, respectively) are identical to the previously discussed cases and there is no evidence of different chemical environment in aliphatic chains of 16-MHDA samples prepared with or without acetic acid, in contrast with the results obtained by Willey \textit{et al.}\textsuperscript{23} Hence, there is no indication of disorder in the monolayer produced without the addition of acetic acid. Carboxylate carbons appear at 288.4 eV, i.e. shifted to lower binding energy with respect to carboxylic groups due to charge transfer and screening effects induced by the interaction between carboxylate groups and $K^+$ ions. The peaks at 288.4 and 285.6 eV binding energy are slightly more intense than expected when taking into account the stoichiometry of the molecule, suggesting the presence of residual acetic acid or acetate species. The potassium signal (not shown) appears as a doublet with the $2p_{3/2}$ maximum at 293.1 eV binding energy and its area is in stoichiometric ratio with the C $1s$ area of the carboxylate group.
Acid-terminated Alkanethiol SAMs on Au(111)

Figure 5.7. X-ray photoemission spectra of C 1s core level region and mathematical reconstruction of the experimental lines of C10, 11-MUA, C16 and 16-MHDA prepared with and without acetic acid and KOH.

The S 2p core level region of the photoemission spectra of the four SAMs is presented in Figure 5.8. In particular, for the case of 16-MHDA we present the S 2p core levels of both the sample prepared only with ethanol and the sample prepared with ethanol + acetic acid and rinsed with KOH. The three S 2p spectra of carboxylic-terminated SAMs are identical to their methyl-terminated counterparts: all spectra are characterized by a doublet with maximum at 162.0 eV binding energy, an intensity ratio 1:2 and a FWHM of 1.2 eV. There was no evidence of free (163.5 eV) or oxidized sulphur (168 eV)\(^{30}\) in any sample, contrarily to what was reported by Wang et al.\(^{24}\) who has observed unbound thiols in carboxylic acid-terminated SAMs prepared only with ethanol.

The observations suggest no difference between SAMs prepared with or without acetic acid plus KOH rinsing and we conclude that 16-MHDA SAM
prepared only with ethanol presents the same chemical characteristics than C16 or 11-MUA so the special preparation treatment with acetic acid plus KOH rinsing is not necessary to achieve an improvement.

Figure 5.8. X-ray photoemission spectra of S 2p core level region and mathematical reconstruction of the experimental lines of C10, 11-MUA, C16 and 16-MHDA prepared with and without acetic acid and KOH.

The intensity of the signal produced by gold photoelectrons is attenuated by the alkanethiol monolayer and this attenuation depends mainly on the SAM thickness: the thicker the film, the larger the substrate signal attenuation. Thus, XPS measurements are a good alternative to estimate the thickness of an alkanethiol monolayer. In the present work, we estimate the SAM thicknesses via the Au 4f core level assuming that the gold peak intensities follow the equation \(31, 32\)

\[
\text{Au}_1 = \text{Au}_0 e^{-d/(\lambda \sin \phi)}
\]
where $Au_1$ is the intensity of gold photoelectrons attenuated by the SAM, $Au_0$ is the intensity of clean gold, $d$ is the SAM thickness, $\lambda$ is the attenuation length (reported as $42 \pm 1.4$ Å for alkanethiols on gold$^{31}$) and $\varphi$ is the take-off angle. Thicknesses calculated by this method are presented in Table 5.1. The results are in good agreement with previous ellipsometry studies on methyl-terminated alkanethiols$^{11, 27, 33}$ and with the calculated values taking into account the C-C distance of fully extended alkyl-chains with $30^0$ tilt respect to the substrate normal. Additionally, 11-MUA and 16-MHDA were investigated by electrochemistry and the thicknesses that were obtained are in accordance with the results of Table 5.1.$^{34}$

The attenuation of the S 2p signal indicates that the sulphur atoms are not exposed to the surface but are at the bottom of the SAM. The relative attenuation of the sulphur signal was similar for C16 and 16-MHDA and larger than for C10 or 11-MUA. This observation can be only explained if we consider that the alkanethiols form a compact film in all four cases.

<table>
<thead>
<tr>
<th>Monolayers</th>
<th>C10</th>
<th>11-MUA</th>
<th>C16</th>
<th>16-MHDA</th>
</tr>
</thead>
<tbody>
<tr>
<td>Thickness (Å)</td>
<td>13 ± 2</td>
<td>15 ± 3</td>
<td>19 ± 3</td>
<td>19 ± 3</td>
</tr>
</tbody>
</table>

Table 5.1. SAM thicknesses estimated by the attenuation of the Au 4f signal.

Recently, Sushko and Shluger investigated the influence of dipole-dipole interactions on the structure of COOH-terminated monolayers using atomistic calculations.$^{35}$ They found that the alkyl-chains and the head-groups of long molecules ($> 11$ carbons) present independent crystalline structures. They concluded that these molecules ‘can simultaneously have a crystalline-like order with respect to the chain backbones and a high degree of disorder with respect to the COOH-groups’. Their calculations help to explain the apparent disagreement between experimental data acquired by different techniques such as infrared spectroscopy$^{18}$ and NEXAFS.$^{36}$

### 5.4 Wettability properties

The wettability of both acid- and methyl-terminated alkanethiols was investigated by measuring the contact angle of water on freshly prepared samples. The values, determined as the average of three identically prepared samples, where at least three points on each one were measured, are presented in Table 5.2. The
high contact angle of 109° and 111° for C10 and C16, respectively, testifies the hydrophobic nature of methyl-terminated monolayers. In contrast, both 16-MHDA (prepared with or without acetic acid + KOH rinse) and 11-MUA present very low contact angles, lower than 12° or 10° respectively, when measured immediately after deposition. Water droplets deposited on acid-terminated SAMs spread very fast, making it difficult to determine an accurate contact angle value. Such behaviour is in agreement with strongly hydrophilic surfaces and suggests that both 11-MUA and 16-MHDA self-assemble on the substrate with their acid groups oriented towards the air-side.8 The water contact angle of the 16-MHDA SAMs prepared with acetic acid and KOH is also very low, consistent with the ionic nature of the surface. Contact angles measurements of 16-MHDA prepared only with ethanol or with ethanol + acetic acid and rinsed with KOH do not manifest any difference in terms of wettability.

The results of Table 5.2 are in good agreement with previously reported values,8 but they differ from the results of other authors,24,37 who found the contact angles of carboxylic-terminated SAMs prepared only with ethanol to be higher. We observed that contact angles of carboxylic-terminated SAMs can be a few degrees higher than those presented in Table 5.2 if freshly prepared samples are measured too soon, i.e. before they are completely dry. Additionally, we noticed that the roughness of the gold substrate influences the quality of the monolayer. Thus, solvent contamination or differences in substrate roughness can explain discrepancies in contact angle data reported in other publications.

<table>
<thead>
<tr>
<th>Monolayers</th>
<th>C10</th>
<th>C16</th>
<th>11-MUA</th>
<th>16-MHDA</th>
<th>16-MHDA (acid+KOH)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Contact angle</td>
<td>109 ± 2°</td>
<td>111 ± 2°</td>
<td>&lt; 10°</td>
<td>&lt; 12°</td>
<td>&lt; 12°</td>
</tr>
</tbody>
</table>

Table 5.2. Water contact angle of the four studied SAMs: C10, C16, 11-MUA and 16-MHDA.

5.5 Conclusions

We have investigated acid- and methyl-terminated self-assembled monolayers of alkanethiols with different alkyl chain length. C10, C16, 11-MUA and 16-MHDA on Au(111) were characterized by STM, XPS and contact angle measurements. Molecular resolution STM images of C16 were achieved for the
Acid-terminated Alkanethiol SAMs on Au(111) 65

first time and both C10 and C16 show ordered domains with \((\sqrt{3} \times \sqrt{3})R30^\circ\) lattice and a c(4x2) superstructure. In contrast, 11-MUA monolayers form smaller ordered domains than n-alkanethiols and regions with a simple \((\sqrt{3} \times \sqrt{3})R30^\circ\) lattice, a c(4x2) superlattice and non-ordered arrangements coexist on the surface. Finally, 16-MHDA presents the morphology of a uniform alkanethiol monolayer with the characteristic single-atom-deep etch pits. In this case, both the thickness of the monolayer and the hydrophilic properties of the surface make it impossible to reach molecular resolution in air. XPS spectra showed peak positions and line-shapes in agreement with the chemical structure of the molecules. The film thicknesses, estimated by XPS, are in good agreement with the values expected taking into account the C-C distance in the alkyl chain and fully extended alkanethiols tilted by 30° with respect to the substrate normal. The water contact angles of methyl-terminated monolayers were very high (~ 110°) because methyl groups create extremely hydrophobic surfaces. In contrast, acid-terminated monolayers presented very low water contact angles (< 12°) as expected for highly hydrophilic surfaces formed when most of the acid groups of 11-MUA and 16-MHDA point upright. 16-MHDA monolayers prepared only with ethanolic solution are as good and uniform as the ones prepared with acetic acid/ethanol and additionally rinsed in KOH. Furthermore, the acetic acid was difficult to remove and appears as contamination on the surface. Hence, we have demonstrated that ordered acid-terminated alkanethiol self-assembled monolayer can be obtained with the same preparation conditions used for methyl-terminated ones, without any other particular treatment.

References

