

Self-Assembled Monolayers on Gold Generated from Aliphatic Dithiocarboxylic Acids

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Self-assembled monolayers (SAMs) were prepared by the adsorption of aliphatic dithiocarboxylic acids (ADTCAs) onto the surface of gold. These new SAMs were characterized by optical ellipsometry, contact angle goniometry, and polarization modulation infrared reflection absorption spectroscopy. The data are consistent with a model in which the ADTCAs generate well-packed and highly oriented monolayer films. Comparison of the wettabilities of these new SAMs to those prepared from normal alkanethiols reveals an unusually large “odd–even” effect when hexadecane is used as the contacting liquid. The origin of this effect is attributed to chelation of the ADTCA headgroup to the surface of gold.

Introduction

Self-assembled monolayers (SAMs) are continuing to draw widespread interest because of their potential use in technological applications.¹ Some areas of current interest include adhesion promotion/resistance,^{2,3} biomaterials fabrication,^{4–7} corrosion resistance,^{8,9} lithographic patterning,^{10,11} and microelectronics fabrication.^{12,13} The most thoroughly examined SAMs are those generated by the adsorption of alkanethiols on gold. Their popularity can be attributed to the ease with which they can be prepared, manipulated, and characterized.^{14–17} When adsorbed from solution onto gold, alkanethiols form close-packed essentially defect-free monolayer films. The sulfur atoms tenably bind to the 3-fold hollow sites of Au(111) with the alkyl chains tilting approximately 30° from the normal to the surface. The overlayer structure is characterized by a $(\sqrt{3} \times \sqrt{3})R30^\circ$ orientation.^{18,19}

The structural features of SAMs on gold are dictated by two major factors: the thiol–gold interaction and the

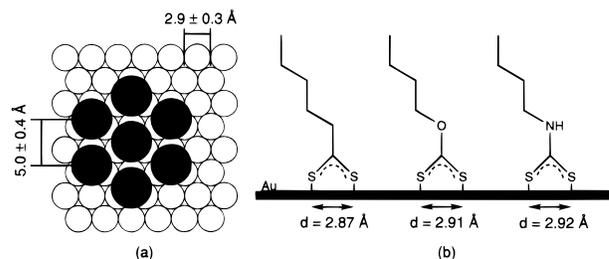


Figure 1. (a) Overlayer structure of *n*-alkanethiols on Au(111). (b) Proposed binding motif for aliphatic chelating moieties.

interchain interactions.^{14–17} The adsorbates bind to the 3-fold hollows to maximize the binding of sulfur to gold (see Figure 1a); the chains tilt to maximize the interchain attractions.^{20,21} Consequently, we felt that it might be possible to influence the structural features of SAMs on gold by changing the nature of the binding of the adsorbate to the hexagonal lattice of gold. Specifically targeted chelating adsorbates, for example, in which the sulfur atoms are restricted in their ability to bind to the 3-fold hollows might generate SAMs with equilibrium structures that are different from normal alkanethiol-based SAMs. Indeed, SAMs on gold have been generated from at least two such species: aliphatic dithiocarbamates and xanthates,^{22,23} assuming that both sulfur atoms in the headgroup attach to the surface of gold (see Figure 1b).²⁴ To our knowledge, however, there has been no systematic comparison of the SAMs generated from these species to those generated from their normal alkanethiol analogues.

This paper describes our preliminary studies of new types of SAMs generated from aliphatic dithiocarboxylic acids, $\text{CH}_3(\text{CH}_2)_n\text{CS}_2\text{H}$ (ADTCAs), where $n = 8–17$. We compare these films to those generated from their *n*-alkanethiol analogues, $\text{CH}_3(\text{CH}_2)_m\text{SH}$, where $m = 9–18$. We chose to examine ADTCAs rather than the analogous dithiocarbamates or xanthates because the ADTCAs are structurally more similar to alkanethiols (Figure 1b). Due

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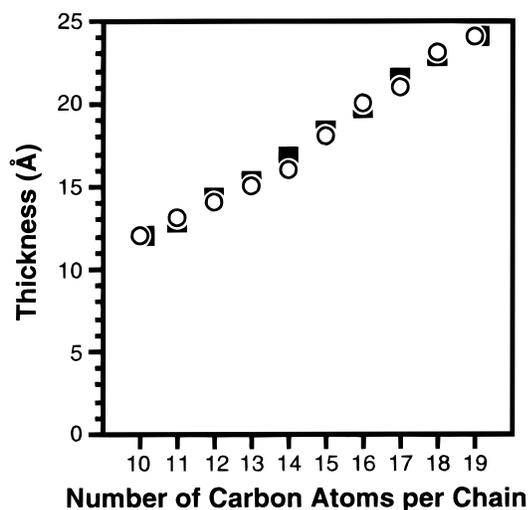


Figure 2. Ellipsometric thicknesses of SAMs generated from dithiocarboxylic acids (filled squares) and alkanethiols (empty circles).

to the potential binding of both sulfur atoms to gold,^{23,25} we anticipated that ADTCA-based SAMs would exhibit unprecedented structural features. Molecular modeling studies showed, for example, that the distance between the centers of the two sulfur atoms in ADTCAs is ca. 2.87 Å.²⁶ Given that the nearest-neighbor spacing measured for Au(111) is 2.9 ± 0.3 Å,²⁷ these studies suggest a different attachment for the ADTCAs than is observed for alkanethiols, where the nearest-neighbor sulfur atoms reside ca. 5.0 Å apart (see Figure 1).^{14–17}

Experimental Section

Materials. Gold shot (99.99%) was purchased from Americana Precious Metals. Chromium rods (99.9%) were purchased from R. D. Mathis Company. Single-crystal silicon (100) wafers, which were polished on one side, were obtained from Silicon Sense, Inc., and rinsed with absolute ethanol (McCormick Distilling Co., Inc.) before use. The liquids used for contact angle measurements were of the highest purity available from Aldrich Chemical Co. and were used without purification. Alkanethiols used to generate the SAMs were either commercially available or synthesized using established methods. The ADTCAs were synthesized via Grignard addition of alkylmagnesium bromides to carbon disulfide (CS₂);^{28,29} experimental details are included as Supporting Information. The fragile nature of some species of dithiocarboxylic acids has been reported.^{30,31} In analyses by ¹H nuclear magnetic resonance (NMR) spectroscopy, we found that initially pure samples of the ADTCAs stored at 0 °C would undergo partial decomposition (e.g., <5%) to unidentified impurities in a matter of weeks. These impurities, however, could be readily removed using the procedures detailed in the Supporting Information. Furthermore, ADTCAs purified in this manner were able to withstand off-site shipping for elemental analysis (roughly 1 week at room temperature) without detectable degradation. The purity of all ADTCAs used for making SAMs was >98%, as judged by ¹H and ¹³C NMR spectroscopy.

Preparation of SAMs. Solutions of the dithiocarboxylic acids and thiols were prepared in weighing bottles that were cleaned

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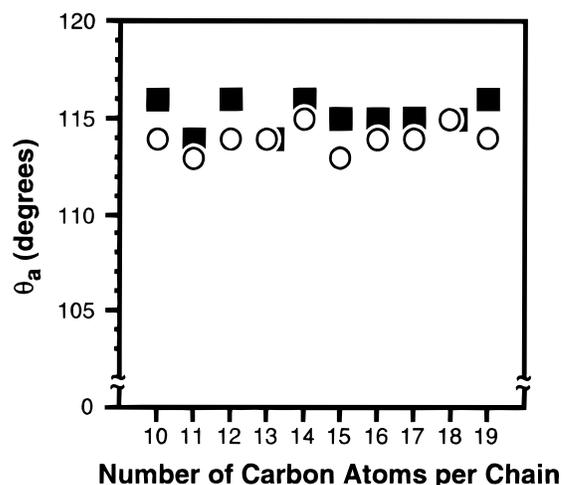


Figure 3. Advancing contact angles of water on SAMs generated from dithiocarboxylic acids (filled squares) and alkanethiols (empty circles).

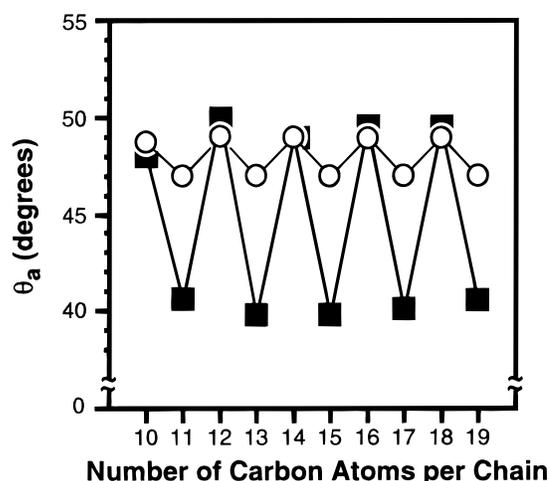


Figure 4. Advancing contact angles of hexadecane on SAMs generated from dithiocarboxylic acids (filled squares) and alkanethiols (empty circles).

by soaking in piranha solution (7:3 H₂SO₄/H₂O₂) for 1 h. *Caution: piranha solution reacts violently with organic materials and should be handled carefully.* The bottles were then rinsed with deionized water and absolute ethanol. The gold substrates were prepared by thermally evaporating ca. 100 Å of chromium onto the polished surfaces of the silicon wafers, followed by evaporating ca. 2000 Å of gold. Deposition pressures were maintained at ca. 1×10^{-7} Torr. Chromium serves to promote the adhesion of gold to silicon.³² The freshly prepared gold-coated wafers were immediately transferred to Fluoroware containers, where they were stored until used. The wafers were cut into slides (ca. 1 cm × 3 cm) with a diamond-tipped stylus. The slides were washed with absolute ethanol and blown dry with ultrapure nitrogen. Ellipsometric data for the bare gold were collected. The slides were then washed with ethanol and immersed in solutions of the respective dithiocarboxylic acids (1 mM in ethanol) or thiols (1 mM in ethanol). All ADTCA solutions were prepared immediately following purification of the acids (typically less than 1 day); only freshly prepared solutions were employed in the formation of SAMs. All substrates were allowed to equilibrate simultaneously for a period of 24 h. The resultant SAMs were thoroughly rinsed with ethanol and blown dry with ultrapure nitrogen before immediate characterization.

Ellipsometric Thicknesses. The thicknesses of the monolayers were measured with a Rudolph Research Auto EL III

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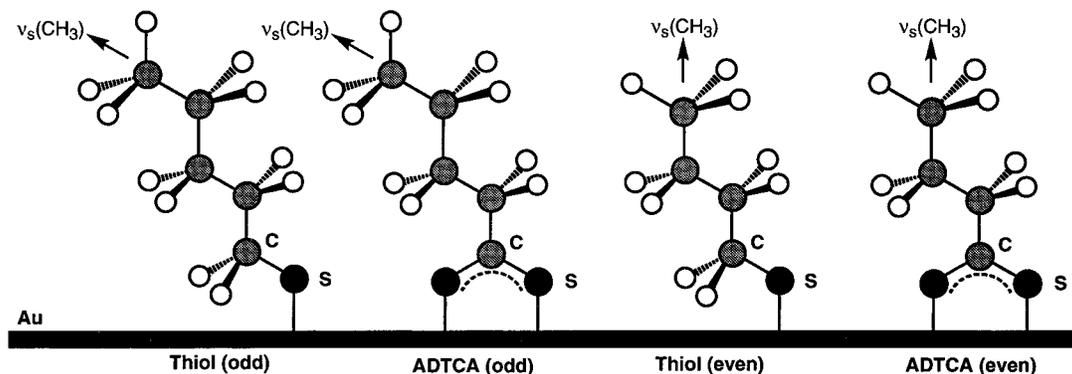


Figure 5. Illustration of the terminal methyl group orientation for adsorbates possessing odd and even numbers of carbon atoms.

ellipsometer equipped with a He–Ne laser (632.8 nm) at an incident angle of 70° . A refractive index of 1.45 was assumed for all films. For a given sample, the data were averaged over three separate slides using three spots per slide.

Contact Angle Wettabilities. Advancing and receding contact angles were measured with a Ramé-Hart model 100 contact angle goniometer. The contacting liquids, hexadecane ($C_{16}H_{34}$, HD) and water (H_2O , W), were dispensed and withdrawn with a Matrix Technologies micro-Electrapipet 25 operated at the slowest possible speed (ca. $1 \mu L/s$). For a given sample, the data were averaged over three separate slides using three drops per slide and measuring angles from opposite edges of each drop. The measurements were performed at 293 K with the pipet tip in contact with the drop.

Infrared Spectroscopy. Polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) data were collected using a Nicolet MAGNA-IR 860 Fourier transform spectrometer equipped with a liquid-nitrogen-cooled mercury–cadmium–telluride (MCT) detector and a Hinds Instruments PEM-90 photoelastic modulator. The p-polarized light was incident at 80° . The spectra were collected for 1000 scans at a spectral resolution of 4 cm^{-1} .

Results and Discussion

Thicknesses of the Films. Measurements of the ellipsometric thicknesses of SAMs can provide a rough estimate of film quality.¹⁴ We compared the thicknesses of SAMs generated from the ADTCAs to the thicknesses of SAMs generated from their alkanethiol counterparts having the same number of carbon atoms. Figure 2 shows that the thicknesses of the two types of films are indistinguishable ($\pm 1 \text{ \AA}$). These results are consistent with a model in which the ADTCAs bind to the surface of gold in a fashion such that the alkyl chains are densely packed and oriented away from the surface.

Wettabilities of the Films. Contact angle measurements respond to changes in the quality and structure of organic thin films.¹⁴ We compared the wettabilities of SAMs generated from ADTCAs to the wettabilities of SAMs generated from the corresponding alkanethiols. The average advancing contact angle of water ($\theta_a \text{ H}_2\text{O}$) for the ADTCA SAMs was $115 \pm 2^\circ$; that for the alkanethiol SAMs was $114 \pm 2^\circ$, and thus indistinguishable (Figure 3). These data suggest that the interfaces formed by both types of SAMs are similarly hydrophobic.

The contact angles of dispersive liquids such as hexadecane (HD) are remarkably sensitive to the orientation and composition of low-energy surfaces generated by the adsorption of organic molecules.^{14,33,34} We compared the advancing contact angles of hexadecane (θ_a^{HD}) observed on the ADTCA SAMs with those observed on the corre-

sponding alkanethiol SAMs (Figure 4). Both types of SAMs exhibit a similar zigzag pattern where the value of the contact angles are higher on films composed of even-numbered carbon chain lengths and lower on films composed of odd-numbered carbon chain lengths. This type of “odd–even” effect has been observed in other studies of alkanethiol-based SAMs and is generally interpreted to reflect the increased wettability of methylene vs methyl groups exposed at the interface (Figure 5).^{33,34} The magnitude of the “odd–even” effect is, however, dramatically greater for ADTCA SAMs, where $\Delta\theta$ ($\theta_a^{\text{even}} - \theta_a^{\text{odd}}$) is approximately 9° ; $\Delta\theta$ for the alkanethiol SAMs is approximately 2° . This difference in magnitude suggests that the structural features of the ADTCA SAMs differ from those of the alkanethiol SAMs.

Characterization by PM-IRRAS. To confirm that the differences in wettability for the odd- and even-numbered ADTCA SAMs are due to orientational differences at the interfaces of these films, we examined two representative ADTCA SAMs by surface IR spectroscopy (PM-IRRAS). If the known “odd–even” effect is responsible for the observed differences in wettabilities, the relative intensities of the methyl symmetric C–H stretch, $\nu_s(\text{CH}_3)$, at 2878 cm^{-1} and the methyl asymmetric C–H stretch, $\nu_a(\text{CH}_3)$, at 2964 cm^{-1} should change as the orientation of the terminal methyl group changes (see Figure 5).^{33,35} Figure 6 shows the PM-IRRAS spectra of SAMs generated from $\text{CH}_3(\text{CH}_2)_{16}\text{CS}_2\text{H}$ (C18S₂H) and $\text{CH}_3(\text{CH}_2)_{17}\text{CS}_2\text{H}$ (C19S₂H). The spectrum of C18S₂H exhibits a $\nu_s(\text{CH}_3)$ stretch of higher intensity than the $\nu_a(\text{CH}_3)$ stretch. This ratio is consistent with a structure in which the terminal methyl group is oriented perpendicular (i.e., normal) to the surface. The spectrum of C19S₂H exhibits a substantial increase in the intensity of the $\nu_a(\text{CH}_3)$ stretch at the expense of the intensity of the $\nu_s(\text{CH}_3)$ stretch. This result is consistent with a tilting of the terminal methyl group away from the surface normal, which would expose the more wettable methylene moieties. Indeed, we observe increased wettabilities (lower contact angles) on the surfaces of the ADTCA SAMs having odd-numbered carbon chain lengths.

The enhanced “odd–even” effect observed for the ADTCA SAMs suggests that the alkyl chains are oriented differently than those of normal alkanethiolate SAMs. It seems plausible that chelation of type shown in Figure 5 could impose structural constraints (e.g., torsional stiffening) that would lead to the observed enhancement (*vide supra*). The potential for chelation in these new SAMs is particularly intriguing due to the known stability afforded by the entropy-driven “chelate effect”.^{36–40} The ability to

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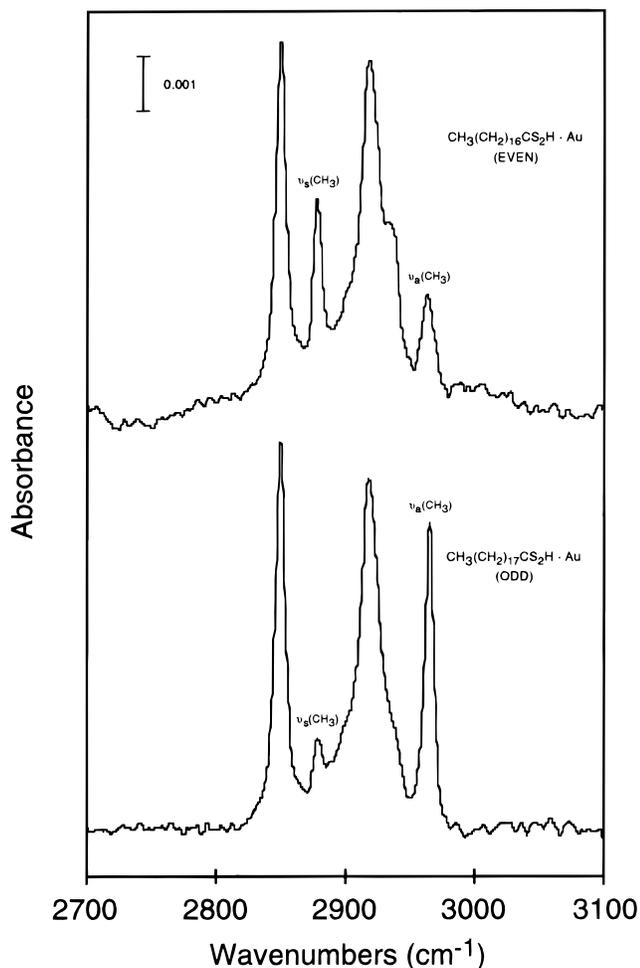


Figure 6. PM-IRRAS spectra of the C–H stretching region for SAMs derived from C18S₂H (upper) and C19S₂H (lower).

generate highly robust SAMs on gold will undoubtedly extend their use in the types of technologies noted in the Introduction. Furthermore, since the key step in our

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synthetic route to aliphatic dithiocarboxylic acids relies on simple Grignard addition to CS₂, the synthesis of ω -functionalized dithiocarboxylic acids (and thus new types of functionalized interfaces) appears tenable as long as compatible (or appropriately protected) ω -functional groups are employed during this step. We will explore these issues in future studies.

Conclusions

A series of aliphatic dithiocarboxylic acids were synthesized and used to generate SAMs on gold. Ellipsometric measurements confirmed that the ADTCAs adsorb onto gold as highly oriented monolayer films. Measurements of the advancing contact angle of water showed that the ADTCAs form hydrophobic interfaces consistent with methyl termination. Measurements of the advancing contact angle of hexadecane showed remarkably large “odd–even” effects for the ADTCA SAMs, which are also consistent with methyl termination. Characterization by PM-IRRAS provided structural support for the “odd–even” effect. Further analyses by PM-IRRAS,^{41,42} atomic force microscopy,²⁷ X-ray photoelectron spectroscopy,²³ and diffraction studies^{18,20} should provide more insight into the structural features (e.g., adsorption sites, chain tilt, and interchain packing) of this new class of SAM.

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Supporting Information Available: Procedures for the synthesis and purification of the dithiocarboxylic acids (4 pages). Ordering information is given on any current masthead page.

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