Tridentate Adsorbates with Cyclohexyl Headgroups Assembled on Gold

Burapol Singhana, Supachai Rittikulsittichai, and T. Randall Lee*

Department of Chemistry and the Texas Center for Superconductivity, University of Houston, Houston, Texas 77204-5003, United States

ABSTRACT: The tridentate adsorbates cyclohexane-cis,cis-1,3,5-triytrimethanethiol (CyTSH) and (cis,cis-1,3,5-trimethylcyclohexane-1,3,5-triy)trimethanethiol (3C1CyTSH) were designed and synthesized. Thin films prepared by the adsorption of these molecules onto the surface of gold were characterized by ellipsometry, contact angle goniometry, polarization modulation infrared reflection absorption spectroscopy, and X-ray photoelectron spectroscopy (XPS). CyTSH was found to generate multilayer thin films with many unbound thiol species and oxidized sulfur moieties (e.g., disulfides and sulfones). In contrast, 3C1CyTSH was found to generate monolayer films in which ~90% of the thiols were bound to the surface of gold (~10% unbound), and there were no oxidized sulfur species. In comparing CyTSH and 3C1CyTSH, the methyl groups of 3C1CyTSH impart rigidity to the structure, which significantly enhances the chemisorption of sulfur to the surface of gold. Ellipsometric measurements and analysis by XPS indicate that the thickness of the self-assembled monolayer formed from 3C1CyTSH is ~5 Å.

INTRODUCTION

Self-assembled monolayers (SAMs) are formed when amphiphilic molecules adsorb spontaneously onto the surface of an appropriate substrate. In particular, SAMs generated by the adsorption of alkanethiols on gold have been widely studied because of their facile generation, manipulation, and characterization.1–3 Furthermore, these SAMs have found use in a variety of applications, such as corrosion resistance,4 biointerface coatings,5 biosensors,6 and nanomedicine,7 as well as adhesion,8 friction and lubrication,9 lithographic patterning,10,11 electrode modification,12 and thin-film transistor applications.13–18

Despite the attractive properties of SAMs, their somewhat fragile nature remains a critical drawback for many applications.19–24 While some studies have reported that alkanethiolate SAMs exhibit moderate stability at room temperature, others have noted that SAMs desorb upon exposure to air in the absence of light over a span of a few days.25 Moreover, normal alkanethiol-based SAMs decompose rapidly upon heating at elevated temperatures (e.g., 80 °C in hexadecane).26–28 They also readily undergo displacement when exposed to organosulfur adsorbates in solution.21,24

To circumvent this problem, researchers have explored several strategies for generating thermally and chemically stable SAMs. One such strategy employed by our research team21,24,26–28 and others33–36 utilizes adsorbates with the capacity for multiple sulfur–gold interactions, which can afford SAMs with enhanced stability through the entropically driven “chelate effect”.21,24,26,28,30 Further, chelating adsorbates can be designed to resist the formation of intramolecular disulfides upon desorption from the surface, which provides additional stability to such multidentate SAMs.21,24,26,28,30

During the course of our earlier studies, we examined the stability of multidentate organosulfur adsorbates both on evaporated “flat” gold and on gold nanoparticles. As a whole, we found that SAMs generated from tridentate adsorbates are more thermally stable than those generated from bidentate adsorbates, which in turn are more stable than those generated from monodentate adsorbates.30,37 Furthermore, independent studies have found that long-chain alkanethiols fail to displace tridentate adsorbates under conditions where monodentate adsorbates were readily displaced.24,38 Of particular relevance, two adamantane-based tridentate adsorbates were used to generate SAMs on gold (see Figure 1a,b);38–40 for these adsorbates, all three thiomethyl legs bind to gold in a fashion similar to normal alkanethiols.39,40 However, save for their noted resistance to displacement,38 there have been no reports of the stability of the films generated from these adsorbates.

![Figure 1. Structures of tridentate adsorbates with cyclohexyl headgroups.](image-url)
In an effort to generate a synthetically accessible and chemically versatile class of multidentate thiol for preparing stable, well-defined SAMs on gold, we chose in the present study to explore a new adsorbate architecture in which a cyclohexane ring serves as a framework for linking thiol headgroups with synthetically variable tailgroups. Figure 1c,d shows the chemical structure of the first two examples of this class of adsorbate, where the top of the cyclohexane ring is unmodified (1c; CyTSH) or modified with three symmetrically equivalent methyl groups (1d; 3C1CyTSH).

There are at least five reasons that motivated us to choose a cyclohexane ring as the linking moiety. First, we anticipated that the geometry afforded by the 1,3,5-substituted cyclohexane ring would allow for adsorption of the headgroups to the surface of gold and simultaneous direction of the tailgroups away from the surface. Second, the three thiomethyl legs of the chelating adsorbate can plausibly bind simultaneously to the gold surface, thereby affording films with enhanced stability. Third, two or three distinct functional groups could be incorporated into the tailgroups of this adsorbate to afford chemically unique hybrid surfaces with functional groups that are homogeneously mixed at the molecular level (rather than phase separated). Fourth, we anticipated that the steric bulk of the cyclohexyl moiety would be sufficiently small to allow dense packing of the tailgroups and concomitant van der Waals stabilization. Finally, in contrast to the tridentate adamantane-thiols, which fail to form well-packed films due to insufficient interchain van der Waals interactions, our tridentate cyclohexyl-based alkanethiols can be synthesized to possess long alkyl tailgroups.

As part of our initial efforts to evaluate the capacity of these tridentate cyclohexyl-based alkanethiols to form SAMs, we describe in this report the self-assembly of CyTSH and 3C1CyTSH on the surface of gold. We characterize the resultant films by ellipsometry, contact angle goniometry, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS).

### EXPERIMENTAL SECTION

**Materials.** Gold (99.9%) shot was purchased from Americana Precious Metals. Chromium rods (99.9%) were obtained from R. D. Mathis Company. Polished single-crystal Si(100) wafers were purchased from NESTEC and rinsed with absolute ethanol (Aaper Alcohol and Chemical Co.) before use. 1,3,5-Benzenetricarboxylic acid (95%), 5% rhodium on activated alumina, boron trifluoride diethyl etherate, methanesulfonyl chloride (puriss, ≥ 99.0%), potassium thioacetate (98%), potassium thiocyanate (ACS reagent, ≥ 99.0%), dimethyl sulfate (≥ 99.8%), and 1,3-dimethyl-3,4,5,6-tetrahydro-2(1H)-pyrimidinone (absolute, over molecular sieve, ≥ 99.0%) were purchased from Sigma-Aldrich. Lithium aluminum hydride (LiAlH₄) was obtained from Alfa Aesar. All reagents were used as received without further purification unless otherwise specified.

**Synthesis of Tridentate Alkanethiol Adsorbates.** The adsorbates cyclohexane-cis,cis-1,3,5-triyethanethiol (CyTSH) and (cis,cis-1,3,5-trimethylcyclohexane-1,3,5-triyl)trimethanethiol (3C1CyTSH) were prepared using the strategy outlined in Scheme 1. Detailed experimental procedures and spectroscopic data are provided in the following paragraphs. While we provide only 1H NMR spectral data for each of the intermediates, we provide a more complete characterization (1H NMR spectroscopy, 13C NMR spectroscopy, FT-IR spectroscopy, and mass spectrometry) for the final adsorbate products CyTSH and 3C1CyTSH.

**cis,cis-Cyclohexane-1,3,5-tricarboxylic Acid (1).** A mixture of 7.50 g (3.57 mmol) of trimesic acid, 1.0 g of 5% rhodium on alumina, and 150 mL of water was hydrogenated at 70 °C and 50 psi of H₂. Uptake was complete in 48 h, and the filtrate was concentrated to give a white solid. Recrystallization from a 1:4 mixture of ethanol/toluene gave 4.50 g (20.8 mmol) of the cis,cis isomer (58% yield). 1H NMR
cis-cis-Trimethylcyclohexane-1,3,5-tricarboxylate (2). Anhydrous methanol was distilled over CaH₂ before use. cis-cis-Cyclohexane-1,3,5-tricarboxylic acid (1.0 g, 4.6 mmol) was heated under reflux for 6 h with boron trifluoride diethyl etherate (4.2 mL) in an excess of dry methanol (50 mL). The reaction mixture was cooled and poured into a saturated sodium bicarbonate solution. The organic phase was then extracted with diethyl ether and dried over Na₂SO₄. Removal of the ether afforded the crude trimethyl ester (1.05 g, 4.07 mmol, 88% yield). ¹H NMR (400 MHz, CD₃OD): δ 3.68 (s, 9H; 3COS₂CH₃), 2.36 (tt, J = 3, 13 Hz; 3H, 3Hₐx), 2.25-2.29 (m, 3H, 3Hₐx). ¹³C NMR (125 MHz, CDCl₃): δ 170.5 (3COS₂CH₃), 139.0 (3COS₂CH₃), 126.2 (3COS₂CH₃), 116.5 (3COS₂CH₃), 116.4 (3COS₂CH₃), 67.9 (3COS₂CH₃), 30.1 (3COS₂CH₃), 27.9 (3COS₂CH₃), 21.2 (3COS₂CH₃). IR (neat oil): 2915, 2892, 2841, 2560 cm⁻¹.

Trimethyl-cis-cis-1,3,5-trimethylcyclohexane-1,3,5-tricarbonyl (6). ⁴,³,⁵ Diisopropylamine was dried over molecular sieves before use. Lithium disopropylamide (LDA) was generated at 0 °C by the addition of 2.5 M BuLi in hexanes (5.11 mL, 12.8 mmol) to diisopropylamine (1.80 mL, 12.8 mmol) in 10 mL of dry diethyl ether. The mixture was stirred at 0 °C for 2 h. Then, 2 mL (21 mmol) of dimethylsulfate was added, and stirring was continued overnight at rt. The solution was washed with water, 1 N HCl, and brine, and it was dried over Na₂SO₄. After removal of the volatiles, 0.85 g of oil was obtained. Fractional recrystallization from 1:1 pentane/diethyl ether afforded the pure cis-cis isomer as a white solid (0.54 g, 1.8 mmol, 47% yield). ¹H NMR (300 MHz, CDCl₃): δ 3.66 (m, 9H; 3SCO₂CH₂), 2.73 (d, J = 15 Hz, 3H, 3Hₐx), 1.21 (m, 9H; 3CH₃), 0.96 (d, J = 15 Hz, 3H, 3Hₐx).

cis-cis-1,3,5-Trimethylcyclohexane-1,3,5-triyltrimethanol (7). This intermediate was prepared in 88% yield as a white solid (0.63 g, 2.9 mmol) from 6 (1.0 g, 3.3 mmol) and LiAlH₄ (1.8 g, 48 mmol) in dry THF (20 mL) using the procedure described above for the synthesis of 3. ¹H NMR (300 MHz, CDOD): δ 3.12 (s, 6H; 3CH₂OH), 1.24 (d, J = 14 Hz, 3H, 3Hₐx), 1.08 (m, 12H; 3CH₃ + 3CH₅). ¹³C NMR (125 MHz, CDCl₃): δ 78.9 (3CH₂OH), 63.0 (3CH₂OH), 56.2 (3CH₂OH), 37.0 (3CH₂OH), 29.1 (3CH₂OH), 26.7 (3CH₂OH), 26.6 (3CH₂OH).

cis-cis-1,3,5-Trimethylcyclohexane-1,3,5-triyl[methylene]trimethanesulfonate (8). This intermediate was prepared in 90% yield as a white solid (2.27 g, 5.04 mmol) from trialetic 7 (1.21 g, 5.59 mmol) in dry THF (100 mL), triethylamine, and methanesulfonyl chloride (3.9 g, 31 mmol) using the procedure described above for the synthesis of 4. ¹H NMR (300 MHz, CDCl₃): δ 3.91 (s, 6H; 3CH₂SO₃CH₂), 3.12 (s, 9H; 3SO₂CH₃), 1.48 (d, J = 14 Hz, 3H, 3Hₐx), 1.34 (d, J = 14 Hz, 3H, 3Hₐx), 1.32 (s, 9H; 3CH₃). ¹³C NMR (125 MHz, CDCl₃): δ 72.9 (s, 6H; 3CH₂SO₃CH₂), 2.36 (s, 9H; 3SO₂CH₃), 1.33 (d, J = 14 Hz, 3H, 3Hₐx), 1.11 (m, 12H; 3CH₃ + 3CH₅).

(cis-cis-1,3,5-Trimethylcyclohexane-1,3,5-triyl)[methylene]trimethanol (9). A mixture of 8 (0.859 g, 1.90 mmol) and potassium thioacetate (KSCa, 6.53 g, 57.2 mmol) in anhydrous DMPU (30 mL) was stirred at 110 °C for 3 days. After cooling to rt, the solution was poured into water and extracted with DCM (3 × 100 mL). The combined organic phases were washed with water several times to remove the DMPU and then washed with saturated brine, dried over MgSO₄ and concentrated to dryness. The crude product was purified by column chromatography on silica gel, eluting with a mixture of 8.3% ethyl acetate in hexanes to afford 9 as a colorless oil (0.21 g, 0.54 mmol) in 40% yield. ¹H NMR (400 MHz, CDCl₃): δ 2.08 (s, J = 6 Hz, 6H; 3CH₂SO₃CH₂), 0.82 (q, J = 12 Hz, 3H, 3Hₐx). ¹³C NMR (125 MHz, CDCl₃): δ 42.3, 41.1, 35.3, 26.70 IR (KBr, neat): 3100, 2952, 2911, 2558 cm⁻¹.

Substrate Preparation. Gold surfaces were prepared by the thermal evaporation of chromium (ca. 100 Å) under high vacuum at a pressure of ~6 × 10⁻⁶ Torr onto silicon wafers. Chromium was used as a primer to promote the adhesion of gold to the surface of silicon. A gold film having a thickness of approximately 2000 Å was deposited on the chromium at a rate of 1 Å/s. The substrates were rinsed with absolute ethanol and dried under a stream of ultrapure nitrogen before use.

Preparation of SAMs. Solutions of the thiols were prepared in beaten bottles that were cleaned by soaking overnight in "piranha solution" (3:1 mixture of concentrated H₂SO₄/30% H₂O₂). Caution: "piranha solution" reacts violently with organic materials and should be handled carefully. The bottles were then thoroughly rinsed with deionized water and absolute ethanol and then dried overnight at 100
°C. The gold-coated wafers were cut into slides (ca. 1 cm x 3 cm) and then rinsed with absolute ethanol and blown dry with ultrapure nitrogen before immersing in the thiol solutions. All substrates were allowed to equilibrate for a period of 48 h. The resultant SAMs were thoroughly rinsed with THF and absolute ethanol and then blown dry with ultrapure nitrogen before characterization.

**Measurements of Ellipsometric Thickness.** The thicknesses of the monolayers were measured using a Rudolf Research Auto ELIII ellipsometer equipped with a He–Ne laser operating at 632.8 nm and an incident angle of 70°. The optical constants of the bare gold were measured immediately after evaporation. For each sample, data collected from measurements on two separate slides with at least three spots per slide were averaged. The thicknesses of the monolayers were calculated assuming a refractive index of 1.45 for all monolayers. The thickness values obtained by ellipsometry were compared to those calculated from XPS measurements (vide infra).

**Contact Angle Measurements.** Contact angles were measured using a Rame–Hart model 100 contact angle goniometer at room temperature (ca. 293 K). The contacting liquids (water, hexadecane, decalin, and disopropyl ether) were dispensed and withdrawn using a Matrix Technologies micro-Electrapette 25 operated at the slowest possible speed (ca. 1 μL/s), and the advancing angle (θ) was measured while the pipet tip was kept in contact with the drop. For each type of monolayer film, contact angles were averaged from the collected measurements on two separate slides using at least three drops per slide.

**Fourier Transform IR Spectroscopy.** The bulk IR spectrum of 3C1CyTSH was collected using a Nicolet Nexus-IR 670 Fourier transform (FT) spectrometer. A 500 mg portion of dry spectra-grade KBr was ground in a clean mortar and pressed to 10 000 L/s), and the advancing angle of 84.0° as a reference binding energy for standard analysis by XPS. Based on previous electron diffraction and low energy helium defraction studies of the structure of normal alkane thiolate SAMs on gold, the sulfur–sulfur spacing is ~5 Å with the sulfur atoms bound to the 3-fold hollow sites on Au(111). To the best of our knowledge, there have been no reports of adsorbates having a cyclohexane framework such as those shown in Figure 1c,d. However, we note that the structurally related adamanathetriithiol derivatives reported by Whitesell and Kitagawa (Figure 1a,b) would also generate SAMs on gold with an S–S spacing of ~5.0 Å, which is identical to the interatomic distance between sulfur atoms in normal alkane thiolate SAMs on Au(111). Based on scanning tunneling microscopy data, the authors proposed that all three sulfur atoms of the adamantathetriithiol were bound to the surface of gold.

These previous studies led us to hypothesize that CyTSH and 3C1CyTSH would also generate SAMs on gold with all three sulfur atoms bound to gold—a condition essential for generating stable monolayer coatings. We therefore sought to characterize the nature of the sulfur atoms in films derived from CyTSH and 3C1CyTSH. To this end, we explored the use of various solvents from which to generate optimal SAMs from these adsorbates, relying on studies by XPS to characterize the nature of sulfur–gold binding (i.e., bound vs unbound thiol). Further, because our ultimate studies will utilize SAMs formed from adsorbates with long and chemically varied tailgroups, we focused our initial survey studies on thin films formed from CyTSH and particularly 3C1CyTSH.

The chemisorption between sulfur and gold surfaces in SAMs can be monitored using the XPS binding energies, which can be used to determine more broadly the chemical composition on the surface. Thus, by monitoring the S2p region of the XPS spectra, the binding of the sulfur headgroup to the gold substrate can be evaluated. In the XPS spectra of SAMs generated from alkane thiols on gold, the binding energy of the S2p1/2 and S2p3/2 peaks for thiols bound to gold is known to be 162 and 163.2 eV, respectively. In contrast, the S2p1/2 and S2p3/2 peaks for unbound thiols or disulfide species on the surface appear roughly at 164 and 165 eV, respectively. Therefore, incomplete adsorbate binding on gold can be identified and quantified by the presence of the S2p peak at 164 eV. Moreover, oxidized sulfur species (S2p BE > 166 eV) can also be detected by XPS. Thus, we used XPS to characterize the SAMs generated from 3C1CyTSH upon adsorption from various organic solvents (Figure 2).

Previous studies of the generation of SAMs from multidentate adsorbates have found that the solvent used for the adsorption can strongly influence the percentage of bound versus unbound sulfur in the resultant SAM. To this end, we first explored the use of ethanol as a solvent from which to adsorb 3C1CyTSH because ethanol is the most widely used solvent for preparing SAMs on gold. The popularity of ethanol can be attributed to its relatively low price, its availability in high purity, and its low toxicity. In addition, ethanol has a low tendency to be incorporated into SAMs and is known to form robust and fully bound normal alkane mono-, di-, and trithiols SAMs on gold. Other solvents that we used to adsorb 3C1CyTSH onto gold included the polar aprotic solvents THF and DMF, which have been used previously to form fully bound bidentate and tridentate SAMs.
on gold.\textsuperscript{30} We also examined the adsorption of 3C1CyTSH from isopropyl ether and toluene.

For all of these studies, the gold substrates were immersed in 1 mM solutions of 3C1CyTSH and allowed to equilibrate for 48 h. The slides were exhaustively rinsed with THF, toluene, and ethanol and then dried under a vigorous stream of ultrapure nitrogen before analysis by XPS.

The XPS spectra of SAMs generated from 3C1CyTSH in various solvents are shown in Figure 2, with a focus on the S\textsubscript{2p} region. For all of the samples, the S\textsubscript{2p} peaks exhibit some degree of intensity at 164 eV, indicating incomplete binding of the adsorbate to gold. The relative amounts of bound and unbound sulfur were deconvoluted using standard XPS software processing and are summarized in Table 1. Although none of the samples show completely bound thiolates for 3C1CyTSH, the adsorption from THF appears to be optimal, with \textasciitilde 90\% of the sulfur atoms bound to gold. Although a comprehensive understanding of the mechanism by which the solvent influences the formation of SAMs on gold remains obscure,\textsuperscript{1} the good solubility of the adsorbates in THF, together with the ability of polar solvents such as THF to stabilize partial charge separation in the adsorption step,\textsuperscript{49} might contribute to the observed superior performance of THF in the generation of SAMs on gold from 3C1CyTSH.

To examine whether the methyl groups play any role in the chemisorption of sulfur to gold, we prepared the CyTSH film in the same manner as that used to prepare the optimal 3C1CyTSH SAM (i.e., using THF as a solvent). XPS spectra of the S\textsubscript{2p} region for the CyTSH films are displayed in Figure 3c, together with the corresponding data for SAMs derived analogously from octadecanethiol (Figure 3a) and 3C1CyTSH (Figure 3b). The XPS spectra of the films derived from CyTSH (Figure 3c) show a high intensity S\textsubscript{2p} peak at \textasciitilde 164 eV, indicating substantial unbound thiol and/or disulfide species (\textasciitilde 80\%) and some bound thiolate (\textasciitilde 20\%) in the film. Further, the peaks at 166–170 eV suggest the presence of oxidized sulfur species (e.g., sulfones).\textsuperscript{45,47} Based on our observations, molecular CyTSH is stable under ambient conditions. However, SAMs derived from CyTSH readily undergo partial oxidation when exposed to oxygen and light.\textsuperscript{50} In an effort to decrease the amount of oxidized sulfur species, we generated films from CyTSH in degassed THF, under nitrogen, and in the absence of light for 48 h at room temperature. Under these “inert” conditions, we found that the amount of oxidized sulfur species and unbound thiol (\textasciitilde 60\%) decreased, while the amount of bound thiolate (\textasciitilde 40\%) increased (see Figure 3d).

On the whole, comparison of the data collected for SAMs derived from 3C1CyTSH and CyTSH suggests that the methyl groups on the cyclohexane ring of 3C1CyTSH significantly enhance the chemisorption of sulfur to gold for this class of adsorbate. It is possible, for example, that the presence of the methyl groups gives rise to minor conformers in which the methylene thiol moieties occupy axial positions (Scheme 2).\textsuperscript{31,52} This arrangement facilitates the binding of the thiols to gold. In contrast, the absence of the methyl groups in CyTSH gives rise to exclusively equatorial conformations for the methylene thiols, which allows for one or more of the methylene thiols to orient away from the surface upon initial chemisorption. This hypothesis is consistent with the XPS data shown in Figure 3. Finally, the presence of oxidized sulfur species (e.g., disulfides and sulfones) in the films formed from CyTSH is likely due to oxidation of the unbound thiols of CyTSH (vide supra). Finally, although the axial hydrogens of bound 3C1CyTSH might come close to the surface of gold, this potential interaction appears to give rise to no significant repulsion, which is supported by the observed high percentage of bound thiolate indicated by XPS for this SAM when adsorbed from THF (\textasciitilde 90\%).

Table 1. Relative Amounts of Bound vs Unbound Sulfur Species Obtained from Deconvolution of the XPS Spectra in Figure 2

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>solvent</th>
<th>% bound thiolate</th>
<th>% unbound thiol</th>
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<tbody>
<tr>
<td>3C1CyTSH</td>
<td>THF</td>
<td>89</td>
<td>11</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>EtOH</td>
<td>79</td>
<td>21</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>i-Pr ether</td>
<td>73</td>
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<td>3C1CyTSH</td>
<td>DMF</td>
<td>70</td>
<td>30</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>toluene</td>
<td>68</td>
<td>32</td>
</tr>
</tbody>
</table>

Chemical and Orientational Analysis by IR Spectroscopy. Figure 4 shows the spectra collected by transmission IR spectroscopy and PM-IRRAS for neat 3C1CyTSH and for the SAM derived from this adsorbate. The S–H vibrations, observed at \textasciitilde 2558 cm\textsuperscript{-1} in the neat transmission IR spectrum,\textsuperscript{58} were absent in the PM-IRRAS spectrum of the SAMs (Figure 4). The loss of the S–H peaks upon adsorption is consistent with the molecules attaching to gold via the three sulfur atoms in a tripodlike, perpendicular orientation.\textsuperscript{39}

For many SAMs, the molecular orientation can be elucidated by monitoring the C–H stretching region of the surface IR spectra.\textsuperscript{27,29,30,53,54} In most cases, the frequency, bandwidth, and intensity of the methylene antisymmetric and symmetric bands (\(\nu_2^{\text{CH}_2}\) at \textasciitilde 2918 cm\textsuperscript{-1} and \(\nu_4^{\text{CH}_2}\) at \textasciitilde 2850 cm\textsuperscript{-1}) and the methyl antisymmetric and symmetric bands (\(\nu_3^{\text{CH}_3}\) at \textasciitilde 2956 cm\textsuperscript{-1} and \(\nu_4^{\text{CH}_3}\) at \textasciitilde 2866 cm\textsuperscript{-1}) are strongly influenced by the
orientation(s) of the adsorbed molecules. For SAMs derived from normal alkanethiols, the \( \nu_{\text{as}} \text{CH}_2 \) and \( \nu_{\text{s}} \text{CH}_3 \) transition dipoles are oriented nearly parallel to the surface normal (true for \( \nu_{\text{s}} \text{CH}_3 \) especially for even-numbered SAMs) leading to strong absorptions for these modes. For 3C3CyTSH, however, the intensity of the \( \nu_{\text{as}} \text{CH}_2 \) band weakens upon adsorption while the intensity of the \( \nu_{\text{s}} \text{CH}_3 \) remains relatively strong (see Figure 4). These results provide strong support that 3C3CyTSH binds to the gold surface with the methylene thiol moieties pointed downward and the methyl groups pointed upward, but tilted from the surface normal (i.e., equatorial rather than axial conformations for the methyl groups; see Scheme 2).

Figure 3. XPS spectra of films generated from (a) octadecanethiol (C18SH) in ethanol, and (b) 3C1CyTSH and (c, d) CyTSH in THF. Ambient laboratory conditions were 25 °C, light, and air. Green and pink lines represent \( S_{2p3/2} \) and \( S_{2p1/2} \) for bound thiolate, respectively. Purple and navy lines represent \( S_{2p3/2} \) and \( S_{2p1/2} \) for unbound thiol and/or disulfide species, respectively.

Scheme 2. Axial and Equatorial Conformations of 3C1CyTSH and CyTSH

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the principle tools used to determine the average monolayer 
Fere to 84.0 eV as a reference. Also, 
set the 
In this procedure, we measured the intensities of the Au4f peak 
values,34 we also used XPS to determine the thickness of 
composition can substantially 
examined. However, since the surface coverage and chemical 


Figure 4. Comparison of the C–H stretching region between the 
transmission FT-IR spectrum of 3C1CyTSH as neat oil and the PM-
IRRAS spectrum of the 3C1CyTSH SAM derived from 3C1CyTSH in 


Figure 5. C–H stretching region of the PM-IRRAS spectra of 
thin films derived from 3C1CyTSH to those of films derived 
from n-octadecanethiol (C18SH) and CyTSH. Notably, the 
band at ~2957 cm⁻¹ is absent in the spectrum for CyTSH, which supports our assignment of this band as ν CH₂ 
for 3C1CyTSH.

Measurements of Film Thickness. Ellipsometry is one of the 
principal tools used to determine the average monolayer 
thickness and follow the progress of the film growth.34 In the 
present study, we assumed a refractive index of 1.45 for all 
films examined. However, since the surface coverage and chemical composition can substantially influence the refractive index 
values,36 we also used XPS to determine the thickness of films. 
In these measurements, the amount of adsorbate on the surface 
of the gold substrate can attenuate the XPS signal for Au. Thus, 
the thickness of monolayer films can be calculated using the 
relative intensities of Au 4f and C 1s peaks from the XPS spectra. 
In this procedure, we measured the intensities of the Au 4f peak 
of the underlying gold substrate for each sample and set the 
binding energy of the Au 4f peak to 84.0 eV as a reference. Also, 
we used the monolayer derived from C18SH (with a known 
thickness of 22 Å)⁴⁸ as a standard for comparison. The film 
thicknesses were calculated using eq 1:

\[
\frac{\delta_{R}^2}{\delta_{S}^2} = \frac{1 - e^{-d_{s}/\lambda_{c}(\text{Au})}}{e^{-d_{s}/\lambda_{c}(\text{Au})}} \frac{1 - e^{-d_{R}^{R}/\lambda_{c}(\text{Au})}}{1 - e^{-d_{R}^{R}/\lambda_{c}(\text{Au})}}
\]

where \(d_{R}\) is the thickness of the C18SH SAM, \(d_{S}\) is the 


Table 2. Thickness of SAMs Determined by Ellipsometry 
and by XPS

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>solvent</th>
<th>thickness (Å)</th>
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<tbody>
<tr>
<td>C18SH</td>
<td>EtOH</td>
<td>21</td>
</tr>
<tr>
<td>CyTSH</td>
<td>THF</td>
<td>13</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>THF</td>
<td>5</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>EtOH</td>
<td>4</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>i-Pr ether</td>
<td>6</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>DME</td>
<td>3</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>toluene</td>
<td>4</td>
</tr>
</tbody>
</table>

*Measured values were reproducible within ±2 Å of the reported values.

that the methods are largely consistent. Notably, 3C1CyTSH 
generates a monolayer film that is thinner than the SAM 
generated by C18SH. This result was expected given that 
3C1CyTSH possesses roughly a 3-carbon chain length while 
C18SH possesses an 18-carbon chain length. Importantly, the 
thickness of the 3C1CyTSH SAM (5 ± 1 Å) is consistent with 
its molecular dimensions calculated by molecular modeling 
assuming a planar conformation.⁶⁷ In contrast, the CyTSH 
adsorbate, which generates films with thicknesses ranging from 11 
to 15 Å, appears to form multilayer films via the formation of 
intermolecular disulﬁdes as indicated by the XPS data in Figure 
3c.d.

Interfacial Wettability. The wettability of the films was 
explored using water, hexadecane, decalin, and disopropyl 
ether as contacting liquids. The results of contact angle 
measurement are displayed in Table 3. The contact angles of 

Table 3. Advancing Contact Angles (\(\theta_a\)) of Water (H₂O), 
Hexadecane (HD), Decalin (DL), and Disopropyl ether (DIPE) 
on SAMs Derived from the Adsorption of C18SH in EtOH and CyTSH and 3C1CyTSH in THF

<table>
<thead>
<tr>
<th>adsorbate</th>
<th>solvent</th>
<th>contact angle ((\theta_a))</th>
<th>HD</th>
<th>DL</th>
<th>DIPE</th>
</tr>
</thead>
<tbody>
<tr>
<td>C18SH</td>
<td>H₂O</td>
<td>114</td>
<td>50</td>
<td>54</td>
<td>...</td>
</tr>
<tr>
<td>CyTSH</td>
<td>HD</td>
<td>74</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>3C1CyTSH</td>
<td>HD</td>
<td>78</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
<tr>
<td>bare gold</td>
<td>HD</td>
<td>74</td>
<td>...</td>
<td>...</td>
<td>...</td>
</tr>
</tbody>
</table>

*The symbol --- indicates that the film was wet by the contacting liquid (\(\theta_a < 10^\circ\)).
the films generated from CyTSH are low (comparable to “bare” gold) due to the presence of oxidized sulfur species as indicated by the XPS analyses described above. In contrast, the low contact angle values for the films generated from 3CICyTSH can be attributed to the fact that these films are extremely thin. Consequently, the probe liquids interact strongly with the underlying gold surface, which enhances the wettability of the films. This interpretation is consistent with XPS and ellipsometric thickness values.

**CONCLUSIONS**

Two tridentate alkanethiols with cyclohexyl headgroups were synthesized and used to prepare thin films on gold, which were characterized by ellipsometry, contact angle goniometry, PM-IRRAS, and XPS. While the adsorption of CyTSH led to multilayer films containing oxidized sulfur species, the adsorption of 3CICyTSH led to monolayer films with ~90% of the sulfur atoms bound to gold. The striking difference can be attributed to the presence of the methyl groups in 3CICyTSH, which restrict the conformational flexibility of the cyclohexane ring and thereby significantly enhance its chemisorption to gold. When taken as a whole, the results suggest that the tridentate 3CICyTSH architecture can be used to generate strongly bound SAMs on gold.

**AUTHOR INFORMATION**

**Corresponding Author**
*E-mail: trlee@uh.edu.*

**Notes**
The authors declare no competing financial interest.

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