

Chelating Self-Assembled Monolayers on Gold Generated from Spiroalkanedithiols

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The formation of self-assembled monolayers (SAMs) on gold from the adsorption of a series of specifically designed 2,2-dialkylpropanedithiol derivatives, $[\text{CH}_3(\text{CH}_2)_n]_2\text{C}[\text{CH}_2\text{SH}]_2$ where $n = 0, 3, 7,$ and $11-15,$ is reported. The SAMs were characterized by optical ellipsometry, contact angle goniometry, and polarization modulation infrared reflection absorption spectroscopy. These data, when compared to those collected on SAMs generated from normal alkanethiols ($\text{CH}_3(\text{CH}_2)_m\text{SH}$) of similar chain length, suggest that the new SAMs are highly oriented and well packed. They exhibit, however, slightly less crystallinity than their alkanethiolate-based analogues. A preliminary description of the kinetics of adsorption and desorption of these new SAMs is presented.

Introduction

The spontaneous adsorption of organic molecules onto solid surfaces leads to the formation of self-assembled monolayers (SAMs).^{1,2} Since structurally and chemically well-defined thin films can be constructed using this technique, SAMs have found use in a number of technologies ranging from corrosion prevention^{3,4} to lithographic patterning.^{5,6} Typical SAMs include alkanethiolates on gold, silver, and copper, as well as carboxylic acids on alumina.^{1,7}

A major objective of our research is to synthesize and study new types of SAMs generated by the adsorption of chelating organosulfur moieties onto gold.^{8,9} Other groups have also explored chelating approaches to SAMs on gold.¹⁰⁻¹⁴ We are motivated by the belief that chelating SAMs will exhibit enhanced stabilities^{15,16} and greater compositional flexibilities than those generated from normal alkanethiols.¹⁷⁻¹⁹ It is known from studies in coordination chemistry, for example, that metal complexes

possessing chelating ligands exhibit enhanced stabilities when compared to their nonchelating analogues.²⁰ We believe that this entropy-driven effect should also characterize SAMs formed from appropriately designed chelating moieties. In addition, because of potential ring strain,²¹ the chelates can be designed to resist the formation of intramolecular disulfides upon desorption from the surface. If the mechanism of decomposition of alkanethiolate-based SAMs on gold proceeds via desorption as disulfides,²² this feature should afford additional stability to the chelating SAMs.

We recently reported the formation of a new class of chelating SAM from the adsorption of aromatic dithiols on gold.⁸ Our studies showed that 1,2-bis(mercapto-methyl)-4,5-dialkylbenzenes can be used to generate well-packed and highly oriented monolayers on gold similar to those generated from corresponding normal alkanethiols having similar chain lengths. Furthermore, preliminary studies of thermal desorption in solution suggest that these new chelating SAMs are more robust than normal SAMs.

As an extension of our studies of chelating SAMs, we report here a new strategy involving the generation of SAMs from 2,2-dialkylpropanedithiols (spiroalkanedithiols, **1-8**) as shown in Figure 1. A major attractive feature of this system is the ease and flexibility of the synthetic approach, which provides the targeted compounds in high yields and purities using relatively few steps (vide infra). Indeed, our synthetic approach, which is based on traditional malonic ester manipulations, offers the facile opportunity to generate a wide variety of substrates, including asymmetric moieties for future studies of homogeneously mixed multicomponent SAMs. Attempts to generate multicomponent interfaces from the adsorption of mixtures of two or more alkanethiols, in contrast, often lead to inhomogeneous mixing¹⁷ as well as islanding.^{18,19}

Studies of spiroalkanedithiol-based SAMs should also allow us to explore one of the remaining controversies

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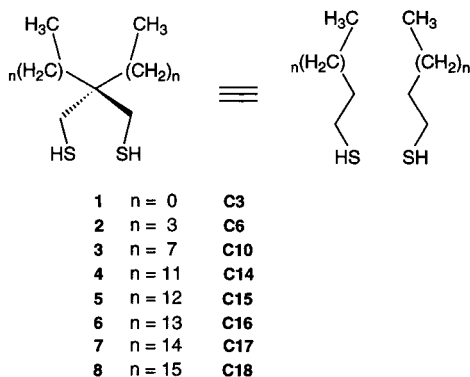


Figure 1. Structures of the spiroalkanedithiols and corresponding normal alkanedithiols used for generating SAMs on gold. For both types of adsorbates, the number of carbon atoms per chain is considered to be the same for a given value of n .

regarding the structure of SAMs on gold. Fenter, Scoles, and colleagues have identified a dimerized structure for the sulfur atoms in normal SAMs on gold.²³ In contrast, others have proposed that the sulfur atoms bind to the 3-fold hollow sites of Au(111) with a spacing of 4.99 Å.^{1,24} Molecular modeling of our spiroalkanedithiols shows that the distance spanned by the two sulfur atoms can extend only as far as 4.8 Å without introducing bond-angle strain.²⁵ The modeling studies suggest, therefore, that the spiroalkanedithiols are incapable of facile binding to gold in the 3-fold hollows. Furthermore, because of ring strain (as much as 3.6 kcal/mol),²¹ the spiroalkanedithiols are unlikely to undergo intramolecular disulfide formation on the surface. Taken together, these factors suggest that the structures of SAMs generated from the spiroalkanedithiols should prove to be unique and might lead to a better understanding of the factors that influence the structural features of normal SAMs on gold.

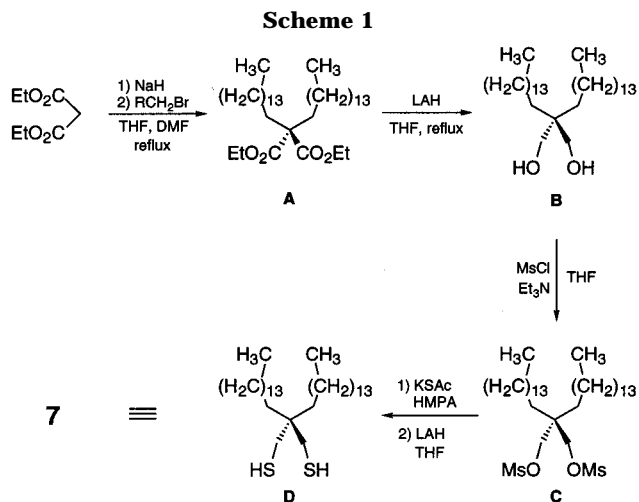
Experimental Section

Materials and Methods. Gold shot (99.99%) was purchased from Americana Precious Metals, and polished single-crystal silicon(100) wafers were purchased from Silicon Sense, Inc. The water (H₂O) and hexadecane (HD) used for the contact angle measurements were of the highest purity available from Aldrich Chemical Co. Dimethylformamide (DMF) and tetrahydrofuran (THF) were purchased from EM Sciences; THF was dried by passage through alumina before use. Hexamethylphosphoramide (HMPA), triethylamine, methanesulfonyl chloride, diethyl malonate, sodium hydride (NaH), lithium aluminum hydride (LAH), and potassium thioacetate (KSAC) were purchased from Aldrich Chemical Co. and used as received. HMPA was dried over calcium hydride and then transferred to a Schlenk flask containing Na under argon. After 24 h, HMPA was distilled and stored under argon. The normal alkanedithiols used in the preparation of SAMs were either commercially available or synthesized using known methods. In the syntheses of the spiroalkanedithiols, the starting bromoalkanes were of the highest purity available from Aldrich Chemical Co. 2,2-Dimethyl-1,3-propanedithiol (**1**) was prepared from 2,2-dimethyl-1,3-propanediol (Acros) using unexceptional methods. Column chromatography was carried out using silica gel (60–200 mesh) purchased from EM Sciences. Thin-layer chromatography (TLC) was carried out using 250-mm-thick Whatman silica gel plates. The eluted TLC plates were analyzed under an ultraviolet lamp or in an iodine chamber. Nuclear magnetic resonance (NMR) spectra were recorded on a General Electric QE-300 spectrometer

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operating at 300 MHz for ¹H and 75 MHz for ¹³C nuclei. The data were collected in CDCl₃ and referenced to δ 7.26 for ¹H and δ 77.00 for ¹³C spectra. Elemental analyses were performed by National Chemical Consulting, Inc. High-resolution mass spectra were obtained at Rice University on a Finniganmat MAT 95 mass spectrometer operating in the EI mode.

Synthesis of Spiroalkanedithiols. The strategy used to synthesize the spiroalkanedithiols is shown in Scheme 1 using compound **7** as a representative target. For each step, a general procedure is provided below; complete analytical data are provided for all dithiol final products.

Diethyl 2,2-Dipentadecylmalonate (A). A solution of NaH (2.40 g, 60.0 mmol) in THF (100 mL) and DMF (30 mL) was prepared at 0 °C under argon. To this solution was added slowly diethyl malonate (3.32 g, 20.7 mmol). The mixture was stirred at room temperature for 15 min, then bromopentadecane (17.48 g, 60.00 mmol) was added, and the mixture was heated under reflux for 6 h. The reaction mixture was concentrated in vacuo, and the resultant oil was suspended in 100 mL of water. The mixture was extracted first with pentane (2 × 100 mL) and then with a 1:1 mixture of pentane/diethyl ether (1 × 100 mL). The organic layers were washed with H₂O (3 × 50 mL), dried over MgSO₄, and evaporated to dryness. The crude products were purified by column chromatography on silica gel (hexane/diethyl ether, 1/0 → 10/1), affording diethyl 2,2-dipentadecylmalonate in 93% yield. ¹H NMR (300 MHz, CDCl₃): δ 4.16 (q, $J = 8.0$ Hz, 4 H, OCH₂), 1.85 (t, $J = 8.3$ Hz, 4 H, CH₂C), 1.45–1.21 (m, 52 H), 1.23 (t, $J = 8.0$ Hz, 6 H, CH₃), 0.88 (t, $J = 8.0$ Hz, 6 H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 172.07, 60.89, 32.07, 31.95, 31.59, 29.93, 29.85, 29.69, 29.54, 29.36, 22.69, 14.11.

2,2-Dipentadecyl-1,3-propanediol (B). Lithium aluminum hydride (1.20 g, 31.7 mmol) was added to a solution of diester **A** (4.60 g, 7.93 mmol) in THF at room temperature, and the reaction mixture was heated under reflux for 2 h. The reaction was quenched with 200 mL of a 1 M HCl solution and stirred for 30 min. The aqueous layer was extracted with diethyl ether (3 × 75 mL). The combined organic layers were washed with a dilute HCl solution (2 × 75 mL) and brine (1 × 75 mL) and then dried over MgSO₄. Removal of the solvents under vacuum afforded crude 2,2-dipentadecyl-1,3-propanediol in 94% yield. ¹H NMR (300 MHz, CDCl₃): δ 3.57 (s, 4 H, OCH₂), 1.42–1.20 (m, 56 H), 0.88 (t, $J = 8.0$ Hz, 6 H, CH₃). ¹³C NMR (75 MHz, CDCl₃): δ 69.57, 31.94, 30.80, 30.58, 29.71, 29.61, 29.54, 29.46, 29.38, 22.69, 14.13.

2,2-Dipentadecyl-1,3-propanedimesylate (C). A solution of diol **B** (3.32 g, 6.69 mmol) and triethylamine (1.69 g, 16.7 mmol) in THF was prepared. To the stirred mixture was added dropwise over 5 min 1.92 g (16.7 mmol) of methanesulfonyl chloride. After the addition was complete, stirring was continued for 2 h. Ice cold water (100 mL) was poured into the reaction mixture to destroy any excess methanesulfonyl chloride. The aqueous layer was separated from the organic layer and extracted with diethyl ether (3 × 50 mL). The organic phases were combined and washed with dilute HCl (1 × 50 mL), H₂O (1 × 50 mL), saturated NaHCO₃ (2 × 50 mL), and H₂O (1 × 50 mL). The organic layer was dried

over MgSO_4 , and the solvent was removed by rotary evaporation to give the crude product in 98% yield. ^1H NMR (300 MHz, CDCl_3): δ 4.03 (s, 4 H, OCH_2), 3.03 (s, 6 H, OMs), 1.41–1.20 (m, 56 H), 0.88 (t, $J = 8.0$ Hz, 6 H, CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 70.47, 37.15, 31.91, 30.07, 29.77, 29.68, 29.55, 29.49, 29.38, 29.31, 22.68, 14.08.

2,2-Dipentadecyl-1,3-propanedithiol (D or 7). Potassium thioacetate (1.38 g, 12.1 mmol) and dimesylate C (3.14 g, 4.82 mmol) were placed in 50 mL of HMPA under argon. The reaction mixture was heated to 120 °C for 20 h under argon. The organic phases were combined with H_2O (100 mL), and the mixture was extracted with diethyl ether (3×100 mL). The organic phases were washed with H_2O (3×100 mL) and then dried over MgSO_4 . The crude products were dissolved in THF, and LAH (457 mg, 12.1 mmol) was added to the reaction mixture at room temperature. The mixture was heated under reflux for 2 h and then quenched under argon with ethanol (20 mL; previously degassed by bubbling with argon). After the reaction mixture was stirred for 10 min, it was acidified to ca. pH 1 with a 1 M HCl solution. The aqueous layer was extracted with diethyl ether (3×50 mL). The combined organic layers were washed with a dilute HCl solution (2×50 mL) and brine (1×50 mL) and then dried over MgSO_4 . The solvents were evaporated under vacuum, and the crude products were purified by column chromatography on silica gel (hexane/diethyl ether, 1/0 → 99/1), affording 2,2-dipentadecyl-1,3-propanedithiol in ca. 82% yield. The products usually contained about 1–5% of the corresponding disulfide. ^1H NMR (300 MHz, CDCl_3): δ 2.52 (d, $J = 9.3$ Hz, 4 H, SCH_2), 1.38–1.20 (m, 56 H), 1.08 (t, $J = 9.3$ Hz, 2 H, SH), 0.88 (t, $J = 7.7$ Hz, 6 H, CH_3). ^{13}C NMR (75 MHz, CDCl_3): δ 39.78, 33.62, 31.93, 30.44, 30.27, 29.70, 29.67, 29.55, 29.48, 29.37, 29.31, 22.70, 14.12. Anal. Calcd for $\text{C}_{33}\text{H}_{68}\text{S}_2$: C, 74.92; H, 12.96. Found: C, 74.76; H, 12.77.

2,2-Dimethyl-1,3-propanedithiol (1). ^1H NMR (300 MHz, CDCl_3): δ 2.54 (d, $J = 9.3$ Hz, 4 H, SCH_2), 1.20 (t, $J = 9.3$ Hz, 2 H, SH), 1.00 (s, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ 35.33, 34.66, 25.07. HRMS calcd for $\text{C}_5\text{H}_{12}\text{S}_2$: 136.0380. Found: 136.0373(3).

2,2-Dibutyl-1,3-propanedithiol (2). ^1H NMR (300 MHz, CDCl_3): δ 2.52 (d, $J = 9.3$ Hz, 4 H, SCH_2), 1.31–1.24 (m, 8 H), 1.16–1.07 (m, 4 H), 1.09 (t, $J = 9.3$ Hz, 2 H, SH), 0.91 (t, $J = 8.0$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ 39.70, 33.34, 30.32, 25.45, 23.33, 14.09. HRMS calcd for $\text{C}_{11}\text{H}_{24}\text{S}_2$: 220.1319. Found: 220.1320(5).

2,2-Dioctyl-1,3-propanedithiol (3). ^1H NMR (300 MHz, CDCl_3): δ 2.51 (d, $J = 9.3$ Hz, 4 H, SCH_2), 1.33–1.10 (m, 28 H), 1.08 (t, $J = 9.3$ Hz, 2 H, SH), 0.88 (t, $J = 7.7$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ 39.79, 33.63, 31.88, 30.44, 30.27, 29.52, 29.37, 29.29, 22.67, 14.10. Anal. Calcd for $\text{C}_{19}\text{H}_{40}\text{S}_2$: C, 68.58; H, 12.13. Found: C, 68.42; H, 12.14.

2,2-Didodecyl-1,3-propanedithiol (4). ^1H NMR (300 MHz, CDCl_3): δ 2.51 (d, $J = 9.3$ Hz, 4 H, SCH_2), 1.33–1.07 (m, 44 H), 1.09 (t, $J = 9.3$ Hz, 2 H, SH), δ 0.88 (t, $J = 7.7$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ 39.78, 33.63, 31.92, 30.45, 30.27, 29.65, 29.56, 29.47, 29.35, 29.29, 22.69, 14.10. A satisfactory analysis was not obtained. Anal. Calcd for $\text{C}_{27}\text{H}_{56}\text{S}_2$: C, 72.90; H, 12.69. Found: C, 72.89; H, 12.14.

2,2-Ditridecyl-1,3-propanedithiol (5). ^1H NMR (300 MHz, CDCl_3): δ 2.51 (d, $J = 9.3$ Hz, 4 H, SCH_2), 1.34–1.07 (m, 48 H), 1.09 (t, $J = 9.3$ Hz, 2 H, SH), 0.88 (t, $J = 7.7$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ 39.75, 33.61, 31.92, 30.42, 30.27, 29.68, 29.66, 29.56, 29.46, 29.37, 29.30, 22.69, 14.11. Anal. Calcd for $\text{C}_{29}\text{H}_{60}\text{S}_2$: C, 73.65; H, 12.79. Found: C, 73.93; H, 12.53.

2,2-Ditetradecyl-1,3-propanedithiol (6). ^1H NMR (300 MHz, CDCl_3): δ 2.51 (d, $J = 9.3$ Hz, 4 H, SCH_2), 1.36–1.08 (m, 52 H), 1.09 (t, $J = 9.3$ Hz, 2 H, SH), 0.88 (t, $J = 7.7$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ 39.76, 33.62, 31.92, 30.46, 30.27, 29.69, 29.67, 29.55, 29.49, 29.37, 29.32, 22.70, 14.12. Anal. Calcd for $\text{C}_{31}\text{H}_{64}\text{S}_2$: C, 74.32; H, 12.88. Found: C, 74.68; H, 12.89.

2,2-Dihexadecyl-1,3-propanedithiol (8). ^1H NMR (300 MHz, CDCl_3): δ 2.51 (d, $J = 9.3$ Hz, 4 H, SCH_2), 1.36–1.07 (m, 60 H), 1.09 (t, $J = 9.3$ Hz, 2 H, SH), 0.88 (t, $J = 7.7$ Hz, 6 H). ^{13}C NMR (75 MHz, CDCl_3): δ 39.79, 33.63, 31.93, 30.46, 30.28, 29.70, 29.66, 29.58, 29.50, 29.37, 29.31, 22.70, 14.12. Anal. Calcd for $\text{C}_{35}\text{H}_{72}\text{S}_2$: C, 75.46; H, 13.03. Found: C, 75.81; H, 13.12.

Preparation of SAMs on Gold. Gold substrates were prepared by thermally evaporating chromium (ca. 100 Å) followed

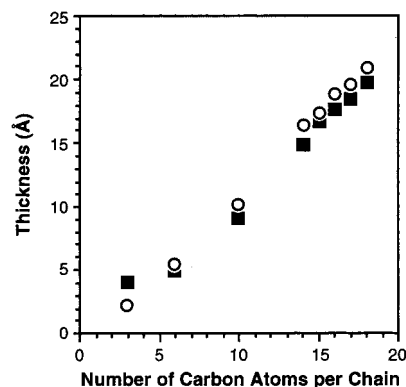


Figure 2. Ellipsometric thicknesses of films generated from spiroalkanedithiols (filled squares) and from normal alkanedithiols (hollow circles).

by evaporating gold (ca. 2000 Å) onto silicon wafers. The gold-coated wafers were cut into slides (ca. 1 cm \times 3 cm) using a diamond stylus. Solutions of the thiols (ca. 1 mM) were prepared in weighing bottles that were precleaned by soaking for 1 h in a "piranha" solution (7.5/2.5 $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$) (caution: "piranha" solution reacts violently with organic materials and should be handled carefully). After being cleaned, the bottles were rinsed with deionized water and absolute ethanol and dried overnight at ≥ 100 °C. The slides were washed with absolute ethanol and dried under a flow of ultrapure nitrogen. The slides were immersed in solutions of the spiroalkanedithiols and normal alkanedithiols dissolved in isooctane and in ethanol, respectively. The monolayers were allowed to equilibrate for a period of 48 h, which is longer than the typical 24-h period (vide infra). The resultant SAMs were exhaustively rinsed with toluene and ethanol and dried under a flow of ultrapure nitrogen before analysis.

Analyses of SAMs. The thicknesses of the SAMs were measured using a Rudolf Research Auto EL III ellipsometer, which was equipped with a He–Ne laser operating at 632.8 nm and an angle of incidence of 70°. Immediately after evaporation, the optical constants for the bare gold were measured. To calculate the thicknesses, we assumed a refractive index of 1.45 for all films. The data were collected and averaged over three separate slides using 3 spots/slide for each type of SAM.

Advancing and receding contact angles of H_2O and HD were measured at 293 K and ambient relative humidity using a Ramé-Hart model 100 contact angle goniometer. The measurements were performed while the pipet tip was kept in contact with the drop. The contacting liquids were dispensed and withdrawn at the slowest possible speed (ca. 1 $\mu\text{L}/\text{s}$) using a Matrix Technologies micro-Electrapette 25. The data were collected and averaged over three separate slides using 3 spots/slide for each type of SAM.

Polarization modulation infrared reflection absorption spectra (PM-IRRAS) were measured 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 operating at 37 kHz. The light was reflected from the sample at an angle of incidence of 80°. The spectra were collected over 256 scans at a spectral resolution of 4 cm^{-1} .

Results and Discussion

To compare SAMs generated from the spiroalkanedithiols to those generated from normal alkanedithiols, we assume that SAMs derived from $[\text{CH}_3(\text{CH}_2)_n]_2\text{C}[\text{CH}_2\text{SH}]_2$ should most readily correspond to those derived from $\text{CH}_3(\text{CH}_2)_{n+2}\text{SH}$. This assumption thus permits a direct comparison of systems in which the total number of carbon atoms per alkyl chain is the same.

Thicknesses and Wettabilities of the Films. Figure 2 provides the ellipsometric thicknesses of SAMs generated from the spiroalkanedithiols and the corresponding normal alkanedithiols. At all chain lengths except C3, the thick-

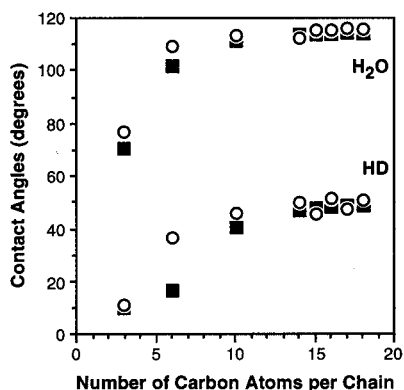


Figure 3. Contact angles of water (H₂O) and hexadecane (HD) on SAMs generated from spiroalkanedithiols (filled squares) and from normal alkanethiols (hollow circles).

Table 1. Values of Advancing (θ_a) and Receding (θ_r) Contact Angles and Hystereses ($\Delta\theta$)^a

SAM adsorbates	θ_{a,H_2O}	θ_{r,H_2O}	$\Delta\theta_{H_2O}$	$\theta_{a,HD}$	$\theta_{r,HD}$	$\Delta\theta_{HD}$
1 (C3)	71	44	27	<10	<i>b</i>	<i>b</i>
2 (C6)	103	84	19	16	<i>b</i>	<i>b</i>
3 (C10)	113	100	13	41	29	12
4–8 (C14–18) ^c	114	103	11	48	37	11
CH ₃ (CH ₂) ₂ SH	77	56	21	<10	<i>b</i>	<i>b</i>
CH ₃ (CH ₂) ₅ SH	109	94	15	37	24	13
CH ₃ (CH ₂) ₉ SH	113	100	13	46	35	11
CH ₃ (CH ₂) _{<i>m</i>} SH ^d	114	103	11	49	38	11

^a The contact angles of water are reproducible within $\pm 2^\circ$ of the reported value; the average contact angles of hexadecane vary more widely ($\pm 3^\circ$) because of the “odd–even” effect (please see text).

^b Receding angles were too low for accurate determination; in these cases, hystereses are undefined. ^c Average values for inclusive chain lengths are reported. ^d Average values for $m = 13–17$ are reported.

nesses of the SAMs generated from the spiroalkanedithiols are reproducibly 1–2 Å lower than those generated from the corresponding normal alkanethiols but are still within the estimated experimental uncertainty (± 2 Å). For both types of films, the thicknesses increase roughly linearly with an increase in the number of carbon atoms; differences in slopes are indistinguishable. The deviation at C3 is perhaps due to the fact that **1** contains no methylene groups. The consequent lack of van der Waals stabilization could lead to films in which the adsorbates are either poorly packed¹⁵ or perhaps oriented more nearly perpendicular to the surface.⁸

The wettability data in Figure 3 and Table 1 show that the average advancing contact angles of water (θ_{a,H_2O}) were $114 \pm 2^\circ$ for the SAMs generated from the longer spiroalkanedithiols (i.e., $\geq C10$). The data for the corresponding normal SAMs were indistinguishable ($114 \pm 2^\circ$), suggesting that both types of SAMs are similarly hydrophobic. Deviations at the shorter chain lengths (i.e., SAMs derived from **1** and **2**) probably result from poor film quality as described above.

The orientation and composition of the moieties that compromise low energy surfaces can be probed with remarkable sensitivity using dispersive liquids such as hexadecane.^{1,26} Indeed, the ability of hexadecane to sense differences in thin films can be seen by examining the contact angles of hexadecane as a function of the chain length of the SAM (Figure 3). While water exhibits low contact angles for the spiroalkanedithiolate SAMs having only the shortest chain lengths ($\leq C6$), hexadecane can sense differences at substantially longer chain lengths

($\leq C10$). Furthermore, the wettability data for hexadecane in Figure 3 and Table 1 show that the SAMs generated from spiroalkanedithiols with chain lengths $\geq C14$ exhibit average values of $\theta_{a,HD} = 48 \pm 2^\circ$, while the normal SAMs with correspondingly long chain lengths exhibit average values of $\theta_{a,HD} = 49 \pm 3^\circ$. The similar magnitude of these values suggests that the SAMs formed from the long-chain spiroalkanedithiols are well-packed and highly oriented, exposing terminal methyl rather than methylene groups at the interface.^{15,26}

In Figure 3, the wettabilities of the normal SAMs exhibit a parity (or “odd–even”) effect as a function of chain length;²⁷ in contrast, the wettabilities of the chelating SAMs exhibit no similar effect. The odd–even effect is generally interpreted to reflect the increased wettability of methylene vs methyl groups exposed at the interface.^{26,28} The absence of an odd–even effect for the spiroalkanedithiolate SAMs could arise from a number of factors such as a greater disorder, different tilt angles, or conformational effects arising from the presence of the tetrasubstituted carbon moiety in the spiroalkanedithiolate SAMs.

As noted above, SAMs generated from compounds having shorter chain lengths exhibit lower contact angles for both water and hexadecane. This phenomenon can plausibly arise from at least two factors. First, interactions between the test liquids and the surface of gold might be greater at the shorter chain lengths.²⁹ Second, the disorder in the films might be greater at the shorter chain lengths.¹⁵ Because values of contact angle hysteresis ($\Delta\theta = \theta_a - \theta_r$) can be used to evaluate the roughness or heterogeneity of a wetted surface,²⁴ we examined the hysteresis of the films under consideration here (Table 1). At chain lengths $\geq C14$, the values are similar for both liquids on all SAMs ($\Delta\theta = 11^\circ$). These results suggest that there are no major differences in the roughness or heterogeneity for long-chain spiroalkanedithiolate SAMs and normal SAMs. We observe, however, a marked increase in the hysteresis of water for the SAMs having shorter chain lengths. This effect is particularly noticeable for the spiroalkanedithiolate SAMs, again suggesting that the short-chain chelating moieties generate poorly ordered SAMs.

Infrared Spectroscopy of the Films. Surface infrared spectroscopy, which in our case involves the specific technique of polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS),³⁰ can be used to provide structural and conformational information regarding organic thin films.³¹ The frequency and bandwidth of the methylene asymmetric C–H stretch ($\nu_a^{CH_2}$) are particularly sensitive to the degree of order (or crystallinity) of the films.^{32,33} Figure 4 shows the PM-IRRAS spectra for the spiroalkanedithiols examined in the present study. As the chain length increases, the $\nu_a^{CH_2}$ stretch decreases from 2926 to 2920 cm^{-1} . This shift provides strong support that the films are more highly ordered at the longer chain lengths.^{32,33} Furthermore, the limiting value of 2920 cm^{-1} is higher than that of normal alkanethiolate SAMs of similar chain lengths,^{32,33} suggesting that the SAMs derived from the spiroalkanedi-

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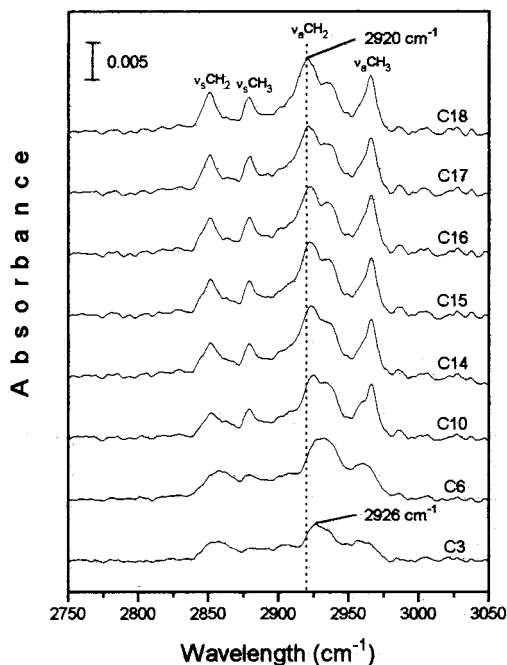


Figure 4. PM-IRRAS spectra of SAMs generated from spiroalkanedithiols as a function of chain length.

thiols, while still highly ordered, are less crystalline than those derived from their normal alkanethiolate analogues. This interpretation rests, of course, on the assumption that the chain tilt and orientation of the spiroalkanedithiolate SAMs are similar to those of normal alkanethiolate SAMs on gold.

PM-IRRAS can also be used to detect the odd–even orientation of the terminal methyl group in SAMs generated from normal alkanethiols.³² The ratio of the intensities of the methyl symmetric C–H stretch ($\nu_s^{\text{CH}_3} \sim 2878 \text{ cm}^{-1}$) and the methyl asymmetric C–H stretch ($\nu_a^{\text{CH}_3} \sim 2965 \text{ cm}^{-1}$) alternates systematically with the orientation of the terminal methyl group. For the spiroalkanedithiolate SAMs, however, the ratio of the intensities of these two peaks is roughly constant over the range of chain lengths examined (Figure 4). This result is consistent with a model in which the new SAMs possess less highly ordered tail groups than normal alkanethiolate SAMs. Before any firm conclusions can be drawn, however, a more detailed analysis of these data is required to resolve issues of chain tilt and orientation in these new films.

Preliminary Observations Regarding Monolayer Equilibration. An equilibration period of 24 h is typically employed in the formation of high-quality SAMs on gold from normal alkanethiols.¹⁵ Indeed, we have found that exposure of freshly evaporated gold to solutions of normal alkanethiols in either ethanol or isooctane for 24 h generates SAMs with contact angles of hexadecane and PM-IRRAS spectra that are characteristic of high-quality SAMs on gold.^{8,9} In contrast, however, we have found that exposure of freshly evaporated gold to solutions of the long-chain spiroalkanedithiols (**4–8**) for 24 h produces SAMs with relatively low contact angles of hexadecane (e.g., $\theta^{\text{HD}} \sim 45^\circ$) and PM-IRRAS spectra that suggest relatively poor crystallinities (e.g., $\nu_a^{\text{CH}_2} \sim 2923 \text{ cm}^{-1}$). If, however, the solutions are allowed to equilibrate for an additional 24 h, the SAMs exhibit the limiting values shown in the present work. Additional equilibration leads to no further changes. While we are as yet uncertain of

the origin of this phenomenon, at least two hypotheses seem plausible: (1) diffusion on the surface might be unusually slow for the chelating adsorbates, requiring longer times for complete film formation, and/or (2) because of the mismatch between the maximum distance spanned by the dithiols (4.8 Å) and the distance between the 3-fold hollow sites on Au(111) (4.99 Å), the underlying surface of gold might be required to undergo a partial reconstruction to permit commensurate binding of the adsorbate and ultimately a highly packed film. Future studies will attempt to distinguish between these hypotheses.

Preliminary Evaluation of the Thermal Stabilities of Spiroalkanedithiolate SAMs. We briefly probed the thermal stability of the spiroalkanedithiolate SAMs by ellipsometry¹⁵ using a comparison of the solution-phase desorption of the SAM derived from **7** to that of the analogous SAM derived from heptadecanethiol. In decahydronaphthalene (DHN) at temperatures ranging from 80 to 90 °C, these studies showed an unexpected and interesting trend: in SAMs that were equilibrated for only 24 h, the stabilities of both SAMs were indistinguishable; if, however, an equilibration period of 48 h were used, the spiroalkanethiolate SAM was the more stable of the two. The latter conclusion was supported by the following ellipsometric results: after heating for 1 h at 90 °C in DHN, 51% of the SAM generated from **7** remained on the surface, while only 30% of the SAM generated from heptadecanethiol remained. These preliminary studies indicate that the new chelating spiroalkanedithiols can be used to generate films that are more thermally robust than those generated from related normal alkanethiols.^{8,34} The kinetics of adsorption and desorption of these and related films will be explored in detail in a future study.

Conclusions

A series of new spiroalkanedithiols was synthesized and used to generate SAMs on gold. The SAMs were characterized by optical ellipsometry, contact angle goniometry, and IR spectroscopy (PM-IRRAS). The results support a model in which the SAMs derived from long-chain spiroalkanedithiols generate well-ordered, densely packed, and highly oriented films having qualities similar to those generated from normal alkanethiols. The new chelating SAMs appear, however, to be slightly less crystalline than their normal alkanethiolate analogues. Preliminary studies of the kinetics of formation of these new SAMs reveal an unusually long equilibration period required to achieve complete monolayer formation. Preliminary studies of desorption in solution indicate that the new SAMs are likely to be more robust than those derived from normal alkanethiols of similar chain length. We are currently exploring the structural and kinetic features of these new films.

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