Interchange between Monolayers on Gold Formed from Unsymmetrical Disulfides and Solutions of Thiols: Evidence for Sulfur–Sulfur Bond Cleavage by Gold Metal[1]

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Reaction of an unsymmetrical disulfide, $HO(CH_2)_{16}SS(CH_2)_3CF_3$, with a gold surface yields a self-assembled monolayer containing approximately equal proportions of the two different thiolate groups. The $S(CH_2)_3CF_3$ group in these mixed monolayers is replaced by $S(CH_2)_{16}CN$ on exposure to a solution of $HS(CH_2)_{16}CN$ in ethanol about 10^3 times more rapidly than the $S(CH_2)_{16}OH$ group, although approximately 70–80% of the latter group is eventually replaced. These observations support the conclusion that disulfides adsorb on the surface of gold with cleavage of their sulfur–sulfur bond to form a new species (a gold thiolate). The two thiolates formed from a single disulfide behave as independent entities in their subsequent reactions.

Introduction

Chemisorption of alkanethiols, RSH, or dialkyl disulfides, RSSR, on gold gives ordered monolayers.[1–5] SAMs (self-assembled monolayers) formed from either precursor are believed to comprise the same species on the gold surface—gold(I) alkyl thiolate ($RS^-Au_3^+$ on these predominately Au(111) surfaces) adsorbed epitaxially on the gold(0) substrate—but the only direct experimental evidence supporting this belief is the observation of indistinguishable S(2p) binding energies for both systems measured by X-ray photoelectron spectroscopy (XPS).[6,7] The objective of the work described in this paper was to compare the reactivity of the surface organosulfur species generated from alkanethiols and dialkyl disulfides in a type of reaction we expected to be senstive to details of bonding to the surface—interchange of these surface organosulfur species with thiols or disulfides in solution.

This study examined the reactivity of species formed on gold from an unsymmetrical disulfide LgSSMd (HO-$(CH_2)_{16}SS(CH_2)_3CF_3$; Lg = long chain; Md = medium chain). We wanted to address two questions (Scheme I): (1) Are both halves of LgSSMd incorporated in the SAM to the same extent when a solution of this disulfide is allowed to react with a bare gold surface? Is the same result observed on a surface already covered with an alkyl thiolate? (2) Do the hypothesized surface species, LgS^-Au^I and MdS^-Au^I, behave as independent entities in their reactions with species in solution, or are their reactivities correlated?

Scheme I. Possible Outcomes for the Reaction of an Unsymmetrical Disulfide with either Gold or Gold with a Chemisorbed SAM
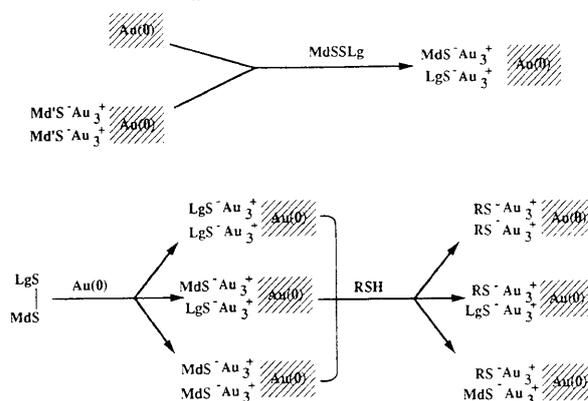
Neither the products released from the surface in these interchange reactions nor the mechanism(s) of the interchange reactions have been established, although data characterizing the kinetics of interchange for a few different SAMs are known.[10–12] Our studies therefore had predominantly an exploratory function and a descriptive character.

Background

Nuzzo et al. examined the XPS spectrum of SAMs prepared from dialkyl disulfides and alkanethiols chemisorbed on gold from solution or from the vapor phase under high vacuum.[7] They observed that the S(2p) binding energy measured by XPS for chemisorbed species derived from dimethyl disulfide was ∼1.5 eV lower than the binding energy for physisorbed multilayers of this disulfide on gold. They argued that the lower binding energy of the chemisorbed species supported the hypothesis that the organosulfur compound coordinates to the surface as an alkyl thiolate. We showed that properties (measured by ellipsometry, XPS and wetting) of SAMs formed on gold

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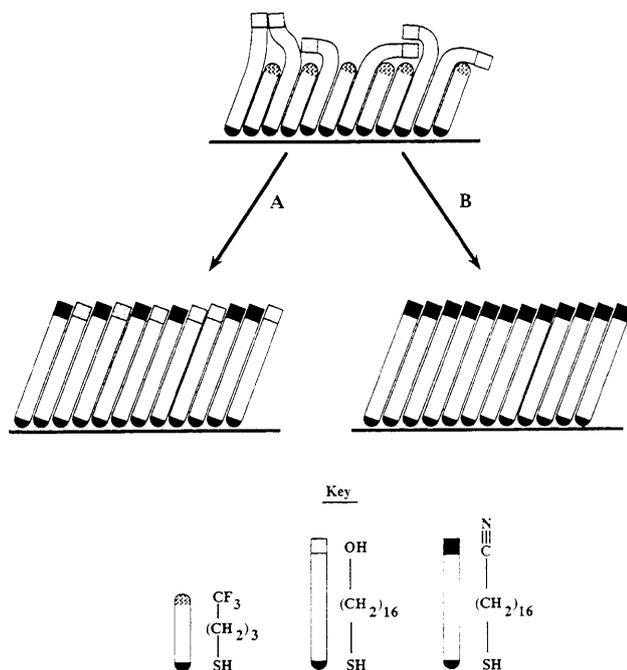(8) Biebuyck, H. A.; Bain, C. D.; Whitesides, G. M. Unpublished results.

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Figure 1. Two possible outcomes for the replacement of species in a SAM formed on gold from $HO(CH_2)_{16}SS(CH_2)_3CF_3$ by $HS(CH_2)_{16}CN$. (A) The $S(CH_2)_3CF_3$ half of the unsymmetrical disulfide is displaced selectively from the gold surface, resulting, for short times of exposure to $HS(CH_2)_{16}CN$, in a monolayer comprising a $\sim$1:1 mixture of species derived from $S(CH_2)_{16}CN$ and $S(CH_2)_{16}OH$. (B) $HS(CH_2)_{16}CN$ nonselectively displaces molecules from the SAM resulting in a correlated loss of species derived from both halves of $HO(CH_2)_{16}SS(CH_2)_3CF_3$.

Table I. Properties of SAMs formed on Gold from Different Precursors of $HS(CH_2)_nR$

	1	$n = 16$ R = OH	$n = 3$ R = CF$_3$
thickness (Å)^a	14 ± 2	20 ± 2	7 ± 2
$\theta_a^{H_2O}$ ^{b}	78	20	118
$\theta_r^{H_2O}$	51	<10^c	104
θ_a^{HD}	18	<10^c	75
θ_r^{HD}	<10^c	<10^c	62
normalized signal^d fluorine	0.47 ± 0.08^e	<0.03	≡ 1
normalized signal^d oxygen	0.46 ± 0.05	≡ 1	<0.03

^{a} Thickness determined by ellipsometry. ^{b} Contact angle in degrees. ^{c} Values of the contact angles less than 10° cannot be determined with any accuracy by the methods used here. These values represent upper limits. ^{d} Normalized intensity of the specified element in the SAM measured by XPS. ^{e} This value is corrected for attenuation of the signal by an overlayer of 6 Å of carbon atoms.[13]

reaction at the surface of the metal generally decreases with increasing chain length of the alkyl thiolate in the SAM.[3]
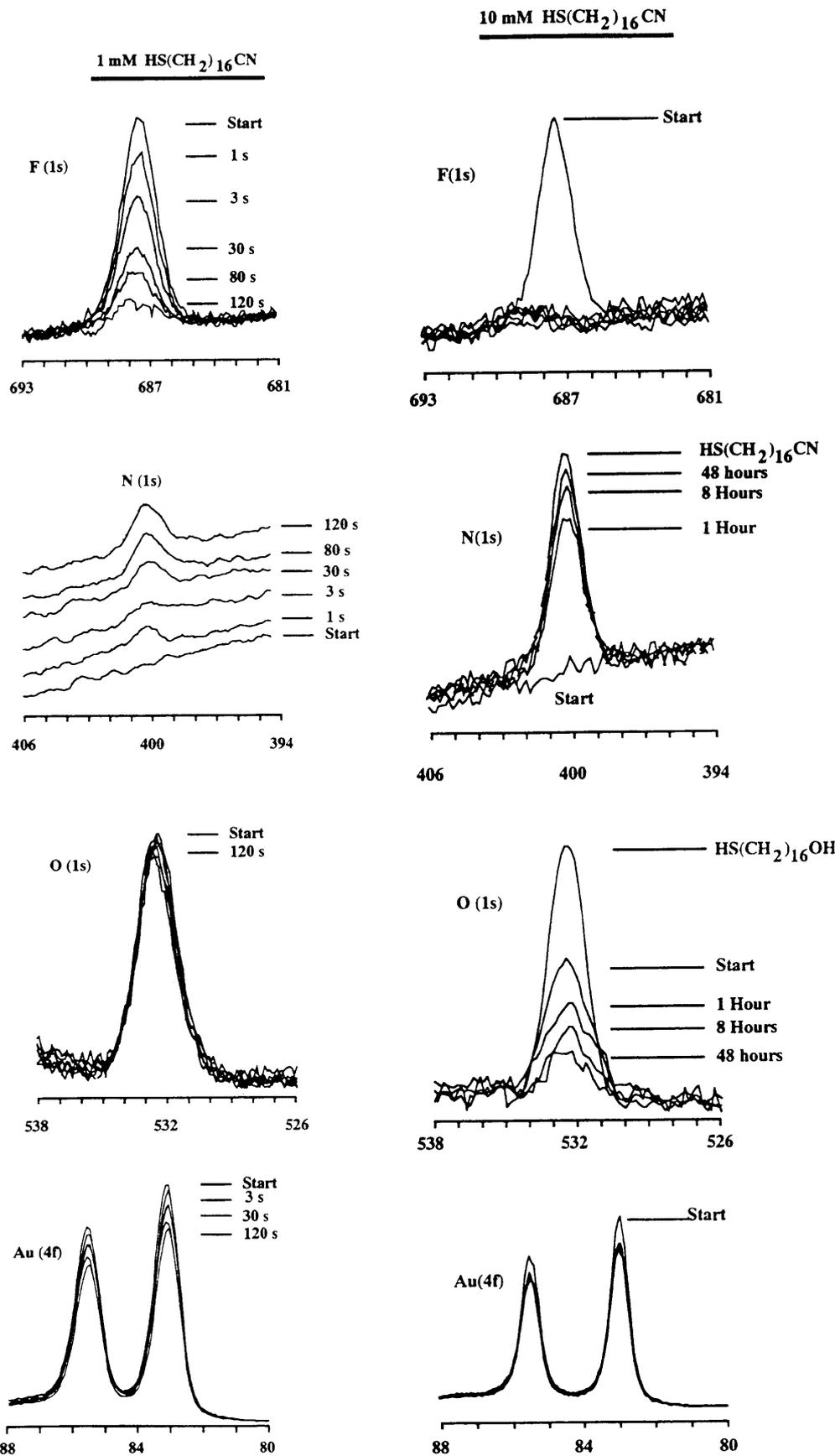
Experimental Design

We wished to have methods of characterizing the processes occurring on the surface that would yield as much information as possible, using relatively simple experiments. Our strategy for addressing the questions outlined in Scheme I was based on using the unsymmetrical disulfide $HO(CH_2)_{16}SS(CH_2)_3CF_3$ (1) to form the monolayer and $HS(CH_2)_{16}CN$ (2) to carry out the replacement. These choices were based on five considerations. First, we wanted one of the two alkyl moieties of the disulfide to be significantly longer than the second. If the organosulfur species derived from the two halves of the disulfide were independent in the SAM, we expected their difference in length and stability to be reflected in a significant difference in their rates of replacement from the SAM by thiol in solution. If the sulfur–sulfur bond of the disulfide remained intact on the surface of gold, however, we expected nonselective replacement of species from the SAM (Figure 1). Second, changes in the composition of monolayers could be assayed by ellipsometry or XPS, using the thickness of the SAM as a measure of this change. Third, we wanted each half of the unsymmetrical disulfide to have a distinct element that could be observed using XPS. Fourth, we wanted an unsymmetrical disulfide that was easily distinguished (by NMR and chromatography) from symmetric disulfides corresponding to either half of the unsymmetrical disulfide. Fifth, we wished to follow incorporation of the thiolate derived from 2 into the SAM by XPS; the nitrogen atom in this compound made that analysis straightforward.

Results and Discussion

Synthesis and Characterization $HO(CH_2)_{16}SS-(CH_2)_3CF_3$. The synthesis of 1 followed a literature preparation of unsymmetrical disulfides by the oxidation of a 1:1 mixture of thiols corresponding to the two halves of 1 with I_2.[9] The unsymmetrical and symmetrical disulfides were easily separated, as determined by thin layer chromatography and NMR, by column chromatography.

SAMs of $HO(CH_2)_{16}SS(CH_2)_3CF_3$. SAMs were formed on gold substrates from 1 mM solutions of 1 in either isooctane or ethanol (see below). After 24 h of equilibration with this solution, the resultant SAM was characterized by XPS, ellipsometry, and its wettability by water and hexadecane. These data are summarized in Table I. The

from solutions of either dialkyl disulfides or alkanethiols were indistinguishable,[8] although we established that SAMs formed from solutions containing $\sim$1:1 mixtures of these molecules had compositions dominated (75:1) by surface species derived from the thiol.[9] In addition we demonstrated that both halves of an unsymmetrical disulfide, $HO(CH_2)_{11}SS(CH_2)_{10}CH_3$, were incorporated in equal proportions in a SAM formed on gold from this molecule.[9] These data were consistent with the hypothesis that thiols and disulfides react at the surface of gold and form the thiolate as a common surface intermediate.

We found previously that either dialkyl disulfides or alkanethiols in solution replaced the organosulfur species in SAMs formed on gold from either dialkyl disulfides or alkanethiols, provided that the group being replaced had the smaller number of methylene groups.[4] The properties of SAMs resulting from replacement of SAMs formed from propanethiol were indistinguishable, after a sufficiently long exposure to the solutions containing the new organosulfur species, from the corresponding properties of SAMs formed on gold by exposure to the longer chain molecule. The rate of replacement of species from SAMs decreases with the length of the alkyl chain of species in the SAM.[4,10]

The opposite type of process—replacement of a long chain alkyl thiolate by a shorter, or equivalent, chain thiol, or disulfide—also occurs, albeit much more slowly.[10–12] In these cases, thiolates in SAMs with ten or more carbon atoms in their alkyl chains were only partially replaced by thiols in solution, even after several weeks of reaction. These data suggest the kinetics of interchange between thiolates in SAMs and thiols in solution are greatly affected by the ability of the SAM to block chemical reaction at the gold surface. Electrochemical studies of SAMs on gold and other metals have established that the rate of chemical

10 mM HS(CH$_2$)$_{16}$CN

1 mM HS(CH$_2$)$_{16}$CN

Figure 2. Intensity of photoelectrons of F(1s), O(1s), N(1s), and Au(4f) measured by XPS for SAMs formed from HO(CH$_2$)$_{16}$SS-(CH$_2$)$_3$CF$_3$ change following exposure of these SAMs to 1 mM (A, left) or 10 mM (B, right) solutions of HS(CH$_2$)$_{16}$CN in ethanol. The nitrogen spectra in part A are offset to improve the clarity of the data.

F(1s) signal in SAMs of 1 was 36 ± 3% of the fluorine signal measured for SAMs formed from HS(CH$_2$)$_3$CF$_3$. Correction of the fluorine signal in SAMs of 1 for

attenuation of the fluorine photoelectron through a disordered layer of 6 Å of methylene groups (due to the presence of species derived from HS(CH$_2$)$_{16}$OH in the
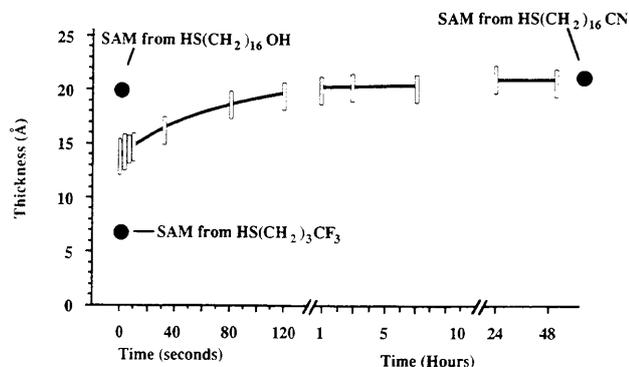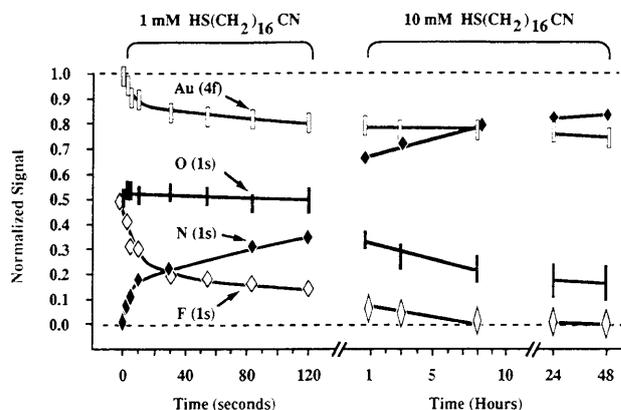
Figure 3. Thickness of SAMs formed from $HO(CH_2)_{16}SS(CH_2)_3$-CF_3 (1) rapidly increases on exposure to a solution of $HS(CH_2)_{16}$-CN in isooctane. Changes measured by ellipsometry in SAMs formed on gold from $HO(CH_2)_{16}SS(CH_2)_3CF_3$ are shown as a function of the time from immersion of the SAM in a 1 mM solution of $HS(CH_2)_{16}CN$ in isooctane. In order to display the data conveniently, the time ordinate is discontinuous; the left part of this scale is linear in seconds; the right part of this scale is linear in hours. The size of the symbols give our best estimate of the error of the measurement.

Figure 4. Normalized signals for the photoelectron peaks for N(1s), F(1s), O(1s), and Au(4f) change relative to each other following immersion of a SAM formed from $HO(CH_2)_{16}SS(CH_2)_3$-CF_3 in either a 1 mM (short times) or a 10 mM (long times) solution of $HS(CH_2)_{16}CN$ in isooctane. Signals for oxygen and nitrogen were normalized to the signals measured for SAMs formed on gold from $HS(CH_2)_{16}OH$ and $HS(CH_2)_{16}CN$, respectively. The signal for gold was normalized to its value in SAMs prior to exposure to $HS(CH_2)_{16}CN$. The signal for fluorine was normalized to its value in SAMs prior to exposure to $HS(CH_2)_{16}$-CN after correction of the signal for attenuation by an overlayer resulting from $S(CH_2)_{16}OH$ in the SAM.[13] We have made the time ordinate discontinuous to display the data conveniently; the left part of this scale is linear in seconds; the right part is linear in hours. The size of the symbols give our best estimate of the error of the measurement.

SAM) gave 47 ± 8% of the intensity of the fluorine signal of SAMs derived from $HS(CH_2)_3CF_3$.[14] These data indicate that species derived from either half of 1 were present in approximately equal proportions in SAMs formed from 1.

SAMs from $HS(CH_2)_2CH_3$, following Replacement by $HO(CH_2)_{16}SS(CH_2)_3CF_3$. We placed SAMs formed from $HS(CH_2)_3CH_3$ (3) in 10 mM solutions of 1 ethanol for 48 h. Examination of the resulting SAMs by XPS, ellipsometry, and contact angles indicated they were indistinguishable from SAMs formed by exposure of bare gold to solutions of 1. This similarity in the properties of SAMs made by these two different reactions suggests the gold surface by itself, or covered by chemisorbed organsulfur species, does not confer preferential reactivity to either of the two sulfur atoms in the unsymmetrical disulfide.

SAMS from $HO(CH_2)_{16}SS(CH_2)_3CF_3$ following Replacement by $HS(CH_2)_{16}CN$ (2). Exposure of SAMs derived from 1 to solutions of $HS(CH_2)_{16}CN$, 2, formed new SAMs incorporating the nitrile group. The composition (Figure 2) and thickness (Figure 3) of these new SAMs changed with the time from immersion in solutions of 2. Measurements by XPS showed that the increase in the thickness of SAMs of 1 exposed to solutions of 2 occurred through selective replacement of $-S(CH_2)_3CF_3$ by $-S(CH_2)_{16}CN$ (Figures 3 and 4) and thus favors outcome A in Figure 1.

Exposure of SAMs of 1 to solutions of 2 also eventually resulted in replacement of $-S(CH_2)_{16}OH$ in the SAM, although the rate of this replacement was much slower than the replacement of $-S(CF_2)_3CF_3$ (Figures 3 and 4); $-S(CH_2)_{16}CN$ replaced most (70–80%), but not all, of the hydroxyl moieties in SAMs of 1 after 48 h. The rate of replacement of these hydroxyl moieties slowed noticeably as their mole fraction decreased in the monolayer (Figure 4). Figure 4 demonstrates that loss of 50% of the $-S(CF_2)_3CF_3$ groups in the SAM is $\sim 10^3$ times faster than loss of 50% of the $-S(CH_2)_{16}OH$ groups. The difference between relative rates of replacement of species derived from $S(CH_2)_3CF_3$ or $S(CH_2)_{16}OH$ in SAMs of 1 agreed with previously published observations suggesting the rate of replacement in monolayers decreases with increasing

thickness of the monolayer and increasing conversion of the SAM.[4,10-12] This decrease in the rate of replacement of species from thick monolayers probably results from two factors. First, sterically restricted access to the surface of gold by thiols or disulfides in solution, and increasing chain–chain interactions, decreases the rate of replacement in thick films. Second, the morphology of the surface of gold probably results in sites with high coordination numbers (>3) that bind thiolate better than sites with low coordination numbers (<3) and therefore reduce the rate of replacement of these thiolates.[13] We found similar effects for the rates of replacement from SAMs of 1 by solutions of 2 in ethanol or isooctane.

Together these data suggest that species in SAMs formed from 1 behave as independent particles on the gold surface. This result supports the hypothesis that gold thiolates form on chemisorption of dialkyl disulfides on gold.

Conclusions

Reaction of an unsymmetrical disulfide $HO(CH_2)_{16}SS$-$(CH_2)_3CF_3$, with a gold surface yields a SAM containing approximately equal proportions of the two possible thiolate groups. The $-S(CH_2)_3CF_3$ group in these mixed monolayers is replaced by $-S(CH_2)_{16}CN$ about 10^3 times more rapidly than the $-S(CH_2)_{16}OH$ group, although a large fraction (70–80%) of the latter group is eventually replaced. A fraction of the $-S(CH_2)_{16}OH$ groups *is* not replaced, even after long exposure; the observation of a kinetically trapped population of thiolate groups is in agreement with work by Chidsey[11] and Fox.[12]

These observations support the conclusion that disulfides adsorb on the surface of gold with cleavage of their sulfur–sulfur bond and form a new species (a gold thiolate). The two thiolates formed from a single disulfide behave as independent entities in their subsequent reactions.

Experimental Section

Materials. Absolute ethanol (Quantum Chemical Corp.) was purged by N_2 or Ar prior to use. Hexadecane (Aldrich, 99%) was

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percolated twice through activated, neutral alumina (EM Science). Water was deionized and distilled in a glass and Teflon apparatus (Pfaltz & Bauer) prior to use. 16-Mercaptohexade-canenitrile and 16-mercaptohexadecanol were available from previous studies. $CF_3(CH_2)_3SS(CH_2)_{16}OH$ was synthesized according to a literature procedure.[9] ^{1}H NMR (500 MHz, $CDCl_3$) δ 3.62 (Q, 2H), δ 2.70 (t, 2H), δ 2.66 (t, 2H), δ 2.21 (m 2H), δ 1.96 (p, 2H), δ 1.64 (p, 2H), δ 1.55 (p, 2H), δ 1.4–1.2 (m, 24H). Anal. Calcd for $C_{20}H_{39}F_3OS_2$: C, 57.66; H, 9.44. Found: C, 57.41; H, 9.59.

Preparation of Substates. Gold substrates were prepared by electron-beam evaporation of 2000 Å of gold (Materials Research Corp., 99.999%) onto 100 mm thick, single-crystal silicon (100) test wafers (Monsanto, MEMC, and Silicon Sense) that had been precoated with 100 Å of chromium (Johnson Mathey, 99.997%; Aldrich, >99.99%) as an adhesion layer between the silicon dioxide and the gold. The substrates were stored in wafer holders (Fluoroware) until used in experiments. Before being added to solutions, the silicon wafers were cut into ~1 cm × 3 cm slides with a diamond-tipped stylus, rinsed with ethanol, and blown dry in a stream of nitrogen. The time between removal of the wafers from the evaporator and immersion in solutions containing thiols or disulfides was generally less than 4 h.

Instrumentation. Ellipsometric measurements were performed on a Rudolf Research Type 43603-200E ellipsometer equipped with a He–Ne laser (λ = 6328 Å) at an incident angle of 70°. Samples were rinsed with ethanol and blown dry in a stream of nitrogen prior to characterization. Values of thickness were calculated using a program written by Wasserman[15], following an algorithm by F. L. McCrackin and co-workers; in the calculation, we used a refractive index of 1.45 for the SAMs.

Contact angles of water and hexadecane were measured on a Ramé-Hart Model 100 goniometer at room temperature and ambient humidity. Advancing and receding contact angles were measured on at least three drops of each liquid per slide; contact angle data in the text represent the average of these measurements. A Micro-Electrapette syringe (Matrix Technologies) was used for dispensing and removing the liquids onto the SAMs (~1 μL/s). The method used for measuring the advancing and receding angles has been described previously.[4]

X-ray photoelectron spectra were obtained on an SSX-100

spectrometer (Surface Science Instruments) using monochromatic Al Kα X-rays. The spot size was 3 mm^2 with an analyzer pass energy of 100 eV for measurements of N(1s), F(1s), and O(1s); spectra were accumulated for 30 min. A 1 mm^2 spot and an analyzer pass energy of 50 eV were used for measurements of C(1s) and Au(4f); these spectra were acquired for 20 and 3 min, respectively. Spectra were fit using a 60% Gaussian/40% Lorentzian function in the computer system of the SSX-100.

Formation of SAMs. Adsorptions were carried out in 25-mL glass weighing bottles that had been cleaned with "piranha solution" (7:3 concentrated H_2SO_4/30% H_2O_2) at 90 °C for 1 h, and rinsed first with distilled water and then with copious amounts of deionized water. **WARNING: Piranha solution should be handled with caution. It should not be allowed to contact significant quantities of oxidizable organic materials. In some circumstances (most probably when mixed with significant quantities of an oxidizable organic material), it has detonated unexpectedly.**[16] The weighing bottles were stored in an oven at approximately 100 °C until use. Adsorptions were carried out in 25 mL of ethanol or isooctane at a total concentration of sulfur of 1 mM. Adsorptions were performed at room temperature for 1 day.

Studies of Kinetics. Studies of rates of formation of SAMs were carried out in either 1 or 10 mM stirred (4 × 8 mm Teflon coated bar at ~5 revolutions per second) solutions of the thiol or disulfide. Samples were placed in solution and removed after a fixed period of time (~1 s) followed by immediate (within 1 s) washes with ethanol (10 mL) and hexane (10 mL). Samples were dried under a stream of nitrogen. Samples were split into two pieces. One piece was placed in a container made of polypropylene and transported to the XPS, where it was immediately (within 20 min) placed under high vacuum, <10⁻⁸ Torr. The thickness of the monolayer by ellipsometry and the contact angles of water and hexadecane were measured on the other piece. This procedure minimized contamination of the monolayer in the laboratory atmosphere.

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