Self-Assembled Monolayers on Gold Generated from Alkanethiols with the Structure RNHCOCH₂SH

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Received December 19, 1994. In Final Form: July 10, 1995

This paper outlines a general synthetic route to alkanethiols useful in forming self-assembled monolayers (SAMs) starting from amines, RNH₂, and converting them, via α-chloroamides RNHCOCH₂Cl, to thiols having the structure RNHCOCH₂SH. The wettability (estimated from contact angles of water and hexadecane) and the thicknesses (as measured by ellipsometry and X-ray photoelectron spectroscopy, XPS) of SAMs having an amide moiety β Au/thiolate were similar to those of SAMs of alkanethiols with similar backbone length on gold. The internal amide group present in SAMs prepared from CF₃CH₂NHCOCOCH₂SH increases their stability against desorption or exchange with hexadecanethiol in ethanol relative to SAMs from CF₃(CH₂)₇SH. The desorption of SAMs from CF₃(CH₂)₇SH was first order in the alkanolate and had a half-life of ~2 h at 10⁻⁹ Torr; SAMs from CF₃CH₂NHCOCOCH₂SH, by contrast, showed no loss after 48 h at ~ 10⁻⁹ Torr. The rate of exchange of a SAM from CF₃CH₂NHCOCOCH₂SH with hexadecanethiol in ethanol was 10⁴-10⁵ times slower than the SAMs from CH₃(CH₂)₇SH or from CF₃(CH₂)₇SH. The susceptibility of a SAM prepared from a short-chain alkanethiol (e.g., CH₃(CH₂)₇SH or CF₃(CH₂)₇SH) to damage by UV was 10 times greater than that observed for a SAM prepared from hexadecanethiol. UV damage of SAMs derived from CH₃(CH₂)₇NHCOCOCH₂SH, followed by protection of the UV-damaged SAM by replacement with hexadecanethiol and etching, gave gold patterns with minimum feature sizes of 5 nm; these sizes were limited by the lithographic procedure used and do not reflect the true edge resolution of this photolithographic method.

Introduction

This paper outlines a general synthetic route to alkanethiols useful in forming self-assembled monolayers (SAMs) on gold starting from structurally complex amines, RNH₂ (eq 1). This work had three objectives. First, we wished to develop a general procedure by which a common class of functionalized organic molecules could be converted to thiols suitable for incorporation into SAMs. The direct introduction of thiols into many organic groups (e.g., by Sn2 reaction or by free radical addition to an olefin) can be problematic, and a straightforward sequence that modified an existing functional group seemed more general. We chose the amine group as the basis for our work. The great majority of the work on SAMs of alkanethiolates (RS⁻) on gold has used the structure HS(CH₂)ₓX⁻ (1) greater structural variations in R would increase the breadth of the field. Second, we wished to determine if the amide moiety β Au/thiolate would stabilize SAMs by forming hydrogen bonds (Figure 1). We chose the susceptibility of short-chain thiols on gold toward exchange with long-chain alkanethiols (CH₃(CH₂)₇SH) in solution as a primary measure of stability. Third, we wished to explore if the amide moiety β to the thiol group would increase the breadth of the field. Two objectives were to determine if the amide moiety β to the thiol group would stabilize SAMs by forming hydrogen bonds (Figure 1). We chose the susceptibility of short-chain thiols on gold toward exchange with long-chain alkanethiols (CH₃(CH₂)₇SH) in solution as a primary measure of stability. Third, we wished to explore if the amide moiety β to the thiol group would stabilize SAMs by forming hydrogen bonds (Figure 1).
cross-section might lead to a useful technology for lithographic patterning.

Patterning SAMs of alkanethiolates on gold surfaces can be accomplished by microcontact printing (μCP),14 microwriting,16 and micromachining.17 SAMs of long-chain alkanethiolates protect gold from etching by CN/O2 techniques and for forming patterns of SAMs on the gold surface, combined with a CN/O2 etch, provide a procedure for patterning gold.16 UV-induced photooxidation of SAMs has been studied by Hemminger and used by him and others as the basis for photolithography with SAMs.18 21 Alkanesulfonates resulting from photooxidation of SAMs on gold were detected by static secondary ion mass spectroscopy (SSIMS)21 and laser-induced desorption-coupled Fourier transform mass spectroscopy (LID-FTMS).19 20 oxidized sulfur species have been detected by X-ray photoelectron spectroscopy (XPS).22 Alkanesulfonates formed by photooxidation are only weakly bound to gold and are thus easily removed from its surface. Selective damage of the SAM resulted from selective illumination, but edge resolution and feature size are currently substantially poorer than can be achieved by μCP.

Here we show that a SAM prepared from CF3CH2NHCOCH2SH exhibits a significantly enhanced stability against thermal desorption (in vacuo) or exchange with hexadecanethiol in ethanol: a monolayer formed from CH3CH2CH2CH2SH is less stable under similar conditions. These data indicate that the internal amide group present in SAMs derived from CF3CH2NHCOCH2SH increases their stability. SAMs from long-chain alkanethiolates also require relatively longer exposures to UV than do SAMs from shorter chain alkanethiolates to give clean etching by CN/O2: the effective rate of UV damage of a SAM prepared from CF3CH2NHCOCH2SH is 10 times greater than that of a SAM prepared from hexadecanethiol; SAMs prepared from CF3CH2NHCOCH2SH may thus be suitable for fabricating patterned gold features (which in turn can serve as chemically robust resists for other types of processing) by UV lithography.

Results and Discussion

Synthesis of Thiols. The synthesis of thiols 4a–g demonstrates a general synthetic route for the formation of ω-substituted alkanethiolates from a range of organic structures containing amine groups. Reactions of amines 1a–g with chloroacetyl chloride yielded 2a–g, respectively (Scheme 1); these amines were chosen in part to represent a range of organic structural types. Substitution of the chloride of 2a–g by thioacetic acid resulted in the thioacetates 3a–g. These, on hydrolysis, gave the thiols 4a–g, respectively (Scheme 1). In the case of compound 3e (with the structure CH2OCOCH2CH2NHCOCH2SCOH), method B rather than method C was chosen to ensure the conversion of the COOH group to the COO− group. The stirring of a suspension of compound 3e in 1 N NaOH solution for 24 h resulted in the hydrolysis of both COOCH3 and SCOH2 groups to the desired product 4e with the structure HOOCC(CH2)11NHCOCH2SH. The reactions proceeded rapidly and in high yield, although in some cases protection of other functional groups present in the molecule was necessary. Commercial availability of a large number of primary and secondary amines and the ease with which amines can be introduced into a range of structures make this method of formation of thiols particularly convenient.

Characterization of Monolayers

Wettability with Water and Hexadecane. The wettabilities of SAMs derived from 4a–g on gold (<1000)

![Figure 1. A hypothetical model of a SAM of alkanethiolates with amide moieties β to the thiol groups. Interchain hydrogen bonds form among the amide groups.](image)

H3C(CH2)11-NHCOCH2SH

4a

HO(CH2)11-NHCOCH2SH

4b

CF3C=O-NHCOCH2SH

4c

HOOCC(CH2)11-NHCOCH2SH

4d

O=N

4e

H2C=CH-NHCOCH2SH

4f

H2C

4g

A were determined by measuring the advancing and receding contact angles, θa and θr, of water (H2O) and hexadecane (HD), respectively (Table 1). Acetic acid was added to ethanolic solutions of thiols 4a–g to minimize the formation of disulfides by base-catalyzed oxidation of the thiolates and thus to facilitate comparison of the resulting SAMs, although disulfides of

(21) This route has been used in the conversion of N,N-dimethyl-hydrazine to N,N-dimethyl-N,N-bismercaptoacetyl-hydrazine. Singh, R.; Whitesides, G. M. J. Org. Chem. 1991, 56, 2332–2337.
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Scheme 1

\[
R^*\text{NHCOCH}_2\text{COCH}_3
\]

Table 1. Contact Angles of Water (H\text{2}O) and Hexadecane (HD) on SAMs and Thickness of SAMs Determined by Ellipsometry and XPS

| SAM prepared from | [AcOH]* mM | H\text{2}O | HD | thickness of SAM (Å) by ellipsometry
<table>
<thead>
<tr>
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<tbody>
<tr>
<td>CH\text{3}CH\text{2}N\text{HCOCH}_2\text{SH}</td>
<td>0, 0.06</td>
<td>117, 116</td>
<td>101, 102</td>
<td>47, 54</td>
</tr>
<tr>
<td>CH\text{3}CH\text{2}NHSH</td>
<td>0, 0.06</td>
<td>118, 117</td>
<td>105, 106</td>
<td>48, 53</td>
</tr>
<tr>
<td>CH\text{3}CH\text{2}N\text{HSS}</td>
<td>0, 0.06</td>
<td>118, 118</td>
<td>106, 106</td>
<td>48, 48</td>
</tr>
<tr>
<td>HO\text{CH}_{2}CH\text{2}N\text{HCOCH}_2\text{SH}</td>
<td>0.06</td>
<td>20, 118</td>
<td>8, 106</td>
<td>10, 53</td>
</tr>
<tr>
<td>HO\text{CH}_{2}CH\text{2}NHSH</td>
<td>0.06</td>
<td>22, 118</td>
<td>8, 106</td>
<td>10, 53</td>
</tr>
<tr>
<td>CF\text{3}CH\text{2}N\text{HCOCH}_2\text{SH}</td>
<td>0.06</td>
<td>99, 99</td>
<td>75, 75</td>
<td>55, 55</td>
</tr>
<tr>
<td>CF\text{3}CH\text{2}NHSH</td>
<td>0.06</td>
<td>88, 99</td>
<td>64, 75</td>
<td>17, 17</td>
</tr>
<tr>
<td>HO\text{CH}_{2}CH\text{2}N\text{HCOCH}_2\text{SH}</td>
<td>0.06</td>
<td>14, 88</td>
<td>9, 99</td>
<td>&lt;10, &lt;10</td>
</tr>
<tr>
<td>HOOCCH\text{2}CH\text{2}N\text{HCOCH}_2\text{SH}</td>
<td>0</td>
<td>16, 16</td>
<td>&lt;10, &lt;10</td>
<td>&lt;10, &lt;10</td>
</tr>
<tr>
<td>HOOCCH\text{2}CH\text{2}NHSH</td>
<td>0.06</td>
<td>59, 59</td>
<td>44, 44</td>
<td>15, 15</td>
</tr>
<tr>
<td>HO\text{CH}_{2}CH\text{2}N\text{HCOCH}_2\text{SH}</td>
<td>0.06</td>
<td>104, 104</td>
<td>95, 95</td>
<td>14, 14</td>
</tr>
</tbody>
</table>

* [AcOH] is the concentration of acetic acid in the solution used for the formation of SAMs. A vacancy in this column means that the thickness was not determined. The thickness of other SAMs was calculated from the Au(4f) signal in XPS using the thickness of SAM of hexadecanethiol as a standard (see Experimental Section). \(d\) Reference 3. * Assumes to be 20 Å. \(c\) Reference 25.

these thiols form SAMs on gold that are similar to those formed from the thiols. Oxidative formation of disulfides occurs primarily by oxidation of the thiolate anion. Since RNHCOCH\text{2}SH (\(pK_a \sim 8\)) is significantly more acidic than alkanethiols RCH\text{2}CH\text{2}SH (\(pK_a \sim 10\)), spontaneous oxidation of compounds 4a-g by O\text{2} is relatively rapid in neutral media; oxidation of these thiols is, however, slower in acidic media. The wetting properties of SAMs prepared from ethanolic solutions of thiols containing acetic acid (\(\sim 0.06 \text{ M}\)) were similar to those prepared from solutions without acetic acid. The presence of the acetic acid thus did not noticeably alter either the rate of the formation or the properties of the SAMs.

The wettabilities of monolayers prepared from thiols: R*NHCOCH2COCH3, NEt3, CH2Cl2 or MeOH, 0 °C, r.t.  ❮R = CH3(CH2)11 ❯R = HO(CH2)r, ❮R = CF3CH2 ❯R = HO{CH2CH2 | CH2CH3} ❮R = CH3OOC(CH2)11 ❯R = O N<,)− \\

Method A: HCl(aq), MeOH, r.t., 12 h — Method B: 1 N NaOH(aq), Ar, r.t., 24 h; 2 HCl(aq) — Method C: 1 NaOMe, MeOH, Ar, r.t., 12 h — Method A: HCl(aq), MeOH, r.t., 12 h — Method C: 1 NaOMe, MeOH, Ar, r.t., 12 h — Method A: HCl(aq), MeOH, r.t., 12 h — Method C: 1 NaOMe, MeOH, Ar, r.t., 12 h — Method A: HCl(aq), MeOH, r.t., 12 h — Method C: 1 NaOMe, MeOH, Ar, r.t., 12 h — Method A: HCl(aq), MeOH, r.t., 12 h — Method C: 1 NaOMe, MeOH, Ar, r.t., 12 h — Method A: HCl(aq), MeOH, r.t., 12 h — Method C: 1 NaOMe, MeOH, Ar, r.t., 12 h
containing the amide moiety were comparable to those prepared from alkanethiols with the same nominal backbone structures, although there were significant differences in the hysteresis between the advancing and receding contact angles. SAMs of 4a, for example, showed a slightly larger hysteresis between the advancing and receding contact angles; a few degrees of either water or hexadecane than did SAMs from hexadecanethiol and octadecanethiol.

**Determination of the Thickness of SAMs.** The thicknesses of SAMs containing the HSCH$_2$CONH group were determined by ellipsometry and XPS; these data are presented in Table 1. The thicknesses of SAMs having an amide moiety β to Au(thiolate) are similar to those of related SAMs lacking this moiety. These data suggest that the formation of the monolayer proceeds by bonding of sulfur to the gold substrate in a manner analogous to that for simpler alkanethiol adsorbates.

**Polarized Infrared External Reflectance Spectroscopy (PIERS) of SAMs from 4a.** Contact angles and ellipsometry establish that many of the SAMs derived from the adsorbates detailed in Scheme 1 have wetting properties and mass coverages comparable to those of structurally related SAMs that lack the amide group in the head group region. This observation suggests that those SAMs that have long alkyl chains might organize themselves with the same ($\sqrt{3} \times \sqrt{3}$R30°) periodicity that those SAMs that have long alkyl chains might organize themselves with the same ($\sqrt{3} \times \sqrt{3}$R30°) periodicity that those SAMs that have long alkyl chains might organize themselves with the same ($\sqrt{3} \times \sqrt{3}$R30°) periodicity that those SAMs that have long alkyl chains might organize themselves with the same ($\sqrt{3} \times \sqrt{3}$R30°) periodicity that an n-alkanethiol SAM. We believe that the character of these spectra is most consistent with a "chain-melting" model.

It is well-known that the d and d band intensities of the bulk n-alkanes are very sensitive to the phase state in which they are measured. The phase I to phase II (rotator) transition of orthorhombic n-alkane crystals is accompanied by a significant decrease in the oscillator strengths of the CH stretching and other low-frequency modes; factors of 2–3 have been noted between the crystalline and the melt states as well. The spectra of 4a shown in Figure 2a are consistent with the intensities one might expect to see for disorganized chains. Additional conformation is obtained from the position of the d band (~2922 cm$^{-1}$); this very high value suggests that gauche conformations are heavily weighted in the structure of these SAMs.

The conformational disordering of the alkyl chain in a SAM of 4a is, at first glance, most unexpected given the results obtained by PIERS studies of numerous long-chain thiol derivatives. The logical inference is that interactions at the head group, such as hydrogen bonding and/or packing restrictions, affect the conformational freedom of these molecules. However, the spectrum in Figure 2b provides a simple explanation. The amide II band of 4a appears at ~1510 cm$^{-1}$. This band is very weak when the amide II band of another conformation is seen in the spectrum of 4a shown in Figure 2a are consistent with the intensities one might expect to see for disorganized chains. Additional conformation is obtained from the position of the d band (~2922 cm$^{-1}$); this very high value suggests that gauche conformations are heavily weighted in the structure of these SAMs.

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The line shape and intensity distribution of the amide II band provide perhaps the best insights into the nature of these SAMs. As noted above, the presence of this intense band, and absence of any mode in the 1450 cm$^{-1}$ region, is only consistent with a largely (if not entirely) trans conformation of the amide.

No other conformations of this group are possible. The intensity/frequency distribution also suggests that the chains are largely hydrogen bonded in the SAM; from the line shape, it would seem that some (although a smaller population) of non-hydrogen-bonded segments may also be present.

The amide II band involves torsional motions of both the N–H and C–N moieties. This coupling in the trans form leads directly to the splitting responsible for the amide III band. Hydrogen bonding in solution and in the solid state shift, but do not eliminate, these bands. Hydrogen bonding typically is reflected in a band centered at ~1550–1560 cm$^{-1}$ for an amide of this structure. This band, in a non-hydrogen-bonded state, would appear at ~1510 cm$^{-1}$. The spectrum in Figure 2a thus reveals conclusively that most segments are hydrogen bonded in the SAM of 4a. This band is asymmetric, however; the low-frequency side shows a pronounced, nonhomogeneous contribution to the line shape. We therefore conclude that
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Figure 3. Space-filling models showing side on views of two molecules of 4a in an all-trans conformation spaced at 5.1 Å and oriented vertically along a hypothetical surface normal vector and (right) canted by 18° from this vector along the nearest neighbor direction. The N–H···O contact shown on the right corresponds to a N–O distance of 2.8 Å.

The most important feature that emerges from the data in Figure 2b is the orientation of the chain that must exist to accommodate (1) the trans conformation of the amide group and (2) the complex chain organizations that must accompany this interchain H-bonding. The model structures shown in Figure 3 adopt the conventions necessary to make this analysis.

We start our analysis from a vantage based on literature precedents. Given its importance to the tertiary structure of proteins, the hydrogen-bonding characteristics of the amide group have been the subject of considerable study. The structures of many systems, both in solution and in the solid state, have been characterized and reported in the literature. The more important features of the current understanding of these interactions remain very much the same as those elegantly described by Pauling in an overview written more than 30 years ago. The amide group adopts a similar hydrogen-bonded arrangement in almost all unsaturated systems. The preferred N–H–O bonding angle is zero degrees. The torsional barrier associated with a distortion from linearity is modest (≈ 0.1–0.2 kcal/mol). The N–O bond distances for the amide N–H–O hydrogen bond tend to fall in a narrow range around 2.8 Å.

If we use these insights to guide an organizational model of the structure formed by 4a on Au, an interesting result is obtained. A linear hydrogen bond can only be formed if a significant perturbation of the packing of the SAM occurs—one which distorts both the chain packing and the typical 3 × 3 R30° overlayer structure presumed to characterize most thiol monolayers on Au. For simplicity of discussion, we assume that the chains are present in a hexagonal overlayer related to the (3 × 3 R30°) structure. As shown in Figure 3, the linear hydrogen bond in such a lattice can only be obtained by a tilt of the molecule in the nearest neighbor direction (seen here side on for two chains). In order for a chain tilt in this direction to yield a linear hydrogen bond and an N–O bond distance of 2.8 Å, the S–S spacing must increase to 5.1 Å (from 4.98 Å); for this structure, the chain tilt cannot exceed 18° (as compared to the ~24–28° chain tilt found for the n-alkanethiol SAMs on Au). As the space-filling model clearly demonstrates, there is no simple arrangement of an all-trans chain that will densely pack within these constraints.

The model shown in Figure 3 is but one of several possible arrangements that yield a linear hydrogen bond of the proper length. The arrangement shown is one that we favor strongly, for several reasons. First, this simple arrangement minimizes the cross-sectional projection of the head group on the Au surface and thus allows a dense chain structure. Second, this orientation allows the construction of long hydrogen-bonded chains and thus allows this attractive interaction to be easily maximized. Third, the trans arrangement at the head group accounts well for the significant projection of the amide II transition moment along the surface normal direction and, thus, for the negligible intensity seen for the amide II, C=O stretching mode. Fourth, the model provides a simple arrangement that yields interchain hydrogen bonding of a sort consistent with the rather typical values of the vibrational frequencies seen for the amide group in these SAMs. The model does require, however, that conformational changes from an all-trans arrangement of the polyethylene chain shown in the figure must occur to maximize the attractive interactions of the chains. This maximization can only be accomplished by relaxing the chains via trans–gauche isomerism. In this regard, the structure shown adequately explains both the low intensity of the d- and d′- modes and the high values of these vibrational frequencies as compared to an ordered alkane phase (the “average” chain tilt is less than that of the normal thiol SAM structure, and the gauche conformer density is relatively high).

Taken together, the simplest interpretation of the data suggests that a modest expansion (~3%) of the sulfur lattice constant is likely obtained for these SAMs and that the organization of the chains is altered as a result. It is therefore likely that the overlayer structure would be incommensurate with respect to the Au lattice spacing. This arrangement would also make it very difficult to accommodate a S–S dimerization as has been recently proposed to occur for n-alkanethiol SAMs on Au. We should also point out that were the hydrogen-bonding arrangement to involve the long linear chains, the data tend to suggest, this hydrogen bonding could not be accommodated within the type of superlattice present in the n-alkanethiol systems.

Finally, we note that many of the qualitative aspects of the data presented here are reminiscent of the results of a study of an amide-containing SAM capped by a long perfluorinated chain that appeared while this paper was under review. The quantitative aspects show some differences, however. We think these differences are entirely consistent with the relatively larger size of the perfluoride side chain and the packing constraints, this difference in size would impose on the organization of the SAM.

The Amide Moiety Stabilizes Short-Chain Thiocyanates against Thermal Desorption. The stability of SAMs toward isothermal desorption in ultrahigh vacuum (~10⁻⁶ Torr) at ambient temperature (~300 K) was investigated by monitoring their composition using XPS. SAMs derived from 4,4,4-trifluorobutanethiol and its disulfide were unstable toward desorption in high vacuum (~10⁻⁹ Torr). Molecules desorbed from the gold surface.

presumably as disulfides, although we did not identify
the desorbing species. This desorption was not caused by
the X-rays or by secondary electrons emitted from the
substrate. 32 no F (1s) or S (2p) signal (< 0.1% F, and < 1% S)
was detected after the samples were ultrahigh vacuum
for 24 h; the same results were obtained even when limited or no X-ray analyses were made at short
times of exposure to vacuum. A small residual C (1s) signal
remained that was similar in binding energy, peak shape,
and intensity to that observed for adventitious contami-
nants present in the chamber and adsorbed onto the
surface of the gold after argon sputtering of its surface.11

The kinetics of the isothermal desorption of SAMs of
4,4,4-trifluorobutanethiol, determined from the decrease
in intensity of the F (1s) signal in XPS, was found to be
first order in the coverage of the alkanethiolate, and the measured half-life of this desorption at 300 K was ~2 h
(Figure 4). SAMs derived from CF3CH2SSCH2(F)CF3
desorbed at rates similar to SAMs derived from CF3CH2SH;
this observation is compatible with the conclusion that thiols and disulfides adsorb on gold and form similar
species.25 The fluorinated component of SAMs formed from
CF3(CH2)2SS(CH2)2OH desorbed much more slowly than the alkanethiolate species in SAMs from CF3(CH2)2SH
(Figure 4). We presume that the increased interaction with the hexadecyl chain present in SAMs derived from the
unsymmetrical disulfide accounts for this difference in stability.

SAMs from 4c on gold, in contrast, showed no change in
the F (1s) signal after being left in ultrahigh vacuum for 48 h (Figure 4). Interchain H-bonding of the amide moiety of 4c probably provides an additional energy barrier
(as high as 5 kcal/mol) and may explain the substantially
higher thermal stability of SAMs formed from 4c compared to that of SAMs formed from the alkanethiolate species in SAMs from CF3(CH2)2SH at 300 K is most unusual. SAMs from CH3SSCH2CH3, when formed in ultrahigh vacuum (UHV), are completely stable at 300 K over periods of many days. The measured heat of
desorption (as CH3SSCH2) is ~32 kcal/mol.36 In the
present instance, if we model the desorption kinetics as

\[ \text{rate} = k \times \text{coverage} \]

being an apparent first-order process and assume an initial
coverage ~4.6 × 10^3 molecules/cm^2, and a pre-exponential factor ~10^{10} s^{-1}, we calculate that the activation energy for desorption is ~24 kcal/mol. This value would represent a substantial perturbation due to the neighboring group interactions of the CF groups. Since the situation is only definable when one assumes a more reasonable second-order rate law. Due to the considerable uncertainty as to what would constitute a proper choice of A in this case, a more complete analysis is not possible on the basis of these data alone.

A SAM Prepared from CF3CH2NHCOCH2SH 4c Is
More Stable against Exchange with Hexadecanethiol in Ethanol Than SAMs Prepared from Either
CH3(CH2)3SH or CF3(CH2)2SH. SAMs prepared from
4c, butanethiol, and 4,4,4-trifluorobutanethiol on gold
were allowed to exchange with hexadecanethiol (5 mM)
in ethanol. The rates of exchange of SAMs prepared from
4c and SAMs prepared from 4,4,4-trifluorobutanethiol were calculated from the F (1s) signal measured by XPS
after correction for the attenuation of this signal due to
differences in the thickness of the monolayer following
exchange (see Experimental Section for a description of the methods used in this calculation). The rate of
exchange of SAMs prepared from butanethiol was calcu-
lated from the C (1s) signal after correction for its
attenuation (see Experimental Section). The rate of
exchange of SAMs prepared from 4c was 10^2 ~ 10^3 times
slower than that of the SAMs prepared from butanethiol
or from 4,4,4-trifluorobutanethiol (Figure 5). Exchange
experiments carried out in weighing bottles, wrapped with
aluminum foil and kept in the dark to exclude the possible
effects of light, were compared to exchange experiments
carried out in weighing bottles from which ambient light
was not excluded. The rates in light or dark were indistinguishable.37 Ambient light did not therefore
contribute to the rate of exchange observed under our
experimental conditions.

The relative stability of SAMs prepared from 4c toward
exchange is probably due to the amide group \( \beta \) to the
thiol/thiolate: intermolecular hydrogen bonding, or changes in bond strength of the thiol/thiolate bond, may increase

\[ \text{rate} = k \times \text{coverage} \]

(37) The glass of the container may screen light of the wavelength
required for the photodamage of monolayers.
the stability of 4c. In order to distinguish the effect of pH on the S–Au bond strength, we measured the rate of exchange of a SAM prepared from thiocetic acid with hexadecanethiol in solution. Thiocetic acid has a $pK_a$ of $\sim 3$. Although this value is 5 orders of magnitude lower than the $pK_a$ of 4c, SAMs prepared from thiocetic acid exchanged with hexadecanethiol at rates similar to SAMs prepared from propanethiol.

The stability of the SAM prepared from 4c with respect to thermal desorption and exchange was compared to that of the SAMs prepared from long-chain thiols since trifluorobutanethiol can be synthesized readily from commercially available starting materials. The stability of SAMs prepared from trifluorobutanethiol is comparable to that of those from hexadecanethiol, although trifluorobutanethiol has a larger molecular weight and larger interplay.

The Rate of Exchange of a SAM Prepared from CH$_3$($CH_2$)$_9$CONHCH$_2$SH 4a with CF$_3$CONH($CH_2$)$_2$SH in Solution Was Comparable to That of a SAM Prepared from Hexadecanethiol. SAMs prepared from 4a and hexadecanethiol on gold were allowed to exchange with CF$_3$CONH($CH_2$)$_2$SH 5 mM in ethanol and in heptane. The rates of exchange of the SAMs with CF$_3$CONH($CH_2$)$_2$SH were calculated from the change in the intensity of the F 1s) signal (see Experimental Section). The rates of exchange of the SAMs from 4a and hexadecanethiol with CF$_3$CONH($CH_2$)$_2$SH in heptane were similar to those in在美国 (see Experimental Section), although only results of exchange in ethanol are shown in Figure 5.

SAMs formed from long-chain alkanethiols exchange more slowly than SAMs formed from short-chain alkanethiols (Figure 5). The effect of the amide group on the rate of exchange of a SAM prepared from 4a was therefore less noticeable than that for SAMs formed from 4c on the time scale used for these experiments. The rate of exchange of the SAM with thiols in ethanol may be dependent on the chain length, the $pK_a$, the presence of functional groups, and the solubility of the thiols in ethanol. SAMs prepared from short-chain thiols, butanethiol, 4,4,4-trifluorobutanethiol, and 4c were allowed to exchange with hexadecanethiol in ethanol, while SAMs prepared from long-chain thiols (4a and hexadecanethiol) were allowed to exchange with CF$_3$CONH($CH_2$)$_2$SH in ethanol. The rate of exchange of SAMs with hexadecanethiol in ethanol cannot be directly comparable with those with CF$_3$CONH($CH_2$)$_2$SH in ethanol although their rates of exchange are plotted on the same graph for convenience.

SAMs of 4c Were Unstable in the Atmosphere of the Laboratory. A monolayer of thiol 4c was unstable to oxidation of its sulfur under ambient conditions (room temperature and pressure and standard laboratory lighting), but this SAM was stable when kept in the dark, as shown by XPS (see Experimental Section). The thiolate in monolayers was 35% and 86% oxidized after 1 and 5 h, respectively, in the atmosphere of the laboratory. The thiolate was oxidized (presumably to a sulfonate) as indicated by the increase in the intensity of XPS S (2p) signal at 168 eV. Sulfonates do not form stable monolayers on gold. The percentage of sulfur remaining in the SAM was similar to the amount of residual nitrogen (within the limits of experimental error); this result suggested that light does not induce cleavage of the amide bond but does induce oxidation of the thiolate to sulfonate. This result provides the most direct evidence that the chain orientation may be important in protecting the thiolate moiety of SAMs from atmospheric oxidation.

Figure 6. The dependence of the rate of damage of a SAM by UV on its thickness and composition. The rates of damage of SAMs prepared from 4a and hexadecanethiol by UV were determined directly by measuring F 1s) signals of the SAMs by XPS. SAMs derived from 4a or hexadecanethiol, after exposure to UV and washing, were dipped into a 5 mM solution of CF$_3$CONH($CH_2$)$_2$SH in ethanol for 5 min. The rates of damage of SAMs prepared from 4a and hexadecanethiol were determined from the fluorescence content, measured by XPS, of these SAMs.

The Rate of UV-Induced Damage of SAMs Depends on the Thickness and the Composition of the Monolayer. UV-damage experiments were performed with the SAMs prepared from 4a, 4c, 4,4,4-trifluorobutanethiol, and $n$-hexadecanethiol on gold. Different samples were placed side by side, 5 mm under the immersion well of the UV lamp, to ensure that all samples were damaged under similar conditions. After exposure to UV light, samples were washed with ethanol, water, and heptane to remove the oxidized sulfur species. Rates of damage of SAMs prepared from short-chain thiols (e.g., 4c) or 4,4,4-trifluorobutanethiol by UV were determined directly from the fluorescence content, measured by XPS, of these SAMs. SAMs derived from long-chain thiols (e.g., 4a) or hexadecanethiol, on gold were dipped into a 5 mM solution of CF$_3$CONH($CH_2$)$_2$SH in ethanol for 5 min after these samples were exposed to UV and washed. Rates of damage of SAMs prepared from 4a or hexadecanethiol were then determined from the fluorescence content, measured by XPS, of these SAMs. This procedure provided a reproducible and sensitive method for determining the extent of their oxidation.

All four SAMs were stable when kept in the dark. No photodamage of the SAMs was observed after the SAMs were exposed to UV for 2 h in a nitrogen atmosphere. An oxidant was therefore necessary, but not sufficient, to cause oxidation at the rates observed in these experiments. Light (probably UV, although the wavelength sensitivity remains unknown) is also required for the oxidation of sulfur in SAMs.

SAMs prepared from 4c and 4,4,4-trifluorobutanethiol were damaged by UV at similar rates, suggesting no discernible effect of the amide group on the rate of oxidation of thiolate to sulfonate for these short chains (Figure 6). SAMs prepared from long-chain thiols (hexadecanethiol and 4a) were damaged more slowly (by $\sim 10$ times) than SAMs formed from short-chain thiols (Figure 6). The alkyl chains of the long-chain thiols probably provide a barrier to penetration of these SAMs by oxygen and therefore retard photooxidation of thiolates in these SAMs. SAMs on copper or silver protect the metal from oxidation, and the rate of oxidation of Ag or Cu depends inversely on the thickness of the SAM. Since the thickness of the SAM prepared from 4a is comparable to that for a SAM prepared from hexadecanethiol, we infer from Figure 6 that the rate of UV-induced oxidation of SAMs from long-chain thiols is dependent on the composition of the monolayer.

UV Lithography Using SAMs Prepared from 4c. Figure 7 demonstrates a strategy for the formation of gold
process (5 pm) was limited by shadowing effects due to features. This method uses three properties of SAMs from 4c: (1) these SAMs can be damaged faster (-10×) than SAMs prepared from hexadecanethiol. (2) These SAMs slowly exchange with thiols in solution (-10⁻²-10⁻³ ×), relative to SAMs from short-chain (four carbons or less) alkanethiols. (3) SAMs formed from 4c do not block the CN/O₂ etch. Figure 8 shows that UV damage of SAMs prepared from 4c, followed by protection of the UV damaged area by hexadecanethiol, and etching away the gold in regions masked from UV light (where SAM from 4c remained) gave gold patterns. The resolution of this process (5 µm) was limited by shadowing effects due to the mask and does not provide a measure of the edge resolution that might be obtained in another experiment.

Conclusions

We have developed a general synthetic route to alkanethiols useful in forming self-assembled monolayers (SAMs) starting from amines, RNH₂, and conversion via a-chloroamides RNHCOCH₂Cl to thiols RNHCOCH₂SH, in overall yields in the range 30–80%. The wettabilities (obtained by measuring the contact angles of water and hexadecane) and the thicknesses (as measured by ellipsometry and X-ray photoelectron spectroscopy) of SAMs having an amide moiety γ to Au thiolate were similar to those of SAMs of alkanethiols with similar backbone length on gold although their chain organizations, as inferred from vibrational spectroscopy, appear to differ in detail. The interchain H-bonding of the amide moiety of the SAM derived from CF₃CH₂NHCOC₂H₅, 4c, seemed to provide additional stabilization; this SAM was significantly more stable than the SAMs from butanethiol or 4,4,4-trifluorobutanethiol against desorption in high vacuum (10⁻¹⁰ Torr) or exchange with hexadecanethiol in ethanol. SAMs from long-chain alkanethiols required longer exposure to UV than SAMs from short-chain thiols to accumulate sufficient damage to give clean etching by CN/O₂. SAMs from 4c may have applications in the fabrication of patterned features by UV lithography; UV damage of SAMs from 4c, followed by protection of the UV damaged area by hexadecanethiol, and etching away the gold in regions masked from UV light, where a SAM from 4c remained, gave gold patterns.

Experimental Section

General. 11-Azido-1-undecanol (3.88 g, 18.18 mmol) was suspended in absolute ethanol before use. Copper grid shielding, as depicted in Figure 7, was used as a mask, followed by protection of the gold in the region exposed to UV by hexadecanethiol and subsequent etching of the gold under the SAM prepared from 4c in masked regions of the SAM.

Figure 7. Schematic illustration of the procedure used to pattern gold using UV lithography of SAMs followed by a CN/O₂ etch.

Figure 8. Scanning electron microscopy (SEM) image of a gold pattern prepared by photopatterning of a SAM from 4c on gold, using a copper grid (line width of about 60 µm) as a mask, followed by protection of the gold in the region exposed to UV by hexadecanethiol and subsequent etching of the gold under the SAM prepared from 4c in masked regions of the SAM.
SAMs on Gold from Alkanethiols

was refluxed overnight. The solution was neutralized slowly with saturated sodium carbonate solution. Ethanol was evaporated in vacuo. Compound 1b precipitated as a white solid from the ethyl acetate/hexane (v/v : 30:70) mixture, which was collected with a Dean-Stark flask, and was redissolved in several times with water. The solid was recrystallized with hexane to give 2.83 g (15.1 mmol, 83%) of 1b. mp 70 - 71 °C; H NMR (400 MHz, CDCl₃) δ 4.09 (q, J = 9.8 Hz, 2H), 1.82 (m, 6H), 1.35 - 1.50 (overlapping resonance, 3H), 0.96 (s, 3H), 18.6 mmol) and chloroacetyl chloride (3.6 mL, 45 mmol) were added to the solution. The solvent was evaporated in vacuo. The pale yellow solid obtained was purified by chromatography with ethyl acetate/hexane (v/v : 50:50 ) to give 5.70 g of a light yellow solid. The solvent was evaporated in vacuo to give 3.81 g (16.6 mmol, 85%) of 1e as a white solid. mp 38 - 40 °C; H NMR (400 MHz, CDCl₃) δ 2.64 (t, J = 7.2 Hz, 2H), 3.37 (t, J = 7.2 Hz, 2H), 3.80 (s, 2H), 6.64 (d, J = 1.6 Hz, 1H), 10.05 (s, 1H). HRMS (FAB) (M + H⁺) calculated for C₇H₁₅NO₂Cl M 175.1938, found m/z 175.1936. Anal. Calcd for C₇H₁₅NO₂Cl: C, 53.20; H, 5.27; N, 6.10. Found: C, 52.10; H, 5.19; N, 6.02.

Methyl 2-Chloroacetamidododecanoate (2e). Compound 2e was prepared from 1e (4.7 g, 6.6 mmol) according to the procedure described for acetamide 2a. The desired product was purified by chromatography on silica gel (ethyl acetate/hexane, v/v : 50:50) to give 1.81 g (20 mmol, 92%) of a white solid, mp 94 - 96 °C; H NMR (400 MHz, CDCl₃) δ 2.62 (t, J = 7.2 Hz, 2H), 3.37 (t, J = 7.2 Hz, 2H), 3.80 (s, 2H), 6.64 (d, J = 1.6 Hz, 1H), 10.05 (s, 1H). HRMS (FAB) (M + H⁺) calculated for C₇H₁₅NO₂Cl M 175.1938, found m/z 175.1936. Anal. Calcd for C₇H₁₅NO₂Cl: C, 53.20; H, 5.27; N, 6.10. Found: C, 52.10; H, 5.19; N, 6.02.

2-Chloro-N(2-(3,4-dihydroxyphenyl)ethyl)acetamide (2d). Acetamide 2d was prepared from 2-(3,4-dihydroxyphenyl)ethylenemalonitrile hydrochloride (the hydrochloride of 1d) according to the procedure described for acetamide 2b. The hydrochloride of 1d (10.05 g, 26 mmol) was dissolved in 30 mL of dichloromethane. After 30 min. during which time a solid precipitated slowly.

Dichloromethane was added to the mixture until all of the solids dissolved. The ice bath was removed after 30 min, and the solution was stirred at room temperature for 2 h. The solvent was evaporated in vacuo. The light yellow solid obtained was dissolved in chloroform (200 mL). The solution was cooled in an ice bath. Triethylamine (4.0 mL, 32.76 mmol) was added, followed by 3.1 mL (39 mmol) of chloroacetyl chloride. The solution was then heated at reflux for 20 h. Water resulting from the esterification was collected with a Dean-Stark flask. The solvent was evaporated in vacuo. The solution was then cooled in an ice bath. Triethylamine (4.0 mL, 29 mmol) was added, followed by 3.1 mL (39 mmol) of chloroacetyl chloride.

The solution was cooled in an ice bath. Triethylamine (4.0 mL, 32.76 mmol) was added, followed by 3.1 mL (39 mmol) of chloroacetyl chloride. The solution was then heated at reflux for 20 h. Water resulting from the esterification was collected with a Dean-Stark flask. The solvent was evaporated in vacuo. The white solid obtained was dissolved in 300 mL of dichloromethane. The organic solution was washed with 1 N NaOH (2 x 50 mL) and brine (50 mL) and dried with anhydrous magnesium sulfate. The solution was then evaporated in vacuo to give 4.12 g (16.6 mmol, 85%) of a white solid: mp 53 - 54 °C; H NMR (400 MHz, CDCl₃) δ 1.13 - 1.45 (overlapping resonance, 4H), 1.35 - 1.60 (overlapping resonance, 2H), 1.30 (t, J = 7.0 Hz, 1H), 0.98 (s, 3H). 4.07 (s, 2H), 6.57 (br, 1H) ppm (CDCl₃) (300 MHz, CDCl₃) (15.7 mmol, 85% of 2a as a white solid: mp 48 - 49 °C; H NMR (400 MHz, CDCl₃) δ 1.15 - 1.5 (overlapping resonance, 14H), 1.65 - 1.85 (overlapping resonance, 1H), 1.35 - 1.5 (overlapping resonance, 4H), 1.85 - 2.15 (overlapping resonance, 2H), 2.15 - 2.8 (overlapping resonance, 2H), 4.11 (s, 2H), 6.89 (d, J = 1.6 Hz, 1H), 10.05 (s, 1H). HRMS (FAB) (M + H⁺) calculated for C₇H₁₅NO₂Cl M 175.1936, found m/z 175.1934. Anal. Calcd for C₇H₁₅NO₂Cl: C, 53.20; H, 5.27; N, 6.10. Found: C, 52.10; H, 5.19; N, 6.02.

2-Chloro-N-(2-(3,4-dihydroxyphenyl)benzyl)acetamide (2f). Compound 2f was prepared from 1f (5.01 g, 28 mmol) according to the procedure described for acetamide 2a. The desired product was purified by chromatography on silica gel (ethyl acetate/hexane, v/v : 50:50) to give 1.56 g (8.9 mmol, 46%) of a white solid: mp 50 - 51 °C; H NMR (400 MHz, CDCl₃) δ 3.95 (q, J = 5.9 Hz, 2H), 1.97 (m, 6H), 1.91 (m, 6H), 1.50 - 1.85 (overlapping resonance, 2H), 4.11 (s, 2H), 6.84 (br, 1H); H NMR (100 MHz, CDCl₃) δ 2.25 (s, 3H), 123.69 (q, J = 276 Hz, 8H), 166.43 (s); HRMS (FAB) (M + H⁺) calculated for C₁₃H₁₁NO₂Cl M 247.0849, found m/z 247.0837. Anal. Calcd for C₁₃H₁₅NO₂Cl: C, 52.50; H, 4.37; N, 3.69. Found: C, 52.50; H, 4.37; N, 3.69.
The solution was stirred under argon for 12 h. After the NMR (400 MHz, CDCl₃) δ 14.06, 22.63, 26.74, 29.18, 29.29, 29.47, 29.51, 29.56, 30.20, 31.56, 33.03, 39.37, 168.72, 195.87. HRMS-FAB (M+H) calecd for C₅₉H₅₂NO₂S m/z 320.2115, found m/z 320.2136. Anal. Caled for C₅₉H₅₂NO₂S: C, 73.64; H, 4.10; N, 4.23. Found: C, 73.64; H, 4.20; N, 4.25.

General Synthesis of (Thiоacetyl)acetamides 3b–3g. Compounds 3b, 3c, and 3e–g were prepared by a procedure similar to that described for 3a. The desired products were obtained as white solids. For 3d, tetrahydrofuran was used as solvent for the reaction, and the desired product 3d was obtained as a light yellow oil.

N-(11-Hydroxyundecyl)-2-(thioacetyl)acetamide (3b). mp 83–84 °C; HRMS-FAB (M+Na) calecd for C₇⁺H₆NO₂SNa m/z 294.1038, found m/z 294.1027. Anal. Caled for C₇⁺H₆NO₂SNa: C, 59.05; H, 9.12; N, 4.00. Found: C, 59.05; H, 9.16; N, 4.05.


N-(11-Hydroxyundecyl)-2-(thioacetyl)acetamide (3d). mp 86–88 °C; HRMS-FAB (M+Na) calecd for C₉⁺H₈NO₂SNa m/z 294.1038, found m/z 294.1027. Anal. Caled for C₉⁺H₈NO₂SNa: C, 59.05; H, 9.12; N, 4.00. Found: C, 59.05; H, 9.16; N, 4.05.

N-(2,3-Dihydroxyphenyl)ethyl)-2-(thioacetyl)acetamide (3e). mp 121–123 °C; HRMS-FAB (M+Na) calecd for C₂₀H₁₈NO₃SNa m/z 368.1872. Found m/z 368.1881. Anal. Caled for C₂₀H₁₈NO₃SNa: C, 59.10; H, 9.4; N, 4.05. Found: C, 59.05; H, 9.12; N, 4.00.

N-(4-(4-Morpholinyl)benzyl)-2-(thioacetyl)acetamide (3f). mp 170–171 °C; HRMS-FAB (M+Na) calecd for C₂₁H₂₂NO₄SNa m/z 388.1574, found m/z 388.1567. Anal. Caled for C₂₁H₂₂NO₄SNa: C, 59.05; H, 9.12; N, 4.00. Found: C, 59.05; H, 9.12; N, 4.00.

N-Dehydroabietyl-2-(thioacetyl)acetamide (3g). mp 48–50 °C; HRMS-FAB (M+Na) calecd for C₂₀H₂₀NO₂SNa m/z 294.1038, found m/z 294.1027. Anal. Caled for C₂₀H₂₀NO₂SNa: C, 59.05; H, 9.12; N, 4.00. Found: C, 59.05; H, 9.16; N, 4.05.

General Synthesis of (Thioacetyl)acetamides 3b–3g. Compounds 3b, 3c, and 3f–g were prepared by a procedure similar to that described for 3a. The desired products were obtained as white solids. For 3d, tetrahydrofuran was used as solvent for the reaction, and the desired product 3d was obtained as a light yellow oil.

N-(11-Hydroxyundecyl)-2-(thioacetyl)acetamide (3b). mp 83–84 °C; HRMS-FAB (M+Na) calecd for C₇⁺H₆NO₂SNa m/z 294.1038, found m/z 294.1027. Anal. Caled for C₇⁺H₆NO₂SNa: C, 59.05; H, 9.12; N, 4.00. Found: C, 59.05; H, 9.16; N, 4.05.


N-(11-Hydroxyundecyl)-2-(thioacetyl)acetamide (3d). mp 86–88 °C; HRMS-FAB (M+Na) calecd for C₉⁺H₈NO₂SNa m/z 294.1038, found m/z 294.1027. Anal. Caled for C₉⁺H₈NO₂SNa: C, 59.05; H, 9.12; N, 4.00. Found: C, 59.05; H, 9.16; N, 4.05.

N-(2,3-Dihydroxyphenyl)ethyl)-2-(thioacetyl)acetamide (3e). mp 121–123 °C; HRMS-FAB (M+Na) calecd for C₂₀H₁₈NO₃SNa m/z 368.1872. Found m/z 368.1881. Anal. Caled for C₂₀H₁₈NO₃SNa: C, 59.10; H, 9.4; N, 4.05. Found: C, 59.05; H, 9.12; N, 4.00.

N-(4-(4-Morpholinyl)benzyl)-2-(thioacetyl)acetamide (3f). mp 170–171 °C; HRMS-FAB (M+Na) calecd for C₂₁H₂₂NO₄SNa m/z 388.1574, found m/z 388.1567. Anal. Caled for C₂₁H₂₂NO₄SNa: C, 59.05; H, 9.12; N, 4.00. Found: C, 59.05; H, 9.12; N, 4.00.

N-Dehydroabietyl-2-(thioacetyl)acetamide (3g). mp 48–50 °C; HRMS-FAB (M+Na) calecd for C₂₀H₂₀NO₂SNa m/z 294.1038, found m/z 294.1027. Anal. Caled for C₂₀H₂₀NO₂SNa: C, 59.05; H, 9.12; N, 4.00. Found: C, 59.05; H, 9.16; N, 4.05.
Table 2. X-ray Photoelectron Spectroscopic Data of SAMs

<table>
<thead>
<tr>
<th>SAM prepared from</th>
<th>F (1s)</th>
<th>O (1s)</th>
<th>N (1s)</th>
<th>C(1s)</th>
<th>Si2p&lt;sup&gt;3/2&lt;/sup&gt;</th>
<th>Si2p&lt;sup&gt;1/2&lt;/sup&gt;</th>
<th>Au4f&lt;sup&gt;7/2&lt;/sup&gt;</th>
<th>Au4f&lt;sup&gt;5/2&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3(CH2)6-NHCOCH3 (4a)</td>
<td>531</td>
<td>399</td>
<td></td>
<td>287, 285</td>
<td>164</td>
<td>162</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td>HO(CH2)12-NHCOCH3 (4b)</td>
<td>533, 531</td>
<td>400</td>
<td></td>
<td>287, 285</td>
<td>164</td>
<td>162</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td>CF3(CH2)6-NHCOCH3 (4c)</td>
<td>688</td>
<td>531</td>
<td>400</td>
<td>292, 287, 286, 284</td>
<td>164</td>
<td>162</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td>CF3(CH2)6SH</td>
<td>687</td>
<td></td>
<td></td>
<td>292, 284</td>
<td>163</td>
<td>161</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td>HO(CH2)12-NHCOCH3 (4d)</td>
<td>533, 531</td>
<td>399</td>
<td></td>
<td>287, 285, 284</td>
<td>163</td>
<td>162</td>
<td>88</td>
<td>84</td>
</tr>
<tr>
<td>HOOC(CH2)16-NHCOCH3 (4e)</td>
<td>533, 532</td>
<td>399</td>
<td></td>
<td>285</td>
<td>163</td>
<td>162</td>
<td>88</td>
<td>87</td>
</tr>
<tr>
<td>CF3(CH2)6-NHCOCH3 (4f)</td>
<td>532, 530</td>
<td>399</td>
<td></td>
<td>287, 286, 285, 284</td>
<td>163</td>
<td>162</td>
<td>87</td>
<td>84</td>
</tr>
</tbody>
</table>

Table 3. Exchange of SAMs Prepared from 4a or from Hexadecanethiol with 5 mM Solution of CF3CONH(CH2)16SH in Heptane

<table>
<thead>
<tr>
<th>SAM prepared from</th>
<th>% exchange after 3 days</th>
<th>% exchange after 10 days</th>
</tr>
</thead>
<tbody>
<tr>
<td>CH3(CH2)6-NHCOCH3 (4a)</td>
<td>4 ± 5</td>
<td>21 ± 5</td>
</tr>
<tr>
<td>HO(CH2)12-NHCOCH3 (4b)</td>
<td>4 ± 5</td>
<td>21 ± 5</td>
</tr>
<tr>
<td>CF3(CH2)6-NHCOCH3 (4c)</td>
<td>&lt; 5</td>
<td>&lt; 5</td>
</tr>
<tr>
<td>CF3(CH2)6SH</td>
<td>23 ± 5</td>
<td>23 ± 5</td>
</tr>
</tbody>
</table>

where Au<sub>d</sub> and Au<sub>d0</sub> are the intensities of the Au<sup>4f<sup>7/2</sup></sub> peak due to a SAM of thickness d and bare gold, respectively, and<sup>(40)</sup> is the incident mean free path of the Au<sup>4f<sup>7/2</sup></sub> photoelectron. <sup>(40)</sup> is equal to 36.5 <sup>(41)</sup>,<sup>(42)</sup> is the angle between the analyzer and the sample. The value Au<sub>d0</sub> was determined using eq 2 for a SAM derived from hexadecanethiol, which has a thickness (d<sub>Au<sub>d0</sub></sub>) of 20 Å. <sup>(40)</sup> is a standard.

Exchange with Thiols in Solution. The exchange of SAMs prepared from butanethiol or 4e with hexadecanethiol was followed by dipping the SAMs in a 5 mM ethanolic solution of hexadecanethiol in a weighing bottle kept in the dark. After a fixed time, the sample was removed from the vial and washed with 10 mL of ethanol, 10 mL of water, and 10 mL of heptane. The percentage exchange of SAM prepared from butanethiol (C4SH) with hexadecanethiol (C16SH) was obtained from the surface composition (x = mol fraction of component n) of the mixed SAM after exchange (eq 3).

% exchange = x<sub>C16SH</sub> × 100%  

To evaluate the surface composition of a SAM against the thickness of a SAM composed of the two thiolates was the simple weighted average of the thicknesses of SAMs derived from the individual thiols (eq 4).<sup>(41)</sup>

\[ d = \frac{x_{\text{C4SH}} d_{\text{C4SH}}} {x_{\text{C16SH}}} + \frac{x_{\text{C16SH}} d_{\text{C16SH}}} {x_{\text{C4SH}}} \]  

Equation 4 assumes that the packing density of the SAM does not change with surface composition. The surface composition was determined by comparing the thickness of the mixed SAM with that of the individual thiols.


Table 4. Data from XPS of a SAM from 4c That Show That This SAM Is Unstable under Standard Laboratory Conditions but Is Stable When Kept in the Dark

<table>
<thead>
<tr>
<th>exposure</th>
<th>normalized intensity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>light&lt;sup&gt;a&lt;/sup&gt;</td>
<td>F(1s)</td>
</tr>
<tr>
<td>time (h)</td>
<td></td>
</tr>
<tr>
<td>as prepared</td>
<td>100</td>
</tr>
<tr>
<td>no</td>
<td>1</td>
</tr>
<tr>
<td>yes</td>
<td>5</td>
</tr>
<tr>
<td>yes</td>
<td>5</td>
</tr>
</tbody>
</table>

<sup>a</sup> Standard laboratory lighting. <sup>b</sup> The observed peak is the combined Si(2p)<sup>b2p</sup> and S(2p)<sup>b2p</sup> peaks of sulfoxides (RSO<sub>2</sub>) which are unresolved for this weak signal. <sup>c</sup> S(2p) peak of gold thiolsates.

The percentage exchange of SAMs derived from 4c or 4,4,4-trifluorobutanethiol with hexadecanethiol was obtained from the surface composition \( \chi_{4c} \) of a monolayer of thickness \( d \) by the following equation:

\[
X_{\text{C16SH}} = \frac{d - d_{\text{C4SH}}}{d_{\text{C16SH}} - d_{\text{C16SH}}} \tag{5}
\]

The thickness of each SAM was calculated from the XPS intensity of its C(1s) peak using eq 6:

\[
C_d = C_w (1 - e^{-bd_0 \sinh \left( \frac{d}{\lambda} \right)}) \tag{6}
\]

where \( C_d \) and \( C_w \) are the intensities of the C(1s) peak due to a monolayer of thickness \( d \) and an infinitely thick layer of hydrocarbon respectively; \( \lambda \) (equal to 35 Å) is the inelastic mean free path of the C(1s) photoelectron. \( C_w \) was determined from a SAM derived from hexadecanethiol \( d' = 20 \) Å using eq 6.

The percentage of exchange of SAMs derived from 4c or 4,4,4-trifluorobutanethiol with hexadecanethiol was obtained from the surface composition \( \chi_{4c} \) of a monolayer of thickness \( d \) and an infinitely thick layer of hydrocarbon using eq 6.

\[
I = (1 - \chi_{\text{C16SH}}) I_f (e^{-\Delta/d_{\text{C16SH}}} + \Delta) \tag{7}
\]

where \( I_f \) is the intensity of the F(1s) peak of SAMs prepared from 4c or 4,4,4-trifluorobutanethiol; \( \Delta \) is the inelastic mean free path of the F(1s) photoelectron. \( \Delta \) is the increase in the thickness of the monolayer resulting from exchange (eq 8). The value \( d_f \) is the thickness of a SAM derived from 4c or 4,4,4-trifluorobutanethiol:

\[
\Delta = \chi_{\text{C16SH}}(d_{\text{C16SH}} - d_f) \tag{8}
\]

The exchange of SAMs prepared from 4c or hexadecanethiol with CF<sub>3</sub>CONH(CH<sub>2</sub>)<sub>11</sub>SH was performed by dipping these SAMs in a 5 mM ethanolic solution of CF<sub>3</sub>CONH(CH<sub>2</sub>)<sub>11</sub>SH for a fixed time. The amount of exchange was determined by comparison of the F(1s) signal of the mixed SAM (\( I_{\text{mix}} \)) obtained after exchange with the intensity \( I_{\text{std}} \) of the F(1s) peak of a SAM derived from CF<sub>3</sub>CONH(CH<sub>2</sub>)<sub>11</sub>SH:

\[
\% \text{ exchange} = \frac{I_{\text{mix}}}{I_{\text{std}}} \times 100\% \tag{9}
\]

The exchange of SAMs prepared from 4c or from hexadecanethiol with CF<sub>3</sub>CONH(CH<sub>2</sub>)<sub>11</sub>SH was performed using the same procedure described for the exchange experiments performed in ethanol (Table 3).

**SAMs from 4c Are Unstable in the Atmosphere of Laboratory.** SAMs from 4c were left under ambient conditions (room temperature and pressure and standard laboratory lighting) for a fixed time. After photodamage, the SAMs were not washed with water or any solvents, and the composition of these monolayers was analyzed immediately by XPS (Table 4). The amount of photoxidation of sulfur in these SAMs was determined by comparison of the XPS intensity of the S(2p)<sup>b2p</sup> peaks of the thiols, respectively, of SAMs before and after their exposure to light.

**UV-Induced Damage of SAMs.** UV damage of SAMs was induced by a Canrad-Hanovia 450 W medium pressure mercury vapor lamp (type 7825-34 from ACE Glass) that was water cooled (type 78548 from ACE Glass). The UV damage experiments were performed with substrates lying side by side, at about 5 mm under the immersion well of the UV lamp, to ensure that SAMs were damaged under similar conditions. After UV-induced damage, the samples of SAMs prepared from 4a or from hexadecanethiol were dipped into a 5 mM ethanolic solution of CF<sub>3</sub>CONH(CH<sub>2</sub>)<sub>11</sub>SH for 5 min and then analyzed by XPS. The percentage of damage was calculated from the F(1s) peak of a SAM obtained at \( I_{\text{std}} \) compared with that of a SAM prepared from CF<sub>3</sub>CONH(CH<sub>2</sub>)<sub>11</sub>SH:

\[
\% \text{ damage} = \frac{I_{\text{mix}}}{I_{\text{std}}} \times 100\% \tag{10}
\]

The percentage of damage of SAMs derived from 4c or from 4,4,4-trifluorobutanethiol was determined by monitoring the decrease in the F(1s) peak \( I_f \) of the SAMs after its exposure to UV for a fixed time (eq 11).

\[
\% \text{ damage} = \frac{(I_{\text{std}} - I_f)}{I_{\text{std}}} \times 100\% \tag{11}
\]

**UV Lithography Using SAMs from 4c.** Photopatterning of SAMs from 4c used a copper grid 0.075 mm thick placed in contact with the SAM as a mask. Lines on the grid were 60 µm wide and 20 µm thick. The sample was placed 2 cm below the UV lamp. After UV-induced damage of the SAM of 4c and dipped into a 5 mM solution of hexadecanethiol for 2 min. The etching was performed using a 1 M KOH/0.1 M KCN solution saturated with oxygen.

**Acknowledgment.** The work at Harvard was supported in part by ARPA and ONR. R.G.N. acknowledges support from the National Science Foundation (CHE-9300995). Mass spectra were obtained by Dr. A. Tyler and N. Niedowski at the Harvard University Chemistry Department Mass Spectrometry Facility. The X-ray photoelectron spectrometer (XPS) is an instrumental facility purchased under the DARPA/URI program and maintained by the Harvard University MRSEC (DMR-94-00396). The SEM was purchased and maintained under the Harvard MRSEC program. The X-ray photoelectron spectrometer (XPS) is an instrumental facility purchased under the DARPA/URI program and maintained by the Harvard University MRSEC (DMR-94-00396). The SEM was purchased and maintained under the Harvard MRSEC program. The NMR facilities at Harvard University were supported by NIH Grant 1-S10RR04870-01 and NSF Grant CHE 88-14019.