(1)

ω-TERMINATED ALKANETHIOLATE MONOLAYERS ON SURFACES OF COPPER, SILVER AND GOLD HAVE SIMILAR WETTABILITIES

Paul E. Laibinis and George M. Whitesides
Department of Chemistry
Harvard University
Cambridge MA 02138

Technical Report No. 40 (December 1991)

Interim Technical Report
(Accepted for publication in the J. Am. Chem. Soc.)

PREPARED FOR DEFENSE ADVANCED RESEARCH PROJECTS AGENCY
1400 Wilson Boulevard
Arlington VA 22209

DEPARTMENT OF THE NAVY
Office of Naval Research, Code 1130P
800 North Quincy Street
Arlington VA 22217-5000

Project No.: a400011dd205
Contract No.: N00014-86-K-0756
Effective Date: 86 September 15
Expiration Date: 92 September 14

Principal Investigator: George M. Whitesides
(617) 495-9430

SECURITY CLASSIFICATION OF THIS PAGE

REPORT DOCUMENTATION PAGE

Form Approved
OMB No. 0704-0188

1a. REPORT SECURITY CLASSIFICATION
Unclassified

1b. RESTRICTIVE MARKINGS

2a. SECURITY CLASSIFICATION AUTHORITY

2b. DECLASSIFICATION / DOWNGRADING SCHEDULE

3. DISTRIBUTION / AVAILABILITY OF REPORT
Approved for public release; distribution unlimited

4. PERFORMING ORGANIZATION REPORT NUMBER(S)
Technical Report No. 40

5. MONITORING ORGANIZATION REPORT NUMBER(S)

6a. NAME OF PERFORMING ORGANIZATION
Harvard University

6b. OFFICE SYMBOL *(If applicable)*

7a. NAME OF MONITORING ORGANIZATION
DARPA

6c. ADDRESS *(City, State, and ZIP Code)*
Office for Sponsored Research
Holyoke Center, Fourth Floor
Cambridge MA 02138-4993

7b. ADDRESS *(City, State, and ZIP Code)*
1400 Wilson Boulevard
Arlington VA 22209-2308

8a. NAME OF FUNDING / SPONSORING ORGANIZATION
ONR

8b. OFFICE SYMBOL *(If applicable)*

9. PROCUREMENT INSTRUMENT IDENTIFICATION NUMBER

8c. ADDRESS *(City, State, and ZIP Code)*
Chemistry Division, Code 1113
Office of Naval Research
Arlington VA 22217-5000

10. SOURCE OF FUNDING NUMBERS

PROGRAM ELEMENT NO.	PROJECT NO.	TASK NO.	WORK UNIT ACCESSION NO.
86-K-0756		a400011dd2	

11. TITLE *(Include Security Classification)*
"w-Terminated Alkanethiolate Monolayers on Surfaces of Copper, Silver and Gold have Similar Wettabilities."

12. PERSONAL AUTHOR(S)
Paul E. Laibinis and George M. Whitesides

13a. TYPE OF REPORT
Technical

13b. TIME COVERED
FROM ________ TO ______

14. DATE OF REPORT *(Year, Month, Day)*
December, 1991

15. PAGE COUNT

16. SUPPLEMENTARY NOTATION

17. COSATI CODES

FIELD	GROUP	SUB-GROUP

18. SUBJECT TERMS *(Continue on reverse if necessary and identify by block number)*

19. ABSTRACT *(Continue on reverse if necessary and identify by block number)*

Long-chain alkanethiols ($HS(CH_2)_nX$) adsorb from solution onto the surfaces of freshly evaporated copper, silver and gold films and form oriented monolayers. Both polar and non-polar tail groups (X) can be accommodated in these adsorptions. Adsorption on all three metals generates self-assembled monolayers (SAMs) exhibiting similar wetting properties, and thus, by inference,

20. DISTRIBUTION / AVAILABILITY OF ABSTRACT
☐ UNCLASSIFIED/UNLIMITED ☒ SAME AS RPT. ☐ DTIC USERS

21. ABSTRACT SECURITY CLASSIFICATION
Unclassified

22a. NAME OF RESPONSIBLE INDIVIDUAL
Dr. Harold Guard

22b. TELEPHONE *(Include Area Code)*
703/696-4311

22c. OFFICE SYMBOL

DD Form 1473, JUN 86 *Previous editions are obsolete.* SECURITY CLASSIFICATION OF THIS PAGE having related oriented structures. XPS data suggest that the ω-terminated *n*-alkanethiolate monolayers, like those derived from simple alkanethiols, are composed of trans-extended chains having orientations on copper and silver that are closer to the perpendicular to the surface than are those on gold. We have prepared and characterized monolayers ("mixed monolayers") by exposure of all three metals to mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$. On all three, the wettability of the interfaces covers the range between the extremes: $\theta_a^{H_2O}$ = ~10° and ~115°. Values of the advancing contact angle of water can be related to their composition by Cassie's expression. The similarity in wettabilities of these surfaces, and the fact that wettability is related to surface composition by a simple linear relationship, both argue that $-CH_2OH$ and $-CH_2CH_3$ functional groups behave approximately independently at the monolayer-air (water) interface. Interactions between functional groups, and substantial variations in the structure of the underlying polymethylene region of the SAM are much less important in determining interfacial free energies than are the areas the functional groups occupy at the interface.

ω-Terminated Alkanethiolate Monolayers on Surfaces of Copper, Silver and Gold Have Similar Wettabilities.[1]

Paul E. Laibinis[2] and George M. Whitesides*

Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Abstract

Long-chain alkanethiols ($HS(CH_2)_nX$) adsorb from solution onto the surfaces of freshly evaporated copper, silver and gold films and form oriented monolayers. Both polar and non-polar tail groups (X) can be accommodated in these adsorptions. Adsorption on all three metals generates self-assembled monolayers (SAMs) exhibiting similar wetting properties, and thus, by inference, having related oriented structures. XPS data suggest that the ω-terminated *n*-alkanethiolate monolayers, like those derived from simple alkanethiols, are composed of trans-extended chains having orientations on copper and silver that are closer to the perpendicular to the surface than are those on gold. We have prepared and characterized monolayers ("mixed monolayers") by exposure of all three metals to mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$. On all three, the wettability of the interfaces covers the range between the extremes: $\theta_a^{H_2O}$ = ~10° and ~115°. Values of the advancing contact angle of water can be related to their composition by Cassie's expression. The similarity in wettabilities of these surfaces, and the fact that wettability is related to surface composition by a simple linear relationship, both argue that $-CH_2OH$ and $-CH_2CH_3$ functional groups behave approximately independently at the monolayer-air (water) interface. Interactions between functional groups, and substantial variations in the structure of the underlying polymethylene region of the SAM are much less important in determining interfacial free energies than are the areas the functional groups occupy at the interface.

Introduction

Long-chain alkanethiols ($HS(CH_2)_nCH_3$) adsorb from solution onto the surfaces of copper, silver, and gold and form densely packed, oriented monolayer films (self-assembled monolayers, SAMs) that are attached to the surface as metal thiolates (RS^-M^+).[3-22] On gold, alkanethiolate monolayers, derived from alkyl thiols or disulfides, have provided systems used for studies of wetting,[6-12] adhesion,[13] protein adsorption[14,15] and electrochemistry.[15-19] These assemblies offer a high degree of control over the thickness of the monolayer, and accomodate a wide range of polar and non-polar tail groups at the opposite terminus of the polymethylene chain from the thiol group (and thus at the interface between the SAM and the vapor or liquid phase contacting it). To date, the self-assembling system reported to be capable of generating the widest variety of organic interfaces is that based on adsorption of ω-substituted alkanethiols on gold.[6-12,14,17,19-21] Here we report that the chemistry described for alkyl thiolates on gold can be readily extended to alkyl thiolates on silver, and, with greater experimental difficulty, to copper. We also provide data that suggests that, while the alkanethiolate monolayers on silver and copper have structures that are distinct from (although closely related to) those formed on gold, similar wettabilities are observed for corresponding SAMs on all three metals. We and others have described extensive structural studies of *unsubstituted* alkanethiolates on gold,[3,16,22] silver[3,4] and copper.[3] The emphasis in the present paper is on alkanethiolates bearing terminal substituents, especially polar ones. Ulman et al.[23] have reported that monolayers formed by adsorption of $HS(CH_2)_{11}OH$ on silver and gold have different wettabilities: $\theta_a^{H_2O}$ ~20° and <10°, respectively. We find the wettability of SAMs on silver and gold derived from hydroxyl-terminated alkanethiols, including those derived $HS(CH_2)_{11}OH$, to be the same, although we have observed higher values of $\theta_a^{H_2O}$ on silver whose surface has oxidized.

Many self-assembling systems now exist that can generate low-energy surfaces;[3-6,24,25] however, the number capable of generating high-energy surfaces, *in one assembly step,* are few. For example, while *n*-alkanoic acids adsorb onto various metal oxides and form oriented, oleophobic monolayers,[25] ω-hydroxy- and ω-amino-alkanoic acids adsorb and form poorly organized films that are not wet by water (probably because they form "looped" structures with polar functionalities in both α- and ω-positions coordinated to the surface). Relatively hydrophilic surfaces ($\theta_a^{H_2O}$ = 30-50°) have been prepared on silica in a two-step procedure: first, adsorption of an alkyltrichlorosilane having a terminal olefin, ester, or alkyl sulfide group on silica;[26-28] second, chemical transformation of the non-polar terminal group into a more polar group (carboxylic acid,[26] alcohol,[26,27] sulfone[28]). This type of system has two disadvantages. First, the monolayers of alkylsiloxanes on silica are probably intrinsically less ordered than SAMs on gold and silver,[29] and are unquestionably more difficult to prepare in highly-ordered form; second, the reactions used to convert functionalities present in these SAMs to more polar forms certainly proceed in yields less than 100%.[30] Thus, the alkylsiloxane monolayers having polar terminal functionality are probably disordered both in structure and in composition at their termini.

In contrast, interfaces that are both polar and highly wettable (alcohols,[6,17,21] carboxylic acids,[6,10,17,21] phosphocholines,[20] amides[21]) have been prepared by adsorption of the corresponding alkanethiols onto gold surfaces. We believed the ability of gold to discriminate between hard and soft[31] tail groups could be extended to surfaces of copper and silver.[32]

In a previous paper,[3] we have shown that *n*-alkanethiols adsorb onto copper and silver and form oriented, densely packed monolayers. These SAMs differ in one respect from those formed on gold; XPS and IR spectroscopy indicated that the alkyl chains are oriented closer to the perpendicular to the surface of the metal on copper and silver than on gold (cant angles, relative to the surface normal are 13° (copper and silver) and 28° (gold)). We note that the SAMs studied in that report[3] and here exhibited no (or little) surface oxide on silver and gold; the monolayers formed on copper were supported on an interphase that contained oxide even though exposure of the unfunctionalized surface to the atmosphere was minimized.

Results and Discussion

Films of copper, silver, and gold were prepared by evaporation of the metals onto pre-cut slides of Cr-primed Si(100) using a resistively heated tungsten filament or an electron beam. The slides were immersed in 1 mM deoxygenated ethanolic solutions[33] of various ω-terminated alkanethiols for 2-12 h and characterized by measurement of contact angle and XPS. Some SAMs on copper (X = CH_3, $CH=CH_2$) were prepared from isooctane and exhibited lower hysteresis than corresponding SAMs formed from ethanol. The evaporated films of copper and silver were transferred to solution under a flow of Ar; films of gold was transferred under air. Table I summarizes the advancing and receding contact angles of water and hexadecane on the resulting SAMs.

In general, the wetting behaviors observed on the monolayers prepared on silver and copper are similar to those prepared on gold; the hysteresis in the contact angles of water is generally greater on the copper surfaces. We believe that this increase is probably due to the roughening of the metal-air (or monolayer) interface that occurs during oxidation and subsequent adsorption of the thiol. We note that the range of wettabilities -- for $\theta_a^{H_2O} = 120°$ to $\theta_a^{H_2O} < 15°$ -- demonstrated on copper, silver, and gold cannot be achieved in other self-assembling systems.

The only organic groups that yielded highly hydrophilic surfaces ($\theta_a^{H_2O} < 20°$) are those that exposed groups capable of hydrogen-bond donation (OH, CO_2H, $CONH_2$). Alkanethiols terminating in X = OH or CO_2H did not always yield SAMs on copper that were as hydrophilic as those formed on gold or silver; for X = OH, SAMs were not wet by water only for long-chain ($n > 16$) adsorbates. Carboxylic acids and alcohols will form monolayers on most (if not all) metal oxides;[24] we believe that the films formed on our slightly oxidixed copper surfaces probably consist, in part, of "looped"[34] and/or "inverted" structures. These overall structures would expose a hydrophobic, disordered interface to the contacting

Table I. Static advancing and receding contact angles of water and hexadecane (HD) on films prepared by adsorption of $HS(CH_2)_nX$ on surfaces of gold, silver and copper

Cmpd #	n	X	Molecular Length^{b}	Contact angles (advancing, receding; in degrees)^{a}					
				Au		Ag		Cu	
				H_2O	HD	H_2O	HD	H_2O	HD
1	2	$(CF_2)_5CF_3$	10	119,106	71,62	121,110	79,60	122,106	81,59
2	11	$OCH_2CF_2CF_3$	17	118,105	71,62	119,111	75,61	119,99	69,44
3	7	$CH_3{}^{c}$	10	112,103	46,35	107,93	45,33	115,98	44,31
4	11	$CH_3{}^{c}$	14	115,104	49,36	113,99	46,35	120,99	46,28
5	17	$CH_3{}^{c}$	20	115,105	48,36	116,103	49,35	120,103	48,32
6	21	$CH_3{}^{c}$	24	117,100	49,38	115,103	49,36	117,102	45,34
7	17	$CH{=}CH_2{}^{c}$	21	105,100	38,28	108,100	44,34	117,96	31,24
8	11	$OCOCF_3{}^{d}$	16	93,83	60,28	93,77	64,32	100,85	58,30
9	10	$CO_2CH_2CH_3$	16	89,77	45,28	89,71	38,19	93,69	31,-
10	11	Cl	13	89,77	<10,-	89,77	<10,-	95,80	<10,-
11	11	OCH_3	15	85,72	37,11	84,66	38,20	87,57	32,-
12	11	CN	14	68,61	<10,-	74,65	<10,-	72,52	<10,-
13	16	CN	19	70,62	<10,-	75,63	<10,-	77,49	<10,-
14	21	CN	24	74,62	<10,-	78,60	<10,-	80,50	<10,-
15	11	$CONHCH_3$	16	76,64	31, -	82,65	29,-	e	e
16	10	CO_2CH_3	15	74,61	38,25	72,64	35,22	70,49	22,-
17	10	OH	13	<15,-	<10,-	<15,-	<10,-	<15,-	<10,-
18	11	OH	14	<15,-	<10,-	<15,-	<10,-	<15,-	<10,-
19	19	OH	22	<15,-	<10,-	<15,-	<10,-	26,-	<10,-
20	22	OH^{f}	25	25,-	<10,-	21,-	<10,-	44,20	<10,-
21	10	$CONH_2$	14	<15,-	<10,-	<15,-	<10,-	<15,-	<10,-
22	15	$CONH_2$	19	<15,-	<10,-	<15,-	<10,-	17,-	<10,-
23	10	CO_2H	14	<15,-	<10,-	<15,-	<10,-	35-50,-	<10,-
24	15	CO_2H	19	<15,-	<10,-	<15,-	<10,-	53,25	<10,-
25	21	CO_2H	25	<15,-	<10,-	<15,-	<10,-	50,25	<10,-

(Table I Cont'd)

[a] HD = hexadecane. A dash indicates a receding contact angles for a contacting liquid that could not be removed from the surface. For these systems, $\theta_r \cong 0°$.

[b] Molecular length is defined as the number of contiguous atoms in the adsorbed molecule comprising the monolayer metal/$S(CH_2)_nX$. These values are used in Figure 1.

[c] The SAM on copper was formed from isooctane. SAMs prepared on copper from this thiol from ethanol routinely exhibited greater hystereses ($\cos\theta_r - \cos\theta_a$) than SAMs adsorbed from isooctane.

[d] Prepared by reaction of entry 18 with 5% trifluoroacetic anhydride/hexanes for 30 s.

[e] SAMs on copper were difficult to obtain in high quality. The wetting properties of our best samples were: $\theta_a^{H_2O} = 65\text{-}75°$, $\theta_r^{H_2O} = 36°$, $\theta_a^{HD} = 17°$, $\theta_r^{HD} \cong 0°$.

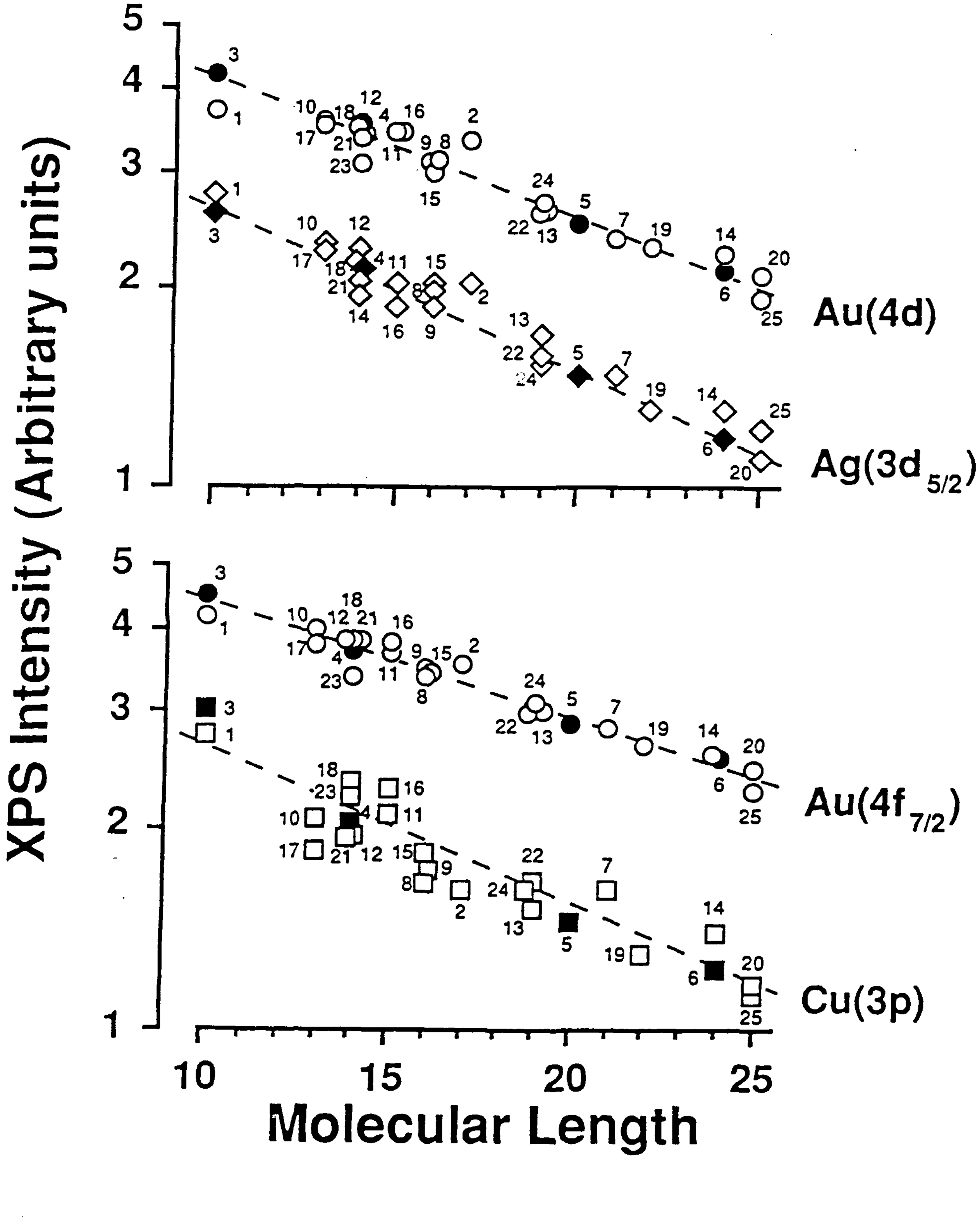
[f] A value of $\theta_a^{H_2O} \approx 20°$ has been reported for SAMs on gold derived from $HS(CH_2)_{21}OH$ (Evans, S. D.; Sharma, R.; Ulman, A. *Langmuir* **1991**, *7*, 156-161).

liquid (vide infra). Alkanethiols terminating in polar groups adsorbed on silver surfaces that contained an oxide interphase also yielded less hydrophilic surfaces; the contact angles reported here on silver (Table I, Entries 17-25) were only obtained when exposure of the evaporated silver to atmosphere was minimized. The adsorption of some fraction of the tail groups to the oxide surface may explain some of the higher contact angles of water observed by Ulman and co-workers for polar organic surfaces formed on silver.[23] We have been able to reproduce the higher contact angles of water reported by Ulman et al. by allowing the silver to oxidize sufficiently before exposure to an ω-hydroxyalkanethiol. Reports by Ulman et al.[23] that wettability of monolayers derived by adsorption of $HS(CH_2)_{11}OH$ on gold and silver are different, and computations rationalizing this reported difference require, in our opinion reanalysis: in our experience, *the wettability of hydroxyl-terminated alkanethiolate monolayers on silver and gold are the same.*

The highly hydrophilic surfaces (X = OH, $CONH_2$ and CO_2H; Entries 17-21) provide an example of the sensitivity of wetting of these systems to structure. Replacement of a hydrogen atom in these structures by a methyl group (X = OCH_3, $CONHCH_3$, CO_2CH_3; Entries 11, 15, 16) is sufficient to change these very hydrophilic surfaces to hydrophobic surfaces ($\theta_a^{H_2O}$ = 70-90°) that are also no longer wet by hexadecane; similar effects have been observed previously.[7,21,35]

The monolayers formed on the three metal surfaces were characterized by XPS to determine their structural similarity to films formed from simple *n*-alkanethiols (Figure 1); XPS can be used as a measure of the thickness of a film by determining the attenuation of photoelectrons from the underlying substrate by the adsorbed layer.[36] We have previously shown for *n*-alkanethiolate monolayers formed on the three metals that conclusions concerning the structure of the SAM drawn from XPS attenuations agreed with those from IR.[3,37] For this study, the variations in head groups complicate comparison; we adopt the convention of comparing the intensities of photoelectrons due to the substrate to the number of atoms that extend from the sulfur to the end of the tail group in the adsorbed molecule (see Table I). While this treatment is qualitative and does not take full account of differences in the structures of the various tail groups, it provides a useful comparison. The degree of attenuation is also a function of the kinetic energy of the photoelectrons,[38] and we compare peaks of similar energies -- that is, in Figure 1, Au(4d) (BE ≈ 1143 eV) with Ag($3d_{5/2}$) (BE = 1119 eV); Au($4f_{7/2}$) (BE = 1402 eV) with Cu(3p) (BE ≈ 1410 eV). Each datum was obtained in ~3 min and the damage to the monolayers in this interval due to exposure to X-rays was negligible. Figure 1 shows that the attenuation, and thus the relative thicknesses of the monolayers containing tail groups of differing polarity but commensurate in size with the polymethylene chains, are similar to those derived from *n*-alkanethiols throughout a series on a particular metal. We stress that the XPS data presented here imply that *the functional groups are supported on a hydrocarbon layer* ($(CH_2)_n$) *that is analogous in thickness and thus in packing density to simple n-alkanethiolate monolayers on*

Figure 1. Intensity of photoelectrons due to the underlying metal substrate for various monolayers adsorbed on the surfaces of copper (□), silver (◇), and gold (○) from absolute ethanol. We define "molecular length" as the number of contiguous atoms in the adsorbate spanning the monolayer. (For example, for metal/$SCH_2CO_2CH_3$ the molecular length would be 6.) The numeric labels refer to compounds listed in Table I. Absolute photoelectron intensities are a function of instrumental parameters and the sets of data have been offset vertically to facilitate comparison; only the slopes are important here. The kinetic energies of photoelectrons for each graph are similar: $Au(4f_{7/2})$ = 1402 eV and Cu(3p) = 1412 eV; Au(4d) = 1143 eV and $Ag(3d_{5/2})$ = 1119 eV. The filled symbols correspond to SAMs derived from *n*-alkanethiols ($X = CH_3$). Dashed lines were determined from linear least square fits to data obtained from adsorption of *n*-alkanethiols on the three metals; the higher slopes obtained on copper and silver demonstrate that the SAMs formed on these metals are oriented closer to the surface normal than those formed on gold: Au(4d) = -0.049 vs. $Ag(3d_{5/2})$ = -0.057; $Au(4f_{7/2})$ = -0.041 vs. Cu(3p) = -0.051.



XPS Intensity (Arbitrary units)
Molecular Length
5
4
3
2
1
10
15
20
25
Au(4d)
Ag(3d 5/2)
Au(4f 7/2)
Cu(3p)

the various metals.[39] These differences in the change in thickness with atomic length between SAMs formed on the three metals suggest that the orientation of the axis of the polymethylene chain is closer to the normal to the surface on copper and silver than on gold. The XPS data do not, however, indicate anything about fine details of structure, especially the orientation of the tail groups. At room temperature, calculations by Hautman and Klein indicate the tail groups to be dynamic and disordered.[40,41]

The XPS attenuation of the films formed on copper by exposure to $HS(CH_2)_nCO_2H$ or $HS(CH_2)_{19,22}OH$ suggests that the packing density of the film approximates a densely packed oriented monolayer. The wettabilities of these films are, however, inconsistent with the formation of an interface comprising densely packed carboxylic acid or hydroxyl groups (vide supra). The films were examined further by XPS. High resolution spectra of the S(2p) region revealed a broad envelope that could not be fit by a single spin-orbital doublet. The presence of intensity at slightly higher binding energies ($\Delta = 1$ eV) from that expected for metal-thiolates suggests that some of the sulfur-containing species are present as thiols. Similar wetting and XPS features could be observed on silver that had been highly oxidized.

Mixed Monolayers Adsorbed from Ethanol Solution. In a further comparison of the characteristics of SAMs on the three metals, we determined contact angles on mixed monolayers[8,9] prepared by adsorbing $HS(CH_2)_{11}CH_3$ and $HS(CH_2)_{11}OH$ from 1 mM ethanolic solutions containing mixtures of these two compounds. The metals were exposed to the contacting solution for 2 h. The wettabilities of the resulting monolayers for various compositions of the solutions and of the resulting SAMs are plotted in Figure 2. The surface compositions were determined from XPS by comparing the intensity of the O(1s) peak in the mixed monolayer to the intensity of the monolayer derived from pure $HS(CH_2)_{11}OH$. Determinations of the surface compositions on copper were complicated by the presence of surface oxide and are therefore slightly less accurate than on gold and silver.[42] The three systems were dynamic: the films incorporated more dodecanethiol and became increasing hydrophobic with extended exposure to the ethanolic solutions. The relation between wettability and surface composition did not change with time and we have included data from longer exposure times in the lower panel of Figure 2.

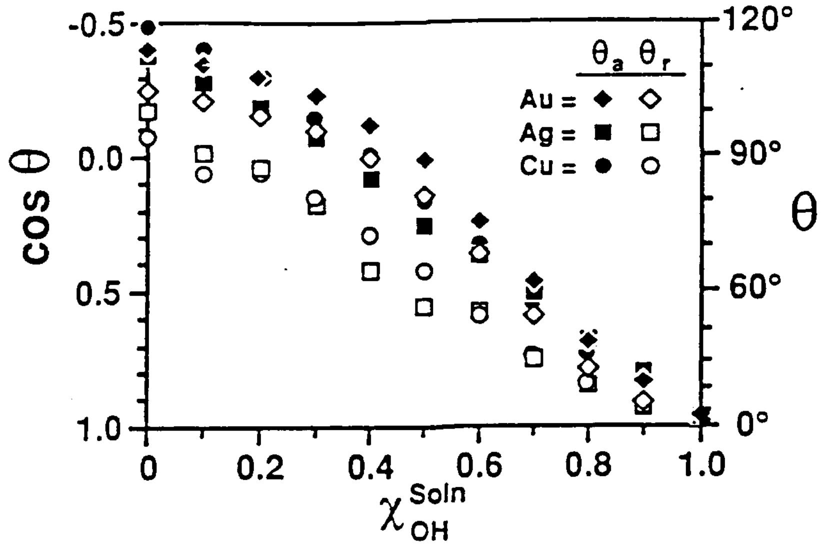
On all three metals, the SAMs exhibited similar wettabilities at the same value of the mole fraction of the hydroxyl-containing component in solution (χ_{OH}^{Soln}) or on the surface (χ_{OH}^{Surf}). The two alkanethiols adsorb on the three metals forming monolayers of similar compositions, and the wettability of these mixed monolayers is better described by Cassie's equation[43] (eq 1), than by eq 2 suggested by Israelachvili and Gee[44] (Figure 2).

$$\cos\theta = f_1\cos_1 + f_2\cos\theta_2 \qquad (1)$$

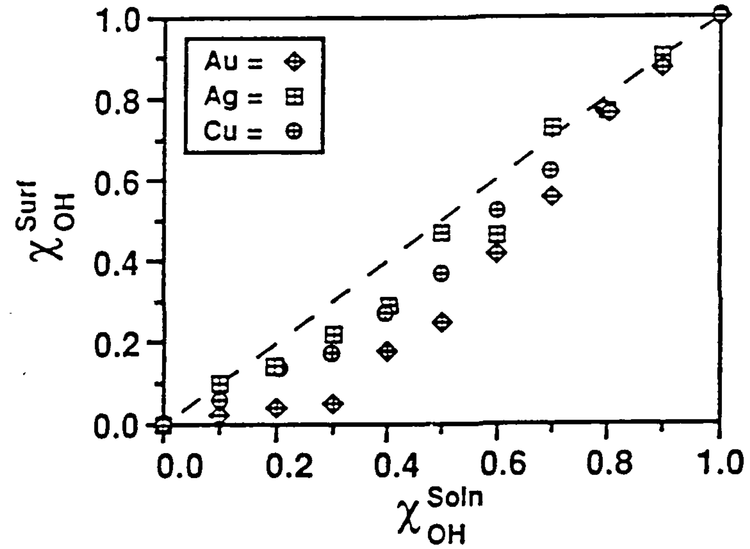
$$(1 + \cos\theta)^2 = f_1(1 + \cos\theta_1)^2 + f_2(1 + \cos\theta_2)^2 \qquad (2)$$

In eq 1 and 2, f_n is defined as the fractional area of the surface that is type *n*, and θ_n as the contact angle on a pure homogeneous surface of type *n*; hydroxyl and methyl groups are sufficiently similar in size that we assume f_n and χ_n^{Surf} are equivalent for the

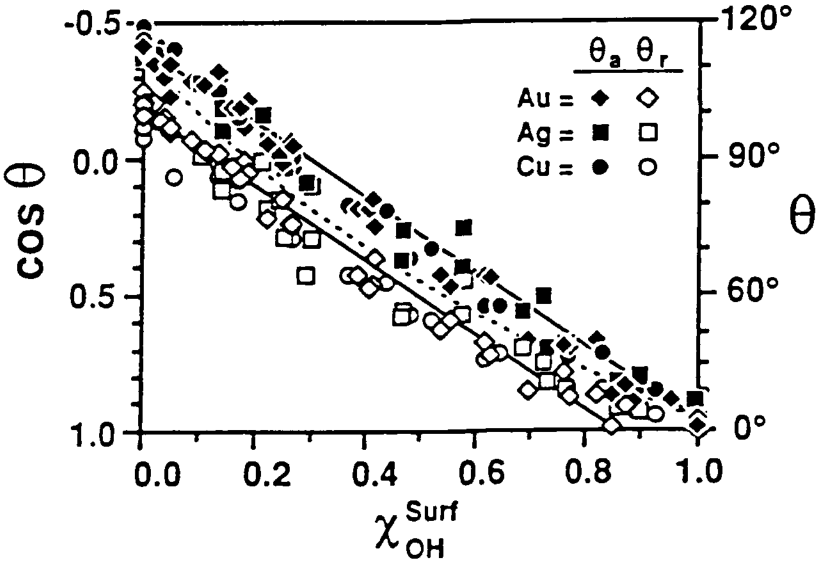
Figure 2. Comparison of monolayers adsorbed on copper (○), silver (□), and gold (◇) from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ dissolved in ethanol after 2 h exposure. Solutions were 1 mM in total thiol concentration. Advancing and receding contact angles (filled and open symbols, respectively) were measured on static drops of water. Surface compositions (patterned symbols) were determined from XPS by scaling the O(1s) signal to that obtained on the pure $HS(CH_2)_{11}OH$-derived monolayer; the background level of oxygen on copper (determined from the pure $HS(CH_2)_{11}CH_3$-derived monolayer) was subtracted from all copper samples prior to analysis.[42] Cassie's equation[43] (solid lines; bottom graph) relates the surface composition linearly to the wettability of the monolayer by water. Israelachvili and Gee's equation[44] (dashed line) does not describe the relation between advancing contact angle and surface composition as well as Cassie's equation. The lowest panel includes data obtained from samples that were exposed to the contacting solutions for 2-48 h.



cos θ
θ
-0.5
0.0
0.5
1.0
120°
90°
60°
0°
0
0.2
0.4
0.6
0.8
1.0
χ_{OH}^{Soln}
θ_a θ_r
Au = ◆ ◇
Ag = ■ □
Cu = ● ○



χ_{OH}^{Surf}
1.0
0.8
0.6
0.4
0.2
0.0
0.0
0.2
0.4
0.6
0.8
1.0
χ_{OH}^{Soln}
Au = ⊕
Ag = ⊞
Cu = ⊖



cos θ
θ
-0.5
0.0
0.5
1.0
120°
90°
60°
0°
0.0
0.2
0.4
0.6
0.8
1.0
χ_{OH}^{Surf}
θ_a θ_r
Au = ◆ ◇
Ag = ■ □
Cu = ● ○

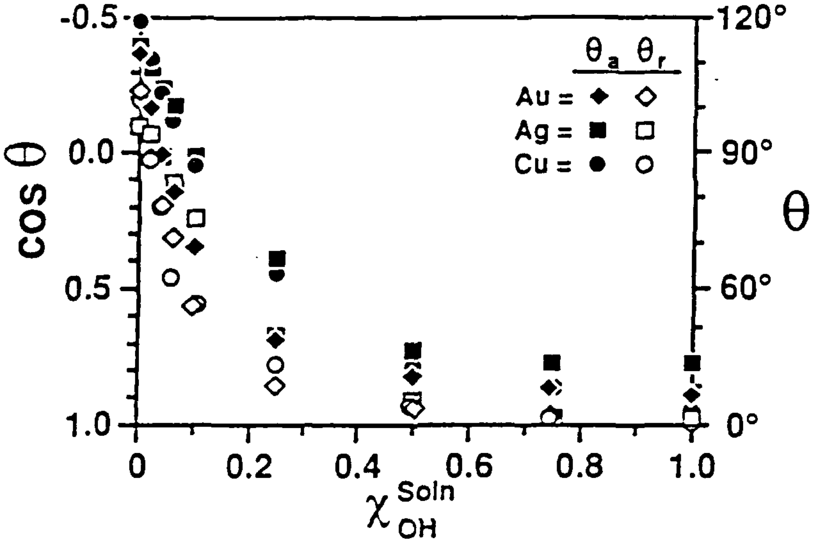
system studied here. We discuss the comparison of these equations further below.

The similarity in surface compositions (χ_{OH}^{Surf}) at a common value of solution composition (χ_{OH}^{Soln}) is remarkable given the differences in the structures of the monolayers, the strength of the various thiolate-metal bonds, and most importantly, the different chemistries that must be occurring during adsorption of the thiols onto surfaces having differing amounts of oxide. This similarity is particularly striking for silver (which has an oxide surface before exposure to thiol), and gold (which does not).

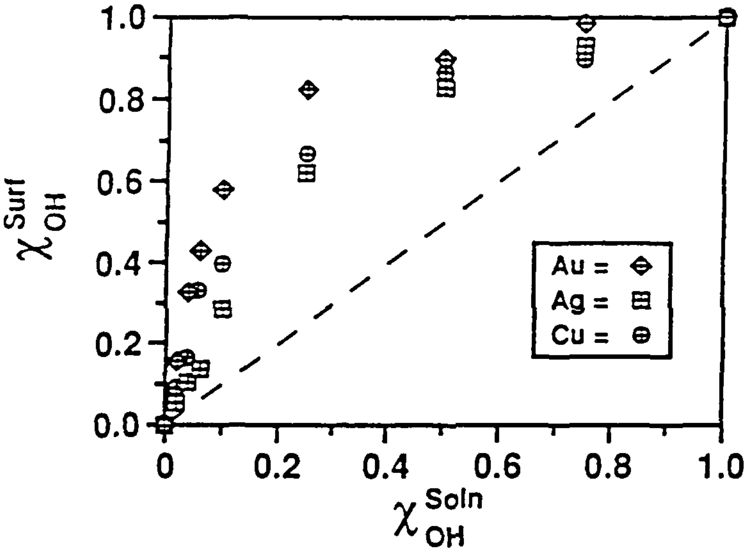
The hysteresis in the contact angles of water appears constant over all surface compositions (and wettabilities) on each of the three metals. This observation suggests that any islanded domains that may have formed have similar size. The hysteresis on each metal, however, is significantly different (Cu > Ag > Au). Since the surface roughness of the metals may be different, hysteresis cannot be related directly to differences in the structures of the monolayers.

Mixed Monolayers Adsorbed from Isooctane Solution. We also examined whether the characteristics of the mixed monolayers on the three metals differed in their response to the solvent used in their preparation. Figure 3 gives data using isooctane as a solvent that parallel those in Figure 2 using ethanol. Bain et al. have shown that the preference of alkanethiols terminated with polar functional groups for a gold surface could be dramatically increased relative to non-polar alkanethiols by using a less polar solvent in adsorption of the SAM.[9] Figure 3 shows that similar

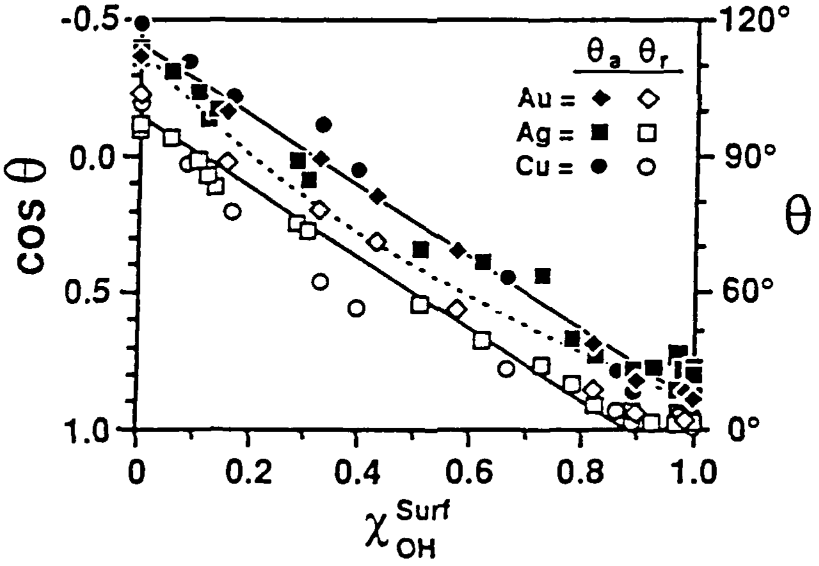
Figure 3. Comparison of monolayers adsorbed on copper (○), silver (□), and gold (◇) from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ dissolved in isooctane after 1 h exposure. Solutions were 1 mM in total thiol concentration. Data were analyzed and are presented as in Figure 2.



-0.5
0.0
0.5
1.0
cos θ
120°
90°
60°
0°
θ
θa θr
Au = ◆ ◇
Ag = ■ □
Cu = ● ○
0
0.2
0.4
0.6
0.8
1.0
χ OH Soln



1.0
0.8
0.6
0.4
0.2
0.0
χ OH Surf
Au =
Ag =
Cu =
0
0.2
0.4
0.6
0.8
1.0
χ OH Soln



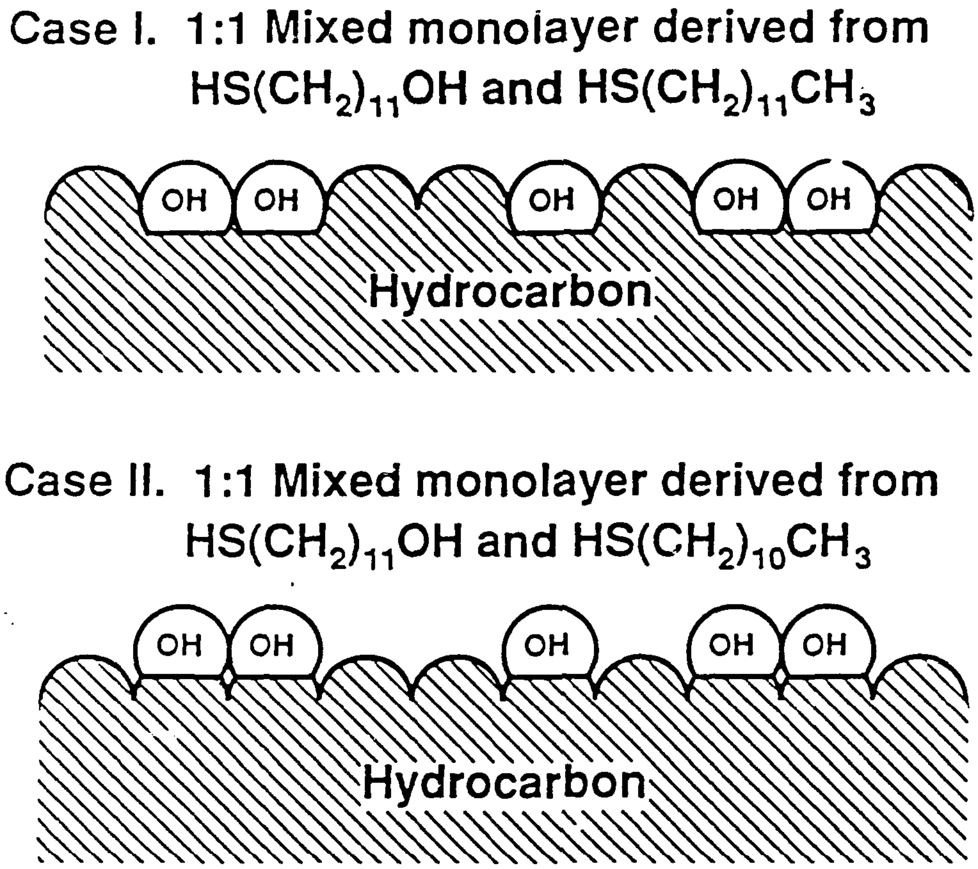
-0.5
0.0
0.5
1.0
cos θ
120°
90°
60°
0°
θ
θa θr
Au = ◆ ◇
Ag = ■ □
Cu = ● ○
0
0.2
0.4
0.6
0.8
1.0
χ OH Surf

behaviors occur on all three metals using isooctane as the solvent for the alkanethiols, and that all three differ in similar ways from monolayers formed from ethanol. While the $-CH_3$ and $-CH_2OH$ terminated thiols competed about equally for the metal surfaces from ethanol, the latter absorbs preferentially from isooctane. With continued exposure to the contacting solution, χ_{OH}^{Surf} increases and the film becomes more hydrophilic. Although the adsorption profiles from isooctane are different from those performed from ethanol, the wetting data are again better described by eq 1 than eq 2 even though the hydrophilicity of the pure hydroxyl surface ($\chi_{CH}^{Surf} = 1.0$) is substantially less from isooctane on all three metals than from ethanol. Adsorption of hydroxyl-terminated thiols onto gold from a non-hydrogen-bonding solvent has been shown to result in SAMs that are less hydrophilic than those formed in ethanol.[9] We do not know the cause of this difference: two possibilities are formation of hydrogen-bonded networks having different structures, or contamination of the polar interface by impurities in solvent.

Ulman[45] has recently proposed the presence of a wetting transition for SAMs on gold derived for mixtures of $CH_3(CH_2)_{11}SH$ and $HO(CH_2)_{11}SH$. The data in Figures 2 and 3 clearly do not support the presence of a wetting transition for water in these mixed monolayers on gold, silver or copper. No significant departures from Cassie's equation were observed with SAMs adsorbed from ethanol or isooctane on any of the three metals studied here.

The Relation Between Wettability and Surface Composition: Cassie vs. Israelachvili-Gee. Israelachvili and Gee[44] have suggested eq 2 as an alternative to eq 1 "whenever the size of chemically heterogeneous patches approach molecular or atomic dimensions." We have shown here that SAMs prepared from mixtures of $CH_3(CH_2)_{11}SH$ and $HO(CH_2)_{11}SH$ are better described by eq 1 than eq 2. In contrast, Bain et al. have shown that mixed SAMs on gold prepared from $CH_3(CH_2)_{10}SH$ and $HO(CH_2)_{11}SH$ are more hydrophilic than Cassie's relation would suggest.[9] We have reanalyzed their data and find that the wettability of the mixed monolayers is well described by eq 2.[46] Why the apparent disagreement in two very similar systems? One possible hypothesis might be that the former system forms SAMs that are highly islanded and the latter does not. While we have no explicit proof concerning the degree of aggregation present in these systems, we feel that the effect can be explained in terms of the differences in the molecular-level heterogeneity present in the two systems, and propose, as one hypothesis, a rationalization based on microscopic roughness.

If one extends Cassie's relation to the molecular level and sums over the *surface areas* of hydroxyl and methyl groups, a difference between the two systems becomes apparent that may be important. The two systems differ by a single methylene in the methyl-terminated alkanethiol (Figure 4). In the system reported here, the mixed monolayer should, on the average, expose the two functionalities at a common molecular height (Case I). The molecular-level surface area should not change over all surface compositions; the surface area of a hydroxyl should be linearly related to its surface composition. We predict a linear relation



Case I. 1:1 Mixed monolayer derived from $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$

Case II. 1:1 Mixed monolayer derived from $HS(CH_2)_{11}OH$ and $HS(CH_2)_{10}CH_3$

Figure 4. Schematic illustration of the surfaces of monolayers derived from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ (Case I) and $HS(CH_2)_{11}OH$ and $HS(CH_2)_{10}CH_3$ (Case II). Cases I and II differ by one methylene in the length of the hydroxyl-terminated chain. Experimentally, the advancing and receding contact angles of water in the two systems are related to the molar fraction of the two components by different expressions: Case I, eq 1; Case II, eq 2. We hypothesize that the difference in wetting may be due to greater exposure of the hydroxyl groups in Case II than in Case I. The diagrams are schematic and oversimplified: both surfaces are disordered to an extent we cannot presently specify.

between wettability and surface composition. In the mixed monolayers studied by Bain et al.,[9] the hydroxyl groups can, on the average, reside above the plane of the methyl surface (Case II). The surface of the mixed monolayer containing two components of different lengths might be microscopically rougher, and have a larger surface area, than for SAMs derived from either of the two components alone. Because the hydroxyl groups extend above the plane defined by the methyl groups, the fraction of the surface area due to hydroxyl groups should be greater than the surface composition of these groups. Cassie's relation (applied at the molecular level) would predict that the SAMs would appear more hydrophilic than estimated from surface compositions.

Conclusions

ω-Terminated alkanethiols form oriented monolayers on copper, silver and gold surfaces that exhibit similar wetting properties, although they differ significantly in structure (specifically in the cant angles of the trans-extended chains: on gold, 28°; on copper and silver, 13°). In particular, we observed no differences in the wettability of hydroxyl-terminated monolayers. This observation is in disagreement with reports by Ulman et al.[23] The three metals accommodate a variety of tail groups; organic surfaces of a wide range of wettabilities ($\theta_a^{H_2O}$ of <15° to ~115°) can be generated on each. Monolayers prepared on each of these metals from mixtures of alkanethiols of similar chain lengths containing different tail groups show similar relations between the compositions or the monolayers and the compositions of the solutions from which they were formed,[47] and exhibit similar wettabilities. The wettability of the mixed monolayers derived from alkanethiols having the same number of methylene groups are better described by the relation of Cassie[43] than of Israelachvili and Gee.[44] No wetting transition was observed on SAMs on gold, silver or copper prepared from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$. This observation disagrees with a recent report by Ulman et al.[45] for SAMs on gold.

Experimental

Materials. 11-Bromo-undecyl t-butyldimethylsilyl ether and most alkanethiols were available from previous studies;[6,21,48] other materials were obtained from Aldrich and used as received unless specified. Octadecanethiol was distilled under reduced pressure prior to use. 1,1,2,2-Dihydrido-perfluorooctyl thiol and 16-mercapto-hexadecanoamide were gifts of Dr. Nandan Rao (Dupont) and Dr. Ralph G. Nuzzo (AT&T Bell Labs), respectively. 16-Cyano-1-hexadecene[49] and 10-undecenamide[50] were prepared by literature procedures. Isooctane was percolated through neutral alumina to remove polar products of oxidation. Absolute ethanol (Quantum Chemical Corp.) and isooctane were deoxygenated with bubbling N_2 for 30 min prior to use. Details of the preparation of the following molecules are given in supplementary material to this journal: 11-(2,2,3,3,3-pentafluoropropoxy)-undecanethiol, ethyl-11-mercapto-undecanoate, 11-cyano-1-undecyl thiol, 16-cyano-1-hexadecyl thiol, 21-cyano-1-heneicosyl thiol, 10-mercapto-1-decanol, 22-mercapto-1-docosanol, and 11-mercapto-undecanamide.

Preparation and Characterization of Monolayers. Procedures were identical with those previously reported;[3] substrates were prepared by evaporation in a cryogenically-pumped electron beam evaporator (base pressure ≈ 8×10^{-8} torr). Single-component monolayers were characterized by wetting and XPS after immersion for 12 h in 1 mM deoxygenated ethanolic solutions. Mixed monolayers were formed from deoxygenated solutions that were 1 mM in total thiol concentration; immersion times for mixed monolayers are as stated in the figure captions.

Acknowledgements. We are grateful to Dr. Nandan Rao (Dupont), Dr. Ralph G. Nuzzo (AT&T Bell Labs), and our colleagues Colin D. Bain and Lana E. Janes for suppplying some of the thiols used in this work, and Drs. Abe Ulman and Steve Evans (Kodak) for useful discussions.

Supplementary Material Available. Details of the preparation of 11-(2,2,3,3,3-pentafluoropropoxy)-undecanethiol, ethyl-11-mercapto-undecanoate, 11-cyano-1-undecyl thiol, 16-cyano-1-hexadecyl thiol, and 21-cyano-1-heneicosyl thiol, 10-mercapto-1-decanol, 22-mercapto-1-docosanol and 11-mercapto-undecanamide (11 pages). Ordering information is given on any current masthead page.

Footnotes and References

1. This research was supported in part by the Office of Naval Research and by the National Science Foundation (Grant CHE-88-12709). XPS spectra were obtained using instrumental facilities purchased under the DARPA/URI program and maintained by the Harvard University Materials Research Laboratory.

2. Shell Pre-doctoral Fellow 1986-87.

3. Laibinis, P. E.; Whitesides, G. M.; Allara, D. L.; Tao, Y.-T.; Parikh, A. N.; Nuzzo, R. G. *J. Am. Chem. Soc.* submitted.

4. Walczak, M. W.; Chung, C.; Stole, S. M.; Widrig, C. A.; Porter, M. D. *J. Am. Chem. Soc.* **1991**, *113*, 2370-2378.

5 Nuzzo, R. G.; Allara, D. L. *J. Am. Chem. Soc.* **1983**, *105*, 4481-4483. Nuzzo, R. G.; Fusco, F. A.; Allara, D. L. *J. Am. Chem. Soc.* **1987**, *107*, 2358-2368.

6. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321-335.

7. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 5897-5988.

8. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 6560-6561. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1988**, *110*, 3665-3666. Bain, C. D.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7164-7175.

9. Bain, C. D.; Evall, J.; Whitesides, G. M. *J. Am. Chem. Soc.* **1989**, *111*, 7155-7164.

10. Bain, C. D.; Whitesides, G. M. *Langmuir* **1989**, 5, 1370-1378.

11. Dubois, L. H.; Zegarski, B. R.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1990**, *112*, 570-579.

12. For reviews, see Bain, C.D.; Whitesides, G. M. *Angew. Chem. Int. Ed. Engl.* **1989**, *101*, 522-528 and Whitesides, G. M.; Laibinis, P. E. *Langmuir* **1990**, *6*, 87-96.

13 Allara, D. L.; Heburd, A. F.; Padden, F. J.; Nuzzo, R. G.; Falcon, D. R. *J. Vac. Sci. Technol. A* **1983**, 376-382. Stewart, K. R.; Whitesides, G. M.; Godfried, H. P.; Silvera, I. F. *Rev. Sci. Instrum.* **1986**, *57*, 1381-1383. Ulman, A.; Tillman, N. *Langmuir* **1989**, *5*, 1418-1420.

14. Pale-Grosdemange, C.; Simon, E. S.; Prime, K. L.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 12-20. Prime, K. L.; Whitesides, G. M. *Science (Washington, DC)* in press.

15. Allen, P. M.; Hill, H. A. O.; Walter, N. J. *J. Electroanal. Chem.* **1984**, *178*, 69-86. Armstrong, F. A.; Hill, H. A. O.; Walton, N. J. *Acc. Chem. Res.* **1988**, *21*, 407-413. Tarlov, M. J.; Bowden, E. F. *J. Am. Chem. Soc.* **1991**, *113*, 1847-1849.

16. Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559-3558.

17. Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* **1990**, *6*, 682-691.

18. Non-electroactive *n*-alkanethiols: Li, T., T.-T.; Weaver, M. J. *J. Am. Chem. Soc.* **1984**, *106*, 6107-6108. Sabatini, E.; Rubinstein, I.; Maoz, R.; Sagiv, J. *J. Electroanal. Chem.* **1987**, *219*, 365-371. Sabatini, E.; Rubinstein, I. *J. Phys. Chem.* **1987**, *91*, 6663-6669. Finklea, H. O.; Avery, S.; Lynch, M.; Furtsch, T. *Langmuir* **1987**, *3*, 409-413. Bunding Lee, K. A.; Mowry, R.;

McLennan, G.; Finklea, H. O. *J. Electroanal. Chem.* **1988**, *246*, 217-224. Rubinstein, I.; Steinberg, S.; Tor, Y.; Shanzer, A.; Sagiv, J. *Nature* **1988**, *332*, 426-429. Creager, S. E.; Collard, D. M.; Fox, M. A. *Langmuir* **1990**, *6*, 1617-1620. Miller, C.; Cuendet, P.; Grätzel, M. *J. Phys. Chem.* **1991**, *95*, 877-886.

19. Electroactive *n*-alkanethiols: Bunding Lee, K. A. *Langmuir*, 1990, *6*, 709-712. Chidsey, C. E. D.; Bertozzi, C. R.; Putvinski, T. M.; Mujsce, A. M. *J. Am. Chem. Soc.* **1990**, *112*, 4301-4306. Obeng, Y. S; Bard, A. J. *Langmuir* **1991**, 7, 195-201. Hickman, J. J.; Ofer, D.; Zou, C.; Wrighton, M. S.; Laibinis, P. E.; Whitesides, G. M. *J. Am. Chem. Soc.* **1991**, *113*, 1128-1132. Chidsey, C. E. D. *Science (Washington, DC)* **1991**, *251*, 919-922. Hickman, J. J.; Ofer, D.; Laibinis, P. E.; Whitesides, G. M.; Wrighton, M. S. *Science (Washington, DC)* in press. Hickman, J. J.; Laibinis, P. E.; Auerbach, D. I.; Zou, C.; Gardner, T. J.; Whitesides, G. M.; Wrighton, M. S. *Langmuir* submitted.

20. Diem, T.; Czajka, B.; Weber, B.; Regen, S. L. *J. Am. Chem. Soc.* 1986, *108*, 6094-6095. Fabianowski, W.; Coyle, L. C.; Weber, B. A.; Granata, R. D.; Castner, D. G.; Sadownik, A.; Regen, S. L. *Langmuir* **1989**, *5*, 35-41.

21. Nuzzo, R. G.; Dubois, L. H.; Allara, D. L. *J. Am. Chem. Soc.* **1990**, *112*, 558-569.

22. Sum-frequency vibrational spectroscopy: Harris, A. L.; Chidsey, C. E. D.; Levinos, N. J.; Loiacono, D. N. *Chem. Phys. Lett.* **1987**, *141*, 350-356. TEM: Strong, L.; Whitesides, G. M. *Langmuir*, **1988**, *4*, 546-558; see ref 17 for a reanalysis of part of the data in this paper. Helium diffraction: Chidsey, C. E. D.;

Liu, G.-Y.; Rowntree, P.; Scoles, G. *J. Chem. Phys.* **1989**, *91*, 4421-4423. Camillone III, N.; Chidsey, C. E. D.; Liu, G.-Y.; Putvinski, T. M.; Scoles, G. *J. Chem. Phys.* submitted. IR spectroscopy: Nuzzo, R. G.; Korenic, E. M.; Dubois, L. H. *J. Chem. Phys.* **1990**, *93*, 767-773.

23. Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir* **1989**, *5*, 101-111. Ulman, A.; Eilers, J. E. *Angew. Chem.* submitted.

24. Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. *J. Colloid Sci.* **1946**, *1*, 513-538. Shafrin, E. G.; Zisman, W. A. *J. Colloid Sci.* **1952**, *7*, 166-177. Sagiv, J. *J. Am. Chem. Soc.* **1980**, *102*, 92-98. Maoz, R.; Sagiv, J. *J. Colloid Interface Sci.* **1984**, *100*, 465-496. Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir*, **1988**, *4*, 365-385.

25. Schulman, F.; Zisman, W. A. *J. Colloid Sci.* **1952**, *7*, 465-481. Bigelow, W. C.; Brockway, L. O. *J. Colloid Sci.* **1956**, *11*, 60-68. Allara, D.L.; Nuzzo, R.G. *Langmuir* **1985**, *1*, 45-52. Schlotter, N. E.; Porter, M. D.; Bright, T. B.; Allara, D. L. *Chem. Phys. Lett.* **1986**, *132*, 93-98.

26. Wasserman, S. R.; Tao, Y.-T.; Whitesides, G. M. *Langmuir*, **1989**, *5*, 1074-1087.

27. Netzer, L.; Sagiv, J. *J. Am. Chem. Soc.* **1983**, *105*, 674-676. Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *99*, 235-241. Netzer, L.; Iscovici, R.; Sagiv, J. *Thin Solid Films* **1983**, *100*, 67-76. Tillman, N.; Ulman, A.; Penner, T. L. *Langmuir*, **1989**, *5*, 101-111.

28. Tillman, N.; Ulman, A.; Elman, J. F. *Langmuir*, **1989**, *5*, 1020-1026.

29. Tillman, N.; Ulman, A.; Schildkraut, J. S.; Penner, T.L. *J. Am. Chem. Soc.* **1988**, *110*, 6136-6144.

30. The wettabilities of the alcohol and carboxylic acid surfaces generated by chemical transformation of less polar terminal groups on alkylsiloxane monolayers ($\theta_a^{H_2O}$ = 30-55°)[26,27] are significantly less than that found on surfaces formed on gold from the corresponding ω-terminated alkanethiols or disulfides ($\theta_a^{H_2O} <$ 15°).[6,10,21]

31. Pearson, R. G. *J. Am. Chem. Soc.* **1963**, *85*, 3533-3539. Huheey, J. E. *Inorganic Chemistry;* Harper & Row: New York, 1978; pp 276-280.

32. For an example of the degree of discrimination possible between hard (-CO_2H) and soft (-SH) adsorbates for hard (Al_2O_3) and soft (Au) surfaces, see Laibinis, P. E.; Hickman, J. J.; Wrighton, M. S.; Whitesides, G. M. *Science (Washington, DC)* **1989**, *245*, 845-847.

33. Ethanol was chosen as the contacting solvent due to its low cost and toxicity, and its previous use to generate alkanethiolate surfaces on gold of a wide range of wettabilities.[5-10,21] Less polar solvents yield ω-hydroxy-alkanethiolate monolayers on gold of decreased hydrophilicity.[9]

34. Allara, D. L.; Atre, S. V.; Ellinger, C. A.; Snyder, R. G. *J. Am. Chem. Soc.* **1991**, *113*, 1852-1854.

35. Wilson, M. D.; Ferguson, G. S.; Whitesides, G. M. *J. Am. Chem. Soc.* **1990**, *112*, 1244-1245.

36. The intensity of the photoelectron peak due to an underlayer decreases exponentially with the thickness of the

overlayer due to inelastic scattering of photoelectrons from the underlayer with the overlayer (Briggs, D.; Seah, M. *Practical Surface Analysis*; Wiley: Chichester, 1983; p 211).

37. IR could also be used to characterize the structure of these monolayers though absolute determination of structure by IR is confounded by choice of a reference state. We believe that once a standard (*n*-alkanethiols) has been evaluated;[3,4,16,21] comparison to it by XPS is not only more convenient but is probably also no less accurate or precise. The thickness of the SAM can be estimated from the attenuation of photoelectrons by the film.[36] Assuming the SAM to contain trans-extended polymethylene chains, the thickness is related to the angle the adsorbate is oriented on the metal. Details pertaining to head group orientation and twisting of the polymethylene chains are, however, determinable by IR and not by XPS.

38. Seah, M. P.; Dench, W. A. *Surf. Interface Anal.* **1979**, *1*, 2-11.

39. Nuzzo et al.[21] have shown by IR that ω-substituted-pentadecanethiolate monolayers on gold have similar structures when the head group is commensurate in size with the polymethylene chain.

40. Hautman, J.; Klein, M. L. *J. Chem. Phys.* **1989**, *91*, 4994-5001.

41. At room temperature, it is difficult to imagine that the tail groups would adopt a single orientation. The structure of alkanethiolate monolayers on gold (by helium diffraction and IR,

respectively) is more crystalline at low temperatures (~100 K) than at room temperature.[22]

42. The different O(1s) peaks overlapped slightly (binding energy, peak width: oxide = 530.4 eV, ~2.0 eV; hydroxyl = 533.0 eV, ~2.0 eV) but could be resolved via chi square analysis of the composite signal.

43. Cassie, A. B. D. *Discuss. Faraday Soc.* **1948**, *3*, 11-16.

44. Israelachvili, J. N.; Gee, M. L. *Langmuir* **1989**, *5*, 288-289.

45. Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E.; Chang, J. C. *J. Am. Chem. Soc.* **1991**, *113*, 1499-1506.

46. Bain et al.[9] assumed a linear relationship between f_{CH} and χ_{CH}^{Surf} which may not be applicable to monolayers derived from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{10}CH_3$ (see text). The wettability of these mixed monolayers can be related to χ_{OH}^{Surf} by eq 2 if one assumes $\chi_{CH}^{Surf} = f_{CH}$.

47. When the two alkanethiols differ in chain length (C_{11} and C_{22}), the surface compositions of monolayers formed on silver and gold from solutions containing mixtures of the two thiols can differ by up to ~40 % (Laibinis, P. E.; Fox, M. A.; Folkers, J. P.; Whitesides, G. M. Manuscript in preparation).

48. Laibinis, P. E.; Janes, L. E.; Prime, K. L.; Nuzzo, R. G.; Whitesides, G. M. Manuscript in preparation.

49. Balanchander, N.; Sukenik, C. *Langmuir* **1990**, *6*, 1621-1627.

50. Aschan, O. *Chem. Ber.* **1898**, *31*, 2344-2350. Dobashi, Y.; Hara, S. *J. Org. Chem.* **1987**, *52*, 2490-2496.

Figure Captions

Figure 1. Intensity of photoelectrons due to the underlying metal substrate for various monolayers adsorbed on the surfaces of copper (□), silver (◇), and gold (○) from absolute ethanol. We define "molecular length" as the number of contiguous atoms in the adsorbate spanning the monolayer. (For example, for metal/$SCH_2CO_2CH_3$ the molecular length would be 6.) The numeric labels refer to compounds listed in Table I. Absolute photoelectron intensities are a function of instrumental parameters and the sets of data have been offset vertically to facilitate comparison; only the slopes are important here. The kinetic energies of photoelectrons for each graph are similar: $Au(4f_{7/2})$ = 1402 eV and Cu(3p) = 1412 eV; Au(4d) = 1143 eV and $Ag(3d_{5/2})$ = 1119 eV. The filled symbols correspond to SAMs derived from *n*-alkanethiols ($X = CH_3$). Dashed lines were determined from linear least square fits to data obtained from adsorption of *n*-alkanethiols on the three metals; the higher slopes obtained on copper and silver demonstrate that the SAMs formed on these metals are oriented closer to the surface normal than those formed on gold: Au(4d) = -0.049 vs. $Ag(3d_{5/2})$ = -0.057; $Au(4f_{7/2})$ = -0.041 vs. Cu(3p) = -0.051.

Figure 2. Comparison of monolayers adsorbed on copper (○), silver (□), and gold (◇) from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ dissolved in ethanol after 2 h exposure. Solutions were 1 mM in total thiol concentration. Advancing and receding

contact angles (filled and open symbols, respectively) were measured on static drops of water. Surface compositions (patterned symbols) were determined from XPS by scaling the O(1s) signal to that obtained on the pure $HS(CH_2)_{11}OH$-derived monolayer; the background level of oxygen on copper (determined from the pure $HS(CH_2)_{11}CH_3$-derived monolayer) was subtracted from all copper samples prior to analysis.[42] Cassie's equation[43] (solid lines; bottom graph) relates the surface composition linearly to the wettability of the monolayer by water. Israelachvili and Gee's equation[44] (dashed line) does not describe the relation between advancing contact angle and surface composition as well as Cassie's equation. The lowest panel includes data obtained from samples that were exposed to the contacting solutions for 2-48 h.

Figure 3. Comparison of monolayers adsorbed on copper (○), silver (□), and gold (◇) from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ dissolved in isooctane after 1 h exposure. Solutions were 1 mM in total thiol concentration. Data were analyzed and are presented as in Figure 2.

Figure 4. Schematic illustration of the surfaces of monolayers derived from mixtures of $HS(CH_2)_{11}OH$ and $HS(CH_2)_{11}CH_3$ (Case I) and $HS(CH_2)_{11}OH$ and $HS(CH_2)_{10}CH_3$ (Case II). Cases I and II differ by one methylene in the length of the hydroxyl-terminated chain. Experimentally, the advancing and receding contact angles of water in the two systems are related to the molar fraction of the two components by different expressions: Case I, eq 1; Case II, eq 2.

We hypothesize that the difference in wetting may be due to greater exposure of the hydroxyl groups in Case II than in Case I. The diagrams are schematic and oversimplified: both surfaces are disordered to an extent we cannot presently specify.

SUPPLEMENTARY MATERIAL

ω-Terminated Alkanethiolate Monolayers on Surfaces of Copper, Silver and Gold Have Similar Wettabilities.

Paul E. Laibinis and George M. Whitesides*

Department of Chemistry
Harvard University
Cambridge, Massachusetts 02138

Materials. All materials were obtained from Aldrich and used as received unless specified below. Thioacetic acid was obtained from Fluka. 11-Bromo-undecene was obtained from Pfaltz & Bauer, NaCN from Fisher, 9-decenol from Alfa, and K_2CO_3 from Sigma. Photolyses were conducted with a 100 W medium pressure Hg lamp. Column chromatographic purifications were performed with 230-400 mesh silica gel (EM Science). Melting points are reported uncorrected. Elemental analyses were performed by Oneida Research Services.

11-(2,2,3,3,3-Pentafluoropropoxy)-undecanethiol (2). Sodium (0.50 g, 22 mmol) was added to a solution of 2,2,3,3,3-pentafluoro-propanol (3.55 g, 23.7 mmol) in 30 mL dist THF and stirred under N_2 for 1 h. A solution of 11-bromo-1-undecene (3.50 g, 15.0 mmol) in 40 mL dist THF was added and the mixture refluxed for 72 h. The reaction was quenched by addition of 30 mL dist H_2O and subsequently extracted with CH_2Cl_2 (3 x 25 mL). The organic extracts were combined and concentrated. 11-(2,2,3,3,3-pentafluoropropoxy)-1-undecene was separated from remaining 11-bromo-1-undecene by chromatography (5% EtOAc/hexanes) and obtained as a colorless liquid (3.02 g, 10.0 mmol, 66%). ^1H NMR ($CDCl_3$, 250 MHz) δ 5.80 (m, 1 H), 4.95 (m , 1 H), 4.93 (m, 1 H), 3.85 (t, J = 13 Hz, 2 H), 3.56 (t, J = 7 Hz, 2 H), 2.02 (quart, J = 6 Hz, 2 H), 1.55 (m, 4 H), 1.2-1.3 (m, 10 H).

A solution of 11-(2,2,3,3,3-pentafluoropropoxy)-1-undecene (2.96 g, 9.8 mmol), 4 mL of thiolacetic acid, and ~10 mg of AIBN were combined in 40 mL of THF and photolyzed for 6 h.[1] The solution was added to 200 mL of dist H_2O and extracted with Et_2O (3 x 50 mL).

The organic extracts were combined, dried over $MgSO_4$ and concentrated to give a yellow oil which was purified by chromatography (5% EtOAc/hexanes) and gave 11-(2,2,3,3,3-pentafluoropropoxy)-1-undecyl thioacetate as a colorless liquid (2.85 g, 7.5 mmol, 77%). ^1H NMR ($CDCl_3$, 300 MHz) δ 3.85 (t, J = 13 Hz, 2H), 3.56 (t, J = 7 Hz, 2 H), 2.84 (t, J = 7 Hz, 2 H), 2.30 (s, 3 H), 1.55 (m, 4 H), 1.31 (t, J = 7 Hz, 1 H), 1.2-1.3 (m, 10 H).

A solution of 11-(2,2,3,3,3-pentafluoropropoxy)-1-undecyl thioacetate (2.74 g, 7.24 mmol) in 30 mL MeOH was deoxygenated with N_2 for 30 min. Granular K_2CO_3 (0.25 g, Sigma) was added and the mixture stirred for 2 h under N_2. The reaction was quenched by addition of 10% aqueous HCl and the title compound separated by extraction with Et_2O (3 x 25 mL). The organic extracts were combined, dried with $MgSO_4$, and concentrated. The oil was purified by chromatography (5% EtOAc/hexanes) and the title compound was obtained as a colorless liquid (1.87 g, 5.56 mmol, 77%). ^1H NMR ($CDCl_3$, 300 MHz) δ 3.85 (t, J = 13 Hz, 2 H), 3.56 (t, J = 7 Hz, 2 H), 2.50 (quart, J = 7 Hz, 2 H), 1.5-1.6 (m, 4 H), 1.31 (t, J = 7 Hz, 1 H), 1.2-1.3 (m, 10 H). Anal. Calcd (Found) for $C_{14}H_{25}F_5OS$: C, 49.99 (50.29); H, 7.49 (7.44); S, 9.53 (9.69).

Ethyl-11-mercapto-undecanoate (9). Ethyl undecenoate (10.6 g, 50.0 mmol), thiolacetic acid (5 mL) and ~5 mg AIBN were combined in 40 mL of THF and photolyzed[1] for 12 h and subsequently concentrated to give a yellow oil. The oil was dissolved in 60 mL abs EtOH and the solution deoxygenated with bubbling N_2 for 30 min. Conc HCl (5 mL) was added and the solution was refluxed for 4 h under N_2. After concentration, the title compound was obtained by vacuum distillation (120-123 °C, <1 torr) as a colorless liquid (7.70 g, 31.3 mmol, 62%). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 4.10 (quart, *J* = 7 Hz, 2 H), 2.50 (quart, *J* = 7 Hz, 2 H), 2.26 (t, *J* = 7 Hz, 2 H), 1.58 (m, 4 H), 1.30 (t, *J* = 7 Hz, 1 H), 1.2-1.3 (m, 12 H), 1.23 (t, *J* = 7 Hz, 3 H). Anal. Calcd (Found) for $C_{13}H_{26}O_2S$: C, 63.37 (63.33); H, 10.64 (10.68); S, 13.01 (13.82).

11-Cyano-1-undecyl thiol (12). A solution of 11-bromo-1-undecene (3.90 g, 16.7 mmol) and NaCN (1.53 g, 31.2 mmol) in 30 mL DMSO were stirred for 4 d.[2] The solution was combined with 50 mL dist H_2O and extracted with Et_2O (3 x 25 mL). The organic extracts were concentrated to give 11-cyano-1-undecene (2.83 g, 15.8 mmol, 94%) as a colorless oil which was not purified further. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.7-5.9 (m, 1 H), 4.95 (m, 1 H), 4.94 (m, 1 H), 2.31 (t, 2 H, *J* = 7 Hz), 2.02 (quart, 2 H, *J* = 7 Hz), 1.64 (m, 2 H), 1.2-1.5 (m, 12 H).

A solution of 11-cyano-1-undecene (2.83 g, 15.8 mmol), thiolacetic acid (3 mL), AIBN (5 mg), and 50 mL MeOH were photolyzed for 12 h.[1] The solution was concentrated and 11-cyano-1-undecyl thioacetate (3.42 g, 13.4 mmol, 85%) obtained by chromatography (10% EtOAc/hexanes) as a colorless liquid. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.87 (t, 2 H, *J* = 7 Hz), 2.34 (t, 2 H, *J* = 7 Hz), 2.32 (s, 3 H), 1.65 (quint, 2 H, *J* = 7 Hz), 1.55 (m, 2 H), 1.2-1.5 (m, 14 H).

A solution of 11-cyano-1-undecyl thioacetate (1.20 g, 4.70 mmol) in 15 mL MeOH was deoygenated with N_2 for 30 min. Granular K_2CO_3 (0.5 g) was added and the mixture was stirred for 3 h under N_2.

The reaction mixture was quenched with 10% HCl and extracted with Et_2O (3 x 20 mL). The organic extracts were combined and concentrated. Chromatography (10% EtOAc/hexanes) afforded 11-cyano-undecyl thiol (480 mg, 2.25 mmol, 48%) and di(11-cyano-undecyl) disulfide (300 mg, 0.71 mmol, 30%) as a colorless liquid and a white solid, respectively. **11-Cyano-undecyl thiol (12).** ^1H NMR ($CDCl_3$, 300 MHz) δ 2.50 (quart, 2 H, J = 7 Hz), 2.31 (t, 2 H, J = 7 Hz), 1.63 (m, 4 H), 1.31 (t, 1 H, J = 7 Hz), 1.2-1.4 (m, 14 H). Anal. Calcd (Found) for $C_{12}H_{23}NS$: C, 67.55 (67.69); H, 10.86 (11.00); N, 6.56 (6.41); S, 15.02 (14.70). **Di(11-cyano-undecyl) disulfide.** M.P. 32-33 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.65 (t, 4 H, J = 7 Hz), 2.31 (t, 4 H, J = 7 Hz), 1.63 (m, 8 H), 1.2-1.45 (m, 28 H). Anal. Calcd (Found) for $C_{24}H_{44}N_2S_2$: C, 67.87 (67.89); H, 10.44 (10.55); N, 6.60 (6.45); S, 15.10 (14.69).

16-cyano-1-hexadecyl thiol (13). A solution of 16-cyano-1-hexadecene[3] (1.21 g, 4.87 mmol), thiolacetic acid (2 g), AIBN (10 mg) and 40 mL THF was photolyzed for 8 h.[1] The solution was concentrated to yield a yellow solid which was purified by chromatography (10% EtOAc/hexanes) to yield 16-cyano-1-hexadecyl thioacetate as a white solid (1.45 g, 4.46 mmol, 92%). M.P. 56-57 °C. ^1H NMR ($CDCl_3$, 250 MHz) δ 2.84 (t, 2 H, J = 7 Hz), 2.32 (t, 2 H, J = 7 Hz), 2.30 (s, 3 H), 1.64 (quint, 2 H, J = 7 Hz), 1.51 (m, 2 H), 1.2-1.5 (m, 24 H). Anal. Calcd (Found) for $C_{19}H_{35}NOS$: C, 70.10 (70.23); H, 10.84 (11.26); N, 4.30 (4.22); S, 9.85 (10.03).

A solution of 16-cyano-1-hexadecyl thioacetate in 50 mL MeOH was deoxygenated with N_2 for 20 min prior to addition of granular K_2CO_3 (1.25 g) and subsequent stirring under N_2 for 2 h. The reaction was quenched by addition of 3 mL conc HCl and 50 mL dist H_2O, and extracted with Et_2O (3 x 20 mL). The organic extracts were combined and concentrated to yield a white solid that contained two primary materials. Separation by chromatography (10% EtOAc/hexanes) afforded 16-cyano-1-hexadecyl thiol (1.09 g, 3.85 mmol, 90%) and di(16-cyano-hexadecyl) disulfide (0.12 g, 0.21 mmol, 10%) as white solids. **16-Cyano-hexadecyl thiol (13).** M.P. 39.5-40 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.50 (quart, 2 H, J = 7 Hz), 2.31 (t, 2 H, J = 7 Hz), 1.61 (m, 4 H, J = 7 Hz), 1.30 (t, 1 H, J = 7 Hz), 1.2-1.5 (m, 24 H). *Anal.* Calcd (Found) for $C_{17}H_{33}NS$: C, 72.02 (72.03); H, 11.73 (11.93); N, 4.94 (4.82); S, 11.31 (12.34). **Di-(16-cyano-hexadecyl) disulfide.** M.P. 61-64 °C. ^{1}H NMR ($CDCl_3$, 300 MHz) δ 2.66 (t, 4 H, J = 7 Hz), 2.32 (t, 4 H, J = 7 Hz), 1.65 (m, 4 H), 1.2-1.5 (m, 52 H). *Anal.* Calcd (Found) for $C_{34}H_{64}N_2S_2$: C, 72.28 (72.50); H, 11.42 (11.76); N, 4.96 (4.94); S, 11.35 (11.76).

21-cyano-1-heneicosyl thiol (14). A solution of 21-bromo-1-heneicosene (974 mg, 2.61 mmol) and NaCN (170 mg, 3.5 mmol) in 15 mL DMSO were stirred at 80 °C for 1 h.^{2} After cooling to R.T., the solution was combined with 35 mL dist H_2O and extracted with hexanes (3 x 20 mL). The organic extracts were combined and concentrated to yield a white solid which was purified by chromatography (20% EtOAc/hexanes) to yield 21-cyano-1-heneicosene as a white solid (784 mg, 2.45 mmol, 94%). M.P. 44-45.5 °C. ^{1}H NMR ($CDCl_3$, 250 MHz) δ 5.80 (m, 1 H), 4.95 (m, 1 H), 4.93 (m, 1 H), 2.31 (t, J = 7 Hz), 2.01 (quart, J = 7 Hz), 2 H), 1.64 (quint, J = 7 Hz, 2 H), 1.2-1.4 (m, 34 H).

A solution of 21-cyano-1-heneicosene (760 mg, 2.38 mmol), thiolacetic acid (2 g), AIBN (10 mg) and 40 mL THF was photolyzed for 2 h.[1] The solution was combined with 40 mL dist H_2O and extracted with Et_2O (3 x 20 mL). The organic extracts were combined and concentrated to give a solid that was purified by chromatography (25% EtOAc/hexanes) to yield 21-cyano-1-heneicosyl thioacetate as a white solid (765 mg, 1.93 mmol, 81%). M.P. 65-66 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.84 (t, 2 H, J = 7 Hz), 2.30 (t, 2 H, J = 7 Hz), 2.29 (s, 3 H), 1.61 (m, 2 H), 1.2-1.5 (m, 36 H).

A solution of 21-cyano-1-heneicosyl thioacetate in 40 mL MeOH was deoxygenated with N_2. Granular K_2CO_3 (0.5 g) was added and the mixture as stirred for 2 h under N_2. The reaction was quenched by addition of 5 mL conc HCl, added to 50 mL dist H_2O and extracted with Et_2O (3 x 25 mL). The organic extracts were combined and concentrated. Purification by chromatography (1:8 EtOAc/hexanes) yielded the title compound as a white solid (451 mg, 1.28 mmol, 69%). M.P. 47-48 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 2.50 (quart, 2 H, J = 7 Hz), 2.31 (t, 2 H, J = 7 Hz), 1.61 (m, 4 H, J = 7 Hz), 1.30 (t, 1 H, J = 7 Hz), 1.2-1.5 (m, 34 H). Anal. Calcd (Found) for $C_{22}H_{43}NS$: C, 74.72 (75.18); H, 12.26 (12.33); N, 3.96 (3.89); S, 9.07 (8.70).

10-Mercapto-1-decanol (17). A solution of 9-decenol (3.21 g, 20.6 mmol), thioacetic acid (2 mL) and AIBN (5 mg) in THF (50 mL) was photolyzed for 12 h.[1] The solution was concentrated, and 10-thioacetyl-1-decanol was obtained by chromatography (15% EtOAc/hexanes) and further purified by recrystallization from hexanes (3.75 g, 16.1 mmol, 79%). M.P. 28.5-29.3 °C. ^1H NMR

($CDCl_3$, 250 MHz) δ 3.61 (t, 2 H, *J* = 7 Hz), 2.83 (t, 2 H, *J* = 7 Hz), 2.29 (s, 3 H), 1.53 (m, 4 H), 1.2-1.4 (m, 12 H). Anal. Calcd (Found) for $C_{12}H_{24}O_2S$: C, 62.02 (62.31); H, 10.41 (10.76); S 13.80 (13.34).

A methanolic solution (50 mL) of 10-thioacetyl-1-decanol (1.43 g, 6.17 mmol) was deoxygenated with bubbling N_2 for 30 min. Granular K_2CO_3 (0.5 g) was added and the mixture stirred for 2 h under N_2. The reaction was quenched with glacial AcOH (2 mL) and added to 50 mL dist H_2O. Extraction with $CHCl_3$ (3 x 25 mL) and purification by chromatography (20% EtOAc/hexanes) gave the title compound as a colorless oil (1.05 g, 5.53 mmol, 90 %). ^{1}H NMR ($CDCl_3$, 300 MHz) δ 3.62 (t, 2 H, *J* = 7 Hz), 2.50 (quart, 2 H, *J* = 7 Hz), 1.45-1.6 (m, 4 H), 1.31 (t, 1 H, *J* = 7 Hz), 1.2-1.4 (m, 12 H).

21-Docosenyl *t*-butyldimethylsilyl ether. A solution of 10-undecylenic magnesium bromide was prepared by dropwise addition of 11-bromo-1-undecene (5.59 g, 24.0 mmol) in 20 mL THF into a flame-dried flask containing Mg and 50 mL THF. The Grignard solution was then added dropwise to a flask containing 11-bromoundecyl *t*-butyldimethylsilyl ether^4 (4.53 g, 12.4 mmol), and Li_2CuCl_4 (0.3 mmol) in 50 mL THF at 0 °C.^{5} The reaction warmed to room temperature overnight. The reaction mixture was added to an aqueous solution of NH_4Cl (30 g in 125 mL dist H_2O) to remove the copper salts. The layers were separated and the aquesous fraction extracted with 50 mL THF. The organic extracts were combined and concentrated to give a yellow oil. The title compound was obtained by chromatography (hexanes followed by 2% EtOAc/hexanes) as a colorless oil (3.92 g, 8.94 mmol, 72%). ^{1}H NMR (CDCl$_3$, 250 MHz) δ 5.80 (m, 1 H), 4.95 (d, 1 H, J = 28 Hz), 4.93 (m, 1 H), 3.57 (t, 2 H, J = 7 Hz), 2.02 (quart, 2 H, J = 7 Hz), 1.49 (m, 2 H, J = 7 Hz), 1.2-1.4 (m, 34 H), 0.87 (s, 6 H), 0.03 (s, 9 H).

21-Docosen-1-ol. A solution of tetrabutylammmonium fluoride in THF (20 mL, 1.0 M) was added to 21-docosenyl t-butyldimethylsilyl ether (3.92 g, 8.94 mmol) in 40 mL THF. The reaction was stirred for 2.5 h and concentrated under reduced pressure. The title compound was obtained by chromatography (1:4 EtOAc/hexanes) as a white solid (2.70 g, 8.32 mmol, 93%). M.P. 60-61°C. ^{1}H NMR (CDCl$_3$, 300 MHz) δ 5.79 (m, 1 H), 4.95 (d, 1 H, J = 32 Hz), 4.93 (m, 1 H), 3.61 (t, 2 H, J = 7 Hz), 2.01 (quart, 2 H, J = 7 Hz), 1.54 (m, 2 H, J = 7 Hz), 1.2-1.4 (m, 34 H).

22-Mercapto-1-Docosanol (20). A solution of 21-docosen-1-ol (2.01 g, 6.21 mmol), thioacetic acid (2 mL), AIBN (2 mg) and THF (50 mL) was photolyzed for 4 h. The reaction mixture was addded to 40 mL dist H_2O and extracted with Et$_2$O (2 x 25 mL). The organic extracts were combined and concentrated to give a white solid. The material was dissolved in MeOH (100 mL) and the solution purge with N_2 for 30 min. Conc HCl (10 mL) was added and the solution refluxed for 4 h. Upon cooling, the product crystallized out and was collected by filtration. The title compound was purified further by recrystallization from hexanes (1.27 g, 3.55 mmol, 57%). M.P. 72-73 °C. ^{1}H NMR (CDCl$_3$, 250 MHz) δ 3.62 (t, 2 H, J = 7 Hz), 2.50 (quart, 2 H, J = 7 Hz), 1.45-1.65 (m, 4 H), 1.31 (t, 1 H, J = 7 Hz), 1.2-1.4 (m, 36 H). Anal. Calcd.(Found) for $C_{22}H_{46}OS$: C 73.67 (73.89); H 12.93 (12.83).

11-Mercapto-undecanamide (21). A solution of 10-undecenamide[6] (3.04 g, 16.6 mmol), thioacetic acid (3 mL), AIBN (5 mg), in 80 mL THF/MeOH (1:1) was photolyzed for 12 h.[1] The reaction mixture was concentrated and gave a solid. Recrystallization from EtOH/H_2O gave 11-thioacetyl-undecanamide as a white solid (3.64 g, 14.0 mmol, 85%). M.P. 91-92 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.42 (br, 2 H), 2.83 (t, 2 H, J = 7 Hz), 2.29 (s, 3 H), 2.19 (t, 2 H, J = 7 Hz), 1.60 (m, 2 H, J = 7 Hz), 1.53 (m, 2 H, J = 7 Hz), 1.2-1.4 (m, 12 H). Anal. Calcd (Found) for $C_{13}H_{25}NO_2S$: C, 60.19 (59.85); H, 9.71 (9.90); N, 5.40 (5.45).

A methanolic solution (40 mL) of 11-thioacetyl-undecanamide (1.06 g, 4.10 mmol) was deoxygenated with N_2 for 30 min. Granular K_2CO_3 (0.3 g) was added and the mixture stirred under N_2 for 12 h. The reaction was quenched by addition of 3 mL glacial acetic acid and added to 50 mL dist H_2O. The title compound was obtained by extraction with $CHCl_3$ (3 x 30 mL) and subsequent concentration. Purification by column chromatography (1% MeOH/$CHCl_3$) gave 11-mercapto-undecanamide as a white solid (0.50 g, 2.3 mmol, 56%). M.P. 90-91 °C. ^1H NMR ($CDCl_3$, 300 MHz) δ 5.57 (br, 2 H), 2.49 (quart, 2 H, J = 7 Hz), 2.20 (t, 2 H, J = 7 Hz), 1.45-1.6 (m, 4 H), 1.30 (t, 1 H, J = 7 Hz), 1.2-1.4 (m, 12 H). Anal. Calcd (Found) for $C_{11}H_{23}NOS$: C, 60.78 (61.01); H, 10.67 (11.01); N, 6.44 (6.36); S, 14.75 (14.60).

Acknowledgement. We gratefully acknowledge our colleague Colin D. Bain for supplying 16-bromo-1-hexadecene and 21-bromo-1-heneicosene.

References

1. Janssen, M. J. in *The Chemistry of Carboxylic Acids and Esters*; Patai, S., Ed.; Interscience: New York, 1969; pp 720-723. Griesbaum, K. *Angew. Chem. Int. Ed. Engl.* **1970**, *9*, 273-287.

2. Friedman, L.; Schechter, H. *J. Org Chem.* **1960**, *25*, 877-879.

3. Balanchander, N.; Sukenik, C. *Langmuir* **1990**, *6*, 1621-1627.

4. Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321-335.

5. Tamura, M.; Kochi, J. *Synthesis* **1971**, 303-305.

6. Aschan, O. *Chem. Ber.* **1898**, *31*, 2344-2350. Dobashi, Y.; Hara, S. *J. Org. Chem.* **1987**, *52*, 2490-2496.

TECHNICAL REPORT DISTRIBITION LIST (June 1991)

Office of Naval Research
Chemistry Division, Code 1113
800 North Quincy Street
Arlington VA 22217-5000

Dr. James S. Murday
Chemistry Division, Code 6100
Naval Research Laboratory
Washington DC 20375-5000

Dr. Robert Green, Director
Chemistry Division, Code 385
Naval Weapons Center
China Lake CA 93555-6001

Dr. Eugene C. Fischer
Code 2840
David Taylor Research Center
Annapolis MD 21402-5067

Dr. Elek Lindner
Naval Ocean Systems Center
Code 52
San Diego CA 92152-5000

Commanding Officer
Naval Weapons Support Center
Attn: Dr. Bernard E. Douda
Crane IN 47522-5050

Dr. Richard W. Drisko
Naval Civil Engineering Laboratory
Code L52
Fort Hueneme CA 93043

Dr. Harold H. Singerman
David Taylor Research Center
Annapolis MD 21402-5067
ATTN: Code 283

Chief of Naval Research
Special Assistant for Marine Corps Matters, Code 00MC
800 North Quincy Street
Arlington VA 22217-5000

Defense Technical Information Center
Building 5, Cameron Station
Alexandria VA 22314

ABSTRACT DISTRIBUTION LIST (June 1991)

Prof. Robert W. Armstrong
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles CA 90024

Dr. Joseph Boyer
Department of Chemistry
University of New Orleans
New Orleans LA 70148

Professor Jerald S. Bradshaw
Department of Chemistry
Brigham Young University
Provo UT 84602

Prof. Ronald Breslow
Department of Chemistry
Columbia University
New York NY 10027

Dr. Duncan W. Brown
Advanced Technology Materials
520-B Danbury Road
New Milford CT 06776

Prof. Cynthia J. Burrows
Department of Chemistry
State University of New York
Stony Brook NY 11794-3400

Professor Peter Chen
Department of Chemistry
Harvard University
Cambridge MA 02138

Prof. Anthony W. Czarnik
Department of Chemistry
Ohio State University
120 West 18th Avenue
Columbus OH 43210-1173

Prof. Peter Dervan
Department of Chemistry
Calif Institute of Technology
Pasadena CA 91125

Prof. Francois N. Diederich
Department of Chemistry
University of California
405 Hilgard Avenue
Los Angeles CA 90024

Prof. Dennis A. Dougherty
Department of Chemistry
Calif Institute of Technology
Pasadena CA 91125

Prof. Kenneth M. Doxsee
Department of Chemistry
University of Oregon
Eugene OR 97403

Prof. Margaret C. Etter
Department of Chemistry
University of Minnesota
207 Pleasant Street SE
Minneapolis MN 55455

Prof. Wilmer K. Fife
Department of Chemistry
Indiana Univ/Purdue Univ
1125 East 38th Street
Indianapolis IN 46223

Prof. Samuel H. Gellman
Department of Chemistry
University of Wisconsin
Madison WI 53706

Prof. Thomas J. McCarthy
Department of Polymer Science
University of Massachusetts
701 Graduate Research Center
Amherst MA 01003

Prof. Arthur E. Martell
Department of Chemistry
Texas A&M University
College Station TX 77843-3255

Prof. William L. Mock
Department of Chemistry
University of Illinois at
Chicago
Chicago IL 60680

Prof. Martin E. Newcomb
Department of Chemistry
Texas A&M University
Box 3578
College Station TX 77843-3255

Prof. Peter Schultz
Department of Chemistry
University of California
Berkeley CA 94720

Prof. Carol Venanzi
Department of Chemistry
New Jersey Inst of Technology
323 King Blvd.
Newark NJ 07102

Prof. Howard W. Whitlock
Department of Chemistry
University of Wisconsin
Madison WI 53706

Prof. Jeffrey D. Winkler
Department of Chemistry
The University of Chicago
5735 S. Ellis Avenue
Chicago IL 60637