Self-Assembled Monolayers of Symmetrical and Mixed Alkyl Fluoroalkyl Disulfides on Gold. 2. Investigation of Thermal Stability and Phase Separation

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The investigation of the thermal stability of self-assembled monolayers of symmetrical and mixed alkyl fluoroalkyl disulfides on gold is reported. The monolayers were annealed in air at temperatures ranging from 60 to 110 °C for several hours and afterward characterized by contact angle measurements, polarized grazing incidence Fourier transform infrared spectroscopy (FTIR), X-ray photoelectron spectroscopy (XPS), and atomic force microscopy (AFM). In mixed alkyl perfluoroalkyl systems evidence was sought for heat-induced phase separation of the alkyl- and perfluoroalkyl-terminated molecules. The ester and amide linkages of the fluorocarbon chains are shown to be less stable than those of the hydrocarbon analogues. Fluoro substituents in α-position to the ester linkage make the ester bond susceptible to hydrolytic cleavage at temperatures between 60 and 70 °C, whereas the corresponding amide and the γ-fluoro-substituted esters remain stable up to 80−100 °C. After annealing for 10 h or longer at these temperatures contact angle measurements, XPS, and FTIR reveal partial loss of fluorocarbon chains in monolayers of symmetrical fluoroalkyl disulfides and mixed alkyl fluoroalkyl disulfides. In contrast, it is still possible to observe ordered domains with AFM in monolayers of mixed alkyl fluoroalkyl disulfides annealed at 100 °C for 17 h. AFM scans in molecular resolution confirm that the lattice constant of the hexagonal lattice remains unchanged (6.2 Å). Since the monolayers of both corresponding symmetrical disulfides show significantly smaller lattice constants, heat-induced phase separation can be excluded. The results indicate nonexisting to very low mobility of the molecules within the layer at higher temperatures. Alternatively, the existence of disulfides rather than thiolates bound to the gold can explain the observations.

Introduction

Understanding and controlling the properties of surfaces and interfaces are of tremendous importance in many kinds of technical applications. Well-organized model systems like self-assembled monolayers (SAMs) of organic molecules on various substrates are therefore of widespread interest.[1,2] SAMs of thiols,[3] disulfides,[4] or thioethers[5] on gold are one class of thoroughly investigated systems. The interest is certainly not limited to the model role of SAMs as models for organic surfaces and interfaces in general.[6] The ease of preparation together with the high degree of order on the molecular level makes these systems attractive for novel applications such as molecular recognition and sensors[7−10] or patterning and nanolithography.[11,12]

In this paper we report the attempt to achieve patterned surfaces of SAMs of mixed alkyl fluoroalkyl disulfides on gold by heat-induced phase separation into monodomains on the surface. In contrast to coadsorption experiments from solutions containing mixtures of thiols, this would lead to systems which are at least close to thermodynamical equilibrium. With suitable ω-functionalized molecules chemistry could be done highly localized within these domains. In combination with other patterning techniques a series of reactors with different functional groups or recognition units could be placed in a predetermined way on the surface.

The motivation for this study was partly to create patterns on the surface of SAMs in the nanometer size regime. In addition, there is some basic interest involved. The nature of the molecular species actually bound to the gold has not been determined unequivocally. The molecules of SAMs derived from thiols and corresponding disulfides were shown to be identical by X-ray photoelectron spectroscopy (XPS).[13] Time of flight secondary ion mass spectrometry (TOF-SIMS)[14] on SAMs of thiols and disulfides as well as exchange experiments of mixed disulfides[15] suggested strongly that thiols and disulfides bind as thiolates to the gold. In Figure 1 the previously accepted reaction scheme is shown. Recently, the existence of a disulfide rather than a thiolate bound to the gold has been postulated on the basis of X-ray diffraction investigations.[16]

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Figure 1. Widely accepted reaction scheme for the reaction of alkanethiols and alkyl disulfides with the gold surface in the process of monolayer formation.
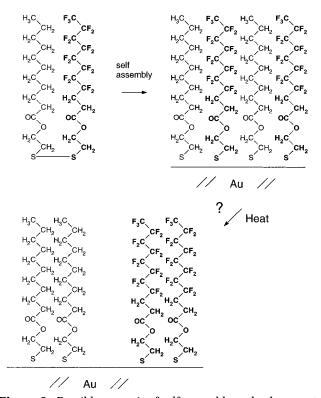
Figure 2. Possible scenario of self-assembly and subsequent heat-induced phase separation into monodomains of SAMs of **13** on the gold surface.

The thermal stability of SAMs of thiols has also been the subject of previous studies.[17,18] Annealing at temperatures below 100 °C leads to an improved molecular order of the SAMs.[9] The morphology of the gold substrate (gold(111)) is altered as well. Annealing leads to the coalescense of the typical etch pits in the gold.[19,20]

As depicted in Figure 2, we investigated whether it is possible to promote mobility of the molecules in the SAM by lowering the interaction between neighboring chains. The interaction between alkyl and perfluoroalkyl chains is lower than that between alkyl chains, or perfluoroalkyl chains, respectively. In other highly ordered systems like liposomes[21] and Langmuir–Blodgett films,[22] this leads to phase separation in mixed alkyl perfluoroalkyl systems. Even at room temperature phase separation could be demonstrated in these cases. At room temperature mixed alkyl perfluoroalkyl disulfides form SAMs on Au(111) with a unique lattice compared to the corresponding symmetrical disulfides. This could be proven by atomic force microscopy (AFM).[23] Thus, the molecules are not mobile at room temperature since no phase separation was observed. Given that the mobility of the thiolates is high enough at temperatures below which desorption becomes competitive, phase separation into monodomains should be feasible. A simulation[24] as well as a thermodynamical treatment of a possible phase separation in monolayers[25] suggest the formation of monodomains in the case of mobile molecules. Since phase separation would require independent behavior of the two parts of the molecule, this would unequivocally prove the cleavage of the sulfur–sulfur bond of the disulfide in the reaction with the gold and the existence of thiolates on the gold surface.

In order to test the approach we investigated the thermal stability of SAMs on gold of three homologous series of mixed alkyl fluoroalkyl disulfides together with the corresponding symmetrical disulfides. The synthesis of the compounds and the monolayer properties of the freshly prepared SAMs have been reported earlier.[23,26] After annealing in air, the SAMs were probed by contact angle, grazing incidence polarized Fourier transform infrared (FTIR), XPS, and AFM measurements.

Experimental Part

Preparation of Substrates. Gold substrates for contact angle measurements and FTIR studies were prepared by evaporation of approximately 3 nm of chromium followed by 120 nm of gold onto cleaned glass slides[26] in a vacuum of 5×10^{-6} mbar in a Balzer evaporation machine. For the XPS measurements silicon wafers were used instead of glass substrates.[27] Au(111) substrates for AFM experiments were prepared by evaporation of gold onto freshly cleaved mica sheets followed by annealing and subsequent quenching to room temperature. The exact procedure has been published before.[23,28]

Preparation of Monolayers. Monolayers were formed by immersing the gold substrates into a dilute solution (1.0 to 5.0 $\times 10^{-4}$ M) of the corresponding compound in methylene chloride. After incubation of 24 h or longer, the samples were removed from the solution, rinsed carefully with pure solvent, and dried in a nitrogen stream.

Annealing in Air. After initial characterization the substrates covered with monolayers were placed on a metal grid in a preheated Heraeus oven at a given temperature. After annealing the SAMs were allowed to cool down to room temperature in a sealed glass container.

Contact Angle Measurements. The advancing and receding contact angles θ_a and θ_r were measured with Millipore water as

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$$\begin{array}{l} S-CH_2-CH_2-O-CO-(CH_2)_{\overline{n}}-CH_3 \\ | \\ S-CH_2-CH_2-O-CO-(CH_2)_{\overline{n}}-CH_3 \end{array}$$

1 (n = 10), **2** (n = 16), **3** (n = 20)

$$\begin{array}{l} S-CH_2-CH_2-O-CO-(CF_2)_8-CF_3 \\ | \\ S-CH_2-CH_2-O-CO-(CF_2)_8-CF_3 \end{array}$$

4

$$\begin{array}{l} S-CH_2-CH_2-O-CO-(CH_2)_{\overline{2}}-(CF_2)_{\overline{7}}-CF_3 \\ | \\ S-CH_2-CH_2-O-CO-(CH_2)_{\overline{2}}-(CF_2)_{\overline{7}}-CF_3 \end{array}$$

5

$$\begin{array}{l} S-CH_2-CH_2-CO-O-(CH_2)_{\overline{2}}-(CF_2)_{\overline{7}}-CF_3 \\ | \\ S-CH_2-CH_2-CO-O-(CH_2)_{\overline{2}}-(CF_2)_{\overline{7}}-CF_3 \end{array}$$

6

$$\begin{array}{l} S-CH_2-CH_2-O-CO-(CF_2)_8-CF_3 \\ | \\ S-CH_2-CH_2-O-CO-(CH_2)_{\overline{n}}-CH_3 \end{array}$$

7 (n = 6), **8** (8), **9** (10), **10** (12), **11** (14),
12 (n = 16)

$$\begin{array}{l} S-CH_2-CH_2-O-CO-(CH_2)_{\overline{2}}-(CF_2)_{\overline{7}}-CF_3 \\ | \\ S-CH_2-CH_2-O-CO-(CH_2)_{\overline{n}}-CH_3 \end{array}$$

13 (n = 9), **14** (10), **15** (12), **16** (14), **17** (16)

$$\begin{array}{l} S-CH_2-CH_2-NH-CO-(CF_2)_{\overline{7}}-CF_3 \\ | \\ S-(CH_2)_{\overline{n}}-CH_3 \end{array}$$

18 (n = 11), **19** (15), **20** (17)

$$HS-CH_2-CH_2-NH-CO-(CF_2)_{\overline{7}}-CF_3$$
21

Figure 3. Investigated compounds and their abbreviations.

a probe liquid on a contact angle microscope (G-1, Krüss, Hamburg). Details can be found in ref 26. The hysteresis was calculated as $-(\Delta \cos \theta)$.

Polarized Fourier Transform Infrared Spectroscopy (FTIR) in Grazing Incidence. The IR data were obtained on a Nicolet 5DXC FTIR spectrometer which was equipped with a FT80 specular reflectance setup (Spectratech Inc.). For details see ref 26.

X-ray Photoelectron Spectroscopy (XPS). The XPS spectra were obtained on a Scienta ESCA 300 Instrument. A high-intensity, 2.8 kW, monochromatic Al Kα ($h\nu$ = 1486.6 eV) radiation source was used and the analyzer slit width and pass energy were set to 0.8 mm and 150 eV, respectively. Spectra were obtained for electron take-off angles of 10° (grazing) and 90° (normal), with the base pressure in the sample chamber maintained at 10^{-9} Torr. Unless otherwise stated the data presented here refer to those obtained at 10°.

Atomic Force Microscopy (AFM). The AFM measurements were performed with a NanoScope III AFM (Digital Instruments) using a liquid cell filled with ethanol. Sharpened tips (Olympus Tokio, 0.09 N/m spring constant) were used for the investigations which were done in contact mode. All the images shown are raw data which were plane fitted. The force between tip and sample was typically 1 nN.

Results and Discussion

The freshly prepared monolayers of all the compounds listed in Figure 3 were investigated by means of contact

Table 1. Contact Angles (H₂O) of Annealed SAMs of Symmetrical Disulfides (1−6)

compound	conditions[a]	θ_a, deg	θ_r, deg	hysteresis
1	as prepared	106	96	0.171
	48 h, 80 °C	106	95	0.188
	24 h, 100 °C	106	91	0.258
2	as prepared	108	101	0.118
	14 h, 80 °C	108	100	0.135
	21 h, 100 °C	103	94	0.155
4	as prepared	116	109	0.113
	19 h, 80 °C	104	95	0.155
5	as prepared	116	107	0.146
	11 h, 80 °C	115	106	0.147
6	as prepared	117	107	0.162
	24 h, 100 °C	117	106	0.178

[a] Selected examples of different annealing experiments were chosen in order to give a general overview.

Table 2. Contact Angles (H₂O) of Annealed SAMs of 18

conditions[a]	θ_a, deg	θ_r, deg	hysteresis
as prepared	114	107	0.114
20 h, 80 °C	113	105	0.132
20 h, 100 °C	108	98	0.170
20 h, 120 °C	102	81	0.364

[a] Selected examples of different annealing experiments were chosen in order to give a general overview.

Table 3. Contact Angles (H₂O) of Annealed SAMs of 9

conditions[a]	θ_a, deg	θ_r, deg	hysteresis
as prepared	112	104	0.133
73 h, 60 °C	112	103	0.150
43 h, 70 °C	103	92	0.196
24 h, 80 °C	103	86	0.295

[a] Selected examples of different annealing experiments were chosen in order to give a general overview.

Table 4

(a) Contact Angles (H₂O) of Annealed SAMs of **13**

conditions[a]	θ_a, deg	θ_r, deg	hysteresis
as prepared	113	104	0.149
73 h, 60 °C	113	102	0.183
43 h, 70 °C	113	104	0.149
24 h, 80 °C	113	101	0.200
20 h, 100 °C	113	101	0.200

(b) Contact Angles (H₂O) of Annealed SAMs of **13−17**

compound	conditions[a]	θ_a, deg	θ_r, deg	hysteresis
13	as prepared	113	104	0.149
	14 h, 100 °C	113	102	0.183
14	as prepared	112	102	0.167
	14 h, 100 °C	110	100	0.168
16	as prepared	112	103	0.150
	14 h, 100 °C	112	101	0.184
17	as prepared	111	100	0.185
	14 h, 100 °C	111	100	0.185

[a] Selected examples of different annealing experiments were chosen in order to give a general overview.

angle measurements and grazing incidence FTIR spectroscopy prior to further annealing experiments. The properties observed for a large number of samples have been published before.[26]

The contact angles give a first hint as to monolayer stability in air at higher temperatures. The values observed are listed in Tables 1−4. Compared to thermal stabilities published in literature before for *n*-alkanethiols, we can confirm a threshold for desorption for comparable SAMs of roughly 100 °C. Exception are only found for SAMs of activated esters of perfluorinated carboxylic acids like compound **4** and the mixed disulfides **7−12**. Here

the hydrolysis of the ester seems to set in before the desorption starts.

Before dealing with the more complicated mixed alkyl fluoroalkyl systems, we want to discuss the symmetric ones. The SAMs derived from symmetrical bis(alkyl) disulfides **1** and **2** are stable at temperatures of 80 °C for prolonged annealing times (longer than 24 h). Prolonged heating at 100 °C or heating at temperatures above 100 °C leads to the destruction of the SAM. The SAMs obtained from the symmetrical bis(fluoroalkyl)disulfides **4**–**6** show different thermal stabilities and thus reflect the different activation of the ester bond toward hydrolysis.[29] Whereas the contact angles of SAMs of **4** decrease at temperatures below 80 °C, the SAMs of **5** remain stable up to 80 °C and higher. The reverse order of the ester bond gives even more stability to the SAMs of **6**. Intermediate stability is observed for SAMs of the perfluorinated thiol **21**.
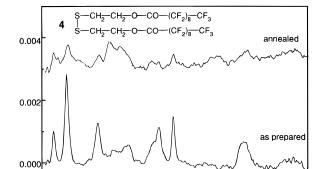
In Tables 2–4 the contact angles of freshly prepared and subsequently annealed SAMs of mixed disulfides are summarized. One can observe the same trend as indicated by the symmetrical compounds before. The SAMs of the amides, e.g., **18**, are stable at 80 °C, whereas at approximately 90 °C desorption or some unknown reaction leads to slow disintegration of the SAM. Monolayers of the activated α-fluoro-substituted esters like those of **9** show the poorest thermal stability. The SAMs are destroyed at temperatures as low as 70 °C. Therefore, they will not be considered suitable candidates for the investigation of possible phase separation.

Monolayers of the less activated esters of compounds **13**–**17** are stable up to 100 °C for annealing times not longer than approximately 10–15 h (Table 4b), although the increasing hysteresis indicates that monolayers of **13** are altered by annealing (Table 4a).

For all investigated SAMs we could not observe any dependence of the thermal stability on chain length of the alkyl chain by contact angle measurements or FTIR experiments.

Since the FTIR measurements in grazing incidence with perpendicularly polarized light are sensitive to the orientation of the molecules in the SAMs, a comparison of the spectra prior to and after annealing should indicate large scale phase separation.[1,30] As demonstrated before,[26] both alkyl and fluoroalkyl chains are oriented much closer to the surface normal direction in the monolayers of the mixed alkyl fluoroalkyl disulfides on gold compared to *n*-alkanethiols. In contrast, the hydrocarbon chains of the molecules in SAMs of the symmetrical bis(alkyl) disulfides are tilted like those in monolayers of *n*-alkanethiols. For molecules with very long alkyl chains like in **2** and **3**, the all-trans conformation could be proven additionally.[26]

In the process of annealing, the desorption of some of the molecules can be assumed even at lower temperatures.[17,18] Partly there is still physisorbed material present. Hence the surface coverage is below 100% for annealed monolayers. If mobility is given and if the mobility results in phase separation into monodomains the alkyl-terminated molecules should be tilted in their domains. These tilted molecules could be detected by means of FTIR.

Figure 4. FTIR spectra of SAM of **4** prior to and after annealing in air for 19 h at 80 °C.
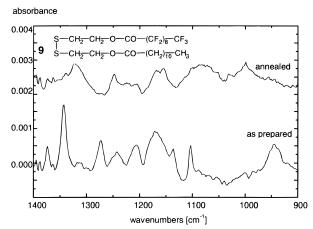

Figure 5. FTIR spectra of SAM of **9** prior to and after annealing in air for 36 h at 100 °C.

In general, the results obtained by FTIR back up the interpretation of the contact angle measurements. The loss of perfluorinated chains in annealed SAMs of the α-fluoro-substituted esters in both symmetric and mixed systems can be confirmed; see Figures 4 and 5. The typical C–F stretching frequencies at about 1375 and 1335 cm^{-1} are drastically reduced.[26] As there are no new bands appearing that can be attributed to perpendicular polarized C–F stretching vibrations, the loss of the chains has to be assumed.

The formation of large scale phase-separated domains seems to be very unlikely as there is no indication at all for pronounced C–H stretching vibrations in any monolayer after nondestructive annealing.[31] For monolayers of the α-fluoro substituted esters, prolonged annealing, which is accompanied by the loss of the fluorinated chains, leads to observable C–H stretching vibrations (absorbance in the order of 1×10^{-3}). We interpret this as the manifestation of additional degrees of freedom of the remaining alkyl chains after the complete loss of the fluorinated ones.[32]

The absence of large scale phase separation can also be observed for monolayers obtained from coadsorptions of dodecanethiol and the perfluorinated thiol **21**. Annealed monolayers of coadsorptions from solutions containing the two thiols in ratios of 1:1, 1:3 and 3:1 (3.0×10^{-4} M total concentration)[26] did not show any evidence for tilted dodecyl thiolate domains. For other systems phase

(29) The activation can be deduced from the pK_a values of similar partially fluorinated carboxylic acids: CF$_3$–COOH pK_a = 0.26; CF$_3$–CH$_2$–COOH pK_a = 3.00; CF$_3$–CH$_2$–CH$_2$–COOH pK_a = 4.15; CF$_3$–CH$_2$–CH$_2$–CH$_2$–COOH pK_a = 4.49; CH$_3$–CH$_2$–CH$_2$–CH$_2$–COOH pK_a = 4.81, from: Kissa, E. *Fluorinated Surfactants*; Marcel Dekker, Inc.: New York, 1994.

(30) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D. *J. Am. Chem. Soc.* **1987**, *109*, 3559.

(31) "Nondestructive annealing" defines the conditions of annealing without excessive loss of fluorinated chains which is detected by decreasing contact angles.
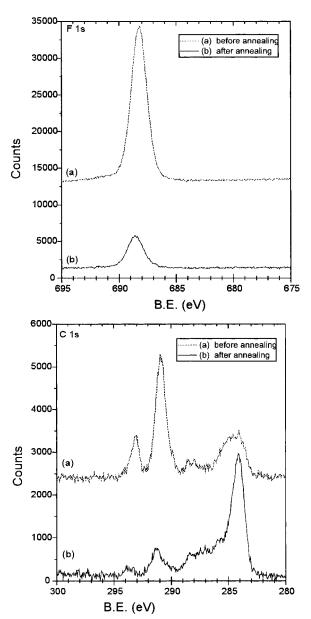
Figure 6. F(1s) and C(1s) XPS spectra of SAM of **5** before (curves a) and after (curves b) annealing for 10 h at 80 °C.

separation has been reported.[33] We assume that our system has a substantially bigger driving force of the molecules to assemble in metastable patches.[25] The molecular structure of the coadsorbed layers of **21** and dodecanethiol is therefore presently investigated by AFM.

XPS measurements were made on monolayers of **1**, **5**, and **13**, both before and after annealing for 10 h at 80 °C in air. Figure 6 shows the F(1s) and C(1s) regions for monolayers of **5** (a) before annealing and (b) after annealing. These spectral regions contain several points of note. Firstly, considering the C(1s) spectra, in the unannealed sample we can see toward lower binding

Table 5. Changes in the O(1s) and F(1s) XPS Signals of Different SAMs upon Annealing for 10 h at 80 °C, Measured with Respect to the Total Carbon Content within the Monolayers

sample	O/C	F/C
5 not annealed	0.29	6.68
5 annealed	0.80	1.38
1 not annealed	0.61	0
1 annealed	0.52	0
13 not annealed	0.75	3.82
13 annealed	2.06	1.71

energy the peaks associated with the alkyl (CH_2) units at ca. 284 eV. The peak is broad and has several contributions, seen as a shoulder toward the high energy side; this is due to the differing nature of the carbons within this molecule. From chemical structure considerations we see that each of the carbons in the lower alkyl chain is unique in terms of its local bonding; thus each gives a slightly different contribution to the total carbon signal. The C(1s) peaks associated with the CF_2 and CF_3 groups occur at much higher binding energies, 291 and 293 eV, respectively, and are thus easily distinguished from the lower carbon portions. Upon annealing, curve b, we see a dramatic change in the C(1s) spectra; in particular we see that there is a considerable loss in the perfluoroalkyl carbon signal. Associated with this decrease we find that the relative intensity of the lower alkyl groups increases, as one would expect since there is now less attenuation due to the removal of the fluorocarbon chains. The loss of fluorcarbon is also clearly seen by the decrease of the F(1s) signal following annealing. Finally, we note that the signal due to the oxygen (O(1s)) increases upon annealing; this is also consistent with our explanation since these groups would now be very close to the surface and hence not attenuated.

Table 5 presents the results for molecules **1**, **5**, and **13**. In each case we present the ratio of the signal of a given species to the total carbon signal. This permits a qualitative discussion of changes occurring due to the annealing process. If "whole" molecules were being lost during the annealing and if the remaining molecules formed ordered domains, this ratio would be constant. We would expect slight changes if they tended toward a disordered state. It is apparent that in all cases the ratio of fluorine to carbon present in the film decreases significantly on annealing. It is thus more likely to be related to the cleavage of the molecules. The decrease in the F/C ratio is associated with an increase in the O/C ratio, which may be accounted for by the reduction of attenuation due to the loss of the overlying fluoroalkyl portion of the molecule. Monolayers of **1**, dialkyl disulfide, showed much smaller changes upon annealing and suggest that the alkyl-substituted derivatives are more stable than those containing the fluoroalkyl derivatives. These results are thus in general agreement with the wetting and FTIR data and are consistent with the picture proposed here of the loss of the fluoralkyl chains through hydrolytic cleavage.[34]

The most convincing proof for the absence of phase separation in annealed monolayers of **13** on gold(111) is obtained from AFM data. We investigated only SAMs of compound **13** because of several reasons.

The visualization of the two-dimensional lattice of freshly prepared SAMs could be achieved previously together with the corresponding symmetrical systems.[23] Since the disulfide contains two chains of equal length,

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(32) This also backs up the hypothesis of the hydrolytic cleavage of the α-fluoro-substituted esters in the monolayers. The annealed SAMs of mixed alkyl fluoroalkyl disulfides can further be compared to annealed SAMs of 2-(*n*-alkanoyloxy)ethyl 2′-hydroxyethyl disulfide, HO−CH₂− CH₂−S−S−CH₂−CH₂−O−CO−(CH₂)ₙ−CH₃ , the precursor molecule to the mixed disulfides.[26] These monolayers show comparable absorbances for the C−H stretching vibrations. When annealing SAMs of 2-(*n*-alkanoyloxy)ethyl 2′-hydroxyethyl disulfide the contact angles increase, *e.g.,* the advancing contact angle θ_a of a SAM of 2-(*n*-dodecanoyloxy)ethyl 2′-hydroxyethyl disulfide increases from 95° to 102° after annealing at 70 °C for 40 h.

(33) Stranick, S. J.; Parikh, A. N.; Tao, Y.-T.; Allara, D. L.; Weiss, P. S. *J. Phys. Chem.* **1994**, *98*, 7636.

(34) The reaction does not proceed in bulk material annealed in air at similar conditions as can be proven by ¹H-NMR spectroscopy. Hence it seems to be an interfacial reaction.

Table 6. AFM Results on Freshly Prepared SAMs of Different Disulfides on Au(111)[23]

compound	lattice constant of the hexagonal lattice, Å
1	5.28
2	5.27[a]
5	5.87
13	6.20

[a] For compound **2** a second lattice of centered rectangular symmetry is found.

Table 7. AFM Results on Annealed SAMs of Compound 13 on Au (111)

annealing conditions	observed monolayer structure
1 h, 60 °C	domains with hexagonal lattice, $d = 6.2$ Å
8 h, 75 °C	domains with hexagonal lattice, $d = 6.2$ Å
16 h, 90 °C	domains with hexagonal lattice, $d = 6.2$ Å
48 h, 90 °C	no ordered monolayer structure
17 h, 100 °C	domains with hexagonal lattice, $d = 6.2$ Å
65 h, 110 °C	no ordered monolayer structure

the surface of the monolayer is easier to image with AFM than disulfides with different chain lengths. In the AFM images obtained the chain ends are visualized; the lattice formed by both $-CH_3$ and $-CF_3$ groups is recognized. The observed lattice constants of the hexagonal lattices formed by freshly prepared SAMs are listed in Table 6. Important is the unique lattice that is formed by **13**. The lattice constant of the hexagonal lattice is bigger than the lattice constants of both the symmetrical bis(alkyl) and the bis-(fluoroalkyl)disulfide. Furthermore, the symmetrical bis-(alkyl)disulfide forms two lattices of different symmetry. Thus, if phase separation occurs, three additional lattice constants should be detected: One for the perfluorinated part and two for the alkyl part.

The linkage of the partly fluorinated chain to the disulfide with an ethyl bridge is the most stable of the three homologous series investigated in this study. Therefore annealing at temperatures close to the threshold for desorption (100 °C) is still possible and investigation by AFM should be able to detect the appearance of different periodicities.

The freshly prepared monolayers were annealed in air at temperatures ranging from 60 to 110 °C for different times (see Table 7). After cooling down to room temperature the substrates were put into the liquid cell of the AFM filled with ethanol and were imaged immediately. Figures 7−9 show AFM scans of a freshly prepared and two differently annealed SAMs of **13** on gold(111) in molecular resolution. Domains in which the packing is good are still frequently observed. The packing distances of the hexagonal lattice remains 6.2 Å; no additional periodicity can be detected in the two-dimensional fast Fourier transforms of the data evaluation procedure.[23,28] Annealing for very long times at temperatures of 110 °C destroys all order in the organic monolayer that can be imaged by AFM. Desorption and hydrolysis of the esters are probably too pronounced under these conditions. As can be seen from the unchanged packing distances for annealed SAMs of **13** (annealing at 100 °C for 17 h) phase separation can be excluded for these systems under the conditions used.

The absence of phase separation in the investigated SAMs of mixed alkyl fluoroalkyl disulfides can be attributed to various reasons. These can be discussed in a speculative way only because the underlying processes are up to now not well understood. We suppose that the mobility of molecules within the monolayer is probably only pronounced at defect sites like vacancies in the lattice
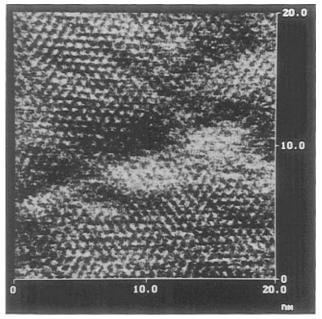

Figure 7. AFM image of a freshly prepared SAM of **13** on gold(111) taken in ethanol. In the middle a domain boundary is visible, in the lower right and the upper left part of the image the hexagonal lattice formed by the $-CH_3$ and the $-CF_3$ groups can be seen.
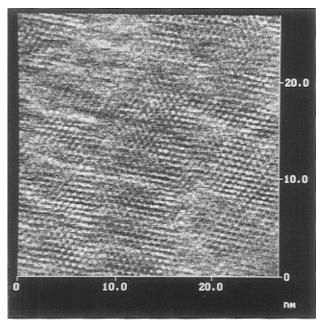

Figure 8. AFM image of an annealed SAM of **13** on gold(111). The monolayer was annealed for 16 h at 90 °C in air. The hexagonal lattice of the mixed disulfide ($d = 6.2$ Å) is recognized inside well-ordered domains.

of the organic material. The mobility of the gold atoms in the top layer is known.[20] The introduction of alkyl and perfluoroalkyl substituents should lower the interaction between unlike chains in the truely mixed system one obtains by the assembly of mixed disulfides. Hence, this should speed up the rate of diffusion of the gold atoms as has been observed for sulfur and chlorine.[35] On the other hand mobility of thiolates was assumed on the basis of STM investigations.[17a,20] Here the mobility of the defects in the gold has been observed in the first place. Mobility of thiolates or disulfides cannot be excluded at the edges

(35) (a) Trevor, D. J.; Chidsey, C. E. D.; Loiacono, D. N. *Phys. Rev. Lett.* **1989**, *62*, 929. (b) Trevor, D. J.; Chidsey, C. E. D. *J. Vac. Sci. Technol. B* **1991**, *9*, 964.

Figure 9. AFM image of an annealed SAM of **13** on gold(111). Although the XPS data show a significant loss of fluorine and hence fluoroalkyl chains in annealed monolayers, the hexagonal lattice of the mixed disulfide ($d = 6.2$ Å) is still recognized inside well ordered domains after annealing for 17 h at 100 °C in air. No monodomains of alkyl or fluoroalkyl chains can be detected.

of the terraces and etch pits. But these areas probably do not represent the interior of the densely packed layer.

In order to further increase the rate of diffusion one runs into the problem of desorption at temperatures around 100 °C. In conclusion, either the mobility does not exist in the interior of the layer or else the rate of diffusion is far too small to be detected, leave alone to be of any use in a patterning as briefly discussed in the introduction.

A second possible explanation could be the recent postulation of disulfides as the molecular species bound to the gold.[16] If there was no cleavage of the sulfur−sulfur bond in the mixed alkyl fluoroalkyl disulfides investigated in this study, a phase separation would not

be expected provided that the disulfide bond remained intact under the annealing conditions applied.

Unfortunately, we are not able to discriminate between the two plausible explanations on the basis of our results. A new approach could for instance include the investigation of similar, but thermally more stable, SAMs. First, the linkage between sulfur functionality and the perfluorinated chain should be only an alkyl segment. Second, the alkyl chain could be functionalized by some azobenzene moiety in ω-position[36] that enhances thermal stability and the attractive interaction between alike molecules.

Conclusions

The thermal stability of a large number of SAMs of symmetrical and mixed alkyl fluoroalkyl disulfides has been investigated by a multipronged approach including contact angle, grazing incidence FTIR, XPS, and AFM measurements. The limited thermal stability of the molecules in the SAMs in air stems on one hand from the different linkage of the perfluorinated chain to the sulfur containing functional group on the other hand from the inherent desorption of thiols and disulfides at temperatures of 100 °C and higher. The α-fluoro-substituted esters are hydrolyzed at 60−70 °C, the amide-based systems are stable up to approximately 90 °C and the γ-fluoro-substituted esters are stable up to 100 °C provided annealing times are not longer than 10 h. The FTIR and AFM experiments do not give any evidence for heat-induced phase separation. There are no tilted alkyl domains detectable in the FTIR, and the unique hexagonal lattice of the mixed alkyl fluoroalkyl disulfides remains unchanged even after annealing for 17 h at 100 °C in air, as confirmed by AFM. The observed behavior can be attributed to nonexisting or very low mobility of molecules in tightly packed SAMs. Alternatively, it cannot be ruled out that disulfides instead of thiolates are bound to the gold substrate.

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(36) SAMs of azobenzenethiols[28] on Au(111) were found to be thermally even more stable than n-alkanethiols. With AFM the periodicity can be still observed for SAMs annealed at 120 °C in air. This is probably due to increased interaction of the aromatic cores compared to the alkyl chains of simple *n*-alkanethiols.