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 fluoroalkyl systems evidence was sought for heat-induced phase separation of the alkyl- and fluoroalkyl-terminated molecules. The ester and amide linkages of the fluoro carbon chains are shown to be less stable than those of the hydrocarbon analogues. Fluorosubstituents 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 fluoro carbon 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 thioethers5 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 role of SAMs as models for organic surfaces and interfaces is of tremendous importance in many systems like self-assembled monolayers (SAMs) of organic 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).7,11 Time of flight secondary ion mass spectrometry (TOF-SIMS)12 on SAMs of thiols and disulfides as well as exchange experiments of mixed disulfides15 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 bond to the gold has been postulated on the basis of X-ray diffraction investigations.16

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.
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 and Langmuir–Blodgett films, 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). 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 as well as a thermodynamical treatment of a possible phase separation in monolayers 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. 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 in a vacuum of $5 \times 10^{-6}$ mbar in a Balzer evaporation machine. For the XPS measurements silicon wafers were used instead of glass substrates. 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.

**Preparation of Monolayers.** Monolayers were formed by immersing the gold substrates into a dilute solution (1.0 to 5.0 × 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 $\theta_a$ and $\theta_r$ were measured with Millipore water as

$$2 \text{CH}_3-(\text{CH}_2)_n\text{SH} \quad \text{Au} \quad \begin{array}{c} \text{S}-(\text{CH}_2)_n\text{CH}_3 \\ \text{S}-(\text{CH}_2)_n\text{CH}_3 \end{array} \quad \text{Au} \quad \begin{array}{c} \text{CH}_3 \\ \text{CH}_3 \end{array} \quad \begin{array}{c} (\text{CH}_2)_n \\ (\text{CH}_2)_n \end{array} \quad \text{S} \quad \text{S}$$

\[ \text{Figure 1.} \text{ Widely accepted reaction scheme for the reaction of alkanethiols and alkyl disulfides with the gold surface in the process of monolayer formation.} \]

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 and Langmuir–Blodgett films, 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). 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 as well as a thermodynamical treatment of a possible phase separation in monolayers 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.

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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 set-up (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 ($\hbar \nu = 1486.6$ 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 Tokyo, 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 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

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

<table>
<thead>
<tr>
<th>compound</th>
<th>conditionsa</th>
<th>$\theta_a$, deg</th>
<th>$\theta_r$, deg</th>
<th>hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>as prepared</td>
<td>106</td>
<td>96</td>
<td>0.171</td>
</tr>
<tr>
<td></td>
<td>48 h, 80 °C</td>
<td>106</td>
<td>95</td>
<td>0.188</td>
</tr>
<tr>
<td></td>
<td>24 h, 100 °C</td>
<td>106</td>
<td>91</td>
<td>0.258</td>
</tr>
<tr>
<td>2</td>
<td>as prepared</td>
<td>108</td>
<td>101</td>
<td>0.118</td>
</tr>
<tr>
<td></td>
<td>14 h, 80 °C</td>
<td>108</td>
<td>100</td>
<td>0.135</td>
</tr>
<tr>
<td></td>
<td>21 h, 100 °C</td>
<td>103</td>
<td>94</td>
<td>0.155</td>
</tr>
<tr>
<td>3</td>
<td>as prepared</td>
<td>116</td>
<td>109</td>
<td>0.113</td>
</tr>
<tr>
<td></td>
<td>19 h, 80 °C</td>
<td>104</td>
<td>95</td>
<td>0.155</td>
</tr>
<tr>
<td>4</td>
<td>as prepared</td>
<td>116</td>
<td>107</td>
<td>0.146</td>
</tr>
<tr>
<td></td>
<td>11 h, 80 °C</td>
<td>115</td>
<td>106</td>
<td>0.147</td>
</tr>
<tr>
<td>5</td>
<td>as prepared</td>
<td>117</td>
<td>107</td>
<td>0.162</td>
</tr>
<tr>
<td></td>
<td>24 h, 100 °C</td>
<td>117</td>
<td>106</td>
<td>0.178</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>conditionsa</th>
<th>$\theta_a$, deg</th>
<th>$\theta_r$, deg</th>
<th>hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>as prepared</td>
<td>114</td>
<td>107</td>
<td>0.114</td>
</tr>
<tr>
<td>20 h, 80 °C</td>
<td>113</td>
<td>105</td>
<td>0.132</td>
</tr>
<tr>
<td>20 h, 100 °C</td>
<td>108</td>
<td>98</td>
<td>0.170</td>
</tr>
<tr>
<td>20 h, 120 °C</td>
<td>102</td>
<td>81</td>
<td>0.364</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>conditionsa</th>
<th>$\theta_a$, deg</th>
<th>$\theta_r$, deg</th>
<th>hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>as prepared</td>
<td>112</td>
<td>104</td>
<td>0.133</td>
</tr>
<tr>
<td>73 h, 60 °C</td>
<td>112</td>
<td>103</td>
<td>0.150</td>
</tr>
<tr>
<td>43 h, 70 °C</td>
<td>103</td>
<td>92</td>
<td>0.196</td>
</tr>
<tr>
<td>24 h, 80 °C</td>
<td>103</td>
<td>86</td>
<td>0.295</td>
</tr>
</tbody>
</table>

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

<table>
<thead>
<tr>
<th>compound</th>
<th>conditionsa</th>
<th>$\theta_a$, deg</th>
<th>$\theta_r$, deg</th>
<th>hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>as prepared</td>
<td>113</td>
<td>104</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>73 h, 60 °C</td>
<td>113</td>
<td>102</td>
<td>0.183</td>
</tr>
<tr>
<td></td>
<td>43 h, 70 °C</td>
<td>113</td>
<td>104</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>24 h, 80 °C</td>
<td>113</td>
<td>101</td>
<td>0.200</td>
</tr>
<tr>
<td></td>
<td>20 h, 100 °C</td>
<td>113</td>
<td>101</td>
<td>0.200</td>
</tr>
</tbody>
</table>

(b) Contact Angles (H2O) of Annealed SAMs of 13 – 17

<table>
<thead>
<tr>
<th>compound</th>
<th>conditionsa</th>
<th>$\theta_a$, deg</th>
<th>$\theta_r$, deg</th>
<th>hysteresis</th>
</tr>
</thead>
<tbody>
<tr>
<td>13</td>
<td>as prepared</td>
<td>113</td>
<td>104</td>
<td>0.149</td>
</tr>
<tr>
<td></td>
<td>14 h, 100 °C</td>
<td>113</td>
<td>102</td>
<td>0.183</td>
</tr>
<tr>
<td>14</td>
<td>as prepared</td>
<td>112</td>
<td>102</td>
<td>0.167</td>
</tr>
<tr>
<td></td>
<td>14 h, 100 °C</td>
<td>110</td>
<td>100</td>
<td>0.168</td>
</tr>
<tr>
<td>16</td>
<td>as prepared</td>
<td>112</td>
<td>103</td>
<td>0.150</td>
</tr>
<tr>
<td></td>
<td>14 h, 100 °C</td>
<td>112</td>
<td>101</td>
<td>0.184</td>
</tr>
<tr>
<td>17</td>
<td>as prepared</td>
<td>111</td>
<td>100</td>
<td>0.185</td>
</tr>
<tr>
<td></td>
<td>14 h, 100 °C</td>
<td>111</td>
<td>100</td>
<td>0.185</td>
</tr>
</tbody>
</table>

a Selected examples of different annealing experiments were chosen in order to give a general overview.
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 symmetrical
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 hydroly-
sis.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 per-
fluorinated 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 ap-
proximately 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.

In the process of annealing, the desorption of some of
the molecules can be assumed even at lower tempera-
tures.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.

The activation can be deduced from the pKₐ values of similar
partially fluorinated carboxylic acids: CF₃-COOH pKₐ = 0.26; CH₃-
CH₂-COOH pKₐ = 3.00; CF₃-CH₂-COOH pKₐ = 4.15; CF₃-
CH₂-CH₂-CH₂-COOH pKₐ = 4.49; CH₃-CH₂-CH₂-CH₂-COOH pKₐ =
4.81, from: Kissa, E. Fluorinated Surfactants; Marcel Dekker, Inc.:

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 mono-
layer 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 × 10⁻⁴). 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 dodecane-thiol 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

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CH₂-CH₂-CH₂-COOH pKₐ = 4.49; CH₃-CH₂-CH₂-CH₂-COOH pKₐ =
4.81, from: Kissa, E. Fluorinated Surfactants; Marcel Dekker, Inc.:

(30) Porter, M. D.; Bright, T. B.; Allara, D. L.; Chidsey, C. E. D.
We can see toward lower binding of note. Firstly, considering the C(1s) spectra, in the monolayers of 2-((CH2)\n-alanoyloxy)ethyl 2′-fluoro-substituted esters in air. Figure 6 shows the F(1s) and C(1s) regions for and 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 energy the peaks associated with the alkyl (CH2) 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 CF2 and CF3 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 fluorocarbon 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 fluoralkyl 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 fluoralkyl 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.

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. Since the disulfide contains two chains of equal length,
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 –CH₃ and –CF₃ 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. 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 fluoralkyl 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 of the organic material. The mobility of the gold atoms in the top layer is known. The introduction of alkyl and perfluoroalkyl substituents should lower the interaction between unlike chains in the truly 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. On the other hand mobility of thiolates was assumed on the basis of STM investigations. 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 of the organic material.
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. 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 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 ρ-fluoro-substituted esters are hydrolyzed at 60–70 °C, of 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 nonexistent 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 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.