

Tribological properties of self-assembled monolayers of fluorocarbon and hydrocarbon thiols and disulfides on Au(111) studied by scanning force microscopy

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Abstract

The tribological properties of highly ordered self-assembled monolayers (SAMs) of fluorocarbon and hydrocarbon thiols and disulfides formed on triangular Au(111) terraces were studied by scanning force microscopy (SFM). Molecular resolution SFM images proved the high degree of lateral order in the films. The magnitude of friction between Si_3N_4 tips and the monolayers measured by SFM was related to the order of the alkane chains. The disorder of the hydrocarbon chains in SAMs of mixed hydrocarbon–fluorocarbon disulfides, or short chain hydrocarbon disulfides, was determined by Fourier transform infrared (FTIR) spectroscopy. Conformational and structural disorder was found to correlate with a significant increase in the magnitude of friction. The correlation between disorder (transition from ‘solid-like’ to ‘amorphous-like’ monolayers) and increase in observed friction force can be interpreted based on models by Yoshizawa et al. [H. Yoshizawa, Y.-L. Chen, J. Israelachvili, J. Phys. Chem. 97 (1993) 4128]. © 1999 Elsevier Science S.A. All rights reserved.

Keywords: Friction; Scanning force microscopy; Self-assembled monolayers

1. Introduction

In recent years, studies of adhesion, friction and lubrication have received increasing attention. Growing interest in these areas is partly due to the expansion of related technologies and to the need of achieving a better understanding of the related scientific issues [1]. Fundamental results regarding lubrication, and the relation between friction and adhesion, were obtained in experiments with the surface forces apparatus [2,3]. Relatively recently, atomic force microscopy (AFM), also called scanning force microscopy (SFM),¹ has proven to be an appropriate technique for measuring the adhesion [5–7] and friction [8] between a very sharp probe (tip) and well-defined model surfaces. The corresponding literature has been recently reviewed by Carpick and Salmeron [9]. For a number of systems, the friction process is relatively well understood. However, in general, the great number of often interrelated parameters which determine adhesion and friction make

predictions difficult or often impossible. These parameters can include interaction of exposed functional groups at surfaces [10–13], orientation of crystal lattices and thus dipoles (*friction anisotropy*) [13–20],² packing densities and energies, order (crystalline, ‘amorphous’) [21,22], number of defects, and mechanical properties [23,24] which result in different contact areas [25] between tip and sample. Several studies focused on the tribological characterization of well-defined model surfaces consisting of Langmuir Blodgett (LB) films and self-assembled monolayers (SAMs) [26]. Xiao et al. [27] and Lio et al. [28] presented studies on several SAMs of organosilanes on mica and organothiols on gold. They proposed that energy dissipation can play a dominating role in determining the magnitude of friction for the monolayers studied. Their observations, however, can be rationalized based on earlier models by Yoshizawa et al. [29] assuming (1) that molecular reorientations in the SAM are included in the definition of interdigitation [29] and (2) that SAMs of thiols on gold can be classified as ‘solid-like’ or ‘amorphous-like’, re-

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¹ For a recent review, see Ref. [4].

² See additional examples in Ref. [9].

spectively, regarding their tribological properties. This classification is analogous with the time–temperature superposition principle describing the mechanical response of the viscoelastic properties of polymeric materials.

In this paper, we report on our results of SFM study on the tribological properties of highly ordered SAMs of fluorocarbon, and hydrocarbon thiols and disulfides formed on triangular Au(111) terraces. These model systems are very suitable for investigating the tribological properties by SFM as the orientation and the order of the hydrocarbon chains, as well as the packing densities and thus the number of active vibrational and rotational modes ('phase state' of the films) [29], can be controlled in the corresponding monolayers [30–33].

2. Experimental

2.1. Substrate and SAM preparation

Evaporated gold substrates (borosilicate glass, 2 nm Cr, 250 nm Au) were purchased from Metallhandel Schröer, Lienen (Germany). Au(111) samples were prepared by flame annealing these gold substrates in a high purity hydrogen flame for 10 min. The substrates consisted of triangular Au(111) terraces which were usually several microns large. Monolayers were prepared by self-assembly in 0.5–1.0 mM solutions of the corresponding thiol or disulfide in dichloromethane (p.a., Merck). The compounds were available from previous studies [30–33]. After at least 12 h of assembly, the samples were taken out of the solution, rinsed carefully with pure solvent and dried in an argon stream.

2.2. Fourier transform infrared (FTIR) spectroscopy

The FTIR spectra were obtained on a Nicolet 5DXC FTIR spectrometer which was equipped with an FT80 specular reflectance setup (Spectratech). The chamber of the instrument was purged with dry air. The spectra were taken with a resolution of 2–4 cm^{-1} (2000 scans).

2.3. SFM

The SFM data were acquired on a NanoScope III Multimode SFM (Digital Instruments (DI), Santa Barbara, CA, USA) equipped with a 10 μm scanner which was placed in a home-built glass chamber purged with dry nitrogen. Commercial silicon nitride cantilevers/tips (DI) with a nominal spring constant of 0.38 N/m were used. Before each experiment, the SFM setup was equilibrated for at least 5 h in order to minimize the thermal drift. Before and after each measurement, freshly cleaved mica was scanned in order to record a reference curve. The friction data were obtained by scanning the sample in 90° to the long axis of the cantilever. 200 nm line scans were performed on SAMs on flat, triangularly shaped Au(111) terraces at a scan rate of 5 Hz (velocity \approx 1.0 $\mu\text{m/s}$) for different set points. The friction force was calculated from

the so-called 'friction loops' [15]. The data were averaged over at least three sets of experiments performed with the same tip/cantilever on different terraces. The lateral force constant was estimated according to the double beam approach, based on scanning electron microscopy (SEM) images of the cantilevers' dimensions using the known elastic constant of the material, as described in Ref. [21]. The radii of the tips used in this study were estimated with a scanning electron microscope (Jeol JSM-T 220A) at a voltage of 20 kV. All the tip radii were found to be in the range of 75 ± 35 nm. In order to avoid artifacts due to different tip radii and spring constants, only results obtained with a single cantilever/tip assembly are presented for the given individual sets of SAMs (see text and figure captions). The quality of the SAMs was checked by recording molecular resolution SFM images on the terraces chosen for friction measurements. Lattice resolution was not possible to achieve for compounds **6** and **9** (Scheme 1).

3. Results and discussion

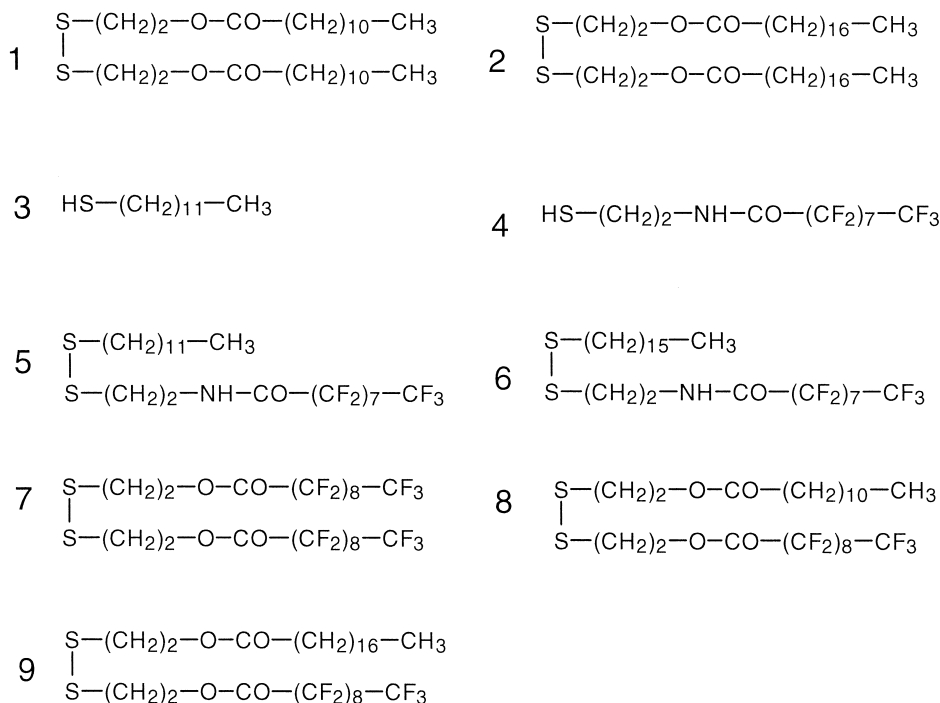
The SAMs investigated by SFM were formed by self-assembly of the thiols and disulfides shown in Scheme 1 onto flame-annealed Au(111) substrates (Fig. 1). As discussed in earlier papers, the structure of the molecules in the SAMs can be varied by the introduction of functional groups within the chain. The SAMs of the compounds in Scheme 1 were investigated previously by a multitude of techniques [30–34]. The lattices formed by various symmetrical and mixed hydrocarbon and fluorocarbon ester disulfides differ significantly from the known lattices of *n*-alkane thiols on Au(111). The lattice distances as well as the symmetry of the disulfides were found to depend on the structure. Consequently, the tilt angle of the molecules and the packing density of the films are different. In the following paragraphs, an attempt is described to correlate these structural differences with the tribological properties.

3.1. Hydrocarbon disulfides

The friction behavior of SAMs, which consists of closely packed hydrocarbon chains, was investigated first. All the SFM experiments were performed on flat, triangularly shaped Au(111) terraces (Fig. 1). The interpretation of earlier friction experiments on Au(111) terraces of smaller size and less perfection was difficult due to significant scatter in the friction data which we attributed to coupling of topography in the friction loops.

The friction forces measured by SFM with a silicon nitride tip on SAMs of disulfides **1** and **2** as well as of dodecane thiol (**3**) are summarized in Fig. 2. Despite insignificant differences in pull-off forces,³ the friction force is clearly different for all these SAMs.

³ Pull-off forces of 45 ± 15 nN were measured for all the hydrocarbon SAMs.



Scheme 1. Compounds used in this study.

The contact angles measured with water were found to be slightly lower than that of SAMs of *n*-alkane thiols ($\theta_a = 106 \pm 2^\circ$ for **1**, $108 \pm 2^\circ$ for **2**, and $109 \pm 2^\circ$ for dodecane thiol, respectively) [30,31]. As mentioned before, the pull-off forces measured did not vary significantly. Thus, any frictional differences that may exist between the hydrocarbon disulfides with $n = 10$ (**1**), $n = 16$ (**2**) and dodecane thiol should be related to structural differences of the SAMs.

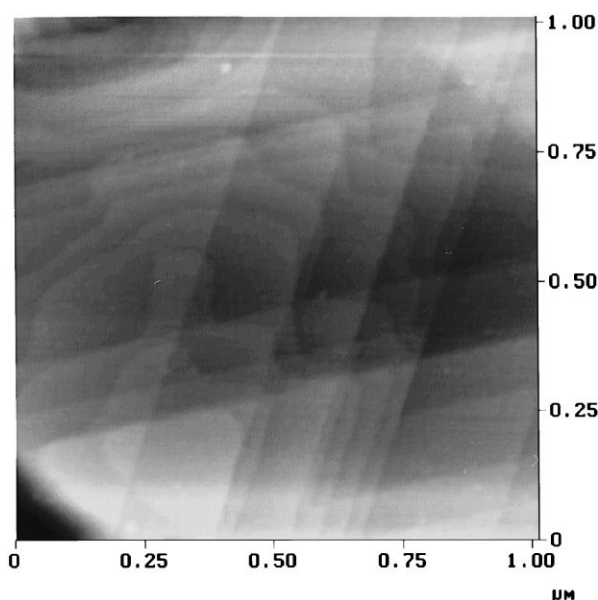
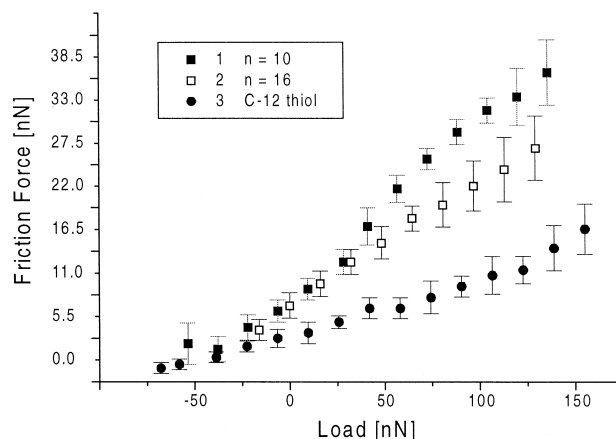


Fig. 1. SFM image of triangular Au(111) terraces (height from dark to bright 5 nm).

The disulfides and dodecane thiol form SAMs on gold with significantly different structural order (as shown by FTIR spectra, Fig. 3). The peak positions for the C–H stretching vibrations indicate that the SAM of the disulfide **1** is more ‘liquid-like’ (see Ref. [26]), whereas SAMs of **2** is more ‘crystal-like’, but still less ordered than that of SAMs of, e.g., octadecane thiol [26]. The better order of **2** as compared to **1** can also be deduced from the progression bands seen in the low energy region of the FTIR spectra (Fig. 3b). These progression bands indicate an all-*trans* conformation of the alkane chains for monolayers of **2** [30,31].

The ester bond can be expected to introduce *gauche* defects in the lower region of the alkane segment. In

Fig. 2. Friction force vs. load plot for dodecanethiol and disulfides **1** and **2**.

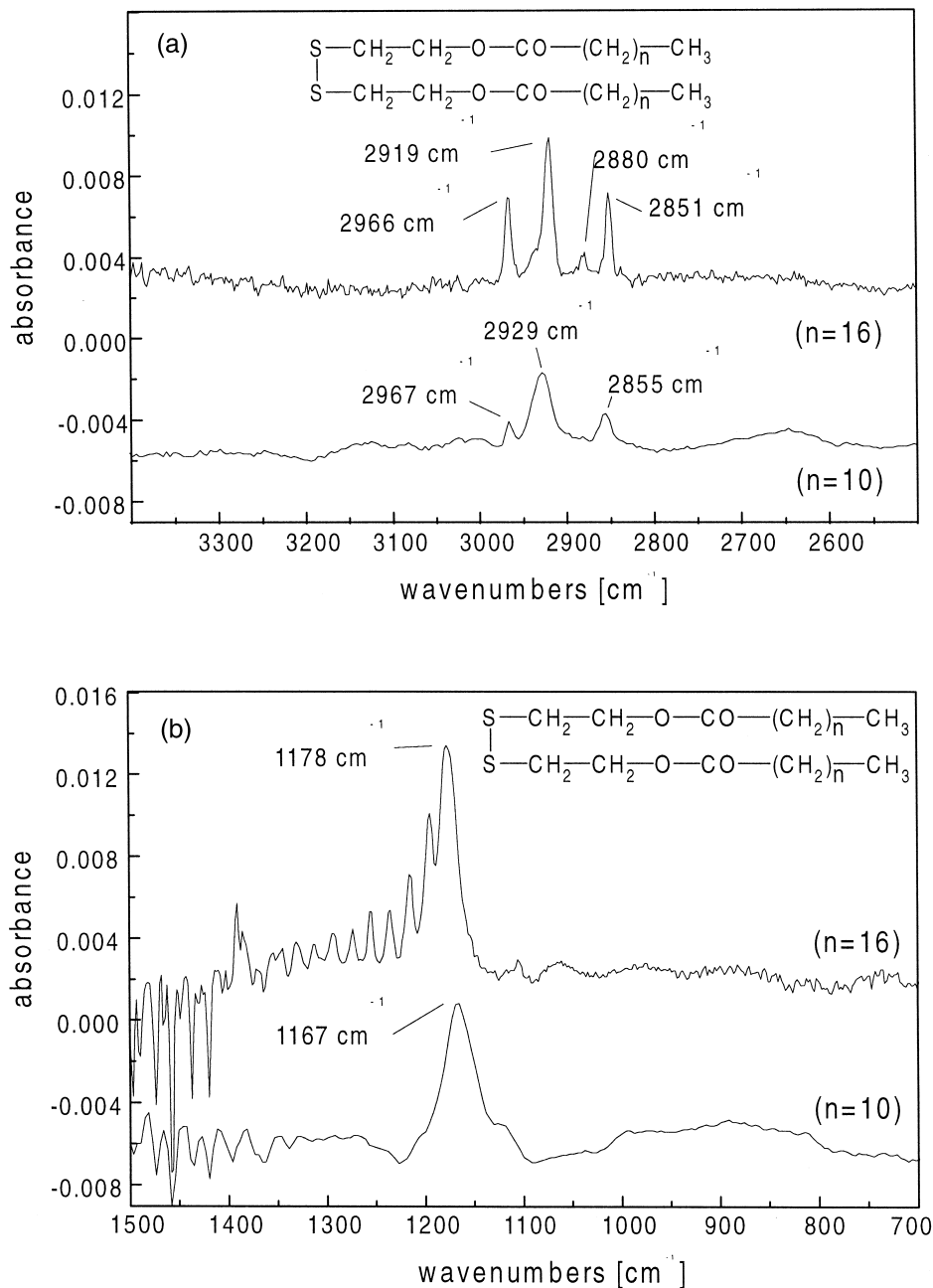


Fig. 3. (a) FTIR spectra of SAMs of compounds **1** and **2** showing the C-H stretching vibrations. The peak width at half maximum is significantly smaller for **2** ($n = 16$). In addition, the peak maxima for **2** are located at lower wavenumbers. Both observations are indicative for a more 'crystalline-like' order in the corresponding SAM of **2**. (b) FTIR spectra of SAMs of compounds **1** and **2** showing the C-O stretching vibration and for **2** ($n = 16$) the progression bands which are typical for an all *trans* conformation of the hydrocarbon chains.

addition, thermal motion causes some disorder near the chain termini [35]. However, the previous arguments (differences in measured contact angles, and peak positions and band widths in FTIR) do not rule out the possibility of the formation of a closely packed layer for molecules of short chain length. By means of SFM, the lattice of these two disulfides and homologues with $n = 8-16$ [32,36], as well as unsymmetrical bis alkane disulfides [37], could be imaged with molecular (lattice) resolution. The nearest

neighbor distances found for disulfides **1** and **2** (see Table 1) [32] suggest that hydrocarbon chain has a slightly increased tilt angle as compared to *n*-alkane thiols (tilt angles of 30° were measured) [26]. As the SAMs show a 2D translational order, the peak positions of SAMs of **1** found in FTIR do not mean that the SAM is in a liquid state (in the sense described for surfactant monolayers in Ref. [29]), but in an 'amorphous' 'phase state'. SAMs of dodecane thiol can be considered to be 'solid-like', while

Table 1
Area per molecule/chain as measured with SFM [31–33]

Compound	Area per molecule/chain [Å ²]
1	24.1
2	24.1
3	21.7
4	28.7
5	33.3
7	29.8
8	33.3

SAMs of **2** are in an intermediate state. The observed magnitude of friction follows the expected trends based on the model of Yoshizawa et al. [29].

3.2. Hydrocarbon–fluorocarbon disulfides

The friction force vs. load plots for the CH–CF system (Fig. 4) show that the friction for the fluorocarbon thiol is larger than that for dodecane thiol. The mixed disulfides, however, show the largest magnitude of friction. The pull-off forces measured were for dodecane thiol (**3**) 47 ± 15 nN, for the fluorinated thiol (**4**) 33 ± 15 nN, and for the mixed disulfides (**5,6**) 46 ± 18 nN, respectively. Thus, no significant differences in the pull-off force values were obtained. In light of the discussion of the structural differences (vide infra), it seems reasonable to attribute the observed large magnitude of friction of the mixed disulfides to additional modes of energy dissipation which can be related to differences in the ‘phase state’ of the SAMs.

For the mixed hydrocarbon–fluorocarbon systems, we have found earlier that the fluorocarbon chain imposes a nearly perpendicular orientation of the alkane chain with respect to the surface normal. A more detailed FTIR analysis by Tsao et al. [38] could resolve the very broad C–H stretching vibrations of these SAMs. The peak positions found in this study are indicative of ‘disordered’ chains. The orientation of the fluorocarbon segment is virtually unchanged as compared to the symmetrical fluo-

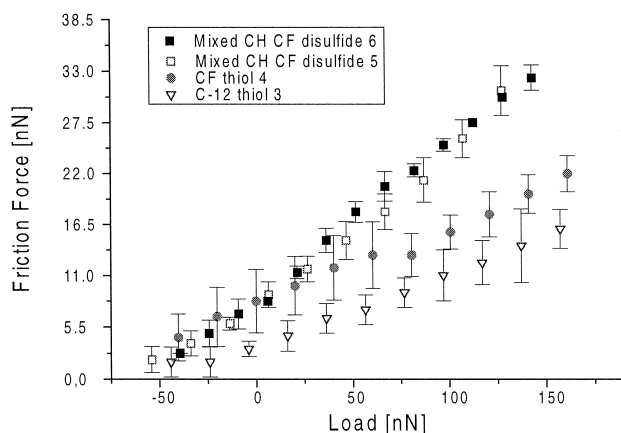


Fig. 4. Friction vs. load plot for SAMs of compounds **3–6**.

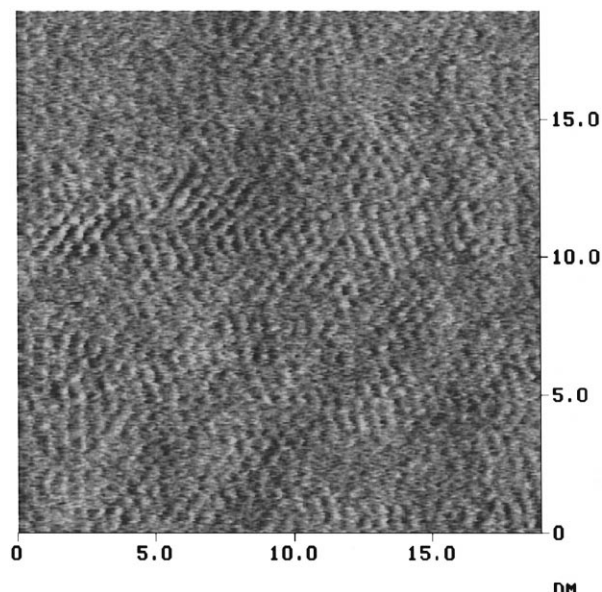


Fig. 5. Unfiltered high resolution SFM (friction) image of the lattice of the mixed hydrocarbon-fluorinated disulfide **5** on Au(111).

rocarbon disulfide [30,31], thus the disordered alkane chain should possess more vibrational and rotational modes than the symmetric compound (*n*-alkane thiol). In addition, SFM analyses of the corresponding lattices indicate the increased freedom of the alkane chains. Mixed CH–CF disulfides form incommensurate lattices with large nearest neighbor distances (6.2 Å) [32,33]. As an example, an unfiltered friction force image of a SAM of **5** is shown in Fig. 5. The image contrast is related to a molecular stick-slip process [15].

A second system of hydrocarbon and fluorocarbon SAMs consists of structurally similar ester disulfides **7–9**. The results of the friction measurements are similar to the results obtained for compounds **3–6**. The structural details,

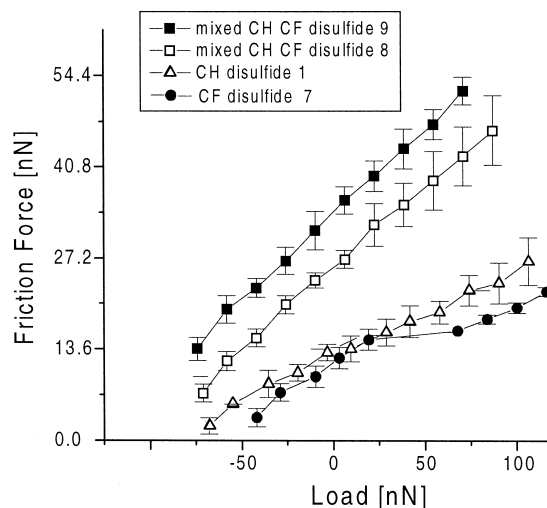


Fig. 6. Friction vs. load plot for SAMs of compounds **1** and **7–9**.

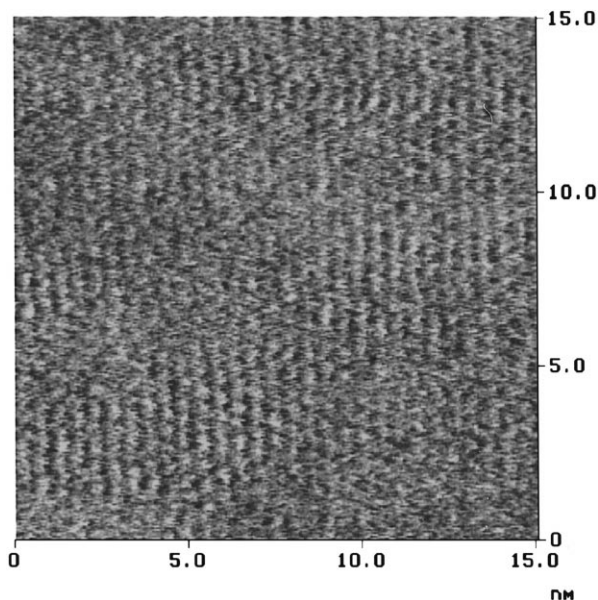


Fig. 7. Unfiltered high resolution SFM (friction) image of the lattice of the fluorinated disulfide **7** on Au(111).

which are very similar to the amide CH–CF system (vide supra) have been discussed before [30,31]. The alkane chains are disordered and oriented close to the surface normal in the mixed systems.

The friction observed in our present experiments shows a dramatic increase when going from the symmetrical hydro- or fluorocarbon SAM to the mixed SAM (Fig. 6).

It is remarkable that the fluorocarbon disulfide has a similar friction as the hydrocarbon analogue. In the literature, there are several examples for studies which indicate significantly higher friction on fluorocarbon compared to corresponding hydrocarbon monolayers [39]. A recent study of SAMs of two structurally very similar molecules estimated the friction of the $-\text{CF}_3$ terminated thiol to be a factor of 4 higher than the corresponding $-\text{CH}_3$ terminated thiol [12].

In addition, the orientation of the lattice of the fluorinated disulfide **7** could be deduced for the first time from images on the Au(111) terraces (Fig. 7). Thus, the SAM of the fluorinated disulfide **7** is highly ordered. The hexagonal lattice observed ($d = 5.8 \pm 0.2 \text{ \AA}$) was oriented parallel to the directions of the terrace edges which correspond to nearest neighbor directions of the Au(111). Thus the tail group lattice can be classified as a commensurate $p(2 \times 2)$ lattice [40].

For all the systems studied here, the pull-off forces as measured by SFM and the advancing contact angles measured with water [30,31] did not correlate with the observed trend found for friction. Thus, unlike for other thin films of hydrocarbon and fluorocarbon molecules, the chemical functionality exposed at the surface of the SAMs is *not* the dominating factor for determining the magnitude of friction. Surface energy, as well as a postulated size

effect of the terminal functional groups [12], cannot account for the observed friction data.

The systems described in this paper varied in the order of the alkane chain as detected, e.g., by FTIR and in area per molecule/chain ('packing density') as measured in molecularly resolved SFM images. In general, the differences in friction correlate with these structural differences. It is reasonable to assume that the increased disorder for 'amorphous-like' SAMs facilitates the excitation of vibrational and rotational modes as compared to more 'solid-like' SAMs.

4. Conclusion

In the SFM study on the tribological properties of highly ordered SAMs of fluorocarbon and hydrocarbon thiols and disulfides formed on triangular Au(111) terraces, the magnitude of friction was correlated with the order of the alkane chains ('phase state'). The disorder of the hydrocarbon chains in SAMs of mixed hydrocarbon–fluorocarbon disulfides or short chain hydrocarbon disulfides, as seen in FTIR spectroscopy, was found to result in a significant increase in the magnitude of friction. The correlation of disorder and increase in observed friction force supports the friction mechanism of energy dissipation in the SAM by vibrational and rotational modes. These observations agree with predictions of models by Yoshizawa et al. assuming that disordered SAMs are 'amorphous-like' and well-ordered SAMs are 'solid-like'.

Acknowledgements

The authors thank Helmut Ringsdorf (University of Mainz, Germany) for stimulating discussions and Mei-Wei Tsao and John F. Rabolt (University of Delaware) for providing additional FTIR data on the mixed systems. This study was financially supported by the Council for Chemical Sciences of the Netherlands Organization for Scientific Research (CW-NWO) in the priority program materials (PPM).

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