Local Packing Environment Strongly Influences the Frictional Properties of Mixed CH_3- and CF_3-Terminated Alkanethiol SAMs on Au(111)

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Compositionally mixed, self-assembled monolayers (SAMs) derived from 16,16,16-trifluorohexadecanethiol and a normal alkanethiol, either hexadecanethiol or pentadecanethiol, were formed on Au(111) substrates. The relative composition of the films was determined using X-ray photoelectron spectroscopy and was found to approximately equal the equimolar composition of the isooctane solution from which they were formed. The frictional properties of the mixed films were measured on the nanometer scale using atomic force microscopy and were observed to decrease when the chain length of the CH_3-terminated component was shortened by one methylene unit (i.e., when hexadecanethiol was replaced by pentadecanethiol). For comparison, the frictional properties of a mixed-chain-length CH_3-terminated SAM derived from hexadecanethiol and pentadecanethiol in a 1:1 ratio was also examined. In contrast to the mixed CF_3/CH_3 system, the latter mixed-chain-length system exhibited relatively higher friction when compared to single-component SAMs derived solely from either hexadecanethiol or pentadecanethiol. For both types of mixed films, the change in frictional properties that occurs as a result of modifying the position of neighboring terminal groups with respect to the surface plane is discussed in terms of the influence of local packing environments on interfacial energy dissipation (friction).

Introduction

In the past decade, organic thin films have been extensively employed in a variety of molecular technologies.[1−4] In particular, fluorinated organic thin films have drawn much attention due to their unique chemical stability and anti-adhesive properties.[5−7] With the emergence of applications and devices relying upon nanotechnology, lubricant films with monomolecular layer thickness are desired. On this scale, molecular properties such as local conformation, dispersion, packing arrangement, and chemical composition can directly influence the performance of the lubricant system. With the increased need for molecularly thin films, additional insight into the molecular-level details of interfacial contacts is required. The development of atomic force microscopy (AFM) has provided a unique opportunity to study interfaces with molecular-scale sensitivity. In this paper, we use AFM to evaluate the relationships between tailgroup packing and the frictional properties of organic thin films, including those with terminal-group fluorination.

In previous work,[8,9] we explored the frictional properties of SAMs having a hydrogenated backbone and terminated with either CH_3 or CF_3 groups. Upon the introduction of fluorine, a 3-fold increase in friction was observed in lateral force microscopy measurements. We attributed this increase to the relatively large size of fluorine compared to hydrogen in the terminal group. In our model, we postulated that the introduction of fluorine leads to enhanced intra- and intermolecular steric interactions for the bulky CF_3-terminated films and that corresponding lateral steric interactions can plausibly occur over distances sufficiently long to permit the propagation of surface phonons. In related work,[10] we examined the frictional properties of mixed SAMs composed of CH_3- and CF_3-terminated alkanethiols with the same chain length (for both even and odd numbers of carbon atoms). We found that the introduction of even small amounts of the CF_3-terminated component led to a substantial increase in the frictional properties of the film compared to that of the single-component CH_3-terminated film. Using the model described above, we rationalized this increase on the basis that the presence of small numbers of bulky terminal groups gives rise to additional steric barriers to the motion of their nearest neighbors. A simple schematic of mixed films with ideally dispersed components showed that the intermolecular interactions between the terminal groups of the vast majority of the film can be influenced by the incorporation of the CF_3 group, even at a level of only 10%.

In the present study, we measure the frictional properties of mixed SAMs composed of CH_3- and/or CF_3-terminated alkanethiols in which the chain length and film termination are systematically varied (Figure 1). Specifically, we compare the frictional properties of a SAM composed of a mixture of 16,16,16-trifluorohexadecanethiol and hexadecanethiol (∼1:1) and a SAM composed of

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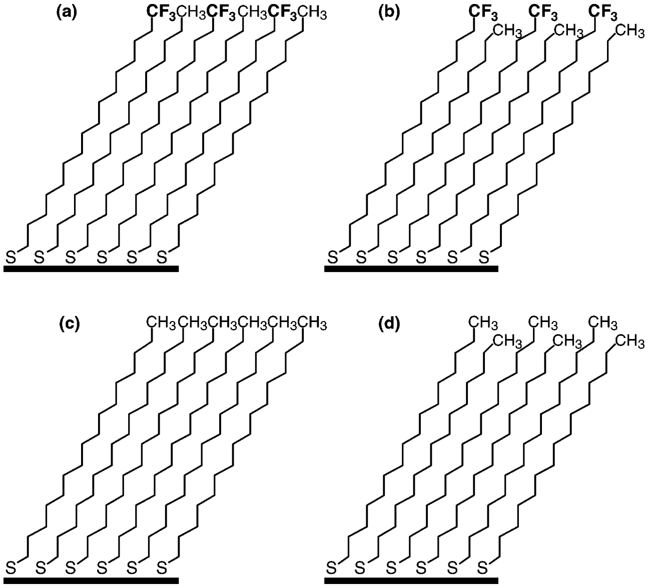

Figure 1. Schematic representation of SAMs on Au(111): (a) F1H15 + H16, (b) F1H15 + H15, (c) H16, and (d) H16 + H15.

the same CF_3-terminated thiol and pentadecanethiol (~1:1). We also compare the frictional properties of a SAM derived from hexadecanethiol to those of a mixed SAM derived from hexadecanethiol and pentadecanethiol (~1:1). The results are discussed in terms of the local packing environment of the film components and the pathways of energy dissipation encountered during a molecular-scale tribological contact.

Experimental Section

Nomenclature. For simplicity, we denote the names of the alkanethiols as follows: 16,16,16-trifluorohexadecanethiol ($CF_3(CH_2)_{15}SH$), F1H15; hexadecanethiol ($CH_3(CH_2)_{15}SH$), H16; and pentadecanethiol ($CH_3(CH_2)_{14}SH$), H15.

Materials. The normal alkanethiols were obtained from Aldrich Chemical Co. and used as received. The trifluoromethyl-terminated alkanethiol was synthesized using an established methodology.[11] The Au(111) substrates were prepared by annealing a gold wire in a flame of H_2/O_2 as described previously.[8,12]

Preparation of SAMs. Mixed monolayers were prepared by immersing gold substrates in 1 mM solutions of either pure alkanethiol or a 1:1 mixture of alkanethiols in isooctane at room temperature for 24 h. Upon removal from solution, the SAMs were rinsed thoroughly with isooctane and ethanol and blown dry with ultrapure nitrogen.

X-Ray Photoelectron Spectroscopy (XPS). XPS measurements were carried out using a PHI 5750 XPS system equipped with a PHI 10-420 toroidal monochromator and a PHI 10-360 hemispherical analyzer. The monochromatic Al source (1486.6 eV) was operated at 350 W, and spectra were collected using a pass energy of 50 eV. The use of a monochromatic X-ray source minimizes the degree of degradation of the organic species during irradiation.[13]

Atomic Force Microscopy. The topographic and frictional properties of the SAMs were measured with a beam-deflection atomic force microscope using a single piezo tube scanner. RHK AFM 100 and RHK STM 100 electronics were used to control the sample position, as well as data collection and processing. The measurement of frictional forces was accomplished by monitoring the lateral torsion of the cantilever as a function of applied load. The detailed procedure has been described in previous publications.[14,15] The present studies employed a Digital Instruments Si_3N_4 probe tip having a force constant of 0.58 N/m. The identical cantilever/tip assembly was used for an entire data set (including all of the different monolayers) in order to allow a precise comparison of frictional properties. Frictional forces are reported as calibrated photodiode responses (arb units) in light of the uncertainty in the cantilever lateral force constant. In all cases, the reported data have been collected at least three times and found to be independent of the order of measurement.

Table 1. Analysis of SAMs by XPS

	surface analysis		percent composition of F1H15	
samples[a]	F 1s XPS area	Au 4f XPS area	solution (%)[b]	surface (%)[c]
F1H15	8935	125802	100	100
H16 + F1H15	4308	114052	50.0	53.2
H15 + F1H15	4213	116539	50.0	50.9

[a] Solvent: isooctane. [b] Calculated from stoichiometries. [c] Determined by XPS.

Results and Discussion

The four types of SAMs prepared on Au(111) for this study and are shown in Figure 1. While three of the SAMs were derived from two-component mixtures of alkanethiols, the H16 SAM was derived from a single alkanethiol (i.e., hexadecanethiol). For additional clarity, we note that H16 + F1H15 and H15 + F1H15 correspond to SAMs containing both CH_3 and CF_3 terminal groups; in contrast, H16 and H16 + H15 correspond to SAMs containing only the CH_3 terminal group.

The surface composition of the mixed monolayers was evaluated by XPS (spectra not shown). The mole fraction of the partially fluorinated component was calculated by the method described in a previous report.[10] Briefly, this procedure entailed integrating the F 1s, C 1s, and Au 4f regions of the spectrum and calculating normalized ratios of the intensities of these elements. Due to the relatively low intensity of the C 1s region associated with the presence of CF_3 species, the calculations of film percent composition have been based upon ratios of F 1s and Au 4f signals and referenced to similar measurements of a single-component F1H15 film. The results of these calculations are presented in Table 1, where the solution and surface compositions of the different monolayers are compared. From Table 1, it can be seen that the percent composition of the CF_3-terminated alkanethiol in the SAMs is similar to that in the isooctane solution.

Before measuring the frictional properties of the SAMs, we collected topographic and lateral force AFM images over two different length scales: 0.5 μm × 0.5 μm and 200 Å × 200 Å. For example, Figure 2 displays the normal and lateral force images, collected at 0 nN applied load, from the H15 + F1H15 monolayer over a 0.5 μm × 0.5 μm area. Over both length scales, the topographic images indicated that the surfaces of all films were smooth and featureless; only the steps and terraces of the underlying gold substrates were observed. The lateral force image of Figure 2b demonstrates a spatial homogeneity across the film surface and provides no indication of islanding of the two film components. The lateral force images of the other films of this study, collected simultaneously with the topographic images, revealed a homogeneous surface character as well. On the basis of these results, we conclude

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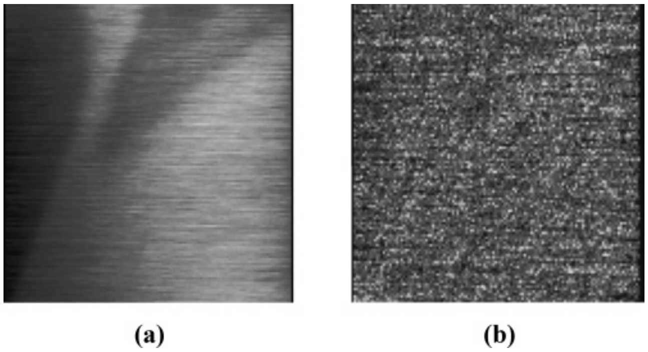

(a) **(b)**

Figure 2. (a) Normal force (topography) and (b) lateral force (friction) images collected at a load of 0 nN external applied load from a 0.5 μm $\times$ 0.5 μm region of the H15 + F1H15 SAM. The relatively homogeneous frictional signal is consistent with the absence of phase separation within the film.

that the CH_3- and CF_3-terminated alkanethiols with identical backbone structures and similar chain lengths are homogeneously mixed without phase separation.

A handful of studies have reported the nanometer-scale phase separation of two-component hydrocarbon SAMs on gold. For example, Tamada et al.[16] observed phase separation by AFM for mixed SAMs of butanethiol and octadecanethiol. In additional AFM studies, we found phase separation within SAMs composed of equimolar quantities of decanethiol and heptadecanethiol.[17] However, the phase separation of two-component mixtures of CH_3-terminated n-alkanethiols of similar length has yet to be observed.[18−21] In particular, Weiss et al.[22] reported homogeneous mixing within SAMs composed of 1-decanethiol ($CH_3(CH_2)_9SH$) and 1-dodecanethiol ($CH_3(CH_2)_{11}SH$), where the chain length difference is two methylene units. These results are consistent with the homogeneous friction images described above and with our conclusion of fully mixed CH_3- and CF_3-terminated SAMs.

The existence of homogeneously mixed CF_3/CH_3 films can be further rationalized by considering the local environment of the terminal CH_3 and CF_3 groups. The XPS results described above indicate that nearly equal amounts of CH_3- and CF_3-terminated alkanethiols are distributed across the Au(111) surface. Two distinct phenomena would encourage the dispersion of these components in the film as opposed to their coalescence. First, since the CF_3 group is bulkier than the CH_3 group, it is energetically favorable that the CF_3 groups be dispersed among the CH_3 groups in the outermost plane of the SAMs, instead of being crowded together. Second, the CF_3-terminated thiols possess an appreciable dipole due to the presence of the electronegative fluorine atoms. Given the mobility of the two components on the surface and within the film,[23,24] neighboring dipoles of two CF_3 groups would tend to repel one another and again drive the dispersion of this component throughout the film.

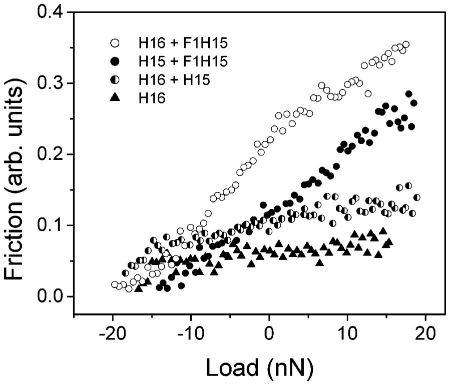

Figure 3. Frictional forces measured with AFM as a function of decreasing load for the single-component and mixed monolayers depicted in Figure 1.

We examined the frictional properties of the four SAMs by measuring the interfacial friction between a silicon nitride probe tip and the surface of the films as a function of applied load. Figure 3 displays the friction−load plots obtained for each film measured under decreasing load conditions. To permit a valid comparison of the frictional properties of the films, the same AFM tip was used for all of the measurements described in this study.

The data of Figure 3 demonstrate that the friction of the mixed F1H15 + H16 monolayer is significantly greater than that of the H16 monolayer. This result is consistent with our previous studies in which an enhancement in friction was observed when introducing CF_3-terminated alkanethiols into monolayers containing hydrogenated components of the same chain length.[10] Figure 3 also shows that when the H16 component is replaced in the mixed film by an alkanethiol that is one carbon shorter, H15, the frictional properties of the mixed SAM is reduced; that is, the friction of the H15 + F1H15 is lower than that of the H16 + F1H15 SAM. With fully dispersed components (i.e., no phase separation), this observation illustrates the remarkable degree to which local packing structure can influence the frictional response of a molecular-scale contact. From Figure 3, we also find that when two CH_3-terminated alkanethiols, differing in length by a single methylene unit, are mixed under conditions leading to an ~1:1 surface composition, the frictional properties of the mixed film are measurably higher than that of the single-component H16 film.[25] Moreover, Figure 4 shows that the frictional properties of single-component H15 and H16 films are indistinguishable. Thus, the higher friction observed for the mixed H15 + H16 film again highlights the high degree of correlation between the local packing environment of hydrocarbon films and their corresponding frictional properties. While some variation in the pull-off force measured *during slide* was encountered for the different film systems, no systematic trend in adhesive properties as a function of chain length was observed, thus suggesting that adhesive character does not dominate the observed differences in friction.

Although the replacement of C16 by C15 in the two different systems leads to opposite trends in the frictional properties, both trends can be rationalized by considering the phenomena occurring at the outermost plane of the

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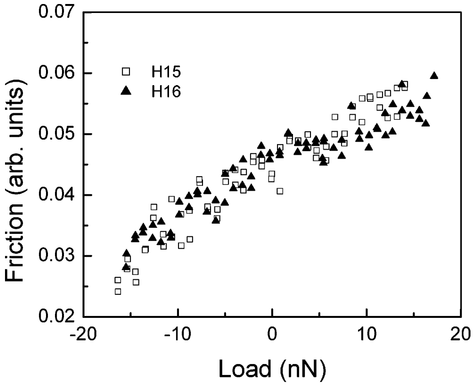

Figure 4. Frictional forces measured with AFM as a function of decreasing load for single-component H15 and H16 monolayers on Au(111).

films (i.e., where the terminal groups reside). Our previous work utilizing AFM and infrared spectroscopy measurements has shown that mixed films composed of CH_3 and CF_3 terminations exhibit indistinguishably different adsorption geometries and chain densities when compared to fully hydrogenated SAMs derived from normal alkanethiols.[8−10] However, an effectively higher *local* packing density must exist in the outermost plane of mixed CF_3/CH_3 films, given that CF_3 groups are larger than CH_3 groups. Thus, for these mixed SAMs, a reduction in the chain length of the CH_3-terminated component can effectively eliminate the additional steric strain associated with the CF_3 group. In our previous work, we have argued that the steric strain in the more densely packed surface plane gives rise to the presence of coupled interactions (repulsions) among terminal groups, which in turn lead to more widespread deformation of the film as the tip is translated across the surface. Furthermore, we have argued that it is the excitation of such modes (deformations), even on a local scale, that gives rise to the enhanced frictional properties of a CF_3-terminated film in comparison to that of the fully hydrogenated analogue. The results presented in Figure 3 provide further support for this model by demonstrating that interfacial friction is reduced when such modes are eliminated, thereby removing a channel of energy dissipation (e.g., the excitation of local phonon modes).[26,27]

As for the trend in friction observed for the H16 vs the mixed H16 + H15 film, the outermost plane of the latter film (Figure 1d) is again less densely packed than that of the former (Figure 1c). It is known that conformationally disordered hydrocarbon films exhibit higher frictional properties than highly crystalline hydrocarbon films.[14−17,28,29] The results of the present study indicate that the influence of local order extends beyond film structure to the level of the local environment of individual molecular components, in the present case, that of terminal groups. In this context, we can argue that the interfacial friction increases for the mixed-chain-length film as a result of the enhanced excitation of rotational and vibrational modes of the methyl groups protruding from the surface plane.[28−30] (We note that this interpretation might also be true for the mixed CH_3 and CF_3 films, but conclude from the data that this phenomenon represents a weaker influence than the elimination of intermolecular steric interactions). This type of energy dissipation has been observed in the molecular dynamics simulations of Harrison et al.[31,32] in the form of enhanced bond length distributions (stretching) of hydrocarbon layers under shear. For the experimental system described here, reducing the local packing density of the surface plane can plausibly enhance the degree to which such modes are excited. Indeed, Harrison et al. have recently observed an enhanced vibrational excitation following molecular-scale slip events occurring at the outermost terminal methyl groups of mixed-chain-length hydrocarbon monolayers.[33] Experimentally, the contribution of this effect to increased interfacial friction was also seen in our systematic study of spiroalkanethiols in which friction directly scaled with the difference in chain length between the two backbone components of the film.[14]

Conclusions

A study of compositionally mixed CF_3- and CH_3-terminated SAMs of varying chain lengths has been used to demonstrate the relationships between the frictional properties and the local structure and environment of the tailgroups. When CF_3-terminated alkanethiols are mixed 1:1 with CH_3-terminated alkanethiols having one fewer methylene group, a measurable reduction in friction is observed with respect to the friction of a SAM composed of similar species with identical chain lengths. In contrast, when two CH_3-terminated alkanethiols differing in chain length by one methylene unit are mixed in a 1:1 ratio, the resulting interfacial friction is slightly higher than that of a single-component CH_3-terminated SAM. Both of these results illustrate how energy dissipation within a nanometer-scale contact depends greatly on the local environment (e.g., composition of nearest neighbors, packing density, molecular-scale roughness) of the contacting species. In the mixed CF_3- and CH_3-terminated SAMs, the reduction in friction upon shortening the fully hydrogenated component likely originates from elimination of the excitation of collective molecular vibrations (e.g., phonons) within the surface plane. The more modest increase in friction that is observed in mixed SAMs of CH_3-terminated components differing in length by one methylene unit is attributed to the enhanced energy transfer between the sliding probe tip and the exposed methyl and methylene groups. The effect of such a mechanism would also be present in the mixed CH_3- and CF_3-terminated system but is apparently outweighed by the reduction of steric strain within the surface plane. Taken together, these results suggest great opportunities for tailoring the frictional properties of nanoscale contacts through careful control of the local structural environment of the outermost plane of the films.

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