Systematic Studies of the Frictional Properties of Fluorinated Monolayers with Atomic Force Microscopy: Comparison of CF₃- and CH₃-Terminated Films

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Molecular-level insight into the frictional properties of fluorinated self-assembled monolayers (SAMs) was achieved by combining two recently developed techniques that operate at the subnanometer scale: control of the interfacial composition through molecular self-assembly and tribological measurements performed with the atomic force microscope. To explore the origin of frictional forces in fluorinated films, the frictional properties of two classes of alkanethiols adsorbed on single crystal gold were measured and compared. In these studies, films of equivalent chain length, packing density and packing energy, but different termination (methyl vs trifluoromethyl), were characterized and investigated. For these films, in which the only detectable difference was the outermost chemical structure/composition, a factor of 3 increase in the frictional response was observed in going from the hydrogenated to the fluorinated film. These results support the conclusion that chemical structure/composition alone plays an integral role in determining the frictional properties of an interface. We propose that the difference in friction arises predominantly from the difference in size of the methyl and trifluoromethyl groups.

Introduction

The stability and properties of molecularly thin organic thin films are of great importance to the performance and activity of surfactants, lipid bilayers, self-assembled monolayers acting as templates or coatings, and advanced lubricant systems. The physical state of thin film systems can be influenced by a number of forces including intermolecular interactions between molecules making up the film, surface interactions in adsorbed films, and solvent interactions in dispersed film systems. When used as ultrathin or boundary layer lubricants, the structural characteristics of organic thin films (molecular conformation, dispersion, packing arrangement, and chemical composition) directly influence the performance of the lubricant system. A clear distinction between these factors is, however, not fully understood.

Until recently, tribological studies have not had access to the molecular-level detail of interfacial contacts. As a result, experimental verification of the molecular factors influencing frictional properties has been lacking. The development of techniques such as atomic force microscopy (AFM) has now provided the opportunity to study tribological interfaces on a truly molecular scale. AFM models a tribological contact by using a probe tip as a model of a single microasperity. Through study of the contact of the tip with systematically well prepared monolayers on atomically flat surfaces, the measured forces can be interpreted in terms of molecular properties of an interface. It is with this approach that we address the study of molecularly thin films of partially fluorinated organic films.

In previous tribological studies using AFM, well-ordered and well-characterized Langmuir−Blodgett (LB) and self-assembled monolayers (SAMs) have been used as models of organic lubricant systems.[2−6] In the present study, we explore the contribution of molecular structure/composition to the interfacial frictional properties through a systematic investigation of two closely related model lubricant systems: SAMs adsorbed on crystalline gold from solutions of tridecanethiol ($CH_3(CH_2)_{12}SH$) and 13,13,13-trifluorotridecanethiol ($CF_3(CH_2)_{12}SH$). We have used AFM to probe the frictional properties of the two monolayers and find a substantial increase in the frictional properties of the film with the introduction of fluorine into the interfacial region. In light of the similarities of the backbone structure of the films, we attribute the frictional increase to the chemical makeup and consequent size of the terminal methyl group.

Experimental Section

SAMs of the two alkanethiols were prepared from 1 mM solutions of the alkanethiol in ethanol on gold substrates containing (111) terraces. Absolute ethanol was purchased from McCormick Distilling Co.; water (HPLC grade) and tridecanethiol ($CH_3(CH_2)_{12}SH$) were purchased from Aldrich Chemical Co.; all were used as received. The synthesis of 13,13,13-trifluorotridecanethiol ($CF_3(CH_2)_{12}SH$) will be described elsewhere.[7] Gold wire (99.9985%) was purchased from Alfa Aesar.

Gold substrates were prepared by annealing a gold wire in an H_2/O_2 flame.[8] Gold wire (1 mm diameter) was melted in the flame until an approximately 1.5−2.0-mm-diameter droplet had formed at the end of the wire. The microball was annealed for a short time in a cooler part of the flame. It was then quenched in HPLC grade water or ethanol. A microball typically contained several large facets between the equator of the ball and the principle axis of the wire. The facets were flat (111) terraces separated by atomic steps. A gold substrate consisting of these (111) terraces was immersed in each 1 mM solution of $CH_3(CH_2)_{12}$-SH and $CF_3(CH_2)_{12}SH$. All AFM experiments were conducted on the atomically flat (111) faces of these gold substrates.

AFM images and measurements were collected with a beam-deflection type microscope using a single tube scanner. In the

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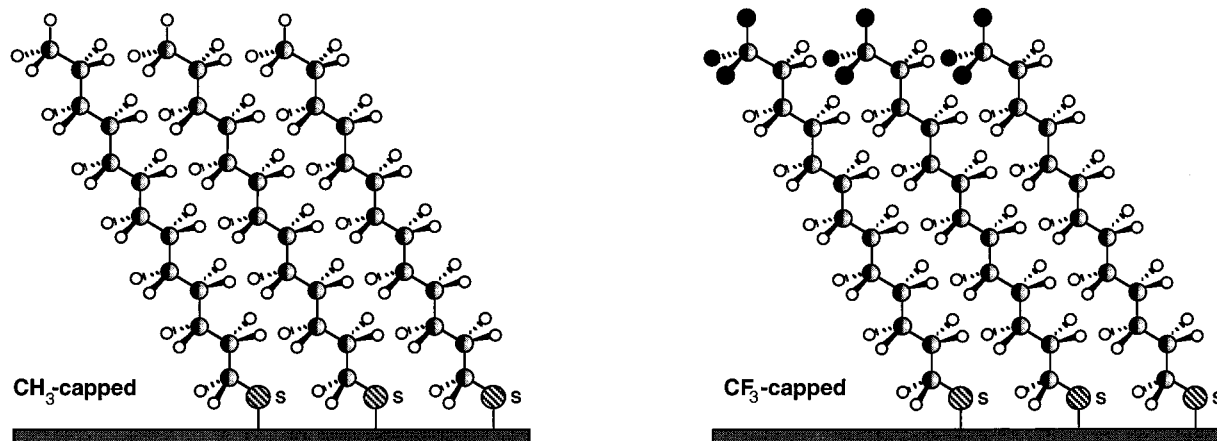
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Figure 1. Schematic representation of SAMs on Au(111) formed from tridecanethiol (left) and 13,13,13-trifluorotridecanethiol (right).

work presented here, the sample position was scanned or moved with respect to the tip position. Data acquisition, control of the microscope head, image processing, and data analysis were carried out using RHK STM 100 control electronics and RHK STiMage 3.31 software. Control and processing of the laser diode signal were performed using an RHK AFM 100.
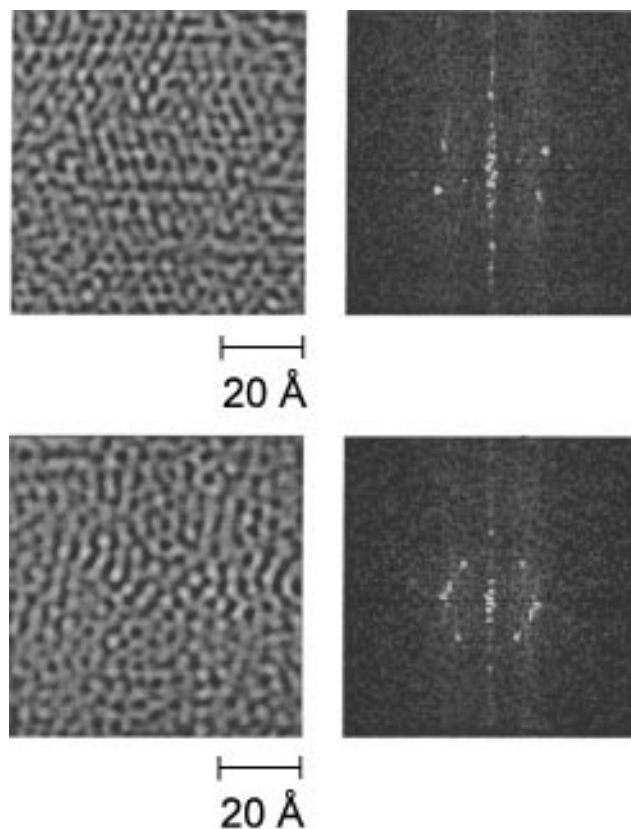
A variety of Park Scientific microlever assemblies were used to access the desired range of forces. Radii of curvature of the various tip assemblies were routinely measured by imaging a reconstructed $SrTiO_3$ substrate standard.[9] Values for the normal force constant (N/m) for the cantilever assemblies were taken from the product specifications. Lateral force constants were estimated by modeling the torsion of a triangular lever assembly and accounting for the specific shape and dimensionality of the lever assemblies. By convention, the sample surface is taken as the $x-y$ plane with the z coordinate lying along the surface normal. The SAMs were imaged by mapping both the normal and lateral deflections of the cantilever as a function of $x-y$ position across the surface. Maximum contrast was obtained in lateral force images.

Friction-load maps were collected in a number of areas on each sample according to procedures described in detail in a previous publication.[10] Briefly, frictional forces were measured as a function of total load (adhesive load plus applied load) by rastering the sample in a lateral direction while first loading and then unloading the sample from the tip. From these maps, average kinetic frictional forces were plotted versus the average applied load during the line scan across the surface. In order to provide for valid comparisons, the same AFM tip was used for both samples, although different tips were used to independently collect the imaging and the friction-load data.

Results

Two types of self-assembled monolayers were prepared on Au(111) surfaces for this study and are shown in Figure 1; the SAM generated from tridecanethiol is denoted as C13 and that generated from 13,13,13-trifluorotride-canethiol is denoted as F-C13. These monolayers are identical in chemical composition and structure with the exception of the terminal methyl groups—one is fully hydrogenated and the other is fully fluorinated. Atomic force microscopy was used to probe the structural and frictional properties of the two SAMs.

Topographic images of the SAMs were collected over large regions of the surface (1 μm $\times$ 1 μm) by detecting the normal deflection of the cantilever as a function of the position across the sample. The films were featureless on this scale, with the exception of the appearance of steps resulting from steps in the underlying gold substrate,

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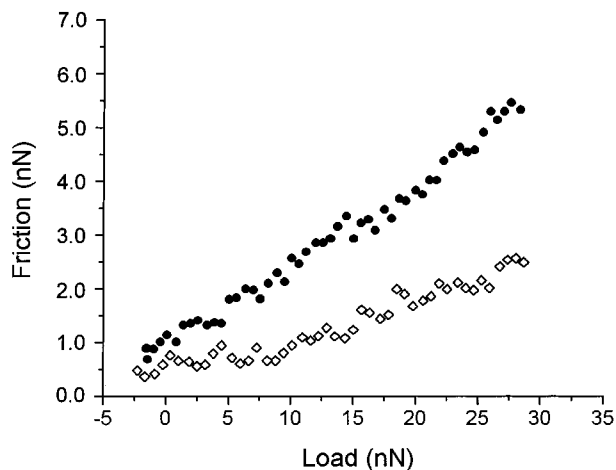

Figure 2. AFM lateral force images of the two self-assembled monolayers demonstrating the presence of order on a molecular scale in both films with a molecular spacing of 4.9 $\pm$ 0.2 Å, tridecanethiol/Au(111) (upper), and 4.8 $\pm$ 0.2 Å, 13,13,13-trifluorotridecanethiol/Au(111) (lower). Shown beside each image is the Fourier transform of the lateral force image revealing the symmetry and from which the average spacing of the molecules within the film can be calculated.

indicating well-formed monolayer structures. On a smaller scale ($\sim$60 Å $\times$ 60 Å), molecular-level features were observed in the lateral force images of both films. Lateral force images, collected by detecting the torsion of the cantilever as a function of sample position, are shown in Figure 2 for the C13 and F-C13 films together with the Fourier transform of each image. The Fourier images clearly reveal the ordered nature of the film systems. Orientational differences between the two films result from different macroscopic orientations of the underlying gold substrate. The measured lattice spacings of the two films are indistinguishable: 4.9 $\pm$ 0.2 Å for C13 and 4.8 $\pm$ 0.2 Å for F-C13. As observed in previous studies of

Figure 3. From friction–load maps acquired on the two films, the average kinetic friction is plotted versus the external applied load. Negative loads arise from adhesive forces between the probe tip and the sample. The frictional response of the film is defined as the force of friction at a specified load. An approximate factor of 3 increase in the frictional response is observed upon moving from a methyl (open diamond) to a trifluoromethyl (closed circle) termination.

SAMs by AFM,[11] lateral force images collected at highloads reveal the structure of the supporting gold substrate with a lattice spacing of 3.0 ± 0.2 Å and confirm that these monolayers are formed by the adsorption of the thiols in a $(\sqrt{3} \times \sqrt{3})R30°$ overlayer structure.[12] The reproducible appearance of a lattice resolution in the AFM data is interpreted as periodicity of the stick–slip behavior of the multiple atom contact between the tip and sample.[13]

The frictional properties of the two monolayers were also measured using atomic force microscopy by measuring frictional forces as a function of the applied load for each system. The results of the frictional measurements for the two films are shown in Figure 3 as a plot of friction versus applied load. The frictional forces were investigated for applied loads up to ~30 nN in an effort to probe the frictional properties of only the outermost portions of the SAMs. Previous studies have shown that substantial deformation of monolayers occurs at loads greater than 30 nN; the threshold for this occurrence depends on the radius of curvature of the probe tip. For the tip radius used here (~400 Å), plastic film deformation was observed only at higher loads; the details of these deformations will be discussed in a later publication. As seen in Figure 3, an approximately linear response is observed in the plot of friction versus applied load. Given the radius of curvature, we believe that this response arises from a multiple asperity contact between the tip and the film surface. The data presented in this figure were measured as a function of decreasing applied load. Negative loads correspond to regimes where an attractive normal force arises from adhesion between the tip and the sample. In the negative load regime, the adhesive forces during sliding are indistinguishable for the two films. We conclude, therefore, that adhesive forces make little or no contribution to the difference in the frictional properties measured for the two films (*vide infra*).[14]

In macroscopic systems, the coefficient of friction is defined as the slope of the plot of friction (y) versus load (x) and is used as a qualifier of the frictional properties

of an interface. In microscopic systems, nonlinearity in friction–load plots has been observed in some systems where deformation of the interface produces a nonlinear relationship between applied load and area of contact.[17] As a result, the meaning of the coefficient of friction is ambiguous in these systems, and relative magnitudes of friction must be compared. Although an approximately linear dependence of friction on load is observed for these films suggesting that no substantial deformation occurs, we discuss only the frictional response (the force of friction at a specified load) of the systems. In the low-load regime investigated here, the frictional response is approximately three times greater for the F-C13 films as compared to the C13 films. Although some statistical variation in frictional response was observed for different regions across the surface, a distinguishable difference between the two films was consistently evident. The radius of curvature of the probe tip was measured before and after each set of frictional measurements. This procedure confirmed that no change in the tip character had occurred during the measurements and thus ensured the precise comparison of the frictional properties of the two films. Furthermore, the frictional properties of the two films were measured as a function of relative humidity (0–60% RH) and showed no dependence on the ambient partial pressure of water above the surface of the films under these conditions.

Discussion

Several studies have investigated the frictional properties of hydrocarbon- and fluorocarbon-based monolayer films.[3,4,18–21] In each of these studies, the fluorinated films consistently exhibited higher frictional properties than those of the hydrocarbon films. Despite the fact that fluorocarbon-based materials exhibit higher frictional properties than analogous hydrocarbon-based materials, fluorocarbons such as Teflon enjoy widespread use as lubricants because of their high chemical, thermal, and mechanical stabilities. Although a number of molecular-level phenomena have been proposed to account for higher frictional properties in fluorinated films,[3,4,18–21] the issue remains controversial. Potential factors contributing to frictional properties on the molecular scale include (i) packing energy, (ii) packing density, (iii) elasticity, (iv) local disorder, and (v) chemical structure/composition.

Packing energies in self-assembled films arise predominantly from intermolecular chain–chain interactions.[22] Packing energies can potentially contribute to frictional properties by allowing for differences in effective areas of contact at equivalent loads. Early AFM frictional measurements of mixed LB bilayer films suggested a higher in-plane cohesive binding (i.e., greater packing energy) for fluorocarbons than for hydrocarbons.[3,4] Es-

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(22) In some systems capable of hydrogen bonding, tail group–tail group interactions are probably important as well.

timates of the intermolecular cohesive energy (derived from the boiling points of hydrocarbons and fluorocarbons),[23] however, suggest that the attractive intermolecular forces between fluorocarbons are less than those for hydrocarbons. Indeed, more recent AFM studies favor this interpretation and argue for a higher packing energy for hydrocarbon rather than fluorocarbon thin films.[5]

Packing densities, which in many cases will mirror packing energies, might also contribute to the frictional properties of monolayer films. In the two-dimensional plane of the film, monolayers less densely packed will experience fewer nearest neighbor interactions per unit area. As a result, the packing energy per unit area will be less, and deeper penetration of the contacting "asperity" into the monolayer at a given load will occur for the less densely packed monolayers. Although early AFM studies attributed the higher friction observed on fluorinated films to (at least in part) a closer packing for the fluorocarbons,[4] X-ray diffraction and other AFM studies have reported greater interchain spacings for fluorinated films relative to their hydrogenated analogs.[24,25]

Elasticity is known to influence the resistance to sliding and thus friction in macroscopic systems.[26] Overney *et al.* have observed that friction and elasticity are correlated in the system of phase-separated monolayers of hydrogenated and fluorinated hydrocarbons.[5] Using AFM, these researchers measured the Young's modulus of the phase-separated films and found that the fluorocarbon areas exhibited both a higher friction and a lower Young's modulus (greater elasticity and lower stiffness) than the hydrocarbon areas of the film. From these results, Overney *et al.* proposed that the fluorocarbon films were more elastic (softer and less rigid) than the hydrocarbon films. This interpretation, however, contradicts a number of studies which contend that fluorocarbon chains,[27-30] including those in monolayer films,[31-33] are *less* elastic (stiffer) than their hydrocarbon counterparts.

Disorder in thin film systems is also believed to influence frictional forces. In studies of alkylsilanes on mica using AFM, Salmeron *et al.* have proposed that nonlinear increases in friction occurring at high loads arise from an increase in the local disorder of the film.[2] By this mechanism, the presence of gauche defects provides additional excitation modes (rotation about the chain axis, bending, the formation of additional gauche defects) to absorb energy, which corresponds to greater frictional forces.

The molecular level properties discussed above are interrelated in most thin film systems. The different (and in some cases contradictory) rationalizations for the greater frictional properties of fluorinated films underscores the complexity of the mechanisms that lead to frictional variations on the molecular scale. In the present

study, we have attempted to examine the influence of chemical structure/composition in the absence of other contributing factors. Our approach focused on two similar, well-defined SAMs of alkanethiols adsorbed on Au(111) surfaces. The targeted SAMs differ in chemical composition only in the terminal methyl group—one being fully hydrogenated and the other fully fluorinated. By design, we have attempted to minimize differences in the properties of packing energy, packing density, elasticity, and disorder.

It is likely that packing energies and elasticities are influenced predominantly by the composition of the backbone of the individual molecular components of the organic thin films. Since the two SAMs studied here have identical backbone structures, any differences in the packing energies or the elasticities of the two films are likely to be insubstantial. Packing density and disorder are related to the local structure of the film. Previous AFM and X-ray diffraction studies of fully fluorinated alkanethiols adsorbed on the Au(111) surface have measured a 5.7 ± 0.2 Å lattice constant, which is consistent with the expected density of the fluorinated films.[23] The lattice spacing of the partially fluorinated SAM in this study is 4.8 ± 0.2 Å and is within experimental error of the lattice constant of the fully hydrogenated SAM.[11] This result might be considered surprising given that the CF_3 group is larger than the CH_3 group by ~40%.[34] We attribute the indistinguishable lattice constants to the identical backbone structures of the two films: the packing energy of the hydrocarbon backbones must dominate the intermolecular interactions in these films.[35,36] From these data and from the images in Figure 2, we conclude that the two monolayers have the same packing density and that both films are well ordered on the molecular scale. Consequently, the only difference in the two films is the chemical structure/composition at the exposed interface.

Having restricted the differences in the films to the nature of the terminal methyl group, there are at least three ways in which this difference might influence frictional forces. First is the adhesion between the tip and the sample. Previous measurements of adhesion on SAMs terminated with chemically distinct functionalities have demonstrated a dependence of adhesive force on chemical composition.[13,37-39] On comparison of the CF_3 and CH_3 terminated films in this study, however, the data of Figure 3 in the negative load regime indicate that the adhesive force during sliding is similar for the two films. While the nature of the relationship between adhesive and frictional forces measured with scanning probe techniques remains obscure, the observed similarities in the negative load regime for the two films suggest that tip–sample adhesion is not a predominant factor in the frictional difference.[13]

A second factor that might contribute to the increase in frictional properties involves the molecular order of

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the film assembly. Previous studies of the chain length dependence of the frictional properties of alkylsilanes have proposed that increases in friction are associated with increased disorder within a thin film system.[2] In turn, disorder within the film structure is associated with defects (kinks, gauche conformations), which act to absorb energy during the sliding process. In the systems studied here, it is possible that point defects (vacancies) exist within the CF_3 films due to the relatively large size of the terminal group. It is also possible that these defects could give rise to additional energy dissipation (as described in ref 2) but remain invisible to the imaging process.[40] We believe, however, that the magnitude of frictional increase measured here would have to be associated with a large number of these defects, which in turn would lead to structural disorder in the film, rendering disordered AFM images (i.e., no lattice resolution). Since we can achieve lattice resolution (see Figure 2), we believe that point defects in the CF_3-teminated films are probably not responsible for the increase in friction observed here.

A third factor to be considered involves the molecular dimensions and the associated energetics (e.g., rotational, vibrational, translational) of the different terminal groups. Indeed, recent molecular dynamics simulations[41,42] and scanning probes studies[2] have interpreted atomic-scale frictional properties in terms of vibrational and rotational energetics. To explore the potential dissipation of energy into rotational modes in our films, we calculated the energy difference and barrier height between *trans* and *gauche* conformations of both the CH_3-CH_2 and the CF_3-CH_2 bonds.[43] These calculations indicated a barrier height between the two states of 14.0 kJ/mol for the CH_3-CH_2 bond and 17.6 kJ/mol for the CF_3-CH_2 bond. Since the rotational barrier of the CF_3-CH_2 bond is larger than that for the CH_3-CH_2 bond, it is possible that the rotational barriers are related to the greater interfacial friction observed for the F-C13 film. The energy difference alone (3.6 kJ/mol), however, might be insufficient to account for the observed differences in friction; moving from C13 to F-C13 corresponds to only a 26% increase in barrier heights, while a 3-fold increase in friction is observed.

We must also consider the relative sizes of the two terminal groups in the context of the adsorption geometry of the two films. We have calculated an effective cross-sectional area of the two terminal groups and estimate the trifluoromethyl group to be ~40% larger: 17.6 Å^2 for CH_3 and 25.4 Å^2 for CF_3.[34] Fourier transform IR studies have shown that alkanethiol films adsorb on the surface of gold with a chain tilt angle of ~30° with respect to surface normal (Figure 1) and that the orientation of the terminal methyl group systematically varies with the number of carbon atoms in the chain.[44] In the present study of an odd-numbered carbon chain, the C–C bond to the terminal methyl group is expected to be oriented ~57°

from the surface normal.[45] In light of the observation that an indistinguishable packing density of the chains was measured for each film, we believe the trifluoromethyl terminal groups in these films experience additional energetic barriers to rotation about the chain axis and additional barriers to translation (or lateral motion) in the plane of the CF_3 groups as they interact more strongly with neighboring chains. Because of the density of packing and the relatively large size of the CF_3 group, this interdigitation or steric interaction should translate to long range (multimolecular) interactions in the plane of the CF_3 groups. These long range motions might correspond to a longer coherence length for the fluorinated films. The longer coherence length would thus serve to provide additional pathways for the dissipation of energy (perhaps through phonon modes)[46] and is consistent with the higher frictional response found in scanning probe experiments performed on these CF_3-terminated SAMs.

Conclusions

This study has demonstrated that frictional properties can be correlated with molecular properties of the self-assembled monolayers, specifically the chemical structure/ composition of the film. Molecular level detail of the frictional properties of fluorinated SAMs was generated by systematic control of the interfacial composition through organic synthesis and molecular scale tribological measurements performed with the atomic force microscope. The frictional response was measured for methyl- and trifluoromethyl-terminated alkanethiols adsorbed on Au(111) surfaces. We found a factor of 3 increase in the frictional properties of these films in going from the hydrogenated to the fluorinated terminal group. In this study, films of equal chain length, adsorption geometry, and packing energy but different termination (methyl vs trifluoromethyl) were investigated. We propose that fluorinated monolayers exhibit higher frictional properties due to tighter packing at the interface, which arises from the larger van der Waals radii of the fluorine atoms. Subsequent steric and rotational factors between adjacent terminal groups give rise to long range multimolecular interactions in the plane of the CF_3 groups. When these energetic barriers are overcome in the film structure, more energy is imparted to the film during sliding and results in higher frictional properties for the fluorinated films.

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