Chapter 4

Interfacial Properties of Specifically Fluorinated Self-Assembled Monolayer Films

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This report describes a systematic exploration of the molecular basis for friction and wettability in organic thin films. The experimental approach relies on the construction of specifically fluorinated self-assembled monolayers (SAMs) generated by the adsorption of terminally fluorinated alkanethiols onto the surface of gold. Analysis of the SAMs by atomic force microscopy (AFM) reveals that the size of the terminal group strongly influences the frictional properties of the monolayers but fails to influence their lattice periodicity. Characterization of the films by polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) shows that the conformational order of the hydrocarbon chains in adsorbates having equivalent numbers of methylene groups are independent of the size of the terminal group. Contact angle measurements reveal the strong influence of oriented surface dipoles on the wettabilities of the films. The indistinguishable frictional response of mixed CF_3- and CH_3-terminated films of varying composition, however, suggests that the surface dipoles exert little, if any, influence upon the frictional properties of the films. Frictional studies of i-Pr-terminated SAMs are consistent with a model in which the size of the terminal group influences the frictional properties.

The widespread commercial use of fluorinated organic films is largely due to their unique interfacial properties [1]. These films have proven to be both chemically and biologically inert, to exhibit high thermal and mechanical stabilities, and to resist oxidation and corrosion. Furthermore, their hydrophobicity and anti-adhesive nature have led to their use in a diverse range of applications. Recently, much interest has focused on understanding the frictional properties of fluorinated films [2-6]. These

studies demonstrated that fluorocarbon films exhibit higher friction than hydrocarbon films. Given the well-known lubricating properties of fluorinated materials such as Teflon, these results might be considered surprising. The enhanced frictional properties of fluorocarbon films have been attributed to a number of phenomena, including differences in the packing energy of hydrocarbons and fluorocarbons, differences in packing density, greater stiffness of fluorocarbons, greater elasticity of hydrocarbons, and the resistance to deformation and rupture of fluorocarbons [2-8]. The widely differing and sometimes conflicting rationalizations suggest that further insight into the physical and chemical contributions to friction in organic films is needed to advance a hypothesis that is both plausible and comprehensive. To this end, we have employed atomic force microscopy (AFM) to explore the frictional response of a series of self-assembled monolayers (SAMs) on Au(111) generated from alkanethiols that possess chemically distinct terminal groups $\omega(CH_2)_nSH$, where $\omega = CF_3$ and CH_3 ($n = 12,13,15$) and $CH(CH_3)_2$ ($n = 13$) [9-14]. Despite the presence of strong interfacial dipole effects in the CF_3-terminated films, we were able to correlate the observed trends in frictional response to the presence of correlated steric interactions among these terminal groups.

Experimental

Generation of SAMs. The SAMs were generated on gold substrates containing (111) terraces by adsorption from 1 mM ethanolic solutions of the appropriate alkanethiol. The gold substrates used for ellipsometry, contact angle goniometry, and PM-IRRAS analyses were prepared by evaporating 2000 Å of gold onto chromium-primed silicon wafers. The gold substrates used for AFM measurements were microballs prepared by annealing a gold wire in a hydrogen/oxygen flame. All substrates were incubated in solution for 24 h. The synthesis of the alkanethiols has been described elsewhere [14].

Contact Angle Wettabilities. A ramé-hart model 100 contact angle goniometer was used to measure the advancing contact angles of contacting liquids on the films. A Matrix Technologies Electrapette 25 operated at the slowest possible speed (*ca.* 1 μL sec⁻¹) was used to dispense the liquids. For a given sample, the data were collected with the pipette tip in contact with the drop and averaged over three separate slides.

Infrared Spectroscopy. A Nicolet MAGNA-IR 860 Fourier transform spectrometer equipped with a liquid nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instruments PEM-90 photoelastic modulator (37 kHz) was used to acquire the polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) data. The spectra were collected using p-polarized light incident at 80° for 1000 scans at a spectral resolution of 4 cm⁻¹.

Atomic Force Microscopy. A homemade beam deflection atomic force microscope equipped with a single tube scanner, an optical deflection scheme, Si_3N_4 tip-cantilever assemblies (Digital Instruments, CA), and RHK AFM 100 and RHK STM 100 electronics was used to measure the lattice constants and frictional properties of

the SAMs under ambient atmospheric conditions (24° C and 40% humidity). Additional experimental details are provided in reference 13.

X-ray Photoelectron Spectroscopy. A PHI 5700 X-ray photoelectron spectrometer equipped with an monochromatic Al Kα X-ray source (hν = 1486.7 eV) incident at 90° relative to axis of a hemispherical energy analyzer was used to obtain X-ray photoelectron spectra of the films at a photoelectron takeoff angle of 45° from the surface and a pass energy of 23.5 eV. The surface concentration of CF_3 groups in the mixed monolayers was determined by integrating the F 1s and Au 4f photoelectron peaks. Additional experimental details are provided in reference 13.

Results and Discussion

Our initial comparison of the frictional properties of fluorocarbon and hydrocarbon films involved the study of SAMs generated from CF_3- and CH_3-terminated tridecanethiols (Figure 1) on gold [9]. Figure 2 shows the frictional response of the films versus the applied load measured by AFM. As the load increases, the frictional response of the CF_3-terminated film exhibits a larger increase than that of the CH_3-terminated film. To rationalize this phenomenon, we considered the following list of possible causes for the frictional difference: (1) differences in the packing density of the two films, (2) differences in film order, (3) differences in the packing energies of the two films, (4) differences in the stiffness or elasticity of the two films, (5) differences in the chemical composition of the terminal groups, and (6) the presence of surface dipoles in the films [15-17]. We then systematically evaluated the influence of each of these factors upon the frictional properties.

First, we probed the structural features of the films by collecting lateral force images using AFM (Figure 3). The lattice structure of both SAMs were hexagonal and exhibited indistinguishable periodicities (~4.9 Å), even though the CF_3 groups are substantially larger than the CH_3 groups (Figure 1) [9,18]. In light of this result, it seems unlikely that differences in either packing density or interfacial order are responsible for the observed differences in friction [19]. Next, we analyzed the band position of the antisymmetric methylene C-H stretch ($v_a^{CH_2}$) by PM-IRRAS to evaluate the conformational order of the chemically identical backbones of the CH_3- and CF_3-terminated adsorbates [13,20]. This band position shifts to higher wavenumbers as the conformational order of the methylene backbones in SAMs decreases (i.e., decreased interchain interactions and increased intrachain gauche defects) [21]. Figure 4 shows that the $v_a^{CH_2}$ band positions of CF_3-terminated and CH_3-terminated films are the same, which suggests that the methylene backbones in both films possess similar degrees of conformational order. Because the two SAMs exhibit indistinguishable degrees of conformational order, the observed difference in frictional properties of the films must arise from factors other than differences in packing energy or film elasticity.

Since the difference in the chemical composition of the terminal groups might be solely responsible for the increased frictional response [22-27], we considered exactly how this difference might influence the frictional response. First, differences in the
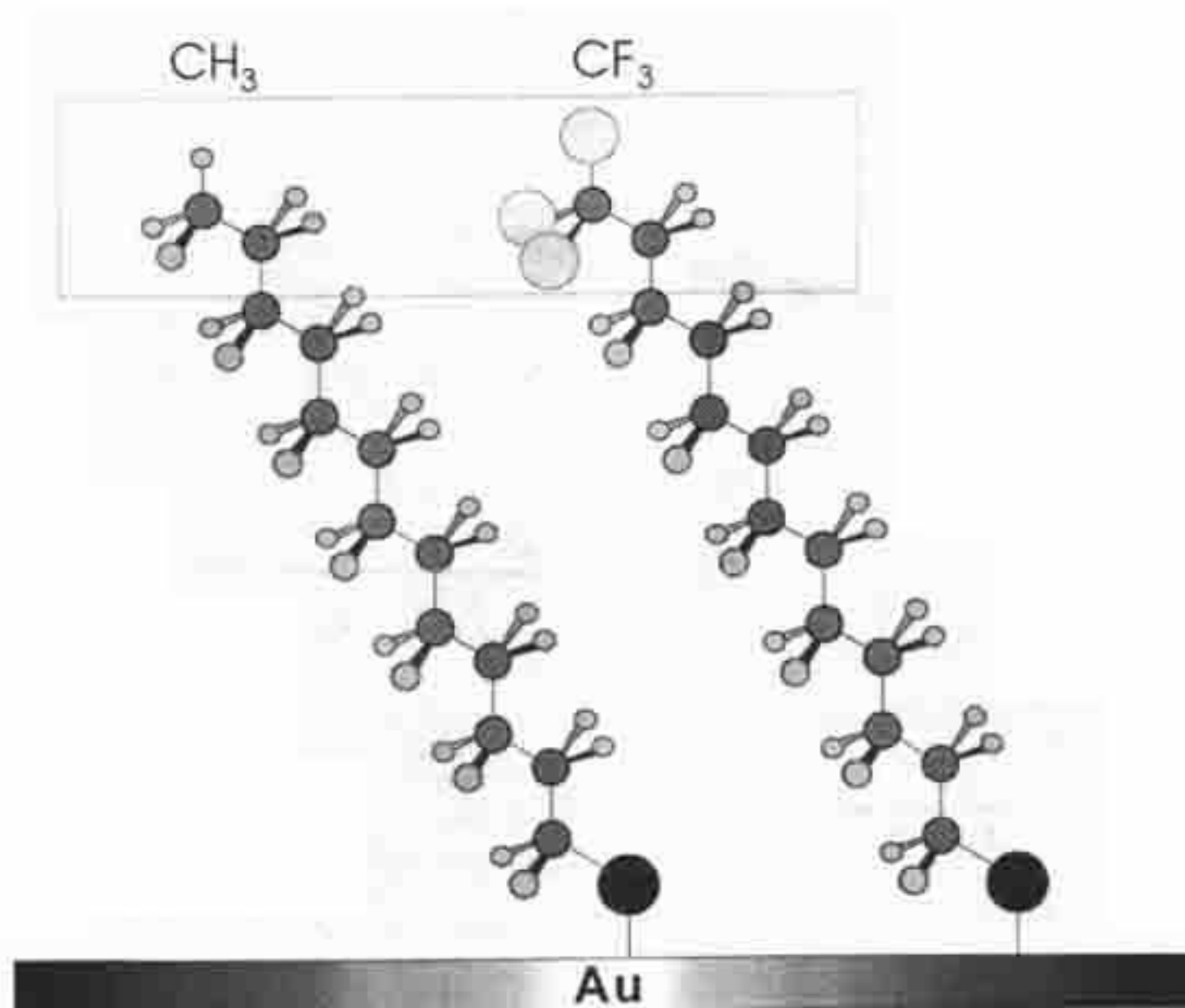
Figure 1. Schematic representation of CH_3-terminated and CF_3-terminated SAMs derived from $\omega(CH_2)_{12}SH$, where $\omega = CH_3$ and CF_3.
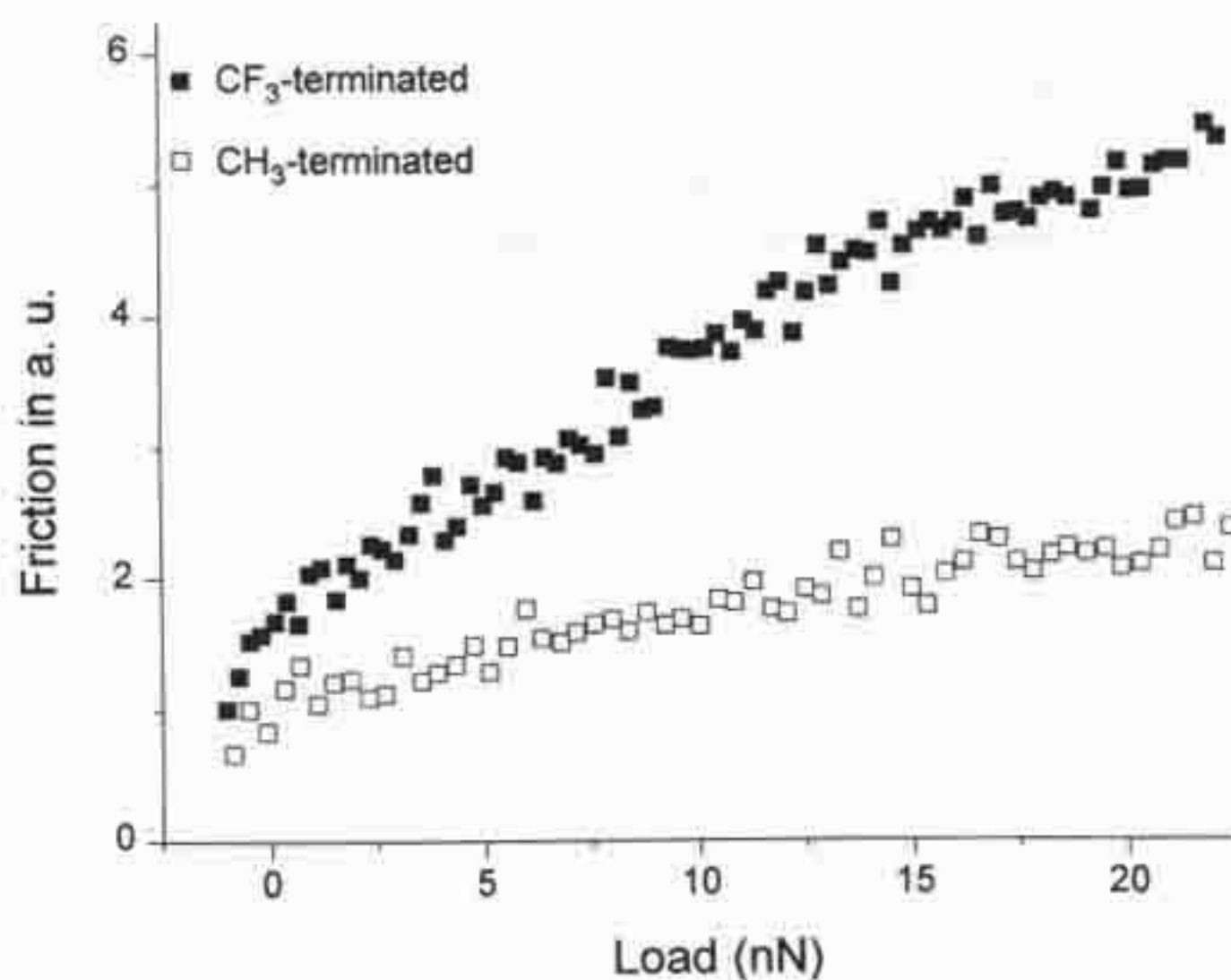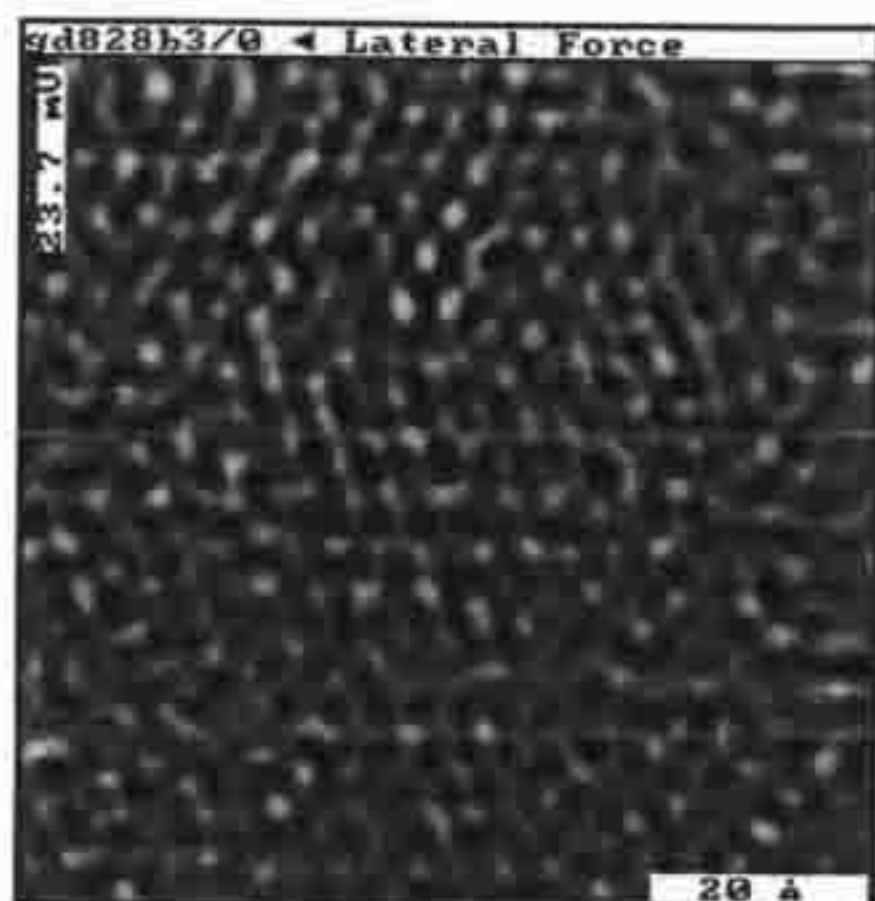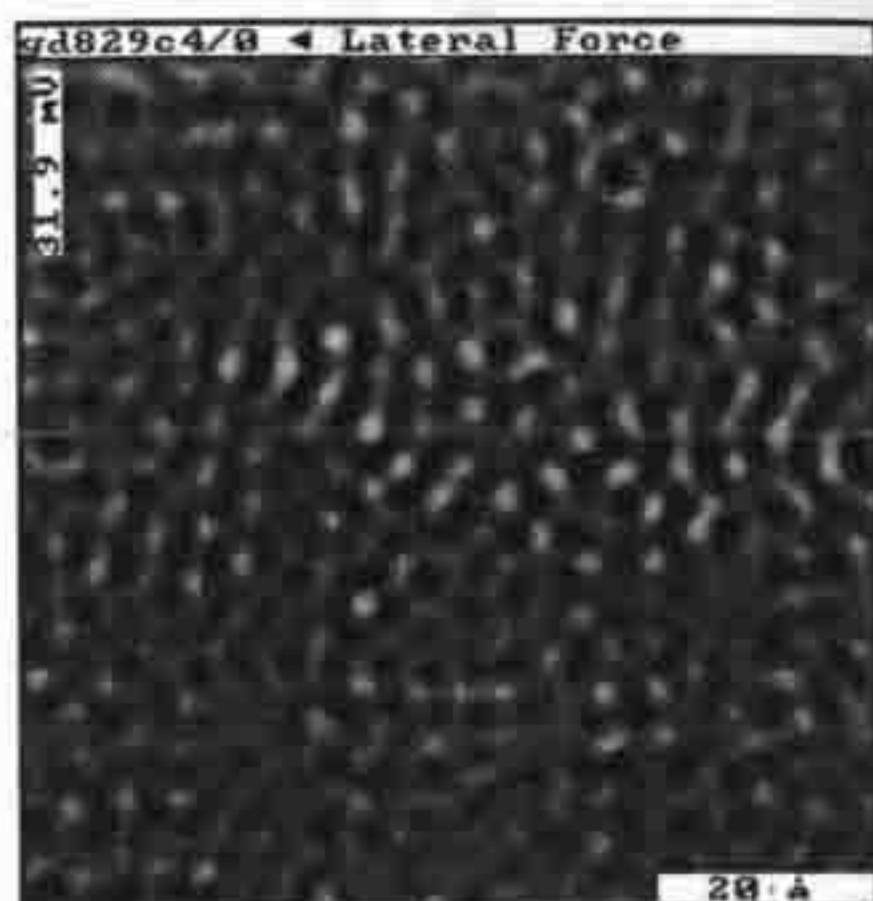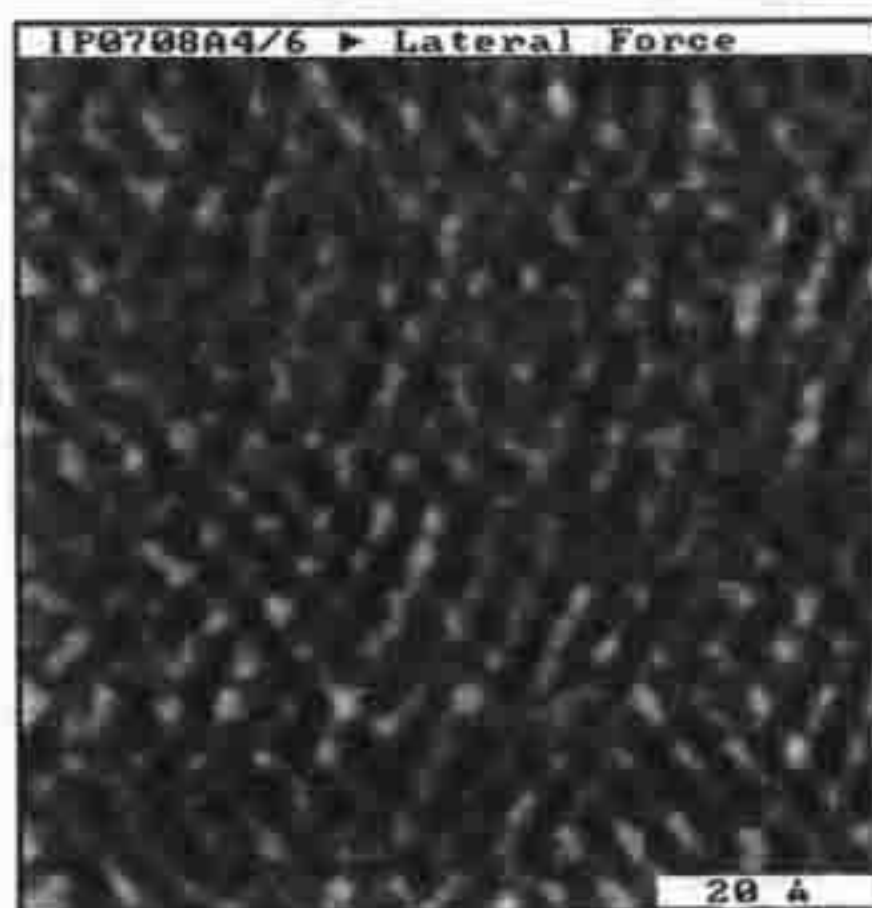

Figure 2. Frictional response of CF_3-terminated (■) and CH_3-terminated (□) tridecanethiol SAMs measured by AFM as a function of decreasing applied load.

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(a) CH$_3$-terminated
4.9 ± 0.2 Å spacing

(b) CF$_3$-terminated
4.8 ± 0.2 Å spacing

(c) *i*-Pr-terminated
5.0 ± 0.2 Å spacing

Figure 3. Lateral force images (80 Å × 80 Å) and lattice constants of (a) CH$_3$-terminated, (b) CF$_3$-terminated, and (c) *i*-Pr-terminated SAMs.
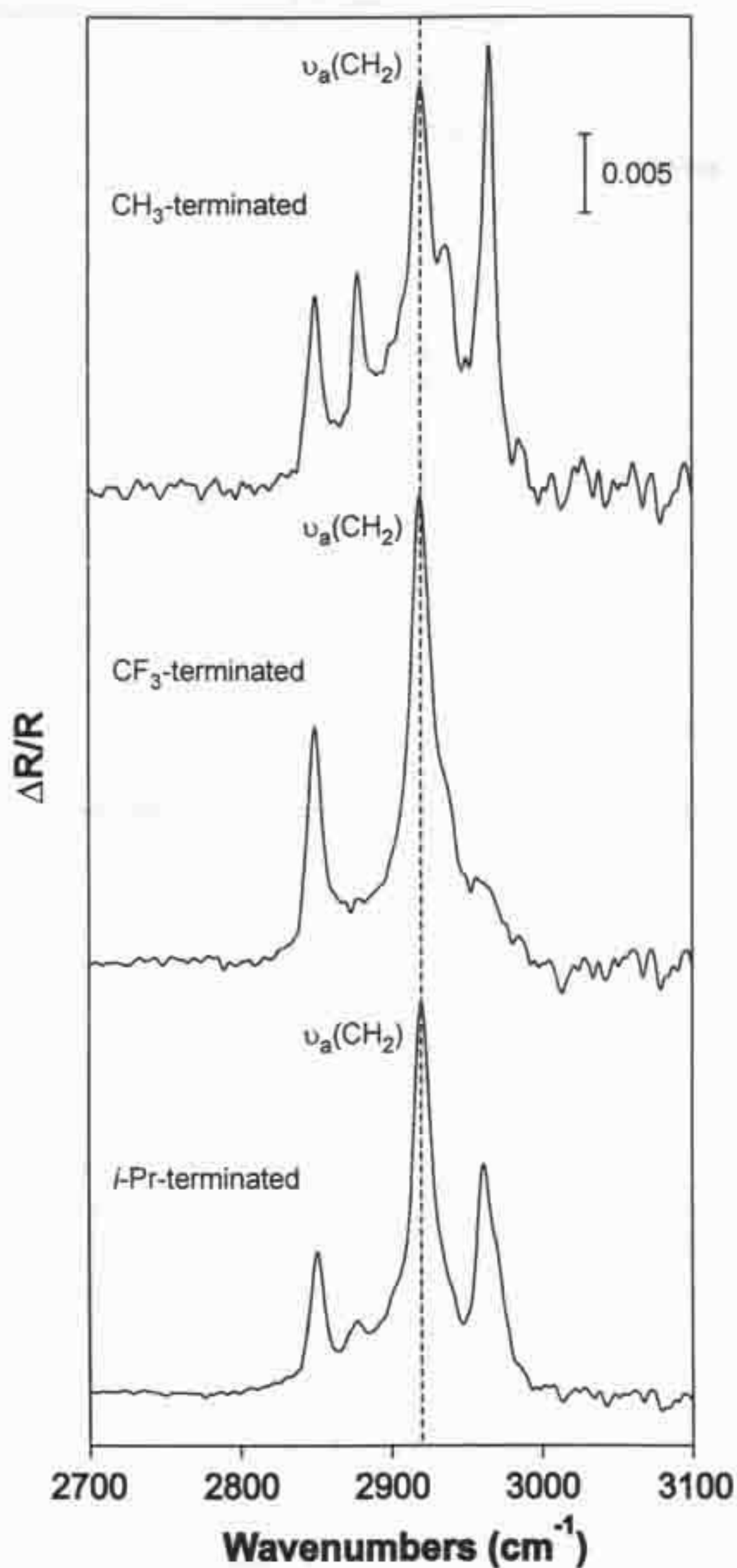
Figure 4. PM-IRRAS spectra of the hydrocarbon stretching region for CH_3-terminated, CF_3-terminated, and *i*-Pr-terminated SAMs derived from $\omega(CH_2)_{13}SH$, where $\omega = CH_3$, CF_3, and $CH(CH_3)_2$. The antisymmetric band position ($v_a^{CH_2}$) is indicated by the dashed line at 2919 cm^{-1}.

conformational order of the terminal groups could lead to increased friction by permitting the dissipation of energy into additional local excitation modes (e.g., gauche defects) [15,17,28,29]. However, our AFM and IR results suggest that CF_3- and CH_3-terminated films possess similar degrees of conformational order. Hence, this factor is an unlikely contributor to the observed frictional difference. Next, a difference in the rotational barriers of the terminal C-C bonds could contribute to the frictional difference [15,17,30,31]. The barrier for rotation about a CF_3-CH_2 bond is indeed higher (by ~26%) than the barrier for rotation about a CH_3-CH_2 bond [13,32]. The magnitude of this increase, however, might not fully account for the observed threefold increase in frictional response. Further studies involving molecular dynamics simulations might lend further insight into the relationships between rotational barriers and the frictional properties of organic thin films [31,33,34].

Another possibility is that differences in adhesion between the AFM tip and the samples give rise to the differences in frictional response [9,22-27,35,36]. Indeed, the introduction of terminal CF_3 groups creates dipoles (aligned with the CF_3-CH_2 bonds) at the surface of the film [16,37]. Evidence for these dipoles is found in the wettability studies of SAMs generated from a series of terminally fluorinated alkanethiols and SAMs generated from an analogous series of normal alkanethiols using contact angle goniometry (Figures 5a and 5b) [11,12,20,37,38]. Due to the weak dispersive interactions between fluorocarbons and hydrocarbons, the nonpolar and weakly polar contacting liquids (hexadecane and methylene iodide, respectively) wet the CF_3-terminated surfaces less than they wet the CH_3-terminated surfaces. Polar protic contacting liquids, such as water and glycerol, however, wet the CF_3-terminated surfaces more than they wet the CH_3-terminated surfaces. To determine whether the observed increase in the wettability of the CF_3-terminated films arose from hydrogen bonding between the liquids and the terminal groups, we conducted further studies with polar aprotic contacting liquids (e.g., acetonitrile, dimethylformamide, and nitrobenzene). The data revealed that the observed increases in wettability arise from factors other than hydrogen bonding because the aprotic liquids, which cannot plausibly hydrogen bond to the CF_3 groups, exhibited the same wettability discrimination (i.e., CF_3-termination was more wettable than CH_3-termination) as the polar protic liquids. We propose instead that the enhanced wettabilities on the CF_3-terminated SAMs are consistent with the presence of oriented CF_3-CH_2 dipoles at the surface of the films. These dipoles strengthen the attractions with the polar contacting liquids through additional dipolar interactions that are absent with the non-polar CH_3-CH_2 moieties at the surface of the CH_3-terminated films [37,38].

Additional support for this hypothesis was provided by the observation of an inverse "odd-even" or parity effect for the wettabilities of polar contacting liquids on the CF_3-terminated films (see Figure 5). The parity effect has been observed in CH_3-terminated monolayer films and arises from the dependence of the orientation of the terminal methyl groups upon the total number of carbon atoms in the adsorbates (i.e., the chain length) [39,40]. Films comprised of adsorbates with odd chain lengths (odd-numbered SAMs) have terminal methyl groups oriented more parallel with respect to the surface of gold than films comprised of adsorbates with even chain
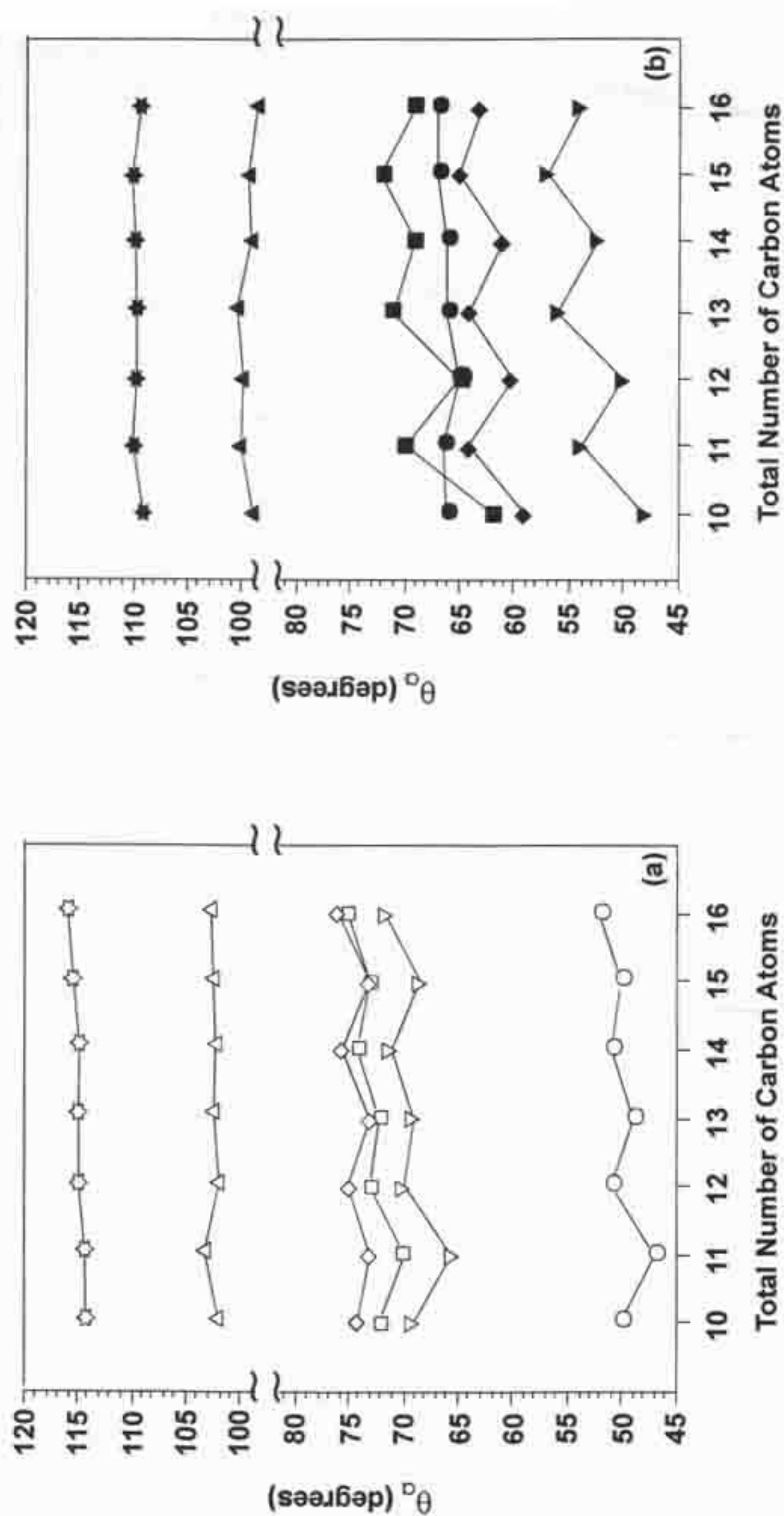
Figure 5. Advancing contact angles of hexadecane ($\bigcirc$, $\bullet$), water ($\star$, $\star$), glycerol ($\triangle$, $\blacktriangle$), acetonitrile ($\triangledown$, $\blacktriangledown$), DMF ($\diamondsuit$, $\blacklozenge$), and nitrobenzene ($\square$, $\blacksquare$) on (a) CH_3-terminated SAMs (open symbols) and (b) CF_3-terminated SAMs (filled symbols).

lengths (even-numbered SAMs). An increase in tilt leads to increased exposure of the underlying methylene moieties that increases the dispersive interactions and consequently increases the wettability for odd-numbered SAMs relative to that for even-numbered SAMs [41,42]. The parity effect for the CF_3-terminated SAMs, however, differs in two respects: (1) it is only observed with polar contacting liquids, and (2) the wettabilites of odd-numbered SAMs are *lower* than the wettabilities of even-numbered SAMs. These two differences can be rationalized by the surface dipole model. First, nonpolar liquids by definition can interact exclusively by dispersive means and should therefore be insensitive to polar changes in the surfaces. Second, the more parallel orientation of the terminal groups in odd-numbered SAMs should allow the terminal dipoles to partially compensate one another by aligning themselves in a head-to-tail fashion (Figure 6). This compensation would lead to an overall decrease in the magnitude of the electrostatic field presented at the surface of odd-numbered SAMs, which would diminish the interaction with a polar contacting liquid and thus diminish the wettability of the film. The near-perpendicular orientation of the dipoles in even-numbered SAMs offers little opportunity for compensation and thus presents stronger electrostatic fields and enhanced wettabilities [37].

While our contact angle measurements demonstrated the strong influence of these surface dipoles on the wettabilities of CF_3- versus CH_3-terminated films, AFM measurements of tip-sample adhesion revealed little evidence for the contribution of surface dipoles to the frictional properties of the films [9,22-28]. The pull-off forces between the AFM tip and the samples were indistinguishable for both CF_3- and CH_3-terminated films (~12.1 ± 0.9 nN) [28,36,43], which suggests that the AFM tip used in our experiments experiences similar adhesive forces on both types of films [44]. This issue was further examined by studying mixed monolayers of ω-terminated hexadecanethiols on Au in which the surface concentration of the CF_3 groups was systematically increased (0, 15, 22, 38, 51, 75, and 100% as measured by XPS) [13,45]. If surface dipoles were responsible for the observed frictional difference, then the frictional response of these mixed films would be expected to increase progressively with an increase in the surface concentration of CF_3 groups, assuming that the CF_3 groups are randomly dispersed among the CH_3 groups. To determine whether the mixed monolayers consisted of large domains of randomly mixed CF_3- and CH_3-terminated adsorbates or of phase-segregated domains of single-component islands, we collected lateral force images of these films. If the CF_3- and CH_3-terminated adsorbates did in fact phase segregate, one would expect to see islands of contrasting lateral force in these images due to the different frictional responses of the two terminal groups [25]. Lateral force images of the mixed films, however, were homogeneous over the investigated areas (0.5 μm × 0.5 μm) and revealed no evidence of domain formation [36,45]. Figure 7 shows the lateral force image for the 51% CF_3 film and is representative of all the images obtained on the mixed films. These results suggest that, under the conditions used for film formation, random mixing of the different terminal groups occurs. Remarkably, the frictional responses of the mixed films failed to increase with the increasing surface concentration of CF_3 groups. The friction-load plots of the mixed films revealed that just a 15%
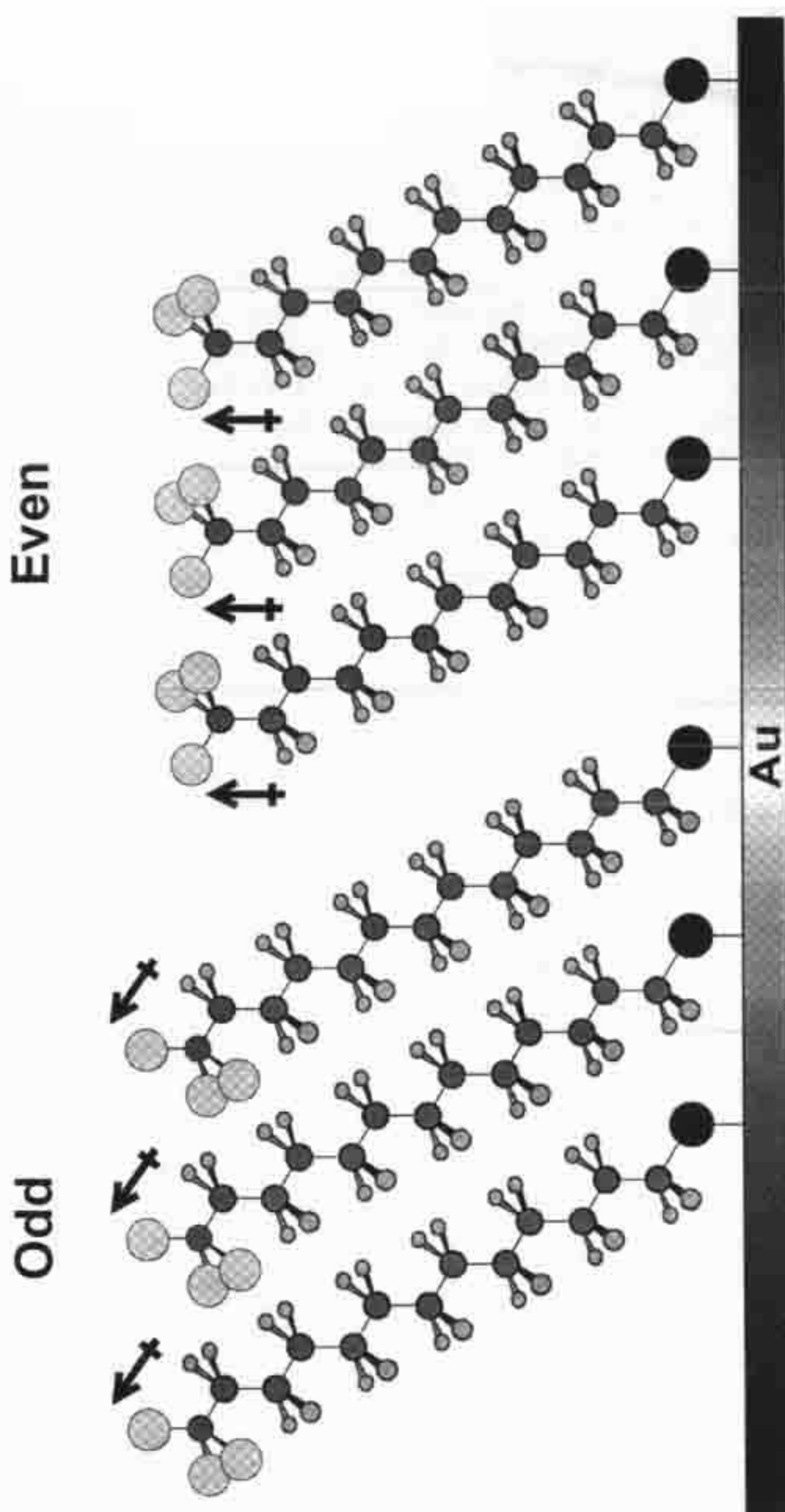
Figure 6. Schematic representation of the odd-even effect on the orientation of the CF_3-CH_2 surface dipoles in CF_3-terminated SAMs on gold. (Note: The depicted structure serves only to illustrate the relative alternation of the average terminal group orientation as a function of chain length.)

concentration of CF_3 groups induces an increase in frictional response to values that are significantly higher than that of the CH_3-terminated film (Figure 8). Furthermore, films with higher concentrations of CF_3 groups all exhibit frictional responses that are indistinguishable from the response for the 15% CF_3 film. These data argue against the influence of CF_3-CH_2 surface dipoles upon the increased frictional response of the CF_3-terminated films and suggest that a threshold of surface fluorination gives rise to the higher frictional response.

Perhaps the most significant difference between terminal CF_3 vs. CH_3 groups is the greater steric bulk of the CF_3 group [9,18]. The fact that the lateral force images for the two films exhibit indistinguishable periodicities despite the larger cross-sectional area of the CF_3 group demonstrates that the film structure within the fluorinated monolayer must accommodate the increased bulk without changing the lattice spacing [9,13]. As a consequence, the intermolecular interactions of the terminal groups with their nearest neighbors should be greater in the fluorinated films. Consequently, the local movement of the terminal CF_3 groups should be highly correlated with the motion of neighboring moieties. These correlated motions might give rise to long range intermolecular lateral and rotational interactions that provide additional pathways for the dissipation of energy, which in turn lead to the higher frictional response for the CF_3-terminated films. Since this model limits itself to interactions at the terminal portion of the films, we believe that it is consistent with the structural characterizations of film order, which argue that the underlying backbones are structurally indistinguishable. This model can also be used to rationalize the results from the mixed monolayer studies. In an idealized hexagonal surface structure for a perfectly mixed 10% CF_3-terminated film (Figure 9), the CF_3 groups could interact sterically with a majority of the film structure through nearest-neighbor interactions with the surrounding CH_3 groups. These interactions serve to increase the "effective" packing density of the terminal groups and give rise to long range correlated interactions that enhance the frictional response [13].

Given our hypothesis that the frictional responses of ω-substituted SAMs are greatly influenced by the size of the terminal groups, we evaluated the frictional response of a SAM terminated with isopropyl groups (i-Pr), which afford no strong terminal dipoles (due to their purely non-polar aliphatic composition), and like CF_3 groups, are sterically larger than CH_3 groups (Figure 10) [13,18,46]. The wettability of this film by water (advancing contact angle = 115°) reveals that the i-Pr-terminated films are as hydrophobic as the CH_3-terminated films. Moreover, neither of these films expose oriented dipoles at the surface. The higher wettability by hexadecane of the i-Pr-terminated film (advancing contact angle = 41°) compared to that of the CH_3-terminated film (advancing contact angle = 49°) suggests that the i-Pr groups possess a higher surface free energy than the CH_3 groups [47]. Analyses of the i-Pr-terminated film by AFM (Figure 3) and PM-IRRAS (Figure 4) showed that the lattice spacings and the conformational order, respectively, of the film were indistinguishable from those of the CF_3- and CH_3-terminated films. Given the relatively large size of the i-Pr group, these results highlight the fact that the monolayer structure can accommodate a significant amount of steric bulk at the surface.

Figure 7. Lateral force image (0.5 μm × 0.5 μm) of a mixed monolayer with a surface concentration of 51% CF_3 groups and 49% CH_3 groups as determined by XPS. The observed constancy of the lateral force suggests that the film components are well mixed over this area.
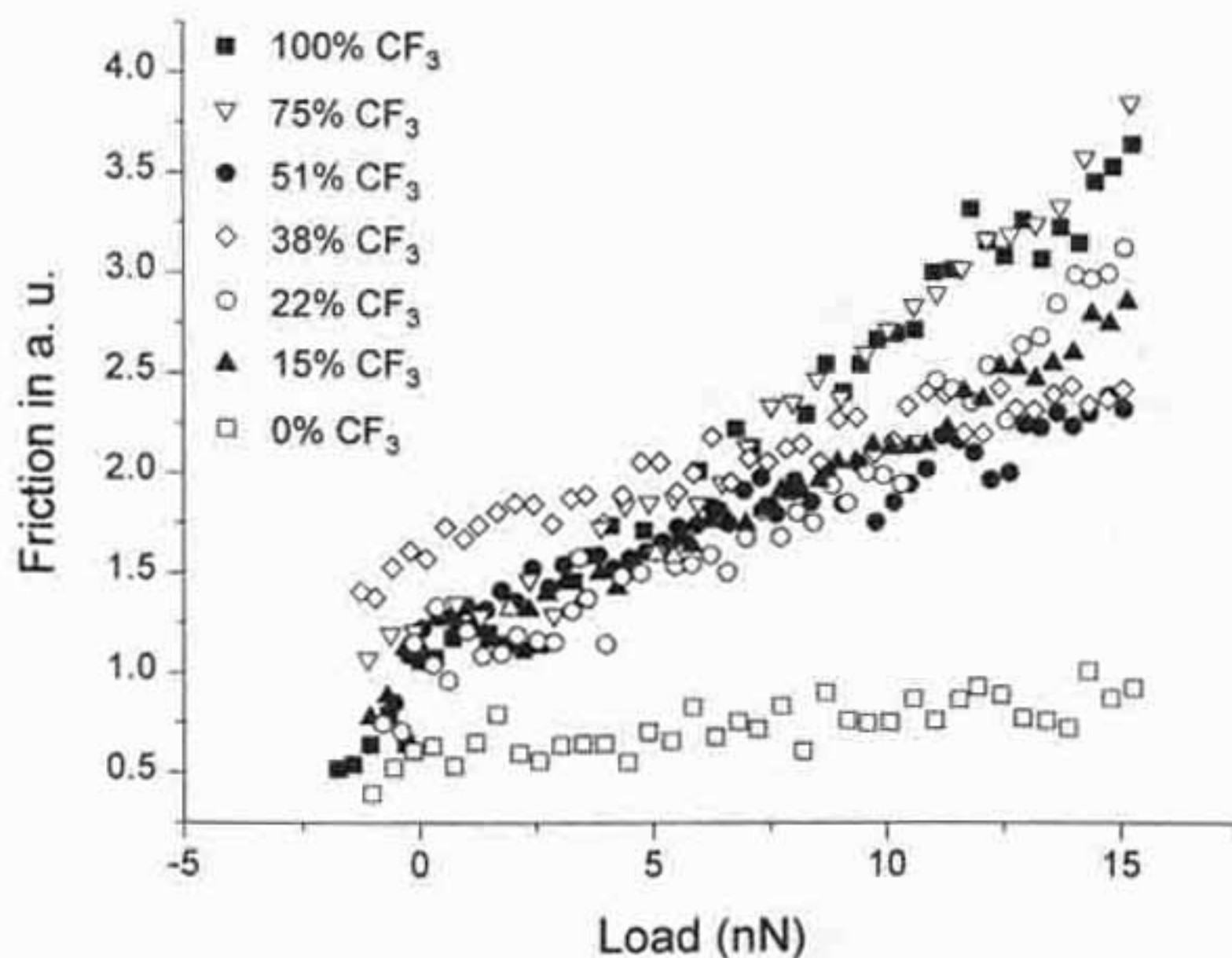

Figure 8. Frictional response of mixed monolayers derived from CF_3-terminated and CH_3-terminated hexadecanethiols (0% CF_3: □, 15% CF_3: ▲, 22% CF_3: ○, 38% CF_3: ◇, 51% CF_3: ●, 75% CF_3: ▽, and 100% CF_3: ■) measured by AFM as a function of decreasing applied load.
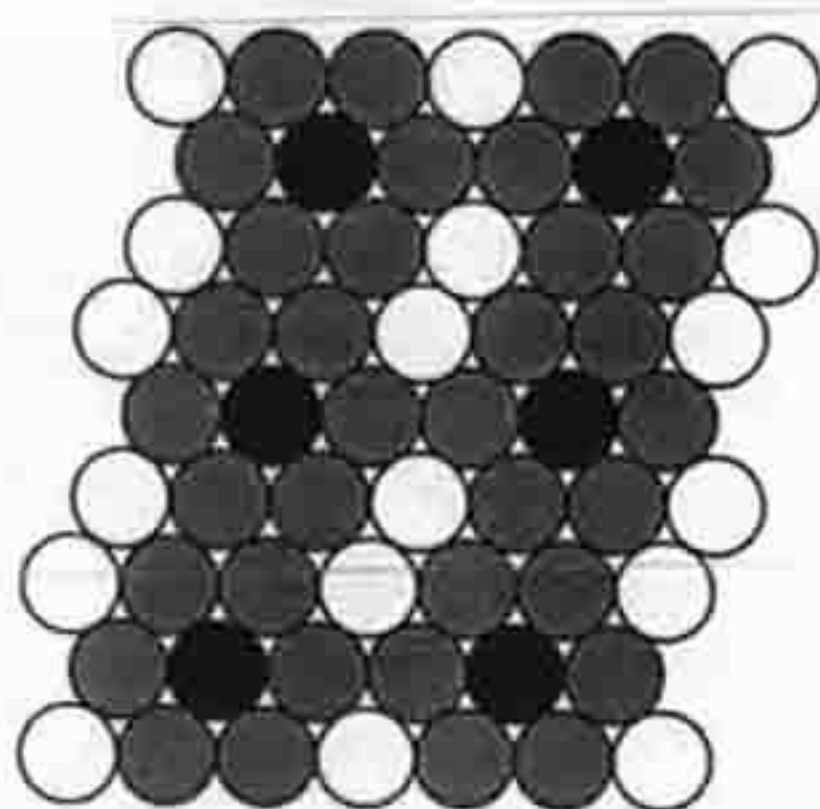
Figure 9. Schematic representation of the degree of multimolecular influence in a hexagonal lattice structure for an ideally mixed monolayer containing 10% CF_3 groups. The filled circles represent CF_3 groups, and the shaded circles represent nearest neighbor CH_3 groups influenced by the steric bulk of adjacent CF_3 groups.
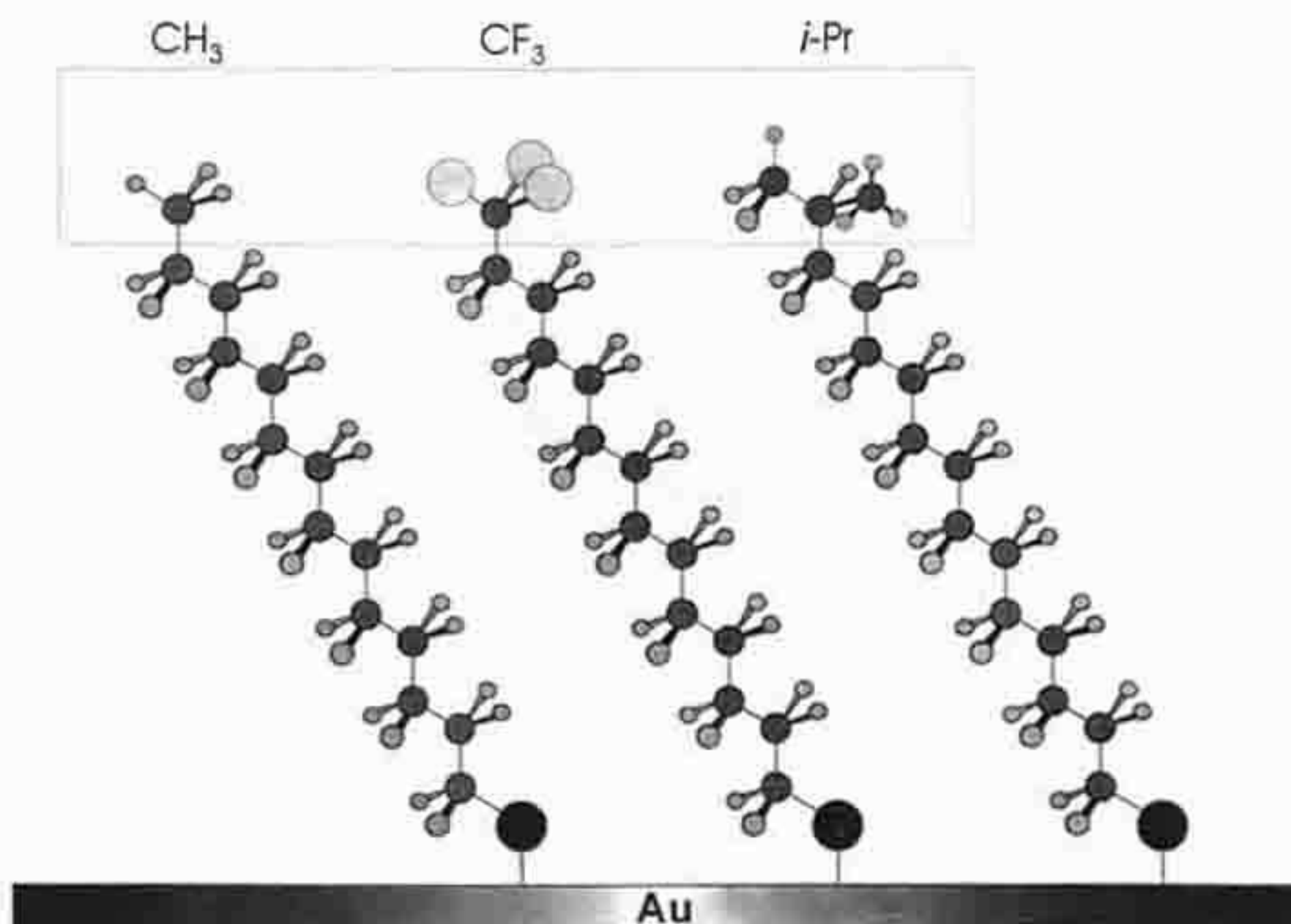

Figure 10. Schematic representation of CH_3-terminated, CF_3-terminated, and *i*-Pr-terminated SAMs derived from $\omega(CH_2)_{13}SH$, where $\omega = CH_3$, CF_3, and $CH(CH_3)_2$.

Figure 11 shows friction versus load plots of CF_3-, i-Pr-, and CH_3-terminated SAMs. Like the CF_3-terminated film, the i-Pr-terminated film exhibits a frictional response that is greater than that of the CH_3-terminated film. Since the lattice spacing, conformational order, and chemical composition of the films are the same, this higher frictional response can be rationalized in terms of the additional steric interactions that accompany the larger size of the i-Pr group. The results are consistent with a model in which the frictional responses of the i-Pr and CF_3-terminated films are influenced by the increased sizes of their terminal groups relative to those of a CH_3-terminated film. Studies to further explore these systems are currently underway in our laboratories.

Conclusions

We prepared and characterized a series of SAMs generated from ω-substituted alkanethiols to explore the relationship between film structure/composition and the interfacial properties. The lattice spacings and the conformational order of CF_3- and CH_3-terminated SAMs comprised of adsorbates having methylene backbones of equivalent length were found to be similar. Friction-load maps, however, collected by AFM showed that the CF_3-terminated SAMs have higher frictional responses than the CH_3-terminated SAMs. The contribution of the greater rotational barrier about a CF_3-CH_2 bond compared to a CH_3-CH_2 bond to the frictional response was considered; however, the 26% greater rotational barrier is perhaps insufficient to account for the threefold increase in frictional response. The potential influence of surface dipoles on interfacial properties was probed by evaluating the wettabilities of CF_3-terminated SAMs and CH_3-terminated SAMs. The results revealed strong interactions between oriented surface dipoles and polar contacting liquids. The similar frictional responses of mixed CF_3- and CH_3-terminated monolayers with progressively increasing surface concentrations of CF_3 groups suggest, however, that the influence of surface dipoles fails to contribute significantly to the enhanced friction of CF_3-terminated SAMs. Lateral force images and antisymmetric methylene band positions obtained for an i-Pr-terminated SAM, which also possesses a larger terminal group than that of the CH_3-terminated SAMs, were indistinguishable from those of CF_3- and CH_3-terminated SAMs and suggest that the lattice periodicity and methylene conformational order, respectively, of these ω-substituted films are unaffected by the size of the terminal functional group. Furthermore, contact angle measurements revealed that the i-Pr-terminated SAM is wet more by hexadecane and wet equivalently by water when compared to the CH_3-terminated SAM. The i-Pr-terminated SAM, which posseses no oriented terminal dipoles, exhibited a greater frictional response than that of the CH_3-terminated SAM. Overall, these results are consistent with a model in which the friction of the CF_3- and i-Pr-terminated SAMs are influenced by the relatively large size of their terminal functional groups. We are currently exploring chain length effects that alter the orientation of the terminal groups (odd-even effects) and the use of larger terminal groups (phenyl, $tert$-butyl) to gain further insight into the frictional responses of these ω-substituted films.

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Acknowledgments

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46. Previously (see reference 13 and reference 3 therein), the size of the *i*-Pr group was underestimated due to an erroneous omission of the contribution of the hydrogen $HC(CH_3)_2$ in calculating the cross-sectional area.

47. As in reference 38, the surface free energies of the SAMs (γ_s^d) were estimated from the advancing contact angles of hexadecane (θ_a) using the following relationships (discussed in van Oss, C. J.; Chaudhury, M. K.; Good, R. J. *Chem. Rev.* **1988**, *88*, 927): $W_a = \gamma_L(1 + \cos \theta_a)$, $W_a = W_a^d + W_a^p$, and $W_a^d = 2(\gamma_L^d \gamma_S^d)^{1/2}$, where W_a^d and W_a^p are the dispersive and polar components, respectively, of the work of adhesion (W_a) between the contacting liquid and the SAM, $W_a^p = 0$ (assuming that the interactions between hexadecane and the SAMs are entirely dispersive), and the surface free energy of hexadecane is $\gamma_L = \gamma_L^d = 27.5$ mJ m^{-2}. The following values were obtained: γ_S^d (CH_3-terminated film) = 18.9 ± 0.3 mJ m^{-2}, γ_S^d (CF_3-terminated film) = 13.6 ± 0.3 mJ m^{-2}, and γ_S^d (*i*-Pr-terminated film) = 21.2 ± 0.3 mJ m^{-2}. The value of γ_S^d (CF_3-terminated film) might be underestimated by hexadecane due to the non-ideal nature of the dispersive interactions between hydrocarbons and fluorocarbons, but no more than 4 mJ m^{-2}, which was determined through the use of *cis*-perfluorodecalin as the non-polar contacting liquid in the estimation of γ_S^d.