

## Surface Dipoles Influence the Wettability of Terminally Fluorinated Organic Films

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### ABSTRACT

The correlation of differences in the wettabilities of partially fluorinated self-assembled monolayers (SAMs) to changes in the chemical structure and composition of the films was explored by contact angle goniometry and polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS). SAMs of simple alkanethiols ( $\text{CH}_3(\text{CH}_2)_n\text{SH}$  with  $n = 9-15$ ) and their  $\text{CF}_3$ -terminated analogs ( $\text{CF}_3(\text{CH}_2)_n\text{SH}$  with  $n = 9-15$ ) were prepared by adsorption from solution onto evaporated gold. Advancing contact angles of hexadecane were measured on both the terminally fluorinated surfaces and the hydrocarbon surfaces. These data were compared to those obtained using a series of polar aprotic contacting liquids. As expected, the contact angles of hexadecane were higher on the  $\text{CF}_3$ -terminated SAMs than on the  $\text{CH}_3$ -terminated SAMs. The contact angles of the polar aprotic solvents, however, were measurably lower on the  $\text{CF}_3$ -terminated SAMs than on the  $\text{CH}_3$ -terminated SAMs. These observations were rationalized on the basis that the introduction of the  $\text{CF}_3$  terminal groups yields oriented surface dipoles that interact with the dipoles of the polar contacting liquids. Further support for this model was provided by the observation of an inverse parity ("odd-even") effect in the wettabilities of the polar aprotic solvents on the  $\text{CF}_3$ -terminated surfaces. Analysis by PM-IRRAS revealed that both types of films consist of predominately trans-extended alkyl chains with relatively few gauche defects in a densely packed arrangement. The high degree of order is consistent with the detection of the parity effect, where small changes in the orientation of the tail groups can be sensed by contact angle measurements only in highly ordered organic thin films. The significance of the dipole-oriented dipole interaction in describing interfacial wettabilities is discussed.

### INTRODUCTION

Fluorinated organic materials enjoy widespread use in a variety of interfacial applications due to their attractive surface properties [1]. Understanding how these interfacial properties are affected by structural or chemical changes in the material will facilitate the generation of tailored fluorocarbon surfaces. The preparation of self-assembled monolayers through the spontaneous adsorption of alkanethiols from solution onto gold offers atomic control over the chemical and physical structure of organic surfaces [2,3]. When coupled with the use of contact angle goniometry as a means of probing interfacial interactions [4], and PM-IRRAS as a means of elucidating structural order [2,5], this system provides an attractive approach to monitoring the changes in surface properties that accompany systematic alterations of the composition and structure of organic thin films.

In previous studies, we examined a series of SAMs generated from  $\omega,\omega,\omega$ -trifluoromethylalkanethiols ( $\text{CF}_3(\text{CH}_2)_n\text{SH}$  with  $n = 9-15$ ) and compared their properties to those of SAMs generated from the corresponding normal alkanethiols ( $\text{CH}_3(\text{CH}_2)_n\text{SH}$  with  $n = 9-15$ ) [6]. The results revealed that the  $\text{CF}_3$ -terminated surfaces were less wettable by nonpolar or weakly polar contacting liquids (hexadecane and methylene iodide, respectively), but surprisingly more wettable by polar contacting liquids (water and glycerol) than were the  $\text{CH}_3$ -terminated

surfaces. We proposed that oriented  $\text{CF}_3\text{-CH}_2$  surface dipoles were responsible for this effect. By using a combination of nonpolar, polar aprotic, and polar protic solvents, we further explored the plausibility of this hypothesis [7]. This particular combination of contacting liquids allowed us to estimate the dispersive and polar contributions to the overall interfacial energies for the aforementioned series of  $\text{CF}_3$ -terminated and  $\text{CH}_3$ -terminated SAMs.

In the present study, we further explore the influence of oriented surface dipoles by examining the wettabilities of these films using a series of polar aprotic contacting liquids (acetonitrile, dimethylformamide, and nitrobenzene) and correlating the observed wettabilities with the structural order of the films, which is evaluated by PM-IRRAS measurements. The results are consistent with a model in which the observed trends in wettability reflect electronic and structural changes in the outermost portions of the films.

## EXPERIMENT

### Materials

The materials and methods used to evaporate thin films of gold onto the polished surfaces of silicon wafers have been described previously [8]. The liquids used for contact angle measurements were of the highest purity available, and were used without further purification. The simple alkanethiols used to prepare the SAMs were either commercially available or synthesized using common methods. The details of the synthesis and characterization of the partially fluorinated alkanethiols have been described elsewhere [9].

### Preparation of SAMs

Solutions of the thiols were prepared in weighing bottles that were previously cleaned with piranha solution (7:3  $\text{H}_2\text{SO}_4/\text{H}_2\text{O}_2$ ) for 1 h. *Caution: piranha solution reacts violently with organic materials and should be handled carefully.* The bottles were thoroughly rinsed with deionized water and absolute ethanol before use. Gold-coated silicon wafers (ca. 1 cm  $\times$  3 cm) were then immersed in solutions of the respective thiols (1 mM in ethanol). All substrates were allowed to equilibrate in solution for 24 hours. Before characterization, the SAMs were thoroughly rinsed with ethanol and blown dry with ultra-pure nitrogen.

### Contact Angle Wettabilities

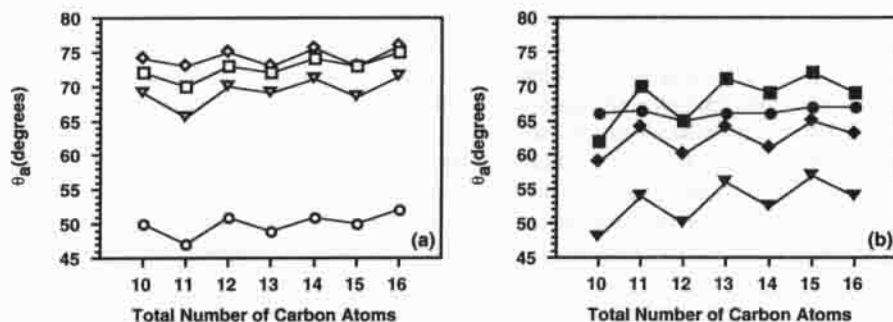
Advancing contact angles were measured with a ramé-hart model 100 contact angle goniometer. The contacting liquids were dispensed and withdrawn with a Matrix Technologies micro-Electrapipette 25 operated at the slowest possible speed (ca. 1  $\mu\text{L/s}$ ). For each SAM, contact angles were averaged over three separate slides using three drops per slide, and by measuring angles from opposite edges of each drop. The measurements were performed at 293 K with the pipette tip maintaining contact with the drop.

### Infrared Spectroscopy

Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS) data were collected with 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. The spectra were collected over 1000 scans with p-polarized light at an 80° angle of incidence. The spectral resolution was 4  $\text{cm}^{-1}$ .

## RESULTS

Our previous findings revealed that the contact angles of hexadecane were *ca.* 18° higher on the CF<sub>3</sub>-terminated surfaces than on the CH<sub>3</sub>-terminated surfaces [6,7]. We anticipated this result due to the known weakness of the dispersive interactions between hydrocarbons and fluorocarbons [10]. We were surprised to find, however, that the contact angles of water and glycerol were lower on the fluorinated surfaces than on the hydrocarbon surfaces, which could perhaps be rationalized by the presence of hydrogen bonding between the protic solvents and the terminal trifluoromethyl groups [11]. In the present work, we explore this issue further by examining the wettabilities of CF<sub>3</sub>- and CH<sub>3</sub>-terminated surfaces with liquids that are unable to hydrogen bond with fluorine atoms: acetonitrile, dimethylformamide (DMF), and nitrobenzene (Figures 1a and 1b). Interestingly, these liquids also show wettabilities on the CF<sub>3</sub>-terminated surfaces that are enhanced relative to the CH<sub>3</sub>-terminated surfaces. From these results, we conclude that an effect other than hydrogen bonding must be primarily responsible for the increased interactions on the fluorinated films.

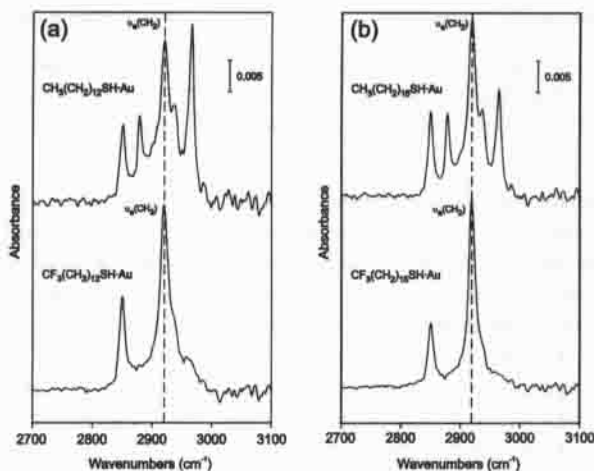


**Figure 1.** Advancing contact angles of hexadecane (●), acetonitrile (▼), DMF (◆), and nitrobenzene (■) on SAMs formed from (a) *n*-alkanethiols (CH<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH with *n* = 9-15; open symbols) and (b) CF<sub>3</sub>-terminated alkanethiols (CF<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH with *n* = 9-15; filled symbols).

Contact angle measurements are known to be sensitive to the local order at an interface [4]. The observation of a parity ("odd-even") effect for hexadecane wettabilities on CH<sub>3</sub>-terminated SAMs of alkanethiols on gold provides an example of the remarkable level of sensitivity (Figure 1a). The phenomenon is proposed to arise from the change in orientation of the terminal methyl group as the number of carbon atoms in the alkyl chains alternates between odd and even. Lower contact angles are obtained on CH<sub>3</sub>-terminated SAMs having an odd number of total carbon atoms due to an orientation that exposes the more wettable methylene moieties [12]. Further illustrating the degree of order in these films, Figure 1a shows a similar parity effect for all three polar aprotic liquids. We note that the interactions between all test liquids and the CH<sub>3</sub>-terminated films are strictly dispersive in nature.

Using the same test liquids, Figure 1b shows the wettability data obtained on the analogous  $\text{CF}_3$ -terminated SAMs. While the parity effect is undiscernable using hexadecane as the contacting liquid, all three polar aprotic liquids exhibit a pronounced parity effect. It is interesting to note, however, that the parity effect is inverted for these films: lower contact angles are obtained on  $\text{CF}_3$ -terminated SAMs having an *even* number of total carbon atoms. Given that the underlying moieties for both  $\text{CH}_3$ - and  $\text{CF}_3$ -terminated films are  $\text{CH}_2$  groups, these results suggest that the nature of the parity effect in the  $\text{CF}_3$ -terminated films is not strictly dispersive in nature. Furthermore, the existence of a parity effect suggests a highly ordered interface for these films.

The conformation and orientation of the alkyl adsorbates that comprise SAMs can be examined by infrared reflection absorption spectroscopy [2,5]. In particular, the frequency of the asymmetric methylene stretch can be used to indicate the degree of *trans*-extension and crystalline packing of the alkyl backbone. Shifts from the standard value of  $2919\text{ cm}^{-1}$  for crystalline polyethylene to higher frequencies are interpreted to arise from an increase in the disorder of the alkyl chains [13,14]. To compare the degree of order in the  $\text{CF}_3$ -terminated SAMs to that in the  $\text{CH}_3$ -terminated SAMs, we analyzed the films of both series by PM-IRRAS. Figures 2a and 2b show the spectra of odd (total number of carbon atoms = 13) and even (total number of carbon atoms = 16) SAMs from both series. For both odd and even SAMs, the frequency of the  $\nu_a(\text{CH}_2)$  stretch in both the fluorinated and hydrocarbon films appears at  $2919\text{ cm}^{-1}$ . These results suggest that the terminal  $\text{CF}_3$  group induces no detectable disorder in the alkyl backbone. Peak positions for the shorter total chain lengths (12 carbon atoms and below) occur at higher frequencies (e.g.,  $2921\text{ cm}^{-1}$ ), but they are indistinguishable for both the fluorinated and hydrocarbon series (data not shown). Previously collected atomic force microscopy (AFM) images of films from both series show that the spacing between the head groups are also indistinguishable (*ca.*  $5.0\text{ \AA}$ ) [15]. Collectively, these analyses indicate that the SAMs of both series possess similar degrees of structural order. Consequently, the differences observed in the interfacial wettabilities of  $\text{CF}_3$ - and  $\text{CH}_3$ -terminated SAMs can be evaluated as a function of the chemical composition at the interface.



**Figure 2.** PM-IRRAS spectra of  $\text{CF}_3$ - and  $\text{CH}_3$ -terminated SAMs having (a) odd-numbered chains and (b) even-numbered chains.

The substitution of a  $\text{CF}_3$  group for a  $\text{CH}_3$  group gives rise to a strong terminal dipole [16]. Hydrocarbon SAMs generated from  $\text{CF}_3$ -terminated adsorbates should thus possess an ordered arrangement of surface dipoles oriented away from the substrate. Accordingly, the dipoles of the molecular species that comprise the polar contacting liquids can interact with the surface dipoles in an attractive manner that enhances wettability. Our observation of an inverse parity effect for the polar aprotic liquids on the fluorinated films (see Figure 1b) supports this model. A change in orientation of the terminal dipole can be used to rationalize the alternation (Figure 3). SAMs comprised of adsorbates with an even total number of carbon atoms have their terminal dipoles oriented relatively normal to the surface and arranged parallel to each other. The contacting polar liquids will thus interact strongly with the surface dipoles to yield relatively low contact angles. SAMs, however, generated from thiols with an odd total number of carbon atoms possess terminal dipoles that are tilted further from the surface normal and arranged with respect to their nearest neighbors in a manner that facilitates partial dipolar compensation. As a result, the electrostatic field at the surface of the odd-numbered SAMs will be diminished relative to the field of the even-numbered SAMs. Consequently, the interaction between the polar liquids and the surface will be relatively weak, leading to relatively high contact angles. Since the contact angles for hexadecane on the fluorinated surfaces are largely (if not solely) dispersive in nature, the data show no variation with dipole orientation.

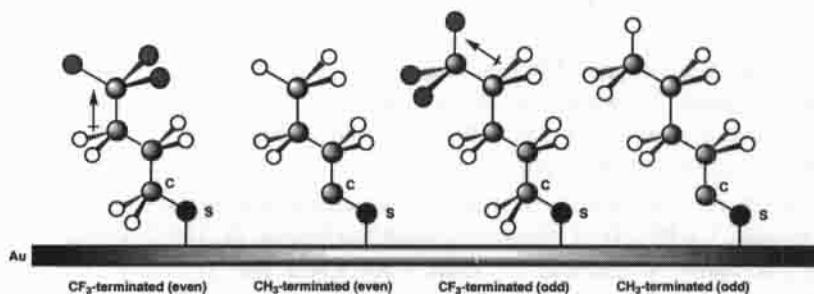


Figure 3. Illustration of the parity ("odd-even") effect for  $\text{CF}_3$ - and  $\text{CH}_3$ -terminated SAMs.

## CONCLUSIONS

The wettabilities of a series of terminally fluorinated SAMs generated from  $(\text{CF}_3(\text{CH}_2)_n\text{SH})$  with  $n = 9-15$  and a series of hydrocarbon analogs  $(\text{CH}_3(\text{CH}_2)_n\text{SH})$  with  $n = 9-15$  were measured using hexadecane and three polar aprotic contacting liquids. The wettability of hexadecane on the fluorinated surfaces was less than that on the hydrocarbon surfaces due to relatively weak dispersive interactions between hydrocarbons and fluorocarbons. In contrast, the wettabilities of the polar aprotic solvents on the fluorinated surfaces was *greater* than that on the hydrocarbon surfaces. We propose that oriented surface dipoles in the fluorinated films give rise to the latter phenomenon. For both  $\text{CF}_3$ - and  $\text{CH}_3$ -terminated films, the observation of parity effects in the wettability data and the high degree of crystallinity indicated by PM-IRRAS measurements suggest that both types of films are well packed and highly ordered. Furthermore, the inverse parity effect observed on the  $\text{CF}_3$ -terminated SAMs provides additional support for the influence of surface dipoles on the interfacial wettabilities of organic thin films.

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## REFERENCES

1. F. Garbassi, M. Morroca, E. Occhiello, Polymer Surfaces, Wiley, Chichester, (1994).
2. R.G. Nuzzo, L.H. Dubois, D.L. Allara, *J. Am. Chem. Soc.*, 112, 558 (1991).
3. C.D. Bain, G.M. Whitesides, *J. Am. Chem. Soc.*, 110, 3665 (1988).
4. A. Ulman, An Introduction to Ultrathin Organic Thin Films, Academic, Boston, (1991).
5. M.R. Anderson, M.N. Evaniak, M. Zhang, *Langmuir*, 12, 2327 (1996).
6. Y.F. Miura, M. Takenaga, T. Koini, M. Graupe, N. Garg, R.L. Graham, Jr., T.R. Lee, *Langmuir*, 14, 5821 (1998).
7. M. Graupe, M. Takenaga, T. Koini, R. Colorado, Jr., T.R. Lee, *J. Am. Chem. Soc.*, submitted.
8. R. Colorado, Jr., R.J. Villazana, T.R. Lee, *Langmuir*, 14, 6337 (1998).
9. M. Graupe, T. Koini, V.Y. Wang, G.M. Nassif, R. Colorado, Jr., R.J. Villazana, H. Dong, Y.F. Miura, O.E. Shmakova, T.R. Lee, *J. Fluorine Chem.*, in press.
10. M.K. Chaudhury, *Mat. Sci. Eng.*, R16, 97 (1996).
11. The strength of a C-F...H hydrogen bond has been estimated to be as high as 2.4 kcal/mol: J.A.K. Howard, V.J. Hoy, D. O'Hagan, G.T. Smith, *Tetrahedron*, 52, 12613 (1996).
12. H. Sellers, A. Ulman, Y. Shnidman, J.E. Eilers, *J. Am. Chem. Soc.*, 115, 9389 (1993).
13. R.G. Snyder, H.L. Strauss, C.A. Elliger, *J. Phys. Chem.*, 86, 5145 (1998).
14. M.D. Porter, T.B. Bright, D.L. Allara, C.E.D. Chidsey, *J. Am. Chem. Soc.*, 109, 3559 (1987).
15. H.I. Kim, T. Koini, T.R. Lee, S.S. Perry, *Langmuir*, 13, 7192 (1997).
16. E.G. Shafrin, W.A. Zisman, *J. Phys. Chem.*, 61, 1046 (1957).