

Structure, Wettability, and Electrochemical Barrier Properties of Self-Assembled Monolayers Prepared from Partially Fluorinated Hexadecanethiols

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Received: April 21, 2003; In Final Form: June 30, 2003

We report the preparation and characterization of self-assembled monolayers (SAMs) derived from the adsorption of partially fluorinated hexadecanethiols ($\text{CF}_3(\text{CF}_2)_{n-1}(\text{CH}_2)_m\text{SH}$; $n = 2, 4, 6, \text{ and } 8$; $n + m = 16$) onto the surface of gold. The quality of the SAMs, as measured by electrochemical impedance spectroscopy, was found to be sensitive to the solvent used as SAMs prepared in dichloromethane exhibited higher resistances and lower capacitances than those prepared in liquid CO_2 . The extent of fluorination was observed to influence the wettability, structure, and capacitance of the films without significantly affecting their charge-transfer resistance or their stability against exchange by a competing adsorbate. Reflectance-absorption infrared spectra showed that the fluorocarbon chains were oriented more normal to the surface for $n = 8$ but more parallel to the surface for $n = 2$. Advancing contact angles of hexadecane increased sharply with fluorination from $n = 0$ to 4 but slightly with additional fluorination, suggesting that hexadecane is insensitive to CH_2 groups that are buried by >4 fluorinated carbon atoms. We also were able to model the dielectric properties of these partially fluorinated SAMs as two capacitors in series: one due to the outer fluorocarbon region and one due to the inner hydrocarbon region. The dielectric constants of the fluorocarbon and hydrocarbon regions of these SAMs were quantified as ~ 1.7 and ~ 2.3 , respectively, and were comparable to the values for the pure polymer counterparts.

Introduction

Self-assembled monolayers (SAMs) prepared from the chemisorption of alkanethiol derivatives from solution onto a variety of metal surfaces¹ have been used to create protective barrier films^{2–6} and to alter surface properties that influence wettability,^{7–10} biological adsorption,¹¹ and friction.¹² The use of alkanethiol derivatives is particularly advantageous in these applications because of the inherent synthetic flexibility in preparing thiol adsorbates having various terminal groups, which allows systematic investigations of the fundamental relationships between surface structure/composition and the corresponding interfacial properties.¹³

Until recently, SAMs used for barrier films had been primarily prepared from methyl-terminated n -alkanethiols, because of their commercial availability and the low-energy, hydrophobic surfaces that these hydrocarbon adsorbates generate.^{2–6} Nonetheless, SAMs prepared from partially fluorinated thiols are known to be less permeable to aqueous ions,¹⁴ and fluorocarbon-based films, in general, are known to offer advantages over hydrocarbon coatings in terms of rigidity, oleophobicity, and thermal stability.^{10,15} These advantages have spurred several recent studies on the barrier properties of partially fluorinated alkanethiols on gold^{16–18} and silver¹⁹ surfaces using electrochemical

methods. Barbour and Lennox^{16,17} used impedance spectroscopy in the absence of redox active species to show that SAMs prepared on gold from $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$ act as ionic insulators but exhibit capacitances that are a bit higher than those of SAMs prepared from normal alkanethiols of similar thickness.¹⁷ An important advantage of the $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$ SAMs compared to SAMs terminated with $-\text{CH}_3$, $-\text{OH}$, and $-\text{CO}_2\text{H}$ groups is their enhanced stability against ion/water penetration when biased to negative potentials.¹⁶ These studies, however, did not address the influence of fluorocarbon chain length on the electrochemical properties of the SAMs nor did they use other analytical techniques to probe the properties of the films.

Because of the technological importance of fluorinated monolayers,^{20,21} Lee and co-workers have developed synthetic strategies to prepare alkanethiols having varying degrees of fluorination.²² These authors have also characterized the corresponding partially fluorinated SAMs to study the effects of fluorination on wettability,^{15,23} friction,¹² microstructure,^{10,24–26} and thermal stability.¹⁰ Some of their important findings include the fact that increasing the length of the hydrocarbon chain on a terminally fluorinated alkanethiol ($\text{CF}_3(\text{CF}_2)_{10}(\text{CH}_2)_m\text{SH}$) improves the thermal stability of the resulting monolayer and increases its oleophobicity.¹⁰ Their work indicates that the properties of the film can be tailored by simply changing the chain length of the assembling molecule without altering the chemical nature of its terminal group. Lee and co-workers were also able to demonstrate that the wettability and frictional properties of SAMs can be substantially altered by adding just one $-\text{CF}_3$ group to the end of an n -alkanethiol.^{12,15,23} These studies have provided fundamental insight into how a perfluoro-

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rocarbon terminal group, which has a larger cross section than a polymethylene chain, influences the properties of a molecular film.

Naud et al.¹⁸ have examined the effect of fluorination on the capacitance of SAMs on gold prepared from $\text{CF}_3(\text{CF}_2)_{n-1}(\text{CH}_2)_m\text{SH}$ ($n = 4, 6, 8,$ and 10 ; $m = 2$ and 11). Through the sole use of capacitance measurements by cyclic voltammetry in the absence of redox probes, they have postulated that short fluorinated chains ($n = 4$) are unable to organize along the surface normal, independent of the length of the polymethylene tether, whereas longer fluorinated chains ($n = 8$ and 10) do indeed organize along the surface normal. In general, the SAMs prepared by Naud et al.¹⁸ behaved as ideal capacitors, and they used measured capacitance values to estimate the thickness of the SAMs.

In the work described here, we have combined electrochemical impedance spectroscopy (EIS), contact angle goniometry, and reflectance-absorption infrared spectroscopy (RAIRS) to correlate the effects of fluorination on the structure, wettability, and barrier properties of partially fluorinated SAMs. We also examine the influence of solvent on the preparation of these SAMs and their tendency to exchange when exposed to different solvents containing a competing thiol. The motivation behind this work is to determine how solvent and fluorination can be selected to enable the preparation of high-quality partially fluorinated barrier films with tailored properties. To this end, we have used hexadecanethiols with systematically varying degrees of fluorination ($\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ and $\text{CF}_3(\text{CF}_2)_{n-1}(\text{CH}_2)_m\text{SH}$, denoted as FnHmSH , with $n + m = 16$) to maintain a constant chain length of the adsorbate while incrementally increasing the length of the fluorocarbon chain. Specifically, the four partially fluorinated alkanethiols that we investigate here are F2H14SH , F4H12SH , F6H10SH , and F8H8SH .

In addition to using dichloromethane, we have also chosen to explore the use of liquid CO_2 for the formation of SAMs with varying degrees of fluorination. Adding fluorinated functional groups to compounds tends to greatly increase their solubility in CO_2 ,^{27–31} and therefore, we would expect CO_2 to have a profound influence on the preparation of SAMs from partially fluorinated adsorbates. Furthermore, we have previously shown that liquid and supercritical CO_2 can be used to prepare hydrocarbon n -alkanethiolate SAMs on gold surfaces that have greater packing densities, fewer defects, and superior electrochemical blocking capabilities than films formed from solvents such as ethanol exhibited.³² We were also able to control the properties of the films simply by using binary mixtures of organic solvents with CO_2 .³³

In a recent related study, Efimenko et al.³⁴ employed partially fluorinated and hydrocarbon chlorosilane precursors to produce SAMs on silica surfaces using liquid CO_2 as solvent. They found that the hydrocarbon chlorosilane adsorbates formed an ordered film much more rapidly than the partially fluorinated adsorbates did. The authors attributed these changes to the favorable interactions of CO_2 with the partially fluorinated adsorbates. Here, we propose to gain additional insight into the role of CO_2 in the preparation and properties of SAMs from partially fluorinated alkanethiols.

Experimental Section

Materials. Gold shot (99.99%) and silicon(100) wafers were obtained from J&J Materials (Neptune City, NJ) and Montco Silicon (Royersford, PA), respectively. Chromium-coated tungsten rods were obtained from R. D. Mathis (Long Beach, CA). Partially fluorinated alkanethiols [$\text{CF}_3(\text{CF}_2)_{n-1}(\text{CH}_2)_m\text{SH}$ with

$n + m = 16$ and $n = 2, 4, 6,$ or 8] were prepared using the materials and procedures described by Lee and co-workers;²² the nonfluorinated hexadecanethiol [$\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ denoted as C_{16}SH] was purchased from Aldrich. High purity isooctane, ethanol, dichloromethane, hexadecane, and 2,2,2-trifluoroethanol were used as received from Aldrich. Potassium ferricyanide ($\text{K}_3\text{Fe}(\text{CN})_6$) and potassium ferrocyanide trihydrate ($\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$) were used as received from Aldrich. Grade-5 CO_2 (BOC Gases) was also used as received. Deionized water (16.7 M Ω) was purified with a Modu-Pure system.

Sample Preparation. Chromium (100 Å) and gold (1500 Å) were evaporated sequentially in a diffusion-pumped chamber (operating pressure of 4×10^{-6} Torr) onto silicon (100) wafers. For SAMs formed in organic solvents, evaporated gold substrates were immersed into solutions containing 0.2 mM of a thiol in the solvent at 25 °C and 1 bar for a fixed time. Once removed, substrates were rinsed with the pure solvent and dried in air. Exchange experiments were performed by first exposing the gold substrates to a 0.2 mM dichloromethane solution of the partially fluorinated thiol for 48 h. The substrates were removed, rinsed with pure dichloromethane, dried with N_2 , and then exposed to a 1 mM solution of C_{16}SH in either ethanol, 2,2,2-trifluoroethanol, isooctane, or liquid CO_2 for 24 h.

SAM Formation in CO_2 . SAMs generated in CO_2 were prepared without stirring in a 10-mL vessel. In a typical experiment, a gold substrate (ca. 3 cm \times 1 cm) was rinsed with methylene chloride, dried in air, and placed in the reactor. A small amount of thiol was placed in the vessel before the vessel was sealed to produce a 0.2 mM solution when the system was pressurized. Once sealed, low-pressure CO_2 was briefly flushed through the vessel, and then an Isco 260D syringe pump was used to pressurize the reactor with CO_2 . Pressurization occurred in less than 20 s. After a fixed time of exposure, the pressure of the system was lowered slowly to ensure that the thiol would not precipitate from solution and produce a physisorbed film on the surface of the monolayer. To further discourage thiol precipitation, approximately 60 g of pure CO_2 was flushed through the reactor during the lowering of the pressure. The depressurization process was only a small fraction of the experimental time and considered to be insignificant. Once removed from the reactor, the substrate was rinsed with dichloromethane and dried in air.

Reflectance-Absorption Infrared Spectroscopy (RAIRS). IR spectra were obtained in single-reflection mode with a Bio-Rad Excalibur infrared spectrometer containing a universal reflectance attachment. The p-polarized light was incident at 80° from the surface normal. The reflected light was detected with a narrow-band MCT detector cooled with liquid nitrogen. Spectral resolution was 2 cm^{-1} after triangular apodization. Spectra were referenced to those of SAMs prepared on gold from octadecanethiol- d_{37} , and 1000 scans of both sample and reference were collected.

Electrochemical Impedance Spectroscopy. Electrochemical impedance measurements of SAM-coated gold samples were performed with a CMS300 electrochemical impedance system (Gamry Instruments) interfaced to a personal computer. A glass cell equipped with a gold-coated silicon counter electrode and a Ag/AgCl /saturated KCl reference electrode contained an aqueous solution of 0.1 M Na_2SO_4 , 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, and 1 mM $\text{K}_4\text{Fe}(\text{CN})_6 \cdot 3\text{H}_2\text{O}$. The measurements were conducted at the open circuit potential with a 5 mV ac perturbation that was controlled between 50 mHz and 20 kHz. Film resistance and capacitance values were determined by fitting the EIS data with

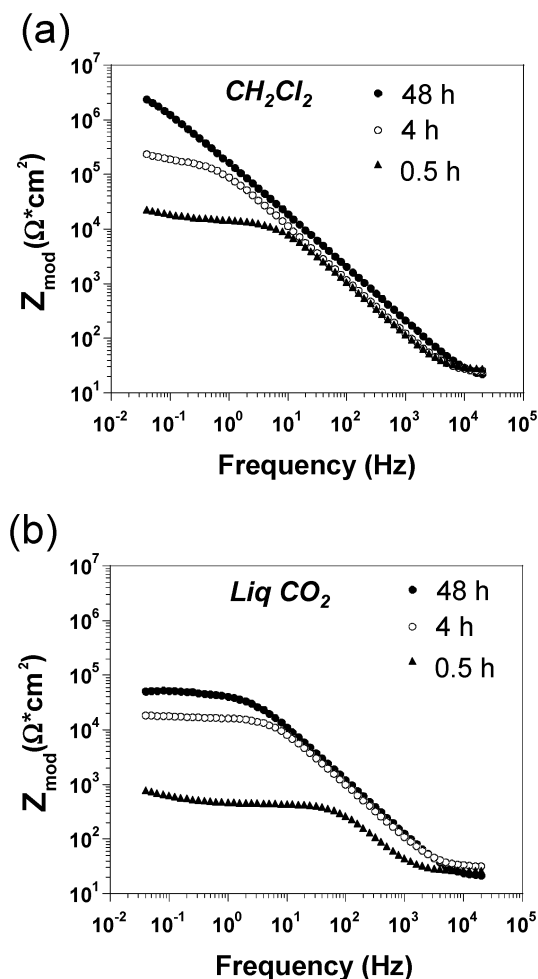


Figure 1. Impedance data in the form of Bode magnitude plots obtained after exposure of gold to F8H8SH (0.2 mM) in (a) CH_2Cl_2 or (b) liquid CO_2 for different times. The impedance data were obtained in an aqueous solution containing 0.1 M Na_2SO_4 , 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, and 1 mM $\text{K}_4\text{Fe}(\text{CN})_6$.

an equivalent circuit⁵ that consists of a solution resistance in series with a parallel combination of interfacial capacitance and charge-transfer resistance using software provided by Gamry. For poorly blocking monolayers, the equivalent circuit was modified to contain a Warburg component in series with the charge-transfer resistance, both of which are in parallel with an interfacial capacitance term.^{35,36}

Wetting Measurements. Advancing contact angles were measured on static drops of hexadecane with a Ramé-Hart manual goniometer. Hexadecane was advanced at $\sim 1 \mu\text{L}/\text{s}$ prior to measurement via an attached syringe supplied by Ramé-Hart. The syringe tip remained submerged in the drop during the measurement. For a given sample, both sides of $\sim 5 \mu\text{L}$ drops were measured at two separate locations.

Results and Discussion

Influence of Solvent and Adsorption Time on the Properties of the Films. To assess the effects of solvent and adsorption time on the barrier properties of partially fluorinated SAMs, we examined the impedance spectra of SAMs formed from F8H8SH, the most highly fluorinated alkanethiol in this study, using both dichloromethane (25 °C and 1 bar) (Figure 1a) and liquid CO_2 (25 °C and 103 bar) (Figure 1b) as solvents for exposure times of 0.5, 4.0, and 48 h. We have previously shown that pressure alone does not affect the properties or rate of SAM

formation.³² The electrochemical impedance spectra in Figure 1 are in the form of a Bode magnitude plot, which is a log–log plot of impedance modulus (Z_{mod}) versus frequency. At high frequencies, the impedance spectra are dominated by solution resistance. At moderate frequencies, the impedance spectra exhibit linear behavior with a slope that approaches -1 , consistent with a capacitive response in which the impedance modulus varies as $1/(2\pi fC)$, where f is frequency and C is capacitance. At lower frequencies, the impedance modulus is nearly independent of frequency and approximates the resistance of the SAM against the diffusion of soluble redox probes, which were $\text{K}_4\text{Fe}(\text{CN})_6$ and $\text{K}_3\text{Fe}(\text{CN})_6$.

In Figure 1a, the impedance data indicate that the resistance of the SAMs prepared from F8H8SH in CH_2Cl_2 increases with adsorption time. In fact, the resistance for the SAM formed for 48 h is sufficiently high that it is not observed (no leveling off at low f) on the Bode plot but can be estimated on a Nyquist plot (not shown). Based on fits of these data to a Randles model,⁵ we have estimated the resistance of these films as 0.02, 0.2, and 3 $\text{M}\Omega \text{ cm}^2$ after exposures of 0.5, 4, and 48 h, respectively. This increase of resistance with time is consistent with the gradual filling in and quenching of ion conducting defects within the SAM as the chains in the film approach an equilibrium structure. Further increases in adsorption time (> 100 h) exhibited no additional improvement (data not shown) over that for SAMs formed for 48 h. The capacitance of these films decreases with adsorption time: 1.35 $\mu\text{F}/\text{cm}^2$ for 0.5 h, 1.30 $\mu\text{F}/\text{cm}^2$ for 4 h, and 0.90 $\mu\text{F}/\text{cm}^2$ for 48 h. This trend is consistent with the evolution to a lower dielectric barrier film that more effectively excludes water.

SAMs formed from F8H8SH in liquid CO_2 also show increased resistance and decreased capacitance with adsorption time; however, the quality of the SAMs formed in CO_2 is significantly lower than those prepared in CH_2Cl_2 at identical exposure times. This observation is highlighted by uniformly lower resistances (500 $\Omega \text{ cm}^2$ for 0.5 h, $2 \times 10^4 \Omega \text{ cm}^2$ for 4 h, and $5 \times 10^4 \Omega \text{ cm}^2$ for 48 h) and uniformly higher capacitances (4.91 $\mu\text{F}/\text{cm}^2$ for 0.5 h, 1.50 $\mu\text{F}/\text{cm}^2$ for 4 h, and 1.44 $\mu\text{F}/\text{cm}^2$ for 48 h) for SAMs prepared in CO_2 when compared to those for SAMs formed in CH_2Cl_2 (vide supra). A 0.5-h exposure to F8H8SH in CO_2 produced an especially low impedance with a Warburg component at lowest frequencies, indicating a film with an unusually high density of defects. The advancing contact angle of hexadecane on this film was 79°, measurably lower than that of 83° for a well-formed SAM from F8H8SH, suggesting an incomplete film after the 0.5 h exposure.

The inferior quality of the films adsorbed from CO_2 is consistent with the enhanced solvation of fluorocarbons in liquid CO_2 , which can plausibly inhibit the crystallization of the fluorocarbon chains into a densely packed SAM. Dannenberger et al.³⁷ have shown that solvents that interact more strongly with alkanethiols exhibit diminished rates of SAM formation. For the specific case of fluorocarbon adsorbates in CO_2 , Efimenko et al.³⁴ used near-edge X-ray absorption fine structure (NEXAFS) and contact angles to show that partially fluorinated trichlorosilanes are slower to order when formed in CO_2 versus less solvating organic solvents. It appears from the results described herein and those of Efimenko et al.³⁴ that CO_2 is a poor choice of solvent for the preparation of partially fluorinated monolayer films because this solvent exhibits such a high affinity for fluorocarbon adsorbates. Nonetheless, we have previously shown that liquid and supercritical CO_2 are good solvent choices for the preparation of highly blocking SAMs from hydrocarbon adsorbates.³²

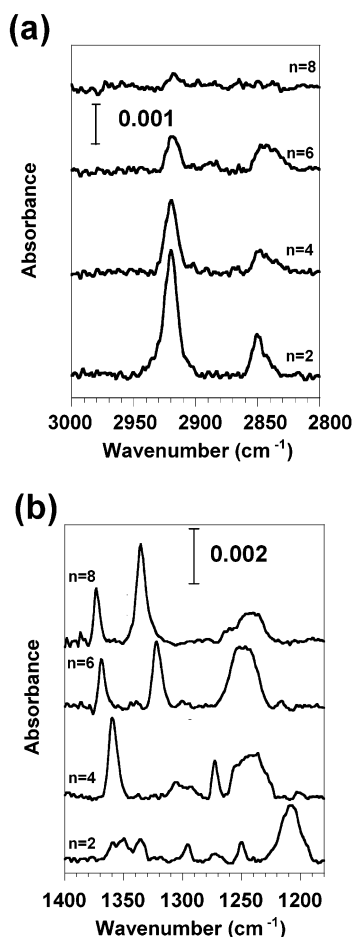


Figure 2. Reflectance-absorption infrared spectra of the (a) C–H and (b) C–F stretching regions for SAMs prepared by exposure of gold to 0.2 mM F_nH(16-*n*)SH in CH₂Cl₂ for 48 h. The spectra have been offset vertically for clarity.

Influence of the Degree of Fluorination on the Properties of Partially Fluorinated SAMs. We have used reflectance-absorption infrared spectroscopy (RAIRS) to examine the structure of partially fluorinated SAMs. Figure 2 shows the C–H and C–F stretching regions of infrared spectra for SAMs formed after 48 h exposure to 0.2 mM solutions of F₂H₁₄SH, F₄H₁₂SH, F₆H₁₀SH, and F₈H₈SH in CH₂Cl₂. In Figure 2a, the two dominant peaks in the C–H region correspond to the asymmetric (~2919 cm⁻¹) and symmetric (~2850 cm⁻¹) methylene (CH₂) stretching bands. The positions of these peaks are consistent with highly crystalline, trans-extended hydrocarbon chains. As expected, these peaks exhibit a pronounced decrease in intensity as the number of methylene groups within the assembling chains decreases.

The two dominant sets of peaks in Figure 2b correspond to C–F stretching vibrations that exhibit transition dipole moments parallel (1300–1380 cm⁻¹) and perpendicular to (1190–1270 cm⁻¹) the fluorocarbon helical axis.³⁸ These bands are referred to as axial ($\nu_{\text{ax}}^{\text{CF}_2}$) and perpendicular ($\nu_{\text{pd}}^{\text{CF}_2}$) CF₂ stretching bands, respectively. The intensities of these bands provide information regarding the orientation of the fluorocarbon chains within the SAM. For example, if the fluorocarbon chains are oriented normal to the surface, only the axial component will overlap with the electric field vector and will be observed in the IR spectrum. Based on the relative intensities of $\nu_{\text{ax}}^{\text{CF}_2}$ and $\nu_{\text{pd}}^{\text{CF}_2}$ bands in Figure 2b, the fluorocarbon chains appear to be oriented nearly normal to the surface for F₈H₈SH but progressively more tilted for adsorbates having lesser degrees of

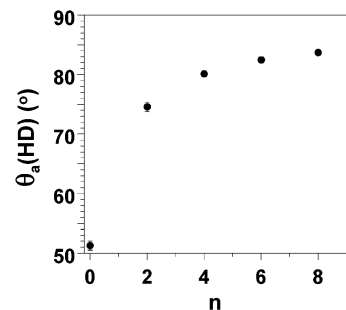


Figure 3. Influence of fluorocarbon chain length (*n*) on the advancing contact angle of hexadecane for SAMs prepared by exposure of gold to 0.2 mM F_nH(16-*n*)SH in CH₂Cl₂ for 48 h. When no error bar is visible, the error is approximated by the size of the symbol.

fluorination. This trend, which is consistent with those observed for related partially fluorinated SAMs on gold,^{18,38} reflects the complex interplay between hydrocarbon packing forces, fluorocarbon packing forces, and the preferred sulfur–gold bonding geometries.²⁶ The first and second axial bands ($\nu_{\text{ax}}^{\text{CF}_2}$) at ~1300–1330 and ~1370 cm⁻¹ are of particular interest in characterizing the helical structure of fluorocarbons. As shown in Figure 2b, the position of these axial bands increases in wavenumber as the chain is increasingly fluorinated. Colorado et al.³⁸ have correlated these changing band positions to the length of the fluorocarbon helix. Therefore, the wavenumbers can be used to provide information reflecting the thickness of the fluorocarbon layer.

We measured the contact angle of hexadecane to qualitatively assess the surface composition and structure of these partially fluorinated SAMs. Although the contact angles of water on fluorocarbon and hydrocarbon surfaces are similar in magnitude, the hexadecane contact angles are widely different on these surfaces and are therefore useful to evaluate partially fluorinated monolayers that contain both hydrocarbon and fluorocarbon segments. An example of the distinct differences is shown in Figure 3, where the advancing contact angle of hexadecane on a methyl-terminated C₁₆S–Au surface (taken to be *n* = 0 in Figure 3) is 51°, whereas that on SAMs prepared from partially fluorinated thiols ranges from 74 to 83°, depending on the degree of fluorination. The observed increase in contact angle with increasing fluorination is consistent with the IR analysis above, which indicates an increase in the length of the fluorocarbon helix. The fact that the measured contact angles are relatively insensitive to increased fluorination beyond *n* = 6 suggests that the fluorocarbon layer is sufficiently thick and densely packed such that the wetting of hexadecane is unaffected by the underlying methylene (CH₂) groups. Previous work by Laibinis et al.⁹ has estimated the depth to which hexadecane can sense an underlying molecular group (e.g., an ethereal oxygen) as 3–4 CH₂ units. For the unique system examined here, we estimate the depth to which hexadecane can sense an underlying methylene group is ~4–6 CF₂ units.

We have used EIS to characterize the capacitance (Figure 4) and charge-transfer resistance (Figure 6) of these partially fluorinated SAMs prepared by exposure to a 0.2 mM solution of the thiol in CH₂Cl₂ for 48 h. The impedance spectra were collected in an aqueous solution containing 0.1 M Na₂SO₄, 1 mM K₃Fe(CN)₆, and 1 mM K₄Fe(CN)₆, and the resulting spectra were fit with a Randles model equivalent circuit to quantify capacitance and resistance. Figure 4a shows the influence of fluorination on the measured capacitance. For partially fluorinated SAMs, the capacitance decreases with increasing fluorination, suggesting either an increased thickness or an effectively lower dielectric constant of the films as more carbon atoms are

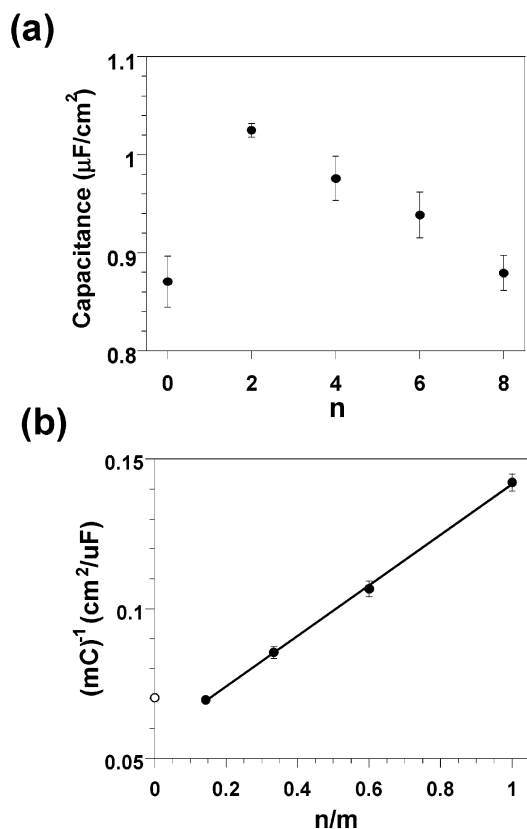


Figure 4. (a) Influence of fluorocarbon chain length (n) on the capacitance of SAMs prepared by exposure of gold to 0.2 mM FmH-(16- n)SH in CH_2Cl_2 for 48 h. The resistance values were determined by a least-squares fit of the impedance spectra with a Randles model. (b) Based on eq 4, a plot of $(mC)^{-1}$ versus n/m for the partially fluorinated SAMs should yield a straight line with a slope of $d_{\text{CH}_2}/\epsilon_0\epsilon_{\text{CH}_2}$ and an intercept of $d_{\text{CF}_2}/\epsilon_0\epsilon_{\text{CF}_2}$. The line represents a least-squares fit to the data and exhibits a correlation coefficient of 0.997. The open symbol represents the $(mC)^{-1}$ value for a nonfluorinated SAM prepared from C_{16}SH , which clearly fails to fall along the linear extrapolation of the partially fluorinated SAMs.

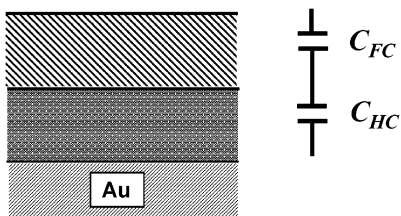


Figure 5. Two-layered model used to describe the capacitance of these partially fluorinated SAMs, as given by eqs 1–3. The fluorocarbon and hydrocarbon layers are modeled as capacitors in series.

fluorinated. Colorado et al.³⁸ have previously shown that the ellipsometric thicknesses of these films are essentially constant with increasing fluorination despite the more normal orientation of the fluorocarbon segments. Therefore, the decrease of capacitance with n is more likely due to a lower overall dielectric constant as n increases, consistent with the fact that fluorocarbon polymers such as poly(tetrafluoroethylene) exhibit lower dielectric constants ($\epsilon = 1.9$ – 2.1) than hydrocarbon polymers such as polyethylene ($\epsilon = 2.3$).³⁹ Surprisingly, the capacitance for the SAM prepared from unsubstituted C_{16}SH ($n = 0$) is lower than those for the partially fluorinated SAMs and fails to follow the observed trend. This result is consistent with that of Barbour and Lennox,¹⁶ who observed that methyl-terminated n -alkanethiols formed SAMs that exhibited lower capacitances than those for partially fluorinated SAMs of similar thickness.

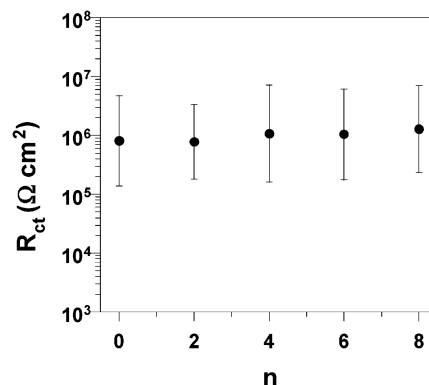


Figure 6. Influence of fluorocarbon chain length (n) on the charge-transfer resistance of SAMs prepared by exposure of gold to 0.2 mM FmH-(16- n)SH in CH_2Cl_2 for 48 h. The resistance values were determined by a least-squares fit of the impedance spectra with a Randles model.⁵

To determine the dielectric constants for the fluorocarbon and hydrocarbon regions based on the capacitance data shown in Figure 4a, we model the partially fluorinated SAM as a bilayer consisting of a hydrocarbon region nearest the metal surface and a fluorocarbon region at the solution/SAM interface (Figure 5). Similar to Naud et al.,¹⁸ we have neglected the capacitances of the thiol headgroup and the SAM–solution interface because of their relatively high values (low values for inverse capacitance). The measured capacitance (C) of the SAM can then be expressed as two capacitances in series

$$\frac{1}{C} = \frac{1}{C_{\text{FC}}} + \frac{1}{C_{\text{HC}}} \quad (1)$$

where C_{FC} and C_{HC} represent the capacitances of the fluorocarbon and hydrocarbon regions, respectively. Based on a Helmholtz model of the interface,² these capacitances can be written as

$$C_{\text{FC}} = \frac{\epsilon_{\text{CF}_2}\epsilon_0}{nd_{\text{CF}_2}} \quad (2)$$

$$C_{\text{HC}} = \frac{\epsilon_{\text{CH}_2}\epsilon_0}{md_{\text{CH}_2}} \quad (3)$$

where ϵ_0 is the permittivity of vacuum and d_{CH_2} and d_{CF_2} are the incremental thicknesses of each methylene or perfluoromethylene unit, taken as 1.18 and 1.23 Å, respectively.³⁸ Combining eqs 1–3 and dividing each term by m yields

$$\frac{1}{mC} = \frac{d_{\text{CH}_2}}{\epsilon_{\text{CH}_2}\epsilon_0} + \frac{d_{\text{CF}_2}}{\epsilon_{\text{CF}_2}\epsilon_0} \frac{n}{m} \quad (4)$$

which is in a convenient slope-intercept form.

To test the validity of the capacitance model in eq 4, we have taken the data from Figure 4a and plotted $(mC)^{-1}$ versus n/m in Figure 4b. The extremely high linearity (correlation coefficient = 0.997) of these data suggests that eq 4 does indeed describe the layered composition of these partially fluorinated alkanethiolate SAMs. The slope of the plot in Figure 4a yields a dielectric constant for the fluorocarbon region (ϵ_{CF_2}) of ~ 1.7 . Fluorocarbon polymers typically exhibit dielectric constants of 1.9–2.1, with the lower values in this range corresponding to polymers with CF_3 groups in the side chain.³⁹ The dielectric constant of ~ 1.7 observed here is likely due to the predominate effect of the $-\text{CF}_3$ group in each molecular chain, suggesting

TABLE 1: Influence of the Degree of Fluorination on the Exchange of Fluorinated SAMs

adsorbate	coverage ^{a,b}
F2H14SH	0.50
F4H12SH	0.57
F6H10SH	0.57
F8H8SH	0.67

^a SAMs were exposed to 1 mM C₁₆SH in ethanol for 24 h.

^b Approximate errors are ± 0.05 based on the standard deviation of results from multiple independent preparations.

that the terminal group has a significant affect on the overall dielectric constant as well as the capacitance of the film. This lower dielectric constant may also reflect the lower density of the fluorocarbon segments constrained within the SAM as compared to macromolecular chains in the bulk state. The intercept in Figure 4a yields a dielectric constant for the hydrocarbon region (ϵ_{CH_2}) of ~ 2.3 , which is identical to that reported for polyethylene films.³⁹ The data point at $n/m = 0$ corresponds to that for a SAM prepared from nonfluorinated C₁₆SH which, again, fails to follow the trend exhibited by the partially fluorinated SAMs. The lower capacitance of the nonfluorinated SAM might reflect the more insulating nature of the methyl group (compared to a methylene group) combined with a different structure of the hydrocarbon chains in the absence of the fluorinated groups. Dielectric constants of methyl-terminated *n*-alkanethiolate SAMs have been reported as ~ 2.1 , measurably lower than that for polyethylene.^{5,40}

Figure 6 shows the influence of fluorination on the charge-transfer resistance of the partially fluorinated SAMs. Across different experiments, the reproducibility of resistance measurements for these SAMs was less than that of capacitance measurements as indicated by the larger error bars in Figure 6 compared to those in Figure 4. Nevertheless, neither across all five repeated experiments nor within any one experiment did we observe any significant trend in resistance based on the extent of fluorination. Resistance measurements are more sensitive to the defect density within a SAM than are capacitance measurements,⁴¹ and the relatively high resistance values shown in Figure 5 indicate that all of the films studied, regardless of the extent of fluorination, are highly blocking with extremely low defect densities. These results suggest that partially fluorinated SAMs, which exhibit enhanced stabilities in comparison with hydrocarbon SAMs,¹⁰ would provide outstanding barrier properties to impact applications such as corrosion inhibition and lithographic etch resists.

Influence of Solvent and Fluorination on Exchange. A SAM will lose some of its adsorbates when exposed to a solution of a competing adsorbate because of exchange or displacement reactions. The stability of a SAM against exchange has been related to its defect content,^{42–44} solvent-adsorbate interactions,⁴⁵ and interchain interactions.^{43,46,47} The present system can provide fundamental information on the exchange process because varying the fluorocarbon chain length affects both interchain interactions and solvent-adsorbate interactions while the defect content of these monolayers is similar, as suggested by Figure 6. Thus, we have investigated the exchange of partially fluorinated hexadecanethiols by exposure to a 1 mM solution of nonfluorinated C₁₆SH in ethanol for 24 h (Table 1). We estimated the coverage of the partially fluorinated adsorbates (ϕ_{CF}) after the exposure by using the measured hexadecane contact angles and Cassie’s equation

$$\cos \theta_{\text{meas}} = \phi_{\text{CF}} \cos \theta_{\text{CF}} + (1 - \phi_{\text{CF}}) \cos \theta_{\text{CH}} \quad (5)$$

TABLE 2: Effect of Solvent on Exchange^{a,b}

solvent	F2H14SH coverage	F8H8SH coverage
isooctane	0.89	0.92
liq CO ₂	0.85	0.91
ethanol	0.50	0.67
trifluoroethanol	0.69	0.63

^a SAMs prepared from F2H14SH or F8H8SH on gold were exposed to 1 mM C₁₆SH in the listed solvents for 24 h. ^b Approximate errors are ± 0.05 based on the standard deviation of results from multiple independent preparations.

where θ_{meas} is the measured advancing contact angle of hexadecane, θ_{CF} is the contact angle on the pure partially fluorinated SAM, and θ_{CH} is the contact angle on the pure nonfluorinated C₁₆ SAM. For all partially fluorinated SAMs, the coverage of the fluorinated adsorbates (ϕ_{CF}), which is initially at 1.0, decreases upon exposure to C₁₆SH after 24 h. In general, Table 1 shows that increased fluorination produces a SAM that is more stable against displacement by a competing adsorbate, although the differences observed here are modest. The partially fluorinated SAMs studied here are significantly more stable against exchange than those composed of HS-(CH₂)₁₁OCH₂CF₂CF₃, where 80% of the SAM was displaced within 24 h under identical conditions.⁴⁸ The greater chain length and the absence of the ether linkage in the current study produces a more crystalline structure, as shown by RAIRS, that might be responsible for stabilizing the SAMs against exchange. The slight differences in stability with increased fluorination, as shown in Table 1 perhaps arise from enhanced levels of interchain interactions and/or poor solubility of the partially fluorinated adsorbates in ethanol, both of which should improve the stability of the SAM against exchange.

To address the various mechanistic aspects of the exchange process, we varied the solvent to examine its interactions with both the immobilized adsorbate and the competing adsorbate in solution. Table 2 shows the influence of solvent on the exchange of two different partially fluorinated SAMs (prepared from F2H14SH and F8H8SH) with 1 mM C₁₆SH. Both SAMs exchange to a lesser degree when exposed to less polar solvents, such as isooctane and liquid CO₂ (103 bar), than when exposed to ethanol and 2,2,2-trifluoroethanol. The tendency for the SAMs to exchange less in liquid CO₂, a good solvent for fluorocarbons, than in ethanol, an inferior solvent for fluorocarbons, suggests that the interactions between solvent and immobilized adsorbate are less important than those between the solvent and the competing adsorbate. For example, long-chain alkanethiols are known to be much less soluble in polar solvents such as ethanol than in alkanes.⁴⁵ The less favorable interactions between C₁₆SH and ethanol or 2,2,2-trifluoroethanol can plausibly promote interactions between the nonpolar thiol and the low-energy surface of the partially fluorinated SAMs. Surfactants and long chain alcohols form highly ordered bilayer structures on low-energy surfaces in water,⁴⁹ and alkanethiols have been proposed to form bilayer structures on low-energy surfaces in ethanol.⁴⁰ The weak interactions between these polar solvents and the competing adsorbate, coupled with the high interfacial free energy between the fluorinated surface and the polar solvent, might effectively increase the concentration of the competing thiol at the vicinity of the metal surface and thereby promote displacement.

Conclusions

Our results suggest that the quality of partially fluorinated monolayer films prepared from F_nH_mSH is sensitive to solvent

and that the use of a strong solvent for fluorocarbons leads to films with inferior properties. By using partially fluorinated hexadecanethiols, we have been able to address in a systematic manner the influence of fluorination on the structural and electrochemical properties of monolayer films. Increasing the extent of fluorination results in an orientation of the fluorocarbon helical axis that is more normal to the metal surface and also reduces the capacitance of the monolayer because of the presence of a thicker region of low-dielectric fluorocarbon near the SAM/aqueous interface. Increasing the extent of fluorination does not significantly influence the charge transfer resistance of the films, which is uniformly high, or their tendency to exchange when exposed to solutions of $n\text{-C}_{16}\text{SH}$. The use of more polar solvents does promote exchange, which is consistent with a decreased solubility of the competing adsorbate that enhances its concentration at the SAM/solution interface.

Acknowledgment. We thank the National Science Foundation (G.K.J. and R.D.W., Grant CTS-0203183; T.R.L. Grant DMR-9700662) for financial support of this work. Additional support for T.R.L. was provided by the Robert A. Welch Foundation (E-1320) and the Texas Advanced Research Program (003652-0307-2001). We would also like to thank Thomas C. Kopec of Villanova University for assistance in performing experiments.

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