STRUCTURAL MODIFICATION OF PARTIALLY FLUORINATED ALKANETHIOLS: THEIR IMPACT ON THE PROPERTIES OF FLUORINATED SELF-ASSEMBLED MONOLAYERS

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In Partial Fulfillment

of the Requirements for the Degree of

Doctor of Philosophy

By

Oussama Zenasni

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Dedicated to my parents and my wife, Mohammed Zenasni, Houaria Chwirif, and Ismahan Lounas For the love and the outstanding support during my

Academic endeavor.

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ABSTRACT

The ability to fine-tune structural parameters for partially fluorinated alkanethiols opens avenues for the fabrication of fluorinated films with certain targeted physical properties. This dissertation focuses on the modification of fluorinated alkanethiols in order to provide new types of fluorinated self-assembled monolayers (SAMs) as model films to study their physical properties. In one study, we developed a new fluorinated surfactant that bears a methyl terminal group; $CH_3(CF_2)_6(CH_2)_nSH$ (H1F6HnSH where n = 10, 11). This amphiphile created an unprecedented HC–FC dipole at the SAMs interface. When comparing the structural properties of SAMs of H1F6H11SH to those of octadecanethiol and 18,18,18-trifluorooctadecanethiol, films generated from H1F6H11SH were found to have a well-packed underlying hydrocarbon assembly. However, this property disrupts the orderliness of the perfluorinated segments, which gives rise to anomalies in the interfacial properties when comparing even and odd numbered chains.

To draw a deeper understanding of the role of the underlying fluorinated segment, we synthesized and generated monolayers from alkyl-capped partially fluorinated alkanethiols; $H(CH_2)_n(CF_2)_6(CH_2)_{11}SH$ (HnF6H11SH; where n = 3, 4, 5). These films revealed three important findings: 1) the HC–FC dipole ceases to affect the wetting behavior of the films as it is buried underneath the alkyl unit, 2) the orientation of the terminal methyl follows an odd-even trend as a function of the size of the upper alkyl segment and 3) a disordered interface is generated when extending the alkyl cap to five hydrocarbons.

A separate study involves the manipulation of the interfacial properties of SAMs by introducing three new surfactants that are highly fluorinated with a small propyl unit as an alkyl spacer: $F(CF_2)_n(CH_2)_3SH$, FnH3, where n = 8, 10, 12. An evaluation of the performance of the FnH3 series in relation to the known SAMs using ellipsometry, XPS, and wettability analysis, indicate that the newly fluorinated surfactants not only behave similar to those formed with the shorter ethyl spacer, but they also provide an improved packing structure. Such work expands the scope of molecules that generate films that are close to a completely perfluorinated surface, while improving the packing ability of the adsorbates.

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Chapter 1: The Impact of Fluorination on the Structure and Properties of Self-Assembled Monolayer Films¹

1.1. Introduction

Over the past two decades, fluorinated thin films have continued to draw the interest of scientists, engineers, and application specialists. The ability to generate such films via the adsorption of fluorinated amphiphiles on either coinage metals or oxide interfaces has provided a vital tool to modify surfaces in various technologies such as corrosion prevention,¹ microelectromechanical systems (MEMS),² and biomaterials coatings.^{3,4} Much of this attention draws from the fact that the introduction of a fluorocarbon segment in an amphiphile changes important physical properties of the generated films, including friction and wettability,^{5–7} and work function and capacitance.^{8–10} Furthermore, depending on the size of the perfluorinated segment, the thermal stability of the resulting film can also be enhanced.¹¹

Self-assembled monolayers (SAMs) derived from the adsorption of partially fluorinated organic thiols on gold have become a widely used platform for studying fluorinated organic thin films (FSAMs), and are frequently evaluated in light of their nonfluorinated counterparts (HSAMs). For both types of monolayer systems (Scheme 1.1), the spontaneous adsorption of the organosulfur headgroup is followed by the alignment/packing of the tailgroups, which allows for maximum interchain van der Waals (vdW) interactions. As a substrate, gold makes for an excellent platform for these

¹ Reproduced with permission from Zenasni, O.; Jamison, A.C.; Lee, T. R. *Soft Matter.* **2013**, *9*, 6356. Copy Writes RSC 2013. Please See Appendix 1 for more details.

fundamental studies due to its inertness and relative ease of handling in a laboratory environment; moreover, SAMs derived from the adsorption of organosulfur adsorbates on gold allow detailed structure-property studies at the nanoscale that are not readily feasible on substrates that are technologically more useful and typically more heterogeneous. Since HSAMs have been studied extensively, numerous reviews on this topic can be found in the literature.^{12–15}

Scheme 1.1. The Formation of SAMs via the Adsorption of Organothiols on Gold



The ability to functionalize alkanethiol chains with endgroups bearing the most electronegative atom also opens avenues to exploring the use of SAMs in a variety of technologies.¹⁶ This research has been enabled by the facile preparation of terminally fluorinated compounds and the incorporation of these adsorbates into FSAMs, allowing for systematic studies on the impact of such fluorine incorporation on the properties of organic thin films.^{17–19} For example, SAMs derived from highly perfluorinated alkanethiols on gold are poorly wet by both both water and oil, revealing increased hydrophobicity and oleophobicity when compared to SAMs derived from their normal alkanethiol counterparts. Furthermore, highly fluorinated FSAMs are more thermally stable, better antibiofouling agents, and more biologically and chemically inert when

compared to HSAMs. On the other hand, the addition of limited fluorination to the adsorbate structure changes the properties of the resulting monolayers in unique ways. Notably, the introduction of a trifluoromethyl group to the thiolate chains gives rise to an oriented dipole at the SAM interface that dramatically influences the physical properties of the resulting films.^{16,20,21} Furthermore, increasing the number of fluorinated carbons at the terminus of the chain can transform the resulting FSAM film so that its interfacial characteristics are comparable to that of polytetrafluoroethylene (PTFE). In this account, we aim to present research that reveals how the structure of the fluorinated thiol adsorbates dictates the properties of the generated films, with an emphasis on film structure, interfacial energy, electronic properties, and thermal stability. This review also endeavors to link the knowledge gained from these fundamental studies to the use of FSAMs as a model for fluorinated amphiphiles in a variety of applications.

1.2. Influence of Adsorbate Architecture on Monolayer Structure

Many of the unique geometrical features of FSAMs arise from the replacement of C–H bonds by C–F bonds, which are the strongest organic covalent bonds known (105.4 kcal mol⁻¹).²² The nature of the two bonds are completely different, with hydrogen being slightly less electronegative than carbon (2.1 vs. 2.5, respectively) and fluorine being markedly more electronegative (4.0 on the Pauling scale).^{22,23} Consequently, the C–F bond exhibits electrostatic character, which leads to strong dipole interactions, but generally not H-bonding.²² The positive charge density on the carbon due to the polarization of the C–F bond increases with progressive replacement of hydrogen with fluorine, which is consistent with the shortening in the C–F bond length upon going from

fluoromethane to difluoromethane to trifluoromethane.^{22,24} Furthermore, the H–C–H bond angle changes depending on the number of fluorine atoms connected to the central carbon, reflecting a shift in electron density toward the fluorine atoms. Non-fluorinated methane has an H-C-H bond angle of 109.5°, which changes to 110.2° for fluoromethane as compared to 113.8° for difluoromethane.²² In the case of adding multiple fluorine atoms along a hydrocarbon chain, the polarization of the C–F bond influences the geometry of the chain such that the gauche conformation in 1,2-difluoroethane is favored by 0.5–0.9 kcal mol⁻¹ due to hyperconjugation of the σ_{C-H} orbital with the σ_{C-F}^* orbital.²² A computational analysis conducted for long chains with multiple mono-fluorinated carbons in all syn conformations indicated that the fluorine atoms were inclined to adopt a helical arrangement that produced 1,2-gauche alignments while avoiding 1,3-diaxial repulsions between fluorine atoms.²⁵

Importantly, the conformational alignments for fully fluorinated chain are strongly influenced by relative atomic sizes of hydrogen and fluorine, with the van der Waals (vdW) radius for hydrogen being ~1.2 Å and that of fluorine ~1.47 Å.^{26,27} While the greater size of fluorine gives rise to unequal spacing between sterically repulsed fluorines along an extended CF₂ chain, the overall chain conformation reflects a compromise between steric, structural, and orbital influences.²⁸ For shorter chain lengths, this effect leads to a dihedral angle for \angle F–C–C–F that ranges from 46–49° versus 60° for \angle H–C–C–H in the all anti-zigzag structure observed for well-ordered hydrocarbon chains.²⁹ Thus, in the case of extended perfluorinated segments, a helical structure is favored instead of the planar all *trans*-extended conformation of saturated

alkyl chains. This phenomenon was revealed in an early X-ray diffraction study in which perfluorinated polymers were found to exhibit a 180° twist for every 13 chain atoms.²⁸ Thus, the fluorocarbon chain is said to adopt a helix conformation of 13/6 (units per turn), where the equivalent of 6 turns (zig-zags) occurs in 13 CF₂ units.³⁰ A 15/7 helix has also been reported, the result of a slight untwisting of the 13/6 helix due to a first-order transition at 19° C.³⁰ Consequently, short perfluorinated chains exhibit a rigid rod-like structure in contrast to the more conformationally flexible hydrocarbon chains. The vdW diameter of the two systems is also different, with ~5.6 Å for perfluorinated chains and ~4.2 Å for hydrocarbon chains.

The impact of limited levels of fluorination on the structure of thin films formed through self-assembly can be found in the literature from the 1950's and 1960's. They include molecular structures with varying degrees of terminal fluorination (e.g., CF₃ groups), but the insight gained with these studies was limited by several factors, including the instrumental methods available at the time.^{33–35} Since the development of modern SAM research techniques and the shift to thiol adsorbates on metal surfaces,^{36,37} a large variety of SAM systems have been analyzed. CF₃-terminated films have served as useful models for evaluating the effect of minimal fluorination on the properties of FSAMs. Variation solely at the terminus can preserve the structural characteristics of HSAMs, such as packing density, lattice spacing, and the ordering of the film.^{38–41} Pflaum *et al.* evaluated the differences in structure for CF₃-terminated versus CH₃-terminated monolayers using scanning tunneling microscopy (STM), surface-grazing incidence X–ray diffraction (GIXD), and helium scattering.¹⁶ Their STM results, which concentrated predominantly on decanethiol and ω,ω,ω -trifluorodecanethiol, showed that

in the close-packed phase (standing-up phase), the interchain distance of CF₃-terminated SAMs is equal to that found in an HSAM (~5 Å). However, while CF₃-terminated films have a rotational six-fold symmetry, they lack a long-range order as compared to HSAMs, which have $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer structure. The GIXD and X-ray reflectivity results in this study confirmed the lack of long-range order in CF₃-terminated films. The differences were attributed to the larger vdW radius of the CF₃ endgroup (~2.7 Å) compared to the CH₃ endgroup (~2.0 Å).^{16,42}

Additionally, it has been suggested for CF₃-terminated chains that the shift in electron density toward the fluorine atoms leads to charge repulsion among the end groups, thus perturbing the molecular order of the films at the surface-vacuum interface, making them less well-defined compared to the interface of HSAM films.¹⁶ However, increasing the number of methylenes in the alkyl spacer, which increases the vdW interactions between the alkyl chains, lessens the impact of charge repulsions, as has been shown in several other studies on the molecular packing of CF3-terminated SAMs.^{38–41} In addition, Kim and co-workers have shown that the size of the terminal group also affects the frictional properties of the film.^{38,41} Specifically, CF₃-terminated SAMs exhibit a higher frictional response than their CH₃-terminated analogs. This conclusion was supported by studies of isopropyl-terminated SAMs, which also exhibited an elevated frictional response.⁴¹ Furthermore, while the bulky isopropyl endgroup influenced the interfacial properties of the films, PM-IRRAS data confirm that the hydrocarbon backbone in all of these films aligned in well-packed structures with relative degrees of crystallinity that were indistinguishable.

Knowledge regarding how the molecular structure of fluorinated alkanethiols impacts the packing structure of the resulting FSAMs is crucial to understanding the interfacial properties of the films. While the study of completely fluorinated alkanethiols on gold remains elusive due to synthetic limitations, the influence of the aforementioned geometrical changes to the fluorocarbon chains is revealed in the differences in lattice structures of SAMs of alkanethiols with extended perfluorinated segments versus aliphatic alkanethiols on Au(111).^{43–46} Alves and Porter used atomic force microscopy (AFM) to show that perfluorinated alkanethiols bearing a short methylene segment, $CF_3(CF_2)_8(CH_2)_2SH$ (F8H2SH), form a (2×2) adlayer with a nearest-neighbor distance Independently, Liu et al. using AFM and GIXD, found that SAMs of ~5.8 Å.⁴³ $CF_3(CF_2)_n(CH_2)_2SH$ (FnH2SH) on Au(111), where n = 5, 7, 11, adopt a hexagonal lattice with a nearest-neighbor distance of 5.7 ± 0.2 Å.⁴⁴ While the lattice spacing found in these studies was similar, the latter authors concluded that the "packing is incommensurate or at most only close to the high-order commensurate $c(7 \times 7)$ structure." They also noted a 30° rotation of the fluorinated chains with respect to the Au(111) lattice.44 The structure of these adsorbates differs from the well-studied system of HSAMs on gold, which form a $(\sqrt{3} \times \sqrt{3})R30^\circ$ adlayer on Au(111) with a nearest-neighbor distance ~ 5.0 Å.^{47,48} The differences in the two systems arise from the fact that the perfluorocarbon segments form rigid helices, in contrast to the conformationally flexible chains of HSAMs, with the larger vdW diameter of the former influencing the surface structure.41,44

The tilt angle of the perfluorinated segments of FSAMs also differs from that of HSAMs, reflecting systematic changes in the monolayer organization required to produce a well-packed film.⁴⁴ Using a variety of surface techniques, Lenk *et al.* studied FSAMs

having short methylene spacers (i.e., derived from $CF_3(CF_2)_8C(O)N(H)CH_2CH_2SH$; **F8AmdH2SH**).⁴⁹ These authors noticed that when comparing the intensities of the vibration bands associated with a resultant dipole parallel or perpendicular to the fluorocarbon helix ($v_{ax}^{CF_2}$ and $v_{pd}^{CF_2}$, respectively) in the surface IR of the FSAM as compared to that obtained from a KBr pellet of the free thiol, the increase in the relative intensities of the axial bands indicated that the FSAM fluorinated segments were aligned almost normal to the surface. Frey *et al.* calculated the tilt angle of the fluorinated helix in FSAMs, including those derived from $CF_3(CF_2)_9(CH_2)_2SH$ (**F10H2SH**), using angledependant near-edge X-ray absorption fine structure spectroscopy (NEXAFS) and found it to be ~11° from the surface normal.⁵⁰ On the other hand, the alkane chains in HSAMs tilt ~30° from the surface normal.⁵¹ The difference in the tilt angle of the fluorocarbon versus hydrocarbon chains of the respective monolayers has been attributed to the size of the perfluorinated chains as compared to normal hydrocarbon chains.^{31,43}

Notably, the reported tilt angles provide additional insight into the nature of the surface alignment. Chidsey *et al.* concluded that in order for the fluorinated segments in a SAM formed from F8H2SH to assume a densely packed commensurate adlayer similar to an HSAM, the chains must tilt ~16° from the surface normal.³¹ Thus, a reduction in the tilt angle might indicate a failure of the thiolate headgroups to adopt consistent spacing on the Au(111) surface. In addition, a recent STM study by Patole *et al.* examined the SAMs formed from CF₃(CF₂)₅(CH₂)₂SH (**F6H2SH**) versus that of the equivalent HSAM on Au(111).⁴⁶ **F6H2SH** adopts a $p(2\times2)$ structure with nearest neighbor spacing of 5.7 Å, which is in agreement with the results observed in previous studies. The authors also noticed a height variation in the one-dimensional molecular alignment of these FSAMs as compared to the HSAMs. While the PM-IRRAS data

correlated well with those observed in earlier work done on FSAMs with small methylene spacers, molecular modeling calculations showed the possibility of different tilt angles of the chains due to different adsorption sites in the $p(2\times2)$ registry. Further support was provided by their simulated STM image, which showed height differences that were in agreement with their experimental work.⁴⁶

Additional research has focused on the structure of several series of FSAMs generated from combinations of increased terminal fluorination and/or variation in the length of the underlying methylene spacer. If the monolayer film is considered a bilayer system, the ordering of the film varies according to the size of underlying alkyl segment. The tilt angle for the hydrocarbon moiety increases to maximize interchain vdW interactions, thus influencing the packing structure and and the orientation of the fluorinated segment. Tamada et al. have shown that for FSAMs generated from $CF_3(CF_2)_9(CH_2)_nSH$ (F10HnSH, where n = 2, 6, 11, 17, 33), increasing the number of methylene units leads to a distorted AFM image (see Figure 1.1).⁴⁵ While the nearestneighbor distance is 5.9 ± 0.1 Å, consistent with what has been observed in other FSAMs,^{43,44} the hexagonal ordering of the molecules at the surface becomes poorly defined as n increases. These researchers also observed a shift in the binding energy of the C 1s spectra from X-ray photoelectron spectroscopy (XPS) of these monolayers to a higher binding energy. This shift was attributed to charging that results from secondary electrons generated in the XPS process being trapped in the monolayer, an indication of an increase in packing density for the hydrocarbon chains as the number of methylene units increases from 2 to 33. Thus, the observed disorder in the AFM images as the chain lengths increased was rationalized by an increase in the packing of the hydrocarbon segment as a function of increasing n due to higher vdW attractive forces among the alkyl

chains. This effect brings the hydrocarbon segments closer to each other on average, which leads to increased disordering in the overlying perfluorinated segments as they are pressed to fit their larger vdW diameter chains into alignments dictated by the underlying hydrocarbon assembly.



Figure 1.1. Increase in blurriness in AFM images for FSAMs as the number of methylene units increases from two in (a) **F10H2SH** to eleven in (b) **F10H11SH**. Also, one-dimensional schematics for the FSAM derived from (c) **F10H2SH** and (d) **F10H11SH**. The AFM images are reproduced with permission from Ref. 45.

These observations correlate with observations by Fukushima and co-workers in their polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) analysis of these FSAMs.⁵² The antisymmetric CH₂ stretch ($v_a^{CH_2}$) appears at 2919 cm⁻¹ for n = 11, 17, and 33, whereas the $v_a^{CH_2}$ appears as a broad peak from 2920 to 2930 cm⁻¹ for n = 6. Based on earlier studies of HSAMs, the position and width of the $v_a^{CH_2}$ band reflects the structural conformation along the alkyl chain; specifically, the band shifts to lower energy and sharpens when the chains are more crystalline (i.e., a predominantly *trans*-extended alignment for the chains), with the peak appearing near 2918–2919 cm⁻¹.^{51,53,54} Therefore, the value of $v_a^{CH_2}$ in Fukushima's study indicates that for n = 11, 17, and 33, the methylene units are predominantly *trans*-extended, whereas for n = 6, there is a greater presence of gauche conformations, and the underlying alkyl chain assembly is more "liquid-like". As for the tilt angle for the hydrocarbon segments in such FSAMs, Frey *et al.* found averages of 32° for **F10H11SH** and 38° for **F10H17SH** based on results from angle-dependent NEXAFS.⁵⁰

The authors also observed systematic changes in the IR spectra in the region of the C–F vibrations. Using the relative band intensity for $v_{ax}^{CF_2}$ and $v_{pd}^{CF_2}$ and the surface selection rules, a stepwise increase in the intensity of the perpendicular band to that of the axial band with the increased number of methylenes is consistent with an increase in the tilt of the fluorocarbon helix. Further, based on these IR studies, increasing the number of methylene units from n = 2 to n = 33 increases the order of the hydrocarbon segment; however, it also induces a slight disorder in the orientation of the terminal fluorocarbon helices. Frey *et al.* used angle-dependent NEXAFS to calculate the tilt angle of the perfluorodecyl groups in FSAMs of CF₃(CF₂)₉(CH₂)_nSH (F10HnSH, where n = 2, 11, 17) on gold, finding 11° for F10H2SH, 20° for F10H11SH, and 24° for F10H17SH.⁵⁰ Colorado *et al.* have also used PM-IRRAS data to evaluate the structure of FSAMs having a constant total chain length and where the underlying hydrocarbon backbone was

held constant.⁵⁵ These investigations revealed that the position of the axial bands ($v_{ax}^{CF_2}$) increases systematically with the number of fluorocarbons in the chain regardless of the chain tilt, suggesting that the $v_{ax}^{CF_2}$ band position can be used to determine the length of the perfluorocarbon segment of FSAMs.

The ability to generate binary mixed monolayers can be used to tune the interfacial properties of a film. To describe the properties, Cassie's law is often invoked, where the net character of the interface proportionately reflects the character of the component parts according to the relative presence of the adsorbates in the film.^{12,56} Li et al. generated SAMs from a mixture of 16,16,16-trifluorohexadecanethiol (F1H15SH) and normal pentadecanethiol or hexadecanethiol via co-adsorption from isooctane.⁵⁷ The resulting surface composition approximately equaled the solution composition. Furthermore, AFM images showed large areas of homogenously formed surface and no domains or "islands". Islanding, however, is known to occur for mixed SAMs of perfluorinated thiols when the two adsorbates possess a substantial difference in structure, such as a large difference in (1) total chain length or the length of the perfluorinated segment of the adsorbates, (2) the solubility of the adsorbates, or (3) the packing characteristics of the adsorbates.⁵⁸⁻⁶¹ For example, Tsao *et al.* reported that the co-adsorption of F8AmdH2SH and F8H11SH from solution gives rise to mixed SAMs where the surface composition of F8H11SH is higher than that in solution due to competitive adsorption and the greater surface stability offered by the methylene units in the longer chain.⁵⁹ Patole *et. al* investigated the exchange process between normal octanethiol and fluorinated octanethiol (F6H2SH).⁶² Aside from the dissimilarity in chemical structure, octanethiol forms a close-packed monolayer with a $(\sqrt{3} \times \sqrt{3})R30^{\circ}$ adlayers on Au(111), where as F6H2SH forms a less densely packed structure based on a

 $p(2\times2)$ adlayer. The authors found that the formation of a **F6H2SH** SAM followed by exchange with octanethiol leads to a homogenous distribution of octanethiol throughout the film. In contrast, when the octanethiol SAM is formed first, the exchange by **F6H2SH** occurs with the formation of domains. This difference suggests that the exchange processes are easier for films with relatively loose packing structures.⁶² However, covalently linking the two adsorbate chains can be used to overcome the issues of disproportionate adsorption and domain formation (see Figure 1.2).^{63–66}



Figure 1.2. Structure of adsorbates where fluorocarbon and hydrocarbon chains are linked covalently by means of a disulfide bond (**left**) or a double-chained monothiol (**right**).

1.3. Impact of Adsorbate Architecture on Surface Energy

One important application of fluorinated films centers on their use as coatings that are non-wettable and/or anti-adhesive.⁶⁷ Highly fluorinated organic materials are more hydrophobic and oleophobic than their hydrocarbon counterparts.^{68,69} Recent theoretical work on water solvation of perfluorocarbons and hydrocarbons has found that the

increase in hydrophobicity of the former is due to the greater diameter of these chains, which gives rise to a larger energy penalty for hydration.⁷⁰ In a hydrocarbon medium, the attractive dispersive interactions are weaker among fluorocarbons and hydrocarbons than between hydrocarbons alone.^{20,71} While this phenomenon is consistent with contact angle studies of highly fluorinated FSAMs, which are poorly wettable by both water and hydrocarbon liquids,³¹ the wettability of SAMs (and thus the interfacial surface free energy) are greatly affected by the degree of fluorination and the total chain length of the thiol adsorbates. In an exceptional case, Lee and co-workers demonstrated that CF₃terminated SAMs exhibit lower contact angles with polar contacting liquids than their hydrocarbon analogues.^{20,72} While some researchers speculated that such an outcome was tied to hydrogen bonding between fluorines at the interface and susceptible contacting liquids, a systematic study of the wettability of FSAMs derived from CF₃terminated alkanethiols, $CF_3(CH_2)_nSH$ with n = 9-15, and their HSAM analogues, $CH_3(CH_2)_nSH$ with n = 9–15, with a variety of contacting liquids, showed that the increases in wettability of polar liquids on such SAMs is due to the presence of a dipole at the hydrocarbon–fluorocarbon (R_H – R_F) junction. These results are in line with the observations of Zisman and co-worker, who proposed that this interaction was due to a force field dipole generated at the interface of the film.^{35,73}

As illustrated in Figure 1.3, the CF₃-terminated FSAMs are more wettable toward all polar contacting liquids than the analogous HSAMs. The fact that these minimally fluorinated films are more wettable, even with polar aprotic contacting liquids, suggests a phenomenon other than hydrogen bonding. Furthermore, for this FSAM series, chains with odd-numbered carbon chains are less wettable by polar aprotic liquids than those
with even-numbered carbon chains. The authors rationalized this parity or "odd-even" effect by noting that the R_H - R_F dipole at the interface in even-numbered SAMs is oriented roughly parallel with the surface normal (i.e., pointed toward the contacting liquid), while the R_H - R_F dipole in odd-numbered chains is oriented more perpendicular to the surface normal (i.e., head-to-tail with neighboring - CH_2 - CF_3 groups), thus minimizing the interaction of the dipole with the contacting liquid. Notably, the tilt of the dipoles in the odd-numbered chains enables them to compensate one another and reduce the magnitude of the net dipole field. Consequently, the dipole interaction with a polar aprotic contacting liquid is greater for the even-numbered SAMs than for the odd-numbered SAMs. Related odd-even phenomena have been observed in many SAM systems and summarized in a comprehensive review.⁷⁴ For nonpolar contacting liquids, the CF₃-terminated SAMs are less wettable than analogous HSAMs, which is consistent with weaker dispersive interactions between the fluorocarbon-terminated chains and the nonpolar contacting liquids.^{20,71,72}



Figure 1.3. (a) Advancing contact angle data for hexadecane (\bigcirc), acetonitrile (\bigtriangledown), DMF (\diamondsuit), water (\blacktriangle), and glycerol (\blacksquare) on SAMs generated from CF₃(CH₂)_nSH n = 9–15 (filled symbols) and CH₃(CH₂)_nSH = 9–15 (open symbols).⁷² (b) Schematic representation of homologous series of CF₃-terminated normal alkanethiolate adsorbates. The inset in (b) represents the orientation of the CF₃-terminal groups (R_H–R_F dipole) in odd and even numbered carbon chains. Figure 1.3a was reproduced by permission from Ref. 72.



Figure 1.4. Schematic representation of four series of SAMs used to evaluate the effect of terminal fluorination on FSAM surface energy. Series 1.1 are CF₃-terminated FSAMs ($CF_3(CH_2)_mSH$ where m = 12–15), Series 1.2 are partially fluorinated hexadecanethiol FSAMs ($F(CF_2)_n(CH_2)_mSH$ where n = 1–10 and m = 15–6), Series 1.3 are HSAMs with chain lengths analogous to CF₃-terminated FSAMs ($H(CH_2)_xSH$ where x = 13–16), and Series 1.4 are terminally fluorinated FSAMs where the fluorocarbon segments were systematically increased while the hydrocarbon segment was held constant ($F(CF_2)_n(CH_2)_{11}SH$, where n = 0–10).

The unique contact angle data collected on the CF₃-terminated FSAMs generated interest in studies of surface free energy as a function of the degree of terminal fluorination. Colorado et al. evaluated the importance of the interfacial dipole using wettability studies with a variety of contacting liquids.²⁰ The FSAM series used in this study was composed of $F(CF_2)_n(CH_2)_mSH$ where n = 1 and m = 12-15 (Series 1.1) and where n = 1-10 and m = 15-6 (Series 1.2), as shown in Figure 1.4. Both of these series were compared to HSAMs of the form $H(CH_2)_xSH$ where x = 13-16 (Series 1.3). From the collected data, the authors also determined that all CF₃-terminated SAMs of Series 1.1 are more wettable toward polar liquids than the HSAMs of Series 1.3, reinforcing the conclusions of the earlier study by Lee and co-workers.⁷² Furthermore, upon burying the R_H-R_F dipole in Series 1.2, the authors observed an increase in the contact angle values as the degree of terminal fluorination increased up to five fluorocarbons.²⁰ For the rest of the series, the polar contacting liquids showed no detectable response to the buried dipole. Similar results were observed in a separate study on a series of FSAMs that maintained a constant alkyl chain length beneath the fluorinated segments, $F(CF_2)_n(CH_2)_{11}SH$ (**FnH11SH**), where n = 0-10 (Series 1.4 in Figure 1.4).⁷⁵ Both of these studies indicate that the contact angles are more affected by the number of fluorocarbons in the terminal segment than the total chain length, assuming the latter provides sufficient distance between the perfluorinated segment and the underlying gold substrate.76

For these studies, the increase in contact angle values with increasing fluorination correlates with a reduction in the surface free energy of the FSAMs. Two key studies have shown how the measured changes in contact angles associated with the burying of a R_H-R_F dipole correlates to the surface free energy by calculating the work of adhesion for

these liquids on the FSAMs. Figure 1.5a shows the data collected for polar contacting liquids, where the polar component of the work of adhesion decreases systematically with increased fluorination, following the contact angle trends. Figure 1.5b shows that the value of the polar work of adhesion decreases for the series of FSAMs until four fluorocarbons, where it plateaus. At this point, the contacting probe liquid no longer senses the buried dipole of the R_H - R_F junction, and the interfacial interactions are merely dispersive in nature.⁷⁵ This result is similar to that obtained with Series 1.2.²⁰



Figure 1.5. (a) Contact angle values of water (\blacksquare), glycerol (\blacklozenge), acetonitrile (\triangledown), DMF (\blacktriangle), DMSO (\bigstar), and nitrobenzene ($\textcircled{\bullet}$) on FSAMs generated from Series 1.4 (FnH11SH). (b) The corresponding values of the dispersive work of adhesion (upper panel) and the polar work of adhesion (lower panel) of these liquids on Series 1.4. Reproduced by permission from Ref. 75.

The interaction of nonpolar liquids with fluorinated SAMs having an increasing degree of fluorination reveals the contributing factors that impact the calculated dispersive forces for such a series of SAMs. Specifically, the contact angles of nonpolar hydrocarbon and fluorocarbon contacting liquids have been observed to increase progressively on SAMs derived from **F1H11SH** to **F10H11SH**.^{20,75} Here, the liquids

interact not only with the outer most molecular layer, but also with the underlying methylenes. either hydrocarbon (phase-compatible) fluorocarbon or (phaseincompatible). This trend was rationalized by Colorado and co-workers using Hamaker theory, for which the dispersive energies at a surface are due not only to the type of molecular structures present at the interface, but also to the packing densities. For this series of FSAMs in which the length of the underlying hydrocarbon chain is held constant at C11 as shown in Figure 1.4 (Series 1.4), the termini of the fluorocarbon chains are less densely packed as the distance between the interface and the densely packed transextended hydrocarbon chains become greater, lessening the interfacial dispersive interaction energies. The generality of this phenomenon is further supported by a more recent study by Takenaga *et al.* of FSAMs derived from $CF_3(CF_2)_n(CH_2)_{12-n}SH$ (where n = 0, 1, 2, 3, and 9), which found that the magnitude of the Lifshitz-van der Waals interactions (γ^{LW}) decreases as the value of n increases.⁷⁷ In short, the studies collectively show that the surface energies decrease as the degree of fluorination increases, which consequently leads the films to become progressively more hydrophobic and oleophobic.^{20,75,77}

1.4. Effect of Adsorbate Architecture on Electron-transfer Properties

Certain key properties of organic electronic devices (e.g., lifetime and peak performance) are strongly influenced by the interface between the organic material and a metal or metal oxide surface.^{10,78} For example, charge injection in organic semiconductors depends on energy-level matching between the electrode and the contacting organic material.¹⁰ A large mismatch between the Fermi level of the metal

electrode and the highest occupied molecular orbital (HOMO) or lowest unoccupied molecular orbital (LUMO) level of the organic material leads to a barrier to the transport of holes or electrons, respectively.⁷⁹ The barrier can have a significant impact upon product design for polymer light-emitting diodes (LEDs), ambipolar field-effect transistors (FETs), or photovoltaic (PV) cells. The self assembly of amphiphilic molecules as an intervening monolayer for the inorganic-organic interface has been shown to provide a means of tuning the Fermi level or work function of an inorganic electrode, thus mitigating difficulties encountered in Fermi level matching of the electrode to conduction or valance bands of the organic layer.^{80–83} This tuning process is made more comprehensive by the fact that alkanethiolate and perfluoroalkanethiolate SAMs produce surface dipoles of opposite directions, thus providing a means of either decreasing (HSAM) or increasing (FSAM) the work function of the coated surface.^{21,79} Furthermore, SAMs can alter the morphology (interfacial organization/alignment) of the organic semiconducting layer owing in part to the change in surface energy for the SAMmodified inorganic interface, leading to reported improvements in product fabrication and device performance.⁷⁸ Reviews that discuss changes in device performance with respect to specific inorganic electrodes and coating materials can be found in the literature.^{10,84} In this section, we focus mainly on what happens to the vacuum level of gold in response to the adsorption of partially fluorinated thiols.

Upon the formation of a SAM, the change in work function of a metal (M) surface arises from the alignment of two dipoles that are present: the M–S dipole (reflecting the influence of the Au–S bond) and the oriented molecular dipole of the adsorbates (the R_{H} – R_F dipole in our FSAM studies).⁸⁵ Therefore, the change in the work function can be written as the sum of the two dipoles multiplied by the grafting density of the monolayer (N), which depends on the monolayer structure of the SAM on the metal.⁷⁹

$$\Delta \phi = -N \left[(\mu_{\perp \text{SAM}} / \varepsilon_{\circ} \kappa_{\text{SAM}}) + (\mu_{\text{M}-\text{S}} / \varepsilon_{\circ} \kappa_{\text{M}-\text{S}}) \right]$$
(1.1)

For Equation 1.1, the change in the effective M–S dipole, represented by the term ($\mu_{M-S}/\varepsilon_{o}\kappa_{M-S}$), is almost independent of the alkyl moiety. Whereas, the change in the molecular dipole, ($\mu_{sAM}/\varepsilon_{o}\kappa_{SAM}$), is strongly influenced by the chemical nature of the alkyl chains in the monolayer.

Figure 1.6 illustrates how the work function of a metal surface can be tuned depending on the chemical nature of the adsorbate molecules.^{79,86} Figure 1.6B shows that an HSAM decreases the work function, which can lower the electron-injection barrier.^{79,86} In contrast, Figure 1.6C shows that an FSAM increases the work function, which can lower the hole-injection barrier.



Figure 1.6. Schematic alignment difference between the work function of the metal (Φ_M) and the HOMO/LUMO levels of the organic semiconductor at the metal/organic interface. The +/- indicates the direction of the interface dipole generated by the SAM. (A) Electron-injection barrier (Φ_e) and hole injection barrier (Φ_h) for untreated surface. (B) HSAM creates an interface dipole (with direction toward the substrate) that lowers the electron-injection barrier (Φ_e) . (C) FSAM creates an interface dipole (with direction away from the substrate) that lowers the hole-injection barrier (Φ_h) . Adapted from Ref. 79.

To evaluate the contribution of both dipoles on the work function of gold, Rusu *et al.* modeled the adsorption of different thiolates on Au(111) using density functional theory.⁸⁵ Their study examined both fluorinated and normal alkanethiols, finding that the dipole contribution from the Au–S bond is approximately the same for all systems, and that the work function is independent of the adsorption site on the Au(111) surface. The authors also noted that the weakly polar nature of the Au–S bond means that its contribution to the overall surface dipole is small.^{80,85} However, changing the metal

surface to Ag gives rise to a greater influence on the overall work function due to the more highly polarized Ag–S bond.^{79,87}

On the other hand, the effect of the intrinsic molecular dipole, associated with the remainder of the adsorbate, on the work function is evident for both HSAMs and FSAMs, although their effects are opposite.⁷⁹ Studies by de Boer *et al.* compared the influence of well-ordered SAMs on the net work function using SAMs derived from hexadecanethiol and 1H,1H,2H,2H-perfluorodecanethiol (**F8H2SH**) on gold and silver.⁷⁹ Figure 1.7 shows that FSAMs formed from **F8H2SH** increase the work function of both metal systems; in contrast, HSAMs formed from hexadecanethiol decrease the work function of both metal systems. The major feature contributing to the difference centers on the relative direction of the molecular dipole, μ_{SAM} , compared to the M–S dipole, μ_{M-S} . In FSAMs, the two dipoles are pointing in the same direction, which serves to increase the effective work function. In HSAMs, however, the two dipoles are pointing in opposite direction. Additionally, the value of the effective M–S dipole is generally smaller than the molecular dipole for HSAMs. Therefore, the adsorption of HSAMs leads to a decrease in the work function on gold.⁷⁹



Figure 1.7. Value of the work function of gold and silver with and without HSAMs and FSAMs. Reproduced with permission form Ref. 79.

Alloway *et al.* have evaluated the influence of SAMs on the work function of gold as a function of the degree of fluorination (see Figure 1.8).²¹ Comparison of UVphotoemission spectra (UPS) of HSAMs formed from a progressive series of alkanethiols (C3SH to C18SH) show a negative shift in the low kinetic energy (KE) photoemission edge as the length of the alkanethiol chains increase, reflecting the influence of the oriented molecular dipole pointing toward the metal surface (positive dipole). However, the addition of only one CF₃ unit shifts the low-KE photoemission edge to the positive direction, providing excess compensation for the balance of the alkyl chain. Furthermore, this shift to positive values in the low-KE photoemission edge increases in magnitude with an increase in the number of terminal fluorocarbon units, and also appears to mirror the influence of the buried transition dipole upon the interfacial surface energy as described in Section 3.^{20,21,75,77}



Figure 1.8. (a) UV-photoemission spectra for unmodified gold along with a series of HSAMs on gold (C_nSH ; n = 3, 8, 10, 18). The inset represents the shift in the low-KE photoemission edge for these SAMs. (b) UV-photoemission spectra for unmodified gold along with a series of FSAMs on gold ($F_nH_{16-n}SH$; n = 0, 1, 2, 4, 10). The inset represents the shift in the low-KE photoemission edge for these SAMs. Reproduced with permission from Ref. 21.

In addition, Alloway and co-workers also examined SAMs derived from a series of alkanethiols terminated with a single CF₃ group (CF₃(CH₂)_nSH, where n = 12–15) and observed that the shift in the low-KE photoemission edge of the CF₃-terminated SAMs depended on the total number of carbons in the chain of these well-ordered films. Surprisingly, the shift was greater for adsorbates having an odd number of carbon atoms than those having an even number of carbon atoms by ~0.3 eV. This "odd-even" effect was attributed by the authors to the relative orientation of the individual C–F bonds in the adsorbates with respect to the surface normal. Apparently, the C–F bonds in the adsorbates with odd-numbered chain lengths are on average more parallel to the surface normal than the C-F bonds in the adsorbates with even-numbered chain lengths, which

makes for a more efficient escape orientation for exiting low-KE photoelectrons.²¹ This model assumes that the underlying alkyl chains are crystalline (i.e., densely-packed and trans-extended), and is consistent with surface-induced dissociation (SID) studies of FSAMs, which revealed that the neutralization probability is lower for adsorbates with odd-numbered chain lengths than for those with even- numbered chain lengths.⁸⁸



Figure 1.9. Vacuum-level shift as a function of surface composition of F2H16SH in binary SAMs (i.e., F2H16SH and hexadecanethiol). The precision of the measurements is shown by the agreement of the two trials. Reproduced with permission from Ref. 81.

Mixed SAMs can also be used to tune the effective work function of gold. Alloway et al. studied binary SAMs derived from CF₃CF₂(CH₂)₁₄SH (F2H16SH) and CH₃(CH₂)₁₅SH deposited on gold via co-adsorption from solution.⁸¹ The XPS data shows that the surface composition follows the concentration of the deposition solution for most ratios of the two adsorbates. Furthermore, as shown in Figure 1.9, the shift in the vacuum level adopts a linear trend with the change in the F2H16SH concentration on the surface. This correlation between the effective work function and the surface

concentration of **F2H16SH** enables the effective work function to be tuned up to ± 0.1 eV.⁸¹



Figure 1.10. Schematic drawing of changes in the work function as a consequence of the change in the surface composition of the decanethiol-**F8H2SH** gradient. Black rectangles represent the fluorinated helix of **F8H2SH**. Adapted from Ref. 89.

Similarly, Venkataraman and co-workers examined the work function of gold upon the adsorption of mixed monolayers of decanethiol and perfluorinated decanethiol (**F8H2SH**) prepared through a gradient method.⁸⁹ This study relied upon the conclusion that the net interfacial dipole at any point is related to the molar surface concentration of the two components at that point.⁸⁹ Kelvin probe force microscopy (KPFM) showed a gradual decrease in surface potential going from the one-component HSAM, to the decanethiol-rich section of the gradient, to the **F8H2SH**-rich section, and finally to the one-component FSAM. Furthermore, the difference between the surface potentials of the

one-component SAMs, the two extremes, is consistent with the change in work function for these SAMs on gold reported by de Boer and co-workers.^{79,89} Thus, as shown in Figure 1.10, their results indicate that the variation of the net effective dipole moment for the surface is based on the composition of the two thiols in the decanethiol-**F8H2SH** gradient, which changes in tandem with the work function in a manner that is parallel to the change in the vacuum level (ΔE_v).⁸⁹

1.5. Influence of Adsorbate Architecture on Film Stability and Barrier Properties

The incorporation of SAMs into everyday technologies has been hampered by their relatively poor thermal stability. Thermal stability studies of HSAMs have shown that these films become disordered at temperatures approaching 100 °C;⁵⁴ furthermore, SAMs desorb slowly under ambient conditions and rapidly under extreme conditions. To enhance the thermal stability of HSAMs, researchers have employed, among several strategies, multidentate surface binding through multiple headgroups to enhance the S–Au interaction.^{90,91} Multidentate adsorbates, where two or three sulfur atoms per adsorbate bind to the gold surface, have been shown to enhance the resistance to desorption of SAMs.^{91–96} However, SAM films generated from dithiols and trithiols produce alkyl tailgroup alignments that are, depending on the nature of the headgroup, slightly or substantially less ordered than those formed from single-chained monothiol adsorbates. For adsorbates with large headgroups, the increase in the bulkiness of the headgroups forces the hydrocarbon tailgroups apart, making the monolayer liquid-like, which could be detrimental for applications where a well-oriented chain assembly is

needed to create a net dipole for SAMs used to modify the work function of a metal surface.

Incorporating fluorinated segments in alkanethiol adsorbates has also been shown to enhance the thermal stability of SAMs.^{11,52} In studies of partially fluorinated alkanethiol adsorbates, an increase in the length of either the hydrocarbon segment or the fluorocarbon segment led to an increase in the thermal stability for the films. To evaluate each effect separately, systematic investigations of the stability of FSAMs in air and in solution were undertaken.^{11,52} In initial work by Fukushima and co-workers.⁵² thermal desorption studies in air of FSAMs derived from $F(CF_2)_{10}(CH_2)_nSH$, where n = 2, 6, 11, 17, 33, and the length of the fluorocarbon moiety was held constant (F10HnSH), revealed that adsorbates having longer hydrocarbon chains resisted desorption in air better than those having shorter hydrocarbon chains.⁵² In this system, any differences in the thermal stability of the films can be attributed to interchain vdW interactions, which are known to increase with increasing alkyl chain length.⁹⁷ In addition, increasing the length of the fluorocarbon moiety while keeping the length of the hydrocarbon spacer constant at 6 units (F8H6SH and F10H6SH) or 17 units (F10H17SH and F13H17SH) also led to an increase in thermal stability.⁵² An important finding from these initial studies was that the fluorocarbon segments were more effective at stabilizing the films than were the hydrocarbon segments.

In more recent studies, Yuan *et al.* examined the desorption of three series of FSAMs in both decalin and perfluorodecalin at 80 °C for 1.5 hours.¹¹ The first series of SAMs (Series 1.5) was derived from **FmH11SH** where m = 1-10 (i.e., variable fluorocarbon length and constant hydrocarbon length). The second series of SAMs

(Series 1.6) was derived from **F10HnSH** where n = 2-6, and 11 (i.e., constant fluorocarbon length and variable hydrocarbon length). The third series of SAMs (Series 1.7) was derived from F(CF₂)x(CH₂)ySH where x = 1-10 and y = 16 - x (i.e., constant total chain length with variable fluorocarbon length and variable hydrocarbon length). While the thermal stability was observed to increase with increasing the total chain length for all SAMs, studies of the Series 1.7 SAMs showed that the replacement of CH₂ groups with CF₂ groups led to an increase in the thermal stability. As a whole, these studies demonstrate that fluorinated adsorbates offer more stability to organic thin-films than their hydrocarbon analogs -- an important consideration for technologies that require robust nanoscale coatings such as those used in corrosion inhibition,¹ MEMS devices,^{98–} ¹⁰⁰ biosensors,^{3,4} and electrode modification (*vide infra*).

SAMs, which behave as electronic insulators due to their low conductivity,¹⁰¹ can also serve as an ionic barrier, and depending on the nature of the terminal group, might behave as an ideal capacitor.^{102–104} As a capacitor, the gold surface functions as one plate, and the physisorbed electrolytes at the film's interface serve as the second plate.¹⁰² Boubour and Lennox evaluated the effect of the terminal group (CH₃, OH, COOH) of ω terminated hexadecanethiols as well as the chain length of HSAMs (CH₃(CH₂)_nSH, where n = 7–15) on the barrier properties of SAMs and compared them to the FSAM derived from **F8H2SH** using electrochemical ac impedance spectroscopy (EIS).^{102,103} The authors observed that **F8H2SH** FSAMs have a higher capacitance (2.19 ± 0.02 μ F cm⁻¹) than the corresponding HSAMs (1.55 ± 0.01 μ F cm⁻¹).^{102,103} Naud *et al.* evaluated the effect of the degree of fluorination on the ion-insulation property of FSAMs derived from **FnHmSH** (n = 4, 6, 8, 10 and m = 2, 11).¹⁰⁵ Based on their findings, FSAMs with short fluorocarbon segments, both **F4H11SH** and **F4H2SH**, deviate from an ideal capacitor behavior due to the inability of the terminal fluorocarbon segment to align close to the surface normal, thus allowing anions to penetrate though the film. On the other hand, increasing the length of the fluorocarbon segment allowed for the generation of monolayers resistant to ion permeation, as indicated by their constant capacitance value per electrolyte system regardless of the scan rate.

Similarly, Jennings et al. evaluated the barrier properties of FSAMs derived from partially fluorinated hexadecanethiols, FnHmSH (where n = 2, 4, 6, 8; n + m = 16) using EIS.9 Their investigation included SAMs formed in dichloromethane (DCM) and in liquid CO₂. The capacitance of F8H8SH FSAMs was observed to decrease with increasing incubation time, which indicates the generation of a defect-free film with longer incubation times. Also, F8H8SH FSAMs prepared in DCM exhibited a higher resistance and a lower capacitance than those generated in CO₂, indications of a higher quality film.⁹ This conclusion regarding the quality of the FSAMs formed in DCM was further supported by HD contact angle measurements, 83° for F8H8SH FSAMs formed in DCM compared to 79° for those formed in liquid CO₂.⁹ Solvent effects during film formation was attributed for the variance in film guality owing to a more efficient solvation of the fluorinated species in liquid CO_2 , which might hinder the formation of a densely packed film.⁹ The authors also observed a decrease in the film's capacitance as the number of fluorocarbons increased, which correlates with a lowering of the dielectric constant of the FSAMs with increasing fluorination.⁹ These observations, in addition to the improved thermal stability, low surface energy, and chemical inertness of the fluorinated films, expand the scope of possible applications of fluorinated thin films (vide supra).

1.6. Existing and Emerging Applications of Fluorinated Organic Thin Films

Fundamental studies of FSAMs derived from the adsorption of organothiols on gold have helped to shape a comprehensive picture of how the specific placement of fluorocarbons in organic thin films can dictate interfacial properties. Nanoscale tuning of adsorbate structures have laid the groundwork for the use of fluorinated amphiphiles having mercapto and other headgroups, not only on noble metal surfaces, but also on other technologically important surfaces such as silica and glass.^{106–108} In particular, the low surface energy of FSAM films having extended perfluorocarbon segments has contributed to the development of superhydrophobic coatings through the use of highly fluorinated alkylsiloxane adsorbates,^{109,110} which are also used as coatings in microelectronic devices.^{111–113}

More recently, thiol-based FSAMs have been used to coat metal nanoparticles.¹¹⁴ While the FSAM coating is likely to impart enhanced stability to the nanoparticles (*vide supra*), the coating also renders the nanoparticles poorly soluble in both water and organic media.^{115,116} To solve this problem, researchers have developed synthetic routes to functionalize fluorinated adsorbates at both ends.¹¹⁷⁻¹¹⁹ The incorporation of a hydrophilic tailgroup above the fluorinated helix increases nanoparticle solubility in polar media, allowing for the generation of the first water-soluble fluorinated gold nanoparticles (see Figure 1.11a).¹²⁰



Figure 1.11. (a) Synthesis of water-soluble gold nanoparticles capped with partially fluorinated SAMs. Adapted from Ref. 120. (b) Structures of partially fluorinated adsorbates used to prepare nanoscale protein-resistant surface coatings along with comparable OEG-based adsorbates. Adapted from Ref. 121.

The unique character imparted by a buried perfluorinated segment can also be found in efforts to generate biofouling-resistance on two-dimensional substrates.¹²¹ SAMs generated from the carboxylate- and OEG-terminated partially fluorinated alkanethiols shown in Figure 1.11b afforded surfaces with higher reduction of nonspecific protein adsorption when compared to an OEG-surface with analogous thickness.¹²¹

One potential problem with the use of FSAMs in coating applications centers on their susceptibility to low-energy electron radiation damage.¹²² In a study of FSAMs of $CF_3(CF_2)_9(CH_2)_nSH$, where n = 2, 11, 17, damage due to low electron radiation led to the loss of fluorinated segments, especially the CF₃ terminal group. While controlled application of such processes could be useful in lithographic patterning, it could also hinder the use of FSAMs as lubricants at rubbing interfaces.¹⁷ Researchers have tackled

this issue by using a bilayer system in which the top layer forms a lubricant film that contains the perfluorinated chains that also serve as a healing layer for the underlying FSAMs.¹²³ Another approach to solving this problem is the use of perfluorinated terphenyl-based FSAMs. Although irradiation of such FSAMs with low-energy electrons (10 eV) cleaves C–F bonds, the process leads to the cross-linking of the outmost phenyl layer as shown in Figure 1.12, producing films that are remarkably stable.¹²⁴



Figure 1.12. Electron-induced modification in FSAMs on gold derived from perfluoroterphenyl alkanethiols. Adapted from Ref. 124.

In summary, the insight gained from the research highlighted here allows for new advances in the design of nanoscale fluorinated coatings. CF₃-terminated adsorbates create a surface dipole that can interact with polar contacting liquids, but this phenomenon diminishes as the fluorinated segment is lengthened, leading to an interface with wettability comparable to that of PTFE. Variation in the length of the fluorocarbon segment in both single-component FSAMs and in mixed SAMs with alkanethiolate-diluted partially fluorinated adsorbate content offers control over the electronic properties of metal interfaces in organic electronic devices. Further, the lengthy perfluorocarbon segments enhance the stability and barrier properties of monolayer films. As the scope of fluorinated amphiphiles continues to expand with the development of synthetic

methodologies that allow more sophisticated architectures (e.g., functionalization at both ends of the fluorinated helix), unprecedented types of interfaces with unique characteristics that are well controlled, highly reproducible, and technologically relevant are waiting to be developed.

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1.8. Dissertation Contents

The work presented in the chapters that follow focuses on the synthesis of new partially fluorinated alkanethiols and their use in modifying the interfacial properties of self-assembled monolayers. Two chapters involve the incorporation of alkyl terminal groups atop partially fluorinated alkanethiols. This work is the aftermath of knowledge gained from all studies conducted on fluorinated SAMs over the past two decades. Another study involves expanding the scope of molecules that generate a nearly all fluorinated surface.

Chapter 2 highlights the use of a new type of methyl-caped, partially fluorinated alkanethiol in generating SAMs. A comparison of the properties of these films to those of CF_3 -terminated films and normal alkanethiol SAMs indicate that the effect of the HC–

FC dipole at the surface termini causes an increased interaction between the films interface and polar liquids. **Chapter 3** is a continuation of the aforementioned work, where the HC–FC dipole is progressively buried underneath an alkyl terminal group to determine the extent of the effect this dipole has on the interfacial properties of the SAMs. **Chapter 4** involves a study that examines the role of increasing the methylene spacer in perfluorinated alkanethiols on the structural and interfacial properties of the generated monolayers. This work shows that these molecules are an attractive alternative to the known perfluorinated alkanethiols used in a variety of applications, such as field transistors and anti corrosion, since the latter offers an improvement in packing and interfacial properties. The insight gained from the above-mentioned studies is summarized Chapter **5**.

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Chapter 2: Methyl-terminated Partially Fluorinated Alkanethiols: The Synthesis of Truly Unique Surfactants and the Preparation of Self-Assembled Monolayers that Present an Unprecedented Interfacial Dipole

2.1. Introduction

The ability to decorate the tailgroups of partially fluorinated chains with different functional moieties opens up new avenues for the use of fluorinated amphiphiles as seeds for a new generation of fluorinated materials. Modifications that have created a sandwich of the fluorinated segment, like the recently reported PEG-terminated fluorinated thiols, gave rise to the first type of water-soluble partially fluorinated gold nanoparticles.^{1,2} And the application of other forms of spatial distribution of fluorinated moieties in a larger network have led to a better understanding of the influence that such limited levels of fluorinated aromatic tetrazoles and carboxylic acids in metal organic frameworks (MOFs), a project that produced a highly fluorinated MOF with superhydrophobic character.⁴ Research involving fluorinated films has also gained from such advancements in organic synthesis. Using click chemistry, Cai and coworkers have developed means for creating microarrays on fluorinated surfaces.⁵

Investigations involving self-assembled monolayers (SAMs) of thiols on gold surfaces continue to serve as model systems for determining how structural features of fluorinated amphiphiles can help tailor the physical and interfacial properties of the resulting surfaces. Fundamental studies of fluorinated self-assembled monolayers, FSAMs, have shown that fluorinated alkanethiols surpass their hydrocarbon analogues in key characteristics such as chemical and biological inertness, thermal stability, and oleoand hydrophobicity.^{6,7} Such properties are inherent in these structures owing in part to the fundamental characteristics of the C–F bond (extremely polar but with a bond strength of 105.4 kcal per mole),⁸ as well as the stiff helical geometry of the perfluorinated chains.^{9–11} In addition, the extended perfluorocarbon chains have a larger surface area compared to their hydrocarbon counterpart.¹²

Over a decade ago, Lee and coworkers introduced a series of trifluoromethylterminated alkanethiols.¹³ SAMs of such molecules on gold surfaces exhibited similar structural features to their normal alkanethiol counterparts.^{14–16} The length of the methylene spacers strictly governs the crystallinity of both types of films. Furthermore, despite the differences in the sizes of the terminal methyl groups, the underlying alkyl chains possess the same arrangement as the alkyl chains of alkanethiolate SAMs on a gold lattice.¹⁷ However, the interfacial properties of such chains are indeed altered by the change in the chemical makeup of the tailgroup. The CF₃-terminated SAMs are less hydrophobic than normal hydrocarbon SAMs due to the dipole residing at the FC–HC junction.¹⁸ Colorado *et al.* have investigated this phenomenon using a series of CF₃terminated SAMs (CF₃(CH₂)_nSH, where n = 12–15) and compared it to that of normal alkanethiolate SAMs where the FC–HC dipole is steadily buried in the film by increasing the size of FSAMs where the FC–HC dipole is steadily buried in the film by increasing the size of the fluorinated moiety, while keeping the chain length constant at 16 backbone carbons $(F(CF_2)_n(CH_2)_mSH)$, where n = 1-10 and m = 15-6; FnHmSH).¹⁹ The outcomes of these studies indicate that all FSAMs formed from terminally fluorinated thiols are more oleophobic than their nonfluorinated analogues due to the non-ideal dispersive interactions between fluorocarbons and hydrocarbons. On the other hand, CF₃terminated SAMs are more wettable by polar liquids than normal alkanethiolate SAMs. Furthermore, the former exhibits an inverse odd-even effect by polar aprotic liquids than what is commonly seen with hydrocarbon liquids on normal alkanethiolate SAMs. According to Colorado and Lee, it is this finding that supports the presence of the FC-HC dipole in CF₃-terminated SAMs, and that its orientation is dictated by the orientation of the terminal perfluoromethyl group. Hence the total number of carbons in the chain results in an observed odd-even effect for polar aprotic contacting liquids that corresponds with the non-compensated strength of the interfacial dipole, as illustrated in Figure 2.1. Furthermore, burying the FC–HC dipole in the film by varying the number of fluorocarbons and hydrocarbons in the FnHmSH series of FSAMs results in a decrease in the wetting ability of polar liquids on these monolayers. This was confirmed by another wettability study on an additional series of fluorinated SAMs $(F(CF_2)_n(CH_2)_{11}SH)$, where n = 1–10; FnH11SH), where the wettability of contacting liquids decreased with an increasing size of the fluorinated segment, and that the wetting behavior of those contacting liquids plateaus at five fluorocarbons and beyond.²⁰ Other interfacial properties of FSAMs, such as adhesion and friction, are also altered by the chemical nature of the terminal group. Fluorinated monolayers have shown to exhibit low adhesive properties.^{21–23} However, AFM studies have shown that CF₃-terminated

SAMs have a higher coefficient of friction due to the larger van der Waals (vdW) diameter of the terminal group (~5.6 Å), and that the bulkier chain ends are locked in a confined spatial arrangement due to the efficient packing of the underlying alkyl spacers – lattice spacing of chains in the two types of films is ~ 4.8 Å.^{14,17,24}

For the current investigation, the first example of a SAM formed with a reversed interfacial dipole (HC-FC) is examined. Taking the knowledge gained from the earlier work with FSAMs, we chose to explore the effect of reversing the terminal dipole in a fluorinated alkanethiol (FnHmSH) by producing a methyl capped-partially fluorinated alkanethiol (H1F6HmSH), as shown in Figure 3.1. The featured molecule used in this study has been tailored to include specific structural parameters and is of the form $CH_3(CF_2)_6(CH_2)_{11}SH$ (H1F6H11SH). The length of the fluorocarbon segment is set at six fluorocarbons in order to reduce the effect of the FC–HC dipole, associated with the transition at the alkyl spacer, on the interfacial properties for the resulting monolayer. The number of methylene spacers is set at eleven to insure minimal effect from the underlying gold substrate on the wetting behavior of contacting liquids on the exposed This chain length also allows for the generation of a monolayer with a interface. minimal amount of gauche defects in the hydrocarbon region of the film, thus lowering the chances for the generation of a disordered film. Films produced from H1F6H11SH will be compared to those of *n*-octadecanethiol (H18SH) and 18,18,18trifluorooctadecanethiol (F1H17SH); normal and CF₃-terminated alkanethiol analogues bearing the same total number of carbons in the chain. The study also includes $CH_3(CF_2)_6(CH_2)_{10}SH$ (H1F6H10SH), *n*-heptadecanethiol (H17SH), and 17,17,17-tri-



Figure 2.1. Illustrations of FSAMs formed from the deposition of methyl-terminated partially fluorinated thiols; (a) **H1F6H10SH** and (b) **H1F6H11SH**, as well as FSAMs that are generated from CF_3 -terminated alkanethiols; (c) **F1H17SH** and (d) **F1H16SH**, and SAMs formed from normal alkanethiols; (e) **H18SH** and (f) **H17SH**. All of the SAMs were prepared on gold surfaces.

fluoroheptadecanethiol (**F1H16SH**) as molecules with an odd number of carbons in the alkyl chain, to determine if any odd-even effect might be associated with the new types of surfactants. The properties of the SAMs analyzed in this study will be characterized using optical ellipsometry, X–ray photoelectron spectroscopy (XPS), polarization modulation infrared reflection-adsorption spectroscopy (PM-IRRAS), and contact angle goniometry.

2.2 Experimental Section

2.2.1 Materials and Methods

Gold shot (99.999%) was purchased from Americana Precious Metals. Chromium rods (99.9%) were purchased from R. D. Mathis Company. Polished singlecrystal Silicon (100) wafers were purchased from Silicon Wafer Enterprises and rinsed with absolute ethanol (Aaper Alcohol and Chemical Co.) before use. Tetrahydrofuran (THF), dichloromethane (DCM), and diethyl ether (Et₂O), from Avantor Performance Materials (Macron Chemicals and J.T. Baker), along with Toluene from Sigma Aldrich, were dried by distilling over calcium hydride (Sigma-Aldrich). The other solvents, methanol (MeOH), hexanes, and acetone (from Avantor Performance Materials); diethylene glycol (DEG), dichloroethane (DCE), dimethoxyethane (DME), α,α,α trifluorotoluene, and ethyl acetate (from Sigma Aldrich); and ethanol (EtOH – Aaper Alcohol and Chemical Co.), were either used as received or degassed by purging with nitrogen gas. Butenyl magnesium bromide (3-BuenylMgBr), methanesulfonyl chloride (MsCl), azobisisobutyronitrile (AIBN), lithium aluminum hydride (LiAlH₄), tributyltin hydride (Bu₃SnH), borane tetrahydrofuran complex (BH₃⁻THF), *p*-toluenesulfonyl chloride (TsCl), triethylamine (Et₃N), *p*-toluenesulfonic acid (PTSA), dihydropyran (DHP), and 1,4,7,10,13-pentaoxa-cyclopentadecane (15-Crown-5), were all purchased from Sigma Aldrich and used as received. Dimethyl perfluorosuberate (Synquest Labs); trifluoroethyl iodide (Cole); cesium fluoride (CsF – Sigma Aldrich); (trifluoromethyl) trimethylsilane (CF₃-TMS – Oakwood Products); 9-decen-1-ol (TCI America); 10undecen-1-ol and potassium thioacetate (KSAc; both from Sigma Aldrich); were used as received. The lithium copper chloride (Li₂CuCl₄) solution was prepared from lithium chloride (LiCl) and copper (II) chloride (CuCl₂) which were each obtained from Acros Chemicals.

Potassium hydroxide (KOH – Sigma Aldrich); hydrochloric acid (HCl), sodium iodide (NaI), and sulfuric acid (H₂SO₄ – all from J.T. Baker); hydroiodic acid (HI) and zinc dust (Fischer); potassium iodide (KI - EMD Chemicals); sodium hydroxide (NaOH), silver oxide (Ag₂O), glacial acetic acid (AcOOH), hydrogen peroxide (30% H_2O_2), ammonium chloride (NH₄Cl), and iodine (I₂ – all from Mallinckrodt Chemicals), were all used as received.

Octadecanethiol (C18SH) was from Sigma-Aldrich. Heptadecanethiol was prepared by a procedure found in the literature.²⁵ Chloroform-*d* was purchased from Cambridge Isotope Laboratories and used for all NMR spectra. The silica gel used for column chromatography was obtained from Sorbent Technologies.
2.2.2. Synthesis of Methyl-Terminated Partially Fluorinated Alkanethiols and Terminally Fluorinated Alkanethiols.

12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorooctadecane-1-thiol

(H1F6H11SH) and 11,11,12,12,13,13,14,14,15,15,16,16-dodecafluoroheptadecane-1-thiol (H1F6H10SH) were prepared following the synthetic route outlined in Scheme 2.1. 18,18,18-trifluorooctadecane-1-thiol (F1H17SH) was synthesized following the detailed procedure shown in Scheme 2.2. 17,17,17-trifluoroheptadecane-1-thiol (F1H16SH) was synthesized following an alternative procedure shown in Scheme 2.3. All thiols were stored under an argon atmosphere prior to use.

Scheme 2.1. Synthetic Route for the Preparation of 12,12,13,13,14,14,15,15, 16,16,17,17-dodecafluorooctadecane-1-thiol (**H1F6H11SH**) and 11,11,12,12,13,13, 14,14,15,15,16,16-dodecafluoroheptadecane-1-thiol (**H1F6H10SH**).



Scheme 2.2. Synthetic Route for the Preparation of 18,18,18-trifluorooctadecane-1-thiol (F1H17SH).



Scheme 2.3. Synthetic Route for the Preparation of 17,17,17-trifluoroheptadecane-1-thiol (F1H16SH).



methyl 2,2,3,3,4,4,5,5,6,6,7,7-*dodecafluoro-7-iodoheptanoate* (1). In a 2-neck round bottom flask equipped with a condenser and an addition funnel, dimethyl perfluorosuberate (10.085 g; 24.119 mmol) was dissolved in MeOH (50 mL). A

solution of KOH (0.541 g; 9.64 mmol) in MeOH (10 mL) was added drop-wise, and the resulting mixture was heated to 50 °C for 2.5 h. After cooling the reaction to room temperature, the reaction was quenched with 1 M HCl (12 mL), followed by the addition of water (50 mL). The product was then extracted with Et₂O (3×150 mL). The combined organic phases were washed with water (1×100 mL) and brine (1×100 mL), dried over MgSO₄, and evaporated to dryness by rotary evaporation.

The crude mono-*F*-carboxylic acid was then dissolved in α,α,α -trifluorotoluene (50 mL), followed by the addition of Ag₂O (2.46 g; 10.6 mmol). The mixture was heated to 75 °C for 5 h. After that, the reaction was filtered at 50 °C to remove excess unreacted oxide, and was then washed with hot acetone (50 mL). The filtrate was evaporated to dryness using rotary evaporation, and the crude mixture was washed with boiling hexanes to recover unreacted dimethyl perfluorosuberate.

The perfluorinated silver salt of the monoester, white crystals, was dried under high vacuum for 24 h, and then placed in a 50 mL Schlenk flask with iodine (8.76 g; 34.3 mmol) and heated at 100 °C for 24 h. The reaction was then cooled to -30 °C, at which CO₂ was slowly allowed to vent out. The product was then dissolved in Et₂O (200 mL), and washed with 10% aqueous NaHSO₃ (2 × 100 mL), followed by water (1 × 100 mL) and brine (1 × 100 mL), and then dried over MgSO₄. The solvent was then filtered though a silica plug and evaporated to dryness by rotary evaporation to give methyl 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-7-iodoheptanoate in a 33% yield from the starting diester. ¹H NMR (500 MHz, CDCl₃): δ 4.06 (s, 3 H) *methyl* 2,2,3,3,4,4,5,5,6,6,7,7-*dodecafluoro-18-hydroxy-9-iodooctadecanoate* (2*a*). In a 100 mL pear-shaped Schlenk flask equipped with a condenser, methyl 7-iodoperfluoheptanoate (1) (3.822 g; 7.864 mmol), AIBN (10 mol %) and 10-undecane-1-ol (1.875 g; 11.01 mmol) were dissolved in DCE (20 mL). The system was degassed with three cycles of a standard freeze-pump thaw procedure. After warming to room temperature, the reaction mixture was heated to 85 °C for 8 h. After 8 h, the reaction was cooled to room temperature and an additional 10 mol % of AIBN was added under argon, followed by the same degassing method. The system was heated again to 85 °C for 8 h. After cooling the reaction to room temperature, the solvent was evaporated and the crude mixture was purified by column chromatography on silica gel using hexanes / ethyl acetate (70 / 30) as the eluent system to give methyl 2,2,3,3,4,4,5,5,6,6,7,7dodecafluoro-18-hydroxy-9-iodooctadecanoate (**2a**) in a 53% yield. ¹H NMR (500 MHz, CDCL₃): δ 4.32 (m, 1H), 3.99 (s, 3H) 3.64 (m, 2H), 2.72–2.96 (m, 2H), 1.71– 187(m,2H). 1.53–1.58 (m, 2H), 1.24–1.42 (broad m, 12H)

methyl 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-17-hydroxy-9-iodoheptadecanoate
(2b) ¹H NMR (500 MHz, CDCL₃): δ 4.33 (m, 1H), 3.98 (s, 3H) 3.64 (m, 2H), 2.72–2.96 (m, 2H), 1.70–1.85 (m, 2H), 1.54–1.59 (m, 2H), 1.23–1.44 (broad m, 10H).

2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorooctadecane-1,18-diol (3a). To a solution of **2a** (2.719 g; 7.864 mmol) in THF (20 mL) were added glacial acetic acid (100 mL) and zinc dust (4.076 g; 62.14 mmol) under the flow of argon at room temperature. The reaction mixture was stirred for 40 h and then filtered through a bed of Celite. The

Celite pad was washed with 200 mL of hot Et_2O . The filtrate was washed with water (3 × 100 mL), saturated aqueous NaHCO₃ (2 × 100 mL), and brine (1 × 100 mL), and dried over MgSO₄. The solvent was then removed by rotary evaporation to dryness.

The crude hydroxy-ester was dissolved in dry THF (10 mL) and added drop-wise to a stirring slurry of LiAlH₄ (0.473 g; 12.5 mmol) in THF (20 mL) at -20 °C. The reaction was stirred for 6 h under argon while maintaining the temperature around -10 °C. The reaction was then quenched at -20 °C using water (25 mL), and then acidified with 1M aqueous HCl solution. The mixture was then extracted with Et₂O (3 × 150 mL). The combined organic phases were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried over MgSO₄, and evaporated to dryness by rotary evaporation. The crude diol was purified by column chromatography on silica gel using hexanes / ethyl acetate (70 / 30) to give 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorooctadecane-1,18-diol (**3a**) in a 70% yield. ¹H NMR (500 MHz, CDCl₃): δ 4.05 – 4.12 (m, 2 H,), 3.64 (q, *J* = 6.18 *Hz*, 2 H), 1.98 – 2.09 (m, 3 H), 1.53 – 1.62 (m, 4H), 1.24 – 1.40 (m, 14H), 1.20 (t, *J* = 5.50 Hz, 1 H).

2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptadecane-1,17-diol (**3b**) ¹H NMR (500MHz, CDCl₃): δ 4.05 – 4.13 (m, 2H), 3.64 (q, *J*= 6.19 Hz, 2H), 1.94 – 2.09 (m, 3H), 1.54 – 1.62 (m, 4 H), 1.25 – 1.40 (m, 12 H). 1.19 (t, *J* = 5.50 Hz, 1 H).

2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorooctadecane-1,18-diyl bis(4-toluenesulfonate) (4a). To a stirred solution of **3a** (1.1 g; 2.2 mmol) and TsCl (3.340 g; 17.52 mmol) in anhydrous DCM at 0 °C was added Et₃N (1.8 mL; 13 mmol) drop-wise. The reaction was then warmed to room temperature and stirred for 24 h. After that, DCM was evaporated, and the crude compound was redissolved in Et₂O (200 mL), followed by the addition of ice-cold water (100 mL). The layers were separated and the organic layer was washed with 1M HCl (1 × 100 mL), water (1 × 100 mL), and brine (1 × 100 mL), and dried over MgSO₄. After the evaporation of the solvent by rotary evaporation, the crude product was purified by chromatography on silica gel using hexanes / ethyl acetate (90 / 10) to give 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluorooctadecane-1,18-diyl bis(4-toluenesulfonate) (**4a**) in an 82% yield. ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, *J* = 8.02 Hz, 2H), 7.78 (d, *J* = 8.02 Hz, 2H), 7.38 (d, *J* = 8.02 Hz, 2H), 7.34 (d, *J* = 8.02 Hz, 2H), 4.45 (t, *J* = 13.17 Hz, 2 H), 4.01 (t, *J* = 6.59 Hz, 2 H), 2.47 (s, 3 H), 2.44 (s, 3 H), 1.96 – 2.07 (m, 2 H), 1.51 – 1.65 (m, 4H), 1.22 – 1.35 (m, 14 H)

2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoroheptadecane-1,17-diyl bis(4toluenesulfonate) (**4b**) ¹H NMR (500 MHz, CDCl₃): δ 7.82 (d, *J* = 8.02 Hz, 2H), 7.78 (d, *J* = 8.02 Hz, 2H), 7.38 (d, *J* = 8.02 Hz, 2H), 7.34 (d, *J* = 8.02 Hz, 2H), 4.45 (t, *J* = 13.17 Hz, 2 H, *OCH*₂*CF*₂), 4.01 (t, *J*=6.59 Hz, 2 H, *OCH*₂), 2.47 (s, 3 H), 2.44 (t, 3 H), 1.96 – 2.07 (m, 2H), 1.55 – 1.65 (m, 2 H,), 1.22 – 1.34 (m, 12 H).

2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1,18-diiodooctadecane (5a). Perfluoro ditosylate (4a) (1.456 g; 1.796 mmol) and NaI (8.075 g; 53.87 mmol) were dissolved in DEG (70 mL) and heated to 160 °C for 24 h. After cooling the reaction to room temperature, water (100 mL) was added and the mixture was extracted with ethyl acetate

 $(3 \times 150 \text{ mL})$. The combined organic layers were washed with half-saturated brine (2 x 100 mL), dried over MgSO₄, and the solvent was then removed by rotary evaporation.

The crude product was then dissolved in a mixture of acetic acid (50 mL) and 48% HI solution (10 mL) and heated to 95 °C for 24 h. After cooling, water (50 mL) was added and the mixture was extracted with Et₂O (3 × 150 mL). The combined organic layers were washed with water (3 × 100 mL), saturated aqueous NaHCO₃ (2 × 100 mL), and brine (1 × 100 mL), and dried over MgSO₄. The solvent was then removed by rotary evaporation. The crude product was purified by column chromatography on silica gel using hexanes / ethyl acetate (95 / 5) to give 2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1,18-diiodooctadecane (**5a**) in a 54% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.63 (t, *J* = 17.36 Hz, 2 H), 3.18 (t, *J* = 7.05 Hz, 2 H), 1.98 – 2.09 (m, 2 H), 1.78 – 1.84 (m, 2 H), 1.53 – 1.61 (m, 2 H), 1.25 – 1.42 (m, 14 H).

2,2,3,3,4,4,5,5,6,6,7,7-dodecafluoro-1,17-diiodoheptadecane (**5b**) ¹H NMR (500 MHz, CDCl₃): δ 3.63 (t, *J* = 17.36 Hz, 2 H), 3.18 (t, *J* = 7.05 Hz, 2H), 1.98 – 2.09 (m, 2H), 1.78–1.84 (m, 2H), 1.52 – 1.61 (m, 2H), 1.25 – 1.42 (m, 12 H).

S-(*12*, *12*, *13*, *14*, *14*, *15*, *15*, *16*, *16*, *17*, *17*-dodecafluoro-18-iodooctadecyl)

ethanethioate (6a). In a 2-neck round bottom flask equipped with a condenser and an addition funnel, **5a** (1.189 g; 1.646 mmol) was dissolved in absolute ethanol (100 mL) (previously degassed). KSAc (0.376 g; 3.29 mmol) was separately dissolved in absolute ethanol (20 mL) (previously degassed), and added drop wise to the stirred ethanolic solution of **5a** under argon over 10 min. The reaction was heated to 60 °C and

maintained at that temperature for 3 h. After the reaction was cooled to room temperature, water (100 mL) was added to the solution and the resulting mixture was extracted with Et₂O (3 × 100 mL). The organic phases were combined and washed with water (1 × 100 mL) and brine (1 × 100 mL), and then dried over MgSO₄. The solvent was removed by rotary evaporation to give S-(12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-18-iodooctadecyl) ethanethioate (**6a**) in a 95% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.63 (t, *J* = 17.18 Hz, 2H), 2.85 (t, *J* =7.39, 2H), 2.32 (s, 3H), 2.02 – 2.07 (m, 2H), 1.51 – 1.61 (m, 4 H), 1.26 – 1.42 (m, 14 H).

S-(11,11,12,12,13,13,14,14,15,15,16,16-dodecafluoro-17-iodoheptadecyl) ethanethioate (**6b**) ¹H NMR (500 MHz, CDCl₃): δ 3.63 (t, *J*=17.18 Hz, 2 H, *CF*₂*CH*₂*I*), 2.85 (t, *J*=7.39, 2 H, *SCH*₂), 2.32 (s, 3 H), 1.97 – 2.09 (m, 2H, *CF*₂*CH*₂), 1.51 – 1.59 (m, 4 H), 1.23 – 1.39 (m, 12 H).

12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorooctadecane-1-thiol

(H1F6H11SH). The thioacetate (**6a**) (1.051 g; 1.568 mmol) and AIBN (10 mol %) were dissolved in anhydrous toluene. The reaction was heated to 60° C under argon, and then Bu₃SnH (1.3 mL; 4.9 mmol) was added drop-wise for 15 min. The reaction was then further heated to 85° C and stirred at that temperature for 6 h. After cooling to room temperature, the reaction was diluted with Et₂O (100 mL) and filtered through a short bed of silica to remove any Bu₃SnI salt. Excess of Bu₃SnH was removed by flash chromatography on silica gel using hexanes / ethyl acetate (95 / 5) as the eluent.

The dehalogenated thioacetate was then dissolved in dry THF (50 mL) and added drop-wise to a stirring slurry of LiAlH₄ (0.131 g; 3.45 mmol) in THF (10 mL) at -10 °C.

The reaction was stirred 8 h under argon while maintaining the temperature at ~ -10 $^{\circ}$ C. The reaction was quenched at -10 °C using water (25 mL, previously degassed), and was then acidified with $1M H_2SO_4$ solution (previously degassed). The mixture was extracted with Et_2O (3 × 100 mL). The combined organic phases were washed with water $(1 \times 100 \text{ mL})$ and brine $(1 \times 100 \text{ mL})$, dried over MgSO₄, and evaporated to dryness by rotary evaporation. The crude thiol was purified by column chromatography silica gel (hexanes) give 12,12,13,13,14,14,15,15,16,16,17,17on to dodecafluorooctadecane-1-thiol (H1F6H11SH) in an 85% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.52 (q, J = 7.33 Hz, 2 H), 1.99 – 2.10 (m, 2 H), 1.84 (t, J = 19.01 Hz, 3 H), 1.56 - 1.64 (m, 4 H), 1.25 - 1.37 (m, 14 H). ¹³C NMR (125 MHz, CDCl₃): δ 34.13, 30.85-31.21 (t, J = 22.5 Hz), 30.39 (s), 29.14-29.80 (m), 28.45 (s), 24.75 (s), 20.19 (s), 18.41-18.80 (t) Broad peaks at δ 108.90-118.57 (6 C) are characteristic of a long perfluorocarbon chain.^{26 19}F NMR (470 MHz, CDCl₃): δ -106.21 (m, 2 F), -114.34 (m, 2 F), -121.84 (m, 4 F), -123.63 (m, 2 F), -124.13 (m, 2 F).

11,11,12,12,13,13,14,14,15,15,16,16-dodecafluoroheptadecane-1-thiol (H1F6H10SH). ¹H NMR (500 MHz, CDCl₃): δ 2.52 (q, J= 7.33 Hz, 2H, SCH_2), 1.78 – 2.08 (m, 2 H.), 1.83 (t, J= 18.90 Hz, 3 H), 1.54 – 1.60 (m, 4 H), 1.28 – 1.36 (m 12 H). ¹³C NMR (125 MHz, CDCl₃): δ 34.11(s), 30.85-31.21 (t), 30.40 (s), 29.11-29.49 (m,), 28.43 (s), 24.74 (s), 20.19 (s), 18.41-18.81 (t) Broad peaks at δ 110.71–118.56 are characteristic of a long perfluorocarbon chain.^{26 19}F NMR (470 MHz, CDCl₃): δ -106.22 (m, 2 F), -114.31 (m, 2 F), -121.84 (m, 4 F), -123.61 (m, 2 F), -124.11 (m, 2 F). *12-iodododecan-1-ol.* 12-Bromododecan-1-ol (2.5 g; 9.4 mmol) and potassium iodide (15.6 g; 94.0 mmol) were dissolved in 100 mL of acetone, and the reaction mixture was refluxed for 24 h. After that, acetone was removed via rotary evaporation, and the reaction mixture was redissolved in Et₂O (200 mL). This organic solution was washed with water (100 mL), followed by brine (100 mL), and dried over MgSO₄. After filtration, the solvent was removed by rotary evaporation and dried under vacuum to afford 12-iodododecan-1-ol in a 99% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.64 (m, 2H), 3.18 (t, *J* = 7.05 Hz, 2 H₂), 1.76 – 1.86 (m, 2 H), 1.51 - 1.60 (m, 2 H), 1.19 – 1.39 (m, 16 H).

Hexadec-15-en-1-ol. 12-iodododecan-1-ol (2.91 g; 9.32 mmol) and dihydropyran (1.3 mL; 14 mmol) were sequentially added to 100 mL of dichloromethane containing PTSA (0.177 g, 0.932 mmol). The reaction mixture was stirred at room temperature for 4 h. The reaction was then diluted with hexanes (200 mL) and washed twice with half-saturated brine (2×100 mL) to remove the catalyst. The organic phase was dried over MgSO₄, and the solvent was removed by rotary evaporation to give 2-((12-iodododecyl)oxy)tetrahydro-2H-pyran, which was dried under vacuum and carried to the next step without purification.

In a two-neck flask equipped with an addition funnel, the crude iodide was dissolved in 100 mL of dry THF under argon. To that solution, 4.6 mL of 0.10 M solution (0.46 mmol) of Li_2CuCl_4 in THF were added. The mixture was cooled to 0 °C, and a 0.5 M solution of 3-butenylmagnesium bromide in THF (38 mL; 19 mmol) was added drop-wise over 15 min. The reaction was then warmed and stirred at room

temperature under argon for 12 h. The reaction was quenched with 25 mL of saturated NH₄Cl, followed by 25 mL of water. The mixture was extracted with Et_2O (3 × 100 mL), and the combined organic layers were washed with brine (1 × 100 mL), dried over MgSO₄. The solvent was removed with a rotary evaporator.

The crude alkene was dissolved in 100 mL of ethanol containing PTSA (0.212 g; 1.11 mmol), and stirred at 55 °C for 3h. Upon completion, ethanol was removed by rotary evaporation, and the crude product was redissolved in Et₂O (200 mL), washed with half-saturated brine (3 × 100 mL), and dried over MgSO₄. The solvent was evaporated to dryness by rotary evaporation. The crude product was purified by silica gel chromatography using hexanes / ethyl acetate (80 / 20) as the eluent to give hexadec-15-en-1-ol in a 79% yield from the iodo-alcohol. ¹H NMR (500 MHz, CDCl₃): δ 5.77 – 5.85 (m, 1H), 4.91 – 5.01 (m, 2 H, *CHCH*), 3.64(t, *J* = 6.53 Hz, 2 H), 2.01 – 2.05 (m, 2 H), 1.53 – 1.59 (m, 2 H), 1.19 – 1.38 (m, 22 H).

18,18,18-trifluorooctadecan-1-ol. In a 100 mL pear-shaped Schlenk flask, hexadec-15-en-1-ol (1.761 g; 7.325 mmol), AIBN (4 mol %) and trifluoroethyl iodide (2.31 g; 11.0 mmol) were combined. The system was degassed with three cycles of a standard freeze-pump thaw procedure. After warming to room temperature, the reaction mixture was heated to 85 °C for 3 h. After 3 h, an additional equivalent of the iodide and AIBN were added under argon, followed by the same degassing method. The system was heated again to 85 °C for 3 h. This process was repeated six times. The percent conversion of the alkene was monitored by ¹H NMR spectroscopy of a small sample prior to each addition of the iodide and AIBN. After 90 % conversion of the alken-1-ol, the crude iodoalcohol was dissolved in 70 mL of glacial acetic acid and zinc dust (6.55 g; 100 mmol) under the flow of argon at room temperature. The reaction mixture was stirred for 40 h and then filtered through a bed of Celite. The Celite pad was then washed with 200 mL of hot Et_2O . The filtrate was washed with water (3 × 100 mL), saturated aqueous NaHCO₃ (1 × 100 mL), and brine (1 × 100 mL), and dried over MgSO₄. The solvent was removed by rotary evaporation.

To remove the remaining olefinic starting material, the crude fluorinated alcohol was dissolved in 30 mL of anhydrous THF and cooled to 0 °C under argon. A 1M solution of BH₃ in THF (6.0 mL; 6.0 mmol) was added slowly over 10 min. The mixture was warmed to room temperature and stirred under argon for 12 h. The reaction was then quenched by adding a solution of 5 M aqueous NaOH (5 mL) dissolved in 30% H₂O₂ (15 mL), and the resulting solution was stirred for 1 h at room temperature. The mixture was extracted with Et₂O (3 × 100 mL), and the combined organic layers were washed with 1 M aqueous HCl (1 × 100 mL), water (1 × 100 mL), and brine (1 × 100 mL), and dried over MgSO₄. The solvent was removed by rotary evaporation, and the residue purified by silica gel chromatography using hexanes / ethyl acetate (80 / 20) as the eluent to give 18,18,18-trifluorooctadecan-1-ol in a 50 % yield from the starting olefin. ¹H NMR (500 MHz, CDCl₃): δ 3.63 (t, *J* = 6.7 Hz, 2 H), 1.99 – 2.10 (m, 2 H,), 1.50–1.58 (m, 4 H), 1.25 – 1.41 (m, 26 H).

18,18,18-trifluorooctadecane-1-thiol (F1H17SH). 18,18,18-trifluorooctadecan-1ol (0.794 g; 2.45 mmol) was dissolved in anhydrous THF under argon, and the solution was cooled to 0 °C in an ice bath. NEt₃ (1.0 mL; 7.3 mmol) was added slowly, and the resulting mixture was stirred for 30 min at 0 °C. Subsequently, MsCl (0.76 mL; 9.8 mmol) was added drop-wise. The reaction was allowed to warm to room temperature and stirred for 6 h. The reaction was then quenched with 50 mL of ice-cold water. The product was extracted with Et₂O (3 × 100 mL) and the combined organic phases were washed with 1M HCl (1 × 100 mL), water (1 × 100 mL), and brine (1 × 100 mL). The organic layer was dried over anhydrous MgSO₄, followed by removal of the solvent by rotary evaporation.

The crude product was dried under high vacuum overnight and redissolved in 100 mL of absolute ethanol (previously degassed) under argon. KSAc (0.851 g; 7.45 mmol) was then added to the solution and the mixture was refluxed for 6 h. After cooling the reaction to room temperature, water was added (100 mL), and the product was extracted with Et_2O (3 × 100 mL). The organic phases were combined and washed with water (1 × 100 mL) and brine (1 × 100 mL), and then dried over MgSO₄. Removal of the solvent by rotary evaporation afforded the crude thioacetate, which was dried and carried to the next step without purification.

The crude thioacetate was dissolved in dry THF (50 mL) and added dropwise to a stirring slurry of LiAlH₄ (0.151 g; 3.98 mmol) in THF (10 mL) at 0 °C. The reaction was stirred at room temperature for 6 h under argon. The reaction was then quenched at 0 °C using water (25 mL, previously degassed), and the resulting solution was acidified with 1M H₂SO₄ solution (previously degassed). The mixture was then extracted with Et₂O (3 × 100 mL). The combined organic phases were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried over MgSO₄, and then evaporated to dryness by rotary evaporation. The resulting thiol was purified by column chromatography on silica gel (hexanes) to give 18,18,18-trifluorooctadecane-1-thiol (**F1H17SH**) in a 69% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.51 (q, *J* = 7.45 Hz, 2 H), 2.00–2.07 (m, 2 H), 1.51 – 1.66 (m, 4 H), 1.19 – 1.42 (m, 27 H). ¹³C NMR (125 MHz, CDCl₃): δ 34.15 (s), 33.93 (s), 33.71 (s), 29.62 – 29.75 (m), 29.47 (s), 29.28 (s), 29.18 (s), 28.79 (s), 28.48 (s), 24.77 (s), 21.92 (s).

2-((16-iodohexadecyl)oxy)tetrahydro-2H-pyran. 16-iodohexadecan-1-ol (4.51 g; 12.2 mmol) and dihydropyran (1.7 mL; 19 mmol) were added to 100 mL of dichloromethane containing PTSA (0.233 g, 1.22 mmol). The reaction mixture was stirred at room temperature for 4 h. The reaction was then diluted with hexanes (200 mL) and washed twice with half-saturated brine (2 × 100 mL) to remove the catalyst. The organic phase was dried over MgSO₄, and the solvent was removed by rotary evaporation to give 2-((16-iodohexadecyl)oxy)tetrahydro-2H-pyran, which was dried under vacuum and carried to the next step without further purification. ¹H NMR (500 MHz, CDCl₃): δ 4.56 – 4.58 (m, 1H), 3.84 – 3.89 (m, 1 H), 3.70 – 3.75 (m, 1 H), 3.48 – 3.51 (m, 1 H), 3.36 – 3.40 (m, 1 H), 3.18 (t, J=7.05 Hz, 2 H), 1.78–1.88 (m, 4 H), 1.51 – 1.60 (m, 4 H), 1.21 – 1.27 (m, 26 H).

17,17,17-trifluoroheptadecan-1-ol. 15-Crown-5 (8.0 g; 36 mmol) was added with vigorous stirring to CsF (3.20 g; 21.1 mmol), which had been dried under vacuum

for 2 h. This was followed by the addition of 20 mL of anhydrous DME to the mixture with vigorous stirring. After cooling the solution mixture to -20 °C (ice / NaCl mixture), a solution of 2-((16-iodohexadecyl)oxy)tetrahydro-2*H*-pyran (3.0 g; 6.6 mmol) and TMS-CF₃ (4.0 g; 28 mmol) in 10 mL DME was added to the reaction mixture slowly over 5 min. The reaction was then warmed to room temperature and left stirring for 12 h. After that, 100 mL of hexanes was added to the reaction mixture, which resulted in precipitate formation that was filtered off. The filtrate was washed with half-saturated brine (1 x 100 mL) and the organic layer was dried over MgSO₄. The solvent was then evaporated to dryness by rotary evaporation.

The crude fluorinated pyran was then dissolved in 100 mL absolute ethanol containing PTSA (2.0 g; 12 mmol), and stirred at 55 °C for 3h. The ethanoic solution was then removed by rotary evaporation, and the crude product was redissolved in Et₂O (200 mL), washed with half-saturated brine (3 × 100 mL), and dried over MgSO₄. The solvent was evaporated to dryness by rotary evaporation to give 17,17,17-trifluoroheptadecan-1-ol in an 82 % yield. ¹H NMR (400 MHz, CDCl₃): δ 3.63 (t, 2 H, *OCH*₂), 2.01 (m, 2 H, *CH*₂*CH*₂), 1.51 – 1.57 (m, 4 H), 1.25 – 1.32 (m, 24 H).

17,17,17-trifluoroheptadecane-1-thiol (*F1H16SH*). *17,17,17-*

trifluoroheptadecan-1-ol (1.80 g; 5.80 mmol) was dissolved in 50 mL anhydrous THF under argon. The solution was then cooled to 0 °C in an ice bath. NEt₃ (1.4 mL; 10 mmol) was slowly added to the cooled solution, and the resulting mixture was stirred for 30 min at 0 °C. MsCl (1.5 mL; 19 mmol) was then added dropwise, and the reaction

was allowed to warm to room temperature and stirred for 6 h. The reaction was quenched with 50 mL of ice-cold water. The product was extracted with Et_2O (3 × 100 mL) and the combined organic phases were washed with 1M HCl (1 × 100 mL), water (1 × 100 mL), and brine (1 × 100 mL). The organic layer was dried over anhydrous MgSO₄, followed by removal of the solvent by rotary evaporation.

The crude product was dried under high vacuum overnight, and then dissolved in 100 mL of absolute ethanol (previously degassed) under argon. KSAc (2.32 g; 20.3 mmol) was added to the solution, and the mixture was refluxed for 6 h. After cooling the reaction to room temperature, water was added (100 mL) to the reaction, and the product was extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with water (1 × 100 mL) and brine (1 × 100 mL), and then dried over MgSO₄. Removal of the solvent by rotary evaporation afforded the crude thioacetate, which was dried and carried to the next step without purification.

The crude thioacetate was dissolved in dry THF (50 mL) and added dropwise to a stirring slurry of LiAlH₄ (0.154 g; 4.06 mmol) in THF (10 mL) at 0 °C. The reaction was then stirred at room temperature for 6 h under argon. The reaction was quenched at 0 °C using water (25 mL, previously degassed), and the resulting solution was then acidified with 1M H₂SO₄ solution (previously degassed). This mixture was extracted with Et₂O (3 × 100 mL). The combined organic phases were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried over MgSO₄, and evaporated to dryness by rotary evaporation. The crude thiol was purified by column chromatography on silica gel (hexanes) to give 17,17,17-trifluoroheptadecane-1-thiol (**F1H16SH**) in a 53 % yield. ¹H NMR (500 MHz, CDCl₃): δ 2.51 (q, J= 7.33 Hz, 2 H, *SCH*₂), 2.02 – 2.07 (m, 2 H, *CF*₃*CH*₂), 1.50 – 1.63 (m, 4 H), 1.22 – 1.35 (m, 24 H), 0.876 (t, J=7.05 Hz, 1 H). ¹³C NMR (125 MHz, CDCl₃): δ 124.09–130.07 (q), 39.28 (s), 34.15 (s), 33.92 (s), 33.70 (s), 33.48(s), 31.69 (s), 29.61-29.73 (m), 29.46(s), 29.12-29.27 (d), 28.79 (s), 28.48 (s), 24.75 (s), 21.92(m), 14.22 (s)

2.2.3. Preparation of Monolayers

Gold substrates were prepared by thermal evaporation of the metals (chromium and gold) onto Si(100) wafers under vacuum at a pressure $\leq 6 \times 10^{-5}$ torr. The chromium layer of 100 Å was deposited on the silicon surface to aid in the adhesion of a subsequent 1000 Å layer of gold.²⁶ To optimize film formation, the gold was deposited at a rate of 1 Å/s. The substrates were rinsed with absolute ethanol, dried with ultra-pure nitrogen gas, and used promptly after cleaning. Thiol solutions, at 1 mM concentration in absolute ethanol, were prepared in glass vials that had been previously cleaned with piranha solution and rinsed thoroughly with deionized water, followed by absolute ethanol. [Caution: Piranha solution is highly corrosive, should never be stored, and should be handled with extreme care.]. Two freshly cut and cleaned gold slides (3 cm × 1 cm) were inserted into each of the solutions. The thin film samples were allowed to equilibrate for 48 h. SAMs produced from H1F6HnSH (n = 10, 11) were then allowed to equilibrate at 40 °C for an additional period of 24 h. Following the equilibration period, all SAMs were rinsed with THF, then absolute ethanol and dried with ultra-pure nitrogen gas before characterization.

2.2.4. Characterization of Monolayers

Ellipsometric Thickness Measurements. The thicknesses of the monolayers were determined using a Rudolph Research Auto EL III ellipsometer equipped with a He-Ne laser (632.8 nm). The incident angle was fixed at 70°. The refractive index of the sub-layer was set to 1.45, in accordance with the established protocol.²⁷ The calculated thickness for each sample was the average of the data collected for measurements made at six points (i.e., three different points for each slide).

X-ray Photoelectron Spectroscopy (XPS). XPS spectra of the SAMs were obtained using a PHI 5700 X-ray photoelectron spectrometer with monochromatic Al K α X-ray source (hv = 1486.7 eV) incident at 90° relative to the axis of the hemispherical energy analyzer. Spectral data were collected using a take off angle of 45° from the surface and a pass energy of 23.5 eV. The binding energies were referenced to the Au 4f_{7/2} peak at 84.0 eV.

Wettability Measurements. A ramé-hart model 100 contact angle goniometer was employed to measure the contact angles of the various liquids on the generated films using a Matrix Technologies micro-Electrapette 25 set at the slowest speed of 1 μ L/s. The following contacting liquids were dispensed (to obtain an advancing contact angle, θ_a) and withdrawn (to obtain a receding contact angle, θ_r) on the surface of the SAMs: water (H₂O), *n*-hexadecane (HD), *N*,*N*-dimethylformamide (DMF), decalin (DC), 1bromonaphthalene (BNP), and perfluorodecalin (PFD). The measurements were performed at room temperature (293 K) with the pipette tip remaining in contact with the drop throughout the procedure. The reported data for each sample was the average of measurements obtained from two slides, with three points per slide with data collected at both edges of the liquid drop.

Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS). Surface IR spectra were collected using a Nicolet Nexus 670 Fourier transform spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instrument PEM-90 photoelastic modulator. The incident angle of the p-polarized light reflected from the sample was set to 80° with respect to the surface normal. The spectra of the C-H stretching region (2700-3100 cm⁻¹) were collected using 512 scans at a spectral resolution of 4 cm⁻¹.

2.3. Results and Discussion

The performance of the H1F6HnSH FSAMs was compared to that of normal alkanethiols with an equivalent carbon count in the molecular chain (H18SH and H17SH). These SAMs are fully characterized in the literature and provide a point of reference for the complete data set for this series of SAMs when formed on the same batch of vapor deposited gold. To provide an appropriate comparison for the influence of the unique interfacial dipole of the new FSAMs, we have included two CF_{3} -terminated alkanethiols (F1H17SH and F1H16SH) bearing the same number of carbons to the above-mentioned molecules.

2.3.1. Ellipsometric Assessment of SAM Formation

The SAMs of the newly designed methyl-capped partially fluorinated alkanethiols (H1F6HnSH; n = 11, 10) were developed in ethanol initially for 48 hours –

established literature on fluorinated alkanethiols indicate that ethanol is the appropriate liquid for developing this form of FSAM.²⁰ The first set of ellipsometric measurements provided thickness data for the new FSAMs that were short of the anticipated thicknesses, while the other SAMs prepared for this experiment were in line with anticipated film thicknesses. In order to improve the packing of the new thiolated molecules on gold, all of the SAMs were further equilibrated in ethanol at 40 °C for an additional 24 h.²⁸

The average thicknesses of the SAMs measured after equilibration in ethanolic solution for 48 h are shown in Table 2.1. The thicknesses of the SAMs generated from normal alkanethiols (H18SH and H17SH) are within experimental error of the literature values, 22 Å and 20 Å for H18SH and H17SH, respectively.^{25,28} The CF₃-terminated SAMs produced measured thicknesses of 21 Å and 20 Å for F1H17SH and F1H16SH, respectively. Since prior research into CF₃-terminated alkanethiolate SAMs has shown that these adsorbates form films that are generally about 1 Å shorter than their normal alkanethiolate counterparts, the obtained values appear to be appropriate for these molecules.²⁹ And the additional equilibration time (i.e., 24 h) produced no effect on the thickness of the final monolayer film (data not shown). On the other hand, the initial thickness values (i.e., after 48 h) for the methyl-capped fluorinated thiols were 17 Å and 16 Å for H1F6H11SH and H1F6H10SH, respectively. The increase in thickness from H1F6H10SH to H1F6H11 is in line with the increase of one methylene unit (~1.1 Å per CH₂ unit).^{25,30} However, after the additional equilibration time at 40 °C, the measured thicknesses show an increase of 2 Å for H1F6H11SH and 1 Å H1F6H10SH.

Adsorbate	48 h at 25 °C	Additional 24 at 40 °C
H1F6H11SH	17	19
H1F6H10SH	16	17
F1H17SH	21	
F1H16SH	20	
H18SH	22	
H17SH	20	

Table 2.1. Ellipsometric Data for SAMs Formed from Methyl-capped Fluorinated

 Alkanethiols, Normal Alkanethiols and CF₃-terminated Alkanethiols

Ellipsometric data were obtained with an error of ± 1 Å.

The results obtained from the methyl-capped fluorinated films correspond to those of partially fluorinated alkanethiol films with similar structures.^{30,31} Unlike the current study, the FSAMs formed from analogous structures developed to well-packed films within 48 h in ethanol.^{20,32} Considering that the carbon backbone for the H1F6HnSH FSAMs are equivalent to that of the corresponding HnSH or F1HnSH films, and the perfluorinated segment for similarly structured adsorbates has been reported to exhibit a reduced tilt from normal as compared to the hydrocarbon segment, the films' thicknesses were anticipated to be close to their comparative offsets.^{26,31} This reduction in film thickness could reflect a lower chain density for the H1F6HnSH FSAMs as compared to the other SAMs analyzed in this study. Due to the larger size of the fluorinated helix (with a diameter of 5.6 Å vs 4.2 Å for a hydrocarbon chain), the fluorinated chains are expected to occupy less space on the gold lattice, as was shown by an AFM analysis in an earlier report.³³ Furthermore, structural studies on SAMs of

partially fluorinated alkanethiols (F10Hn; where n = 11, 17, 33) have shown that an increase in length for the alkyl spacer results in some disordering for the fluorinated layer, and that the increase in vdW interactions among the methylene spacers results in an increase in tilt for the fluorinated chains.^{26,33} The aforementioned reasons could result in a lower chain density, which translates to lower thicknesses for the H1F6HnSH FSAMs. In order to address this concern, additional analysis of the films thickness is provided in the following section.

2.3.2. XPS Analysis of the Composition of the SAMs

XPS analysis of SAMs reveals the chemical nature of the atoms on the surface as well as insight into the structural features of the monolayers being investigated.³⁴ Survey spectra obtained for the given SAMs show the presence of only Au, C, F, and S for the H1F6HnSH and F1HnSH SAMs, while HnSH SAMs only show Au, C, and S. Note that the H1F6HnSH SAMs were analyzed by XPS after equilibrating the SAMs for an additional 24 h at 40 °C. The binding energies of the elements are shown in Table 2.2. The S 2p region for all the SAMs investigated herein (see Figure 2.2) reveals that a peak associated with bound sulfur is positioned at ~ 162 eV. This characteristic peak has been assigned to the S $2p_{3/2}$ binding energy for sulfur bound to gold.³⁵ The absence of peaks at ~164 eV, a binding energy associated with the sulfur of unbound thiol, indicates that the rinse procedure used to clean the SAMs is sufficient to remove unbound thiol from the surface. In addition, a successful rinse procedure insures that the thickness values discussed in the earlier section are representative of monolayers bound to the gold surface.

	Peak Position (eV)						
	C 1s (CH2)	C 1s (CF2)	C 1s (CF3)	F1s	S 2p _{3/2}		
H1F6H11SH	284.7	291.1		688.4	161.8		
H1F6H10	284.6	291.1		688.3	161.9		
F1H17SH	284.7		292.7	688.2	162.0		
F1H16SH	284.8		292.7	688.3	161.9		
H18SH	284.9				161.9		
H17SH	284.9				161.9		

Table 2.2. XPS Peak Position for H1F6HnSH, F1HnSH, and HnSH SAMs on Gold



Figure 2.2. XPS spectra for the S 2p region of the investigated SAMs: H18SH (black), H17SH (black dash), F1H17SH (red), F1H16SH (red dash), H1F6H11SH (blue), and H1F6H10SH (blue dash).



Figure 2.3. XPS spectra for the C 1s region of the investigated SAMs: H18SH (black), H17SH (black dash), F1H17SH (red), F1H16SH (red dash), H1F6H11SH (blue), and H1F6H10SH (blue dash).

Aside from determining the chemical composition of a monolayer, XPS analysis can be used to qualitatively examine the chain density of the molecules that form a monolayer. Figure 2.3 shows the C 1s region of all SAMs prepared for this study. The C 1s spectra of the H1F6HnSH FSAMs reveal two peaks characteristic of CF_2 and CH_2 units.^{26,33} The C1s peak corresponding to the CH_2 units for both of these FSAMs is shifted to a lower binding energy as compared to those of the HnSH and F1HnSH SAMs. Additionally, the binding energy of the C 1s peak for the CH_2 units for H1F6H10SH is lower than that of H1F6H11SH. Such a shift in binding energy is indicative of changes in packing density of the thiolates on the gold surface. The first observation is in line with the increased vdW diameter of the fluorinated helix as compared to the hydrocarbon chain; this causes them to occupy a larger space on the gold lattice as opposed to that occupied by a normal alkanethiolate or CF₃-terminated alkanethiolate adsorbate.^{14,21,33} On the other hand, the shift in the C 1s peak for the CH₂ units for the **H1F6H10SH** FSAM to a lower binding energy with respect to that of the **H1F6H11SH** FSAM indicates that increasing the methylene spacer improves the packing density of the chains in the monolayer. It has been previously observed in monolayer films of chains that are similar in chemical structure that well-packed films would act as good insulators, thus retarding the processes of completely discharging secondary electrons generated by XPS irradiation. This then translates into an increase in the binding energy of their emitted electrons. On the other hand, loosely pack chains behave as poor insulators.^{33,36,37}



Figure 2.4. XPS spectra for the F 1s region of the investigated SAMs: H18SH (black), H17SH (black dash), F1H17SH (red), F1H16SH (red dash), H1F6H11SH (blue), and H1F6H10SH (blue dash).

Figure 3.4 shows the F 1s spectra of the SAMs. The H1F6HnSH and F1HnSH SAMs show an F 1s peak originating from the fluorine atoms on the CF₂ and CF₃ groups, respectively. Note that the binding energy of F1H17SH and F1H16SH is lower than that of H1F6H11SH. Frey *et al.* have described the change in the binding energy of the F 1s electrons as a function of the monolayer's thickness, as a consequence of increasing the distance of the core hole from the screening electrons of the substrate, a final state effect.²⁶ In a separate account on SAMs of FnHmSH (n + m = 16), Colorado and coworkers noted an increase in the attenuation of Au 4f signal as the number of fluorocarbons increased, while the film's thickness was maintained at a constant value.³¹ This same trend was also observed in their FnH11SH SAMs (n = 1-10). Similarly, in the data presented herein, the addition of fluorocarbons in H1F6HnSH SAMs seems to have a larger role in the final state effect than the increased monolayer thickness of the F1HnSH SAMs, leading to the observed shift in F 1s binding energy. Note, this is also evident in the increase in the broadening of the C 1s (CH₂) peak of the H1F6HnSH SAMs. Finally, the shift in the F 1s spectra of H1F6H10SH FSAM to a lower binding energy than that of H1F6H11SH likely indicates a better insulating layer and packing density in the H1F6H11SH FSAMs (vide supra).^{33,36,37} Taking into account all of the collected XPS data, the packing density of the SAMs formed from the H1F6HnSH adsorbates appears to be less than that of the HnSH and the F1HnSH SAMs, and there is an apparent enhancement in packing density in the H1F6H11 FSAMs vis-à-vis the H1F6H10SH FSAMs.

2.3.3. PM-IRRAS Analysis of the Relative Crystallinity of the SAMs

The relative conformational order and chain orientation for alkanethiolate selfassembled monolayer films can be determined using surface IR. The crystalline nature of SAMs has been characterized based on the position of the antisymmetric methylene C-H stretching band ($v_{as}^{CH_2}$).^{27,38,39} The appearance of this band at ~2918 cm⁻¹ is an indication of a relatively crystalline monolayer with alkyl moieties adopting an all *trans*extended conformation similar to that of paraffin wax. However, shifts of this band to a higher wavenumber indicate a less ordered SAM – a monolayer with gauche defects. Figure 2.5 and 2.6 shows the PM-IRRAS spectra for the C–H stretching region of the SAMs studied herein. **H18SH** SAMs have a $v_{as}^{CH_2}$ band at 2918 cm⁻¹, which is consistent with a relatively crystalline monolayer with *trans*-extended chains. The **H1F6H11** FSAM also



Figure 2.5. PM-IRRAS spectra in the C–H stretching region for SAMs generated from the adsorption of H18SH (black), H1F6H11SH (black dash), H1F6H10SH (red), and

H17SH (red dash) on gold surfaces. SAMs of HnSH serve as a reference for the shifts in the bands associated with the methylene C-H stretching vibrations. exhibits a $v_{as}^{CH_2}$ band at 2918 cm⁻¹, and the film formed from H1F6H10SH exhibits a $v_{as}^{CH_2}$ band at 2919 cm⁻¹. This is consistent with IR studies that analyzed FnH11SH FSAMs, and to the SAMs in this study formed from F1HnSH, as shown in Figure 2.6.^{20,40} Based on the above-mentioned data, the hydrocarbon spacer of H1F6H11SH exhibits a conformational order that is as crystalline in nature as the alkyl chains of the H18SH SAMs. In addition, the hydrocarbon spacer of H1F6H11SH is more ordered than that of H1F6H10SH. The latter statement is in agreement with the results obtained from XPS, where the shift to a lower binding energy for the C 1s peak of the H1F6H10SH FSAM indicated a more disordered film than that of H1F6H11SH.



Figure 2.6. PM-IRRAS spectra in the C–H stretching region for SAMs generated from the adsorption of H1F6H11SH (black), H1F6H10SH (black dash), F1H16SH (red), and F1H17SH (red dash) on gold surfaces.

2.3.4. Contact Angle Study of the Interfacial Properties of the SAMs

Highly fluorinated surfaces enjoy an extremely low surface energy that manifests in their high degree of repellency towards both water and oil.^{6,7,41} This has motivated surface scientists to incorporate fluorinated chains into a variety of materials in an effort to minimize their interfacial energy, thus creating surfaces with low adhesion and coefficients of friction.^{22,23} Accordingly, FSAMs formed from terminally fluorinated alkanethiols have been used to study the effect of the degree of fluorination on surface wettability. This research led to the conclusion that the dipole associated with the fluorinated end of the adsorbates forming CF₃-terminated SAMs causes the surfaces to be less hydrophobic than those of normal alkanethiolate SAMs.¹⁸⁻²⁰ To expand the aforementioned knowledge on the role of an interfacial dipole to that of an HC-FC dipole on surface interfacial energy, the wettability of FSAMs formed from the H1F6HnSH molecules have been probed by a variety of polar liquids including a polar protic liquid (water - H_2O , $\gamma_{LV} = 72.8 \text{ mN/m}$),⁴² a polar aprotic liquid (dimethylformamide – DMF, γ_{LV} = 34.4 mN/m),⁴³ and a bulky hydrocarbon liquid with a localized dipole (bromonaphathalene - BNP). We have also probed the new FSAMs with nonpolar liquids including a liquid formed from a long alkyl chain (hexadecane – HD, $\gamma_{LV} = 27.1 \text{ mN/m}$,⁴³ a bulky bicyclic hydrocarbon liquid (decalin - DC $\gamma_{LV} = 29.4$ mN/m (trans); 31.7 mN/m (cis)),⁴³ and a bulky bicyclic perfluorinated liquid (perfluorodecalin – PFD, $\gamma_{LV} = 19.2 \text{ mN/m}$).⁴⁴ The corresponding values are presented in Table 3.3 where they are compared to the SAMs formed from HnSH and F1HnSH. The advancing contact angle data for the HnSH SAMs show that the H18SH SAM is less wettable than that of **H17SH**, which is consistent with observations reported in the literature.¹⁹ This phenomenon is largely due to the orientation of the terminal methyl group, which is more aligned with the surface normal in **H18SH** SAMs than **H17SH** monolayers. For the alkanethiolate films with an odd number of carbons in the alkyl chain backbone, where the methyl group is more tilted away from the surface normal, there is a greater degree of interfacial contact with the alkyl chain because of an increased interfacial exposure of the last methylene unit in the chain.⁴⁵ This causes the films formed from odd-numbered chains in thiolate SAMs to be more wettable than the ones formed from even-numbered chains, as displayed in Figure 2.7.

	H ₂ O	DMF	BNP	DC	HD	PFD
H18SH (even)	116	72	67	54	48	38
H17SH	116	68	65	49	44	30
H1F6H11SH (even)	109	45	68	57	48	
H1F6H10SH	108	54	75	65	58	
F1H17SH (even)	112	59	76	69	63	
F1H16SH	113	62	82	70	62	

Table 2.3. Advancing Contact Angles (θ_a , °) for Various Contacting Liquids Measured on SAMs Formed from H18SH, H17SH, H1F6H11SH, H1F6H10SH, F1H17SH, and F1H16SH

^a Contact angle data are the average of at least 12 measurements reproducible within \pm 1°. -- indicates a contact angle \leq 15°, which means that the film is fully wetted by the given liquid.

Aside from the anticipated increase in wettability of the F1HnSH SAMs by polar liquids, as compared to that of HnSH SAMs, due to the FC–HC dipole, the data in Table 3.3 show an inverted odd-even effect for the SAMs with a CF₃ terminus. For these films, even-numbered chains are more wettable than odd ones. According to Colorado *et al.*, this phenomenon is caused by the orientation of the terminal CF₃ group (*vide supra*), which is directed toward the contacting liquid in SAMs with even-numbered chains and away from it in SAMs with odd-numbered chains.^{19,20,43}



Figure 2.7. Contact angles of water (\blacktriangle) and DMF (\triangledown) on SAMs of HnSH, H1F6HnSH, and F1HnSH formed on gold.

To evaluate the role of the inverted dipole (HC–FC) in the newly designed FSAMs of H1F6HnSH, we first will compare the wettability data of the **H1F6H11SH**

SAMs to those of H18SH and F1H17SH. The values for the advancing contact angles for polar liquids composed of small molecules are lower on the H1F6H11SH films than on those formed from H18SH and F1H17SH. Furthermore, H1F6H11SH SAMs are far more wettable than the other two films when in contact with the polar aprotic liquid (DMF). The latter is due to the weaker cohesive forces in DMF vis-à-vis water whose molecules experience an increase in cohesive forces owing to hydrogen bonding. At a glance, these results indicate that the methyl-capped partially fluorinated alkanethiolate FSAMs are less hydrophobic than their normal alkanethiolate counterparts due to the dipole at the HC-FC termini. On the other hand, the difference in wettability trends of the polar liquids on H1F6H11SH and F1H17SH SAMs likely reflect the influence of the chemical composition of the outermost methyl group, as well as the spatial arrangement of the outer atomic layer at the liquid-solid interface. The CF₃ groups for SAMs formed from F1HnSH have been shown to pack tightly, while the CH₃ termini of the H1F6H11SH FSAMs are likely loosely packed owing to the larger vdW radii of the underlying perfluorinated segments.^{14,21,33} Therefore, the probing liquids can intercalate in the outer most layer of the monolayer. Based on earlier studies on F10HnSH SAMs, the interchain distance of the fluorinated chains is ~ 5.8 Å.³³ On the other hand structural studies of F1HnSH SAMs have shown that their interchain distance is ~ 4.9 Å (based on the lattice spacing of this type of film measured by AFM).^{14,21} Thus, probing liquids can insert themselves below the outermost layer which gives rise to an increase in wetting by the smaller polar molecules on H1F6H11SH (109° for H₂O and 45° for DMF) as compared to the F1H17SH SAM (112° for H₂O and 59° for DMF). Examining the

wettability data for BNP (bulky liquid with a localized dipole), there seems to be support for the insertion argument. The inability of the BNP molecules to insert themselves below the outermost methyl layer reduces the interaction of the dipole of this liquid with the surface dipoles on **H1F6H11SH** (68°) and **F1H17SH** SAMs (76°) (Figure 2.8). This results in the interaction of BNP with these surfaces to be more in line with a nonpolar liquid than a polar one, as can be seen by its contact angle on the SAM formed from **H18SH** (67°). Nonetheless, **H1F6H11SH** SAMs are more wettable with BNP than **F1H17SH** films. This is due to the difference in the chemical nature of the terminal group, where the CF₃ units in **F1H17SH** SAMs lead to non-ideal dispersive interactions between fluorocarbons in the film and hydrocarbons in BNP.

The contact angle values obtained for liquids whose surface interactions are dominated by dispersive forces (HD, DC) on **H1F6H11SH** indicate that the chains are indeed well packed as was also determined by the IR analysis (*vide supra*). This is most clearly revealed by the inability of hexadecane to intercalate between the chains of the **H1F6H11SH** SAMs. To evaluate the oleophobic character of the methyl-terminated fluorinated FSAMs, wettability data of decalin (a bulky hydrocarbon liquid) on the **H1F6H11SH** SAMs (57°) shows that they are more oleophobic than the **H18SH** films (54°), as shown in Figure 2.8. A driving force for such phenomenon could be the presence of the perfluorocarbon segment, which lies almost at the interface, along with the steric bulk of these perfluorocarbons, which should reduce the intercalation of liquid molecules within the chain assembly. In the **H1F6H11SH** monolayer system, the smaller radius of the CH₃ groups on top of the larger fluorocarbon helix would also contribute to the underlying CF₂ units interacting with liquids in contact with these FSAMs. This would lead to a reduced wetting behavior for hydrocarbon liquids on the **H1F6H11SH** SAMs due to the aforementioned non-ideal dispersive interactions between hydrocarbons and fluorocarbons.



Figure 2.8. Advancing contact angle values of BNP (\star), DC (\blacksquare), HD (\blacklozenge), and PFD (\blacklozenge) on SAMs derived from HnSH, H1F6HnSH, and F1HnSH on gold.

The addition of **H1F6H10SH** to the set of SAMs evaluated herein provides insight into the anomalies present in the structural and interfacial properties of these newly derived SAMs due either to the number of methylenes in the alkyl spacer or the total number of carbons present in the H1F6HnSH chains. In earlier sections, the underlying methylene units have shown that the hydrocarbon moiety in **H1F6H11SH** FSAMs is better packed and more crystalline than that of the **H1F6H10SH** FSAMs.

The wettability data shown in Table 3.3 indicate that the H1F6H11SH FSAM is more wettable than that of the **H1F6H10SH** FSAM for all the liquids used in this study except H₂O, which produced results that were statistically equivalent for the two FSAMs. Based on the XPS and IR data discussed in earlier sections, chains in the H1F6H10SH FSAMs are less densely packed and the alkyl segment is less ordered for this monolayer as compared to that in the H1F6H11SH film. As mentioned earlier in this section, this has produced an effect on the measured interfacial energies of these new monolayers. However, the observed differences between the H1F6H11SH SAMs and those of H1F6H10SH cannot be directly assigned as a consequence of a chain-carbon number effect on the orientation of the terminal group, as is the case in *trans*-zigzagged thiolated SAMs. The fluorinated segment, with a half-turn helix at 6 fluorocarbons, could result in the methyl unit being oriented in a manner different from that of a CF₃ or a CH₃ unit at the terminus of a *trans*-extended alkane chain. Thus, the observed odd-even effect could be the result of a combination of factors, among which includes the slight disorder caused in H1F6H10SH SAMs due to the reduced number of CH₂ units, as well as the exposure of the underlying fluorocarbons at the film's interface, which seems to be greater in the FSAMs of H1F6H10SH than that of H1F6H11SH FSAMs.

2.4. Conclusions.

The new type of methyl-capped partially fluorinated alkanethiols (H1F6HnSH) were successfully synthesized and used to generate methyl-terminated partially fluorinated FSAMs on gold. Ellipsometric analysis confirmed that such monolayers are best developed in ethanol for 48 h, followed by further equilibration at 40 °C for 24 h. XPS analysis confirmed the formation of monolayers with all sulfur atoms bound to

gold. When compared to normal alkanethiolate SAMs (HnSH), XPS analysis of C 1s binding energy indicates that the packing density of H1F6HnSH FSAMs is less than that of the HnSH SAMs. Such an effect would probably arise from the increased vdW diameter of the fluorinated helix, resulting in an increased interchian distance. Nonetheless, the alkyl spacers of H1F6HnSH FSAMs adopt a trans-extended conformation as indicated by the antisymetric C-H stretching vibration of the methylene units in the PM-IRRAS spectra. The wettability data helped construct a general impression about the effect that having an inverted dipole (HC-FC) at the interface of H1F6HnSH FSAMs had on interfacial energy. These films are less hydrophobic than their hydrocarbon counterparts. Furthermore, the wetting behavior of polar aprotic liquids is greater for the H1F6HnSH films than for those of F1HnSH. We attribute this effect to the larger diameter of the fluorinated layer underneath the terminal methyl unit, which allows for the small polar molecules to intercalate into the film. The wettability of dispersive contacting liquids show that the H1F6HnSH FSAMs have an oleophobic character that is \geq to that of the HnSH SAMs. Such behavior has led us to conclude that the underlying fluorocarbon units might be exposed to the FSAM interface. The latter is further supported by the odd-even effects observed between the H1F6H11SH FSAMs and that of H1F6H10SH, where the latter behaves similarly to an F1HnSH SAM when contacted by hydrocarbon contacting liquids (a measure of interfacial dispersive forces). These findings open new avenues to be explored, including an investigation of the surface orientation of the methyl terminal group in the H1F6HnSH FSAMs, as well as the frictional properties exhibited by these films, recognizing that having a small alkyl tail group placed on a fluorinated film might reduce interfacial friction.
2.5. References

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Chapter 3: Alkyl-capped Partially Fluorinated Alkanethiols: An Evaluation of the Effect of the HC–FC Dipole on the Properties of the Corresponding Thin Films

3.1. Introduction

Over the past few years, fluorinated organic thin films have seen a broad increase in use in nanotechnology. Their ability to perform as nanoscale lubricants makes them a prime choice as coatings for nanoelectromechanical systems (NEMSs) and microelectromechanical systems (MEMSs).¹⁻³ Such applications have generally involved fluorinated self-assembled monolayer (FSAM) films that were assembled from partially perfluorinated alkyl silanes, a thin film format that can be challenging to apply. However, the knowledge gained from these application oriented studies of fluorinated films has allowed researchers to develop a better understanding of these highly robust coatings that possess low adhesive characteristics.^{4–6} In a recent report, such perfluorinated films on silica have yielded surfaces with better frictional properties than Teflon.^{3,7} Furthermore, in organic electronics, coating electrodes with perfluorinated amphiphiles changes the work function of such surfaces, which can help reduce the charge transfer barrier between an overlying conjugated polymer and the coated electrode.⁸⁻¹⁰ But the application of fluorinated thin films is not limited to electronics devices; the incorporation of such fluorinated films in biomaterials can create nonbiofouling surfaces exhibiting reduced adsorption of non-specific proteins.^{11,12}

Of the known self-assembled monolayer (SAM) formats, those that are comprised of thiolates on gold have been the most widely studied as model systems to comprehend the effect that structurally tailored adsorbates have on the physical properties of the resulting films.¹³⁻¹⁶ Research involving partially fluorinated alkanethiols has revealed a variety of avenues towards the design of molecules that can generate surfaces with certain desired properties.^{4,17} Such surfaces include perfluorinated SAMs formed from $F(CF_2)_n(CH_2)_2SH$ where the films' properties reflect the dominance of the large perfluorinated segment, as compared to the short alkyl spacer.^{18–21}. Such segmented structuring of fluorocarbon/hydrocarbon adsorbates has enabled detailed studies into the true nature of the role that limited levels of fluorination exert upon the interfacial properties of the coated substrate. The pioneering work of Colorado and coworkers on partially fluorinated SAMs of the form $F(CF_2)_n(CH_2)_{11}SH$ where n = 1-10 (FnH11SH) have shown that many of the physical properties of such films are a function of the degree of fluorination present in the molecule.^{22–25} Furthermore, the structural features of these SAMs, such as the films' relative crystallinity and chain density, are a function of the size of the alkyl spacers.^{26–27} In addition, a recent study on the thermally induced solution desorption of such SAMs indicates that the enhancement of van der Waals (vdW) interactions of the hydrocarbon sub-layer and the high degree of crystallinity that is enjoyed by perfluorinated segments result in the formation of fluorinated SAMs with an improved thermal stability.²⁵

In the previous report, we introduced methyl-terminated partially fluorinated SAMs of the form $CH_3(CF_2)_6(CH_2)_nSH$ where n = 10,11 (H1F6HnSH), as the first examples of FSAMs where the perfluorinated segment was sandwiched between two hydrocarbon segments, producing an HC–FC dipole at the interface of the film. The films' formation was confirmed by XPS analysis, which also indicated that both of these FSAMs were slightly less densely packed than those of octadecanethiol (**H18SH**), due in part to the larger size of the fluorinated helix (~5.6 Å) as compared to the underlying hydrocarbon chain (~4.2 Å).²⁸ Both types of films are illustrated in Figure 3.1.



Figure 3.1. Illustration of SAMs generated from H1F6H11SH and H18SH on gold.

With the H1F6HnSH FSAM structure, the presence of the larger perfluorinated segment immediately under the terminal methyl group exposes contacting liquids to the underlying CF₂ units at the surface of the film. In our first study on this form of adsorbate, this phenomenon resulted in an improved oleophobic character for a bulky hydrocarbon contacting liquid (decalin) on the **H1F6H11SH** SAMs as compared to that of **H18SH**. And the influence of the HC–FC dipole at the chain termini for **H1F6H11SH** monolayers appeared to contribute to an improved wettability for this FSAM by polar liquids as compared to the SAM formed from **H18SH**. Yet the data gathered in the initial study fell short from providing definitive results regarding which influence (if any) was the most important factor in defining the surface energy of these films; the HC–FC dipole, the presence of the perfluorinated moiety near the interface, or the general ordering of the FSAM. To help provide clarity and to assist in the evaluation of the distance at which the HC–FC dipole ceases to influence the interfacial properties of the

self-assembled films, we have synthesized and generated SAMs of alkyl-capped fluorinated thiols of the form $H(CH_2)_n(CF_2)_6(CH_2)_{11}SH$ (HnF6H11; where n = 3, 4, and 5; H3F6H11SH, H4F6H11SH, and H5F6H11SH, respectively). The questions that we aim to answer are: (1) what is the length of the top alkyl segment at which the HC-FC dipole loses it effect on wettability; (2) what is the length of the top alkyl segment at which the underlying perfluorinated segment no longer impacts wettability; and (3) what is the effect of extending the alkyl-capping segment on the ordering of the resulting FSAMs? Question (2) reflects the important role that different contributions to surface energy can play in the analysis of contact angle data. Along with the three new adsorbates, we have also included both H1F6H11SH and H18SH films to provide perspective in our efforts to monitor the behavior of the HnF6H11SH thiols as new surfactants for forming FSAMs. The molecules included in this study are shown in Figure 3.2. SAMs formed from the four HnF6H11SH molecules, along with that of H18SH as a reference film, have been prepared and these monolayers have been analyzed using optical ellipsometry, contact angle goniometry, polarization modulation infrared reflection-adsorption spectroscopy (PM-IRRAS), and X-ray photoelectron spectroscopy (XPS).



Figure 3.2. Molecular structure of the HnF6H11SH and the **H18SH** adsorbates investigated in this study.

3.2. Experimetal Section

3.2.1. Materials and Methods

Gold shot (99.999%) was purchased from Americana Precious Metals. Chromium rods (99.9%) were purchased from R. D. Mathis Company. Polished singlecrystal Silicon (100) wafers were purchased from Silicon Wafer Enterprises and rinsed with absolute ethanol (Aaper Alcohol and Chemical Co.) before use. Tetrahydrofuran (THF) and diethyl ether (Et₂O) were purchased from Avantor Performance Materials (Macron Chemicals and J.T. Baker), were dried by distilling over calcium hydride (Sigma-Aldrich). The other solvents, methanol (MeOH), hexanes, and acetone (from Avantor Performance Materials); dichloroethane (DCE) and ethyl acetate (from Sigma Aldrich); and ethanol (EtOH – Aaper Alcohol and Chemical Co.), were either used as received or degassed by sparging with nitrogen gas. methanesulfonyl chloride (MsCl), azobisisobutyronitrile (AIBN), lithium aluminum hydride (LiAlH₄), triethylamine (Et₃N), allyl alcohol, palladium on carbon (Pd/C), and methyl 10-undecenoate, were all purchased from Sigma Aldrich and used as received. 1,6-diiodoperfluorohexane (Synquest Labs), 5-bromo-1-pentene, 4-bromo-1-butene and potassium thioacetate (KSAc; all from TCI America), were used as received. Hydrochloric acid (HCl) and sulfuric acid (H₂SO₄ – from J.T. Baker); zinc dust (Fischer); potassium iodide (KI - EMD Chemicals); glacial acetic acid (AcOOH - Mallinckrodt Chemicals), were all used as received.

Octadecanethiol (**H18SH**) was from Sigma-Aldrich. Heptadecanethiol (**H17SH**) was prepared by a procedure found in the literature.²⁹ Chloroform-*d* was purchased from Cambridge Isotope Laboratories and used for all NMR spectra. The silica gel used for column chromatography was obtained from Sorbent Technologies.

3.2.2. Synthesis of Terminally Alkylated Partially Fluorinated Alkanethiols.

12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorodocosane-1-thiol (H5F6H11SH) and 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorohenicosane-1-thiol (H4F6H11SH) were synthesized following the detailed procedure shown in Scheme 3.1. 12,12,13,13,14,14,15,15, 16,16,17,17-dodecafluoroicosane-1-thiol (H3F6H11SH) was synthesized following the procedure shown in Scheme 3.2. H1F6H11SH was synthesized according to the procedure outlined in Chapter 2. All fluorinated mercaptans were stored under argon atmosphere prior to their use in SAMs formation.

Scheme 3.1. Synthetic Route for the Preparation of 12,12,13,13,14,14,15,15, 16,16,17,17-dodecafluorodocosane-1-thiol (H5F6H11SH) and 12,12,13,13,14,14, 15,15,16,16,17,17-dodecafluorohenicosane-1-thiol (H4F6H11SH).



Scheme 3.2. Synthetic Route for the Preparation of 12,12,13,13,14,14, 15,15,16,16,17,17-dodecafluoroicosane-1-thiol (H3F6H11SH).



12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-10,17-diiodoheptamethvl decanoate (1). In a 100 mL pear-shaped Schlenk flask, the starting 1,6diiodoperfluorohexane (1.68 g; 3.03 mmol), AIBN (10 mol %) and methyl 10undecenoate (0.40 g; 2.0 mmol) were dissolved in DCE (20 mL). The system was degassed with three cycles of a standard freeze-pump-thaw procedure. After warming to room temperature, the reaction mixture was heated to 85 °C for 5 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The product was purified by silica gel chromatography using hexanes /ethyl acetate (95 / 5) as the eluent to 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-10,17give methvl diiodoheptadecanoate (1) in a 60% yield. ¹H NMR (500 MHz, CDCl₃): δ 4.32 (m, 1 H, *CHICH*₂), 3.66 (s, 3 H), 2.70 – 2.95 (m, 2H, *CH*₂*CF*₂), 2.30 (t, J= 7.56 Hz, 2 H, $C(O)CH_2$, 1.71 – 1.85 (m, 2 H, CHICH₂), 1.51 – 1.63 (m, 4 H), 1.24 – 1.42 (m, 8 H). 96

¹⁹F NMR (470 MHz, CDCl₃): δ - 58.8 (m, 2 F), -111.8 - -115.2 (m, 4 F; CF₂I and CF₂CH₂), -120.91 (m, 2 F), -121.45 (m, 2 F), -123.50 (m, 2 F).

methyl 22-bromo-12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-10,19diiododoco-sanoate (2a). In a 100 mL pear-shaped Schlenk flask, *F*-iodoester 1 (0.70 g; 0.93 mmol), AIBN (10 mol %) and 5-bromo-1-pentene (0.28 g; 1.9 mmol) were dissolved in DCE (20 mL). The system was degassed with three cycles of a standard freeze-pump thaw procedure. After warming to room temperature, the reaction mixture was heated to 85° C for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The product was purified by silica gel chromatography using hexanes /ethyl acetate (90 / 10) as the eluent to give methyl 22-bromo-12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-10,19-diiododocosanoate (**2a**) in an 86% yield. ¹H NMR (500 MHz, CDCl₃): δ 4.30 – 4.34 (m, 2 H), 3.66 (s, 3 H), 3.43 – 3.45 (m, 2 H), 2.73 – 2.92 (m, 4 H), 2.30 (t, J= 7.56 Hz, 2 H), 2.11 – 2.19 (m, 1 H), 1.92 – 2.04 (m, 3 H), 1.72 – 1.84 (m, 2 H), 1.60 – 1.63 (m, 2 H), 1.51 – 1.56 (m, 1 H), 1.23 – 1.42 (m, 9 H). ¹⁹F NMR (470 MHz, CDCl₃): -111.16 – -114.78 (m, 4F), -121.56 (m, 4F), -123.56 (m, 4F).

methyl 21-bromo-12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-10,19-diiodohenicosanoate (**2b**) 88% yield. ¹H NMR (500 MHz, CDCl₃): δ 4.49 – 4.51 (m, 1 H), 4.30 – 4.35 (m, 1 H), 3.66 (s, 3 H), 3.59 – 3.61 (m, 1 H), 3.46 – 3.51 (m, 1 H), 2.75 – 3.04 (m, 4 H), 2.30 (t, *J*= 7.56 Hz, 2 H, *C(O)CH*₂), 2.22 – 2.34 (m, 2 H), 1.72 – 1.83 (m, 2 H, *CH*₂*ICH*), 1.51 – 1.63 (m, 4 H), 1.18 – 1.42 (m, 8 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -110.5 – -114.8 (m, 4 F), -121.54 (m, 4 F), -123.53 (m, 4 F).

methyl 22-bromo-12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorodocosanoate (3a). In a 250 mL pear-shaped Schlenk flask, intermediate **2a** (0.72 g; 0.80 mmol) was dissolved in glacial acetic acid (50 mL). A minimal amount of THF was added to help dissolve the fluorinated ester. Zinc dust (1.570 g; 23.94 mmol) was added to the mixture, and the system was degassed with three cycles of a standard freeze-pump thaw procedure. After warming to room temperature, the reaction was stirred for 48 h. The reaction mixture was then diluted with THF (50 mL) and filtered through a bed of Celite. The Celite pad was washed with 200 mL of hot Et_2O . The filtrate was washed with water $(3 \times 50 \text{ mL})$, saturated aqueous NaHCO₃ $(1 \times 50 \text{ mL})$, and brine $(1 \times 50 \text{ mL})$, and dried over MgSO₄. The solvent was then removed by rotary evaporation and the product was dried under high vacuum for 24 h to give methyl 22-bromo-12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorodocosanoate (**3a**) in a 96% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.66 (s, 3 H), 3.42 (t, J= 6.70 Hz, 2 H, CH_2Br), 2.30 (t, J = 7.56 Hz, 2 H, C(O)CH₂), 1.98 - 2.13 (m, 4 H, CH₂CF₂), 1.87 - 1.93 (m, 2 H, CH_2CH_2Br), 1.54 – 1.64 (m, 8 H), 1.24 – 1.37 (m, 12 H)

methyl 21-bromo-12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorohenicosanoate (**3b**) 94% yield (**3b**) ¹H NMR (500 MHz, CDCl₃): δ 3.66 (s, 3 H), 3.43 (t, J = 6.70, 2 H, *CH*₂*Br*), 2.30 (t, J = 7.56, 2 H, *C(O)CH*₂), 2.13 – 1.91 (m, 6 H), 1.78 (m, 2 H), 1.62 – 1.54 (m, 4H), 1.35 (m, 12 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.30 (m, 4 F), -121.78 (m, 4 F), -123.58 (m, 4 F)

methyl 12,12,13,13,14,14,15,15,16,16,17,17-*dodecafluoro-22-iododocosanoate* (4*a*). F-bromo-ester (**3a**) (0.50 g; 0.77 mmol) and potassium iodide (0.640 g; 3.86 mmol) were dissolved in 25 mL of acetone. The reaction mixture was refluxed for 24 h. Afterwards, acetone was removed via rotary evaporation, and the reaction mixture was redissolved in Et₂O (200 mL). The organic layer was washed with water (100 mL), followed by brine (100 mL), and dried over MgSO₄. After filtration, the solvent was removed by rotary evaporation and the product was dried under vacuum to afford methyl 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-22-iododocosanoate (**4a**) in 97% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.66 (s, 3 H), 3.20 (t, *J*=6.87 Hz, 2 H, *CH*₂*I*), 2.30 (t, *J*=7.56 Hz, 2 H, *C(O)CH*₂), 2.01 – 2.11 (m, 4 H), 1.83 – 1.89 (m, 2 H), 1.43 – 1.65 (m, 8 H), 1.25 – 1.36 (m, 12 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.32 (m, 4 F), -121.78 (m, 4 F), -123.59 (m, 4 F).

methyl 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-21-iodohenicosanoate (**4b**) in 95% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.66 (s, 3 H), 3.20 (t, *J*=6.87 Hz, 2 H, *CH*₂*I*), 2.30 (t, *J*= 7.56 Hz, 2 H, *C(O)CH*₂), 1.98 – 2.10 (m, 4 H), 1.91 (m, 2H), 1.71 – 1.78 (m, 2 H), 1.54 – 1.63 (m, 4 H,), 1.20 – 1.43 (m, 12 H). ¹⁹F NMR (470 MHz, CDCl₃): δ - 114.28 (m, 4 F), -121.77 (m, 4 F), -123.58 (m, 4 F).

12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorodocosan-1-ol (5a). In a 250 mL RB-flask *F*-iodo-ester **4a** (0.52 g; 0.75 mmol) was dissolved in glacial acetic acid (50 mL). A minimal amount of THF was added to help dissolve the fluorinated ester. Zinc dust (0.730 g; 11.1 mmol) was added under a flow of argon, and the reaction mixture was stirred at room temperature for 40 h. The reaction mixture was then diluted

with THF (50 mL) and filtered through a bed of Celite. The Celite pad was washed with 200 mL of hot Et_2O . The filtrate was then washed with water (3 × 50 mL), saturated aqueous NaHCO₃ (1 × 50 mL), and brine (1 × 50 mL), and then dried over MgSO₄. The solvent was then removed by rotary evaporation. The crude product was dried under high vacuum for 24 h and carried to the next step without further purification.

The crude *F*-methyl ester was dissolved in anhydrous THF (50 mL) and added dropwise to a stirring slurry of LiAlH₄ (0.110 g; 2.90 mmol) in THF (10 mL) at 0 °C. The reaction was then warmed to room temperature and stirred for 6 h under argon. The reaction was quenched at 0 °C using water (20 mL), followed by 1M aqueous HCl solution (20 mL). The mixture was then extracted with Et₂O (3 × 100 mL). The combined organic layers were washed with water (1 × 100 mL) and brine (1 × 100 mL), and dried over MgSO₄, and evaporated to dryness by rotary evaporation. The product was purified by column chromatography on silica gel (hexanes / ethyl acetate; 75 / 25) to give 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorodocosan-1-ol (**5a**) in a 95% yield from **4a**. ¹H NMR (500 MHz, CDCl₃): δ 3.63 (q, *J*= 6.30 Hz, 2 H, *OHCH*₂), 1.98 – 2.09 (m, 4 H), 1.54 – 1.61 (m, 6 H), 1.25 – 1.37 (m, 18 H), 0.91 (t, *J*= 7.05 Hz, 3 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.34 (m, 4 F), -121.80 (m, 4 F), -123.63 (m, 4 F),

12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorohenicosan-1-ol (**5b**) 76% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.64 (t, J= 6.70 Hz, 2 H, *OHCH*₂), 1.98 – 2.10 (m, 4 H), 1.55 – 1.58 (m, 6 H), 1.28 – 1.41 (m, 16 H), 0.95 (t, J = 7.22 Hz, 3 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.32 (m, 4 F), -121.80 (m, 4 F), -123.62 (m, 4 F). *S*-(*12*, *12*, *13*, *13*, *14*, *14*, *15*, *15*, *16*, *16*, *17*, *17*-*dodecafluorodocosyl*) ethanethioate (6a). *F*-alcohol **5a** (0.384 g; 0.708 mmol) was dissolved in anhydrous THF under argon, and the solution cooled to 0 °C in an ice bath. NEt₃ (0.3 mL; 2 mmol) was added slowly, and the resulting mixture was stirred for 30 min at 0 °C. Subsequently, MsCl (0.3 mL; 4 mmol) was added dropwise. The reaction was allowed to warm up to room temperature and stirred for 12 h. The reaction was then quenched with 50 mL of ice-cold water. The product was extracted with Et₂O (3 × 100 mL) and the combined organic phases were washed with 1M aqueous HCl (1 × 100 mL), water (1 × 100 mL), and brine (1 × 100 mL). The organic layer was dried over anhydrous MgSO₄, followed by removal of the solvent by rotary evaporation.

The crude product was then dissolved in a blend of ethanol / THF (60:40) (100 mL), which had been previously degassed under argon. KSAc (0.875 g; 7.66 mmol) was added to the solution, and the mixture was refluxed for 6 h. After cooling the reaction to room temperature, water was added (100 mL), and the product was extracted with Et₂O (3×100 mL). The organic phases were combined and washed with water (1×100 mL) and brine (1×100 mL), and then dried over MgSO₄. Removal of the solvent by rotary evaporation afforded the crude thioacetate, which was purified by column chromatography on silica gel (hexanes / ethyl acetate; 95 / 5) to give S-(12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorodocosyl) ethanethioate (**6a**) in an 89% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.85 (t, *J* = 7.39 Hz, 2 H, (CO)*SCH*₂), 2.32 (s, 3 H),

2.00 – 2.05 (m, 4 H), 1.54 – 1.58 (m, 6 H), 1.26 – 1.43 (m, 18 H), 0.91 (t, J= 7.05 Hz, 3 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.34 (M, 4 F), -121.80 (m, 4 F), -123.63 (m, 4 F). *S*-(12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorohenicosyl) ethanethioate (**6b**) in 83% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.85 (t, J = 7.39 Hz, 2 H, *OHCH*₂), 2.32 (s, 3 H), 2.02 – 2.06 (m, 4 H), 1.54 – 1.58 (m, 6 H), 1.26 – 1.41 (m, 16 H), 0.94 (t, J = 7.39 Hz, 3H). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.33 (m, 4 F), -121.80 (m, 4 F), -123.46 (m, 4 F).

12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorodocosane-1-thiol

(H5F6H11SH). Thioacetate **6a** (0.38 g; 0.63 mmol) was dissolved in dry THF (30 mL) and added dropwise to a stirring slurry of LiAlH₄ (0.072 g; 1.9 mmol) in THF (5 mL) at - 10 °C. The reaction was stirred at approximately -10 °C for 6 h under argon. The reaction was then quenched at -10 °C using water (25 mL, previously degassed), and was acidified with a 1M H₂SO₄ solution (previously degassed). The mixture was then extracted with Et₂O (3 × 100 mL). The combined organic phases were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried over magnesium sulfate, and evaporated to dryness by rotary evaporation. The resulting thiol was purified by column chromatography on silica gel (hexanes / ethyl acetate; 99/ 1) to give 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorodocosane-1-thiol (**H5F6H11SH**) in an 85% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.52 (q, *J* = 7.33 Hz, 2 H, *SCH*₂), 2.00 – 2.09 (m, 4 H, *CH*₂*CF*₂), 1.55 – 1.74 (m, 6 H), 1.19 – 1.42 (m, 19 H), 0.91 (t, J= 7.05 Hz, 3 H). ¹³ C NMR (125 MHz, CDCl₃): δ 34.13 (s), 31.31 (s), 31.18 (m), 31.01 (m), 30.87 (m),

29.14-29.54 (m), 28.45 (s), 24.75 (s), 22.37 (s), 19.87-20.20 (d), 13.91 (s). Broad peaks at δ 108.73–120.64 are characteristic of a long perfluorocarbon chain (*Israel J. Chem.* **2000**, *40*, 81).

12,12,13,13,14,14,15,15,16,16,17,17-dodecafluorohenicosane-1-thiol (H4F6H11SH) in 91% yield. (H4F6H11SH) ¹H NMR (500 MHz, CDCl₃): δ 2.52 (q, J= 7.45 Hz, 2 H, *SHCH*₂), 1.94 – 2.12 (m, 4 H), 1.52 – 1.65 (m, 6 H), 1.27 – 1.46 (m, 16 H), 0.95 (t, J= 7.39 Hz, 3 H). ¹³C NMR (125 MHz, CDCl₃): δ 39.25 (s), 34.5 (s), 30.58-31.22 (m), 29.00-29.54 (m), 28.45-28.58 (d), 24.74 (s), 22.23-22.35 (d), 20.20 (s), 13.78 (s), 4.05 (s). Broad peaks at δ 108.93–120.59 are characteristic of a long perfluorocarbon chain (*Israel J. Chem.* 2000, *40*, 81). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.36 (m, 4 F), -121.82 (m, 4 F), -123.64 (m, 4 F).

methyl 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-20-hydroxy-10,19diiodoico-sanoate (7). In a 100 mL pear-shaped Schlenk flask, F-iodoester 1 (0.85 g; 1.1 mmol), AIBN (10 mol %) and allyl alcohol (0.13 g; 2.2 mmol) were dissolved in DCE (20 mL). The system was degassed with three cycles of a standard freeze-pump-thaw procedure. After warming to room temperature, the reaction mixture was heated to 85° C for 12 h. After cooling to room temperature, the solvent was removed by rotary evaporation. The product was purified by silica gel chromatography using hexanes /ethyl 30) acetate (70)eluent system give methyl / as the to 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoro-20-hydroxy-10,19-diiodoicosanoate (7) in a 93% yield. ¹H NMR (500 MHz, CDCl₃): δ 4.43 (m, 1 H), 4.32 (m, 1 H), 3.79

(m, 2 H, OCH_2), 3.66 (s, 3 H), 2.70 – 3.06 (m, 4 H), 2.30 (t, J = 7.56 Hz, 2 H, $C(O)CH_2$), 2.06 (t, J = 6.87 Hz, 1 H), 1.71 – 1.85 (m, 2 H), 1.51 – 1.63 (m, 2 H), 1.24 – 1.42 (m, 10 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -111.2 – 114.9 (m, 4 F), -121.57 (m, 4 F), -123.58 (m, 4 F).

methyl 12,12,13,13,14,14,15,15,16,16,17,17-*dodecafluoroicos-19-enoate* (8). To a solution of 7 (0.85 g; 1.0 mmol) in THF (20 mL), was added glacial acetic acid (50 mL). Zinc dust (2.06 g; 31.4 mmol) was added under a flow of argon, and the reaction mixture was stirred at room temperature for 40 h. The reaction mixture was then diluted with THF (50 mL) and filtered through a bed of Celite. The Celite pad was washed with 100 mL of hot THF. The filtrate was then diluted with Et₂O (200 mL), washed with water (3 × 100 mL), saturated aqueous NaHCO₃ (1 × 100 mL), and brine (1 × 50 mL), and dried over MgSO₄. The solvent was removed by rotary evaporation to give *methyl* 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoroicos-19-enoate (8) in a 90% yield. ¹H NMR (500 MHz, CDCl₃): δ 5.79 (m ,1 H), 5.32 (m, 2 H), 3.66 (s, 3 H), 2.84 (m, 2 H), 2.29 (t, *J* = 7.56 Hz, 2 H), 1.98 – 2.10 (m, 2 H), 1.55 – 1.63 (m, 2 H), 1.21 – 1.37 (m, 14 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -113.17 (m, 2 F), -114.32 (m, 2 F), -121.80 (m, 4 F), -123.16 (m, 2 F), -123.60 (m, 2 F).

12, 12, 13, 13, 14, 14, 15, 15, 16, 16, 17, 17-dodecafluoroicosan-1-ol (9). The perfluorinated olefin **8** (0.51 g; 0.94 mmol) was dissolved in anhydrous THF (50 mL) and added dropwise to a stirring slurry of LiAlH₄ (0.107 g; 2.82 mmol) in THF (10 mL) at 0 °C. The reaction was then warmed to room temperature and stirred for 6 h under argon. The reaction was then quenched at 0 °C using water (20 mL), followed by the addition of

1M aqueous HCl solution (20 mL). The mixture was then extracted with Et_2O (3 × 100 mL). The combined organic layers were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried over MgSO₄, and evaporated to dryness by rotary evaporation. The crude alcohol was carried to the next step without further purification.

The crude alcohol was dissolved in MeOH (30 mL) and added to a slurry of Pd/C (10%; 0.1 equivalent). The mixture was placed under hydrogen (1 atm) and stirred at room temperature for 12 h. The reaction was filtered through a bed of Celite, which was then washed with Et₂O (100 mL). After removal of solvent by rotary evaporation, the product was purified by silica gel chromatography using hexanes / ethyl acetate (70 / 30) as the eluent system to give 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoroicosan-1-ol (**9**) in a 66% yield. ¹H NMR (500 MHz, CDCl₃): δ 3.64 (t, J=6.70 Hz, 2 H, *OHCH₂*), 1.98 – 2.08 (m, 4 H), 1.55 – 1.65 (m, 6 H), 1.14 – 1.41 (m, 14 H), 1.01 (t, J=7.22 Hz, 3 H). ¹⁹F NMR (470 MHz, CDCl₃): δ -114.36 (m, 4 F), -121.83 (m., 4 F), -123.74 (m, 4 F).

S-(*12*, *13*, *13*, *14*, *14*, *15*, *15*, *16*, *16*, *17*, *17*-dodecafluoroicosyl) ethanethioate (10). Alcohol **9** (0.32 g; 0.62 mmol) was dissolved in anhydrous THF (20 mL) under argon, and the solution was cooled to 0 °C in an ice bath. NEt₃ (0.26 mL; 1.9 mmol) was added slowly, and the resulting mixture was stirred for 30 min at 0 °C. Subsequently, MsCl (0.24 mL; 3.1 mmol) was added dropwise. The reaction was allowed to warm to room temperature and stirred for 12 h. The reaction was then quenched with 50 mL of ice-cold water. The product was extracted with Et₂O (3 × 100 mL) and the combined organic phases were washed with 1M aqueous HCl (1 × 100 mL), water (1 × 100 mL), and brine $(1 \times 100 \text{ mL})$. The organic layer was dried over anhydrous MgSO₄, followed by removal of the solvent by rotary evaporation.

The crude product was then dissolved in anhydrous ethanol (50 mL), which had been previously degassed under argon. KSAc (0.345 g; 3.02 mmol) was added to the solution, and the mixture was refluxed for 6 h. After cooling the reaction to room temperature, water was added (100 mL), and the product was extracted with Et₂O (3 × 100 mL). The organic phases were combined and washed with water (1 × 100 mL) and brine (1 × 100 mL), dried over MgSO₄, and the solvent was removed by rotary evaporation. The crude product was purified by column chromatography on silica gel (hexanes / ethyl acetate; 95 / 5) to give S-(12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoroicosyl) ethanethioate (**10**) in a 98% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.85 (t, *J* = 7.39 Hz, 2 H, *SCH*₂), 2.32 (s, 3 H), 1.98 – 2.08 (m, 6 H), 1.52 – 1.66 (m, 4 H), 1.26 – 1.36 (m, 14 H), 1.02 (t, *J* = 7.39 Hz, 3 H). ¹⁹F NMR (470 MHz, CDCl₃): δ - 114.31 (m, 4 F), -121.80 (m, 4 F), -123.66 (m, 4 F).

12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoroicosane-1-thiol (H3F6H11SH). Thioacetate **10** (0.30 g; 0.52 mmol) was dissolved in dry THF (30 mL) and added dropwise to a stirring slurry of LiAlH₄ (0.059 g; 1.6 mmol) in THF (5 mL) at -10 °C. The reaction was stirred at ~ -10 °C for 6 h under argon. The reaction was then quenched at -10 °C using water (25 mL, previously degassed), followed by acidification with 1M H₂SO₄ solution (previously degassed). The mixture was then extracted with Et₂O (3 × 100 mL). The combined organic phases were washed with water (1 × 100 mL) and brine (1 × 100 mL), dried over magnesium sulfate, and evaporated to dryness by rotary evaporation. The resulting thiol was purified by column chromatography on silica gel (hexanes / ethyl acetate; 99/ 1) to give 12,12,13,13,14,14,15,15,16,16,17,17-dodecafluoroicosane-1-thiol (**H3F6H11SH**) in a 50% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.51 (q, *J*= 7.42 Hz, 2 H, *SCH*₂), 1.99 – 2.08 (m, 4 H), 1.57 – 1.67 (m, 6 H), 1.24 – 1.42 (m, 15 H), 1.01 (t, *J*= 7.42 Hz, 3 H).

3.2.3. Preparation of Monolayers

Gold substrates were prepared by thermal evaporation of the metals (chromium and gold) onto Si (100) wafers under vacuum at a pressure $\leq 6 \times 10^{-5}$ torr. The chromium layer of 100 Å was deposited on the silicon surface to aid in the adhesion of a subsequent 1000 Å layer of gold.²⁶ To optimize film formation, the gold was deposited at a rate of 1 Å/s. The substrates were rinsed with absolute ethanol, dried with ultra-pure nitrogen gas, and used promptly after cleaning. Thiol solutions at 1 mM concentration in absolute ethanol were prepared in glass vials that had been previously cleaned with piranha solution and rinsed thoroughly with deionized water, followed by absolute ethanol. [*Caution: Piranha solution is highly corrosive, should never be stored, and should be handled with extreme care.*]. Two freshly cut and cleaned gold slides (3 cm × 1 cm) were inserted into each of the solutions. The thin film samples were allowed to equilibrate for 48 h. SAMs of **HnF6H11SH** (n = 1, 3, 4, and 5) were then allowed to equilibrate at 40 °C for an additional period of 24 h. Following the equilibration period all SAMs were rinsed with THF, then absolute ethanol and dried with ultra-pure nitrogen gas before characterization.

3.2.4. Characterization of Monolayers

Ellipsometric Thickness Measurements. The thicknesses of the monolayers were measured using a Rudolph Research Auto EL III ellipsometer equipped with a He-Ne laser (632.8 nm). The incident angle was fixed at 70°. The refractive index of the sublayer was set to 1.45, in accordance with the established protocol.³⁰ The calculated thickness value for each sample was the average of the data collected for measurements made at six points (i.e., three different points for each slide).

X-Ray Photoelectron Spectroscopy (XPS). XPS spectra of the SAMs were obtained using a PHI 5700 X-ray photoelectron spectrometer with monochromatic Al K α X-ray source (hv = 1486.7 eV) incident at 90° relative to the axis of the hemispherical energy analyzer. Spectral data were collected using a take off angle of 45° from the surface and a pass energy of 23.5 eV. The binding energies were referenced to the Au 4f_{7/2} peak at 84.0 eV.

Wettability Measurements. A ramé-hart model 100 contact angle goniometer was employed to measure the contact angles of the various liquids on the generated films. Using a Matrix Technologies micro-Electrapette 25 set at the slowest speed of 1 μ L/s, the following contacting liquids were dispensed (advancing contact angle, θ_a) and withdrawn (receding contact angle, θ_r) on the surface of the SAMs: water (H₂O), *n*-hexadecane (HD), *N*,*N*-dimethylformamide (DMF), decalin (DC), 1-bromonaphthalene (BNP), and perfluorodecalin (PFD). The measurements were performed at room temperature (293 K) with the pipette tip in contact with the drop throughout the procedure. The reported data for each sample was the average of measurements obtained from two slides, three points per slide. Data was collected at both edges of the liquid drop.

Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM–IRRAS). Surface IR spectra were collected using a Nicolet Nexus 670 Fourier transform spectrometer equipped with a liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instrument PEM-90 photoelastic modulator. The incident angle of the p-polarized light reflected from the sample was set to 80° with respect to the surface normal. The spectra of the C–H region stretching region (2700-3100 cm⁻¹) were collected using 512 scans at a spectral resolution of 4 cm⁻¹.

3.3. Results and Discussion

3.3.1. Measurement of Monolayers Thickness by Ellipsometry

Monolayers of the HnF6H11SH series (n = 1, 3–5) were developed in ethanol and equilibrated for 48 h at room temperature. After the initial film development, they were further equilibrated for 24 h at 40 °C. In Chapter 2, we demonstrated that the thickness of the FSAM formed from **H1F6H11SH** improved after further equilibration at 40 °C for 24 h, therefore, these conditions were also used for the rest of the HnF6H11SH series. After the equilibration time, we evaluated the resulting changes in the monolayers' thicknesses using optical ellipsometry. The collected thickness data for the HnF6H11SH FSAMs are provided in Table 3.1. There is an observed increase in the thickness across the series

with an increase in the length of the terminal alkyl moiety. The values are 17 Å, 20 Å, 21 Å, and 26 Å for the FSAMs formed from **H1F6H11SH**, **H3F6H11SH**, **H4F6H11SH**, and **H5F6H11SH**, respectively. It should be noted that further equilibration of the HnF6H11SH FSAMs at 40 °C for 24 h produced an increase for the **H1F6H11SH** FSAM from 17 Å to 19 Å, as indicated in the previous study. On the other hand, the further equilibration time at an elevated temperature proved detrimental to the thicknesses of the other HnF6H11SH FSAMs (n = 3–5). As a consequence, the thicknesses of these monolayers were reduced by an average of ~ 3 Å for the **H3F6H11SH** and **H4F6H11SH** FSAMs and by ~ 1 Å for the **H5F6H11SH** FSAM. The latter change is within the experimental error generally associated with this instrumental technique (± 2 Å).²²

Adsorbate	48 h at 25 °C	Additional 24 at 40 °C
H1F6H11SH	17	19
H3F6H11SH	20	17
H4F6H11SH	21	17
H5F6H11SH	26	25
H18SH	22	
H178H	20	

Table 3.1. Ellipsometric Data for the FSAMs of Alkyl-Capped Fluorinated Alkanethiolsfrom the HnF6H11SH series, and the Normal Alkanethiolate SAM, HnSH

Ellipsometric data were obtained within ± 1 Å.

However, changes to the thickness in the monolayers of H3F6H11SH and H4F6H11SH could be a result of temperature induced disorder in the chains of the monolayer. Therefore, we chose to equilibrate the HnF6H11SH FSAMs (n = 3-5) at

room temperature similar to **H18SH** SAMs, which have a thickness in agreement with literature values of 22 Å.³¹

The shift in thickness of the HnF6H11SH monolayers is ~ 1 Å per added methylene unit for the films where n = 1, 3, and 4. This is followed by a significant increase in the thickness of the monolayer for the FSAM formed from **H5F6H11SH**. Comparing the thickness of the **H1F6H11SH** monolayer to that of **H18SH** (i.e., owing to the equivalent carbon count in the alkyl chain), the FSAM formed from **H1F6H11SH** has a film thickness that is ~ 3 Å less than the normal alkanethiolate SAM. This reduction was rationalized in Chapter 2 as reflecting disorder in the fluorinated segments of the monolayers. However, an estimated value for the thickness of an **H22SH** SAM would be ~ 26 Å; a thickness value that would be in agreement with that obtained from the **H5F6H11SH** monolayer. Therefore, based on the data obtained for this set of SAMs, it is possible to rationalize these observations as resulting from changes in the orientation and packing densities of the adsorbate chains. However, other experimental evidence will be needed to back up such an assertion, as further explained in the following section.

3.3.2. XPS Analysis of the Monolayer Films

XPS analysis of the FSAMs formed form the HnF6H11SH molecules reveals trends that appear to support the conclusion about film ordering reached in the previous section. The XPS spectral region presented in Figure 3.3 has a featured doublet assigned to the S $2p_{3/2}$ and S $2p_{1/2}$ binding energies that are present in a 2:1 ratio. The peak at ~162 eV has been assigned to the S $2p_{3/2}$ binding energy and is associated with thiolate sulfur bound to gold.³² For this series of FSAMs, the only peaks in this region of the XPS spectra are those of the thiolate sulfurs bound to gold. Therefore, the absence of a

peak at ~ 164 eV indicates that unbound sulfur or disulfide are not present in these SAMs.³² From this data, it is apparent that ethanol can be used as the deposition solvent for the generation of HnF6H11SH SAMs, as indicated in the previous study.



Figure 3.3. S 2p XPS spectra collected from SAMs derived from HnF6H11SH (n = 1, 3–5) and HnSH (n = 17, and 18).

The C 1s region of the XPS spectra for the HnF6H11SH FSAMs is presented in Figure 3.4. Two distinctive peaks appear in the spectra which have been assigned to the C 1s binding energy of the CF₂ moieties (~ 291 eV) and to that of the hydrocarbons (~284 eV). Table 3.2 provides the peak positions for the C 1s binding energy for the HnF6H11SH and HnSH SAMs. In normal alkanethiolate SAMs, shifts in the C 1s position to a higher binding energy in a series with an increasing number of methylene spacers have been attributed to an increase in the packing density of the chains of these

monolayers.^{33,34} The same trend has been observed in an XPS analysis of the C 1s peaks associated with the CH₂ units in partially fluorinated SAMs.²⁸ Examination of the C 1s (CH₃/CH₂) peak position of the FSAM formed fron **H1F6H11SH** and the **H18SH** SAM shows that the peak position shifts to a lower binding energy in the **H1F6H11SH** FSAM, which appears to indicate that the alkyl chains in this film are slightly less ordered than those found in the **H18SH** SAM. Such a conclusion would be in accord with the interpretation of the data made from the ellipsometric thickness values presented in the prior section. Additionally, there is a distinct asymmetry associated with this peak for the **H1F6H11SH** FSAM, which might indicate that the perfluorocarbon moiety is impacting the binding energies for the hydrocarbons nearest the perfluorocarbon chain. However, this distinct distortion of the peak shape is not present in the spectra for the other FSAMs formed from the HnF6H11SH series of thiols.

	Peak Position (eV)				
Adsorbate	C 1s (CH ₃ /CH ₂)	C 1s (CF ₂)	F 1s		
H1F6H11SH	284.7	291.1	688.4		
H3F6H11SH	284.6	291.0	688.3		
H4F6H11SH	284.9	290.9	688.3		
H5F6H11SH	284.9	291.0	688.3		
H18SH	284.9				
H17SH	284.9				

Table 3.2. XPS Peak Positions for C 1s of HnF6H11SH and HnSH SAMs and F 1s for HnF6H11SH SAMs



Figure 3.4. XPS spectra for (a) the C 1s spectral region and (b) the F 1s spectral region, collected from SAMs derived from HnF6H11SH (n = 1, 3-5) and HnSH (n = 17, and 18).

For **H3F6H11SH** FSAM, the binding energy of the C 1s (CH₃/CH₂) peak also shifts to a lower value of 284.6 eV, and the associated band appears to exhibit a slight asymmetry. However, the FSAMs formed from the HnF6H11SH thiols with the longer alkyl chain termini, where n = 4 and 5, have C 1s (CH₃/CH₂) at the same spectral peak positions as that of the alkanethiolate reference SAM. Additionally, while the C 1s (CH₃/CH₂) bands associated with the **H4F6H11SH** and **H5F6H11SH** FSAMs are broader than that of the **H18SH** SAM, they appear to be symmetric about the peak position. However, both the XPS and thickness data for these films produce trends associated with the changing terminal alkyl chain lengths that do not provide a proportional correlation with the change in the size of the terminal alkyl units. This could be the result of packing anomalies for the terminal alkyl chains, which might play a part in the broadening of the C 1s (CH₃/CH₂) peaks as compared to those of the HnSH SAMs in Figure 3.4. Note that the broadening of this peak for HnF6H11SH FSAMs decreases as n increases. The latter is further support that the chains of HnF6H11SH FSAMs pack better as the size of the terminal alkyl moiety increases.

Peaks associated with the fluorinated segments present in the XPS spectra for the C 1s (CF₂) and F 1s binding energies are displayed in Figure 3.4, and they exhibit an apparent shift to lower binding energies with an increase in the length of the terminal alkyl group. Similar trends have been observed in partially fluorinated alkanethiolate SAMs where the binding energies of the fluorinated segments increased with an increase in the size of the underlying methylene chain.²⁶ According to the literature, such an effect could be a result of the increased distance between the excited atoms (C or F) and the gold substrate.^{26,28,35} However, all the HnF6H11SH SAMs have the same number of methylene units, thus the same distance from the gold surface. A more plausible explanation is based on changes in the packing of the fluorinated segments due to the

increasing upper alkyl chain segment. As mentioned earlier in this section, increasing the length of the terminal alkyl segment results in an increased ordering of these hydrocarbon chains in the HnF6H11SH FSAMs. This assertion is supported by both the XPS analysis and the thickness measurements. Furthermore, given that the alkyl segment have a smaller diameter than the fluorinated ones, such improvement in packing structure of the overlying hydrocarbon segments would likely result in an increasingly disordered fluorinated sublayer. Thus, the shift observed in the binding energies of the C 1s (CF₂) and F 1s in the XPS spectra for the HnF6H11SH FSAMs where n > 1 is probably due to a decrease in the packing efficiency of the fluorinated chains.

3.3.3. PM-IRRAS Analysis of the Relative Crystallinity of the Monolayers

The orientation of the terminal group and the conformational order of the chains in organic monolayers have been studied by PM-IRRAS. The C–H stretching vibration region of the IR spectra is shown in Figure 4.Y. The position of the methylene C–H stretching bands has been used as an indicator of the relative crystallinity of the alkyl segment of typical thiolate SAMs. In normal alkanethiolate SAMs, the methylene C–H antisymmetric vibration ($v_{as}^{CH_2}$) has been reported to appear at ~2918 cm⁻¹ in relatively crystalline SAMs.³⁰ On the other hand, these bands shift to ~2924 cm⁻¹ in the presence of a liquid-like monolayer. As shown in table 3.5, the position of the $v_{as}^{CH_2}$ peak shifts slightly as the length of the terminal alkyl segment increases. These bands appear at 2918 cm⁻¹ for FSAMs formed from H1F6H11SH and H3F6H11SH, and 2919 cm⁻¹ and 2920 cm⁻¹ for the H4F6H11SH and H5F6H11SH FSAMs, respectively. Since the number of methylene units below the fluorinated helix in the HnF6H11SH FSAMs is kept constant at 11, we anticipate that these films have a similar ordering for the underlying alkyl segment, leading to a conclusion that the shift in peak position is more representative of the terminal alkyl group. This observation is further supported by the increased broadening in these peaks as n increases.



Figure 3.5. PM-IRRAS spectra for the C–H stretching region collected on SAMs derived from H18SH (black), H1F6H11SH (black dash), H3F6H11SH (red), H4F6H11SH (dash red), and H5F6H11SH (blue).

The methyl antisymmetric, $v_{as}^{CH_3}$, peaks appear at 2976, 2969, and 2966 cm⁻¹ for **H3F6H11**, **H4F6H11** and **H5F6H11**, respectively. Note that, the position of $v_{as}^{CH_3}$ bands shift to lower value as n increases and the value of the $v_{as}^{CH_3}$ bands approaches that of H18 at 2964 cm⁻¹. The trend observed for the methyl symmetric stretching bands is similar to the antisymmetric bands, as highlighted in Table 3.3. Such shifts are in line with the reduction of the electron withdrawing effect the fluorinated chains have on the terminal methyl groups; this is due to the increasing distance between the two caused by

the increase in the alkyl chain in the top layer. In addition, the broadening of these peaks has been attributed to the methyl termini being loose.³¹

	$v_{as}^{CH_2}$ (cm ⁻¹)	$v_s^{CH_2}(cm^{-1})$	$\nu_{as}^{CH_3}(cm^{-1})$	$\nu_s^{CH_3}(cm^{-1})$
H1F6H11SH	2918	2850		
H3F6H11SH	2918	2850	2976	2887
H4F6H11SH	2919	2850	2969	2881
H5F6H11SH	2920	2854	2966	2881
H18SH	2918	2850	2964	2878

Table 3.3. Peak Positions for the C–H Stretching Vibrations for the HnF6H11SHFSAMs and the H18SH SAM as Determined by PM-IRRAS

In the PM-IRRAS spectra shown in Figure 3.5, the intensity of the methyl C-H stretching vibration peaks change as a function of the number of carbons in the upper alkyl segment. With the exception of the IR spectra for the **H1F6H11SH** FSAM, whose methyl C-H stretching peaks could not be detected, the intensities of the methyl antisymmetric C-H stretch (at ~ 2976 - 2964 cm⁻¹) in adsorbates with an odd number of carbons in the terminal alkyl segment (**H5F6H11SH** and **H3F6H11SH**) are greater than the adsorbates with an even number (**H4F6H11SH**). The change is opposite for the methyl symmetric C-H stretch (around 2881 – 2887 cm⁻¹) whose intensity is higher in even (**H4F6H11**) than odd (**H5F6H11SH** and **H3F6H11SH**) adsorbates. Such changes are related to the orientation of the terminal methyl group with respect to the surface normal. Based on the surface selection rules, vibrations that change dipole moments

perpendicular to the surface are detected due to the enforcement between those dipoles and the image charges induced by the adsorbed molecule.^{36,37} For such a phenomenon to happen, the terminal methyl group for the **H5F6H11SH** and **H3F6H11SH** FSAMs align primarily away from the surface normal (parallel to the surface) than in the case of the **H4F6H11SH** FSAM. Such an orientation will align the vibration's dipole for the antisymmetric methyl C-H stretching vibration more perpendicular to the surface for the **H5F6H11SH** and **H3F6H11SH** films. On the other hand the symmetric stretching vibration will have a dipole that is aligned more parallel to the surface, hence the diminishment of that band for the **H3F6H11SH** and **H5F6H11SH** FSAMs.³⁸

3.3.4. Contact Angle Study of the Interfacial Properties of the Monolayers

The wetting behavior of a variety of contacting liquids on a surface helps shape a comprehensive picture of the interfacial energy and heterogeneity of organic films. In an effort to assess the extended effect of the HC–FC dipole buried underneath the alkyl moiety in the FSAMs of HnF6H11SH, we used water (polar protic), DMF (polar aprotic), and BNP (large molecules with a localized dipole) as contacting liquids. The results, as highlighted in Table 3.4, show that the degree of hydrophobicity increases in the series of HnF6H11SH FSAMs as n increases from 1 to 5. Note that the **HSF6H11SH** FSAM enjoy the same level of hydrophobicity as the **H18SH** SAM. The contact angle of DMF also reduces as the alkyl terminal groups increases in size. The contact angle of DMF, as shown in Figure 3.6, has a minimum value that occurs on the **H1F6H11SH** FSAM of 45°. This value increases to 62° for the **H3F6H11SH** FSAM and 66° for **H4F6H11SH**. However, FSAMs of **H5F6H11SH** show a greater wetting behavior (60°) than the previous two films. Such an increase in the wettability could result from an increased

disorder in the top alkyl segment, thus leading to an increase in the dispersive interaction between the contacting liquid and the upper interface of the film. The wettability of these SAMs by BNP seems to support the aforementioned argument. The advancing contact angle increases on the **H1F6H11SH** film (68°) as compared to the **H18SH** SAMs (67°), as has been observed in our earlier study. However, increasing the size of the top alkyl unit increases the wettability of the HnF6H11SH FSAMs with BNP, as shown in Table 3.4. This increase is clearly due to the rise in favorable interactions (namely dispersive forces) between the liquid and the alkyl terminal group. Furthermore, due to the exposure of the CF₂ units underneath the terminal methyl group in the **H1F6H11SH** FSAM, BNP has a smaller contacting angle on this SAM as compared to the other HnF6H11SH FSAMs; this is a result of non-ideal dispersive interactions.^{39,40}



Figure 3.6. Advancing contact angle values of water (\blacktriangle) and DMF (\triangledown) collected on SAMs derived from **H18SH** and HnF6H11SH (n = 1, 3–5) on gold.

The interactions between the exposed interface of these SAMs and the nonpolar contacting liquids (DC, HD, and PFD), as shown in Figure 3.7, are mainly of dispersive in nature. These interactions provide information regarding the nature of the ordering of the outer alkyl segment as well as the exposure of the underlying CF₂ units. The contact angle values of the nonpolar liquids on the H18SH SAM (48° for HD, 54° for DC and 38° for PFD) are in agreement with the reported data in the litiratue.^{31, 39–41} For HD on the H1F6H11SH FSAM the value is also 48°, which can be attributed to a combination of the exposure of the liquid to the underlying CF₂ units, along with intercalation around the methyl terminal group. This is supported by the wetting behavior of PFD on **H1F6H11SH** SAMs. These SAMs are completely wettable by PFD (CA \leq 15°), which indicates that the liquid is interacting with the fluorinated segment underneath.^{39,40} Burying the CH–CF dipole by increasing the size of the terminal groups result in increased interactions between the top alkyl moiety and the hydrocarbon liquids. This is shown by the enhanced wetting behavior of HD on these SAMs. However, the upper alkyl segment seems to be disordered, or less packed than that of the H18SH SAMs. The contact angles of HD and DC on H5F6H11SH SAMs, 36° and 26° respectively, is indicative that the pentyl terminal groups are producing a liquid like interface, which allows for greater interactions between the DC and HD molecules with the films interface. Note that the former has a higher contact angle value than the latter due to the bulkiness of DC molecules, which inhibits its intercalation between the disordered chains of the FSAMs. The increase in disorder of the terminal groups of the H5F6H11SH FSAMs are also supported by the PM-IRRAS data shown in the previous section.



Figure 3.7. Advancing contact angle values of BNP (\star), DC (\blacksquare), HD (\blacklozenge), and PFD (\blacklozenge) collected on SAMs derived from **H18SH** and HnF6H11SH (n = 1, 3–5) on gold.

	Table 3.4 .	Wettability	measurements on	HnF6H11SH	SAMs and	l H18SH SAMs
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	H ₂ O	DMF	BNP	DC	HD	PFD
H18SH	116	72	67	54	48	38
H1F6H11SH	109	45	68	57	48	
H3F6H10SH	113	62	67	52	45	
H4F6H11SH	115	66	65	50	45	
H5F6H11SH	116	60	61	36	26	20
3.4. Conclusions

Newly designed alkyl-capped partially fluorinated thiols have been successfully synthesized and used to generate new type of FSAMs. The formation of these monolayers was confirmed by XPS analysis. Thickness measurements of the HnF6H11SH FSAMs indicate that increasing the terminal alkyl segment gives rise to a thicker film, however at a lower rate as compared to the trends observed in the FnHmSH or HnSH films. Furthermore, XPS analysis indicates that while the hydrocarbon moiety seems show an increase in packing density, as indicated by a shift in binding energy of electrons emitted from the hydrocarbon segments, there is an induced disorder in the fluorinated part of the film. This could be the outcome of an increase in vdW interactions in the terminal alkyl segment as its length increases. PM-IRAAS analysis of the methylene antisymmetric C-H stretching vibration indicates an increased disorder in the chains of the H5F6H11SH FSAMs. Since all HnF6H11SH films have an equal number of methylene units in the underlying alkyl spacer, such disorder, whether present in the upper alkyl segment or in the fluorinated moiety below it, could be the result of changes in chain alignments for these two segments as they work to maximize their packing. Furthermore, PM-IRRAS analysis of the methyl symmetric C-H stretching bands of the HnF6H11SH FSAMs point towards an odd-even effect that is a function of the number of carbons in the extended alkyl moiety. H3F6H11SH and H5F6H11SH films show a higher intensity for this C–H stretching vibration (band at ~ 2960 - 2967 cm⁻¹) than H4F6H11SH FSAMs. This indicates that the methyl units in the H5F6H11SH and H3F6H11SH films are oriented more tilted away from the surface normal as compared to

the methyl moieties of the **H4F6H11SH** films. Based on the wettability data for the polar liquids on the HnF6H11SH FSAMs, increasing the size of the terminal alkyl segment screens the effect of the HC–FC dipole at the upper junction. This would indicate that the terminal alkyl moieties are sufficiently oriented to reduce the proximity of the liquids to the HC-FC dipole. In addition, contact angle values for dispersive liquids indicate that the interaction between the upper interface and the contacting liquids increases with an increasing size for the terminal alkyl moiety. However, the increased wettability of the **H5F6H11SH** film by nonpolar liquids raises questions regarding the orientation and ordering of the terminal alkyl chains, which appears to lean towards having a disordered interface based upon the IR data.

3.5. References

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Chapter 4. Self-Assembled Monolayers on Gold Generated from Fluorinated Alkanethiols Bearing Only Three Methylene Units in the Alkyl Spacer

4.1. Introduction

Fluorinated thin films serve as vital tools for modifying the surfaces of nanoscale devices. Such modifications include the adsorption of fluorinated amphiphiles on coinage metals as a means of corrosion prevention,¹ on metal oxides to reduce stiction in microelectromechanical (MEMS) devices,² and on medical implants as biomaterial coatings.^{3,4} The motivation to use these surfactants is tied to the ability of perfluorocarbon segments to transform the physical properties of an interface, such as the wettability, friction, and barrier properties of the resulting surfaces.^{5,6,7} Such modifications allow for the generation of films that exhibit low surface energy with coefficient's of friction that are a quarter of that of polytetrafluoroethylene (PTFE).⁸ In addition, the fact that the molecules of these thin films are chemically bound to the surface offers an advantage over the polymeric counterpart, namely PTFE, when used as a nanoscale coating for lubrication.

Self-assembled monolayers (SAMs) generated from the adsorption of fluorinated alkanethiols (FSAMs) on gold have been used as model thin films for evaluating the structural influences that determine the properties of organic films. Adsorption of these sulfur-based molecules leads to the sulfur headgroups binding covalently in an array on the Au(111) surface.^{9–13} The alkyl spacer tilts to maximize interchain van der Waals (vdW) interactions, stabilizing the film. Thiolate SAMs formed on gold offer key

advantages over other adsorbate/substrate combinations because of the inertness of gold as well as the moderately stable S–Au bond, with both of these characteristics allowing for greater control over experimental parameters and reproducibility of results. Therefore, this combination allows for a more complete assessment of the effect of chain modification on film properties as compared to other systems. Thus, concerning FSAMs, the ability to precisely control the number of fluorocarbons presented at the end of the chain allows a surface scientist to produce an FSAM film with specific interfacial character.

An additional structural characteristic can be found in FSAMs of the form $F(CF_2)_n(CH_2)_2SH$, abbreviated as FnH2, where $n \ge 6$. Due to the large van der Waals diameter of the perfluorocarbon segments, the chains are spaced ~5.7 Å apart, a larger spacing than that of hydrocarbon chains for SAMs on gold (~4.9 Å).^{14,15} Therefore, films of such adsorbates pack with their chains oriented roughly perpendicular to the surface, with a tilt angle $\sim 11^{\circ}$ from the surface normal, as opposed to well packed HSAMs where the tilt angle is $\sim 30^{\circ}$.^{16,17} These fluorinated thiolates form monolayers that adopt either a $c(7 \times 7)$ or $p(2 \times 2)$ hexagonal lattice, as compared to alkanethiolate SAMs (HSAMs) with a $(\sqrt{3} \times \sqrt{3})$ R30 hexagonal lattice.^{18,19} The impact of the larger van der Waals radii of the perfluorinated segments has also been credited with influencing the effective interfacial energy (dispersive energy) for the exposed surface of these thin films because the density of the terminal CF₃ groups has been reported to reduce with an increase in the length of the perfluorinated segments for FSAMs with equivalent alkyl spacers.²⁰ Wettability studies of FSAMs generated from thiols of the form F(CF₂)_n(CH₂)_mSH (FnHm, where the length of the fluorocarbon and hydrocarbon segments were varied, but the total chain length was held constant) versus FSAMs generated from thiols of the form $F(CF_2)_n(CH_2)_{11}SH$ (FnH11, where the length of the fluorocarbon segment was varied but the hydrocarbon chain was held constant), indicated little additional influence from these extended fluorocarbon segments upon the measured contact angles with changes in the underlying SAM structure.^{20,21} However, the interaction between a polar contacting liquid with each of the monolayers in the two series decreases with an increasing number of fluorocarbons until n = 5. Colorado *et al.* have attributed this observation to the burying of the dipole moment associated with the fluorocarbon-hydrocarbon (FC-HC) junction within the surface's interface.^{20,22} With the current study, the length of the perfluorocarbon segments would preclude the FC-HC dipole from impacting the collected contact angle data.

The research that is the focus of this paper investigates the manipulation of the structural and interfacial properties of FSAMs by introducing three new surfactants that are highly fluorinated with only a propyl unit as an alkyl spacer ($F(CF_2)_n(CH_2)_3SH$, the FnH3 series, where n = 8, 10 12, yielding **F8H3**, **F10H3**, and **F12H3**, respectively). SAMs formed from these new surfactants are compared to those formed from the thiols of the FnH2 series ($F(CF_2)_n(CH_2)_2SH$, where n = 8, 10, 12, yielding **F8H2**, **F10H2**, and **F12H2**, respectively), whose characteristics have been extensively investigated. Due to the small number of methylenes in the spacers of FnH2 FSAMs, their conformational arrangement on the surface becomes largely dictated by the size of the fluorocarbon helix. Molecular resolution microscopic studies have shown that such adsorbates give rise to a well-defined hexagonal lattice structure, which can be distorted by increasing the number of methylene units.¹⁸ The physical properties of such films are also directly affected by the size of the fluorocarbon segment. Films of **F8H2** have shown a low degree of wettability by both water and oil. And when such predominantly perfluorinated

surface structures are accompanied by a microscale increase in surface roughness, they can produce superhydrophobic surfaces; water contact angles $\geq 150^{\circ}$.^{23,24} Another study that displayed the benefits of the FnH2 system involves the ability to generate binarymixed monolayers from such surfactants. These include SAMs with fluorinated and nonfluorinated thiols, and those composed of two different fluorinated thiols. The first type of binary mixed SAM was realized from the adsorption of disulfides with two dissimilar chains, or from adsorbing a nonfluorinated thiol onto a monolayer of **F6H2**.^{25–} ²⁷ As for the second type, Tsao *et al.* showed that dual-component SAMs of **F8H11** and **F8H2** led to island formation, where the monolayers consisted predominantly of the long chains; in contrast, a mixture of **F8H2** and that of $F(CF_2)_8C(O)N(H)(CH_2)SH$ (**F8**) also gave phase-separated domains, but neither adsorbate was favored. Both types of monolayers are technologically relevant since they allow for an improvement in the tuning of the electronic and physical properties of FSAMs.^{28–31}

Nevertheless, prior work on FSAMs have shown that films of such adsorbates possess some defects at the metal-thiol interface due to the spacing restrictions imposed by the larger vdW diameter of the fluorocarbon helix being so close to the substrate. Thus, by extending the methylene spacer to three, as shown in Figure 4.1, we aimed to evaluate the effect of such a change on the conformational order of the adsorbate chains as well as upon the interfacial properties of the resulting films. The new films formed from the FnH3 series are characterized using optical ellipsometry, contact angle goniometry, polarization modulation infrared reflection-adsorption spectroscopy (PM-IRRAS), and X–Ray photoelectron spectroscopy (XPS). In addition, they are compared to SAMs formed from FnH2, where n = 8, 10, 12, which possess an analogous chemical structure and will allow for the detection of any odd-even effect on either the structural or

interfacial properties. SAMs formed from octadecanethiol (C18) are used as reference standards for this study.



Figure 4.1. Schematic illustrations of perfluorinated FSAMs on gold that possess either three or two methylene spacers.

4.2. Experimental Section

4.2.1. Materials and Methods

Gold shot (99.999%) was purchased from Americana Precious Materials. Metals. Chromium rods (99.9%) were purchased from R. D. Mathis Company. Polished single-crystal Silicon (100) wafers were purchased from Silicon Wafer Enterprises and rinsed with absolute ethanol (Aaper Alcohol and Chemical Co.) before use. n-Octadecanethiol (C18) was purchased from Sigma-Aldrich and used as received. The starting materials 1-iodo-1H,1H,2H,2H-perfluorodecane (94%), 1-iodo-1H,1H,2H,2Hperfluoro-dodecane (94%), and 1-iodo-1H,1H,2H,2H-perfluorotetradecane (90%) were purchased from SynQuest Laboratory. Iodoperfluorooctane (98%), iodoperfluorodecane (98%), and iodoperfluorododecane (97%) were purchased from SynQuest Laboratory. Triethylamine (NEt₃), potassium thioacetate (KSAc), lithium aluminum hydride (LiAlH₄), allyl alcohol (99%), tributyltin hydride (Bu_3SnH), and methanesulfonyl chloride (MsCl) were purchased from Sigma-Aldrich Co. and used as purchased. Azobisisobutyronitrile (AIBN) was purchased from Sigma-Aldrich Co. and was recrystallized from methanol prior to use. Solvents used in the synthesis, 1,2dichloroethane (DCE), tetrahydrofuran (THF), diethyl ether (Et₂O), toluene, and hexanes, were purchased from either Sigma-Aldrich or Avantor Performance Materials and used as received, unless stated otherwise. Magnesium sulfate $(MgSO_4)$ was purchased from J. T. Backer Co., and sulfuric acid (H_2SO_4) was purchased from MACRON. Column chromatography was performed using silica gel (40-60 µm), and thin-layer chromatography (TLC) was carried out using 200 µm-thick silica gel plates, both obtained from Sorbent Technologies, Inc. The developed TLC plates were visualized using molybdenum blue staining solution. Contacting liquids were of the highest purity available; n-hexadecane (HD) was purchased from Aldrich Chemical Co. and water was generated from a Milli-Q Water System with resistance of 18.2 M Ω (Millipore Corporation).

4.2.2. Synthesis of the Adsorbates

Synthesis of Perfluorinated Alkanethiols. Perfluorinated alkanethiols with spacers formed from three methylene units were synthesized using the method illustrated in Scheme 4.1. The perfluorinated alkanethiols with spacers formed from two methylene units were synthesized according to a procedure found in the literature.³² Because 1H,1H,2H,2H-perfluorotetradecanethiol has not been previously reported in the literature, the synthesis of this compound is also included in this subsection.

Scheme 4.1. Synthetic Scheme for the Preparation of the Perfluorinated Alkanethiol Adsorbates of the Form $F(CF_2)_n(CH_2)_3SH$, where n = 8, 10, 12 (the FnH3 series).



4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecan-1-ol (1a). In a 100 ml pear shaped Schlenk flask the starting 1-iodoperfluorooctane (5.00 g, 9.16 mmol), AIBN (10 mol %) and allyl alcohol (0.8 mL; ~12 mmol) were dissolved in DCE (30 mL). The system was degassed with three cycles of a standard freeze-pump thaw procedure. After warming to room temperature, the reaction mixture was heated to 85 °C for 8 h. After 8 h, the reaction was cooled to room temperature and an additional equivalent of AIBN was added under argon, followed by the same degassing method. The system was heated again to 85 °C for 8 h. The reaction percent conversion of perfluorinated iodide was monitored via ¹⁹F NMR. The reaction was then transferred to a 250 mL round bottom flask, and the solvent was removed via rotary evaporation. The crude product was dissolved in anhydrous toluene, and AIBN (10 mol %) was added. The reaction was heated to 60 °C and then Bu₃SnH (3.5 mL; 13 mmol) was added drop-wise for 15 min. The reaction was then further heated to 85 °C and stirred at that temperature for 12 h. After solvent removal, the crude product was dissolved in anhydrous Et₂O (200 mL). Excess of the stannane was removed under vacuum. Tributyltin iodide was converted to tributyltin fluoride by adding KF (1.246 g; 13.24 mmol), followed by stirring the resultant mixture at room temperature for 12 h. The mixture was filtered and the solvent was removed by rotary evaporation. The crude product was carried to the next step without further purification.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecan-1-ol (1a). ¹H NMR (400 MHz, CDCl₃): δ 3.74 (m, 2 H, *OCH*₂), 2.21 (m, 2 H, *CF*₂*CH*₂), 1.86 (m, 2 H, *CH*₂*CH*₂).

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecan-1-ol (1b). ¹H NMR (500 MHz, CDCl₃): δ 3.75 (q, *J* = 5.73 Hz, 2 H, *OCH*₂), 2.22 (m, 2H *CF*₂*CH*₂), 1.87 (m, 2 H, *CH*₂*CH*₂).

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15 - pentacosafluoropentadecan-1-ol (1c). ¹H NMR (500 MHz, CDCl₃): δ 3.75 (q, *J* = 5.54 Hz, 2 H, *OCH*₂), 2.22 (m,2 H, *CF*₂*CH*₂), 1.87 (m, 2 H, *CH*₂*CH*₂)

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl methanesulfonate (2a). To a solution of alcohol **1a** (5.00 g; 10.5 mmol) in anhydrous THF (50 mL) at room temperature, NEt₃ (4.4 mL; 32 mmol) was added while stirring. The resultant mixture was cooled to 0 °C under argon. After cooling, MsCl (8.1 mL; ~10 mmol) was added while stirring. The reaction was allowed to warm to room temperature and stirred for 6 h. The reaction was then quenched with ice-cold water (50 mL). The product was extracted with Et₂O (3 × 100 mL) and the combined organic phases were washed with 1M aqueous HCl (1 × 100 mL), water (1 × 100 mL), and brine (1 × 100 mL). The organic layer was dried over anhydrous MgSO₄, followed by removal of the solvent by rotary evaporation to yield the crude product crystals. Triturating these crystals in hexanes (50 mL) afforded the pure mesylate.

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl methanesulfonate (2a) 69% yield. ¹H NMR (500 MHz, CDCl₃): δ 4.32 (t, *J* = 6.02 Hz, 2 H, *OCH*₂), 3.04 (s, 3 H, S*CH*₃), 2.25 (m, 2 H, *CF*₂*CH*₂), 2.09 (m, 2 H, *CH*₂*CH*₂) **4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecyl** methanesul**fonate (2b) 80% yield.** ¹H NMR (500 MHz, CDCl₃): δ 4.32 (t, *J* = 6.01 Hz, 2 H, *OCH*₂), 3.04 (s, 3 H, S*CH*₃), 2.25 (m, 2 H, *CF*₂*CH*₂), 2.09 (m, 2H, *CH*₂*CH*₂),

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15 - pentacosafluoropentadecyl methanesulfonate (2c) 78% yield. ¹H NMR (500 MHz, CDCl₃): δ 4.32 (t, J = 6.02 Hz, 2 H, *OCH*₂), 3.04 (s, 3 H, *SCH*₃), 2.25 (m, 2 H, *CF*₂*CH*₂), 2.09 (m, 2 H, *CH*₂*CH*₂)

S-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl) ethanethioate (3a). In a 3-neck round bottom flask equipped with a condenser and an addition funnel, mesylate **2a** (1.0 g; 1.8 mmol) was dissolved in a blend of THF/ethanol (1:1) (100 mL) under argon. KSAc (0.616 g; 5.40 mmol) was dissolved in absolute ethanol (20 mL) (previously degassed), and added drop-wise to the stirred mesylate solution under argon over 10 min. The reaction was refluxed for 7 h. After the reaction was cooled to room temperature, water (100 mL) was added to the solution and the resulting mixture was extracted with Et₂O (3 × 100 mL). The organic phases were combined and washed with water (1 × 100 mL), brine (1 × 100 mL), and then dried over MgSO₄. After evaporation of the solvent, the crude product was purified by column chromatography on silica gel (hexanes/DCE, 9/1).

S-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecyl) ethanethioate (3a) 73% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.95 (t, *J* = 7.16 Hz, 2 H, *SCH*₂), 2.35 (s, 3 H, *C*(*O*)*CH*₃), 2.15 (m, 2 H, *CF*₂*CH*₂), 1.90 (m, 2 H, *CH*₂*CH*₂). *S*-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecyl) ethanethioate (3b) 67% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.95 (t, *J* = 7.16 Hz, 2 H, *SCH*₂), 2.35 (s, 3 H, *C(O)CH*₃), 2.15 (m, 2 H, *CF*₂*CH*₂), 1.90 (m, 2 H, *CH*₂*CH*₂).

S-(4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,14,14,15,15,15 - pentacosafluoropentadecyl) ethanethioate (3c) 82% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.95 (t, *J* = 7.16Hz, 2 H, *SCH*₂), 2.35 (s, 3H, C(O)CH₃), 2.15 (m, 2 H, *CF*₂*CH*₂), 1.90 (m, 2 H, *CH*₂*CH*₂).

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane-1-thiol

(F8H3SH). The perfluorothioacetate **3a** (0.5 g; 0.9 mmol) was dissolved in dry THF (50 mL) and added drop-wise to a stirring slurry of LiAlH₄ (0.106 g; 2.80 mmol) in THF (10 mL) at 0 °C. The reaction was stirred at room temperature for 6 h under argon. The reaction was then quenched at 0 °C using water (25 mL, previously degassed), and was acidified with 1M H₂SO₄ solution (previously degassed). The mixture was then extracted with Et₂O (3 × 100 mL). The combined organic phases were washed with water (1 × 100 mL) and brine (1 × 100 mL), and dried over MgSO₄, filtered and evaporated to dryness. The crude thiol was purified by column chromatography on silica gel (hexanes).

4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,11-heptadecafluoroundecane-1-thiol (F8H3) 73% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.63 (q, J = 7.25 Hz, 2 H, *SCH*₂), 2.23(m, 2 H, *CF*₂*CH*₂), 1.93 (m, 2 H, *CH*₂*CH*₂), 1.38 (t, J = 8.02 Hz, 1 H, *CH*₂*SH*) ¹³C NMR (125 MHz, CDCl₃): δ 29.32-29.76 (t, J = 22.04 Hz,), 24.68(s), 24.00(s) Broad peaks at δ 107.62–120.41 are characteristic of a long perfluorocarbon chain.¹⁶ **4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,12,12,13,13,13-henicosafluorotridecane-1-thiol (F10H3)** 86% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.62 (q, *J* = 7.22 Hz, 2 H, *SCH*₂), 2.23 (m, 2 H, *CF*₂*CH*₂): 1.93 (m, 2 H, *CH*₂*CH*₂), 1.37 (t, *J*= 8.08 Hz, 1 H, CH₂*SH*), ¹³C NMR (125 MHz, CDCl₃ 40 °C): δ 29.45-29.81 (t, *J* = 23.05 Hz), 24.70 (s), 23.89 (s). Broad peaks at δ 107.62–120.41 are characteristic of a long perfluorocarbon chain.¹⁶ **4,4,5,5,6,6,7,7,8,8,9,9,10,10,11,11,2,12,13,13,14,14,15,15,15** - **pentacosafluoropenta-decane-1-thiol (F12H3)** 90% yield. ¹H NMR (500 MHz, CDCl₃): δ 2.62 (q, *J* = 7.22 Hz, 2 H, *SCH*₂), 2.23 (m, 2H, *CF*₂*CH*₂), 1.92 (m, 2 H, *CH*₂*CH*₂), 1.37 (t, *J* = 8.08 Hz, 1 H, *SH*), ¹³C NMR (125 MHz, CDCl₃ at 40 °C): δ 29.45-29.80 (t, *J* = 22.25 Hz), 24.70 (s), 23.88 (s,). Broad peaks at δ 107.62–120.41 are characteristic of a long perfluorocarbon chain.¹⁶

IH,*IH*,*2H*,*2H*-*perfluorotetradecanethiol (F12H2).* In a 3-neck round bottom flask equipped with a condenser and an addition funnel, 1-iodo-1H,1H,2H,2H-perfluorotetradecane (1.0 g, 1.3 mmol) was dissolved in a blend of THF/ethanol (2:1) (100 mL) under argon. KSAc (0.29 g; 2.6 mmol) was dissolved in absolute ethanol (20 mL) (previously degassed), and added to the stirred solution of starting material under argon over 10 min. The reaction was then refluxed for 7 h. After cooling, water (100 mL) was added to dissolve the potassium iodide salt. The mixture was extracted with Et₂O (3 × 100 mL), and the combined organic layers were washed with brine (1 × 100 mL), and then dried over MgSO₄. The solvent was removed via rotary evaporation and then the crude compound was dried under high vacuum for 12 h.

The resulting crude thioacetate was dissolved in dried THF (50 mL) and added slowly to a stirred suspension of LiAlH₄ (0.1 g; \sim 2.6 mmol) in THF (10 mL) at 0 °C. The

mixture was then stirred at room temperature for 10 h under argon. After that, the reaction was quenched with water (25 mL) (previously degassed) at 0 °C and acidified with 1M aqueous H₂SO₄ solution (25 mL) (previously degassed). The reaction solution was then extracted with Et₂O (3×100 mL). The combined organic layers were washed with water (1×100 mL), brine (1×100 mL), dried over MgSO₄ and then filtered. The solvent was removed using rotary evaporation. The crude product was purified by column chromatography on silica gel (hexanes) to give 1H,1H,2H,2H-perfluorotetradecanethiol in 68% yield from the starting iodide.

1H,1H,2H,2H-perfluorotetradecanethiol (F12H2). ¹H NMR (500 MHz in CDCl₃) δ 1.6 (t, 1H, J = 8 Hz, SH), δ 2.4 (m, 2H, J=8 <u>CH₂CF₂</u>), δ 2.77 (m, 2H, <u>CH₂SH</u>). ¹³C NMR (125 MHz in CDCl₃): δ 15.7 (<u>CH₂SH</u>), δ 36.0 (m, <u>CH₂CF₂</u>). Broad peaks at δ 107.62–120.41 are characteristic of a long perfluorocarbon chain.¹⁶

4.2.3. Preparation of SAMs

Gold substrates were prepared by thermal evaporation of the metals (chromium and gold) onto Si(100) wafers under vacuum at a pressure $\leq 6 \times 10^{-5}$ Torr. The chromium layer of 100 Å was deposited on the silicon surface to aid in the adhesion of a subsequent 1000 Å layer of gold.¹⁶ To optimize film formation, the gold was deposited at a rate of 1 Å/s. The substrates were rinsed with absolute ethanol, dried with ultra-pure nitrogen gas, and used promptly after cleaning. Thiol solutions at 1 mM concentration in absolute ethanol were prepared in glass vials that had been previously cleaned with piranha solution and rinsed thoroughly with deionized water, followed by absolute ethanol. [*Caution: Piranha solution is highly corrosive, should never be stored, and* should be handled with extreme care.]. Two freshly cut and cleaned gold slides ($3 \text{ cm} \times 1 \text{ cm}$) were inserted into each of the solutions. The thin film samples were allowed to equilibrate 48 h, after which they were rinsed with absolute ethanol and dried with ultrapure nitrogen gas before characterization.

4.2.4. Characterization of SAMs

Ellipsometric Thickness Measurements. The thicknesses of the monolayers were measured using a Rudolph Research Auto EL III ellipsometer equipped with a He-Ne laser (632.8 nm). The incident angle was fixed at 70°. The refractive index (RI) of the sublayer was set to 1.45, in accordance with the established protocol. ¹⁷ Thickness measurements for the fluorinated films were also acquired with optical constants determined using 1.33, an RI value associated with perfluorinated structures.³³ The calculated thickness value for each sample was the average of the data collected for measurements made at six points (i.e., three different points for each slide).

X-ray Photoelectron Spectroscopy (XPS). XPS spectra of the SAMs were obtained using a PHI 5700 X-ray photoelectron spectrometer with monochromatic Al K α X-ray source (hv = 1486.7 eV) incident at 90° relative to the axis of the hemispherical energy analyzer. Spectral data were collected using a take off angle of 45° from the surface and a pass energy of 23.5 eV. The binding energies were referenced to the Au $4f_{7/2}$ peak at 84.0 eV.

Wettability Measurements. A ramé-hart model 100 contact angle goniometer was employed to measure the contact angles of water (H₂O) and *n*-hexadecane (HD) on the SAMs. The contacting liquids were dispensed (advancing contact angle, θ_a) and withdrawn (receding contact angle, θ_r) on the surface of the SAMs using a Matrix Technologies micro-Electrapette 25 at the slowest speed of 1 µL/s. The measurements were performed at room temperature (293 K) with the pipette tip in contact with the drop. The reported data for each sample were the average of measurements obtained from two slides working with three points per slide, collecting data at both edges of the drop.

Polarization Modulation Infrared Reflection Absorption Spectroscopy (PM-IRRAS). Surface IR spectra were collected using a Nicolet Nexus 670 Fourier transform spectrometer equipped with liquid-nitrogen-cooled mercury-cadmium-telluride (MCT) detector and a Hinds Instrument PEM-90 photoelastic modulator. The incident angle of the p-polarized light reflected from the sample was set to 80° with respect to the surface normal. The spectra of the C-F region were collected using 2048 scans at a spectral resolution of 4 cm⁻¹. The peak intensity for the spectra of the C-H stretching region was too weak to provide reliable data.

4.3. Results and Discussion

After successfully synthesizing the new fluorinated adsorbates (FnH3 series), we tested their performance in forming perfluorinated monolayer films. To help assess the performance of these FSAMs, we prepared comparable fluorinated thiols (FnH2 series), which have the same length for the fluorinated segments, but only bear two methylene units as a spacer between the fluorinated chain and the thiolate headgroup on the gold interface. We anticipated that the increase in the spacer length could offer better packing for the molecules, yet allow the fluorinated chains to still maintain their upright orientation with respect to the gold surface. Thus to evaluate such properties, we utilized

XPS to analyze the atomic concentration on the gold surface and PM-IRRAS to study the perfluoro-helix orientation for each of the FSAMs in the study. Furthermore, we measured the films' thicknesses and evaluated their wetting behavior to provide a complete set of data for determining the impact on these films from such a minor change in structure.

4.3.1. Ellipsometric Thicknesses of the Films

Variation in the thickness of organic thin films is often detected using ellipsometry, with numerous studies showing how this technique can be used to examine trends in thin film thickness for a homologous series of thiolate SAMs.^{12,34} Therefore, the two series of FSAMs were examined by ellipsometry to determine if they produced similar trends and if the thickness values were concomitant with the addition of a single methylene unit to the FnH3 FSAMs. As for the SAM formed from C18, its thickness was compared to prior measurements collected on our instrument which provided an average thickness of 21 Å for this reference SAM for data collected on seven samples over a one year timeframe.³⁵ Table 4.1 shows the thickness data for FSAMs formed from the FnH3 series and the corresponding FnH2 series, along with the data for the SAMs formed from C18. For the measurements taken utilizing a refractive index of 1.45, the ellipsometric data indicates an increase in the thickness of the film going from F8H3 (11 Å), to F10H3 (13 Å), to F12H3 (16 Å); an increment of ~ 1.2 Å per CF₂ unit. A similar trend is apparent in the data for the FnH2 series: 10 Å, 12 Å, 15 Å for n = 8 through 12, respectively. Both sets of data align with prior published research which reported a change of ~ 1.23 Å per CF₂ unit, a value associated with an average increase in the length of the perfluorinated segment for a homologous series of FSAMs.³⁴ When comparing the thickness data of the FnH3 series to that of FnH2, the data indicate that the FnH3 thiols produce films that are \sim 1 Å thicker, a number that is in line with the increase in chain length by one methylene unit.³⁴

FSAM Adsorbate	1.45 Refractive Index	1.33 Refractive Index
F8H3	11	13
F10H3	13	16
F12H3	16	20
F8H2	10	13
F10H2	12	15
F12H2	15	19
C18	21	

Table 4.1. Ellipsometric Data for FSAMs Formed from the FnH3 and FnH2 Series asCompared to the C18 SAMs

4.3.2. XPS Analysis of the Films

Analysis of the chemical composition of organic films by X-ray photoelectron spectroscopy not only provides an understanding of the elemental content of the monolayer, but also insight into the ordering of these systems. For the current project, the binding energy of the sulfur headgroup to the substrate was used as a reference point to determine the type of sulfur moieties present in the monolayer. All the FSAMs of the FnH3 series exhibited only S2p binding energies of 162.0 eV ($2p_{2/3}$) and 163.2 eV ($2p_{1/2}$),



Figure 4.2. XPS spectra for each of the FSAMs of the FnH3 series: a) the S 2p spectral region, b) the C 1s spectral region, and c) the F 1s spectral region.

as shown in Figure 4.2a, which have been previously assigned to thiolate sulfurs bound to gold.^{36,37} Absent from these spectra are the characteristic peaks associated with sulfur either as an unbound thiol or a disulfide (peaks typically found at 163.5-164 eV)^{18,37,38} or in an oxidized state (generally located at ~168 eV).³⁹ Therefore, analysis of the XPS spectra confirms the formation of the monolayers, the absence of any non-adsorbed species present in the film, and the integrity of these adsorbates upon the assembly of the FSAM.

The C1s spectra for the FnH3 FSAMs provided in Figure 2.2b reveal three C1s peak positions corresponding to the carbons of CF₃ at 293.2 eV, CF₂ at ~290.8 eV, and CH₂ at ~284.8 eV, as shown in table 4.2. Note that the intensity of the peaks corresponding to the CF₂ carbons increases in a manner proportional to the increase in the number of CF₂ units in the monolayer. This trend is also observed in the peaks corresponding to the F1s binding energy, Figure 4.2c, where the intensity of the peaks increase proportionally to the increasing number of fluorine atoms on the chain. Furthermore, these trends are also found in the XPS spectra for the FSAMs of the FnH2 series, as shown in Figure 4.3.

	FnH3 (eV)		FnH2 (eV)			
Peak	n = 8	n = 10	n = 12	n = 8	n = 10	n = 12
C 1s (CF ₃)	293.2	293.2	293.2	293.0	293.2	293.2
C 1s (CF ₂)	290.8	290.8	290.9	290.7	290.9	291.0
C 1s (CH ₂)	284.6	284.8	284.7	284.8	284.7	284.8
S 2p _{3/2}	162.0	162.0	162.0	162.0	162.0	162.0
F 1s	688.2	688.2	688.2	688.1	688.2	688.2

Table 2.2. XPS Peak Position for FnH3 and FnH2 FSAMs



Figure 4.3 XPS spectra for each of the FSAMs of the FnH2 series: a) the S 2p spectral region, b) the C 1s spectral region, and c) the F 1s spectral region.

To evaluate the packing density of FnH3 on gold, we have reviewed the ratio of the area under the peaks (their peak intensities) for the S2p peaks for the FnH3 FSAMs as compared to the FnH2 FSAMs, using the peak intensity for Au4f to normalize the values. Table 4.3 shows this data along with the composite ratios for C1s/Au4f and F1s/Au4f for the FSAMs of the FnH3 and FnH2 series. The ratios of the normalized sulfur peaks increase as the number of fluorocarbons increases; 0.93 for n = 8, 1.01 for n = 10, and 1.05 for n = 12. This would appear to indicate that the packing characteristics of the FnH3 FSAMs with the longer perfluorinated segments are better than those of the FnH2 series, particularly in light of the increased attenuation of the sulfur signal on the FnH3 series. To provide an alternative perspective on the surface packing, we also generated the C1s/Au4f ratios for the two series. This produced 1.07 for n = 8, 1.13 for n = 10, and 1.01 for n = 12. For this data set, we anticipated values that reflected the presence of an additional carbon atom for the FnH3 series. However, the value for the F12H3 FSAM for this dataset fails to align with the data obtained with the S2p/Au4f ratios. On the other hand, the depth and number of F1s electrons is the same for a given size of the fluorocarbon chain between the two series (i.e., F8H3 and F8H2). Therefore, changes in the normalized F1s ratios per fluorocarbon chain size would better correlate to changes in the packing density of the fluorinated helix as the number of methylene spacers increase from two to three. For our data (1.00 for n = 8, 1.05 for n = 10, and 1.01 for n = 12) we show a small increase in the ratios as the methylene spacer in the perfluorinated adsorbate increases, a slight improvement in the packing of the films — a phenomenon observed in other partially fluorinated alkanethiols bearing a large number of fluorocarbons.¹⁸

Fn	(S2p/Au4f) _{FnH3} / (S2p/Au4f) _{FnH2}	(C1s/Au4f) _{FnH3} / (C1s/Au4f) _{FnH2}	(F1s/Au4f) _{FnH3} / (F1s/Au4f) _{FnH2}
n = 8	0.93	1.07	1.00
n = 10	1.01	1.13	1.05
n = 12	1.05	1.01	1.01

Table 4.3. Ratios of the S2p, C1s, and F1s XPS Peak Intensities for the FnH3 FSAMs as Compared to Those of FnH2, Using the Peak Intensity for Au4f to Normalize the Values

4.3.3. Wettabilities of the Films

For perfluorinated thin films, the wettability of the surfaces have typically been probed with contacting liquids such as water (H₂O) and *n*-hexadecane (HD) to provide a measure of the interfacial hydrophobicity and oliophobicity. Furthermore, because such contact angle measurements on self-assembled monolayer films are highly sensitive to small differences in the interfacial structure of the SAMs, additional insight into the nature of the alignment of the adsorbates within the film can sometimes be discerned from the data.²⁰ This is particularly true for the current sets of FSAMs where the influence of the transition dipole is buried far enough within the film that it should have no impact upon the surface energy at the interface.^{20,40} Assuming that the films expose perfluorinated surfaces of equivalent adsorbate density and surface ordering, the contact angle data should reveal only the influence of the fluorinated film with a possible minor role from the underlying substrate.²⁰

FSAM Adsorbate	H ₂ O (adv. / rec.)	HD (adv. / rec.)
F8H3	115 / 105	76 / 56
F10H3	116 / 106	76 / 60
F12H3	118 / 106	78 / 59
F8H2	115 / 104	73 / 56
F10H2	116 / 106	76 / 60
F12H2	117 / 106	77 / 60
C18	114 / 104	49 / 40

Table 4.4 Wettability Data for FSAMs Formed from the FnH3 and FnH2 Series asCompared to the C18 SAMs

The advancing contact angles (θ_a) of H₂O (a polar protic solvent) and HD (a nonpolar hydrocarbon solvent) measured on the FSAMs of both series are shown Table 4.4. FSAMs of the FnH3 series and those of FnH2 show the same high degree of hydrophobicity and oleophobicity, with contact angle values $\geq 115^\circ$ for H₂O and $\geq 73^\circ$ for HD. Note that all of the FSAMs are less wettable than the **C18** SAMs for both liquids, even though the latter is a well-packed film formed from the nanoscale equivalent of paraffin wax. For both series of films, the water contact angles increase with increasing n, yielding data that is statistically equivalent for chains of equal perfluorcarbon length (between the two series), yet the data clearly provides a steady increase in contact angle as the perfluorocarbon segment lengthens. The effect of the monolayer's thickness on its wettability might reflect a diminishment in the influence of the underlying gold substrate on the contacting liquid upon an increase in thickness. Such forces have been reported to dissipate with increasing film thickness.²⁰ From the perspective of a direct comparison of the θ_a H₂O data for these two sets of FSAMs, there

does not appear to be any indication of the presence of odd-even contact angle effect between the two series.

Similar trends can be seen with the contact angle data for HD, however, there are indications that the SAMs formed from the FnH3 thiols might be better organized than those of FnH2. Such variances in the wettability data could result from minor changes in the ordering of the monolayer films owing to the slight increase in the length of the alkyl spacer. In particular, the average θ_a HD contact angle for **F8H3** (76°) is noticeably higher than that of **F8H2** (73°), as shown in Figure 4.4, which could be an indication that the FSAMs formed from the shortest of the perfluorocarbon chains benefit from an increase in distance between the wider diameter of the perfluorocarbon moieties (as compared to the hydrocarbon segments) and the preferred lattice bonding sites on gold for thiols (vide supra).



Figure 4.4. Advancing contact angles (θ_a) for hexadecane on FnH3 and FnH2 monolayers.

4.3.4. PM-IRRAS Analysis of the Films

Surface IR spectra generally reveal information about self-assembled monolayer film organization and orientation of the individual chains within the film. Due to the small number of methylene units in these chains, the C-H vibration bands proved to be too weak to make reliable measurements. This limits the ability to use the collected PM-IRRAS data for determining the relative order within these thin films. However, analysis of the C-F stretching region in the PM-IRRAS spectra proved more fruitful. The bands between 1240 to 1280 and 1330 to 1380 cm⁻¹, designated as $v_{pd}^{CF_2}$ (vibrational mode for CF₂ with a transition dipole perpendicular to the helical axis) and $v_{ax}^{CF_2}$ (vibrational mode for CF_2 with a transition dipole parallel to the fluorocarbon helical axis), respectively,^{18,41}) provides evidence that *all* the chains are oriented largely perpendicular to the surface for these FSAMs. The data also appear to indicate the presence of a slight decrease in the tilt of the chains as the size of the fluorocarbon helix increases. Based on the relative intensity of the two bands ($v_{ax}^{CF_2}$ to $v_{pd}^{CF_2}$) for the collected spectra shown in Figure 4.5; the relative intensity of the two bands increases with the size of the fluorocarbon helix. Such a change would indicate a decrease of the tilt angle of the helix from the surface normal.²¹ However, the exact tilt angle can not be determined from this technique since we are unable to quantitatively compare the absolute intensities of a given vibration mode between spectra due to the signal modulation associated with the PM-IRRAS method.



Figure 4.5. PM-IRRAS spectra for the C-F stretching region of the films generated from the FnH3 series: (a) **F8H3**, (b) **F10H3**, and (c) **F12H3** right.

Comparing the peak positions of the FnH3 FSAMs to those of FnH2, $v_{ax}^{CF_2}$ bands appear at exactly the same wavenumber for a given perfluoroalkyl segment regardless of the number of underlying methylene units. As shown in Figure 4.6, the peak positions of these bands shift with an increasing number of fluorocarbon units and seem to be specific to the helix size -- a phenomena that has been noted previously.²¹



Figure 4.6. Peak positions of the $v_{ax}^{CF_2}$ bands as a function of fluorocarbon units in the FSAMs formed from the FnH3 and FnH2 series.

4.4. Conclusions

Two series of perfluoroalkane thiols with short hydrocarbon spacers were synthesized and used to generate self-assembled monolayers on gold. The ellipsometric measurements confirmed the formation of monolayer films. This conclusion is supported by the XPS data, which shows the presence of only bound sulfur. The PM-IRRAS data shows that the relative intensity of $v_{pd}^{CF_2}$ to $v_{ax}^{CF_2}$ indicates the chains are oriented largely perpendicular to the surface. Furthermore, FnH3 FSAMs were compared to the known FnH2 FSAMs. Using XPS analysis spectral peak intensities, a comparison of the ratio of the F1s/Au4f and S2p/Au4f for the FnH3 FSAMs to those of FnH2 FSAMs shows a slight increase in packing density at the gold surface for the longer FnH3 FSAMs. Comparing wettability data of HD on films from both series further supports the conclusion that the increase in the length of the methylene spacer allows for an improved arrangement of the thiolates on the gold surface. This work expands the scope of molecules that produce a nearly fully perfluorinated interface, producing a new series of FSAMs whose chains are packed better than the current FnH2 adsorbates while maintaining an upright orientation relative to the surface.

4.5. References

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Chapter 5. Conclusions

5.1. Conclusions

The adsorption of fluorinated amphiphiles on metal and metal-oxide surfaces has been utilized to create fluorinated thin films in a variety of technologies. These films have attractive features including high oleophobicity, hydrophobicity, as well as biological and chemical inertness. The work described in this dissertation concentrated on fluorinated self–assembled monolayers (SAMs) from partially fluorinated alkanethiols on gold. Specifically, we utilized synthetic protocols to custom design new types of adsorbates that manipulate surfaces either by: altering the arrangement of molecules on the surface to improve packing, or by manipulating the energies at the monolayer interface through the introduction of a specific type of dipole. All generated surfaces were characterized using optical ellipsometry, contact angle goniometry, polarization modulation infrared reflection-adsorption spectroscopy (PM-IRRAS), and X–ray photoelectron spectroscopy (XPS).

In Chapter 2, we introduced a methyl-capped partially fluorinated alkanethiol in the form of $CH_3(CF_2)_6(CH_2)_{11}SH$ (**H1F6H11SH**). These adsorbates generated a unique, inverted HC–FC dipole at the monolayers' interface. The structure of this adsorbate was designed in such a way that the underlying methylene units provide a sufficient distance from the gold substrate. It also generates a crystalline hydrocarbon segment, thus limiting the effect of films crystalinity on the generated properties. The length of the fluorocarbon is set to six units to limit the effect of the lower dipole at the FC–HC
junction on the interfacial properties of this new type of films. To evaluate changes in the interfacial properties triggered by the HC-FC dipole in H1F6H11SH SAMs, we directly compared these monolayers to films of normal alkanethiols $(CH_3(CH_2)_{17}SH;$ **H18SH**) and CF₃-terminated alkanethiols (CF₃(CH₂)₁₇SH; F1H17SH). We also included SAMs of molecules with an odd-numbered carbon chain (H1F6H10SH, **H17SH**, and **F1H17SH**) to shed light on anomalies caused by an odd-even effect. The generation of H1F6HnSH monolayers was achieved in ethanol as a solvent of choice, and an extended equilibration at 40 °C for 24 h. This extended equilibration resulted in an increase in the thickness of the monolayers. However, the **H1F6HnSH** films had a lower thickness than those of HnSH and F1HnSH. We have attributed the lower thickness to the slight reduction in chain density of H1F6HnSH SAMs due to the increase in the van der Waals diameter of the fluorinated segment as opposed to that of a hydrocarbon chain. XPS analysis of the S 2p binding region confirmed the formation of the monolayer, and that these films do not contain unbound thiol, or disulfide contaminations. Furthermore, analysis of the C 1s binding region indicates that the H1F6HnSH SAMs are less densely packed than those of HnSH. Nevertheless, PM-IRRAS analysis of the C–H stretching region indicates that the underlying methylene spacers of H1F6HnSH SAMs are well ordered. Having said that, both XPS and PM-IRRAS results point towards improved packing in the chains of **H1F6H11SH** SAMs versus H1F6H10SH SAMs. The wettability data indicate that of the new types of SAMs of **H1F6HnSH** films are more wettable by polar liquids than the **F1HnSH** and HnSH SAMs. The increase in wettability, compared to the HnSH SAMs, is due to the presence of the HC–FC dipole at the terminus of **H1F6HnSH** SAMs. On the other hand, we have rationalized such behavior to be due to increased spacing between the terminal methyl groups, since they are residing on chains with a larger vdW diameter compared to F1HnSH. With respect to dispersive liquids, H1F6HnSH SAMs have shown an improved oleophobic character with bulky liquids than HnSH SAMs. However they are more wettable than **F1HnSH** SAMs due to the non-ideal dispersive interaction between the fluorinated interface in F1HnSH SAMs and the hydrocarbon liquids. These observations led us to postulate that the change in wetting behavior of nonpolar liquids on H1F6HnSH SAMs compared to HnSH SAMs is partially due to the presence of the underlying fluorinated segment that is felt by the contacting liquid. This postulation was enforced by the observed anomalies between the wettability data of H1F6H11SH SAMs and that of H1F6H10SH films. The latter difference is partially due to the fluorinated segment being exposed at the interface, which could be caused by the slight disorder in the chains of H1F6H10SH SAMs indicated by other analyses in this study. However, we were unable to stipulate with certainty that the odd-even anomalies observed in wetting behavior is due the magnitude or the orientation of the HC-FC dipole. A conclusion that led to the work presented in Chapter 3.

The work presented in Chapter 3 is an expansion of Chapter 2, where we tried to answer the inquiries regarding the effect of the HC–FC dipole in **H1F6H11SH** SAMs as well as the effect of the underlying fluorinated segment on the interfacial properties of these SAMs. Therefore, we synthesized a series of alkyl-capped fluorinated molecules where we buried the HC–FC dipole monotonically by increasing the length of the terminal alkyl segment (H(CH₂)_n(CF₂)₆(CH₂)₁₁SH (**HnF6H11**; where n = 3, 4, and 5; **H3F6H11SH**, **H4F6H11SH**, and **H5F6H11SH**, respectively). SAMs of the HnF6H11SH series were compared to that of H1F6H11SH and H18SH. Thickness measurements indicate that the additional equilibration of HnF6H11SH films (n = 3-5) at 40 °C for 24 h resulted in a reduction of the monolayers' thickness. Furthermore, even those that were equilibrated at room temperature for 48 h, had an increased thickness trend that did not match what was observed for normal alkanethiols or partially fluorinated thiols whose chain length was varied monotonically. XPS analysis supported the formation of monolayers with sulfur bound to gold. However, changes in the binding energies of C 1s from CF₂ units and F 1s in **HnF6H11SH** SAMs indicate that the increased size of the alkyl units result in an improvement in packing of the hydrocarbon region (indicated by C1s of CH₃/CH₂ peaks) but it reduces the packing of the fluorinated segments. This was supported by the results from the PM-IRRAS analysis where the methylene antisymetric stretch shifts to a higher wavenumber as a function of the size of the upper alkyl moiety. The wetting behavior of polar liquids of HnF6H11SH films indicates that the effect of the HC-FC dipole diminishes with increasing the size of the terminal alkyl chain. Also, the contact angle values for dispersive liquids on these films reduce with increasing the terminal alkyl moiety. While this finding indicates that the upper alkyl unit is ordered enough to block the effect of HC-FC dipole, the wetting behavior of the dispersive liquids increased on H5F6H11SH SAMs. The latter observation raises questions regarding the ordering of the terminal alkyl moiety, especially since the PM-IRRAS data suggest an increase in disorder as size of the alkyl group increases.

In Chapter 4 we have introduced three new highly prefluorinated alkanethiols with three methylene units as alkyl spacers FnH3; $F(CF_2)_n(CH_2)_3SH$, where n = 8, 10, 12

designated as F8H3, F10H3, F12H3 respectively. These molecules were compared to those with two methylene spacers FnH2; $F(CF_2)_n(CH_2)SH$, where n = 8, 10, 12 referred to as F8H2, F10H2, F12H2 respectively. The motivation behind this work was to evaluate the effect of such a change on the conformational order of the adsorbate's chains as well as upon the interfacial properties of the resulting films. The ellipsometric measurements and XPS analysis confirmed the formation of monolayer films from both series of thiols. Furthermore, PM-IRRAS analysis on the C–F stretching region shows that chains in the FnH3 series are oriented largely perpendicular to the surface. Additionally, wettability data of water and hexadecane on the FnH3 series shows a high hydrophobic and oleophobic character in these chains. In addition, XPS analysis on the normalized peak intensity of F 1s, C 1s, and S 2p in FnH2 and FnH3 SAMs indicate that there is a slight increase in packing density for chains with an additional methylene spacer. This was supported by the decreased wetting behavior of hexadecane on the FnH3 surfaces. The significance of this work is that the FnH3 molecules produce a nearly fully perfluorinated surface, with an enhanced packing density than the known FnH2 adsorbates.

Appendix 1. List of Publications

- "Superhydrophobic Perfluorinated Metal–Organic Frameworks" Chen, T.-H.; Popov,
 I.; Zenasni, O.; Daugulis, O.; Miljanić, O. Š. *Chem. Commun.*, **2013**, *49*, 6846–6848.
- "The Impact of Fluorination on the Structure and Properties of Self-Assembled Monolayer Films" - Zenasni, O.; Jamison, A. C.; Lee, T. R.; *Soft Matter.* 2013, *9*, 6356–6370.
- "Fibrillar Self-Organization of a Line-Active Partially-Fluorinated Thiol within Binary Self-Assembled Monolayers" - Jamison, A. C.; Zhang, S.; Zenasni, O.; Schwartz, D. K.; Lee, T. R. *Langmuir*, 2012, 28, 16834–16844.
- "Asymmetric Thioethers as Building Blocks for Chiral Monolayers" Jewell, A. D.; Tierney, H. L.; Zenasni, O.; Lee, T. R.; Sykes, E. C. H. *Top. Catal.* 2011, *54*, 1357– 1367.