

The impact of fluorination on the structure and properties of self-assembled monolayer films

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The adsorption of partially fluorinated amphiphiles on metal/metal oxide surfaces allows for the generation of specifically fluorinated thin-film interfaces. Such surfaces are often compared to polytetrafluoroethylene (PTFE), which exhibits a low surface energy, accompanied by biological and chemical inertness, making perfluorinated interfaces applicable to a wide range of technologies. In thin-film research, self-assembled monolayers derived from fluorinated alkanethiols (FSAMs) serve as well-defined systems that can be used to evaluate the physical and chemical properties of interfaces produced with varying degrees of fluorination. The characteristics of these surfaces have been attributed to both the chemical composition of the individual molecular adsorbates and the consequent structural features associated with monolayers formed from these unique partially fluorinated adsorbates. Specifically, this review seeks to correlate the structural and interfacial properties of FSAMs on gold with the structure/composition of the fluorinated moiety present in the adsorbed molecules and to highlight how the degree of fluorination influences the interfacial ordering of the individual alkanethiolate chains and the vacuum energy levels of the modified metal substrate. Additionally, the thermal stability of these organic thin films is analyzed as a function of adsorbate structure. Included are highlights of some of the studies in which FSAMs, formed from a variety of new types of surfactants, were used to modify colloidal systems, to generate anti-adhesive materials, and to enhance the stability of fluorinated thin films toward low-energy electron degradation.

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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 micro-electromechanical 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,

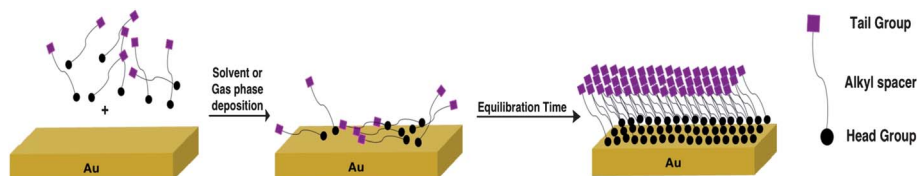
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Dr. Andrew C. Jamison, originally from Shreveport, Louisiana, received a B.B.A. degree from Texas Wesleyan College in 1982. His experience in the paint industry encouraged him to broaden his education, leading to B.S. and Ph.D. degrees in Chemistry from the University of Houston. Working with Prof. Lee, his research has centered on the impact of partially fluorinated adsorbates upon the character of self-assembled monolayer films.



Scheme 1 The formation of SAMs via the adsorption of organothiols on gold.

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 non-fluorinated counterparts (HSAMs). For both types of monolayer systems (Scheme 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 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}

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 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.

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



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scale surface coatings that inhibit corrosion and resist biofilm formation.

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 $\sigma_{\text{C-H}}$ orbital with the $\sigma_{\text{C-F}}^*$ 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 $\angle \text{F-C-C-F}$ that ranges from 46–49° *versus* 60° for $\angle \text{H-C-C-H}$ 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.^{16,17,31,32}

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, polarization modulation infrared reflection absorption spectroscopy (PM-IRRAS) data confirm that the hydrocarbon backbone in all of these films aligned in well-packed structures with conformational order that was 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, CF₃(CF₂)₆(CH₂)₂SH (**F8H2SH**), form a (2×2) adlayer with a nearest-neighbor distance ~ 5.8 Å.⁴³ Independently, Liu *et al.* using AFM and GIXD, found that SAMs of CF₃(CF₂)_{*n*}(CH₂)₂SH (**F*n*H2SH**) 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 $\text{CF}_3(\text{CF}_2)_8\text{C}(\text{O})\text{N}(\text{H})\text{CH}_2\text{CH}_2\text{SH}$; **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 ($\nu_{\text{ax}}^{\text{CF}_2}$ and $\nu_{\text{pd}}^{\text{CF}_2}$, 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 $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_2\text{SH}$ (**F10H2SH**), using angle-dependant near-edge X-ray absorption fine structure spectroscopy (NEXAFS) and found it to be $\sim 11^\circ$ from the surface normal.⁵⁰ On the other hand, the alkane chains in HSAMs tilt $\sim 30^\circ$ 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 and Loicono 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 $\sim 16^\circ$ 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 $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_2\text{SH}$ (**F6H2SH**) *versus* that of the equivalent HSAM on Au(111).⁴⁶ **F6H2SH** adopts a $p(2 \times 2)$ 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 $p(2 \times 2)$ 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 the orientation of the fluorinated segment. Tamada *et al.* have shown that for FSAMs generated from $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_n\text{SH}$ (**F10H n SH**, where $n = 2, 6, 11, 17, 33$), increasing the number of methylene units leads to a distorted AFM image (see Fig. 1).⁴⁵ While the nearest-neighbor 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.

These observations correlate with observations by Fukushima and co-workers in their PM-IRRAS analysis of these FSAMs.⁵² The antisymmetric CH_2 stretch ($\nu_{\text{a}}^{\text{CH}_2}$) appears at 2919 cm^{-1} for $n = 11, 17$, and 33 , whereas the $\nu_{\text{a}}^{\text{CH}_2}$ 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 $\nu_{\text{a}}^{\text{CH}_2}$ 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 $\nu_{\text{a}}^{\text{CH}_2}$ 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 $\nu_{\text{ax}}^{\text{CF}_2}$ and $\nu_{\text{pd}}^{\text{CF}_2}$ 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 $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_n\text{SH}$ (**F10H n SH**, 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 ($\nu_{\text{ax}}^{\text{CF}_2}$) increases systematically with the number of fluorocarbons in the chain regardless of the chain tilt, suggesting that the $\nu_{\text{ax}}^{\text{CF}_2}$ 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



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

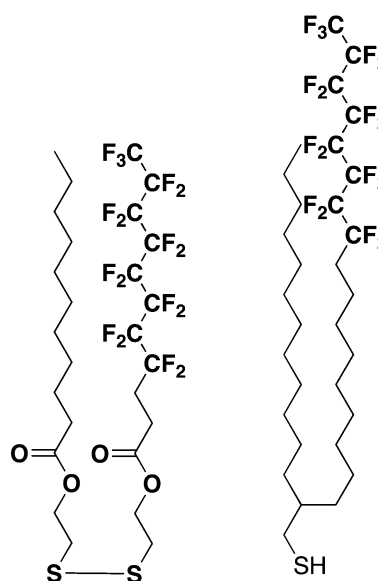


Fig. 2 Structure of adsorbates where fluorocarbon and hydrocarbon chains are linked covalently by means of a disulfide bond (left) or a double-chained monothiol (right).

used to overcome the issues of disproportionate adsorption and domain formation (see Fig. 2).^{63–66}

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 CF₃-terminated 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 CF₃-terminated alkanethiols, CF₃(CH₂)_nSH with *n* = 9–15, and their HSAM analogues, CH₃(CH₂)_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 Fig. 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 –CH₂–CF₃ 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}

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 and Lee 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(CF₂)_n(CH₂)_mSH where *n* = 1 and *m* = 12–15 (Series 1) and where *n* = 1–10 and *m* = 15–6 (Series 2), as shown in Fig. 4. Both of these series were compared to HSAMs of the form H(CH₂)_xSH where *x* = 13–16 (Series 3). From the collected data, the authors also determined that all CF₃-terminated SAMs of Series 1 are more wettable toward polar liquids than the HSAMs of Series 3, reinforcing the conclusions of the earlier study by Lee and co-workers.⁷² Furthermore, upon burying the R_H–R_F dipole in

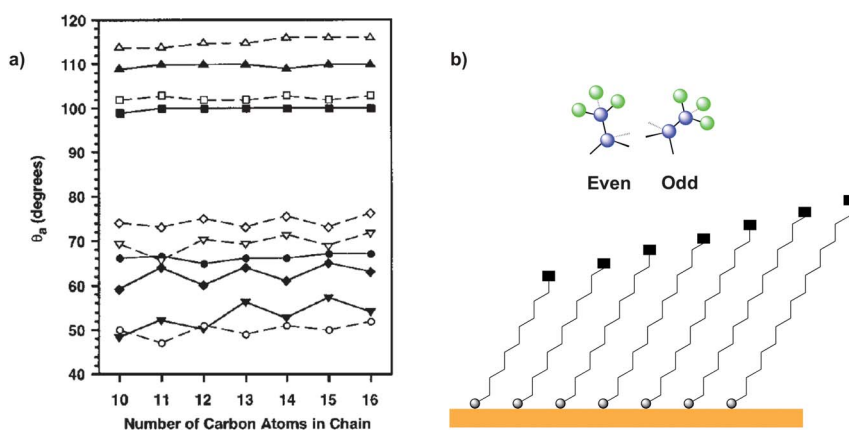


Fig. 3 (a) Advancing contact angle data for hexadecane (●), acetonitrile (▼), DMF (◆), water (▲), and glycerol (■) on SAMs generated from CF₃(CH₂)_nSH *n* = 9–15 (filled symbols) and CH₃(CH₂)_nSH *n* = 9–15 (open symbols).⁷² (b) Schematic representation of homologous series of CF₃-terminated normal alkanethiolate 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. (a) was reproduced by permission from ref. 72.

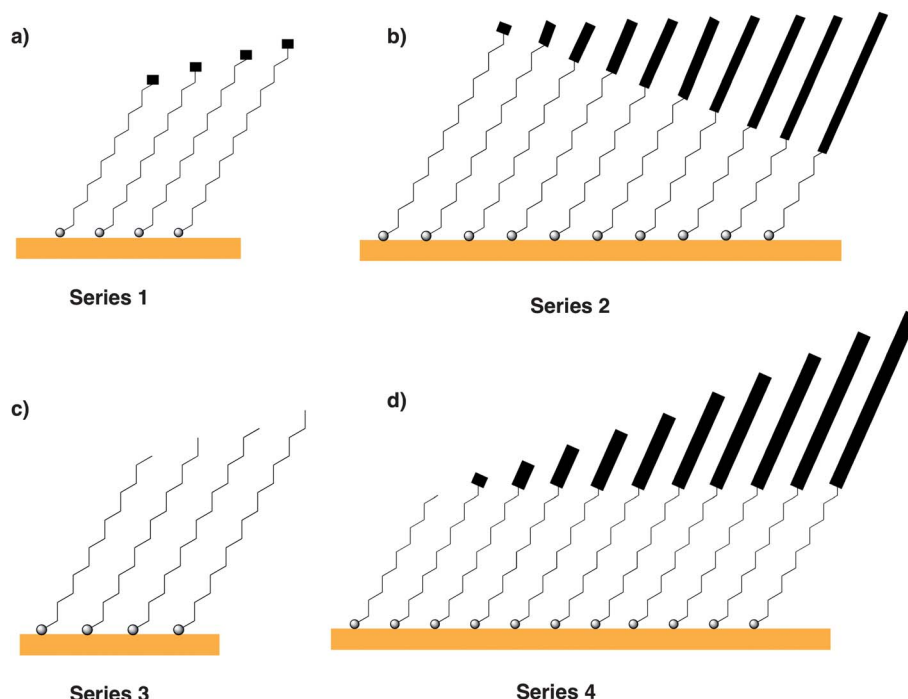


Fig. 4 Schematic representation of four series of SAMs used to evaluate the effect of terminal fluorination on FSAM surface energy. Series 1 are CF₃-terminated FSAMs (CF₃(CH₂)_mSH where $m = 12-15$), Series 2 are partially fluorinated hexadecanethiol FSAMs (F(CF₂)_n(CH₂)_mSH where $n = 1-10$ and $m = 15-6$), Series 3 are HSAMs with chain lengths analogous to CF₃-terminated FSAMs (H(CH₂)_xSH where $x = 13-16$), and Series 4 are terminally fluorinated FSAMs where the fluorocarbon segments were systematically increased while the hydrocarbon segment was held constant (F(CF₂)_n(CH₂)₁₁SH, where $n = 0-10$).

Series 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(CF₂)_n(CH₂)₁₁SH (**FnH11SH**), where $n = 0-10$ (Series 4 in Fig. 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. Fig. 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. Fig. 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 2.²⁰

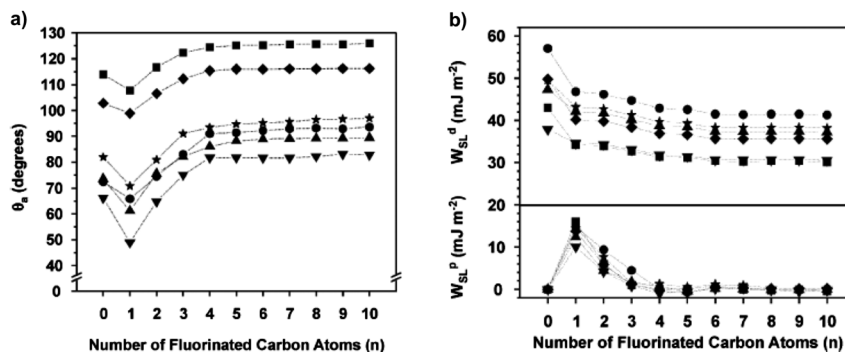


Fig. 5 (a) Contact angle values of water (■), glycerol (◆), acetonitrile (▼), DMF (▲), DMSO (★), and nitrobenzene (●) on FSAMs generated from Series 4 (**FnH11SH**). (b) The corresponding values of the dispersive work of adhesion (upper panel) and the polar work of adhesion (lower panel) of these liquids on Series 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) or fluorocarbon (phase-incompatible). 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 Fig. 4 (Series 4), the termini of the fluorocarbon chains are less densely packed as the distance between the interface and the densely packed *trans*-extended 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 $\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_{12-n}\text{SH}$ (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}

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 perfluoroalkaneethiolate 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 SAM-modified 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 $\text{R}_\text{H}-\text{R}_\text{F}$ dipole in our FSAM studies).⁸⁵ Therefore, the change in the work function can be written as the sum of the two

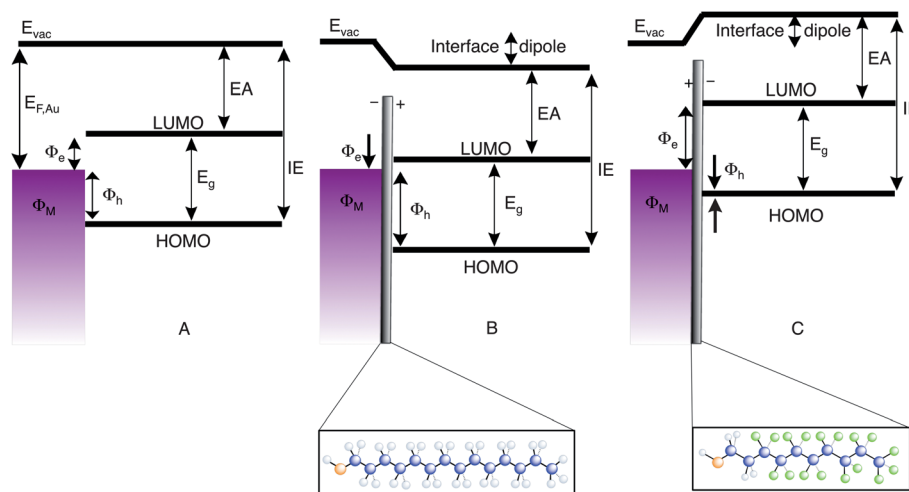


Fig. 6 Schematic alignment difference between the work function of the metal (Φ_M) and the HOMO/LUMO levels of the organic semiconductor at the metal-organic interface. The $+/-$ indicates the direction of the interface dipole generated by the SAM. (A) Electron-injection barrier (Φ_e) and hole injection 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.

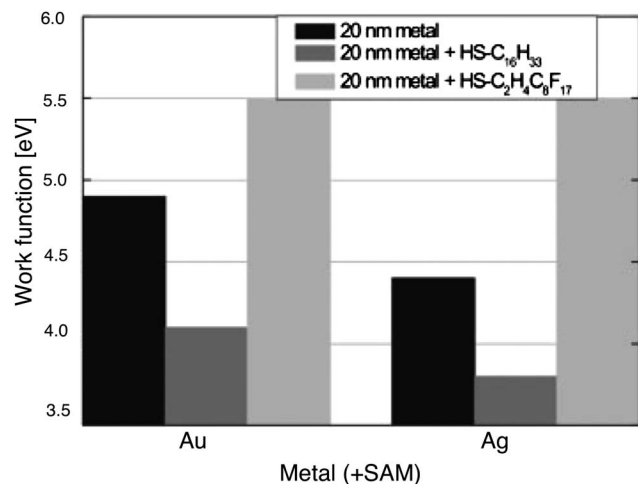


Fig. 7 Value of the work function of gold and silver with and without HSAMs and FSAMs. Reproduced with permission from ref. 79.

dipoles multiplied by the grafting density of the monolayer (N), which depends on the monolayer structure of the SAM on the metal.⁷⁹

$$\Delta\phi = -N[(\mu_{\perp\text{SAM}}/\epsilon_0\kappa_{\text{SAM}}) + (\mu_{\text{M-S}}/\epsilon_0\kappa_{\text{M-S}})] \quad (1)$$

For eqn (1), the change in the effective M-S dipole, represented by the term $(\mu_{\text{M-S}}/\epsilon_0\kappa_{\text{M-S}})$, is almost independent of the alkyl moiety. Whereas, the change in the molecular dipole, $(\mu_{\perp\text{SAM}}/\epsilon_0\kappa_{\text{SAM}})$, is strongly influenced by the chemical nature of the alkyl chains in the monolayer.

Fig. 6 illustrates how the work function of a metal surface can be tuned depending on the chemical nature of the adsorbate molecules.^{79,86} Fig. 6B shows that an HSAM decreases the work function, which can lower the electron-injection barrier.^{79,86} In contrast, Fig. 6C shows that an FSAM increases the work function, which can lower the hole-injection barrier.

To evaluate the contribution of both dipoles on the work function of gold, Rusu and Brocks 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 1*H*,1*H*,2*H*,2*H*-perfluorodecanethiol (**F8H2SH**) on gold and silver.⁷⁹ Fig. 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, $\mu_{\perp\text{SAM}}$, compared to the M-S dipole, $\mu_{\text{M-S}}$. 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

Alloway *et al.* have evaluated the influence of SAMs on the work function of gold as a function of the degree of fluorination (see Fig. 8).²¹ Comparison of UV-photoemission 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

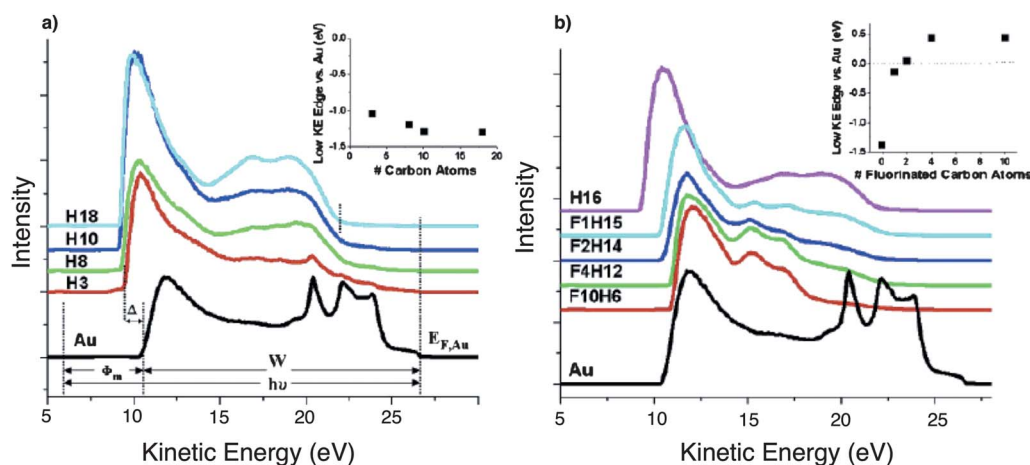


Fig. 8 (a) UV-photoemission spectra for unmodified gold along with a series of HSAMs on gold (C_nSH; $n = 3, 8, 10, 18$). The inset represents the shift in the low-KE photoemission edge for these SAMs. (b) UV-photoemission spectra for unmodified gold along with a series of FSAMs on gold (F_nH_{16-n}SH;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

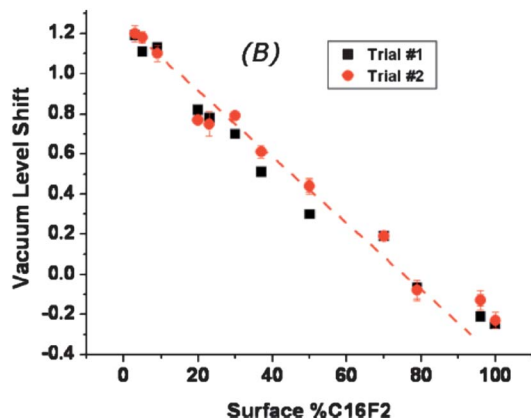


Fig. 9 Vacuum-level shift as a function of surface composition of **F2H16SH** in binary SAMs (i.e., **F2H16SH** and hexadecanethiol). The precision of the measurements is shown by the agreement of the two trials. Reproduced with permission from ref. 81.

addition of only one CF_3 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}

In addition, Alloway and co-workers also examined SAMs derived from a series of alkanethiols terminated with a single CF_3 group ($\text{CF}_3(\text{CH}_2)_n\text{SH}$, where $n = 12\text{--}15$) and observed that the shift in the low-KE photoemission edge of the CF_3 -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

Mixed SAMs can also be used to tune the effective work function of gold. Alloway *et al.* studied binary SAMs derived from $\text{CF}_3\text{CF}_2(\text{CH}_2)_{14}\text{SH}$ (**F2H16SH**) and $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ 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 Fig. 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

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 Fig. 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

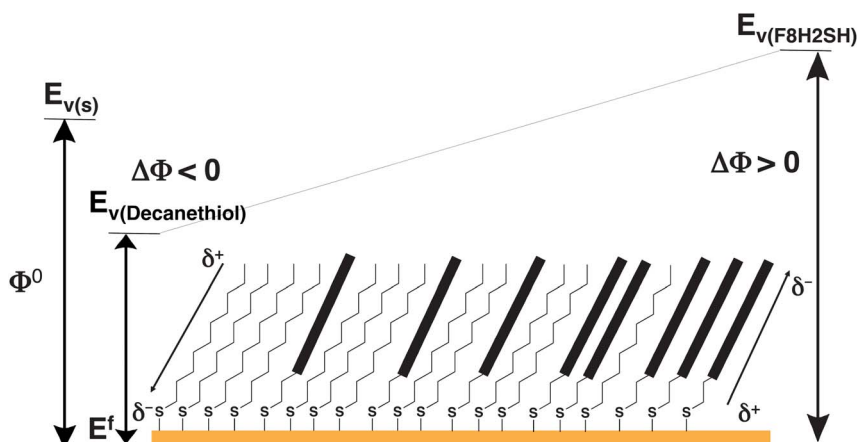


Fig. 10 Schematic drawing of changes in the work function as a consequence of the change in the surface composition of the decanethiol-**F8H2SH** gradient. Black rectangles represent the fluorinated helix of **F8H2SH**. Adapted from ref. 89.

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 (**F10H n SH**), 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 5) was derived from **F m H11SH** where $m = 1–10$ (*i.e.*, variable fluorocarbon length and constant hydrocarbon length). The second series of SAMs (Series 6) was derived from **F10H n SH** where $n = 2–6$, and 11 (*i.e.*, constant fluorocarbon length and variable hydrocarbon length). The third series of SAMs (Series 7) was derived from $F(CF_2)_x(CH_2)_ySH$ 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 7 SAMs showed that the replacement of CH_2 groups with CF_2 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 (CH_3 , OH , $COOH$) of ω -terminated hexadecanethiols as well as the chain length of HSAMs ($CH_3(CH_2)_nSH$, 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 ($2.19 \pm 0.02 \mu F cm^{-1}$) than the corresponding HSAMs ($1.55 \pm 0.01 \mu F cm^{-1}$).^{102,103} Naud *et al.* evaluated the effect of the degree of fluorination on the ion-insulation property of FSAMs derived from **F n H m SH** ($n = 4, 6, 8, 10$ 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 through 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, **F n H m SH** (where $n = 2, 4, 6, 8$; $n + m = 16$) using EIS.⁹ Their investigation included SAMs formed in dichloromethane (DCM) and in liquid CO_2 . 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 CO_2 , 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 CO_2 .⁹ Solvent effects during film formation was attributed for the variance in film quality 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*).

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 Fig. 11a).¹²⁰

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 Fig. 11b afforded surfaces with higher reduction of nonspecific protein adsorption when compared to SAMs derived from analogous OEG-terminated alkanethiols.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 $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_n\text{SH}$, where $n = 2, 11, 17$, damage due to low electron radiation led to the loss of fluorinated segments, especially the CF_3 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 Fig. 12, producing films that are remarkably stable.¹²⁴

In summary, the insight gained from the research highlighted here allows for new advances in the design of nanoscale fluorinated coatings. CF_3 -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

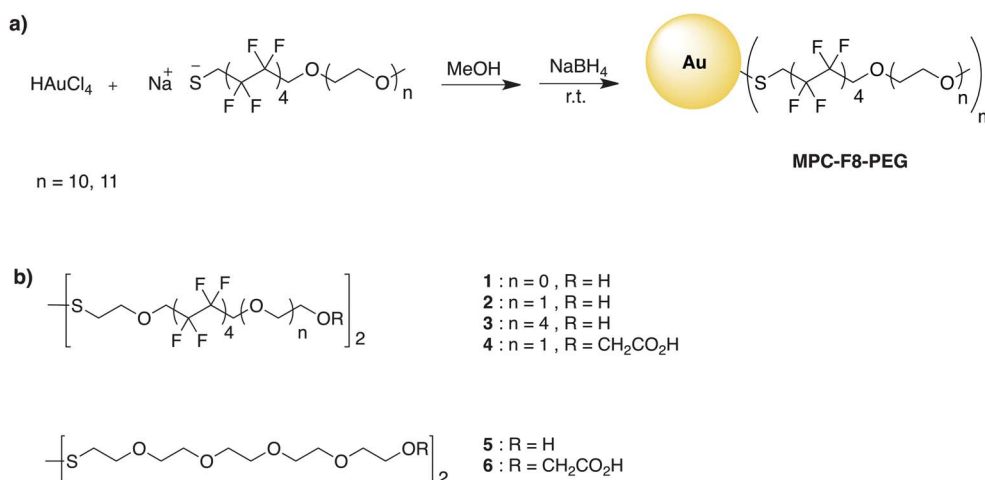


Fig. 11 (a) Synthesis of water-soluble gold nanoparticles capped with partially fluorinated SAMs. Adapted from ref. 120. (b) Structures of partially fluorinated adsorbates used to prepare nanoscale protein-resistant surface coatings along with comparable OEG-based adsorbates. Adapted from ref. 121.

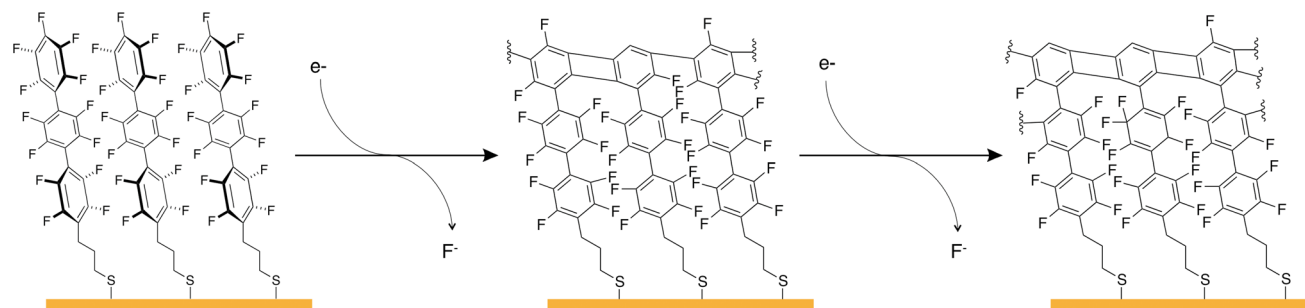


Fig. 12 Electron-induced modification in FSAMs on gold derived from perfluoroterphenyl alkanethiols. Adapted from ref. 124.

characteristics that are well controlled, highly reproducible, and technologically relevant are waiting to be developed.

Acknowledgements

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