Fluorinated self-assembled monolayers: composition, structure and interfacial properties

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Abstract

Over the past several years, various fluorinated self-assembled monolayers (F-SAMs) on gold have been used to study the interfacial properties of fluorocarbon interfaces. This review focuses on the structures of selected F-SAMs and describes how the structures relate to various interfacial properties, such as wettability, friction, X-ray induced damage and ion-surface collisions. © 2003 Elsevier Ltd. All rights reserved.

Keywords: Fluorinated self-assembled monolayers (F-SAMs); Wettability; Friction; X-Ray induced damage; Ion-surface collisions

1. Introduction

The continuing trend toward the nanoscale miniaturization of devices requires an increase in the surface-to-bulk ratio of materials. In theory, miniature devices that incorporate soft organic materials, such as polymers and lubricants, can access size regimes at the molecular, (i.e. subnanometer) level. For many nanoscale applications involving soft organic materials and their surfaces, which are typically disordered by nature, researchers have employed self-assembled monolayers (SAMs). Indeed, SAMs have been used in a variety of applications, such as microfluidics [1], nanolubrication [2,3], corrosion prevention [4], and molecular sensing [5]. A particular area of interest lies in the use of fluorocarbon-based SAMs as nanoscale coatings materials [6]. Due to their ubiquitous use, this review will focus only on fluorocarbon-based SAMs derived from the adsorption of fluorinated alkanethiols onto the surface of gold.

In standard organic chemistry textbooks (even at the graduate level), the sections devoted to fluorocarbon chemistry are typically brief. Moreover, since the chemistry of fluorine, which is the most electronegative element at 3.98 on Pauling scale [7], differs substantially from the other halogens, its chemistry remains highly specialized. Because of the low steric requirements and good overlap of atomic 2s-, 2p-orbitals, the carbon-

fluorine bond is the strongest known involving carbon (466 kJ/mol) [8], which perhaps rationalizes the poor ability of fluorine to act as a leaving group like other halogens. Furthermore, the size of fluorine (covalent radius of 72 nm vs. 37 nm for hydrogen) [8] allows it to replace hydrogen in many organic molecules. Methodologies for the introduction of fluorine into organic molecules are, however, limited to certain functional groups, and the corresponding reaction conditions are typically severe [9].

Another unusual property of fluorocarbons centers on the weakness of the intermolecular attractive forces (or cohesive energies) [10]. This phenomenon likely arises from the low polarizability and high ionization potential of the carbon-fluorine bond. Accordingly, fluorinated molecules exhibit surprisingly low boiling points, (e.g. perfluorohexane at 57 °C vs. hexane at 69 °C) [8], small refractive indices, (e.g. perfluorohexane at 1.2515 vs. hexane at 1.3750) [11], and weak surface tensions, (e.g. perfluorohexane at 11.4 dyn/cm vs. hexane at 17.9 dyn/cm) [8] when compared to their hydrocarbon counterparts. This latter feature is quite unique and depends dramatically on the structure and the degree of fluorination.

In contrast, fluoropolymers have been widely studied due to their widespread use in various technologies and industries. The costs of fluorinated monomers, difficulties in the processing of fluorinated polymers, (e.g. high crystallinity and low solubility), and their valuable interfacial properties have prompted the vigorous devel-

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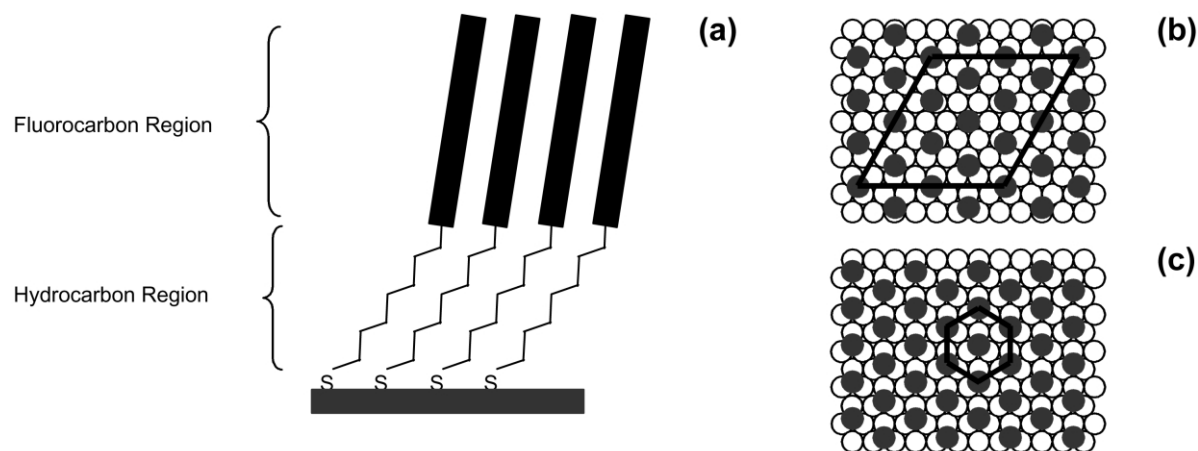
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Fig. 1. (a) Illustration of the pseudo-bilayer structure of partially fluorinated SAMs on gold. (b) Commonly observed c(7×7) packing structure of F-SAMs, showing the ∼5.9 Å spacing of the tailgroups. (c) Ubiquitous ($\sqrt{3} \times \sqrt{3}$) R 30° packing structure of normal hydrocarbon SAMs, showing the 5.0 Å spacing of the tail groups.

opment of fluorinated thin films as alternative materials. In contrast to hydrocarbon or siloxane coatings, fluorocarbon coatings exhibit repellency toward both water and oil; consequently, droplets of both water and hexadecane will 'bead up' when deposited on fluorinated surfaces [12].

Several key unresolved issues hinder the further development of fluorocarbon coatings in nanodevice applications. Foremost is the need to understand the fundamental relationships between fluorocarbon structure and the corresponding interfacial properties. Zisman and co-workers first broached this topic more than 40 years ago in studies of Langmuir-type fluorinated carboxylic acid monolayers [13••,14]. The topic lay largely dormant until the advent of fluorinated self-assembled monolayers (F-SAMs) on gold, which are the focus of this review.

2. Composition and structure

Although the structural features of SAMs derived from the adsorption of normal alkanethiols onto gold have been established, the corresponding structural features of F-SAMs remain a topic of research. In particular, since most fluorinated alkanethiols consist of both hydrocarbon and fluorocarbon regions, F-SAMs derived from them possess a pseudo bilayer structure (Fig. 1a), which serves to complicate any structural description. For example, the length, tilt and conformational order of the hydrocarbon chain are needed, as are the length, tilt and degree of helicity of the fluorocarbon chain. Furthermore, characterization of the packing structure of the SAM requires knowledge of the lattice spacing, the lattice point group and the orientation of the tail group lattice with respect to the Au(111) lattice.

Given that the van der Waals diameter of a helical fluorocarbon chain is 5.7 Å vs. 4.2 Å for a trans-extended hydrocarbon chain, the lattice spacings of highly perfluorinated F-SAMs is greater than that of normal hydrocarbon SAMs (5.9 Å vs. 5.0 Å as illustrated in Fig. 1b and c, respectively) [15]. However, for fluorocarbon tailgroups too short to support a helix, the lattice constants of F-SAMs are indistinguishable from those of hydrocarbon SAMs [16–19•]. Detailed lattice measurements of F-SAMs have shown that these films adopt high order commensurate c(7×7) or p(2×2) lattice structures [15,20•,21,22•,23,24]. In these studies, most F-SAMs possess a short linker group (e.g. ester, amide or hydrocarbon) between the sulfur headgroup and the fluorocarbon tailgroup. A surprising and still unexplained rotation of 30° exists between the molecular lattice of the tailgroup and the underlying gold lattice [20•]. Schonherr and Vancso proposed chain-length dependence, but the origin of the phenomenon remains unresolved [21,25,26].

Tamada and co-workers reported that an increase in the length of the hydrocarbon segment gives rise to increased disorder in the AFM images of highly perfluorinated F-SAMs (i.e. where the outer 8–10 carbons are fluorinated) [27•]. They argued that as the length of the alkyl chain is increased, the interchain interactions become dominated by alkyl–alkyl interactions, which lead to an increase in the tilt angle of the hydrocarbon segments to accommodate the large fluorocarbon tailgroups. As the tilt angle of the hydrocarbon segment increases, the number of defects and domain boundaries among the fluorinated tailgroups increases, leading to an apparent disordering at the interface. In studies of these F-SAMs by surface IR spectroscopy, Fukushima and co-workers observed a shift of the antisymmetric band toward lower wavenumber (indicating higher conformational order) upon increasing the length of the hydrocarbon chain, regardless of the length of the
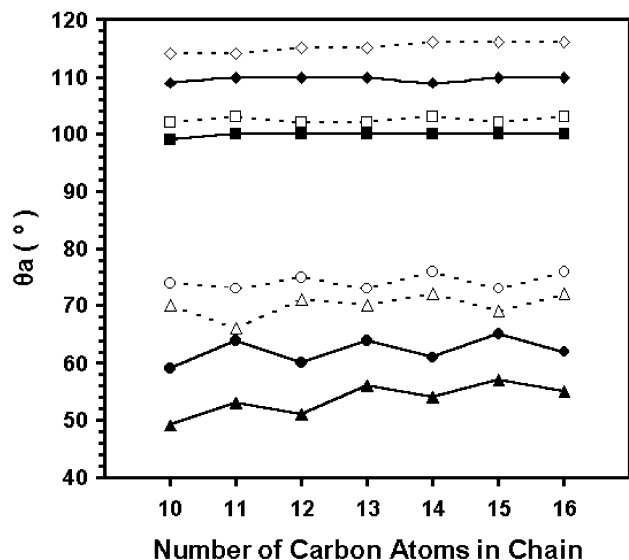
Fig. 2. Advancing contact angles of polar protic (water $\diamond$, glycerol $\square$) and polar aprotic (DMF $\bigcirc$, acetonitrile $\triangle$) liquids on SAMs formed from n-alkanethiols ($CH_3(CH_2)_nSH$ with $n=9$–15; open symbols) and CF_3-terminated alkanethiols ($CF_3(CH_2)_nSH$ with $n=9$–15; filled symbols).

fluorocarbon segment [28]. Thus, as a whole, an increase in the length of the hydrocarbon segment leads to an apparent increase in the conformational order of the hydrocarbon chains, but a decrease in the conformational order of the fluorocarbon tailgroups.

Analysis of the fluorocarbon region by IR spectroscopy revealed that as the hydrocarbon length increased for a constant fluorocarbon length, the symmetric and antisymmetric CF_2 bands shifted toward higher wavenumber and increased in intensity [19•]. The bands at ~ 1220 cm^{-1} and ~ 1150 cm^{-1} correspond to a transition dipole moment perpendicular to the helix axis, leading to the conclusion that the fluorocarbon chains become more tilted as the length of the buried hydrocarbon segment is increased [29]. Studies by Genzer and co-workers using NEXAFS confirmed this interpretation and further found that the tilt angle of the fluorocarbon tailgroup was proportional to its own length [30].

The helical structure can be evaluated using the position of the first and second axial CF_2 stretching vibrations (1315–1345 cm^{-1} and 1365–1375 cm^{-1}, respectively) which both correspond to a change of dipole, parallel to the helical axis. These bands shift toward higher wavenumber as the length of the fluorocarbon segment increases, regardless of the length of the hydrocarbon segment. Thus, the position of these bands, which appear insensitive to minor changes in orientation with respect to the surface, can be used to evaluate the size of the helix [19•].

3. Wettability and friction

Contact angle measurements of CH_3- and CF_3-terminated SAMs have revealed a strong influence of oriented dipoles on the wettabilities of the latter films. Although the replacement of CH_3 by CF_3 was expected to decrease the wettabilities of polar contacting liquids, the opposite effect was observed [31]. For example, both polar protic (water, glycerol) and polar aprotic (acetonitrile, DMF) liquids wetted the CF_3-terminated SAMs more than their CH_3-terminated counterparts (Fig. 2) [32]. This phenomenon was attributed to the presence of oriented surface dipoles along the CF_3–CH_2 molecular axis; the CF_3-terminated surfaces present an ordered array of dipoles that interact with the molecular dipoles in the contacting liquid, leading to a decrease in the contact angles [33••,34••]. In these studies, hydrogen bonding was found to have no significant effect on the wettability of fluorinated SAMs.

The concept of surface dipoles was also apparent in the wettabilities of CF_3-terminated SAMs, having odd and even chain lengths. Specifically, the contact angles of polar aprotic liquids on the CF_3-terminated SAMs were observed to exhibit a systematic variation with odd and even chain lengths (Fig. 3) [33••]. An even-numbered chain presents at the surface an array of dipoles oriented nearly normal to the substrate surface; in contrast, odd-numbered chains give rise to surface dipoles that are substantially more tilted, partially compensating each other [35]. Consequently, the greater force field at the surface of even-numbered SAMs gives rise to the diminished contact angles, (i.e. enhanced
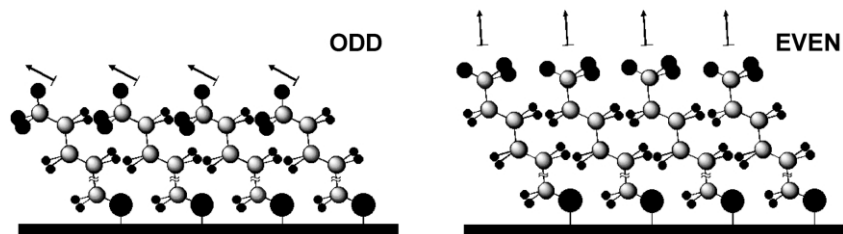

Fig. 3. Illustration of the parity effect for CF_3-terminated SAMs on gold.
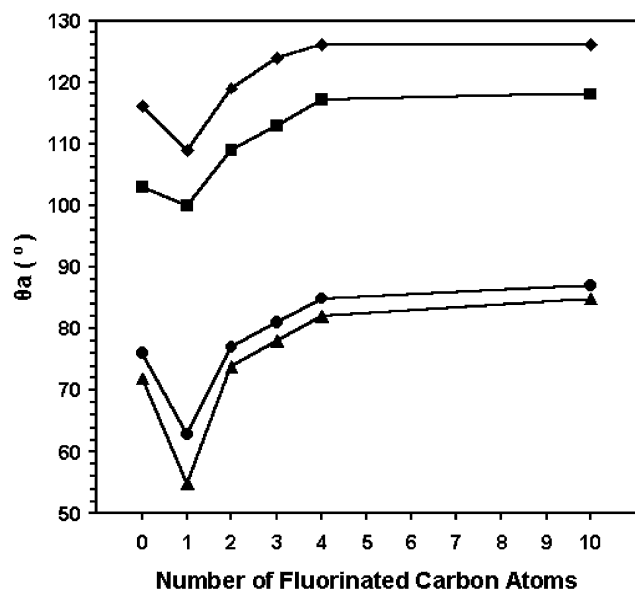
Fig. 4. Advancing contact angles of polar protic (water ♦, glycerol ■) and polar aprotic (DMF ●, acetonitrile ▲) contacting liquid on SAMs formed from progressively fluorinated hexadecanethiols.

wettabilities) observed for the polar aprotic contacting liquids. Furthermore, increasing the degree of fluorination in a series of hexadecanethiols, which effectively leads to a progressive burying of the hydrocarbon-fluorocarbon dipole, shows that the contact angles progressively increase until reaching a plateau (Fig. 4). These observations provide strong evidence for the role of oriented dipole–dipole interactions in dictating the wettabilities of partially fluorinated organic thin films.

While the contact angle measurements demonstrate the strong influence of surface dipoles upon the wettabilities of F-SAMs, measurements of friction by AFM showed no such correlation [25,36•,37]. In particular, the frictional response of CF_3-terminated films was observed to be approximately three times that of CH_3-terminated films. The most obvious correlation responsible for the increase in friction was the molecular size of the tailgroup [38,39•]. To test this hypothesis, isopropyl-terminated (iPr) SAMs were prepared and evaluated; an isopropyl group is isosteric to a CF_3 group, but chemically similar to a CH_3 group [40,41]. A comparison of the frictional properties of SAMs formed from CH_3-, CF_3- and iPr-terminated thiols were consistent with a model in which the size of the terminal group (rather than the chemical nature) dictates the frictional responses of F-SAMs.

4. X-Ray induced damage and ion-surface collisions

The effects of X-ray and electron irradiation on fluorinated surfaces are technologically relevant. For example, fluorocarbon-based lubricants used in hard disk

drives undergo deterioration due to exposure to low-energy electrons evolving at the interface between the disk and the reader [42]. Fundamental studies by X-ray photoelectron spectroscopy (XPS) found that photo and secondary electrons comprise the predominant source of damage, while primary X-rays cause little or no damage [43,44]. In separate studies, Frey and co-workers examined the effects of low energy electron irradiation (10 eV) on a series of F-SAMs, $CF_3(CF_2)_9(CH_2)_nSH$ ($n=$ 2,11,17) [45]. All parts of the monolayers showed evidence for electron-induced damage. The major observations were that (1) substantial fluorine was abstracted, including elemental fluorine; (2) no terminal CF_3 moieties survived the irradiation; and (3) carbon-containing fragments emanate exclusively from the fluorocarbon region. As a whole, these studies led to the conclusion that crystalline F-SAMs sustain less damage than those that are more liquid-like.

In relevant work, XPS is often used to evaluate the structure and chemical composition of organic thin films. For F-SAMs, a prerequisite for this type of study is to understand the interaction of electrons with fluorocarbons. A measure of this behavior is the attenuation length (λ) of the emanating electrons as a function of their kinetic energy. For hydrocarbon films, Whitesides and then Wilkes used SAMs, generated from normal alkanethiols of increasing length to determine the attenuation length ($\lambda = 40 \pm 3$ Å at 1403 eV) of photoelectrons with kinetic energies in the range 140–1400 eV [46,47]. The most logical approach to apply these studies to fluorinated films would be to study fully fluorinated SAMs, but no synthetic approach is available. Partially fluorinated F-SAMs offer a more complex case because their internal structure contains both fluorocarbon and hydrocarbon segments. Frey et al. studied the variations of $C1s(CF_2)$, $C1s(CF_3)$, and $F1s$ peak intensities across the series $CF_3(CF_2)_{10}(CH_2)_xSH$ and concluded that the thickness and/or packing density of the fluorocarbon layer was independent of the length of the alkyl spacer [48•]. As described above, the tilt angle is a function of the length of the alkyl spacer; consequently, the thickness cannot remain constant when the length of the alkyl spacer is changed.

To provide a direct and precise measurement of the attenuation length of photoelectrons in F-SAMs, Colorado and Lee chose to evaluate the series $CF_3(CF_2)_n(CH_2)_{11}SH$ in which the packing densities and chain tilts were known. The attenuation length of photoelectrons found for this series of F-SAMs was $\lambda = 40 \pm 3$ Å (at 1403 eV), which is indistinguishable from that for SAMs derived from normal alkanethiols. Apparently, the lower packing density of fluorocarbon vs. hydrocarbon chains precisely counteracts the increase in size upon replacing hydrogen with fluorine.

F-SAMs have also been used with success as targets for low-energy (10–200 eV) ion-surface collisions

[49,50]. In normal-incidence ion-surface collisions, the projectile ion interacts with multiple chemical groups on the surface with transfer of impact energy into the surface and into the internal energy of the ion. SAMs were used for this particular application due to their barrier properties: they prevent neutralization of the ion beam—a common cause of reduced throughput if bare metal is used. Due to their higher ionization potential, F-SAMs are less susceptible to damage by ions than are hydrocarbon SAMs. The specific interest in F-SAMs lies in their ability to transfer efficiently the kinetic energy of the projectile ion into internal energy, as demonstrated by the groups of Wysocki and Cooks [51–54]. This characteristic was attributed to the stiffness of the fluorocarbon helix and/or to the effective mass increase (when compared to hydrocarbon SAMs). Wysocki and co-workers compared CH_3-, CF_3-, CF_3CF_2- and C10F21-terminated SAMs and found that the effective mass of the terminal group was the predominant factor determining the extent of kinetic energy transferred into internal energy; they also observed a moderate influence due to the underlying group(s) [55•]. Indeed, ion–surface reactions are primarily sensitive to the nature of the terminal groups, but evidence of ion penetration through a few atomic layers has been observed [56]. Ion–surface reactions can also sense differences in terminal group orientation, such as the odd–even effect in CF_3-terminated SAMs [55•].

Cooks and co-workers have found that fluorinated SAMs can be used as substrate for a new technique of surface modification known as 'soft landing' [57•]. In this technique, intact polyatomic ions are deposited on a surface using low energy ion beams and can be released undamaged from the fluorinated matrix using ion sputtering or thermal desorption. Capture at the surface is favored when the ions bear bulky substituents that facilitate steric trapping in the matrix. Depending on the nature of the ion and the surface, the ratio of soft landing to surface-reaction can potentially be tuned to obtain specific surface modifications.

5. Conclusions

From this abbreviated summary, it is apparent that many questions remain regarding the influence of fluorination upon the properties of organic thin films. When considering various technological, economical and environmental standpoints, it is important to minimize the amount of fluorine needed to achieve the targeted material properties. Specifically, further efforts are needed to design appropriate systems that maximize the effects of incorporating fluorocarbon segments into organic thin films. From a more fundamental perspective, fluorocarbon chemistry has generally suffered from a lack of interest due to the peculiar behavior of fluorocarbons vs. hydrocarbons. At the same time, however, technological interest has motivated advances in the field of fluoropolymers. A specific deficiency in these materials is their relatively poor stability toward radiation, leading, for example, to the rapid loss of water repellency for fabric coatings exposed to sunlight. Studies of F-SAMs thus offer a means to reduce or suppress the damage and thereby lead to materials with improved properties.

Acknowledgments

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•　of special interest
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