

Unsymmetrical Spiroalkanedithiols Having Mixed Fluorinated and Alkyl Tailgroups of Varying Length: Film Structure and Interfacial Properties

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Abstract: A custom-designed series of unsymmetrical spiroalkanedithiols having tailgroups comprised of a terminally fluorinated chain and a hydrocarbon chain of varying lengths were synthesized and used to prepare self-assembled monolayers (SAMs) on gold substrates. The specific structure of the adsorbates was of the form $[\text{CH}_3(\text{CH}_2)_n][\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_8]\text{C}[\text{CH}_2\text{SH}]_2$, where $n = 7, 9,$ and 12 (designated as **F8H10-C10**, **F8H10-C12**, and **F8H10-C18**, respectively). The influence of the length of the hydrocarbon chain in the bidentate dithiol on the structure and interfacial properties of the monolayer was explored. A structurally analogous partially fluorinated monodentate alkanethiol and the corresponding normal alkanethiols were used to generate appropriate SAMs as reference systems. Ellipsometric thickness measurements showed an unexpectedly low film thickness for the SAMs derived from the bidentate adsorbates, possibly due to disruptions in interchain packing caused by the fluorocarbon chains (i.e., phase-incompatible fluorocarbon-hydrocarbon interactions), ultimately giving rise to loosely packed and disordered films. Analysis by X-ray photoelectron spectroscopy (XPS) were also consistent with a model in which the films were loosely packed; additionally, the XPS spectra confirmed the attachment of the sulfur headgroups of the bidentate adsorbates onto the gold substrates. Studies of the SAMs by polarization modulation-infrared reflection-adsorption spectroscopy (PM-IRRAS) suggested that as the length of the hydrocarbon chain in the adsorbates was extended, a more ordered surface was achieved by reducing the tilt of the fluorocarbon segment. The wettability data indicated that the adsorbates with longer alkyl chains were less wettable than those with shorter alkyl chains, likely due to an increase in interchain van der Waals forces in the former.

1. Introduction

Over the last three decades, self-assembly has developed into a technique that is widely used to generate well-defined organic thin films on metal substrates [1-3]. The resultant films, denoted as self-assembled monolayers (SAMs), offer great potential for use in a number of applications such as corrosion inhibition [4-8], lithographic patterning [9-10], biomaterials fabrication [11-17], and microelectronic device manufacturing [18-21]. In particular, alkanethiolate-based monolayers on gold substrates are the most studied system due to their reproducible ordered structures and relatively simple preparation procedures [22,23]. The interfacial properties of the organic surfaces such as wettability [24,25], adhesion [26-29], and friction [30-36] can be controlled by varying the structure of the adsorbate employed.

Much of the previously mentioned research has been obtained from ω -terminated alkanethiols (monothiol-based adsorbates), which provide a single point of contact between the sulfur headgroup and the metal surface. Alternatively, other types of adsorbates having multiple headgroup-metal interaction points have also been developed and studied [37-39]. Bidentate adsorbates have been introduced into surface chemistry due to their ability to enhance the stability of thin films formed on solid substrates [40]. The enhanced stability exhibited in films derived from multidentate adsorbates has been attributed to an entropy-driven phenomenon known as the "chelate effect", which is a key strategy used to enhance metal-ligand complexes in inorganic materials [41-43]. The entropy change upon binding one bidentate ligand to a multivalent metal atom is more favorable than the process of binding two monodentate ligands, leading to a more stable complex. This concept can be readily applied to films derived from organic molecules covalently bound to surfaces by incorporating multiple attachment points on the adsorbate to create multiple interactions between the adsorbate and the metal surface.

Several examples of designs of such bidentate adsorbates, which have been used to enhance film stability on metal substrates, include aromatic-based bidentate adsorbates [44-47], spiroalkanedithiolate-based adsorbates [48-51], and trithiolate-based adsorbates [52-57]. Using the spiroalkanedithiol (SADT) structure, well-packed and highly oriented SAMs can be generated by utilizing an adsorbate structure having a pair of relatively long alkyl chains [48]. A major attractive feature of this design is the relatively simple synthetic approach, which can open new avenues for the synthesis of a large variety of adsorbates. A recent example includes the

development of film compositions where two phase-incompatible groups were incorporated into the same molecule, yielding homogeneously mixed SAMs [50,51].

In a previous report, we studied the synthesis and characterization of SAMs generated from a prototype unsymmetrical partially fluorinated SADT [50]. The structure consisted of the spiro-dithiol headgroup connected with two different tailgroups (i.e., one hydrocarbon and one partially fluorinated), as shown in Figure 1. This specific design was motivated by the potential development of thin film fluorinated surfaces to mimic poly(tetrafluoroethylene). The discovery of poly(tetrafluoroethylene) (PTFE) by Plunkett in 1938 [58] has led to the extensive use of fluoropolymers in various applications due to their chemical inertness, thermal and mechanical resistance, and low adhesion [59]. Therefore, fluorocarbon-based films can offer certain advantages over hydrocarbon-based films in terms of chemical resistance, chain rigidity, thermal stability, hydrophobicity, and oleophobicity [60-62]. For this report, two new fluorinated bidentate dithiols were synthesized having the molecular structures shown in Figure 1.

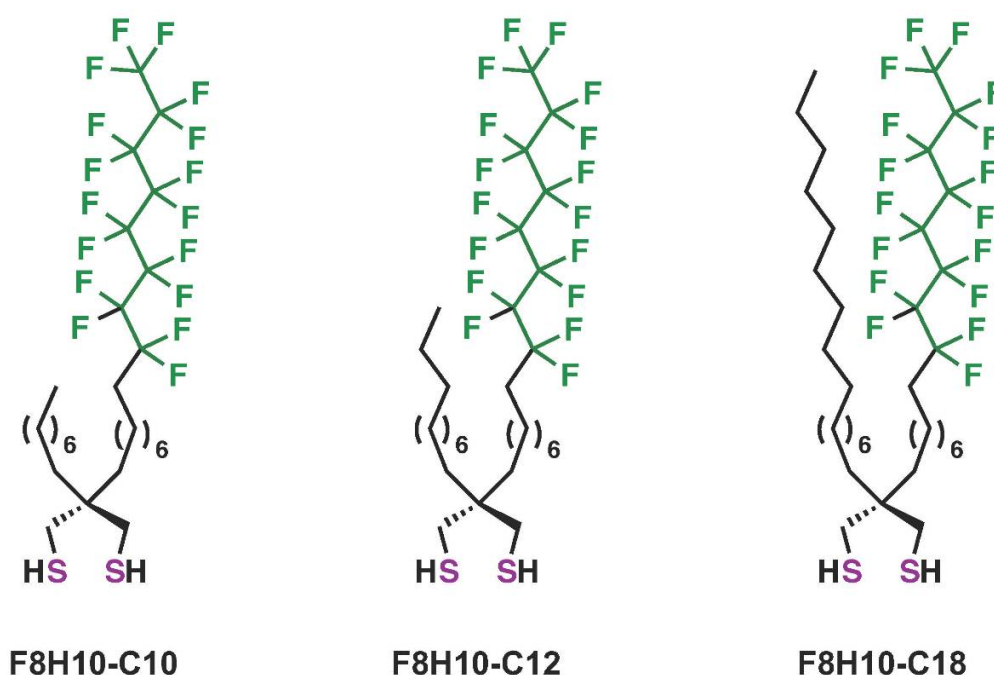


Figure 1. Molecular structures of the unsymmetrical partially fluorinated spiroalkanedithiols (F8H10-C m , $m = 10, 12,$ and 18) examined in the present study: **F8H10-C10**, **F8H10-C12**, and **F8H10-C18**.

Notably, the original prototype in Figure 1, $[\text{CH}_3(\text{CH}_2)_7][\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_8]\text{C}[\text{CH}_2\text{SH}]_2$ (**F8H10-C10**), possesses a partially fluorinated chain and a shorter hydrocarbon chain having the same number of hydrocarbon units as that in the partially fluorinated chain. This original adsorbate was designed to form SAMs in which the helical fluorinated chains (van der Waals diameter of ~ 5.6 Å) [63] would not be subjected to the packing constraints typically observed in SAMs derived from the corresponding monothiol, but instead pack on top of the underlying well-packed trans-extended alkyl chains (van der Waals diameter of ~ 4.2 Å) [64]. To explore further the effects of molecular structure on the packing density and interfacial properties of SAMs derived from this class of adsorbate, the present study examines SAMs derived from the partially fluorinated spiroalkanedithiols in Figure 1 (i.e., **F8H10-C12** and **F8H10-C18**, respectively). In efforts to examine the effects of hydrocarbon chain length on film properties, we incorporated systematically longer hydrocarbon chains in these two new adsorbate molecules. A schematic representation illustrating a well-organized SAM for each of the studied adsorbates is shown in Figure 2.

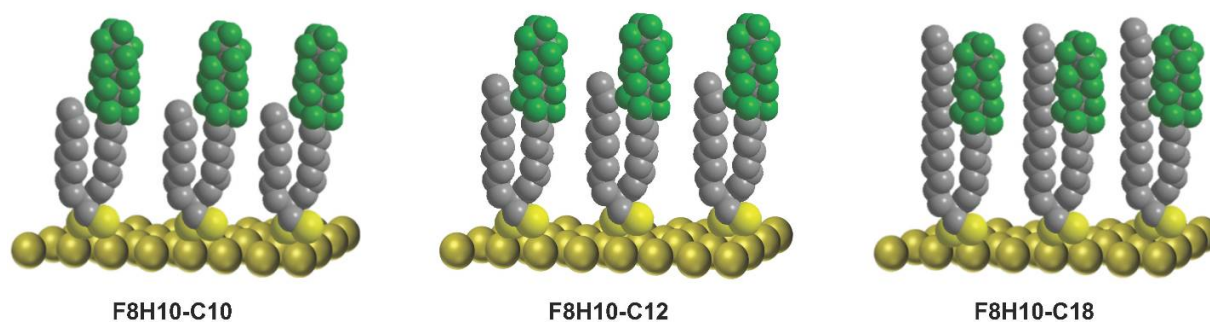


Figure 2. Illustration of idealized SAMs on gold derived from **F8H10-C10**, **F8H10-C12**, and **F8H10-C18**.

Further, we compared the **F8H10-Cm** SAMs to SAMs derived from the corresponding monodentate *n*-alkanethiols: $\text{CH}_3(\text{CH}_2)_n\text{SH}$, where $n = 10, 12,$ and 18 (**C10SH**, **C12SH**, and **C18SH**, respectively) and the structurally analogous partially fluorinated monodentate thiol $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{10}\text{SH}$ (**F8H10SH**). We characterized the structure and the interfacial properties of all SAMs using ellipsometry, X-ray photoelectron spectroscopy (XPS), polarization modulation infrared reflection-adsorption spectroscopy (PM-IRRAS), and contact angle goniometry.

2. Results and Discussion

The **F8H10-Cm** SAMs were allowed to equilibrate at room temperature for 48 h in DMF prior to characterization. Previous work on related SADT SAMs developed in DMF yielded films with optimal qualities (i.e., relatively ordered, less wettable with a well-packed monolayer film) [50]. We also prepared SAMs from the corresponding monodentate thiols to serve as reference systems. For instance, we assumed that the data from SAMs derived from **F8H10-C10** could be readily compared to those derived from **C10SH** and **F8H10SH**. This assumption allows a direct evaluation of the SADT SAMs against SAMs of analogous structural character. Consequently, we prepared SAMs derived from the normal alkanethiols **C10SH**, **C12SH**, and **C18SH** along with the structurally analogous fluorinated **F8H10SH** for comparison with the SAMs derived from **F8H10-C10**, **F8H10-C12**, and **F8H10-C18**, respectively.

2.1. Film Thicknesses

Preliminary confirmation of SAM formation on metal substrates can be determined by measuring the thickness of the film using ellipsometry [50]. Table 1 shows the thicknesses obtained for all of the SAMs. The SAMs derived from the monodentate thiols gave values that correspond to those reported in the literature, 10, 12, 22, and 18 Å for the **C10SH**, **C12SH**, **C18SH**, and **F8H10SH** SAMs, respectively [65-67].

Table 1. Ellipsometric Thickness Measurements for SAMs on Gold Derived from the Monodentate Thiols and the **F8H10-Cm** Dithiols

| Adsorbate | Thickness (Å) |
|------------------|---------------|
| C10SH | 10 ± 2 Å |
| C12SH | 12 ± 2 Å |
| C18SH | 22 ± 2 Å |
| F8H10SH | 18 ± 2 Å |
| F8H10-C10 | 14 ± 2 Å |
| F8H10-C12 | 16 ± 2 Å |
| F8H10-C18 | 21 ± 2 Å |

Comparison of the thickness values obtained for the monodentate SAMs and the **F8H10-Cm** SAMs indicates that the **F8H10-Cm** SAMs exhibit thickness values that are consistent with the formation of monolayer films. Furthermore, as the alkyl chain length is increased systematically in the series, **F8H10-C10**, **F8H10-C12**, and **F8H10-C18**, the thicknesses increase systematically as well: 14 Å, 16 Å, and 21 Å, respectively. The observation that the thickness of the **F8H10-C18** SAM is comparable to that of the **C18SH** SAM (i.e., 21 Å vs. 22 Å, respectively) suggests that the chains in the **F8H10-C18** SAM are densely packed. Furthermore, the lower thickness values observed for the **F8H10-C10** and **F8H10-C12** SAMs compared to that for the **F8H10SH** SAM (18 Å) are consistent with a model in which the alkyl chains in the bidentate films underlay a fluorocarbon chain that is loosely packed with room to undergo significant chain tilt in order to maximize interchain van der Waals interactions with neighboring fluorocarbon moieties [50].

2.2. Analysis of the Films by XPS

Figure 3 provides the XPS spectra of the S 2p, C 1s, and F 1s regions for the SAMs derived from **F8H10SH** and the **F8H10-Cm** adsorbates. Figure 3A shows that the S 2p region is comprised of a doublet corresponding to the S 2p_{3/2} and S 2p_{1/2} photoelectrons. Previous research on SAMs derived from *n*-alkanethiols on gold has shown that the S 2p_{3/2} peak with a binding energy of ~162.0 eV is representative of a bound thiolate, while the S 2p_{3/2} of an unbound sulfur or a disulfide appears at ~164.0 eV [68]. The same observation has also been made for SAMs derived from partially fluorinated alkanethiols adsorbed on gold substrates [50,63]. For the **F8H10SH** SAM and the **F8H10-Cm** SAMs, the observed S 2p_{3/2} peak position suggests that all sulfur moieties in the films are bound to the surface of gold.

The C1s spectra for the **F8H10SH** and the SADTs are shown in Figure 3B, and reveal three peaks characteristic of CH₂, CF₂, and CF₃ units at ~ 285 eV, 292 eV, and 294 eV, respectively [63,67]. Comparison of the C1s (CH₂) peak positions of the **F8H10-Cm** SAMs to those of the **F8H10SH** shows a systematic decrease in the binding energy as the length of the hydrocarbon chain increases. The densely packed SAMs derived from **F8H10SH** and those from **F8H10-C10** exhibit a binding energy of 284.7 eV, while the SAMs derived from **F8H10-C12** and **F8H10-C18** exhibit values of 284.5 eV and 284.4 eV, respectively. The lower binding energies of the **F8H10-C12** and **F8H10-C18** SAMs compared to the **F8H10SH** and **F8H10-C10** SAMs are indicative of a lower hydrocarbon chain packing density in the former films [73]. Further, the shift to lower

binding energies in the **F8H10-C12** and **F8H10-C18** SAMs as the length of the hydrocarbon chain is increased can be plausibly attributed to phase-incompatible fluorocarbon-hydrocarbon interactions in these films. Overall, the relative alkyl chain density of the fluorinated adsorbates decrease as follows: **F8H10SH** ~ **F8H10-C10** > **F8H10-C12** > **F8H10-C18**.

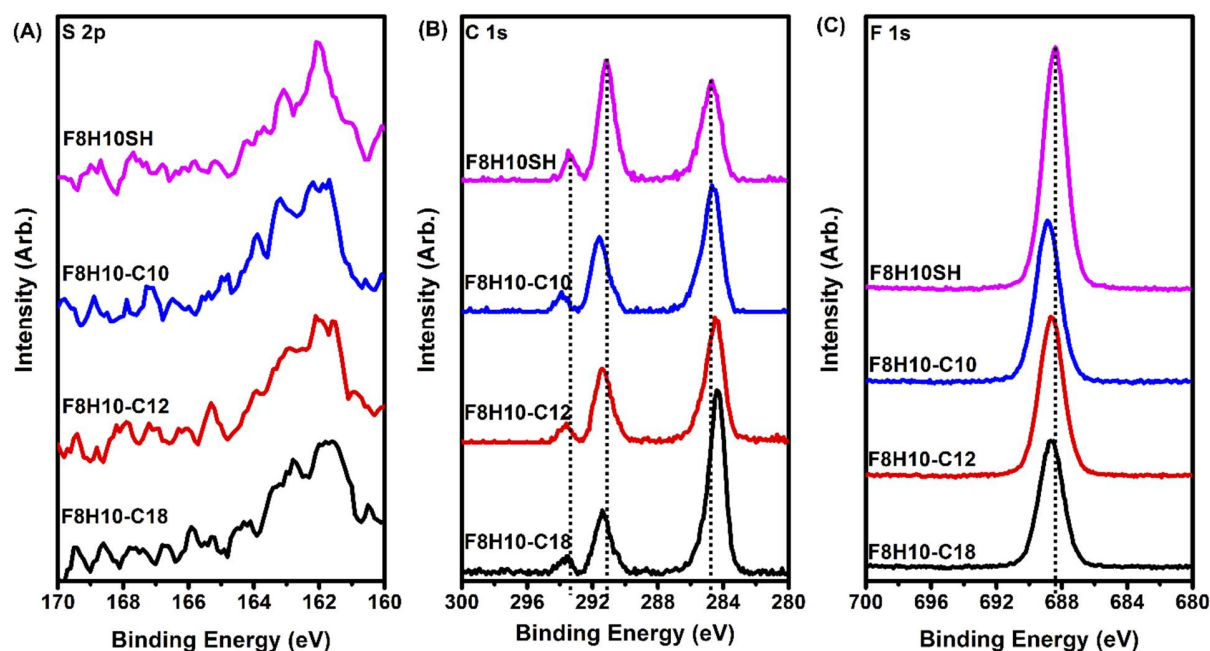


Figure 3. XPS spectra collected from SAMs derived from **F8H10SH** and **F8H10-C_m** ($m = 10, 12, \text{ and } 18$) for the (A) S 2p, (B) C 1s, and (C) F 1s regions.

Several studies on SAMs derived from *n*-alkanethiols have shown that the position of the C 1s peak can be used as a rough measurement of surface coverage for the adsorbates on the substrate [63,67,69-71]. In a series of *n*-alkanethiols with successively increasing chain length, the binding energy of the C 1s photoemission shifts to a higher value when the alkyl chain length is increased, which is attributable to an increase in the packing density of the alkyl chains [69,70,72]. As shown in Figure 4 and Table 2, we observe the same trend for SAMs derived from *n*-alkanethiols on gold: the C 1s (CH₂) peak shifts from 284.7 eV for **C10SH** to 284.8 eV for **C12SH** to 285.3 eV for **C18SH**. The higher binding energy of the densely packed alkanethiolate monolayers have an increased resistance to photoelectron emission from the surface during the irradiation process, shifting the peak position to a higher binding energy [69,70,72].

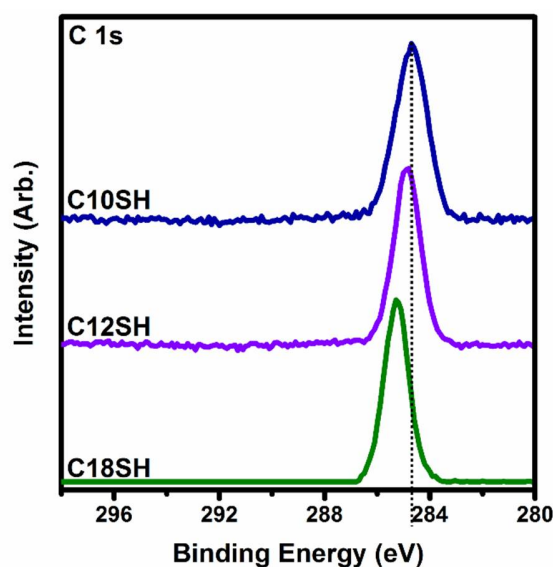


Figure 4. XPS spectra of the C 1s region collected from SAMs derived from the normal alkanethiols, **C10SH**, **C12SH**, and **C18SH**.

Table 2. XPS Peak Positions for the C 1s and F 1s Regions for the Partially Fluorinated SAMs

| Adsorbate | Peak Position (eV) | | | |
|------------------|----------------------------|----------------------------|----------------------------|-------|
| | C 1s (CH ₂) | C 1s (CF ₂) | C 1s (CF ₃) | F 1s |
| C10SH | 284.7 | - | - | - |
| C12SH | 284.8 | - | - | - |
| C18SH | 285.3 | - | - | - |
| F8H10SH | 284.7 | 291.2 | 293.5 | 688.4 |
| F8H10-C10 | 284.7 | 291.6 | 293.9 | 688.9 |
| F8H10-C12 | 284.5 | 291.4 | 293.6 | 688.7 |
| F8H10-C18 | 284.4 | 291.4 | 293.6 | 688.7 |

Considering the peak positions of the fluorinated components (CF₂, CF₃, and F peaks) in the XPS spectra -- Figure 3B, 3C, and Table 2 -- the C 1s (CF₂ and CF₃) and F1s peaks shift to higher

binding energies as compared to those of the **F8H10SH** film in the following order: **F8H10SH** < **F8H10-C18** \leq **F8H10-C12** < **F8H10-C10**, which can be ascribed to the structural parameters of each adsorbate on the substrate. Frey *et al.* and Tamada *et al.* also observed these shifts to higher binding energies of the fluorinated components in their studies of partially fluorinated alkanethiol SAMs when the length of the underlying hydrocarbon chain was increased [63,67]. The authors rationalized this phenomenon by relating a screening effect for the core excited atoms in conjunction with the distance between the core hole and the substrate. The surface charge generated from the photoelectron emission of a core carbon or a fluorine atom in the fluorocarbon segment during X-ray irradiation can be discharged by the electrons in the substrate, which can move to screen the core hole within the film [74]. If the distance between the core hole and the substrate increases, the monolayers may not be discharged completely; therefore, an increase in thickness of the hydrocarbon segment below the fluorocarbon layer was responsible for the shift to higher binding energies of the C 1s (CF₂), C 1s (CF₃), and F 1s peaks [63].

Comparison of the C 1s peaks for the CF₂, CF₃, and the F 1s peaks for the SAMs derived from **F8H10SH** and the bidentate SADTs shows that the **F8H10SH** SAM exhibits the lowest binding energies (~291.2 eV, 293.5 eV, and 688.4 eV), while the **F8H10-C10** SAM exhibits the highest binding energies (~291.6 eV, 293.9 eV, and 688.9 eV), with the **F8H10-C18** and **F8H10-C12** SAMs in between (~291.4 eV, 293.6 eV and 688.7 eV). While it is tempting to try to draw conclusions regarding the chain packing in the hydrocarbon segments from these data, we recognize that the electronic environment of the fluorocarbon chains might vary greatly in these films as the fluorocarbon chains are densely packed for the **F8H10SH** SAM, loosely packed for the **F8H10-C10** SAM, and probably somewhere in between for the **F8H10-C18** and **F8H10-C12** SAMs. Further insight regarding the orientation of the hydrocarbon and fluorocarbon chains in these films can be obtained from the interpretation of the PM-IRRAS data, which are discussed in a later section [61].

Another aspect of the XPS data that can be analyzed to obtain quantitative results is the intensity of the peak, specifically to reveal the adsorbate density and composition on the substrate [63,75]. Table 3 shows the normalized intensities for the C 1s (CH₂), C 1s (CF₂ + CF₃), and F 1s peaks of each fluorinated adsorbate used in this study; for simplicity, the intensities were normalized with respect to the C 1s (CF₂ + CF₃) and the F 1s peak intensities, respectively, of the

F8H10SH SAM. The peak intensity increase observed for the CH₂ component of the bidentate dithiols relative to the **F8H10SH** adsorbate is affected by the addition of the second hydrocarbon chain (i.e., an increased number of CH₂ units) for each of the respective adsorbates. The C 1s (CF₂+CF₃) and F 1s peak intensities for the **F8H10-Cm** SAMs are weaker than those of the **F8H10SH** SAM, which can be attributed to the packing density of the fluorocarbon chains of the SAMs (i.e., **F8H10SH** > **F8H10-Cm**) [63]. The diminished intensity and/or packing density can also be attributed to the steric bulk and consequently greater space occupied by the branched hydrocarbon chains of the bidentate adsorbates, which can plausibly lead to diminished fluorocarbon density at the interface.

Among the **F8H10-Cm** SAMs, the relative packing density of the fluorocarbon chain decreases as the hydrocarbon chain length increases, as judged by the F 1s peak intensities shown in Figure 3 and Table 3 in the following order: **F8H10-C10** ≥ **F8H10-C12** > **F8H10-C18**. It should be noted that the addition of the two methylene units along the hydrocarbon chain for **F8H10-C12** might disturb the fluorocarbon chain order and/or packing; however, the effect appears to be minimal with regard to changes in overall structure and interfacial properties (i.e., thickness, packing density, and wettability, which will be described subsequently) between the **F8H10-C12** and **F8H10-C10** SAMs. The structure of the **F8H10-C18** film, on the other hand, is influenced by phase-incompatible fluorocarbon-hydrocarbon interactions in the terminal portions of this SAM, which contributes to chain disorder, and thus leads to a more loosely packed SAM.

Table 3. XPS Intensities for C 1s and F 1s Regions of Each Fluorinated SAM

| Adsorbate | C 1s ^a (CH ₂) | C 1s ^a (CF ₂ +CF ₃) | F 1s ^b |
|------------------|---|--|-------------------|
| F8H10SH | 0.96 | 1.00 | 1.00 |
| F8H10-C10 | 1.16 | 0.72 | 0.72 |
| F8H10-C12 | 1.07 | 0.71 | 0.69 |
| F8H10-C18 | 1.50 | 0.57 | 0.55 |

^a Peak intensities were normalized with respect to the intensity of the fluorocarbon components (i.e., CF₂ + CF₃) in the C 1s region of the **F8H10SH** SAM.

^b Peak intensities were normalized with respect to the intensity of the F 1s region of the **F8H10SH** SAM.

2.3. PM-IRRAS Analysis of the Films.

The PM-IRRAS spectra for the C-H and C-F stretching regions are depicted in Figures 5 and 6, respectively. The C-H stretching modes are known to be sensitive to the conformational order (i.e., crystallinity) of the hydrocarbon chains [76], while the C-F vibrations can provide information regarding the orientation of the fluorinated segments in fluorocarbon films [61]. The position of the antisymmetric ($\nu_{\text{as}}^{\text{CH}_2}$) methylene C-H stretching bands has been used as a means to determine the conformational order of a SAM [76]. For a well-ordered (crystalline) film, the $\nu_{\text{as}}^{\text{CH}_2}$ peak appears at 2918 cm^{-1} ; however, the $\nu_{\text{as}}^{\text{CH}_2}$ peak for a disordered (liquid like) film appears at 2924 cm^{-1} [65]. For the SAMs derived from the *n*-alkanethiols, the $\nu_{\text{as}}^{\text{CH}_2}$ band positions were observed at 2920, 2919, and 2918 cm^{-1} for the **C10SH**, **C12SH**, and **C18SH** SAMs, respectively (see Figure 5). Consistent with the literature data, the degree of conformational order in these SAMs increased with an increase in alkyl chain length [65]. Also apparent in the spectra is the C-H vibrations originating from the methyl groups at 2965 cm^{-1} for the $\nu_{\text{as}}^{\text{CH}_3}$ band and 2878 cm^{-1} for the $\nu_{\text{s}}^{\text{CH}_3}$ band.

For the fluorinated adsorbates, the $\nu_{\text{as}}^{\text{CH}_2}$ of the **F8H10SH** SAMs appears at 2919 cm^{-1} , consistent with a conformationally ordered film. However, the SAMs derived from the SADTs showed a significant shift of the $\nu_{\text{as}}^{\text{CH}_2}$ band to higher wavenumbers: 2923 cm^{-1} for **F8H10-C10**, 2924 cm^{-1} for **F8H10-C12**, and 2925 cm^{-1} for **F8H10-C18**. The higher wavenumber suggests that the hydrocarbon chains in the bidentate SAMs are less conformationally ordered than those in the monodentate SAMs. This observation can be attributed to a reduction in the chain packing density due to the branched nature of the adsorbates. The presence of hydrocarbon chains of identical length *below* the fluorocarbon segment of the **F8H10-C10** SAMs perhaps, allows the alkyl chains to be more densely packed relative to those in the **F8H10-C12** SAM and especially compared to the **F8H10-C18** SAM, where the phase-incompatible fluorocarbon-hydrocarbon interactions disrupt the monolayer packing, which is consistent with the XPS data (vide supra). Another aspect of the spectra to note is the absence of the C-H stretches associated with the methyl group for the **F8H10-C10** and **F8H10-C12** SAMs. The absence of those peaks can be attributed to their location underneath the fluorocarbon portion, a situation that appears to limit the methyl vibrations to coincide with the surface selection rules (i.e., only vibrations causing changes in the transition dipole moment perpendicular to the surface can be detected) [77], leaving these vibrations undetected by the PM-IRRAS measurement.

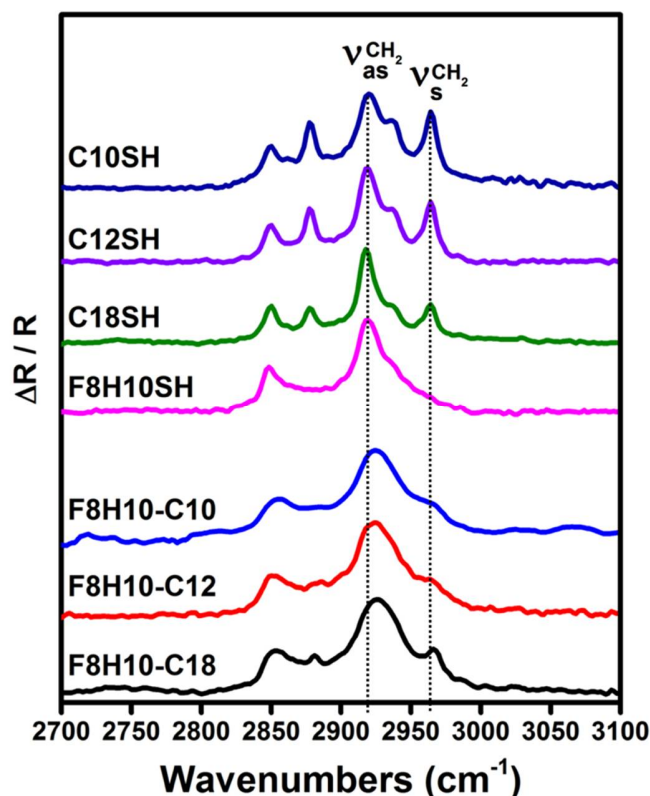


Figure 5. PM-IRRAS spectra in the C-H stretching region for SAMs generated from the alkanethiols, **F8H10SH**, and the **F8H10-Cm** adsorbates used in this study.

The bands arising from the C-F vibrations in the region from 1000 to 1400 cm^{-1} (shown in Figure 6 and discussed below), were assigned based on literature examples using similar fluorocarbon materials [60,63]. Additionally, an estimate of the orientation of the fluorocarbon segments can be obtained by comparing the relative intensities of bands associated with transitions perpendicular and parallel to the fluorinated helix, $\nu_{\text{pd}}^{\text{CF}_2}$ and $\nu_{\text{ax}}^{\text{CF}_2}$ respectively (*vide infra*) [63,78,79]. The band at 1150 cm^{-1} has been assigned as the symmetric C-F stretch of the CF_2 , while those at 1205 and 1250 cm^{-1} to the antisymmetric C-F stretches [60,80]. Complicating our analysis of the C-F spectra is the overlap of other vibrational modes, including C-C bond stretching and C-C-C bending at $\sim 1220 \text{ cm}^{-1}$ [60,81]. The bands in the 1150-1270 cm^{-1} range can be attributed to the stretches whose transition dipole moments are perpendicular to the fluorocarbon chain, $\nu_{\text{pd}}^{\text{CF}_2}$ [61]; correspondingly, the bands at 1336 and 1373 cm^{-1} have been identified as stretches with a transition dipole moment parallel to the fluorocarbon helical axis [61]. When the

fluorocarbon chains are oriented perpendicular to the surface (i.e., less tilted from the surface normal), the intensity of the $\nu_{\text{ax}}^{\text{CF}_2}$ bands are enhanced relative to that of the $\nu_{\text{pd}}^{\text{CF}_2}$ bands. On the other hand, when the fluorocarbon chains are oriented along the surface (i.e., more tilted from the surface normal), the intensity of the $\nu_{\text{ax}}^{\text{CF}_2}$ bands are diminished relative to that of the $\nu_{\text{pd}}^{\text{CF}_2}$ bands.

Based on this analysis, the higher intensity of the $\nu_{\text{ax}}^{\text{CF}_2}$ band relative to the $\nu_{\text{pd}}^{\text{CF}_2}$ band observed for the **F8H10SH** SAM leads to the conclusion that the fluorocarbon helix is oriented nearly perpendicular to the surface. In contrast, the film generated from **F8H10-C10** shows a strong reduction in the relative intensities of $\nu_{\text{ax}}^{\text{CF}_2}$ bands when compared to the $\nu_{\text{pd}}^{\text{CF}_2}$ bands in its spectra, suggesting a highly tilted fluorocarbon chain. The relative intensities of the $\nu_{\text{ax}}^{\text{CF}_2}$ and $\nu_{\text{pd}}^{\text{CF}_2}$ bands for the SAMs derived from **F8H10-C12** and **F8H10-C18** show similar intensities in their respective bands, indicating a fluorocarbon segment with an intermediate degree of tilt. These observations suggest that the latter bidentate SADT SAMs can support the neighboring fluorocarbon chains in a more upward orientation than is found in the **F8H10-C10** SAM.

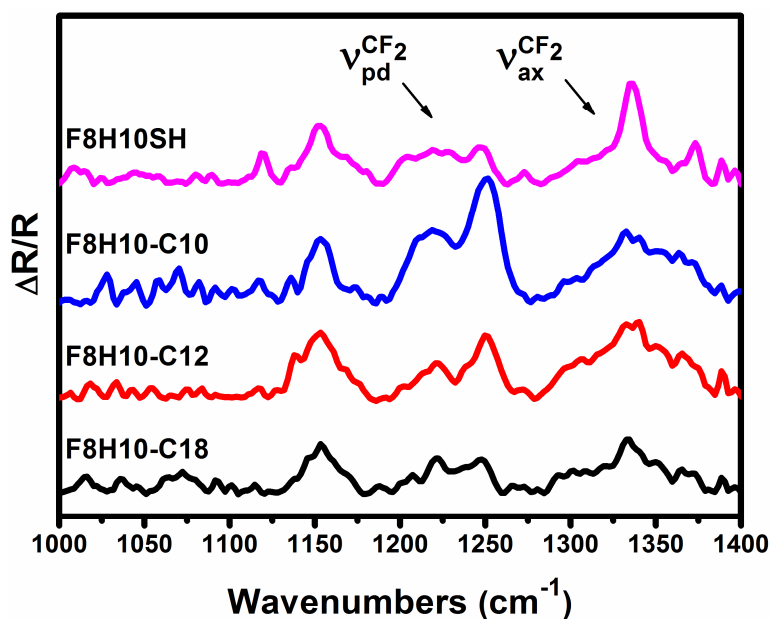


Figure 6. PM-IRRAS spectra of the C-F stretching region for SAMs generated from the **F8H10SH** and **F8H10-Cm** adsorbates used in the study.

2.4. Wettability of the Films

Contact angle measurements are convenient tools for evaluating the wetting properties of organic interfaces. In this study, we measured advancing contact angles (θ_a) for all SAMs using several probe liquids, ranging from nonpolar (hexadecane (HD, $\gamma_{LV} = 27.5$ dynes/cm) and perfluorodecalin (PFD, $\gamma_{LV} = 19.2$ dynes/cm)) [82,83], polar aprotic (*N,N*-dimethylformamide (DMF, $\gamma_{LV} = 37.1$ dynes/cm) and acetonitrile (ACN, $\gamma_{LV} = 29.3$ dynes/cm)) [82,83], to polar protic (water (H₂O, $\gamma_{LV} = 72.8$ dynes/cm)) [82,83], as shown in Figure 7 and listed in Table 4.

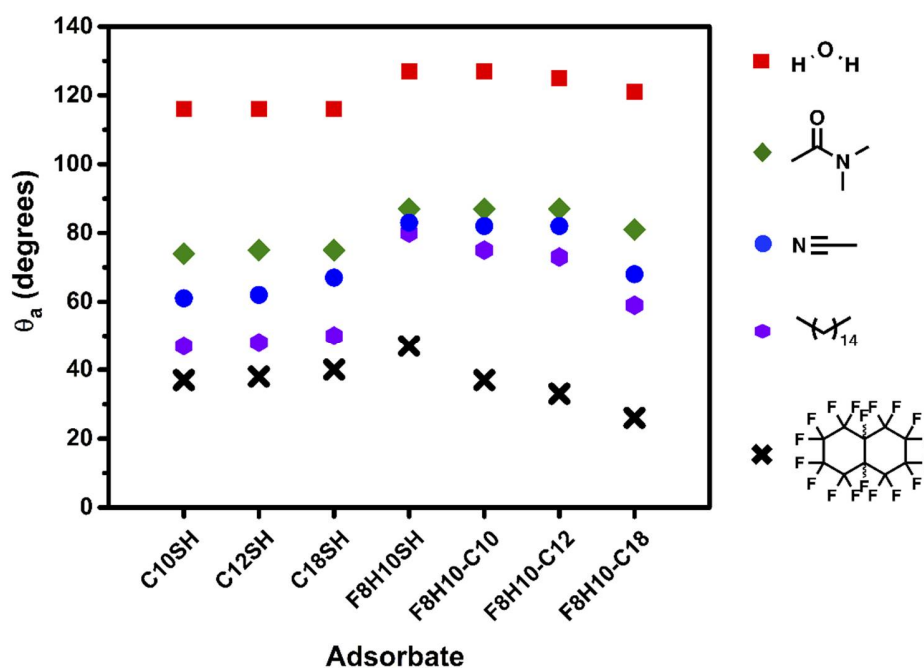


Figure 7. Advancing contact angle data obtained for water (H₂O), *N,N*-dimethylformamide (DMF), acetonitrile (ACN), hexadecane (HD), and perfluorodecalin (PFD) on SAMs derived from the monodentate thiols (C10SH, C12SH, C18SH, and F8H10SH) and the F8H10-Cm dithiols (F8H10-C10, F8H10-C12, and F8H10-C18).

The contact angle values obtained from the SAMs derived from the *n*-alkanethiols (C10SH, C12SH, and C18SH) are similar for each of the probe liquids used, although the SAMs generated from the short-chained adsorbates, C10SH and C12SH, proved to be slightly more wettable (lower θ_a) by the liquids having low surface tensions -- acetonitrile (29.3 dynes/cm), hexadecane

(27.5 dynes/cm) and perfluorodecalin (19.2 dynes/cm) [82,83] -- than the SAM generated from the long-chained adsorbate, **C18SH**. The observed differences in the wettability of the *n*-alkanethiol SAMs by the liquids having low surface tension is in accordance with the conformational order and packing of the adsorbed molecules. The interchain van der Waals forces in a monolayer increase with the addition of more methylene units. The less densely packed SAMs formed from the short-chained adsorbates, **C10SH** and **C12SH**, are more wettable than the more densely packed SAMs derived from the longer-chained adsorbate, **C18SH**. In the SAMs derived from the shorter-chained adsorbates, there is greater atomic contact (dispersive interactions) between the contacting liquid and the SAM interface of the loosely packed SAMs, which leads to a more wettable film [25]. For the SAMs derived from the **F8H10SH**, the contact angle values are higher than those obtained from the **C18SH** film, which is consistent with previously observed values on SAMs derived from partially fluorinated adsorbates with the same degree of terminal fluorination [81,84]. The low surface energy enjoyed by fluorinated interfaces compared to hydrocarbon interfaces is consistent with the higher contact angle values observed on the **F8H10SH** SAM [85-87].

Table 4. Advancing Contact Angles (θ_a , °) on the Indicated SAMs Using Various Probe Liquids with Hysteresis Values ($\Delta\theta = \theta_a - \theta_r$)^a Given in Parentheses

| | H₂O | DMF | ACN | HD | PFD |
|------------------|-----------------------|------------|------------|-----------|------------|
| C10SH | 116 (7) | 74 (9) | 61 (11) | 47 (6) | 37 (8) |
| C12SH | 116 (8) | 75 (10) | 62 (10) | 48 (7) | 38 (8) |
| C18SH | 116 (9) | 75 (9) | 67 (10) | 50 (7) | 40 (9) |
| F8H10SH | 127 (8) | 87 (8) | 83 (10) | 80 (7) | 47 (10) |
| F8H10-C10 | 127 (11) | 87 (9) | 82 (13) | 75 (7) | 37 (11) |
| F8H10-C12 | 125 (8) | 87 (8) | 82 (10) | 73 (7) | 33 (7) |
| F8H10-C18 | 121 (7) | 81 (10) | 68 (11) | 59 (7) | 26 (5) |

^a Receding Angles, θ_r .

For the **F8H10-Cm** SAMs, the contact angle values fall between those of the SAMs derived from their normal alkanethiol and partially fluorinated alkanethiol counterparts, which further suggests the interfacial composition is a mixture of the hydrocarbon and fluorocarbon species in

these SAMs. However, perfluorodecalin shows lower contact angle values for the **F8H10-C12** and **F8H10-C18** SAMs when compared to the hydrocarbon and fluorinated analogs. A preliminary analysis might propose that the lower contact angle observed for PFD on these bidentate SAMs might be due to greater attractive interactions (dispersive interactions) between the fluorinated surface and the fluorinated liquid; however, this observation does not hold true for the **F8H10SH** SAM. Thus, the enhancement in the wettability of the **F8H10-Cm** SAMs is likely due to the low surface tension of perfluorodecalin and the lower packing density of the films. The combination of both effects allows for greater dispersive interactions between the chemically similar fluorocarbon surfaces and liquid, facilitating the intercalation of the liquid molecules into the films.

Figure 7 and Table 4 show that the SAMs derived from the **F8H10-C10**, **F8H10-C12**, and **F8H10SH** adsorbates exhibit similar wettability when in contact with polar contacting liquids, although the **F8H10-C18** SAM was slightly more wettable toward these probe liquids. The lower contact angle values for the **F8H10-C18** SAM likely arise from the diminished packing density of this film, *vide supra*. The decreased packing density of the **F8H10-C18** SAM allows for greater intercalation into the film by small molecules – a trend illustrated by the contact angle values of ACN: 83°, 82°, 82°, and 68° for the series **F8H10SH**, **F8H10-C10**, **F8H10-C12**, and **F8H10-C18**, respectively. A similar but smaller trend in the wettability of H₂O and DMF on the fluorinated SAMs was also observed; however, due to the higher surface tension of the liquids, compared to ACN, a dramatic decrease in the contact angles of the **F8H10-C18** SAM with these liquids was not observed.

The wettability of nonpolar surfaces by nonpolar liquids arises from attractive dispersive interactions, which can reflect the packing density and surface morphology of the monolayers [25]. When nonpolar liquids were used (hexadecane and perfluorodecalin), the contact angles of the **F8H10-C10** and **F8H10-C12** SAMs were comparable, but lower than those obtained on the **F8H10SH** SAM, with the **F8H10-C18** SAM exhibiting the lowest values. The **F8H10-C10** and **F8H10-C12** SAMs displayed similar behavior toward the nonpolar contacting liquids, which corresponds to a predominant exposure of fluorocarbon chains at the interfaces. Nevertheless, the enhanced wettability of the **F8H10-C10** and **F8H10-C12** SAMs as compared to the **F8H10SH** SAM also suggests differences in chain density and orientation between the dithiol adsorbates and

the **F8H10SH** SAM. A more tilted fluorocarbon chain and/or chain disorder can lead to an increase in atomic contact density per unit area on the interfaces, thereby contributing to the enhanced dispersive interactions between the probe liquids and surfaces [25]. The less densely packed structure, with its greater chain tilt and/or disorder in the fluorocarbon chains, is also expected to be more wettable than a more densely packed SAM. On the other hand, the interface of the **F8H10-C18** SAM is composed of a mixture of hydrocarbon and fluorocarbon moieties. The presence of the hydrocarbon moieties at the interface of the respective SAM should plausibly lead to a greater attractive dispersive interaction between hexadecane and the surface when compared to the former two SAMs.

Another important aspect to note from the contact angle data is the contact angle hysteresis ($\Delta\theta = \theta_a - \theta_r$) shown in Table 4, which can be used to indicate the surface roughness or the heterogeneity of an interface [75]. The hysteresis values of the bidentate **F8H10-Cm** SAMs are comparable to the values obtained for the corresponding monodentate SAMs. The calculated values suggest that the **F8H10-Cm** films examined here possess similar roughness/heterogeneity as their monothiol analogues. The contact angle measurements of the **F8H10-Cm** series suggest a mixed interface composed of both phase incompatible groups, proving to be a unique new class of adsorbate in the pursuit of homogeneously mixed dual-component monolayers on metal substrates [39].

3. Materials and Methods

A detailed list of materials and chemicals used to generate the adsorbates and the SAMs on the gold substrates can be found in the Supplementary Information. Complete synthetic procedures and characterization of the adsorbates (^1H , ^{19}F , ^{13}C NMR and HR-MS) are provided in the Supplementary Information. Complete details of the experimental procedures used for the characterization of the monolayers including ellipsometry, XPS, PM-IRRAS, and contact angle goniometry are described in the Supplementary Information.

4. Conclusions

We have examined SAMs generated from a series of unsymmetrical partially fluorinated spiroalkanedithiols having tailgroups comprised of a terminally fluorinated chain and a hydrocarbon chain of varying lengths, **F8H10-Cm** where $m = 10, 12, \text{ and } 18$, and compared them

to the corresponding normal and fluorinated alkanethiols. Analysis from XPS reveal the **F8H10-Cm** adsorbates bind to the gold substrate via both sulfur headgroups. The films revealed interfacial properties corresponding to both the hydrocarbon and fluorocarbon chains incorporated into the adsorbates. The branched nature of these adsorbates was found to influence the resulting films in which moderately ordered, loosely packed SAMs were formed when compared to the single-chained analogs. When considering the influence of the hydrocarbon chain length in the double-chained structure, the impact of the addition of two methylene units appears to be negligible. In contrast, increasing the hydrocarbon chain length to be identical with the partially fluorinated alkyl chain in the **F8H10-C18** adsorbate was found to generate SAMs with a greater degree of loose packing and chain disorder, which can be attributed, at least in part, to phase-incompatible fluorocarbon-hydrocarbon interactions. Finally, the monolayers obtained from the **F8H10-Cm** adsorbates showed no large-scale roughness or heterogeneity, demonstrating the potential for the creation of homogeneously mixed dual-component SAMs from these types of adsorbates.

5. Acknowledgments

We thank the National Science Foundation (CHE-1710561), the Robert A. Welch Foundation (E-1320), and the Texas Center for Superconductivity at the University of Houston for providing generous support for this research.

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