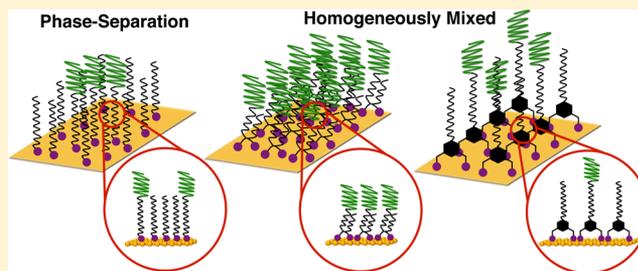


# Homogeneously Mixed Monolayers: Emergence of Compositionally Conflicted Interfaces

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**ABSTRACT:** The ability to manipulate interfaces at the nanoscale via a variety of thin-film technologies offers a plethora of avenues for advancing surface applications. These include surfaces with remarkable antibiofouling properties as well as those with tunable physical and electronic properties. Molecular self-assembly is one notably attractive method used to decorate and modify surfaces. Of particular interest to surface scientists has been the thiolate–gold system, which serves as a reliable method for generating model thin-film monolayers that transform the interfacial properties of gold surfaces. Despite widespread interest, efforts to tune the interfacial properties using mixed adsorbate systems have frequently led to phase-separated domains of molecules on the surface with random sizes and shapes depending on the structure and chemical composition of the adsorbates. This feature article highlights newly emerging methods for generating mixed thin-film interfaces, not only to enhance the aforementioned properties of organic thin films, but also to give rise to interfacial compositions never before observed in nature. An example would be the development of monolayers formed from bidentate adsorbates and other unique headgroup architectures that provide the surface bonding stability necessary to allow the assembly of interfaces that expose mixtures of chains that are fundamentally different in character (i.e., either phase-incompatible or structurally dissimilar), producing compositionally “conflicted” interfaces. By also exploring the prior efforts to produce such homogeneously blended interfaces, this feature article seeks to convey the relationships between the methods of film formation and the overall properties of the resulting interfaces.



## INTRODUCTION

Intermolecular interactions such as van der Waals and London dispersion forces govern much of the interfacial properties of materials that give rise to commonly observed behaviors such as the well-known “like dissolves like” phenomenon that we utilize on a daily basis. For chemists, such rules have enabled the development of an array of tools, specialty materials, and purification processes that provide unquestionable benefits to society. Although such intermolecular forces are generally applied to the three-dimensional world, they are also relevant to two-dimensional systems; for example, the structural quality of organic thin films of molecules assembled on solid substrates is greatly impacted by intermolecular van der Waals interactions.<sup>1</sup> More specifically, self-assembled monolayers (SAMs) composed of a blend of two chemically or structurally different adsorbates tend to undergo phase separation during film formation.<sup>2–4</sup> The resulting phase domains represent the degree of incompatibility between the different molecular components. Thus, the domain size, shape, and structural continuity reflect the relative presence of each component in the film and the interactions at their phase boundaries and with the interface.<sup>2–4</sup> Furthermore, forces exerted by these surfaces (attractive or repulsive) toward contacting matter are dictated by the relative exposure of these patches and their chemical compositions. Note that the applicability of such forces relies

on the ability to control the phase behavior of dissimilar molecular structures on the surfaces.

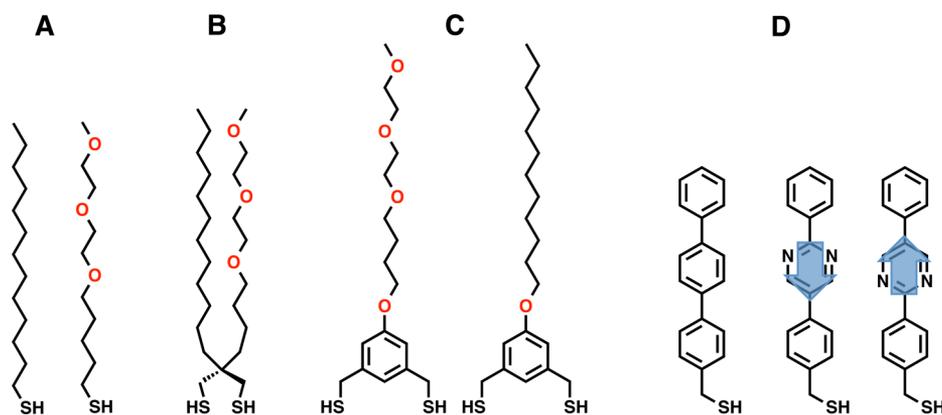
One goal of our recent research efforts in the area of mixed SAMs has been to generate and study unique nanoscale interfaces composed of phase-incompatible chemical entities or other types of dissimilar molecular architectures by means of either designing molecular adsorbates bearing bifunctional moieties or thermodynamic conditions to yield such SAMs, as illustrated in Figure 1.<sup>5,6</sup> For this particular mixed-chain system, we concluded that the intimate blending of the oligoethylene glycol-terminated (OEG-terminated) chain with a hydrocarbon-terminated chain produced films that were more resistant to protein adsorption than a thin film exposing only the hydrocarbon chains but less resistant than a film exposing only the OEG-terminated chains.<sup>5</sup>

Tailoring the SAM composition is essential to monolayer thin-film applications in areas such as protein adhesion/resistance in biological and medical applications,<sup>7–12</sup> friction reduction in microelectromechanical systems (MEMS),<sup>13,14</sup> nanoparticle coatings for colloidal stability,<sup>15,16</sup> controlled topological formation in mixed-adsorbate films,<sup>17,18</sup> and the mimicking of biochemical and biological processes.<sup>19</sup> Alka-

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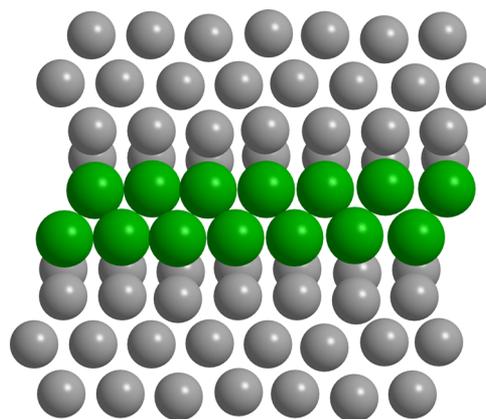


**Figure 1.** Illustration of adsorbates used for generating mixed SAMs from (A) single-tailed adsorbates, (B) a double-tailed adsorbate with a bidentate headgroup, (C) single-tailed adsorbates with bidentate headgroups, and (D) terphenyl-methanethiol molecules bearing a 2,5-pyrimidine moiety. Molecules shown in B and C represent the means for producing a surface with an intimately mixed interface of phase-incompatible chains. Adapted from refs 5, 6, and 25. Copyright 2016 American Chemical Society.

nethiols decorated with polar functional groups have been mixed with normal alkanethiols in order to dilute the presence of the active terminal group. For example, this technique has been used to improve click reactions of azido-terminated SAMs in efforts to install a maleimide group with the ultimate goals of creating a poly(L-lysine) interface,<sup>20</sup> generating a biomimetic protein surface,<sup>21</sup> incorporating ferrocene groups,<sup>22</sup> and reducing steric hindrance in the photoswitching of azobenzenes.<sup>23–25</sup> Separately, the formation of mixed monolayer films via the successive immersion of biomolecule-functionalized surfaces (e.g., DNA) in a secondary thiol solution is an effective tool for minimizing nonspecific adsorption in sensing applications.<sup>26–28</sup> Furthermore, the recently reported work on terphenyl-methanethiol-based SAMs, where the molecules bear a 2,5-pyrimidine moiety in the up and down orientation (Figure 1D), showed that the generation of mixed monolayers of these two adsorbates allows for a controlled tuning of the work function of the metal electrode while simultaneously eliminating any phase separation in the films (i.e., consistent with a homogeneous monolayer film).<sup>25</sup>

Additionally, incorporating the chemical functionalities of two separate adsorbates into one molecular structure influences the interfacial properties of the generated monolayer thin films. For example, our group reported on the ability of a double-chained monothiol linactant—a line-active adsorbate having an unsubstituted hydrocarbon chain and a terminally perfluorinated chain segment—to influence domain formation in binary SAMs.<sup>29</sup> By controlling the ratios of the adsorbates present in the deposition solution, a mixed SAM can be prepared from a combination of the double-tailed linactant and an *n*-alkanethiol, where the mixture forms single-dimensional patterns of the fluorinated chains embedded in the hydrocarbon matrix, as shown in Figure 2.

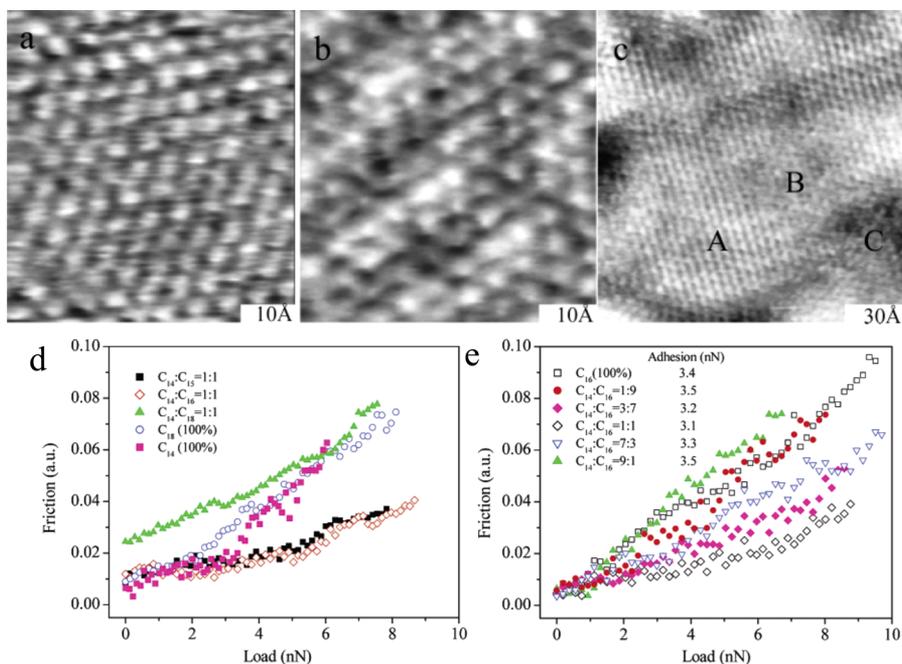
This feature article seeks to highlight methods used to produce compositionally mixed interfaces derived from thiol-based adsorbates. In addition, we discuss both the structural and systematic designs used to overcome incompatibility challenges encountered in nanoscale mixing. We hope that these efforts will inspire others to consider this new and exciting approach to the study and development of compositionally conflicted interfaces.



**Figure 2.** Illustration of a mixed SAM as viewed from above showing how adsorbates with two dissimilar chains avoid the formation of large domains. (Terminally fluorinated chains are represented by filled green circles.) Reproduced with permission from ref 29. Copyright 2012 American Chemical Society.

## ■ PURSUIT OF UNIQUELY BLENDED INTERFACES

**Background.** Prior reports describing the intimate blending of phase incompatible or structurally dissimilar motifs generally involved combining separate adsorbates for each of the surface chains, which led to a loss of homogeneity in the resulting film.<sup>3,4,30,31</sup> Efforts to resolve such problems in our laboratories have primarily involved the design and synthesis of multi-tentate adsorbates bearing a mixture of interfacial chains, an approach to adsorbate design that enhances the stability and homogeneity of the resulting monolayer films. For monolayer films that have produced an interface of phase-incompatible chains, the chains in conflict with each other generally have involved a combination of hydrocarbon chains versus fluorocarbon chains or chains terminated with polar groups such as oligoethylene glycol moieties (OEG).<sup>3,32–35</sup> However, other forms of dissimilarities have also been investigated, with the goal of achieving control of the interfacial characteristics for the resulting films.<sup>36–38</sup> This new emphasis on mixed-component thin-film design builds on more than two decades of fundamental research, which has revealed the challenges encountered in attempting to blend two dissimilar components in a single heterogeneous thin-film assembly.

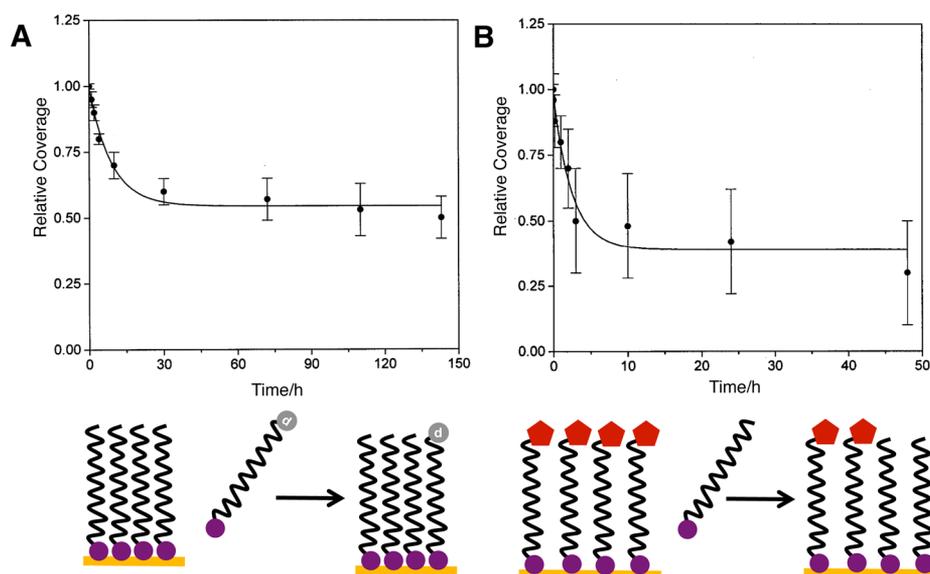


**Figure 3.** STM images of mixed SAMs formed from (a)  $\text{CH}_3(\text{CH}_2)_5\text{SH}$  (C6), (b) a mixture of  $\text{CH}_3(\text{CH}_2)_5\text{SH}$  (C6) and  $\text{CH}_3(\text{CH}_2)_7\text{SH}$  (C8), and (c) a mixture of  $\text{CH}_3(\text{CH}_2)_5\text{SH}$  (C6) and  $\text{CH}_3(\text{CH}_2)_9\text{SH}$  (C10) with A, B, and C indicating the presence of C10, a mixture C6 and C10, and C6, respectively. Friction versus load curves are shown for (d) equimolar mixtures of C14 with C15, C16, and C18 and (e) C14 mixed with C16 at various concentrations. Reproduced with permission from ref 49. Copyright American Chemical Society 2005.

**Hydrocarbon Chains.** Many of the initial systematic studies of self-assembled monolayers involved the use of a homologous series of normal alkanethiols; this history arose largely from the commercial or synthetic accessibility of *n*-alkanethiols and their ability to generate well-ordered films. Therefore, initial attempts at creating and investigating homogeneously mixed SAMs have pursued a number of routes toward film formation, starting with normal alkanethiol chains mixed with either methyl or polar termini; some examples include (1) the coadsorption of different alkanethiols in a single solution,<sup>39–43</sup> (2) the immersion of an alkanethiolate film into the solution of a second alkanethiol in either an exchange or a backfilling process,<sup>33,44,45</sup> and (3) the adsorption of unsymmetrical disulfides.<sup>46,47</sup> With the preparation of binary SAMs from a mixed-thiol solution, several authors have noted that the composition of the adsorbate within the fully formed film departs from those in solution for a number of factors, including ongoing exchange processes with the solution phase, surface migration of the adsorbates (and the associated domain formation, which typically favors the adsorption of one adsorbate over another), and differences in adsorbate solubility. Bain et al. noted that for mixed adsorbate SAMs formed from *n*-alkanethiols of different chain lengths,  $\text{CH}_3(\text{CH}_2)_n\text{SH}$  ( $n = 11, 15,$  and  $21$ ) and  $\text{HO}(\text{CH}_2)_m\text{SH}$  ( $m = 11$  and  $19$ ), the longer chains preferentially adsorb over the shorter chains.<sup>41</sup> Furthermore, nanoscale phase separation can occur between molecules of the same chain length bearing different chemical functionalities at their termini (i.e., different tailgroups).<sup>2,4,30,31,36</sup> Mixed SAMs derived from methyl- and methyl ester-terminated thiols having the same alkyl chain length,  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  and  $\text{CH}_3\text{O}_2\text{C}(\text{CH}_2)_{15}\text{SH}$ , for example, experience similar intermolecular interactions between the alkyl chains, yet still phase separate into two-dimensional assemblies to form separate domains.<sup>30</sup>

Several studies have investigated the factors that control the formation of domains in these types of mixed films. For example, Tamada et al. demonstrated that the deposition conditions can be controlled to form mixed films from *n*-alkanethiols having significantly different chain lengths (a 4 and 18 carbon difference) so that the adsorbates separate into nanometer-scale domains ranging in size from 10 to 20 nm.<sup>31</sup> In a separate study by Chen et al. involving mixed *n*-alkanethiols with similar chain dynamics (a 4 to 10 carbon difference), the authors concluded that phase separation and preferential adsorption (where one adsorbate is preferred over the other) can also be attributed to defects in the gold substrate or to defects that occur as a consequence of the deposition temperature.<sup>48</sup> The authors also suggested that deposition at higher temperatures (e.g., 50 °C or higher) follows a kinetically controlled process, whereas at lower temperatures (e.g., room temperature or lower), it follows a thermodynamically controlled process. In the latter (occurring at low temperatures), the rapid formation of the SAM can lead to either an incomplete film or a film with defects caused by the underlying gold surface. Therefore, adsorbates having shorter chain lengths in such a SAM are readily exchanged by longer chain adsorbates in solution. In contrast, the kinetically controlled process (occurring at high temperatures) leads to a SAM with few defects (i.e., a compact monolayer) unable to undergo exchange with thiols in solution.

In a frictional-force microscopy study of mixed *n*-alkanethiol monolayers that was accompanied by STM imaging, Zuo et al. were able to correlate gauche defects in the film and lubricity.<sup>49</sup> They concluded that there is an enhancement in lubricity when the two *n*-alkanethiol chains have only small differences in chain length (i.e., two methylenes) and fail to phase separate into islands larger than a few molecules, rather than an anticipated increase in friction (Figure 3). The friction versus load graphs in Figure 3d depict this trend on mixed SAMs



**Figure 4.** Relative coverage of (A)  $\text{CH}_3(\text{CH}_2)_{19}\text{SH}$  in a SAM dipped in a  $\text{CD}_3(\text{CH}_2)_{19}\text{SH}$  solution and (B) ferrocene-terminated thiols in a SAM dipped in  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$  solution over time. Adapted with permission from ref 57. Copyright Elsevier 1999.

formed from an equimolar solution of C14 with C15, C16, or C18. Mixed monolayers formed from adsorbates with small differences in chain length (e.g., C14 and C15) showed a reduction in the friction as the load was increased when compared to SAMs derived from only C14. In contrast, when the difference in chain length was large (e.g., C14 with C18), an increase in friction was observed. In addition, their observations led them to conclude that there is a competition between entropy (random ordering) and energy (van der Waals attractions) in which binary mixtures of adsorbate chain lengths with a two methylene chain difference favor homogeneous mixing, whereas the thiolate mixtures with a larger difference in chain length (four methylenes) are inclined to phase segregate, a result that is visible in the STM images in Figure 3. With the increase in domain size, the frictional properties of the resulting mixed film seemed to align with that of a single-component film. The effect of the surface composition of a mixed SAM on the frictional properties is also evident in Figure 3e, where a large difference in the solution concentration of adsorbates, for example, 9:1 and 1:9 C14/C16, gave rise to SAMs predominantly composed of a single type of adsorbate, with frictional properties similar to those of a single-component SAM. In contrast, mixed solution compositions of 3:7, 7:3, or equimolar C14/C16 led to the formation of monolayers with lower frictional responses than that of a single-component SAM. These results were interpreted to indicate that, in addition to the often-encountered phase separation in mixed monolayers formed from the solution-based coadsorption of thiols, the surface composition of adsorbates in the generated mixed SAMs also differed from the ratio of adsorbate molecules in solution.<sup>40,50–55</sup> Thus, homogeneously mixed binary SAMs of monothiols are difficult to obtain from a simple solution-phase codeposition process.

An alternative procedure for forming mixed SAMs takes advantage of exchange processes between surface-bound thiols and those dissolved in solution. In this approach, a preformed monolayer is dipped into a solution containing a different thiol to replace some of the adsorbates in the original monolayer and generate a new mixed-adsorbate film. The rate at which a thiol-

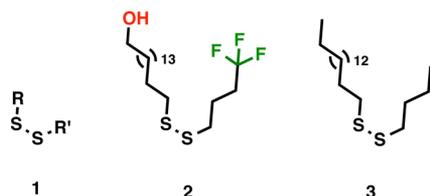
based adsorbate on gold is replaced depends on the quality/packing of the initial SAM.<sup>3,56,57</sup> Chidsey et al. found that the replacement of bound thiols occurs rapidly at defect sites, concluding that the exchange (replacement) rate depends on the packing characteristics of the molecules on the surface, as determined using electrochemical techniques.<sup>56</sup> Separately, Chung et al. quantified the replacement of compact and noncompact monolayers using Fourier transform infrared (FTIR) spectroscopy.<sup>57</sup> In the case of a compact monolayer,  $\text{CH}_3(\text{CH}_2)_{19}\text{SH}$ , being replaced by its deuterated analog,  $\text{CD}_3(\text{CH}_2)_{19}\text{SH}$ , a fast replacement of  $\sim 25\%$  of the monolayer was observed within a 15-min window (Figure 4A). On the other hand, when a noncompact monolayer derived from ferrocene-terminated alkanethiols was replaced with an alkanethiol of the same hydrocarbon chain length,  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$ , a rapid exchange occurred in which  $\sim 55\%$  of the monolayer was replaced within 15 min (Figure 4B).

Intermolecular forces have also been known to exert an effect on the rate of replacement in SAMs. For example, the replacement of *n*-alkanethiolates by carboxy-terminated alkanethiols (i.e., two adsorbates with phase-incompatible termini:  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  and  $\text{HO}_2\text{C}(\text{CH}_2)_{11}\text{SH}$ ) has been described as having first-order kinetics and occurring domainwise rather than randomly.<sup>3</sup> In this type of system, the solubility of the carboxylic acid-terminated adsorbates within the ordered alkanethiolate matrix is low. When the opposite process was tested—a SAM formed from carboxy-terminated adsorbates dipped in a normal alkanethiol solution—the authors found that the adsorbate exchange was much slower. The authors attributed this result to intermolecular H-bonding between the carboxylic acid termini in the existing monolayer. Additional studies using this technique have revealed that exchange processes occur mainly at domain boundaries and gold-defect sites, which limits the effectiveness of this procedure for generating homogeneously blended binary SAMs.<sup>37,38,58</sup>

Another means of generating mixed films is the backfilling method. Spencer and co-workers demonstrated this procedure, which involves the insertion of a gold-coated slide into an initial deposition solution containing one thiol, followed by a slow withdrawal of the slide from the solution.<sup>33</sup> This process

produces a thin monolayer film that is sparsely populated with adsorbates at the end of the slide that was first withdrawn but densely populated at the end that is last to leave the solution. A rapid withdrawal and rinsing procedure can produce an initial array of adsorbates that are evenly distributed across the substrate. Subsequent immersion of the gold substrate into a second thiol solution allows the second thiol to backfill the unoccupied area on the substrate. It is important to note that the backfilling process can also give rise to exchange processes, which might produce inhomogeneity in the resulting mixed films.

In the 1990s, SAMs formed from linear disulfides (i.e., having no cyclic moiety such as structure 1 in Figure 5) were



**Figure 5.** Structures of disulfide adsorbates used for fundamental studies to generate monolayer films.<sup>61,62</sup>

extensively studied and compared to films derived from *n*-alkanethiols. In principle, unsymmetrical disulfides should form homogeneously mixed binary SAMs upon adsorbing to the surface of gold. Investigations by Bain et al. found that films developed from disulfides expose the same chemical termini (functional group) at their interface as SAMs formed from comparable alkanethiols.<sup>46</sup> This particular report also noted a greater presence of disorder in the hydrocarbon segment of disulfide films as compared to films derived from thiols, as concluded from measurements of the contact angles of hexadecane. Additionally, the authors described the adsorption of alkanethiols as being faster than that of disulfides, likely because of the steric hindrance of the disulfide headgroup upon approaching the surface of gold as well as the greater bulk of the disulfide structure in general. This assessment was further confirmed in a separate account by the same authors through wettability comparisons.<sup>59</sup> The latter study revealed that films formed from disulfides are more wettable than those formed from thiols, indicating a slightly disordered film of the former adsorbates due to a less-efficient film-formation process. Chen et al. compared films formed from unsymmetrical and symmetrical disulfides, along with the corresponding thiols, and found that homogeneously mixed films formed from the disulfides with low surface coverage (as expected for disulfides), whereas phase-separated structures were present in the SAMs formed from mixed alkanethiols, although with high surface coverage (as expected for alkanethiols).<sup>60</sup>

Biebuyck et al. examined the adsorption of disulfides, where the length of the two terminally substituted alkyl chains (R and R') was different (i.e., structure 2 in Figure 5).<sup>44</sup> Although XPS results initially revealed approximately equal proportions of the two components on the surface, the authors noted that exposure to an ethanolic solution containing HS(CH<sub>2</sub>)<sub>16</sub>CN led to the preferential displacement of the shorter perfluoromethyl-terminated alkyl chain. Beulen prepared systems involving the adsorption of dialkyl disulfides of different chain lengths (i.e., structure 3 in Figure 5), which revealed a preferential adsorption for the longer chain over the shorter chain over time, a phenomena observed in SAMs formed from

the adsorption of a mixture of alkanethiols.<sup>47</sup> Considering that each of the disulfides noted above produced mixed SAMs composed of stable adsorbates that are subject to exchange processes with adsorbates in solution, the resulting SAMs were also subject to a loss of homogeneity during monolayer development.

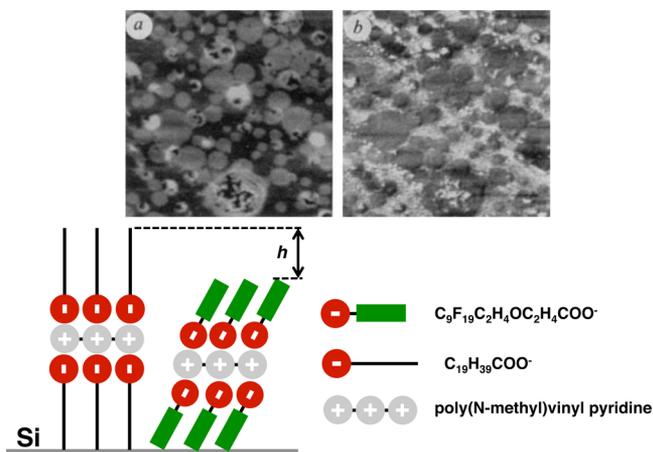
A more precise exchange method that has been investigated in an effort to produce binary mixed interfaces without domain formation starts with single-component SAMs formed from alkanethiolate adsorbates, which are then irradiated with light. This approach, known as the irradiation-promoted exchange reaction (IPER), operates on the basis of removing adsorbates from the surface using irradiation to degrade some of the chains and promote exchange processes that lead to the insertion of a dissimilar adsorbate into the existing SAM.<sup>63,64</sup> Using this method, mixed films have been successfully produced in which the content of the second adsorbate is controlled by the irradiation dose.<sup>64–66</sup> This process appears to produce surfaces having conflicted character, but the resulting thiolate films are assembled with the premise that all of the degraded adsorbates will desorb and be replaced, and that after exchange, only pristine adsorbates will remain in the film.

For the systems reviewed in this section, the structural differences between the chains that produced the mixed films are minor, and van der Waals attractions between alkyl chains play a large role in both stabilizing the assembly and limiting the influence of any structural differences upon domain formation; however, it is apparent that binary thiolate SAMs favor the development of domains.<sup>2–4,29–31,34,36,58,60,67</sup> As detailed in the following sections, increasing the contact area for phase-incompatible moieties within mixed-chain assemblies significantly increases the challenges for producing binary SAMs in which the chains are homogeneously intermixed.

**Fluorocarbon Chains.** The use of fluorinated adsorbates in thin-film technology has enjoyed widespread use in advanced applications because of their (1) hydrophobicity and non-adhesiveness, (2) chemical and biological inertness, (3) thermal and nanomechanical stability, (4) resistance to oxidation and corrosion, and (5) ease of ability to manipulate the structure of the adsorbate synthetically.<sup>68–70</sup> Furthermore, the ability of fluorinated chain segments to beget structural ordering within mixed films that reflects their phase incompatibility with other organic moieties reveals the rigidity and stability that such a segment imparts to the film.<sup>29,71</sup>

Some of the first studies of mixed fluorocarbon–hydrocarbon monolayers arose from research on Langmuir–Blodgett (LB) films of partially fluorinated or perfluorinated carboxylic acids and phosphonic acids mixed with their hydrocarbon counterparts.<sup>71–73</sup> Studies performed with fatty acids having extended hydrocarbon chains mixed with partially fluorinated carboxylic acids, CF<sub>3</sub>(CF<sub>2</sub>)<sub>8</sub>(CH<sub>2</sub>)<sub>2</sub>–O–(CH<sub>2</sub>)<sub>2</sub>COOH, that incorporated either an ether linkage or an ester group produced domains or “islands” within a continuous phase that could be differentiated by their interfacial frictional properties via atomic force microscopy (AFM) (Figure 6).<sup>71,72</sup>

When the two acids were the same length, phase separation was observed in which the alkylated acid formed circular domains within a sea of the partially fluorinated molecules. As the length of the alkylated acid was decreased, the shape of the circular domains became disordered. The authors explained the phase structures observed in these early studies of mixed alkyl/fluoroalkyl films through the influence of attractive dispersive interactions and entropic effects. With the longer chains, the



**Figure 6.** AFM images and a schematic of a bilayer surface generated from an equimolar mixture of fluorocarbon and hydrocarbon carboxylates; the difference in height between the two systems is denoted by  $h$ . (a) Topographical image where the fluorocarbons are the flat portion and the hydrocarbons are the circular structures and (b) the lateral force image of the same area. The bright areas on the image denote areas of higher friction. Adapted with permission from ref 71. Copyright 1992 Nature Publishing Group.

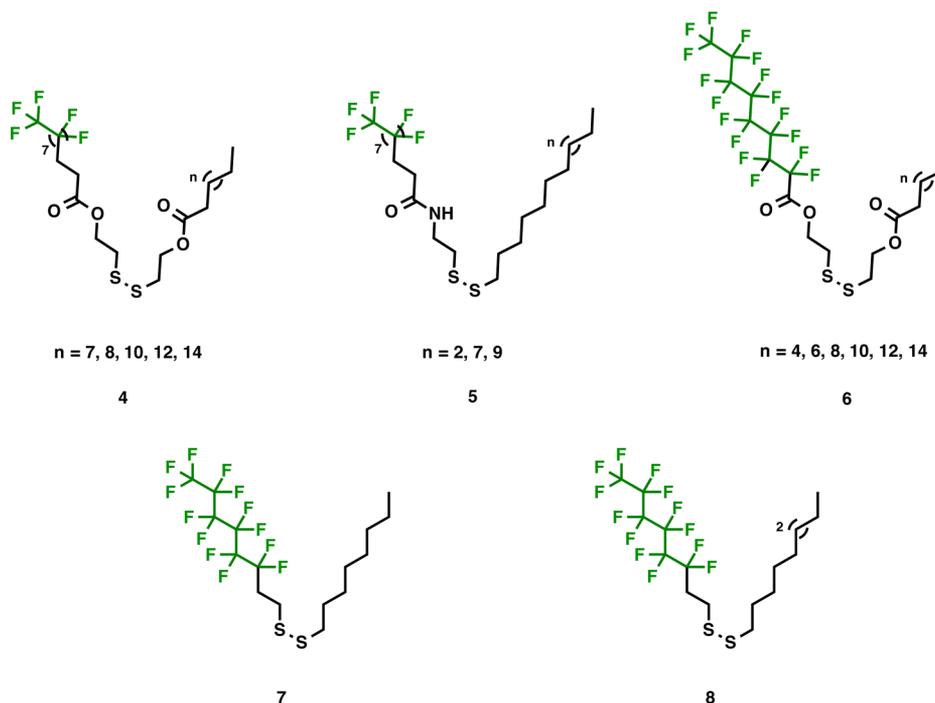
attractive forces between the chains minimized their surface energy, giving rise to circular islands, whereas with the shorter chains, entropy began to favor disordered structures.<sup>71,72</sup> In addition, the perfluorinated structures in these types of films appeared to be less ordered than their longer hydrocarbon counterparts.<sup>73</sup>

A separate study involving mixtures of nonfluorinated  $\text{CH}_3(\text{CH}_2)_{n-2}\text{COOH}$ , where  $n = 18, 20, 22, 24$ , and perfluoropolyether (PFPE) points to phase separation also being dependent upon the chain length of the carboxylic acid along with the surface pressure.<sup>74</sup> Additionally, the size of the

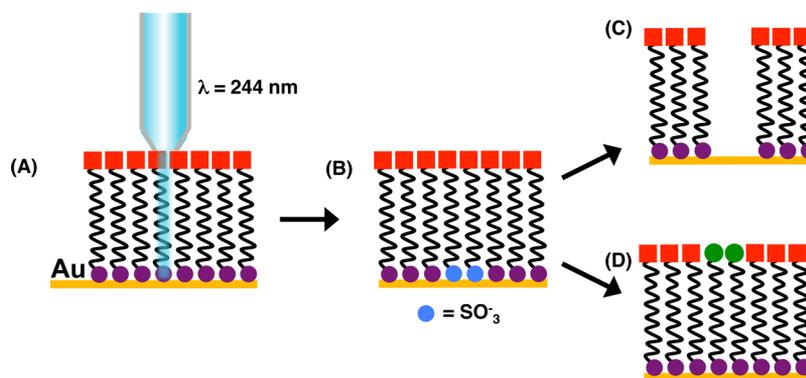
domains that can form in LB monolayers from partially fluorinated phosphonic acid adsorbates [ $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{11}\text{PO}_3\text{H}_2$ ,  $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_6\text{PO}_3\text{H}_2$ ,  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_8\text{PO}_3\text{H}_2$ , and  $\text{CF}_3(\text{CF}_2)_5(\text{CH}_2)_{10}\text{PO}_3\text{H}_2$ ] has been shown to depend on the relative length of the fluorocarbon and hydrocarbon chain segments within the molecular structure, and these adsorbates can form equilibrium-phase structures that persist even in the presence of an excess of a nonfluorinated phase.<sup>75</sup> The authors, Trabelsi et al., concluded in a second study that the larger diameter of the overlying perfluorinated chain segments, as compared to that of the hydrocarbon chain segments (i.e., the alkyl spacers), led to packing arrangements in which the adsorbates splayed to form domain structures with characteristic sizes and dimensions.<sup>18</sup> For all of these partially fluorinated LB films, the perfluorinated chain segments played an important role in the organization of the resulting monolayer film, including the formation of persistent phase structures.

Schönherr et al. studied the adsorption of unsymmetrical disulfides containing terminal alkyl and fluorinated alkane chains and compared the resulting SAMs to monolayers produced from analogous thiols (i.e., structures 4–6 in Figure 7).<sup>76</sup> The authors concluded from contact angle studies that the monolayers derived from the mixed-chain disulfides were well packed and displayed wetting properties that were intermediate to those of single-component SAMs formed from the corresponding  $n$ -alkanethiols.

Ishida et al. explored the films formed from a series of unsymmetrical disulfides having alkane and fluoroalkane chains (i.e., structure 7 in Figure 7).<sup>67</sup> Their study revealed that the cleavage of the S–S bond occurs on the surface of the gold and that the films exhibit phase separation upon annealing for 8 h at 100 °C. Separately, Fujihira and co-workers examined the reductive desorption of mixed-chain disulfides (i.e., structure 8 in Figure 7) on Au(111) electrodes using cyclic voltammetry (CV).<sup>62</sup> These authors found that a high concentration (i.e.,



**Figure 7.** Structures of fluorinated disulfide adsorbates used for fundamental studies in the generation of mixed monolayer films.<sup>32,76</sup>



**Figure 8.** Patterning SAMs on gold surfaces using scanning near-field photolithography. This process includes (A) scanning the SAM using UV light, (B) photochemical oxidation of exposed thiolates to sulfonates, (C) selective etching of gold surfaces, and (D) displacement of the oxidized adsorbate molecule. Reproduced with permission from ref 82. Copyright American Chemical Society 2002.

ranging from 10 to 100  $\mu\text{M}$ ) of the disulfide in solution produced a relatively homogeneous film, but if the adsorption temperature was too high (i.e., 60  $^{\circ}\text{C}$  maximum) or was elevated for too long, phase separation occurred (i.e., separation was visible at 1, 10, and 22 h). Thus, both of these studies are consistent with a model of film development that involves an initial homogeneous distribution of chemical heterogeneity on the surface, followed by temperature-induced surface rearrangement of the adsorbates, leading to phase separation.

As with mixed SAMs of alkanethiols having different chain lengths, mixtures of fluoroalkane and normal alkanethiols [ $\text{CF}_3(\text{CF}_2)_7\text{CONH}(\text{CH}_2)_2\text{SH}$  with  $\text{C}_n\text{H}_{(2n+1)}\text{SH}$  where  $n = 12, 16, 18$ ] produced phase-separated structures, even when developed in solutions with equimolar concentrations.<sup>32</sup> The contributing factors for the resulting film compositions for these mixed-thiolate SAMs are the same as those for mixtures of alkanethiols with different chain lengths (vide supra). Furthermore, such a competitive adsorption phenomenon was also observed in mixed films where both components were terminated with fluorinated alkane chains in which the longer chain was preferentially adsorbed over the shorter chain,  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_{11}\text{SH}$  and  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$ .<sup>77</sup> Similarities between mixed-adsorbate films incorporating only nonfluorinated thiolates versus those including chains with extended fluorinated segments also include the ability to produce homogeneously blended binary SAMs from disulfides, as described in a report by Tsao et al.<sup>32</sup> However, such films are subject to the same exchange/adsorbate migration processes that were noted above. An investigation of the exchange reactions of an alkanethiol SAM,  $\text{CH}_3(\text{CH}_2)_7\text{SH}$ , by a partially fluorinated thiol,  $\text{CF}_3(\text{CF}_2)_6(\text{CH}_2)_2\text{SH}$ , and vice versa gives insight into island formation for each process. First, the replacement of a fluorinated thiolate in a single-component SAM by a normal alkanethiol is a slow process and occurs via the formation of an ordered array, which is likely due to the lack of domain boundaries in such SAMs. Second, the opposite dynamic, which is the replacement of an alkanethiolate in a single-component SAM by a fluorinated thiol, is a much faster process that occurs mainly at domain boundaries. Third, because of the larger size of the fluorinated molecule, fluorinated domains were not observed to be embedded in the hydrocarbon matrix, and a more homogeneous distribution of the embedded adsorbate was observed.<sup>34</sup>

**OEG-Terminated Chains.** Mixed films that incorporate the OEG moiety into the chain terminus with other organic molecules have been shown to have antiadhesive character

toward biomolecules or can be tailored to the specific adsorption of certain proteins for use as biosensors, with promising applications in biomedical research.<sup>7,8,12,35,78–80</sup> The amount of OEG present on the surface plays an important role in the antiadhesive character of these types of films. In a specific example, Prime and co-workers examined the adsorption of several proteins on mixed SAMs composed of an OEG-terminated alkanethiol and a hydroxyl-terminated alkanethiol.<sup>78</sup> The films with a higher concentration of OEG-terminated alkanethiols demonstrated higher resistance to kinetically irreversible, nonspecific protein adsorption. For the films possessing longer OEG moieties, resistance to protein adsorption was achieved even at lower concentration in the films.

The previously described techniques (coadsorption, back-filling, and photolithography) have been used to produce mixed films containing the OEG moiety. Montague et al. used scanning near-field photolithography to pattern a surface and then covalently attach proteins to it.<sup>81</sup> The technique works by generating sulfonates that are formed rapidly, followed by immersion in the second component, but the degradation of the OEG chains, a slower but present reaction, can be problematic. A description of the scanning near-field photolithography process can be found in the literature and is illustrated in Figure 8.<sup>82</sup> Additionally, Zharnikov and co-workers have used IPER to generate mixed SAMs designed for the specific adsorption of avidin in which the composition of the OEG-terminated alkanethiol and biotin-terminated alkanethiol can be controlled by the irradiation dose.<sup>80</sup> The IPER technique has also been applied to pattern films using disulfides terminated with an atom-transfer radical polymerization (ATRP) initiator in efforts to grow complex polymers on the surface, such as poly(ethylene glycol dimethacrylate), a polymer relevant for use in biomedical devices.<sup>83</sup>

It is the combination of antiadhesiveness and hydrophilicity that makes the incorporation of terminal OEG moieties within an adsorbate structure promising for a variety of applications. A recent example where such characteristics have been applied can be found in a recent article by our group, where placing an OEG component between the alkyl spacer of an adsorbate and a terminal maleimide moiety improved the aqueous stability for gold nanoparticles decorated with maleimide-terminated SAMs.<sup>84</sup> This enhanced resistance to aggregation provides added flexibility in handling such nanoparticles when conjugating thiol-terminated biomolecules or other bulky molecules to these particles.

Research efforts with mixed OEG films have sought to create surfaces that have the potential to serve as biosensors.<sup>35,79,85</sup> For example, Jeong and co-workers grafted poly(ethylene glycol methacrylate) brushes from the surface of a mixed SAM and determined that the concentration of the initiator molecule in the SAM dictated the lateral packing density and the overall amount of bound streptavidin.<sup>35</sup> Additionally, Clare and co-workers expanded research on OEG-terminated films by covalently attaching OEG monolayers to silicon and diamond surfaces as a potential electronic biosensor.<sup>79</sup> The technique generated high-quality monolayers on the surfaces and displayed protein resistance similar to that of OEG-terminated surfaces on gold. In addition to successfully generating the monolayers, the authors were able to demonstrate the specific adsorption of avidin to surface-immobilized biotin in the presence of a complex mixture of several proteins.

**Techniques Used to Characterize Mixed SAMs.** Spectroscopy techniques commonly used to characterize mixed SAMs (particularly those outlined in this report) include infrared spectroscopy, UV–vis spectroscopy, and X-ray photoelectron spectroscopy (XPS).<sup>44,46,57,86</sup> Microscopy techniques such as atomic force microscopy (AFM) and scanning tunneling microscopy (STM) are also widely used to characterize mixed-monolayer films.<sup>49,71,72</sup> For example, Pallavicini et al. employed UV–vis spectroscopy to determine the fraction of an absorbing 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene (BODIPY)-functionalized alkanethiol mixed with a normal alkanethiol or a PEGylated alkanethiol, both of which are colorless.<sup>86</sup> Using UV–vis analysis, the authors extracted the exchange constant for the BODIPY alkanethiol and then the constants for the colorless alkanethiols. These constants were then used to calculate the amount of the colorless thiol present on the surface. Separately, Campbell et al. relied on the presence of a fluorescent probe in a binary SAM to gain insight into the surface composition.<sup>87</sup> The approach used by the authors utilized a wet stamping technique to generate a binary SAM from a mixture of a disulfide functionalized with the fluorescent probe and an alkanethiol bearing a hydroxyl or carboxyl group terminus; these groups have the ability to participate in hydrogen bonding. The authors concluded from their studies that the lateral interactions (i.e., hydrogen bonding) have an effect on the composition of the resulting films. In monolayers containing the fluorescent disulfide mixed with the normal alkanethiol, fluorescence was observed in all mixtures containing the disulfide. In contrast, in monolayers containing either the hydroxyl-terminated or carboxyl-terminated adsorbates as part of the mixture, fluorescence was observed only at a certain concentration of disulfide, thus indicating that the ratio of adsorbates on the surface differed from the solution concentration.

An analysis of surface composition has also been studied using electrochemical techniques. The catalytic activity of (2,2,6,6-tetramethylpiperidin-1-yl)oxyl (TEMPO)-terminated mixed SAMs with an alkanethiol has been used to determine the distribution and efficiency of the active moiety.<sup>88,89</sup> The authors used the full width at half-maximum (fwhm) and the peak potential from cyclic voltammetry (CV) to determine the distribution of the active centers. A linear dependency of the fwhm and potential revealed a surface that was homogeneously mixed. On the other hand, a nonlinear dependency pointed to a phase-separated surface. In the case of the mixed TEMPO-based SAMs, a nonlinear relationship was observed. Forster also used CV to monitor the absorption of redox-functionalized

pyridine derivatives on platinum wires; this approach allows for the measurement of the adsorbate ratio.<sup>90</sup> Recently, Capitao et al. were able to achieve a linear dependence between the ratio of adsorbates on the surface and in the solution using the electroassisted deposition method detailed by Sahli et al.<sup>91,92</sup> In addition to creating a surface where the adsorbate ratio is the same as that in solution, one might simultaneously monitor the concentration of the adsorbates on the surface.

**Consequences of Adsorbate Mixing.** Apparent in the details outlined above is that any adsorbate system that produces a mixed-chain monolayer film where the component chains are subject to exchange processes or are able to migrate within the monolayer is subject to domain formation, even if initially deposited from an unsymmetrical linear disulfide as a perfectly homogeneous SAM. This situation is exacerbated when the component parts of the mixed-adsorbate film are significantly different and, like oil and water, naturally phase separate. Therefore, alternative approaches to generating films with such compatibility conflicts have been pursued.

## ■ MULTIDENTATE ADSORBATES AND INTERFACIAL HOMOGENEITY

The stability of ligand–metal complexes can be enhanced through an entropy-driven process known as the chelate effect.<sup>93</sup> For example, previous studies point to the entropy change achieved upon substituting two monodentate ligands with an analogous bis-chelating ligand as the primary driving force for such an exchange.<sup>94</sup> Consequently, if the same technique is applied to chelating thiols on gold, then a greater stability is achieved as compared to having two individual sulfur–gold bond enthalpies and the concomitant interchain van der Waals stabilization.<sup>16,95</sup> Figure 9 provides an overview of the different types of multidentate adsorbates/headgroups that have been used to form stable monolayers on gold with the potential to generate homogeneously mixed conflicted interfaces.

**Cyclic Disulfide Headgroups.** Current research involving SAMs on gold was sparked by the work of Nuzzo and Allara over 30 years ago with the adsorption of a series of symmetrical, cyclic disulfides having the framework of molecule 9 in Figure 9.<sup>96</sup> Monolayer films derived from these adsorbates led to stable, well-packed films,<sup>97</sup> but in these initial studies, the extra stability gained from the chelating character was not considered. In a separate study conducted by Bruening and co-workers, the same dithiane framework was used to create multifunctional films.<sup>98</sup> The authors custom tailored the dithiane base to incorporate two different functional groups to create surfaces having two different interfacial functionalities within the same molecular assembly.

Other commonly used cyclic disulfide anchoring headgroups are those based on thioctic acid (framework 10 in Figure 9). These types of adsorbates have been used as the adhesion layer in bio- or immunosensors,<sup>99–105</sup> molecular electronic applications,<sup>106</sup> and anchors for attaching catenanes to surfaces.<sup>107</sup> A thorough review of the use of thioctic acid and its derivatives to create SAMs as an immobilization platform of biomolecules can be found in the literature.<sup>108</sup> Moreover, researchers have used functionalized thioctic acid derivatives mixed with a diluent alkanethiol to carry out surface reactions, including olefin cross metathesis<sup>109</sup> and glycosylation.<sup>110,111</sup> In these latter reactions, the use of a mixed monolayer improved the overall efficiency of the reaction by reducing the steric interactions around the active site.

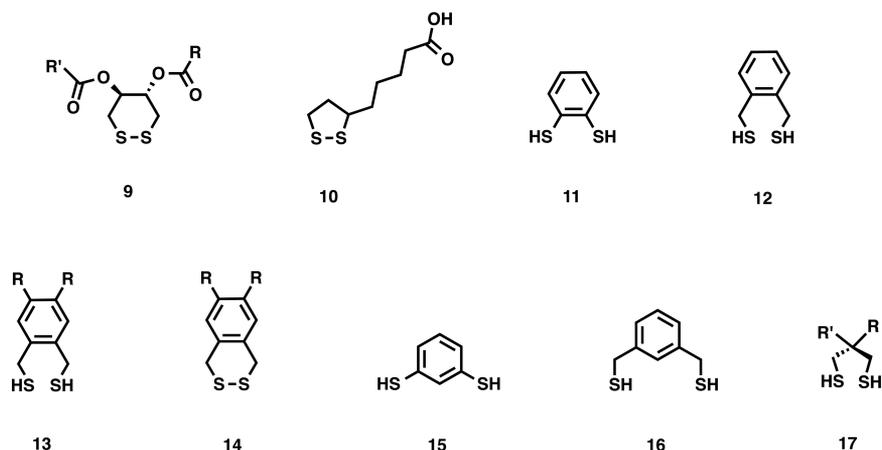


Figure 9. Structures of multidentate adsorbates/headgroups used in efforts to generate stable monolayer films on gold.<sup>6,96,112–118</sup>

### Aromatic Dithiol Headgroups: First Generation.

Researchers sought an alternative approach toward the development of multidentate thiol-based adsorbates through the exploration of molecules having aromatic-based headgroups (i.e., frameworks 11–16 in Figure 9).<sup>112–117,119</sup> Initial work in this area explored the adsorption of 1,2-benzenedithiol (11 in Figure 9) onto gold and silver surfaces.<sup>112</sup> Kinetic studies performed on these types of monolayers revealed a more stable film when compared to the adsorption and desorption rates of octadecanethiol. Using a systematic approach to adsorbate design, our group generated monolayers derived from alkyl-functionalized analogs of adsorbate 12, framework 13, and found that the adsorbates generated “chelating” SAMs that were well-packed and highly oriented.<sup>113</sup> However, monolayer films generated from the corresponding disulfide, framework 14, were less complete and disordered, likely due to constraints introduced by the cyclic disulfide ring.<sup>114</sup> Separate studies by Kim et al. utilized adsorbate 12 to form SAMs on gold surfaces.<sup>115</sup> The authors showed that monolayers formed from 12 yielded highly ordered, well-packed films and attributed the phenomena to the flexibility of the methylene units. As noted in our previous work,<sup>113</sup> the incorporation of the methylene units allows the sulfur atoms to bind to the gold in a manner that avoids steric and torsional strain, as shown in the molecular modeling of the adsorbate, in which the distance between the sulfur atoms can reach 5.0 Å (Figure 10).<sup>113</sup>

1,3-Benzenedithiol 15 and its methylated analog 16 were utilized to form SAMs on both gold and silver nanoparticles.<sup>116,117</sup> The authors found that the coordination of the thiolate groups on the surface (i.e., the number of sulfur

atoms per molecule bound to the metal) was highly dependent on the structure and concentration of the adsorbate. Both sulfur atoms of 15 were found to bind to the metal surface regardless of the concentration of the adsorbate in solution. However, a full binding of sulfur atoms to the metal in SAMs derived from 16 occurred only at lower concentrations. At higher concentrations, there was only a single sulfur–metal bond per adsorbate, which led to a more upright conformation.

**Spiroalkanedithiols.** A second structural design that arose shortly afterward is the bidentate dithiol having structural motif 17, dubbed spiroalkanedithiol.<sup>118</sup> In subsequent studies, the spiro headgroup was coupled with dissimilar tailgroups and utilized for the creation of conflicted interfaces.<sup>5,120,121</sup> Our research group was the first to report the use of the spiro motif to incorporate two alkyl chains of differing lengths to create the first example of a homogeneously mixed film on the molecular level.<sup>120</sup> SAMs derived from spiroalkanedithiols (SADTs) bearing both a 10- and a 17-carbon tailgroup (22) were compared to those derived from SADTs having two equivalent 10-carbon tailgroups (18) and two equivalent 17-carbon tailgroups (20) as well as SAMs derived from their individual *n*-alkanethiol counterparts (19 and 21) and mixtures of the latter *n*-alkanethiols. All of the characterization techniques employed for the SAMs derived from 22 were consistent with a homogeneously mixed film. For example, ellipsometry measurements revealed a thickness for the film derived from 22 in between the thicknesses of the individual films derived from 19 and 21. An evaluation of the degree of conformational order for the films by polarization-modulation infrared reflection adsorption spectroscopy (PM-IRRAS) showed liquidlike character for the unsymmetrical SADT SAMs when compared to that of films derived from the *n*-alkanethiols and the symmetrical SADTs; further analysis by PM-IRRAS revealed that the mixed SAMs at solution ratios of 2 and 3 (i.e., ratio = 19/21) were similar to the SAM derived from the unsymmetrical SADT, 22. Perhaps the most revealing analysis performed was the AFM images (Figure 11). The topographical images offer visual conformation of a homogeneously mixed interface for the unsymmetrical SADT SAM (Figure 11E), whereas domain formation is apparent in the SAM derived from the analogous mixture of *n*-alkanethiols (Figure 11F).

In studies related to those outlined in the Introduction,<sup>5</sup> we utilized the spiroalkanedithiol headgroup to study the effects of blending two mutually incompatible tailgroups composed of hydrocarbon and partially fluorinated chains in efforts to

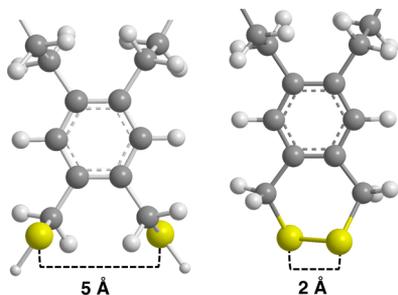
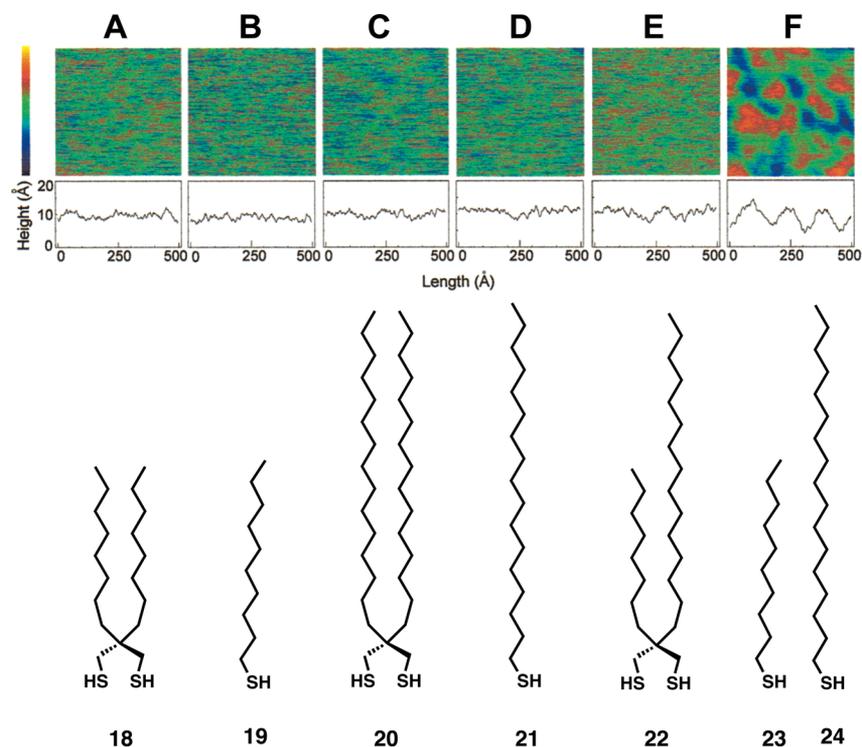
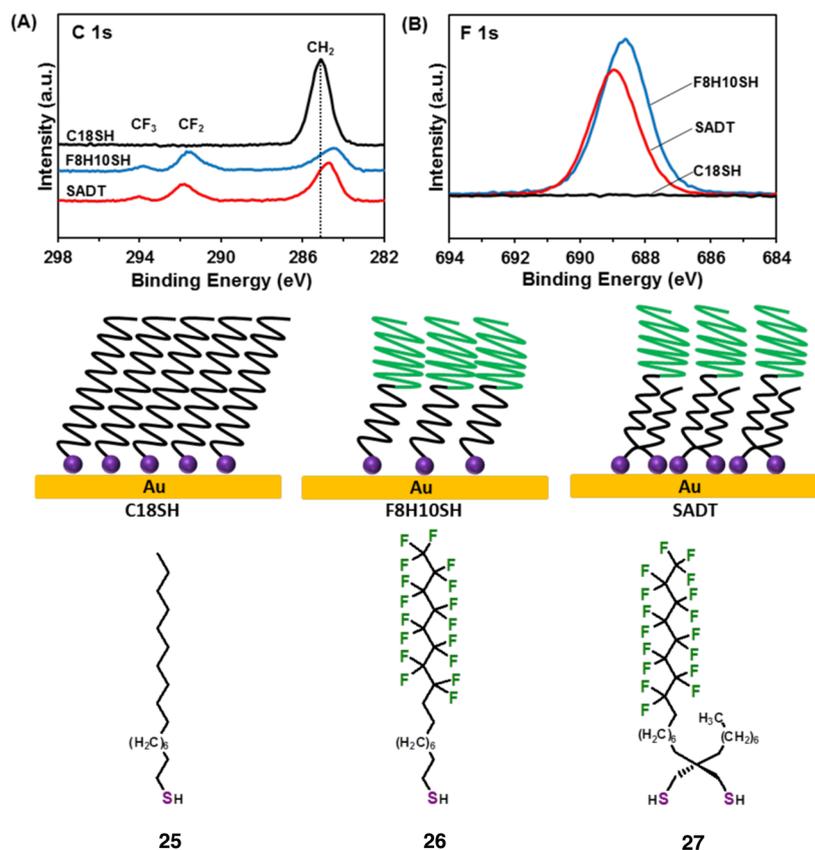


Figure 10. Model depicting the distance between the sulfurs of adsorbates 13 and 14. The model was obtained using MM2 calculations on ChemBio 3D Ultra.



**Figure 11.** AFM images (topographic) of SADT SAMs (A) C10C10(SH)<sub>2</sub> (18), (C) C17C17(SH)<sub>2</sub> (20), and (E) C10C17(SH)<sub>2</sub> (22) along with normal alkanethiols (B) C10SH (19), (D) C17SH (21), and (F) a mixed SAM where [C10SH]/[C17SH] = 2. Reproduced with permission from ref 120. Copyright 2000 American Chemical Society.



**Figure 12.** Homogeneously mixed multicomponent spiro adsorbates for exploring the interfacial properties of surfaces containing well-defined mixtures of hydrocarbons and fluorocarbons. Results of XPS analysis of (A) C 1s and (B) F 1s binding energy regions of normal alkanethiol, partially fluorinated spiroalkanedithiol, and partial fluorinated SAMs. Reproduced with permission from ref 121. Copyright 2015 American Chemical Society.

generate yet another class of conflicted interfaces.<sup>121</sup> A comparison of the SAMs generated from the unsymmetrical SADTs, **27**, to SAMs generated from analogous hydrocarbon, **25**, and partially fluorinated monothiols, **26** (Figure 12), indicates that the custom-designed bidentate adsorbates afford stable monolayers on gold. Furthermore, the analysis of these SAMs by XPS showed that the C 1s peak position for the methylene spacers of the SADT SAMs appeared at a higher binding energy (284.7 eV) than that of the SAM derived from **26** (284.5 eV) (Figure 12A), indicating a denser packing of the hydrocarbon chains in the SADT SAMs. However, the hydrocarbon portion of the SADT SAMs was still less densely packed than that of the SAM derived from **25** (285.0 eV). The enhanced packing density of the chains of the SADT SAMs compared to that of **26** SAMs was also evident in the F 1s binding energies; specifically, the F 1s peak position for the **26** SAMs appeared at a lower binding energy compared to that of SADT SAMs. We rationalized such shifts in the binding energies of the SADT films by considering them to be better insulators than the **26** films, which translates to a slower discharge of the positive holes generated in the core electron ejection process (inhibition of electron flow from the gold surface to the SAMs).<sup>121</sup> Additionally, the analyses suggested that the fluorinated portions of the SADT films were more tilted than those in the **26** films.<sup>121</sup> Thus, by covalently blending these mutually incompatible chains, we were able to reduce the structural constraints of a well-packed partially fluorinated segment (5.8 Å) on the hydrocarbon segment that arise from differences in the chain diameter (5.8 vs 4.2 Å). It is important to note that SAMs derived from mixtures of partially fluorinated alkanethiols and *n*-alkanethiols typically lead to domain formation or "islanding" of the two distinct species within the monolayer film.<sup>29,122</sup> Nevertheless, this research demonstrates that properly designed molecules can be used to generate mixed monolayers having good interfacial homogeneity and low surface energy. The exploration of the interfacial properties (e.g., adhesion and friction) of these new conflicted interfaces is ongoing.

**Dithiocarboxylic Acids and Derivatives.** Aliphatic dithiocarboxylic acids (ADTCAs; **28**, Figure 13) have also

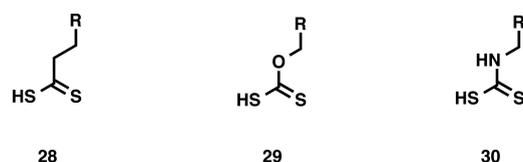


Figure 13. Structures of dithiocarboxylic acids, xanthic acids, and dithiocarbamic acid used in efforts to generate stable monolayer films on gold.<sup>123,125,126</sup>

been explored as multidentate adsorbates for generating SAMs on gold.<sup>123,124</sup> Despite the chelating nature of the adsorbate, SAMs formed from **28** were found to be less stable under air, oxygen, and argon when compared to SAMs derived from *n*-alkanethiols.<sup>124</sup> SAMs on gold derived from xanthic acids (NAXAs; **29**) and dithiocarbamic acids (DTCAs **30**) have also been studied.<sup>125,126</sup> Structurally, SAMs formed from NAXAs were found to exhibit reduced conformational order compared to SAMs formed from ADTCAs; in addition, stability tests revealed a less-stable film when compared to analogous ADTCA SAMs.<sup>125,126</sup> Eckerman et al. utilized an analogue of **30** that bears two different alkyl groups where one has a ferrocene group to study the effect of a mixed monolayer on electron-transfer processes.<sup>127</sup> The dithiocarbamate moiety in DTCAs has also been employed as an organic layer to lower the work function of electrodes.<sup>128</sup> Notably, the relative ease of removal for these types of adsorbates (i.e., **28**–**30**) makes them promising candidates as transient protective inks in orthogonal patterning by soft lithography.<sup>124</sup>

#### Aromatic Dithiol Headgroups: Second Generation.

Combining two of the structural motifs above, our group designed, synthesized, and studied a series of alkyl-terminated aromatic dithiols having a spiro headgroup motif, **31**–**33** (Figure 14), to investigate the relationship between tailgroup chains and headgroup packing densities.<sup>129</sup> From these studies, we concluded that increasing the number of alkoxy chains on the ring led to an increased degree of conformational order with increased van der Waals interactions. Moreover, in addition to the chelate effect, the addition of multiple alkoxy chains gave rise to an enhancement in the overall thermal stability of the SAMs. The aromatic ring in this adsorbate provides a unique platform where two or even three dissimilar tailgroups can be incorporated into a single adsorbate (in contrast to the spiroalkanethiols, where the number of dissimilar tailgroups is limited to two).

In recent breakthrough studies,<sup>6</sup> our group utilized the unmatched stability of SAMs on gold derived from adsorbates having 1,3-bis(mercaptomethyl)phenyl-based headgroups (see framework **34** in Figure 14) to generate conflicted interfaces composed of alkyl, perfluoro, and OEG moieties. In contrast to mixed monolayers derived from functionalized monothiols, which show clear deviations from the solution composition, the surface composition of mixed SAMs generated from these unique bidentate molecules reflects the molar solution concentration of the respective molecules, a reflection of the kinetically controlled film-formation process brought about by the above-mentioned chelating effect. Perhaps more importantly, the interfacial properties of these mixed films are consistent with what one would predict from the solution concentration. After quantitatively analyzing the mixed SAMs by XPS and comparing the XPS data to the wettability data (Figure 15), the results showed that the bidentate system offers

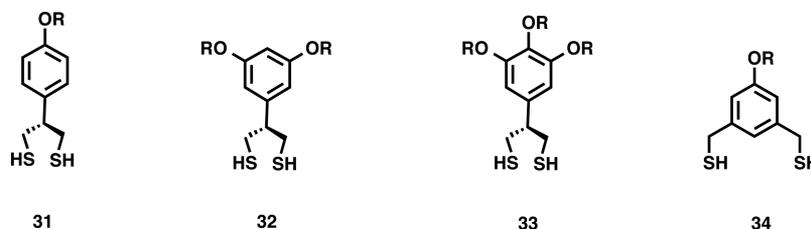
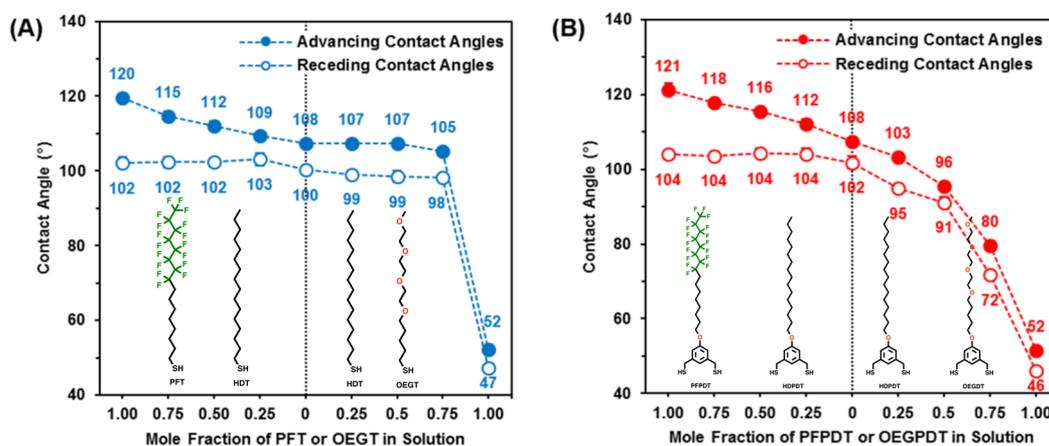


Figure 14. Structures of aromatic dithiol-based adsorbates used to generate stable monolayer films on gold.<sup>129</sup>



**Figure 15.** Wettability data of mixed monolayers of (A) monodentate systems (PFT/HDT and HDT/OEGT) and (B) homogeneously mixed SAMs of bidentate systems (PF PDT/HDPDT and HDPDT/OEGPDT). Reproduced with permission from ref 6. Copyright 2016 American Chemical Society.

a precise way to control the interfacial properties in contrast to the traditional monodentate *n*-alkanethiol system. For the hydrocarbon/OEG-terminated SAMs (right side panels), the change in the contact angle of water on the mixed SAMs formed from the bidentate system (Figure 15B) is more gradual than in the monodentate system (Figure 15A). The more gradual change observed for the bidentate system vs the monodentate system arises from the greater (more precise) control of surface composition afforded by the bidentate adsorbates.<sup>6</sup> Furthermore, a stability assessment of mixed SAMs in the study showed that the monodentate adsorbates (PFT and OEGT) were completely exchanged by hexadecanethiol (HDT) when placed in solutions with high HDT concentration, as indicated by the wettability data. In contrast, however, the bidentate system remained intact, showing constant wettability data even after long incubation times in a 10 mM solution of the displacing adsorbate. Using judiciously selected mixtures of these custom-designed bidentate thiols offers the ability to create thin monolayer films with precisely defined and entirely unique interfacial properties.

**Developing Strategies for Generating Conflicted Interfaces.** As described in the preceding section, the use of adsorbates with multidentate headgroups in the form of either aromatic-based or spiro-based dithiols offers a facile strategy for creating homogeneously mixed interfaces having tunable chemical heterogeneity.<sup>5,6,120,121</sup> Moreover, depending on the desired structural features and chemical compositions of the coated surface, mixed SAMs can be prepared simply by designing and synthesizing multidentate adsorbates with suitable architecture and chemical composition. For instance, SADTs with unsymmetrical tailgroups are likely the best choice for generating homogeneously mixed SAMs having a 50:50 ratio of chemical functionality.<sup>5,120,121</sup> Such adsorbates allow the intimate mixing of chain termini on the surface needed to tune interfacial properties (e.g., wettability, adhesion, and friction) while eliminating the possibility of domain formation.<sup>120,121</sup> Separately, mixed monolayers derived from adsorbates having 1,3-bis(mercaptomethyl)phenyl headgroups represent an alternative approach to mixed interfaces, where the interfacial properties can be tuned simply by adjusting the relative adsorbate concentrations in solution.<sup>6</sup> However, regardless of the type of adsorbate used in generating the SAM (spiro or aromatic dithiol), these monolayer coatings

exhibit enhanced stability when compared to their monothiol-based counterparts, (i.e., they are more resistant to ligand exchange and are more chemically and thermally stable with respect to molecular desorption). Additionally, kinetically controlled film formation from such adsorbates obviates the need for more laborious approaches for the generation of compositionally mixed organic thin films.<sup>33,66</sup>

## CONCLUSIONS

This feature article examines a variety of strategies that have been used to generate stable, compositionally mixed SAMs on gold, including the development of new adsorbates that offer homogeneously mixed conflicted interfaces. Previous efforts to generate high-quality mixed films include the widely studied techniques of the coadsorption of monothiols, backfilling processes, and the adsorption of disulfides; these commonly used techniques have been shown to yield films with phase-separated domains, where the relative concentration of adsorbates on the surface differs from that in solution, films that show preferential adsorption, and films that are susceptible to exchange processes. In contrast, newly developed strategies such as imbedding an internal dipole within a molecule<sup>25</sup> or designing adsorbates with phase-incompatible tailgroups that are structurally connected to the molecule coupled with the incorporation of a dithiol headgroup have been used to generate films having homogeneous mixtures of phase-incompatible species. Furthermore, capitalizing on the enhanced stability of SAMs on gold derived from adsorbates having 1,3-bis(mercaptomethyl)phenyl-based headgroups, mixed thin SAMs derived from these custom-designed molecules resist desorption and are stable against exchange processes. These newly developed adsorbates and film-forming strategies will undoubtedly lead to advances in a variety of applications, including surfaces for selective protein adsorption and/or desorption, nanoparticles with extended circulation time in physiological media, and robust nonadhesive films for antifouling applications.

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## Notes

The authors declare no competing financial interest.

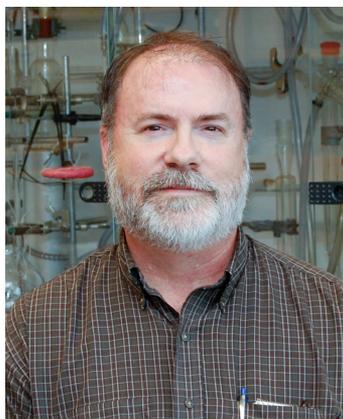
## Biographies



María D. Márquez was born in Houston, Texas. She earned a B.S. degree in chemistry (with minors in French and global business), graduating cum laude from the University of Houston in 2011. She is currently pursuing her Ph.D. in chemistry under the guidance of Professor T. Randall Lee, with a research focus on the structure and properties of organic thin films.



Oussama Zenasni was born in Algiers, Algeria. He earned B.A. degrees in biology and chemistry, graduating cum laude from the University of Houston. He earned his Ph.D. in organic chemistry under the guidance of Professor T. Randall Lee. His postdoctoral research in Professor Wei-Chuan Shih's laboratory focused on developing nanoporous plasmonic sensors for detecting offshore oil spills. His current research focuses on the development of new monolayer coatings for tuning the interfacial properties of surfaces.



Andrew C. Jamison, originally from Shreveport, Louisiana, spent his youth in Houston, Texas. His initial degree, a B.B.A. from Texas Wesleyan College in 1982, reflects his interest in business. However, his career in the paint industry encouraged him to seek a better understanding of chemistry. As a commuter student attending the University of Houston, he obtained both B.S. and Ph.D. degrees in chemistry, the latter under the guidance of Professor T. Randall Lee. His recent research has focused on nanoscale coatings in the form of partially fluorinated self-assembled monolayer films.



T. Randall Lee hails from Daingerfield, Texas. He attended Rice University, earning a B.A. degree in chemistry (magna cum laude), followed by a Ph.D. degree from Harvard University working for Professor George Whitesides. His postdoctoral research was conducted at Caltech under the supervision of Professor Robert Grubbs, where he held an NIH postdoctoral fellowship. Since joining the faculty of the University of Houston, he has pursued research interests that include nanoscale surface coatings, plasmonic nanomaterials, and applied polymeric materials. He currently holds the titles of Cullen Distinguished University Chair in the Department of Chemistry and Associate Dean for Research in the College of Natural Sciences and Mathematics.

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