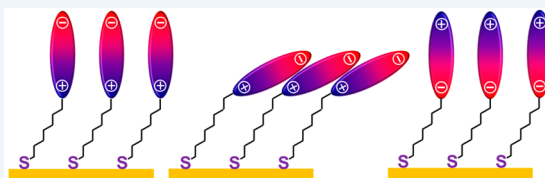


# Surface Dipoles: A Growing Body of Evidence Supports Their Impact and Importance

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**CONSPECTUS:** Surface dipoles arise from differences in the distribution of electron density of interfacial molecular structures as expressed by charge separation. The direction and magnitude of the associated dipole moments directly impact a variety of interfacial phenomena. For example, the wettability of thin film-coated solid surfaces toward polar contacting liquids can be systematically adjusted by reorienting the direction of an array of *interfacial* dipoles, while the vector sum total of all of the dipole moments associated with such thin films can be used to tune the work function of a metal. One method of producing such dipole arrays is by coating a surface with a self-assembled monolayer (SAM), which is a thin organic film of amphiphilic adsorbates that spontaneously assemble on a surface. The interfacial properties of SAMs can be menu-selected by choice of adsorbate structure using  $\omega$ -terminated thiols on gold surfaces as a convenient system for studying and utilizing these properties.



In this Account, we describe the impact of an array of oriented surface dipoles upon the interfacial energy of the thin film bearing such an array. Our analysis of these films divides the subject of surface dipole arrays into three types: (1) those directing a well-defined electronegative pole toward the interface, (2) those incorporating an invertible polar group, and (3) those directing a well-defined electropositive pole toward the interface. With regard to the first category, we analyze the impact of permanent dipoles on the wettability of alkanethiolate SAMs generated from adsorbates possessing well-defined transitions between terminal fluorocarbon and underlying hydrocarbon chain segments. The second category covers recent reports of light-responsive SAMs formed from azobenzene-based adsorbates. Finally, the third category explores a unique example of a dipole array that exposes the positive ends of the interfacial dipoles formed from  $\text{CH}_3$ -terminated fluorocarbon tailgroups. Our analysis of the SAMs formed from these carefully crafted adsorbates encompassing several series of fluorocarbon-containing thiols provides support for a conclusion that oriented surface dipoles exert a significant influence on interfacial energetics and wettability. In contrast to the limited distance from the interface that a surface dipole array will have upon contacting liquids, the work function of a thin film reflects the influence of all the polar groups within the film. Therefore, we also explore the change in the substrate work function for *n*-alkanethiol-modified gold surfaces as a function of molecular length and for other adsorbates as a function of their chemical composition.

## INTRODUCTION

Since the work of Zisman in the late 1950s,<sup>1–3</sup> surface dipoles have been the poor sisters of interfacial science. For example, Fowkes,<sup>4</sup> a renowned pioneer of the field, took note of related work by van Oss, Chaudhury, and Good<sup>5,6</sup> and concluded that all interactions across an interface can be reduced to two types: dispersive and acid–base, naturally assuming that dipole–dipole interactions (Keesom and Debye forces) were too small to contribute significantly to interfacial forces, such as wettability and the work of adhesion. It is important to note that these studies considered the interactions between two condensed phases in which the dipoles were randomized. Further, the thin-film systems investigated in these earlier studies were restricted in their capacity to generate interfaces with well-oriented surface dipole arrays. Consequently, this prevailing opinion stood largely unchallenged until 1999, when we reported the first unambiguous influence of surface dipole effects upon interfacial wettability.<sup>7</sup>

Over the past 17 years, our research group and others have explored the impact of surface dipoles on the physical

properties of surfaces.<sup>7–14</sup> For precise and systematic analysis, we have used functionalized surfaces generated by the spontaneous adsorption of organosulfur-based molecules on gold substrates, forming self-assembled monolayers (SAMs).<sup>15,16</sup> SAMs provide several advantages for investigating the relationship between surface dipoles and surface physical properties. First, SAMs can be used to generate monolayer films that are highly conformationally ordered, with the molecular components precisely oriented within a well-defined array of molecules. Second, the magnitude and direction of the surface dipole moments can be manipulated by the structural modification of the molecular adsorbates. The individual dipoles of adsorbates can be tuned by the nature of the substituents that produce charge separation (e.g., electron-donating or withdrawing groups), by the orientation of these substituents relative to the interface, by the position of the substituents if on a structural component that provides multiple

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bonding sites (e.g., *o*-, *m*-, or *p*-substitution of benzene moieties), by the nature of the moieties used to produce the dipole (i.e., polar groups that might engage in acid–base interactions), and, for adsorbates that are stabilized by an alkyl spacer, by the number of carbon atoms within the alkyl chain (“odd–even” effect).<sup>7–12,14,17,18</sup> Third, SAMs can be formed on various metal surfaces, such as gold and silver, having distinct lattice spacings and electronic properties.<sup>19–27</sup> Accordingly, we can evaluate the impact of surface dipoles, not only on the contacting physical properties of wettability and friction, as influenced by chain densities, but also on the physical properties such as work function that exist independent of interfacial contact. In this Account, we examine the effect of adsorbate dipoles (especially, their magnitude and surface orientation) originating from molecular structure on the wettability and work function of surfaces fabricated by the spontaneous adsorption of selected alkanethiols.

### ■ IMPACT OF SURFACE DIPOLES ON WETTABILITY

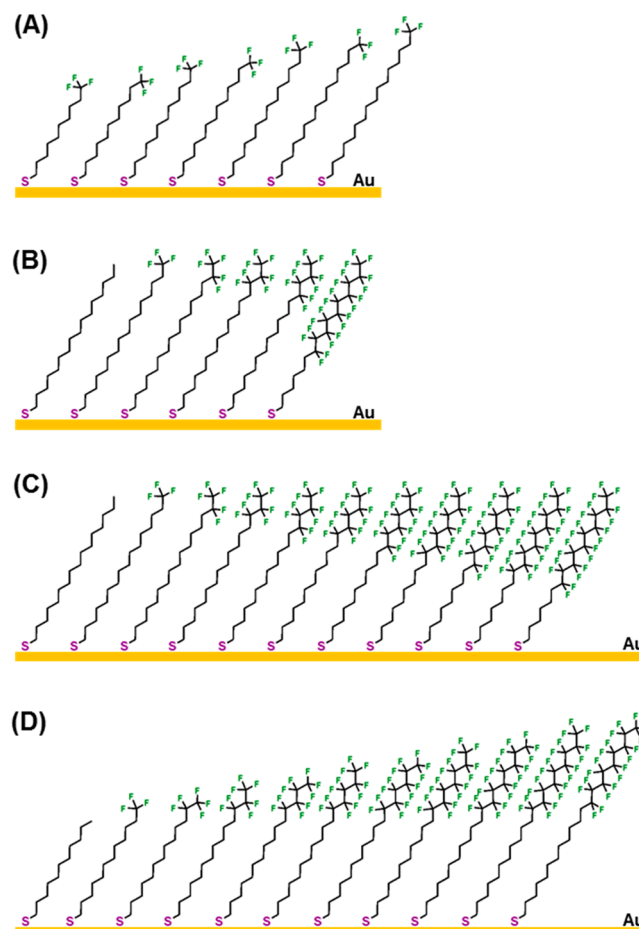
After observing the formation of monolayer films from a particular set of amphiphilic liquids, Zisman noted in 1955 that the resulting surfaces presented an array of methyl groups exhibiting “autophobic” properties, that is, the liquid that formed the monolayer failed to wet the film.<sup>28</sup> An examination of this phenomenon helps clarify the role of surface dipoles upon interfacial energy. For molecules in a liquid state, intermolecular interactions are, for the most part, a reflection of the sampling of attractions and repulsions across the total molecular surface as these structures tumble and collide in constant motion, with the strongest points of attraction and repulsion dominating the molecular interactions. Therefore, a typical molecular modeling program will readily provide a *molecular* dipole moment. For an alkanethiol with a polar moiety at the terminus of an extended alkyl chain, such calculations fail to adequately define the influence of the resulting dipole upon the interfacial properties of the monolayer film. As with Zisman’s films of arrayed methyl groups, the chemical structures with immediate exposure at a surface play a significant role in defining interfacial interactions. This understanding provides the basis for the utilization of the polar surface area parameter for research on the interactions of drug molecules with biological membranes,<sup>29</sup> and the study of molecular surface electrostatic potentials to help elucidate the interactions that give rise to effective anesthetics.<sup>30</sup> Given the myriad of potential applications, the paragraphs below seek to provide additional perspective regarding the role of dipole orientation and interfacial exposure on thin-film surface energy.

#### Dipole Arrays Directing a Well-Defined Electronegative Pole toward the Interface

Fluorinated surfaces are used in applications requiring low wettability, minimal adhesion, and chemical resistance because of their low surface energy and tension and chemical inertness. Generally, water will wet a hydrocarbon surface more than a fluorocarbon surface. However, exceptions to this rule can be found in the literature. Shafrin and Zisman reported a comparative study of the wettability of the outermost surfaces of CF<sub>3</sub>-terminated alkanic acid/alkyl amine monolayers and those of CH<sub>3</sub>-terminated alkanic acid/alkyl amine monolayers on platinum substrates.<sup>2</sup> Their data revealed that the contact angles of water on the CF<sub>3</sub>-terminated films were slightly lower than those on the CH<sub>3</sub>-terminated films, whereas the contact angles of water on surfaces coated with perfluoroalkane

adsorbates were higher than those of the CH<sub>3</sub>-terminated adsorbates. Their studies provided experimental evidence that polar interactions with the CF<sub>3</sub>-terminated films strongly influenced wettability.

To pursue a more comprehensive investigation of the fundamental phenomena that contribute to such wettability differences, we developed two systems. First, we examined fluorinated surfaces generated from several systematically designed series of fluoroalkane thiols on vapor-deposited “flat” gold (Figure 1). Compared with the monolayers prepared by



**Figure 1.** Illustrations of four series of fluorinated self-assembled monolayers used to evaluate the impact of surface dipoles generated from fluorocarbon moieties on wettability: (A) CF<sub>3</sub>(CH<sub>2</sub>)<sub>n</sub>SH, *n* = 9–15; (B) CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>SH and CF<sub>3</sub>(CF<sub>2</sub>)<sub>*m*</sub>(CH<sub>2</sub>)<sub>*n*</sub>SH, *m* = 0–3, 9 and *n* = 15–12, 6; (C) CH<sub>3</sub>(CH<sub>2</sub>)<sub>15</sub>SH and CF<sub>3</sub>(CF<sub>2</sub>)<sub>*m*</sub>(CH<sub>2</sub>)<sub>*n*</sub>SH, *m* = 0–9 and *n* = 15–6; (D) CH<sub>3</sub>(CH<sub>2</sub>)<sub>10</sub>SH and CF<sub>3</sub>(CF<sub>2</sub>)<sub>*n*</sub>(CH<sub>2</sub>)<sub>11</sub>SH, *n* = 0–9. Adapted from refs 7–10.

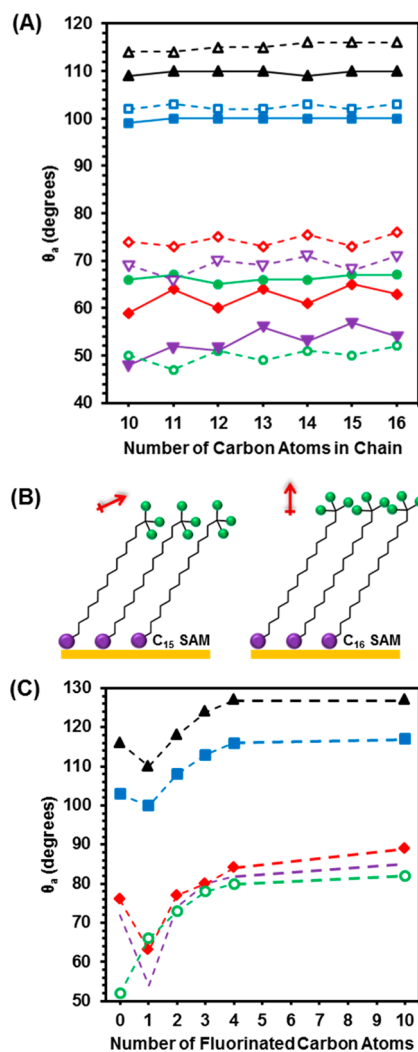
Zisman and co-workers on polished metal surfaces, alkanethiols form densely packed and highly ordered monolayers on freshly evaporated gold surfaces. Second, we employed three different types of contacting liquids (nonpolar, polar protic, and polar aprotic) for systematic studies of the wettability. The collective results generated by use of these contacting liquids (CLs) provide insight into the influence of various factors (dispersive, hydrogen bonding, and dipole–dipole interactions) on surface wettability. The dispersive nature of a surface can be estimated by an analysis of the contact angle data of nonpolar CLs such as hexadecane and decalin. The effect of hydrogen bonding on wettability can be determined by using a combination of polar

protic (such as water and glycerol) and polar aprotic (such as acetonitrile and dimethylformamide) CLs. The contact angles of polar aprotic CLs on surfaces provide further insight regarding the impact of surface dipoles on wettability.

Two of our initial reports exploring the impact of terminally perfluorinated adsorbates on the interfacial energy of SAMs examined the wettability of SAMs generated from  $\omega,\omega,\omega$ -trifluoromethylalkanethiols (series I;  $\text{CF}_3(\text{CH}_2)_n\text{SH}$ ,  $n = 9-15$ , Figure 1A).<sup>7,8</sup> We also collected data from a series of normal alkanethiols ( $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ,  $n = 9-15$ ) for comparison; notably, analysis by atomic force microscopy (AFM) revealed identical lattice spacings (i.e., packing densities) for these films.<sup>31</sup> The advancing contact angles ( $\theta_a$ ) of hexadecane (a nonpolar CL) on  $\text{CF}_3$ -terminated surfaces were higher than those of hexadecane on  $\text{CH}_3$ -terminated surfaces (average  $\Delta\theta_a = \theta_a^{\text{CF}_3} - \theta_a^{\text{CH}_3} = 15^\circ$ ), as we anticipated. However,  $\theta_a$  of water and glycerol (polar protic CLs) on  $\text{CF}_3$ -terminated surfaces was lower than those of water and glycerol on  $\text{CH}_3$ -terminated surfaces (average  $\Delta\theta_a = \theta_a^{\text{CF}_3} - \theta_a^{\text{CH}_3} = -6^\circ$  for water,  $-4^\circ$  for glycerol). Following Zisman,<sup>2</sup> we formulated two hypotheses to rationalize this decrease in contact angle (increase in wettability): (1) the presence of hydrogen bonding between the CLs and the exposed fluorines of  $\text{CF}_3$ -terminated surfaces or (2) the presence of dipole–dipole interactions between the permanent dipoles of the CLs and the oriented dipoles of the terminal  $\text{CF}_3\text{-CH}_2$  moiety of the adsorbates, typically identified in terms of the structural transition between the fluorocarbon and hydrocarbon segments ( $R_F\text{-}R_H$ ). To test these hypotheses, we collected additional contact angle data using polar aprotic CLs such as acetonitrile, dimethylformamide (DMF), and dimethyl sulfoxide (DMSO), which offer little or no capacity for hydrogen bonding to fluorocarbons (Figure 2A). The difference in the advancing contact angles between the  $\text{CF}_3$ -terminated and the  $\text{CH}_3$ -terminated surfaces increased (average  $\Delta\theta_a = \theta_a^{\text{CF}_3} - \theta_a^{\text{CH}_3} < -10^\circ$  in both acetonitrile and DMF), and odd–even effects were observed. Further, the odd–even effect could be rationalized by differences in the dipole direction (i.e., orientation relative to the interface) of the  $\text{CF}_3\text{-CH}_2$  moiety (Figure 2B).

Additionally, we examined the wettability of SAMs generated from alkanethiols having an increasing degree of fluorination (series II;  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  and  $\text{CF}_3(\text{CF}_2)_m(\text{CH}_2)_n\text{SH}$ ,  $m = 0-3, 9$ , and  $n = 15-12, 6$ , Figure 1B).<sup>7</sup> For nonpolar hexadecane, the minimum  $\theta_a$  was observed on the  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  SAM (no terminal perfluorocarbons). In contrast, for polar protic (water and glycerol) and polar aprotic (acetonitrile and DMF) CLs, the minimum  $\theta_a$  was always observed on the  $\text{CF}_3(\text{CH}_2)_{15}\text{SH}$  SAM (Figure 2C), but the values increased thereafter with the increase in fluorination. We attributed the latter trend to a burying of the dipoles ( $R_F\text{-}R_H$ ) within the SAM as the degree of fluorination was increased. As a whole, the contribution of surface dipoles not only rationalizes why polar protic and polar aprotic liquids more readily wet  $\text{CF}_3$ -terminated surfaces than  $\text{CH}_3$ -terminated surfaces but also rationalizes the systematic trends in wettability observed as a function of chain length (Figure 2).

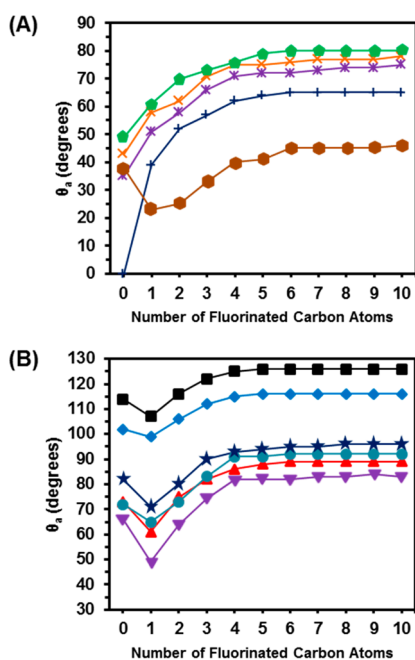
For a more complete understanding of the role that the length of the fluorinated moiety has upon wettability, we performed wettability studies of two more series of progressively fluorinated SAMs. The first series was derived from partially fluorinated alkanethiols whose total chain lengths were held constant (series III;  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  and  $\text{CF}_3(\text{CF}_2)_m(\text{CH}_2)_n\text{SH}$ ,  $m = 0-9$  and  $n = 15-6$ , Figure 1C).<sup>9</sup>



**Figure 2.** (A) Advancing contact angles of hexadecane (●), acetonitrile (▼), dimethylformamide (◆), water (▲), and glycerol (■) on SAMs formed from  $n$ -alkanethiols ( $\text{H}(\text{CH}_2)_n\text{SH}$  with  $n = 10-16$ ; open symbols) and  $\text{CF}_3$ -terminated alkanethiols ( $\text{CF}_3(\text{CH}_2)_{n-1}\text{SH}$  with  $n = 10-16$ ; filled symbols). (B) Illustration of the parity (or odd–even) effect upon the  $R_F\text{-}R_H$  dipole (drawn using the chemist's convention) for  $\text{CF}_3$ -terminated films. (C) Advancing contact angles of hexadecane (○), acetonitrile (▼), dimethylformamide (◆), water (▲), and glycerol (■) on SAMs generated from a hexadecanethiol series:  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$ ,  $\text{CF}_3(\text{CH}_2)_{15}\text{SH}$ ,  $\text{CF}_3\text{CF}_2(\text{CH}_2)_{14}\text{SH}$ ,  $\text{CF}_3(\text{CF}_2)_2(\text{CH}_2)_{13}\text{SH}$ ,  $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_{12}\text{SH}$ , and  $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_6\text{SH}$ . Reproduced with permission from ref 7. Copyright 1999 American Chemical Society.

The second series was generated from fluorinated alkanethiols having a constant methylene spacer chain length and an increasing degree of terminal fluorination (series IV;  $\text{CH}_3(\text{CH}_2)_{10}\text{SH}$  and  $\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_{11}\text{SH}$ ,  $n = 0-9$ , Figure 1D).<sup>10</sup> For our progressively fluorinated SAMs, we observed that the contact angles of nonpolar CLs (heptane, decane, tridecane, and hexadecane) in both series III and series IV increased when the degree of fluorination (number of terminal fluorocarbons) increased from 0 ( $\text{CH}_3$ -terminated alkanethiols) to 10 (Figure 3A). Interestingly, when polar protic (water and glycerol) and polar aprotic (acetonitrile, DMF, DMSO, and nitrobenzene) liquids were used as CLs, minimum contact angles were observed for SAMs formed from  $\text{CF}_3(\text{CH}_2)_{15}\text{SH}$  and  $\text{CF}_3(\text{CH}_2)_{11}\text{SH}$  in series III and series IV, respectively





**Figure 3.** Advancing contact angles of (A) heptane (+), decane (\*), tridecane (x), hexadecane (◊), and *cis*-perfluorodecalin (●) and (B) water (■), glycerol (◆), acetonitrile (▼), dimethylformamide (▲), dimethyl sulfoxide (★), and nitrobenzene (●) on SAMs derived from  $F(CF_2)_n(CH_2)_{11}SH$  for  $n = 1-10$  and  $H(CH_2)_{11}SH$  for  $n = 0$ . Reproduced with permission from ref 10. Copyright 2003 American Chemical Society.

(Figure 3B). These results indicate that interfacial wettabilities of perfluoro-terminated SAMs exhibit little response to the

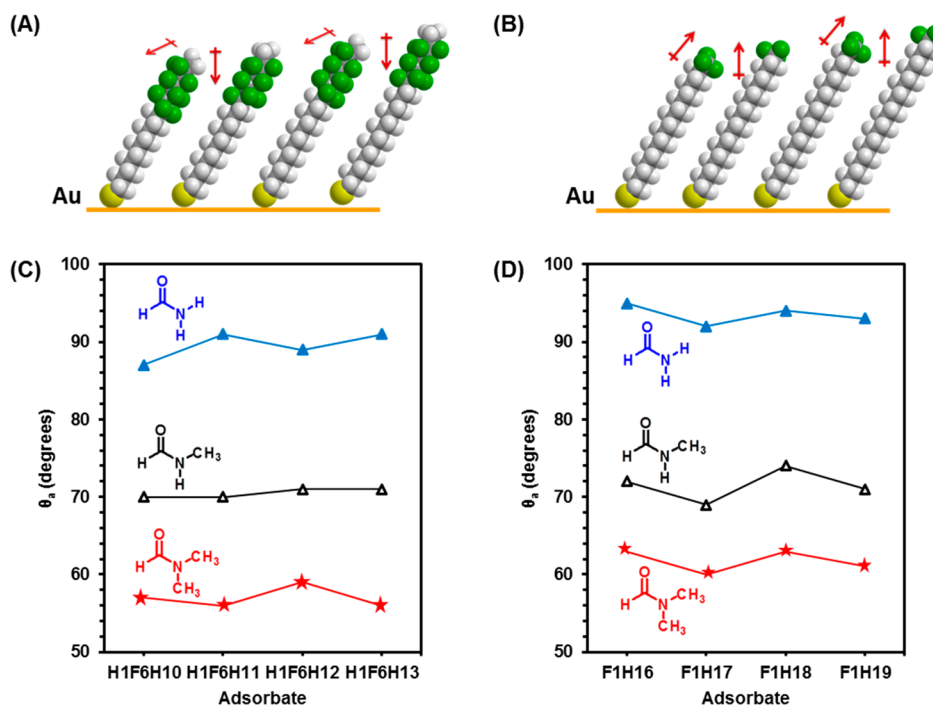
buried dipoles of the SAMs that possess four or more terminal  $CF_2$  moieties, as was also revealed in the results of series II.

### Dipole Arrays Incorporating an Invertible Polar Group

Several research groups have explored the dynamic tuning of surface physical properties using surfaces modified with azobenzene-based molecules.<sup>32–35</sup> The conformational change from *trans* to *cis* for the azobenzene moiety can be induced by UV light (360 nm), while the opposite transition (from *cis* to *trans*) can be induced by visible light (440 nm).<sup>35</sup> Lim and co-workers examined the wettability of silicon surfaces modified by polymers having trifluoromethoxy-substituted azobenzene moieties and found that the interfacial properties were also dynamically changed by the irradiation-induced structural reorganization. The contact angle of water on *cis*-azobenzene-terminated surfaces ( $71^\circ$ ) was lower than that of water on the *trans*-azobenzene-terminated surfaces ( $76^\circ$ ) because the surface-exposed dipole associated with the *cis* isomer is larger than that of the *trans* isomer. These results provide direct experimental evidence that the interfacial wettability can be altered by simple conformational changes that result in different molecular surface dipoles without changing the chemical composition of the organic films.

### Dipole Arrays Directing a Well-Defined Electropositive Pole toward the Interface

Turning direction on its tail, we recently evaluated the wettabilities of SAMs formed from a series of  $CH_3$ -capped, partially fluorinated alkanethiols ( $CH_3(CF_2)_6(CH_2)_nSH$ ,  $n = 10-13$ ; the HC-FC thiols) compared with those of  $CF_3$ -terminated alkanethiol monolayers ( $CF_3(CH_2)_mSH$ ,  $m = 16-19$ ; the FC-HC thiols).<sup>14</sup> For the HC-FC thiols, the underlying fluorinated segment of six perfluorocarbons was chosen to minimize the impact of the buried FC-HC dipole on the



**Figure 4.** Illustrations of the orientation of the dipoles associated with the methyl and trifluoromethyl termini in SAMs of (A)  $CH_3(CF_2)_6(CH_2)_nSH$ ,  $n = 10-13$  (H1F6Hn), and (B)  $CF_3(CH_2)_mSH$ ,  $m = 16-19$  (F1Hm), formed on gold. (Dipole arrows drawn using the chemist's convention.) Advancing contact angles of formamide (▲), methylformamide (△), and dimethylformamide (★) on SAMs generated from (C) H1F6Hn with  $n = 10-13$  and (D) F1Hm with  $m = 16-19$ . Reproduced with permission from ref 14. Copyright 2015 American Chemical Society.

interfacial properties of the resulting monolayers, thereby allowing the terminal HC–FC dipole to be the dominant polar influence on interfacial energy. For the HC–FC films, determination of the orientation of the interfacial HC–FC dipole is complicated by the helicity of the perfluorinated segment; however, as can be discerned from the molecular models in Figure 4A, we concluded that there are distinct terminal dipole orientations, with SAMs having an even number of carbon atoms in their alkyl chains (the *even* SAMs) possessing dipoles more closely aligned with the surface normal. <sup>36</sup> Furthermore, as shown in Figure 4B, the FC–HC surface dipoles of the *even* CF<sub>3</sub>-terminated SAMs are also more closely aligned with the surface normal, producing interfacial dipoles with the opposite polarity. Because the two systems expose arrays of surface dipoles with similar dipole moments, and the *even* SAMs of each series possess dipoles of roughly equivalent orientation, *but opposite polarity*, the contact angle trends observed for the polar *aprotic* contacting liquids were similar for both series (i.e., *even* SAMs were wetted more than *odd*). However, the initial tests with polar *protic* liquids revealed an inverse trend for the HC–FC SAMs compared with the CF<sub>3</sub>-terminated SAMs (i.e., on the CH<sub>3</sub>-capped, partially fluorinated SAMs, *odd* chain lengths were more wettable than *even*).

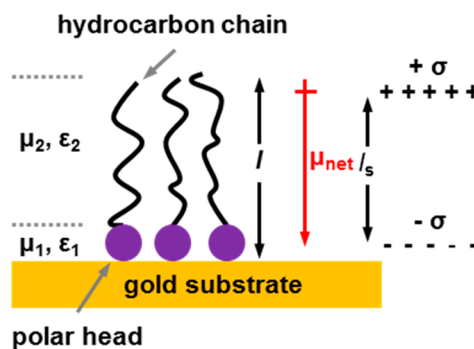
Figure 4C readily illustrates these trends through the contact angle data collected for formamide (FA), methylformamide (MFA), and dimethylformamide (DMF) on both series of SAMs. For these molecules, the ability to hydrogen bond to itself is progressively lost from FA (two H-bonding moieties) to MFA (one H-bonding moiety) to DMF (no capacity). Correspondingly, the wettability trends on the HC–FC alkanethiol monolayers correlate with the number of H-bonding moieties in the molecules. The odd–even trend for DMF on the HC–FC SAMs was the same as that observed in the wettability data for the CF<sub>3</sub>-terminated SAMs in Figure 4D. However, no odd–even effect was observed for the contact angle data of MFA on the HC–FC SAMs. Furthermore, the wettability of FA on the HC–FC SAMs showed an inverted odd–even trend to that observed for FA on the CF<sub>3</sub>-terminated SAMs. From the collected contact angle data, we concluded that when the hydrogen bonding network for a polar *protic* contacting liquid was sufficiently strong to deter interfacial reorientation of the liquid molecules to align with the surface dipoles (e.g., FA), then there was a repulsive interaction between the interfacial liquid molecules and the oriented dipoles at the interface of the SAM. When we reduced the presence of H-bonding moieties in the liquid molecular structure (e.g., MFA), the contact angle data revealed only a partial reorientation of the interfacial liquid molecules, negating the observation of any odd–even trend. Further, when the H-bonding moieties were completely removed from the contacting liquid, eliminating the internal hydrogen-bonding network (e.g., DMF), the odd–even trend reflected the ability of the interfacial liquid molecules to readily reorient in response to the surface dipoles, leading to the same trend observed on the CF<sub>3</sub>-terminated SAMs.

From these data and from a review of SFG studies on the interfacial orientation of water molecules at the liquid–vapor interface,<sup>37</sup> we concluded that the interfacial molecules of a highly hydrogen-bonded liquid were favorably oriented (on the basis of the polarity of their dipoles) with the surface dipoles of the CF<sub>3</sub>-terminated SAMs but unfavorably oriented with those of the HC–FC SAMs. What we have been unable to determine thus far from the collected contact angle data are the relative

magnitudes of the dipole–dipole and hydrogen bonding interactions of the polar *protic* liquids on the HC–FC SAMs. These studies and many others await these newly developed nanoscale materials.

## ■ IMPACT OF SURFACE DIPOLES ON WORK FUNCTION

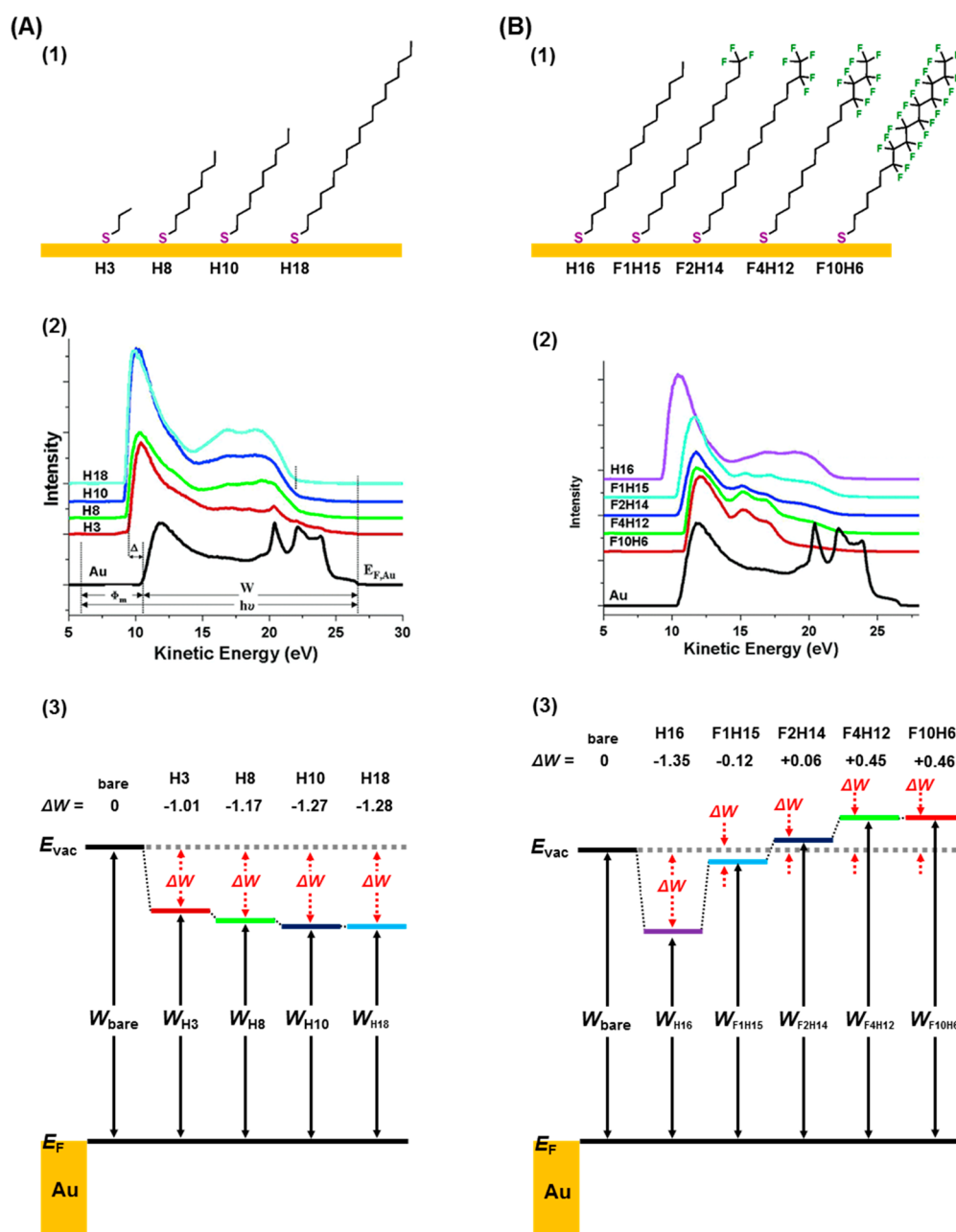
In contrast to the limited effect a deeply buried dipole might have on the interfacial character of a thin film, the same dipole,



**Figure 5.** Illustration of a thiolate monolayer as a dipole sheet. The direction of the apparent dipole moment is shown by  $\mu_{\text{net}}$  and has been drawn using the chemist's convention ( $l_s$ , monolayer thickness;  $\sigma$ , charged planes;  $l_s$ , separation of charged planes;  $\mu_1$  and  $\mu_2$ , dipole moment of the polar headgroup and hydrocarbon chain, respectively;  $\epsilon_1$  and  $\epsilon_2$ , dielectric constants of the polar headgroup and hydrocarbon chain, respectively). Reproduced with permission from ref 20. Copyright 1990 Elsevier Science Publishers.

no matter how far from the interface of the SAM, will greatly affect the overall adsorbate/substrate dipole moment that determines the energy required for an electron to be transported to or from the underlying substrate. The transport of charge carriers (holes or electrons) between metal electrodes and organic active layers is an important process that dictates the performance of organic electronics such as organic electroluminescent switching devices.<sup>38–40</sup> The efficiency of the transport processes is influenced by the optimization of the energy gap between the metal electrodes and the organic materials in contact with them. Generally, metals with large work functions are used as anodes to minimize the energy barrier when holes are injected into an active layer, whereas metals with small work functions are used as cathodes to minimize the energy barrier when electrons are extracted from the active layer.<sup>19</sup> To fine-tune the work function of a metal electrode, many research groups have employed organic thin films, including the incorporation of surface dipoles that are separate from that of the adsorbate–metal bond, by using the self-assembly of molecular adsorbates having permanent dipoles.<sup>20–27</sup>

In 1990, Evans and Ulman performed an initial investigation of the effect of surface dipoles on the work function of metals.<sup>20</sup> These researchers measured the surface potential (contact potential difference) of gold surfaces modified with alkanethiols (CH<sub>3</sub>(CH<sub>2</sub>)<sub>*n*</sub>SH, *n* = 5–21) using the Kelvin probe technique. The surface potential increased with an increase in the chain length of the alkanethiol adsorbates ( $\Delta V = 9.3$  mV per CH<sub>2</sub> unit of the alkyl chain). Based on their experimental results, the investigators proposed a model of a “dipole sheet” on the gold surface: the positive charge of the net dipole was associated with the interface between the hydrocarbon chains and the air,

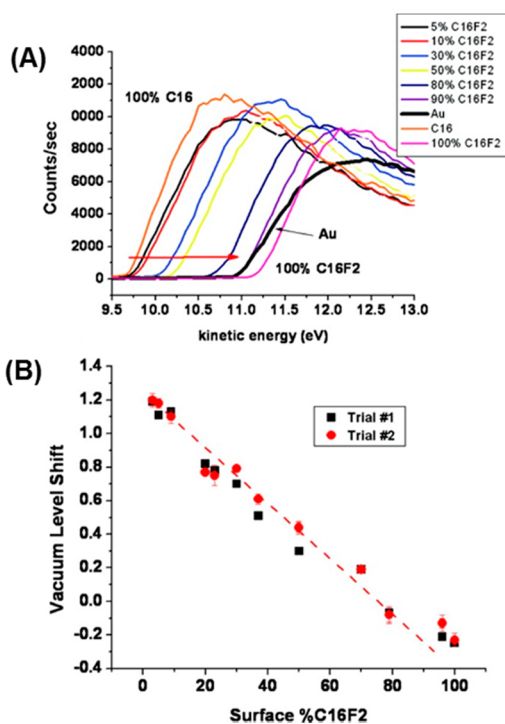


**Figure 6.** (A) (1) Illustration of the adsorbates used to form a series of self-assembled monolayers:  $\text{CH}_3(\text{CH}_2)_2\text{SH}$  (**H3**),  $\text{CH}_3(\text{CH}_2)_7\text{SH}$  (**H8**),  $\text{CH}_3(\text{CH}_2)_9\text{SH}$  (**H10**), and  $\text{CH}_3(\text{CH}_2)_{17}\text{SH}$  (**H18**). (2) UV photoemission spectra for clean Au and Au modified with **H3**, **H8**, **H10**, and **H18**. (3) Schematic diagram of the differences in work function ( $\Delta W$ ) between bare and alkanethiol-modified gold surfaces. (B) (1) Illustration of a series of self-assembled monolayers generated from  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  (**H16**),  $\text{CF}_3(\text{CF}_2)_{15}\text{SH}$  (**F1H15**),  $\text{CF}_3\text{CF}_2(\text{CH}_2)_{14}\text{SH}$  (**F2H14**),  $\text{CF}_3(\text{CF}_2)_3(\text{CH}_2)_{12}\text{SH}$  (**F4H12**), and  $\text{CF}_3(\text{CF}_2)_9(\text{CH}_2)_6\text{SH}$  (**F10H6**). (2) UV photoemission spectra for clean Au and Au modified with **H16**, **F1H15**, **F2H14**, **F4H12**, and **F10H6**. (3) Schematic diagram of the differences in work function ( $\Delta W$ ) between bare and fluorocarbon-terminated alkanethiol-modified gold surfaces.  $E_{\text{vac}}$ ; near-surface vacuum energy,  $E_F$ ; Fermi level energy, and  $W$ ; work function. Reproduced with permission from ref 22. Copyright 2003 American Chemical Society.

where the negative charge of the net dipole was oriented toward the gold surface (Figure 5).

To gain a better understanding of the dynamic role of alkanethiolate SAMs with regard to the work function of a SAM-coated surface, we evaluated the work function of gold surfaces modified with a series of normal alkanethiolate SAMs ( $\text{CH}_3(\text{CH}_2)_n\text{SH}$ ,  $n = 2, 7, 9,$  and  $17$ ; Figure 6, illustration A1) using He(I) UV-photospectroscopy (UPS).<sup>22</sup> A systematic decrease in the low kinetic energy (KE) edge with an increase in the alkyl chain length of the adsorbates was observed in the

UV photoemission spectra (Figure 6, plot A2). These studies allowed an estimation of the difference in the work function ( $\Delta W$ ) between bare and SAM-modified gold surfaces (Figure 6, diagram A3), thereby demonstrating the effect of dipole direction and magnitude from an array of adsorbate dipoles on the work function of metals. In separate studies, Lee used hexadecanethiol-modified gold electrodes as the cathode for organic light-emitting diodes (OLEDs) for promoting the efficiency of the hole injection into the cathode.<sup>23</sup> In these studies, the quantum efficiency (photons/electron) of SAM-

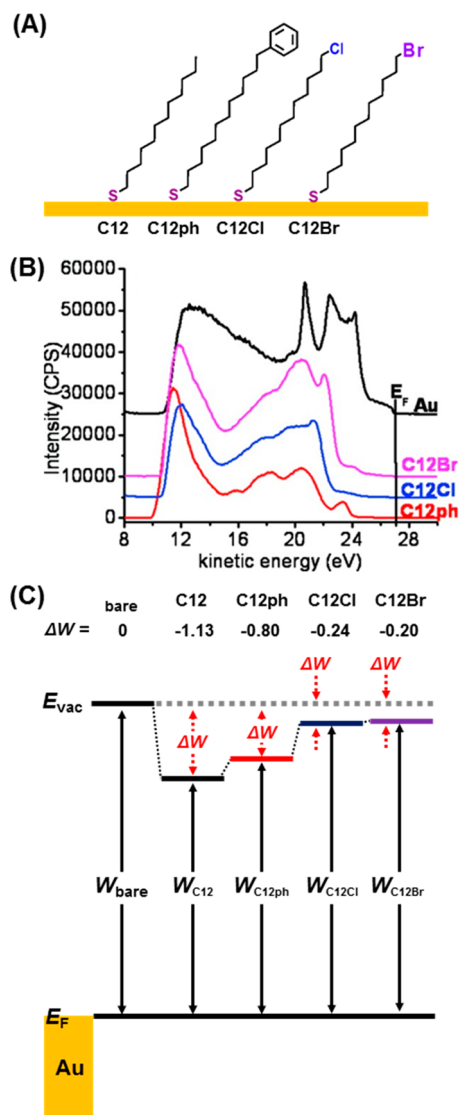


**Figure 7.** (A) Expanded view of the low KE region for UPS of clean Au and Au surfaces modified with mixtures of  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  (C16) and  $\text{CF}_3\text{CF}_2(\text{CH}_2)_{14}\text{SH}$  (C16F2). The effective work function for the Au surface modified with 100% C16F2 is higher than for clean Au (black curve). (B) The vacuum level shift (shift in the low KE edge from part A) as a function of mol % C16F2 in the mixed-thiol films (two trials show the reproducibility of the measurements). Reproduced with permission from ref 26. Copyright 2009 American Chemical Society.

modified gold electrode-adapted OLEDs were shown to be 3 orders of magnitude higher than that in the absence of a SAM.

For exploring the influence of the direction of surface dipoles, we prepared terminally fluorinated alkanethiol adsorbates and applied them to gold surfaces to generate a series of fluorocarbon-terminated self-assembled monolayers ( $\text{CF}_3(\text{CF}_2)_n(\text{CH}_2)_{15-n}\text{SH}$ ,  $n = 0, 1, 3, \text{ and } 9$ ; Figure 6, illustration B1).<sup>22</sup> The surface dipoles for these fluorocarbon-terminated gold surfaces exhibited a polarity opposite to the surface dipoles associated with the hydrocarbon-terminated gold surfaces (i.e., those coated with  $n$ -alkanethiolate SAMs). The low kinetic energy edges of the H16- and F1H5-modified gold surfaces were lower than that of the bare gold surface (abbreviations defined in the caption of Figure 6). However, the low kinetic energy edges of F2H14-, F4H12-, and F10H6-modified gold surfaces were higher than that of the bare gold surface (Figure 6, plot B2). Figure 6, diagram B3 schematically illustrates the increase of the work function of the fluorocarbon-terminated gold surfaces with an increasing number of fluorocarbons.

Interestingly, odd–even effects were observed in the low kinetic energy edges of gold surfaces modified with a series of  $\text{CF}_3$ -terminated alkanethiols ( $\text{CF}_3(\text{CH}_2)_n\text{SH}$ ,  $n = 12\text{--}15$ ).<sup>22</sup> The difference in the low kinetic energy edge between the odd and even chains was  $\sim 0.3$  eV (odd > even). This parity effect provides further evidence that the orientation (relative to the gold surface) of the dipoles associated with the terminal  $\text{CF}_3$  groups impacts the work function of the coated gold surfaces. Separately, de Boer and co-workers examined the influence of



**Figure 8.** (A) Illustration of a series of adsorbates for self-assembled monolayers generated from  $\text{CH}_3(\text{CH}_2)_{11}\text{SH}$  (C12),  $\text{C}_6\text{H}_5(\text{CH}_2)_{12}\text{SH}$  (C12ph),  $\text{Cl}(\text{CH}_2)_{12}\text{SH}$  (C12Cl), and  $\text{Br}(\text{CH}_2)_{12}\text{SH}$  (C12Br). (B) UV photoemission spectra for clean Au and Au modified with C12, C12ph, C12Cl, and C12Br. (C) Schematic diagram of the differences in work function ( $\Delta W$ ) between bare and functionalized gold surfaces: near-surface vacuum energy;  $E_{\text{vac}}$ ; Fermi level energy;  $E_F$ , and work function;  $W$ . Reproduced with permission from ref 26. Copyright 2009 American Chemical Society.

the effective metal–sulfur dipole on the overall work function generated by thiol adsorbates.<sup>24</sup> These researchers found that the difference in the work function between 1H,1H,2H,2H-perfluorodecanethiol-modified silver and  $n$ -decanethiol-modified silver (1.7 eV) was larger than that of the work function between 1H,1H,2H,2H-perfluorodecanethiol-modified gold and  $n$ -decanethiol-modified gold (1.4 eV). The investigators noted that this result was a consequence of the Ag–S dipole moment being larger than the Au–S dipole moment for these SAM-modified metal surfaces. Their studies also led to the elimination of the hole-injection barrier in a polymer light-emitting diode by using the high work function 1H,1H,2H,2H-perfluorodecanethiol-modified silver surface as an anode.

Alloway et al. demonstrated continuous modulation of the work function of gold surfaces using mixed self-assembled



monolayers.<sup>26</sup> The low kinetic energy edge was precisely tuned by changing the ratio between  $\text{CH}_3(\text{CH}_2)_{15}\text{SH}$  (**C16**) and  $\text{CF}_3\text{CF}_2(\text{CH}_2)_{14}\text{SH}$  (**C16F2**) (Figure 7A). The linear relationship between the vacuum level shift of the work function and the percentage of **C16F2** in the mixed SAMs is shown in Figure 7B. The work function of a 100% **C16**-modified gold surface is lower than that of the bare gold surface by  $\sim 1.2$  eV, whereas the work function of a 100% **C16F2**-modified gold surface is higher than that of a bare gold surface by  $\sim 0.2$  eV, allowing modulation of the work function within the range of 1.4 eV.

In related work, Tao and co-workers used SAMs generated from a mixture of  $\text{CH}_3(\text{CH}_2)_9\text{SH}$  (**HDT**) and  $\text{CF}_3(\text{CF}_2)_7(\text{CH}_2)_2\text{SH}$  (**FDT**) to tune the work function of silver.<sup>27</sup> These researchers explored the work function of SAM-modified silver surfaces modulated by changing the ratio between **HDT** and **FDT** within the range of 1.7 eV and also demonstrated the current density of hole-only devices having a configuration of *mixed SAM-modified Ag electrode/organic active layer/bare Ag electrode*, where the composition of the SAMs were systematically varied by the molar ratio of the two adsorbates on the silver surfaces.

The effect of interfacial dipoles associated with phenyl-, chlorine-, and bromine-terminated SAM-modified gold surfaces on the work function was investigated using UPS (Figure 8A).<sup>26</sup> The shifts in the low KE edge of all of the substituted alkanethiol-modified gold surfaces were less negative than that of the *n*-alkanethiol-modified gold surface in the spectra (Figure 8B). The electronegative character of the tailgroups of the adsorbates affected the net magnitude of the dipole moment of the SAM layer, which led to the work functions of the phenyl-, chlorine-, and bromine-terminated SAM-modified gold surfaces being larger than those of the *n*-alkanethiol-modified gold surface (Figure 8C). Taken as a whole, these studies show the effect of the properties of substituents on the work function as well as the importance of the surface dipoles.

## CONCLUSIONS

This Account examined the impact of surface dipoles on the physical properties of interfaces. We showed that the orientation and intensity of *interfacial* dipoles can be tuned by changing the chemical composition and the number of methylenes (odd or even) of the alkyl chains of the alkanethiolate adsorbates used to form SAMs on gold surfaces. As a consequence, the wettability of these surfaces was significantly influenced by the molecular structure of the adsorbates. Interestingly, the wettability of SAM surfaces was also shown to be sensitive to the polarity of an array of interfacial dipoles, as demonstrated by the contact angle data collected for polar protic liquids on partially fluorinated hydrocarbon SAMs bearing either a terminal FC–HC or HC–FC dipole, whereas the work function was affected by the magnitude as well as the direction of the net *adsorbate* dipole moment, including the dipole moment associated with the sulfur–metal bond. In future studies, we will examine the influence of surface dipoles on interfacial properties as a function of various adsorbate headgroups (e.g., thiol, dithiocarboxylate, thiocarbamate, and xanthate) and substrate compositions (e.g., gold, silver, and underpotentially deposited metals).

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### Notes

The authors declare no competing financial interest.

### Biographies

**Han Ju Lee** was born in Chungjusi, South Korea, in 1973. He received a B.S. degree (with top honors) in chemistry from the University of Suwon (South Korea) in 1999 under the direction of Professor Yong-Chan Chung and an M.S. in Chemistry from Sogang University in 2001 under the guidance of Professor Kyung Byung Yoon. After receiving his degree, he developed materials, devices, and processes for liquid crystal displays at Samsung Electronics Co., Ltd., for 9 years. He obtained a Ph.D. degree in Chemistry in 2015 under the guidance of Professor Lee with a research focus on functionalized organic thin films and nanoparticle protectants.

**Andrew C. Jamison**, originally from Shreveport, Louisiana, spent his youth in Houston, TX. 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 a B.S. and Ph.D. degree in Chemistry, the latter under the guidance of Professor 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 Prof. George Whitesides. His postdoctoral research was conducted at Caltech under the supervision of Prof. 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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