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The Wetting of Monolayer Films Exposing Ionizable Acids and Bases[1]

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This paper describes the wetting by water of monolayer films formed by the spontaneous assembly of long-chain alkanethiols, $HS(CH_2)_{10}X$, onto gold surfaces, where X = carboxylate, phosphonate, 5-tetrazolo, 1-imidazolo, or 2-imidazolo. Monolayers were also generated from mixtures of $HS(CH_2)_{10}X$ and $HS(CH_2)_{10}CH_3$. The wetting by water of the single-component and the mixed surfaces was examined as a function of pH. The surfaces uniformly became more wettable at values of pH at which the interfacial groups were charged. Surfaces rich in carboxylic acid groups exhibited an unexpected behavior: the surfaces were less wettable at values of pH between 3 and 7 than at lower or higher values of pH. We attribute this unexpected behavior to conformational changes of the terminal parts of the chain including the carboxylate groups upon partial ionization.

Introduction

Long-chain alkanethiols adsorb onto the surface of gold and form densely-packed, well-ordered monolayer films.[3] The synthesis of thin films using this method permits atomic-level control over the structure and composition of the exposed interface. These thin films are useful for studying a variety of phenomena such as wetting, adhesion, lubrication, and resistance to corrosion. Examining, for example, the wetting of terminally functionalized alkanethiols adsorbed on gold provides a convenient system for studying the fundamentals of ionization of protic acids and bases at the interface between organic solids and water.[4] A knowledge of interfacial acid–base interactions is useful for understanding phenomena such as protein folding,[5] enzymatic catalysis,[6] and the stability of colloids.[7]

Our interest in the wettability of ionizable surfaces began with studies of the wetting of oxidatively functionalized polyethylene ($PE\text{-}CO_2H$).[8-13] These surfaces contained a mixture of polar functionalities, especially carboxylic acid and ketone or aldehyde groups; the acid groups could be derivatized to attach basic moieties. The wettabilities of these surfaces were measured as a function of the pH of the contacting drop of buffered water. Surfaces that contained no ionizable groups were equally wettable at all values of pH, but those that contained ionizable groups became more wettable as they became more ionized. For example, the advancing contact angle of buffered water on $PE\text{-}CO_2H$ was independent of pH at pH 1–5, decreased between pH 5 and 11, and again became independent of pH at pH 11–13.[8,12] Surfaces that contained basic moieties displayed on analogous but opposite trend (that is, the surfaces became more wettable at low pH).[12] We called this type of study a "contact angle titration", and used it to infer values of $pK_{1/2}$ ($pK_{1/2}$ is analogous to pK_a in solution and is defined as the value of the pH of the solution at which the functional groups at the interface are half-ionized).[8,12] For surfaces containing carboxylic acids, values of $pK_{1/2}$ were 3–5 pH units higher than the corresponding values of pK_a; for surfaces containing basic moieties, values of $pK_{1/2}$ were 3–5 pH units lower than the corresponding values of pK_a.[8,12] We attributed the shift in $pK_{1/2}$ relative to pK_a to the difficulty of forming charges at the interface (due perhaps to a low interfacial dielectric constant and/or charge–charge interactions).[8,12]

We subsequently examined the wettability of monolayer films formed by the self-assembly of mixtures of $HS(CH_2)_{10}CO_2H$ and $HS(CH_2)_{10}CH_3$ onto gold.[14] In these films, the carboxylic acid groups were exposed at the outer interface and were surrounded largely by other carboxylic acid groups, by methyl groups, or by mixtures of the two depending on the mole fractions of the two components. We measured the wettability of these surfaces as a function of the pH of the contacting drop of buffered water and found that, as with $PE\text{-}CO_2H$, the advancing contact angle of buffered water was independent of pH at low pH, and to decrease at intermediate values of pH. Unlike $PE\text{-}CO_2H$, however, the monolayer films did not become independent of pH at high values of pH. The surfaces did not "titrate", and we were thus unable to infer values of $pK_{1/2}$, although we were able to infer values of pH at which ionization first occurred.

The work in this paper was motivated by the following questions concerning the titration behavior of monolayer films: (1) Do acid groups with different compositions exhibit titration behavior in SAMs that is similar to that of carboxylic acids? (2) Do ionizable bases positioned at the surface of a monolayer exhibit titration behavior that is analogous but opposite to that of carboxylic acids?

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(2) RIC is an NIH Postdoctoral Fellow (NIH GM-13678).

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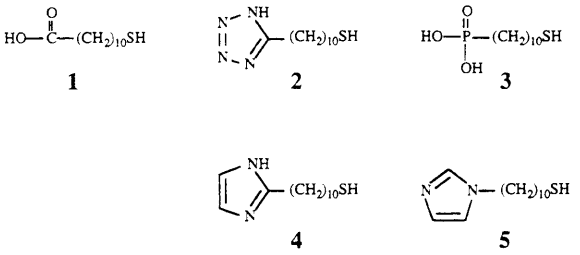
We used the following strategy in an attempt to resolve these questions. First, we synthesized two new alkanethiols having different types of acidic ω-termini: $HS(CH_2)_{10}X$, where X = 5-tetrazolo (**2**) and phosphonate (**3**) instead of carboxylate (**1**). Second, we synthesized two new alkanethiols having basic ω-termini: $HS(CH_2)_{10}X$, where X = 2-imidazolo (**4**) and 1-imidazolo (**5**). Third, we



1 **2** **3**

4 **5**

generated monolayer films from each of these molecules by exposing gold surfaces to ethanolic solutions of the molecules. Fourth, we characterized the composition and thickness of the monolayer films by XPS and examined their titration behavior in the usual way.

We chose the 5-tetrazolo group as an alternative acidic moiety for three reasons: (1) the pK_a of 5-alkyltetrazoles (*ca.* 5.5)[15] falls conveniently within the range of measurement using contact angle titration; (2) since the values of pK_a of 5-tetrazolo groups and carboxylic acid groups are similar, major differences in the titration behavior of carboxylic acid and tetrazole surfaces could not be attributed to differences in pK_a; (3) the 5-tetrazolo group is similar in structure to the 2-imidazolo group. This latter feature facilitates comparison between acidic and basic surfaces.

We chose the phosphonic acid group as an alternative acidic moiety because we wished to examine the wettability of a surface composed of a diprotic acid having values of pK_a that fall within the experimental range of measurement using contact angle titration. The phosphonic acid group meets these criteria because its first and second values of pK_a are *ca.* 3 and 8, respectively.[16]

We chose the 2-imidazolo group as a basic moiety for three reasons. First, since 2-imidazolo groups are less basic than amines, we expected them to be less reactive surface species (especially toward atmospheric carbon dioxide) than amines.[17] Second, the pK_a of 2-alkylimidazoles (*ca.* 8.0)[18] falls within the range of measurement using contact angle titration. Third, attachment of a long hydrocarbon chain to the 2-position of the imidazole was likely to inhibit coordination of the imidazole nitrogens (rather than the thiol) to the gold surface. We thus expected these molecules to generate monolayers of the desired configuration.

Finally, we chose the 1-imidazolo group as a basic moiety for the following reasons: (1) we wished to examine the titration behavior of a second basic surface, and we believed that monolayers derived from the 1-imidazolo isomer would provide a good comparison to those derived from the 2-imidazolo isomer; (2) the synthesis of long-chain alkanethiols having 1-imidazolo groups at the ω-terminus appeared to be relatively simple; (3) the pK_a of 1-alkylimidazoles (*ca.* 7.3)[18] falls within the range of measurement using contact angle titration.

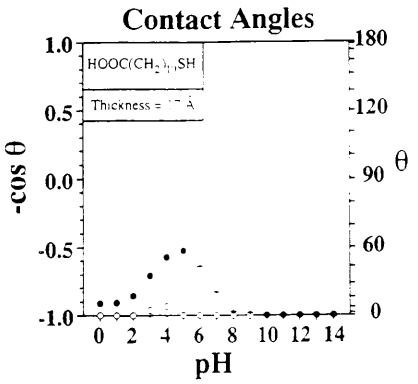


Figure 1. Advancing (●) and receding (○) contact angles measured under cyclooctane on monolayers generated from **1** plotted as a function of the pH of the aqueous buffered drop. The + symbol indicates sessile rather than advancing contact angles (please see the text). The thickness of the monolayers was determined by XPS.

Results

Measurement of Contact Angles. In this paper we report contact angles, θ, that are measured not in air, but rather under an inert, immiscible solvent, cyclooctane. Measuring contact angles under cyclooctane raises them to values that can be measured accurately.[19] Obtaining contact angles in air for SAMs that present very hydrophilic functionalities at the air/monolayer interface is impossible because in air these surfaces are wet by water at all values of pH. Cyclooctane was chosen because it raises the contact angle more than other potentially suitable liquid hydrocarbons and because it can be obtained in high purity at low cost.[20] Additionally, measurement of contact angles under cyclooctane reduces the rate at which the acidic and basic surfaces contaminate. In air the rate of contamination of these surfaces is rapid.

We note here an interesting phenomenon observed on these SAMs: in some of the measurements of advancing contact angles, the advancing edge of the drop continued to move forward after the addition of water to the drop was halted. Initially, the edge of the drop advanced forward across the surface rapidly, and then slowed until it eventually stopped after *ca.* 5 min. Due to the difficulty of measuring accurate advancing contact angles under these circumstances, we report sessile contact angles (that is, the contact angles measured ≥5 min after the addition of water to the drop) instead. We apply the term reactive spreading to describe this behavior.

Acidic Surfaces: Carboxylic Acid Groups. Figure 1 summarizes the contact angle titration of the acidic surface generated from **1**. The receding angles for this surface are zero or near zero for all values of pH. The advancing angles, however, exhibit an unusual trend: at very low pH, the surface is quite wettable, but becomes less wettable up to pH 5; as the pH is increased further, the surface becomes progressively more wettable until it is completely wetted at pH ≥ 10. In past studies of the

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(16) The values of pK_a for phosphonic acids, $R-PO_3H_2$, are typically 2.8 and 8.2 (*Critical Stability Constants*; Smith, R. M., Smith, A. E., Eds.; Plenum: New York, 1989; Vol. 6, p 359–365. Perrin, D. D. *Dissociation Constants of Organic Acids in Aqueous Solution*; Butterworths: London, 1965.

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(20) In ref 14, other liquids were surveyed, including hexadecane, hexane, isooctane, cyclohexane, *cis/trans*-decalin, bicyclohexyl, toluene, benzonitrile, nitrobenzene, butyl acetate, butyl ether, and *o*-dichlorobenzene.

advancing contact angles of water on surfaces of carboxylic acids,[8-14] we have interpreted the greater wettability at high pH to indicate the degree of ionization of the surface: as the surface becomes ionized, it becomes more wettable. We believe this interpretation is also true for the surface generated from 1. The wettability of this surface at pH $\leq$ 5 requires, however, a different rationalization. The following paragraphs describe the several studies that we undertook in an effort to understand the observed "hump" in the titration curve.

First, we questioned whether the hump resulted from interactions between the surface and the species used to buffer the aqueous drop. In an effort to answer this question, we examined the contact angles of drops containing various buffers at a concentration of 0.05 M at the following values of pH: 4 (acetate, phthalate); 7 (phosphate, Tris, HEPES); 10 (borate, carbonate). The type of buffer used had no influence on the observed contact angles. We also questioned whether the hump depended on the ionic strength of the species used to buffer the aqueous drop. We examined the contact angles of drops containing acetate buffer (pH 4), phosphate buffer (pH 7), and borate and carbonate buffers (pH 10) at concentrations of 0.05 and 0.5 M. At pH 4, 7, and 10, the contact angles were indistinquishable at both concentrations of the buffers. Corrosion of the surface by contacting acidic drops probably does not cause the hump because we did not observe humps in the titrations of any of the surfaces containing ionizable groups other than carboxylic acids (*vide infra*). Also, pH 0 and pH 1 solutions composed of sulfuric acid gave results indistinquishable from those obtained with solutions containing HCl. Taken together, these observations suggest that the hump is a real phenomenon rather than an experimental artifact.

In a second set of experiments, we investigated the possibility that the hump results from conformational constraints placed on the carboxylate headgroup by the length of the alkyl chain (i.e., an "odd–even" effect on the orientation of the headgroup).[21] Since the contact angle titration in Figure 1 was conducted on a monolayer having an even number of methylene groups (11-mercaptoundecanoic acid), we examined the contact angle titration of a monolayer having an odd number of methylene groups (16-mercaptohexadecanoic acid). The contact angle titrations on these two surfaces were indistinguishable. We thus conclude that the hump in the titration curve is independent of the chain length of the alkanethiol and that it does not result from an "odd–even" effect.[21]

In a third set of experiments, we investigated the possibility that the hump depends on the cant angle of the alkyl chains in the monolayer film. In self-assembled alkanethiol monolayers on gold, the alkyl chains are tilted *ca.* 27° from the normal to the surface.[22] On silver, however, the alkyl chains are tilted *ca.* 12° from the normal to the surface.[22] We compared the contact angle titrations of monolayer films formed from 11-mercaptoundecanoic acid on silver and on gold, and again found them to be indistinguishable. We thus conclude that the hump is independent of the cant angle of the self-assembled monolayer.

Lastly, we examined the morphology and behavior of the buffered aqueous drops contacting the surfaces. At pH < 5, the drops were spherical, well-defined and stable.

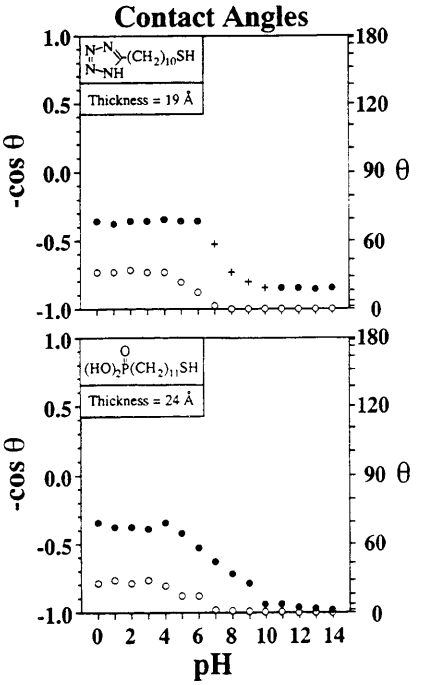

Figure 2. Advancing (●) and receding (○) contact angles measured under cyclooctane on monolayers generated from **2** (top) and **3** (bottom) plotted as a function of the pH of the aqueous buffered drop. The + symbol indicates sessile rather than advancing contact angles (please see the text). The thickness of the monolayers was determined by XPS.

At pH > 8, reactive spreading of the drops was apparent. No reactive spreading occurred at pH < 5.

Acidic Surfaces: Tetrazole and Phosphonic Acid Groups. Figure 2 summarizes the contact angle titrations of the surfaces composed of the tetrazole (**2**) and the phosphonic acid (**3**) moieties. The contact angle titration for the tetrazole **2** resembles the titration curve of an acid in solution and is similar to the advancing contact angle titration previously observed for oxidatively functionalized polyethylene (PE-CO_2H). From the advancing contact angles, we can infer a value of *ca.* 7.5 for $pK_{1/2}$ for the tetrazole. This value is approximately 2 units higher than the measured pK_a of 5-methyltetrazole ($pK_a = 5.5$).[15] The contact angle titration of the surface generated from the phosphonic acid **3** (Figure 2) shows that this surface is generally less wettable than the surface of the carboxylic acid but more wettable than the surface of the tetrazole. Because the advancing contact angles approach (or become) zero at high pH, we cannot infer a value of $pK_{1/2}$ for the monocomponent SAM of **3**. Neither the phosphonic acid nor the tetrazole shows a hump in the titration curve.

Mixed Surfaces with Acidic and Methyl Groups. Figure 3 shows the contact angle titrations of several mixed surfaces of carboxylic acid and methyl groups. As expected, the wettability of these surfaces increases with increasing mole fraction of carboxylic acid in the SAM. In the mixed SAMs with a mole fraction of at least *ca.* 60% carboxylic acid, the hump between pH 3 and pH 7 that we observed in the profile of the advancing contact angle titrations for the monocomponent SAMs of carboxylic acids is present. At mole fractions corresponding to less than *ca.* 60% carboxylic acid, however, the titration profile exhibits no hump: the advancing contact angles are constant at low pH, and steadily decrease through pH 14 without leveling off. These latter surfaces, composed of a lower mole fraction of carboxylic acid groups, show that the onset of ionization appears to occur somewhere in the

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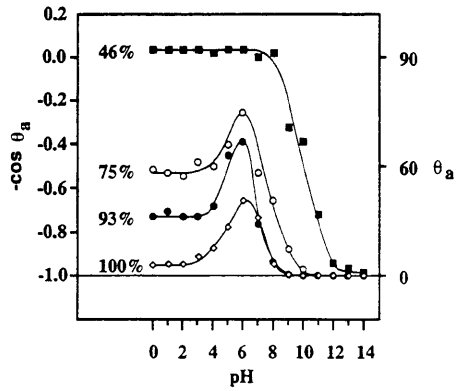


Figure 3. Advancing contact angles of buffered aqueous solutions measured with drops under cyclooctane on mixed monolayers of $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}COOH$, plotted as a function of pH. The curves are labeled by the proportion of the chains in the monolayers that were terminated by a carboxylic acid group. The composition and thickness of the monolayers were determined by XPS. The size of the symbols gives our best estimate of the error of the measurement. The lines drawn through the points are intended to serve as a guide to the eye.

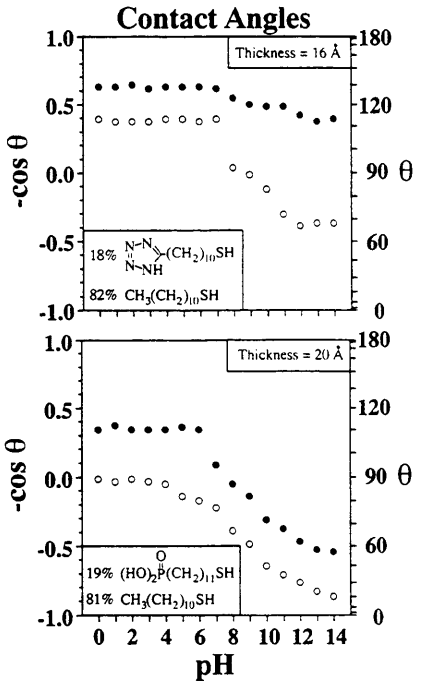


Figure 4. Advancing (●) and receding (○) contact angles measured under cyclooctane on monolayers generated from mixtures of $HS(CH_2)_{10}CH_3$ and **2** (top) or **3** (bottom) plotted as a function of the pH of the aqueous buffered drop. The composition and thickness of the monolayers were determined by XPS.

range pH 6–8, which is 2–4 units above the pK_a of simple carboxylic acids in solution.

Figure 4 shows the advancing and receding contact angles for the SAMs composed of mixtures of tetrazoles and methyl groups and SAMs composed of mixtures of phosphonic acids and methyl groups. The profiles of both the advancing and receding contact angles for these mixed surfaces is shifted to high pH relative to that of the monocomponent surfaces of the acids. For the case of the mixed SAM of the tetrazole and methyl groups, the data in Figure 4 might be interpreted to indicate that the $pK_{1/2}$ for the mixed surface ($pK_{1/2} \sim 10$) is higher than that for the monocomponent surface of the tetrazole ($pK_{1/2} \sim 7.5$).

Basic Surfaces: 2-Alkyl- and 1-Alkylimidazoles. Figure 5 shows the contact angle titrations of the surfaces

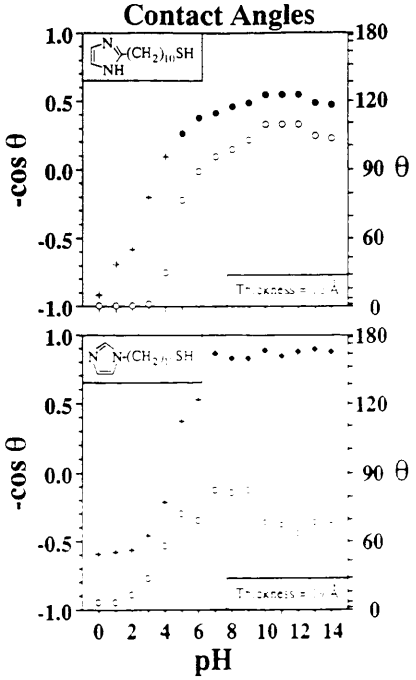


Figure 5. Advancing (●) and receding (○) contact angles measured under cyclooctane on monolayers generated from **4** (top) and **5** (bottom) plotted as a function of the pH of the aqueous buffered drop. The thickness of the monolayers was determined by XPS.

of the imidazoles. For the surface generated from 2-(10-mercaptodecyl)imidiazole (**4**), the data are qualitatively opposite that for the acidic surfaces: the surface becomes progressively more wettable with *decreasing* pH. We interpret this behavior to indicate that as the degree of ionization of the surface increases (in this case, the surface becomes positively charged), the wettability increases.

Since the outermost part of this surface is composed of the relatively nonpolar hydrocarbon portion of the imidazole groups, it is not surprising that this surface is generally less wettable than any of the single component acidic surfaces. Two common features shared by the single component acidic surfaces and this surface are that (1) it is not possible at all values of pH to measure advancing contact angles because of the dynamic behavior of the drop (*vide supra*) and (2) the receding contact angles become zero upon extensive ionization of the surface.

The profiles of the advancing and receding contact angles on this surface suggest that the onset of ionization occurs between pH 9 and 10. This value seems reasonable given that the pK_a of 2-methylimidazole is 8.0.[18] The advancing and receding contact angles also indicate that the wettability of the surface generated from **4** is slightly greater at pH 13–14 than at pH 10–12. The greater wettability at very high pH might result from the partial formation of imidazole anion under these conditions.[23]

Figure 5 also shows the contact angle titration of the surface generated from 1-(10-mercaptodecyl)imidazole (**5**). This surface exhibited anomalous wetting behavior: advancing contact angles measured in the range pH 7–14 were ill-defined because the drop would not readily wet the surface; receding contact angles in the range pH 10–14 were ill-defined because the drop would not readily retreat across the surface. This unusual behavior is due perhaps

(23) For 2-alkylimidazoles, the acidic pK_a is *ca.* 15: Grimmet, M. R. *Adv. Heterocycl. Chem.* **1980**, *27*, 241–326.

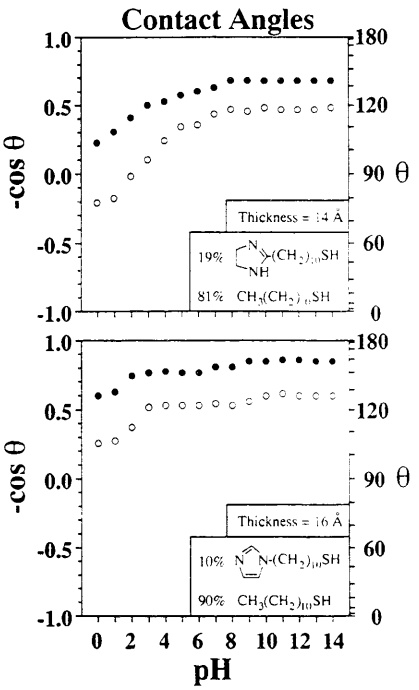


Figure 6. Advancing (●) and receding (○) contact angles measured under cyclooctane on monolayers generated from mixtures of $HS(CH_2)_{10}CH_3$ and **4** (top) or **5** (bottom) plotted as a function of the pH of the aqueous buffered drop. The composition and thickness of the monolayers were determined by XPS.

to carboxylation of the exposed imidazole nitrogen.[24] Despite the anomalies, these data show that the surface is most wettable at low pH and are thus consistent with our hypothesis that the surface becomes more wettable as the degree of ionization increases. We are hesitant to draw further conclusions regarding the surfaces generated from **5**.

Mixed Surfaces with Basic and Methyl Groups. Figure 6 summarizes the contact angle titrations of SAMs composed of mixtures of imidazoles and methyl groups. In contrast to the single component surface generated from **4**, the mixed surface does not exhibit an increase in wettability at pH 13 and 14. Presumably, the presence of the hydrophobic methyl groups disfavors the formation of an imidazole anion at these values of pH.

An examination of the profile of the advancing contact angles shows constant values at high pH and steadily decreasing values from pH 7 through pH 0 without leveling off. The profiles of the receding contact angles for this mixed surface are qualitatively similar. The behavior of these basic surfaces is consistent with the analogous but opposite behavior we observed on several of the acidic surfaces (at high pH, the receding contact angles became constant even though the advancing contact angles continued to decrease with increasing pH, *vide supra*).

By examining the value of pH at which these surfaces become more wettable (as judged from both the advancing and receding contact angles), we infer that the onset of ionization occurs somewhere between pH 6 and 8. In contrast, the onset of ionization for the surface generated solely from **4** occurs between pH 9 and 10 (*vide supra*). This observation suggests that the mixed surface is less basic than the single-component surface.

The contact angle titration in Figure 6 for the mixed surface composed of 1-(10-mercaptodecyl)imidazole and methyl groups is better behaved than that of the monocomponent surface (see Figure 5) composed of 1-(10-mercaptodecyl)imidazole.[25] It is also qualitatively similar to that observed for the mixed surface composed of 2-(10-mercaptodecyl)imidazole and undecanethiol: the wettability is constant at high pH, and then increases with decreasing pH (except at pH 0–1 where both the advancing and the receding contact angles appear to be leveling off). The onset of ionization is difficult to discern from the titration profiles, but it appears to occur somewhere between pH 2 and 10. The pK_a of 1-methylimidazole (7.3)[18] falls within this range.

Discussion

Table 1 summarizes the data from the contact angle titrations of the surfaces examined in this study. With the exception of the surfaces composed of tetrazoles, we cannot directly infer values of $pK_{1/2}$ from the titration curves because we cannot determine with confidence the pH at which complete ionization occurs. For example, the acidic surfaces typically display maximum wettabilities at or near pH 14, and the basic surfaces typically display maximum wettabilities at or near pH 0. Nevertheless, we can estimate minimum (for acidic surfaces) and maximum (for basic surfaces) values of $pK_{1/2}$ by assuming complete ionization at these outer limits. Most of the values of $pK_{1/2}$ in Table 1 were estimated using this assumption.

Figures 1–6 and the data in Table 1 illustrate some of the general themes that have emerged from our investigations. The following paragraphs outline these themes and briefly discuss them.

(*1*) *Ionization of the surfaces increases their wettabilities.* The titration profiles on all of the acidic surfaces examined in this study exhibit an increase in wettability at pH > pK_a. Conversely, the titration profiles on all of the basic surfaces exhibit an increase in wettability at pH < pK_a. We believe that these increases in wettability correspond to ionization of the surfaces: acidic surfaces become more wettable as they become more negatively charged; basic surfaces become more wettable as they become more positively charged.

(*2*) *For acidic surfaces, the value of $pK_{1/2}$ is at least 2 pH units higher than the solution pK_a. For basic surfaces, the value of $pK_{1/2}$ is at least 2 pH units lower than the solution pK_a.* The fact that for acidic surfaces $pK_{1/2} > pK_a$ and that for basic surfaces $pK_{1/2} < pK_a$ probably reflects the greater difficulty of forming charged species at the solid/liquid interface than in water. This difficulty may be due, at least in part, to the relatively low dielectric of the underlying alkyl chains. Independent support for this hypothesis can be found by comparing the values of $pK_{1/2}$ of the pure acidic surfaces to those of the mixed surfaces composed of acidic and methyl groups: for the two examples that we have, the values of $pK_{1/2}$ for the mixed surface (lower dielectric) are greater.

A recent paper by Bryant and Crooks reported the use of differential interfacial capacitance to determine values of surface pK_a (i.e., $pK_{1/2}$) for monolayer films generated by exposing either 4-mercaptopyridine or 4-aminothiophenol to the surfaces of gold electrodes.[26] Using this technique, the authors determined that values of $pK_{1/2}$ for basic functionalities were 2–3 pH units *higher* than values of pK_a for these molecules in solution. Our results, however, suggest that for basic surfaces values of $pK_{1/2}$ should be *lower* than values of pK_a. The discrepancy between the apparent pK_a's of ionizable groups at a surface

(24) Analysis by XPS indicated that the ratio of excess oxygen to nitrogen (O/N) was 3:1. We did not detect excess oxygen in any other surfaces.

(25) Analysis of the mixed surface by XPS shows no excess oxygen.

(26) Bryant, M. A.; Crooks, R. M. *Langmuir* **1993**, *9*, 385–387.

Table 1 [a]

surface	θ_{max},[b] deg advancing	θ_{max},[b] deg receding	ΔpH[c]	onset of ionization (pH)[d] advancing	onset of ionization (pH)[d] receding	pH at θ_{min}[e] advancing	pH at θ_{min}[e] receding	$pK_{1/2}$[f] advancing	$pK_{1/2}$[f] receding	pK_a
carboxylic acid	50–60	10–20	↑	...	...	10 (0°)	...	...	...	4.5[g]
(23% carboxylic acid)	115	92	↑	7–8	6–7	14 (84°)	12 (46°)	10.5	9.5	4.5[g]
5-tetrazole	73	43	↑	6–7	4–5	10 (33°)	8 (0°)	7.5	...	5.5[h]
(18% 5-tetrazole)	132	113	↑	7–8	7–8	13 (113°)	12 (68°)	9.5	9.5	5.5[h]
phosphonic acid	70	40	↑	4–6	3–5	12 (10°)	9 (0°)	7.0	...	2.8, 8.2[i]
(19% phosphonic acid)	112	89	↑	6–7	4–5	14 (57°)	14 (30°)	8.5	8.0	2.8, 8.2[i]
2-imidazole	124	108	↓	9–10	9–10	0 (25°)	2 (0°)	3.0	...	8.0[j]
(19% 2-imidazole)	133	118	↓	7–8	7–8	0 (112°)	0 (78°)	2.5	3.0	8.0[j]
1-imidazole	...	...	↓	...	...	...	...	...	...	8.0[j]
(10% 1-imidazole)	148	127	↓	1–9	2–10	0 (126°)	0 (115°)	2.0	2.5	8.0[j]

[a] The symbol (...) indicates entries for which we were unable to obtain unambiguous values. [b] The value of the maximum observed contact angle. [c] The direction from which to view the titration profile in order to discern the onset of ionization. [d] The value of pH at which the surface becomes more wettable. [e] The value of pH at which the contact angles reach a minimum value when viewed from the direction indicated by the column ΔpH. [f] The value of pH at which the surface is half-ionized. The values reported (except for the tetrazole surfaces) are estimates (please see the text). [g] Reference 14. [h] Reference 15. [i] Reference 16. [j] Reference 18.

obtained from capacitance measurements and from contact angle titration can be rationalized by several arguments. (i) The surface pK_a is a strong function of the electrode potential and can vary about 6 pH units with a potential range of ± 1 E_{pzc}.[26,27] Thus, depending on the conditions of the experiment, the values of pK_a obtained by capacitance measurements can be relevant to electrochemical studies but may not be relevant to the predicting the values of pK_a in organic thin films in the absence of an electrode potential. (ii) Thin films containing the types of functional groups studied by Bryant and Crooks are not well-behaved in our hands. We find that monolayers terminated with amino groups or the 1-imidazolo group undergo rapid contamination (as determined by XPS). (iii) The relatively thin films used by Bryant and Crooks might permit interactions between the basic groups and the surface that are not possible in our thicker films. Direct electrostatic interactions between the basic moieties and the surface (via conjugation) are possible in the films studies by Bryant and Crooks; this type of communication is not possible in our films.

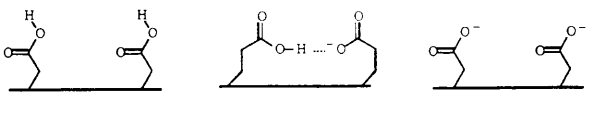
(3) Surfaces of tetrazoles exhibit titration profiles resembling those typically obtained for simple acids and bases in solution. All other surfaces examined in this study exhibit broad titration profiles having no discernible endpoints. Our model for these surfaces is based on the idea that their behavior is analogous to polyprotic acids in solution: the charge–charge repulsion that builds up as the extent of ionization increases causes a shift in the apparent pK_a toward higher values (for acidic surfaces) or lower values (for basic surfaces). Similar phenomena involving carboxylic acid groups forced into close proximity have been observed in solution.[28]

Why do the surfaces containing tetrazole groups behave differently? The answer to this question is not obvious to us, but we do know that the different behavior probably does not arise from structural or steric phenomena: surfaces generated from the structurally similar 2-imidazolo derivatives do not exhibit "well-behaved" titration profiles.

(4) The titration profiles in Figures 1 and 3 of surfaces exposing high concentrations of COOH groups exhibit a "hump": the hump probably arises from conformational changes of the carboxylate groups upon partial ionization. We have made several observations that help us to understand the nature of the hump: (i) It is observed on surfaces composed of >60% carboxylic acid groups. Surfaces composed of lower concentrations of carboxylic acid groups do not have a hump in the titration curve. (ii) It is independent of the composition and ionic strength of the buffer, the length of the underlying alkyl chain (and the consequent orientational differences arising from odd or even numbers of methylene units in these chains), and the cant angle of the monolayer film (SAMs of 1 on silver titrate in identical fashion SAMs of 1 on gold). (iii) It is associated with a marked difference in the morphology of the drop of aqueous buffer in contact with the surface at pH 0–5 in comparison to that observed at pH 8 and above. (iv) It is not observed on any other surfaces, acidic or basic.

We offer two hypotheses to rationalize the existence of the hump. The first hypothesis (the disorder hypothesis) proposes that the onset of ionization induces a sufficient degree of disorder in the monolayer to cause hydrophobic methylene groups to be exposed at the surface (or more correctly, for the hydrophilic COOH and COO–groups to be less exposed). In the absence of unforeseen structural or steric effects, however, induced disorder of this type should be possible for the other ionizable surfaces that we have examined.

The second hypothesis, which we favor, proposes that the hump results from stable hydrogen bonding at intermediate values of pH, which results in the exposure at the surface of carbonyl groups or methylene groups rather than the more hydrophilic COOH or COO– groups. At low pH, the acid groups exist predominantly as the fully protonated species 6. At high pH, however, the acid



6 7 8

groups exist predominantly as the fully deprotonated and negatively charged carboxylate ion 8. The acid and the carboxylate anion are able to form stable hydrogen bonding pairs when the two species are together present on the surface. Therefore, at intermediate values of pH, the formation of stable hydrogen bonds between these species (e.g., 7) would effectively remove both of these hydrophilic groups from the interface and expose instead the more hydrophobic carbonyl or methylene groups.

The titration curves of the surfaces of the phosphonic acid, tetrazole, or the imidazoles do not exhibit a hump. At present we do not understand why these other ionizable surfaces do not show the same bahavior as the surface composed of carboxylic acids. Compared to surfaces of

(27) Smith, C. P.; White, H. S. *Langmuir* **1993**, *9*, 1–3.
(28) Rebek, J., Jr.; Duff, R. J.; Gordon, W. E.; Parris, K. *J. Am. Chem. Soc.* **1986**, *108*, 6068–6070.

carboxylic acids, the surfaces of tetrazoles and imidazoles have tail groups that are larger and less wettable. The wettability of the phosphonic acid, a diprotic acid, probably reflects the presence of P–OH groups at the surface. SAMs of phosphonic acids are not, however, more wettable than SAMs of carboxylic acids. This result, surprising given the pK_a of phosphonic acids in solution and the possibility of having a greater charge density with this group, suggests that inferring properties of these organic interfaces based on their behavior in solution is not always straightforward. This study nevertheless underscores the usefulness of the application of SAMs of alkanethiolates on gold to the synthesis of organic interfaces with a wide range of ionizable functionality.

The work in this paper provides answers to the two questions raised in the Introduction: (1) Acid groups with different compositions exhibit titration behavior in SAMs that is similar, but not identical, to that of carboxylic acids. (2) Ionizable bases positioned at the surface of a monolayer exhibit titration behavior that is analogous but opposite to that of ionizable acids.

Experimental Section

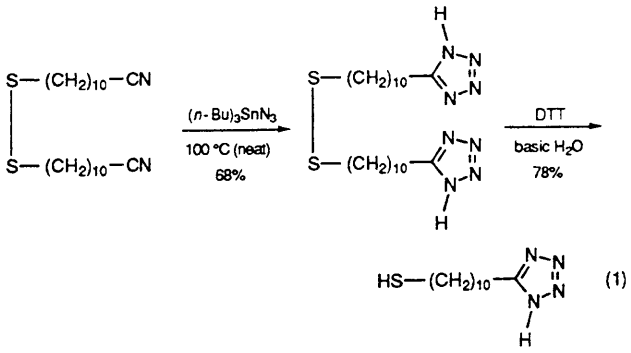
General Information. Ethanol was purchased from either USI or Pharmco and was purged with argon before use. Cyclooctane (Aldrich, 99+%) was saturated with H_2O before use. THF was distilled from Na/benzophenone, and stored under argon. Water (HPLC grade), HCl (0.968 N in H_2O), NaOH (0.995 N in H_2O), NaOH (0.1015 N in H_2O), 1,10-diiododecane (95%), triphenylmethyl chloride (98%), tributyltin chloride (96%), sodium azide (99%), dithiothreitol (99%), potassium *tert*-butoxide (95%), 18-crown-6 (99%), thioacetic acid (tech.), triethyl phosphite (98%), and trimethylsilyl bromide (98%) were purchased from Aldrich. Imidazole (Sigma, 99%), sodium methoxide (Fisher), and *n*-butyllithium (Matheson; 2.1 M in hexane) were used without modification. Undecanethiol was purchased from P&B, and distilled before use. 11-Mercaptoundecanoic acid, 1, was available from a previous study.[29] Tributyltin azide was synthesized according to a procedure from the literature.[30] Undecylenic bromide was purchased from P&B and used without further purification.

The surfaces of gold were prepared by electron-beam evaporation of *ca.* 2000 Å of gold (Materials Research Corp., 99.999%) onto silicon(100) wafers (Silicon Sense) which were precoated with *ca.* 100 Å of chromium (Aldrich, 99.99+%) or titanium (Johnson Mathey, 99.99%) to promote adhesion. Monolayers were formed by immersing small pieces of the freshly prepared gold-coated wafers in deoxygenated ethanolic solutions containing the appropriate thiols in millimolar concentrations. For the mixed surfaces, the molar ratio of acidic or basic thiol to undecanethiol was approximately 1:1. The gold slides were allowed to remain in the ethanolic solution for periods ranging from 15 to 48 h. After removal from solution, the slides were rinsed successively with ethanol, 0.1 N HCl (for acidic surfaces) or NH_4OH solution adjusted to pH 10 (for basic surfaces), distilled water, and ethanol. The ethanol was removed by passing a vigorous stream of N_2 over the slide.

Advancing and receding contact angles were measured under cyclooctane on static drops using a Ramé-Hart Model 100 goniometer. Contacting aqueous solutions were applied (for advancing angles) and withdrawn (for receding angles) using a Matrix Technologies Electrapipette operated at the slowest speed (*ca.* 1 μL/s). Two measurements of the contact angle were performed on opposite edges of at least two drops with the pipet tip touching the drops. The aqueous solutions used for the drops were buffered except at pH 0, 1, and 14. Unless noted otherwise, the concentration of the following buffers was 0.5 M: phosphate (pH 2 3, 6, 7, 8, 11, 12); acetate (pH 4, 5); borate (pH 9, 10); KCl (pH 13).

X-ray photoelectron spectra (XPS) were collected using a Surface Science SSX-100 X-ray photoelectron spectrometer. The compositions of the mixed surfaces were determined by XPS using a method described in a previous paper.[31] The thicknesses of the monolayers were measured by XPS relative to the thickness of a pure monolayer formed from undecanethiol (15 Å) as described previously.[32]

Synthesis of 5-(10-Mercaptodecyl)tetrazole, 2. We synthesized compound 2 using the strategy outline in eq 1.



(1)

2

10,10′-Dithiobis(undecanenitrile). This intermediate was synthesized by oxidation of 11-mercaptoundecanenitrile, a known compound.[33] In a 250-mL round-bottomed flask equipped with magnetic stirring bar, a solution of 11-mercaptoundecanenitrile (3.33 g; 16.7 mmol) in a mixture of 100 mL of methanol and 5 mL of water was oxidized to the disulfide by the slow addition of crystalline I_2 using a spatula. The oxidation was judged to be complete when the solution remained deep brown in color for 30 min. The solution was transferred to a separatory funnel using 250 mL of diethyl ether and 50 mL of water. Several drops of a saturated aqueous solution of sodium thiosulfate were added to decolorize the mixture. The organic phase was isolated, dried with $MgSO_4$, and evaporated to dryness. The crude material was chromatographed on silica gel using 4:1 hexane/diethyl ether. The fractions containing the product were collected, and the solvent was removed by evaporation to give 2.82 g (7.15 mmol; 86% yield) of 10,10′-dithiobis(undecanenitrile) as a light brown oil. ^1H NMR ($CDCl_3$; 500 MHz): δ 2.65 (t, J = 7 Hz, 4 H), 2.30 (t, J = 7 Hz, 4 H), 1.63 (sextet, J = 7 Hz, 8 H), 1.21–1.48 (m, 24 H).

5,5′-(Dithiodi-10,1-decanediyl)bis(tetrazole). This intermediate was synthesized from 10,10′-dithiobis(undecanenitrile) by modification of a procedure from the literature for the conversion of nitriles to tetrazoles.[34] A 5-mL round-bottomed flask was charged with 0.306 g (0.771 mmol) of 10,10′-dithiobis(undecanenitrile) and 0.775 g (2.33 mmol) of tributyltin azide,[30] and a magnetic stirring bar. A reflux condenser was attached, and the system was purged with argon. The flask was placed in an oil bath, and maintained at 100 °C for 10.5 h. The resulting solution consisted of a highly viscous yellow oil and was worked up by rinsing the flask with hexane, placing it in a 500-mL beaker, and carefully crushing it with a hammer. Chloroform (100 mL) and 1.0 N HCl (50 mL) were added to the beaker, and the resulting foamy white mixture was stirred vigorously for 0.5 h. The solution was transferred to a 500-mL separatory funnel using 0.1 N NaOH. The aqueous phase was adjusted to pH 9, and the mixture was shaken. After the layers separated, the aqueous phase was collected and extracted with diethyl ether (2 × 100 mL). The aqueous phase was acidified to pH 1; a white precipitate formed immediately. The precipitate was collected by suction filtration through a medium glass frit, transferred to a 25-mL round-bottomed flask, and placed under vacuum overnight. The yield

(29) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. *J. Am. Chem. Soc.* **1989**, *111*, 321–335.

(30) Kricheldorf, H. R.; Leppert, E. *Synthesis* **1976**, 329–330. **Caution:** this procedure should be performed in a well-ventillated hood to prevent exposure to HN_3.

(31) Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1989**, *93*, 1670–1673.

(32) Laibinis, P. E.; Bain, C. D.; Whitesides, G. M. *J. Phys. Chem.* **1991**, *95*, 7017–7021.

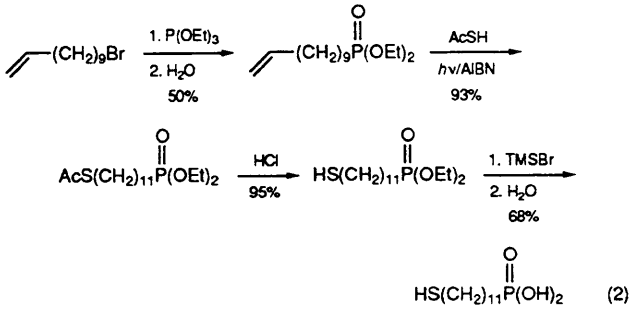
(33) Chidsey, C. E. D.; Loiacono, D. N. *Langmuir* **1990**, *6*, 682–691.

(34) Sisido, K.; Nabika, K.; Isida, T.; Kozima, S. *J. Organomet. Chem.* **1971**, *33*, 337–346. Other procedures were unsuccessful: Finnegan, W. G.; Henry, R. A.; Lofquist, R. *J. Am. Chem. Soc.* **1958**, *80*, 3908–3911. Bernstein, P. R.; Vacek, E. P. *Synthesis* **1987**, 1133–1134.

of 5,5′-(dithiodi-10,1-decanediyl)bis(tetrazole) was 0.253 g (0.524 mmol; 68%). ^{1}H NMR (DMSO-d_6; 300 MHz): δ 2.83 (t, J = 7 Hz, 4 H), 2.64 (t, J = 7 Hz, 4 H), 1.50–1.70 (m, 8 H), 1.15–1.35 (m, 24 H). ^{13}C NMR (1.2 mL of DMSO-d_6 + 0.1 mL of D_2O adjusted to pD 14; 100.6 MHz): 162.3, 38.7, 29.6, 29.47, 29.42, 29.3, 29.1, 29.0, 28.2, 25.2.

5-(10-Mercaptodecyl)tetrazole, 2. Compound 2 was synthesized by conversion of the disulfide (5,5′-(dithiodi-10,1-decanediyl)bis(tetrazole)) to the thiol using dithiothreitol (DTT). A 100-mL round-bottomed flask equipped with a magnetic stirring bar was charged with 0.152 g (0.315 mmol) of the bis(tetrazole), capped with a rubber septum, and purged with a flow of argon. A 50-mL graduated cylinder was charged with 0.292 g (1.89 mmol) of DTT, capped with a rubber septum, and purged with a flow of argon. Degassed water (50 mL) was added to the graduated cylinder, and the solution was bubbled with argon. The aqueous solution was added via cannula to the flask containing the bis(tetrazole); subsequently, a solution of deoxygenated 1.0 N NaOH was added dropwise to dissolve the bis(tetrazole). Analysis of the solution with pH paper indicated that the pH of the solution was *ca.* 8.5. The solution was allowed to stir at room temperature for 2 h; it was then adjusted to pH 1 by the addition of deoxygenated 1.0 N HCl. A white precipitate formed immediately. The suspension was transferred to a 250-mL separatory funnel and extracted with diethyl ether (2 × 100 mL). The organic phase was reduced to *ca.* 50 mL by rotary evaporation and washed with 0.1 N HCl (5 × 50 mL). The solution was dried with $MgSO_4$, filtered, and evaporated to dryness under a flow of argon to give 0.119 g (0.491 mmol; 78% yield) of 2 as a white solid. ^{1}H NMR ($CDCl_3$; 500 MHz): δ 3.06 (t, J = 8 Hz, 2 H), 2.49 (q, J = 7 Hz, 2 H), 1.84 (quintet, J = 8 Hz, 2 H), 1.57 (quintet, J = 7 Hz, 2 H), 1.19–1.41 (m, 13 H). ^{13}C NMR (1.2 mL of DMSO-d_6 + 0.1 mL of D_2O adjusted to pD 14; 125.8 MHz): 162.5, 38.6, 30.4, 30.0, 29.9, 29.6, 29.5, 26.7, 25.4. Anal. Calcd for $C_{11}H_{22}N_4S$: C, 54.51; H, 9.15; N, 23.11. Found: C, 54.54; H, 9.10; N, 22.78.

Synthesis of 11-Mercaptoundecanylphosphonic Acid, 3. The strategy for the synthesis of compound 3 is illustrated in eq 2. This strategy follows an analogous procedure developed for the synthesis of 8-mercaptooctylphosphonic acid.[35]



(2)

3

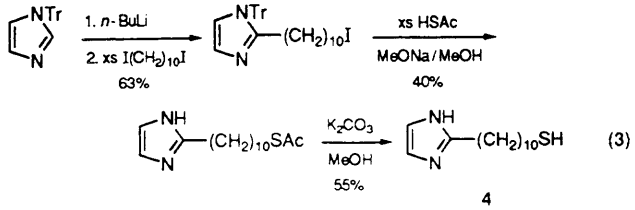
Diethyl 10-Undecenylphosphonate. Undecylenic bromide (11.65 g, 50 mmol) and triethylphosphite (20.7 mL, 0.121 mol) were added under N_2 via syringe to a three-neck flask fitted with a thermometer, a reflux condenser, and a septum. The reaction was brought to reflux with a steady stream of N_2 bubbling into the solution to prevent oxidation of the phosphite. After 24 h, the reaction was cooled to room temperature, and water (50 mL) was added in one portion. This biphasic mixture was stirred for 3 h and extracted with CCl_4. The CCl_4 extracts were combined and washed with H_2O (2×), brine (1×), dried over $MgSO_4$, and concentrated in vacuo to a crude oil (14 g, 97% yield) that was purified by flash chromatography using a gradient of 10/1 hexanes/ethyl acetate to neat ethyl acetate as eluant to yield a clear colorless oil (7.3 g, 50% yield). TLC: R_f = 0.33 in ethyl acetate. ^{1}H NMR (400 MHz, $CDCl_3$): δ 5.72–5.82 (m, 1 H), 4.87–5.0 (m, 2 H), 4.0–4.14 (m, 4 H), 1.96–2.06 (q, 2 H), 1.61–1.75 (m, 2 H) 1.50–1.60 (m, 2 H), 1.15–1.4 (m, 18 H). FABMS (glycerol matrix): 291 (MH^+).

Diethyl 11-(Acetylthio)undecanylphosphonate. A solution of diethyl 10-undecenylphosphonate (1.0 g, 3.5 mmol) in thioacetic acid (1 mL) with AIBN (20 mg) was irradiated with a 200-W high-pressure mercury lamp for 8 h at a distance of 2 in. The reaction was quenched by addition of CCl_4 (30 mL) and H_2O (20 mL). Solid $NaHCO_3$ was added with stirring until the effervescence ceased. The CCl_4 phase was separated, washed with H_2O (1×) and brine (1×), dried over $MgSO_4$, and concentrated in vacuo to a crude oil (1.24 g) that was purified by flash chromatography using a gradient of 1/1 hexanes/ethyl acetate to neat ethyl acetate as eluant to yield a clear colorless oil (1.15 g, 93% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (q, J = 6.5 Hz, 4 H), 2.83 (t, 8 Hz, 2 H), 2.28 (s, 3 H), 1.61 (m, 2 H), 1.45–1.60 (m, 4 H), 1.12–1.38 (m, 20 H). FABMS (glycerol matrix): 367 (MH^+).

Diethyl 11-Mercaptoundecanylphosphonate. A solution of diethyl 11-(acetylthio)undecanylphosphonate (1.15 g, 3.1 mmol) in ethanol (15 mL) and concentrated HCl (aqueous) (10 mL) was flushed with N_2 for 2 min and then heated at reflux under N_2 for 7 h. The reaction was concentrated in vacuo to an oil that was suspended in H_2O (25 mL) and concentrated *in vacuo* again to remove any excess HCl and to yield a clear colorless oil (0.970 g, 95% yield). ^{1}H NMR (400 MHz, $CDCl_3$): δ 4.05 (q, 6.5 Hz, 4 H), 2.48 (q, 8 Hz, 2 H), 1.7 (m, 2 H), 1.55 (m, 4 H), 1.18–1.38 (m, 21 H). FABMS (glycerol matrix): 325 (MH^+), 297 ($MH^+ - CH_2CH_3$).

11-Mercaptoundecanylphosphonic Acid, 3. Trimethylsilyl bromide (0.98 mL; 7.4 mmol) was added under N_2 to a solution of diethyl 11-mercaptoundecanylphosphonate (800 mg, 2.5 mmol) in CH_2Cl_2. The reaction was stirred for 17.5 h under N_2 and heated at reflux for an additional hour. The solvent and excess reagent were removed *in vacuo*, and the resulting oily liquid was hydrolyzed under N_2 by the addition of H_2O (10 mL) followed by stirring for 2 h. The mixture was extracted with CH_2Cl_2 (3×). The CH_2Cl_2 extracts were combined, washed with H_2O (1×), dried over $MgSO_4$, and concentrated in vacuo to a white solid (0.450 g, 68%). ^{1}H NMR (400 MHz, $CDCl_3$): s 9.9 (s, 2 H), 2.53 (q, 8 Hz, 2 H), 1.72 (m, 2 H), 1.59 (m, 4 H), 1.2–1.45 (m, 15 H). FABMS (glycerol matrix): 269 (MH^+). High Resolution FABMS: calcd for $C_{11}H_{25}PO_3S$, 269.1340; found, 269.1324. Anal. Calcd for $C_{11}H_{25}PO_3S$: C, 49.23; H, 9.41. Found: C, 49.31; H, 9.24.

Synthesis of 2-(10-Mercaptodecyl)imidazole, 4. We synthesized compound 4 using the strategy outlined in eq 3.



(3)

4

2-(10-Iododecyl)-1-(triphenylmethyl)imidazole. This intermediate was prepared by modification of a literature procedure.[36] Under argon, 500 mL of THF was added to a flame-dried 1-L round-bottomed flask containing 20.3 g (65.4 mmol) of 1-(triphenylmethyl)imidazole[37] and a magnetic stirring bar. The flask was cooled to 0 °C, and 35 mL (74 mmol) of a solution of *n*-butyllithium (2.1 M in hexane) was added via cannula. The solution was allowed to stir at room temperature for 2 h; it was then added via cannula to a flame-dried 1-L round-bottomed flask containing a magnetic stirring bar, 190 g (482 mmol) of 1,10-diiododecane, and 250 mL of THF. The reaction was allowed to proceed for 20 h at room temperature with stirring. The solution was then concentrated to *ca.* 200 mL by rotary evaporation. Water (200 mL) was added, and the mixture was transferred to a separatory funnel, and extracted with diethyl ether. The organic phases were combined, dried with $MgSO_4$,

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(36) Davis, D. P.; Kirk, K. L.; Cohen, L. A. *J. Heterocycl. Chem.* **1982**, *19*, 253–256.

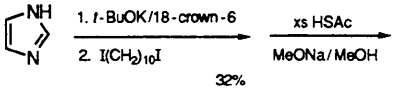
(37) 1-(Triphenylmethyl)imidazole was prepared according to method A in ref 8.

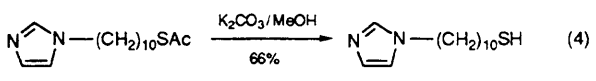
and decolorized with carbon (Norit). After filtration, the solvent was evaporated, and 214.2 g of a brown viscous oil was obtained. Chromatography of this oil on silica gel using a gradient (100% hexane → 2:1:1 hexane/diethyl ether/ethyl acetate) gave 30.3 g of crude product. Chromatography of this material on silica gel using 2:1:1 hexane/diethyl ether/ethyl acetate gave 23.6 g (41.0 mmol; 63% yield) of pure 2-(10-iododecyl)-1-(triphenylmethyl)-imidazole which could be recrystallized as light brown crystals from diethyl ether. ^{1}H NMR ($CDCl_3$; 500 MHz): δ 7.29 (m, 9 H), 7.11 (m, 6 H), 6.93 (d, J = 1 Hz, 1 H), 6.65 (d, J = 1 Hz, 1 H), 3.15 (t, J = 7 Hz, 2 H), 1.87 (t, J = 8 Hz, 2 H), 1.77 (quintet, J = 7 Hz, 2 H), 1.32 (quintet, J = 7 Hz, 2 H), 1.03–1.23 (m, 8 H), 0.96 (quintet, J = 7 Hz, 2 H), 0.86 (quintet, J = 7 Hz, 2 H). ^{13}C NMR ($CDCl_3$; 125.8 MHz): 150.8, 142.7, 129.9, 127.9, 127.7, 125.4, 120.9, 74.6, 33.5, 30.7, 30.4, 29.32, 29.23, 29.17, 29.11, 28.4, 27.5, 7.3. Anal. Calcd for $C_{32}H_{37}N_2I$: C, 66.66; H, 6.47; N 4.86. Found: C, 66.79; H, 6.53; N 4.85.

2-(10-Acetylthiodecyl)imidazole. A 500-mL round-bottomed flask equipped with a magnetic stirring bar was charged with 18.55 g (32.23 mmol) of 1-(triphenylmethyl)-2-(10-iododecyl)-imidazole, 150 mL of methanol, 3.0 mL (42 mmol) of thiolacetic acid, and 2.00 g (37.0 mmol) of sodium methoxide. A reflux condenser was attached, and the system was purged with a flow of argon. The solution was refluxed under argon with stirring for 19 h, after which little starting material remained by analysis by TLC using 9:1 chloroform/methanol. The solution was reduced to a volume of *ca.* 25 mL by rotary evaporation, and was chromatographed on silica gel using 9:1 chloroform/methanol. A slowly eluting fraction (streaking spot with $R_f < 0.2$) was collected and evaporated to dryness. The resulting off-white solid was recrystallized in three portions from either diethyl ether/methanol or methylene chloride/methanol to give 3.60 g (12.8 mmol; 40% yield) of white crystals of 2-(10-acetylthiodecyl)imidazole. ^{1}H NMR ($CDCl_3$; 500 MHz): δ 8.5–9.7 (v br s, 1 H), 6.93 (s, 2 H), 2.83 (t, J = 7 Hz, 2 H), 2.70 (t, J = 8 Hz, 2 H), 2.30 (s, 3 H), 1.71 (quintet, J = 8 Hz, 2 H), 1.53 (quintet, J = 7 Hz, 2 H), 1.21–1.37 (m, 12 H). ^{13}C NMR ($CDCl_3$; 125.8 MHz): 196.2, 148.7, 121.4 (br), 30.6, 29.4, 29.3, 29.20, 29.18, 29.1, 29.0, 28.7, 28.6, 28.5. Anal. Calcd for $C_{15}H_{28}N_2OS$: C, 63.79; H, 9.28; N, 9.92. Found: C, 63.91; H, 9.23; N, 9.86.

2-(10-Mercaptodecyl)imidazole, 4. Compound 4 was synthesized directly from 2-(10-acetylthiodecyl)imidazole by removal of the acetate group under basic conditions. A 100-mL round-bottomed flask equipped with a magnetic stirring bar was charged with 0.100 g (0.724 mmol) of K_2CO_3 and purged with a flow of argon. A separate 100-mL round-bottomed flask containing 0.655 g (2.32 mmol) of the thioacetate and 50 mL of methanol was deoxygenated by bubbling the solution with argon. This solution was transferred via cannula to the flask containing the K_2CO_3. The resulting mixture was allowed to stir for 15 h under an atmosphere of argon. The volume was reduced under vacuum on a Schlenk line, and the concentrated solution was chromatographed on silica gel using ethyl acetate. Several slowly eluting fractions (reactive toward Ellman's reagent, and characterized by a streaking spot with $R_f < 0.2$) were collected and evaporated to dryness to give 0.307 g (1.28 mmol, 55% yield) of 4 as a white solid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.4–9.2 (v br s, 1 H), 6.93 (s, 2 H), 2.71 (t, J = 8 Hz, 2 H), 2.50 (q, J = 7 Hz, 2 H), 1.70 (quintet, J = 8 Hz, 2 H), 1.57 (quintet, J = 7 Hz, 2 H), 1.20–1.40 (m, 13 H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 148.7, 121.2 (br), 39.3, 34.0, 29.41, 29.38, 29.31, 29.27, 29.0, 28.5, 28.3, 24.6. Exact mass calcd for $C_{13}H_{24}N_2S$: 240.1660. Found: 240.1656.

Synthesis of 1-(10-Mercaptodecyl)imidazole, 5. The synthesis of compound 5 is illustrated in eq 4.





(4)

5

1-(10-Acetylthiodecyl)imidazole. This compound was the only isolated intermediate; it was synthesized using the following procedure. A flame-dried 200-mL Schlenk flask was charged with 1.83 g (16.3 mmol) of potassium *tert*-butoxide, 0.452 g (1.71 mmol) of 18-crown-6, 150 mL of diethyl ether, and a magnetic stirring bar. Imidazole (1.031 g, 15.1 mmol) was added, the flask was capped, and the resulting slurry was bubbled with argon, and stirred for 1 h. Separately, a flame-dried 250-mL round-bottomed flask was charged with 23.75 g (60.3 mmol) of 1,10-diiododecane, 50 mL of diethyl ether, and a magnetic stirring bar. After bubbling argon through this solution, the slurry was added via cannula, and the mixture was allowed to stir for 20 h at room temperature. Analysis by TLC using ethyl acetate as the eluant indicated the presence of product (streaking spot with $R_f < 0.2$). Water (50 mL) was added, and the mixture was transferred to a separatory funnel. The layers were separated, and the aqueous phase was extracted twice with 50 mL of diethyl ether. The organic portions were combined, and the volume was reduced to *ca.* 100 mL by rotary evaporation. The solution was extracted once with 100 mL of 1.0 N HCl and twice with 50 mL of 0.1 N HCl. The aqueous layers were combined, adjusted to pH 12, and then extracted with diethyl ether (3 × 100 mL). The organic layers were combined, dried with $MgSO_4$, and filtered into a 500-mL round-bottomed flask. The volume was reduced to *ca.* 100 mL by passing a flow of argon over the solution. The solution was transferred using 150 mL of methanol to a 250-mL round-bottomed flask equipped with a magnetic stirring bar, and the residual diethyl ether was removed by bubbling with argon, and heating the solution in a water bath maintained at 35 °C. Thioacetic acid (2.1 mL, 25.9 mmol) and sodium methoxide (1.51 g, 28.0 mmol) were added. The flask was capped with a rubber septum, and the solution was bubbled with argon, and allowed to stir at *ca.* 35 °C for 45 h. The solution was then concentrated by rotary evaporation and chromatographed on silica gel using 4:1 ethyl acetate/diethyl ether. The fractions containing the product (characterized by a streaking spot with $R_f < 0.2$) were collected and evaporated to dryness. Chromatography of the resulting yellow-orange oil was on silica gel using 2:1 ethyl acetate/diethyl ether and gave 1.35 g (4.78 mmol, 32% yield) of 1-(10-acetylthiodecyl)imidazole as a pale yellow oil that solidifies upon cooling to 0 °C. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.42 (s, 1 H), 7.02 (s, 1 H), 6.87 (s, 1 H), 3.88 (t, J = 7 Hz, 2 H), 2.82 (t, J = 7 Hz, 2 H), 2.29 (s, 3 H), 1.73 (quintet, J = 7 Hz, 10 H), 1.52 (quintet, J = 7 Hz, 2 H), 1.18–1.36 (m, 12 H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 196.0, 137.0, 129.3, 118.7, 47.0, 31.0, 30.6, 29.4, 29.3, 29.1, 29.09, 28.7, 26.5.

1-(10-Mercaptodecyl)imidazole, 5. Compound 5 was synthesized directly from 1-(10-acetylthiodecyl)imidazole by removal of the acetate group under basic conditions. The thioacetate (0.403 g, 1.43 mmol) was added to 50 mL of methanol in a 100-mL round-bottomed flask equipped with a magnetic stirring bar. The solution was degassed by bubbling with argon, and 0.411 g (2.97 mmol) of K_2CO_3 was added through a flow of argon. The flask was capped with a rubber septum, and the reaction was allowed to proceed 20 h with stirring. The solution was evaporated to dryness on a Schlenk line; the resulting brown oil was chromatographed on silica gel using 4:1 ethyl acetate/diethyl ether. The fractions containing thiol (reactive toward Ellman's reagent, and characterized by a streaking spot with $R_f < 0.2$) were collected and evaporated to dryness giving 0.225 g (0.936 mmol, 66% yield) of 5 as a pale yellow oil. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.41 (s, 1 H), 7.00 (s, 1 H), 6.85 (s, 1 H), 3.87 (t, J = 7 Hz, 2 H), 2.47 (q, J = 7 Hz, 2 H), 1.72 (quintet, J = 7 Hz, 2 H), 1.55 (quintet, J = 7 Hz, 2 H), 1.18–1.37 (m, 13 H). ^{13}C NMR ($CDCl_3$, 125.8 MHz): 137.0, 129.3, 118.7, 46.9, 39.0, 33.9, 31.0, 29.2, 28.93, 28.89, 28.2, 26.4, 24.5. Anal. Calcd for $C_{13}H_{24}N_2S$: C, 64.95; H, 10.06; N, 11.65. Found: C, 65.20; H, 9.93; N, 11.50.

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