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Formation of Two-Component Surfaces by the Spontaneous Assembly of Monolayers on Gold from Solutions Containing Mixtures of Organic Thiols[1]

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The formation of ordered, oriented, organic monolayer films by adsorption of long-chain thiols, $HS(CH_2)_nX$, onto gold provides a means of controlling the chemistry and structure of surfaces on an angstrom scale.[3,4] Monolayers formed from a single thiol present a densely packed array of a single functional group at the interface between the monolayer and a liquid or vapor. A controlled degree of disorder can be introduced at this interface by coadsorbing thiols of different chain lengths, with the same[5] or different[6] terminal functionality. Here we demonstrate the synthesis of surfaces comprising a mixture of organic functional groups by the coadsorption of thiols with the *same* chain length but with different tail groups, X. The ability to control the composition of highly structured, multicomponent interfaces has particular potential for examining the interactions between organic functional groups in quasi-two-dimensional systems.

We have studied three simple, binary systems, $HS(CH_2)_{10}CH_3$ and $HS(CH_2)_{10}Z$ (Z = $-CO_2H$, $-CH_2OH$, $-CH_2Br$), chosen to have one polar and one nonpolar component.[7] These pairs were selected for ease of analysis by contact angle and by X-ray photoelectron spectroscopy (XPS). Monolayers were prepared by immersing evaporated gold films, supported on silicon wafers, in solutions of thiols in deoxygenated ethanol overnight at room temperature.[8] The ratio of the two components was varied while maintaining a total concentration of thiol of 1 mM. The compositions of the monolayers were determined from the normalized areas of the O(1s) and Br(3p) peaks in XPS.[9] Carboxylic acids, alcohols, and alkyl bromides coordinate only weakly to gold and do not form monolayers that are stable to washing with ethanol. Consequently, the tail groups do not compete with the thiol in binding to the gold.

Figure 1 (lower) plots the mole fraction in the monolayer, $\chi^P_{surface}$, of the polar component, $HS(CH_2)_{10}Z$, as a function of its mole fraction in solution. In general the compositions of the solution and of the monolayer are not equal: the relationship between $\chi^P_{surface}$ and $\chi^P_{solution}$ depends on the nature of the tail group.[10] Since the intermolecular interactions within a monolayer

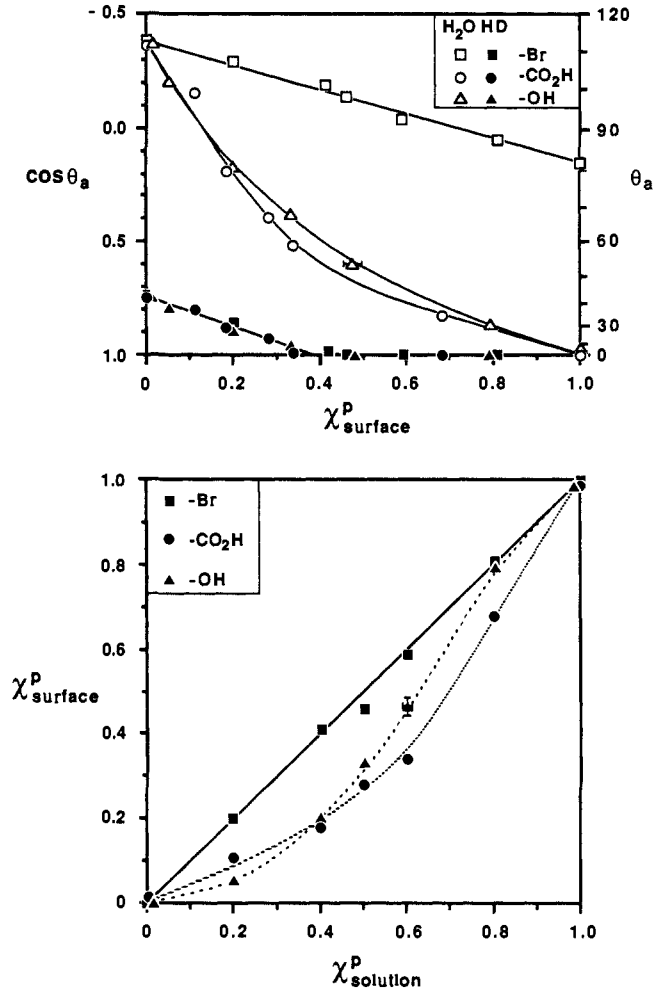

Figure 1. (lower) Composition of monolayers of thiols as a function of the composition of the solutions from which they were adsorbed; (upper) advancing contact angles, θ_a, of water and hexadecane (HD) as a function of the composition of the monolayer. $\chi^P_{surface}$ is the mole fraction on the surface of $HS(CH_2)_{10}Z$ (Z = $-CH_2Br$, $-CH_2OH$, $-CO_2H$) in binary mixtures with $HS(CH_2)_{10}CH_3$; it was determined from the areas of the O(1s) or Br(3p) peaks obtained by XPS. The error bars shown are indicative of the standard deviation of the random errors occurring in the preparation of adsorbate solutions, and in the collection and analysis of XPS data. The errors in the contact angles lie within the symbols.

are often similar to those in a crystal, solubility provides a useful guide to which component will be adsorbed preferentially.[11] $\chi^P_{surface}$ and $\chi^P_{solution}$ are not always related, however, by the simple equilibrium expression expected for an ideal two-dimensional solution; specific interactions within the monolayer clearly play a role in determining the composition.

Figure 1 (upper) shows the advancing contact angles, θ_a, of water and hexadecane as a function of surface composition for the three systems studied. The contact angles vary smoothly with surface composition between the values characteristic of the pure, one-component monolayers.[4] Cassie[12] has shown that if the two components of the surface act independently, then $\cos\theta_a$ is a linear function of the composition of the surface, in the absence of hysteresis. Cassie's law appears to hold for the contact angles of hexadecane on all three pairs over the limited range we could observe and for water on the brominated surfaces, for which dispersion forces are the principal intermolecular interaction. The

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(7) The principle of these studies is generalizable to mixtures of two polar or two nonpolar tail groups or to systems with more than two components.
(8) Reference 4 contains experimental details.
(9) We also measured the intensity of the $Au(4f_{7/2})$ peak as a check on the focus of the spectrometer. The area of the bromine peak collected on the pure $HS(CH_2)_{11}Br$ was corrected by 6% for an abnormally low gold intensity.
(10) The composition of the monolayer appears to be controlled largely by thermodyamics: frequently the minor component in solution is the major component in the monolayer. For longer chains the role of kinetics appears to increase.
(11) Consequently, the choice of solvent has a major influence on the monolayer composition.
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contact angles of water on surfaces containing hydroxyl or carboxylic acid groups, in which specific polar interactions are important, deviate strongly from linearity. The apparent hydrophilicity of the polar tail groups is higher when they are in a nonpolar environment composed largely of methyl groups than when their neighbors are other polar groups. This difference may arise partly from greater electrostatic stabilization in more polar surfaces and partly from intramonolayer hydrogen bonding in surfaces that are rich in hydroxyl or carboxylic acid groups.

We believe that the polymethylene chains in these two-component monolayers are well-packed (in contrast to monolayers assembled from two thiols of different chain lengths), but we have no evidence for any translational order in the tail groups.[13] These monolayers do not phase segregate into macroscopic domains: the resulting nonpolar islands would pin the advancing drop edge and give rise to a deviation from linearity in the contact angles opposite to that observed.[14] In addition, changes in the line width and position of the O(1s) peak in XPS suggest that the local environment of dilute hydroxyl groups is different from that in a pure monolayer.[15]

In conclusion, coadsorption on gold of mixtures of thiols, with the same chain length but different tail groups, produces well-packed monolayers exposing those groups at the surface. Specific interactions between the tail groups cause nonideal behavior both in the composition and the hydrophilicity of the monolayers.

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(13) In addition, highly dipolar tail groups might exhibit orientational disorder if an ordered array engendered a large unfavorable electrostatic interaction.

(14) The size below which islands of different polarity no longer cause hysteresis in the contact angle is not well-established experimentally. Neumann and Good have proposed theoretically that this lower limit is ~0.1 μm (Neumann, A. W.; Good, R. J. *J. Colloid Interface Sci.* **1972**, *38*, 341-358).

(15) The O(1s) peak of the hydroxyl group in the monolayer with $\chi^{P}_{surface} = 0.05$ was 0.3 eV narrower and shifted 0.4 eV to higher binding energy compared to the pure hydroxyl-terminated monolayer. One possible explanation is that very dilute hydroxyl groups are not hydrogen-bonded. The extent to which the molecular distribution in the monolayer deviates from a statistical mixture is unclear.

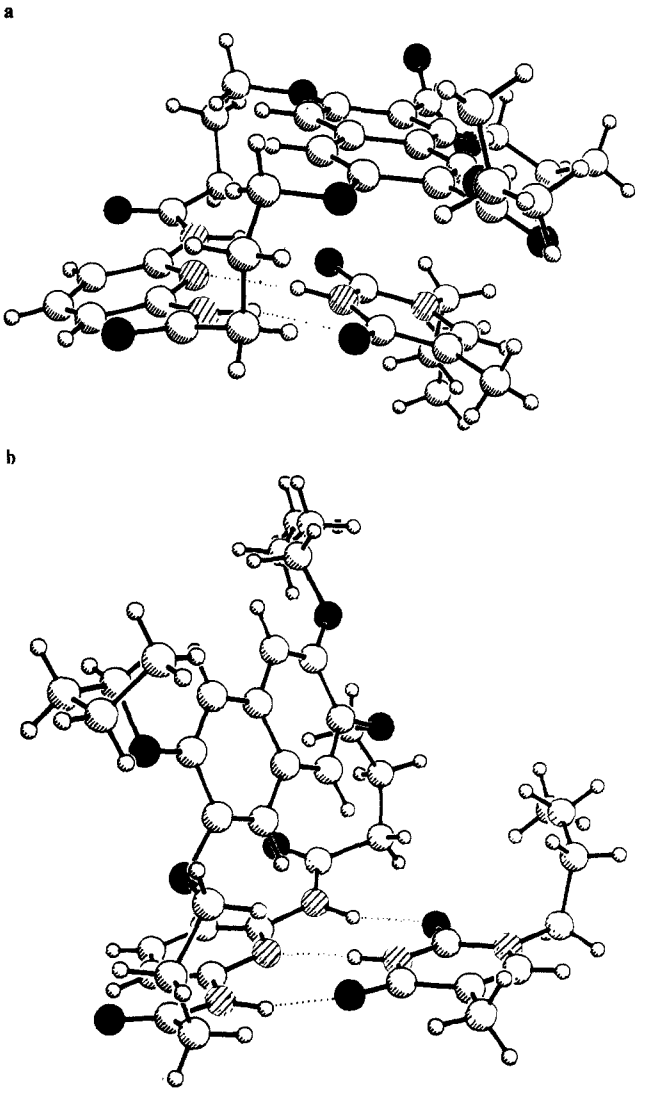

Figure 1. (a) Side view of X-ray structure of **4**:**6**. (b) Side view of X-ray structure of **5**:**6**.

Aromatic-Aromatic Interactions in Molecular Recognition: A Family of Artificial Receptors for Thymine That Shows Both Face-to-Face and Edge-to-Face Orientations

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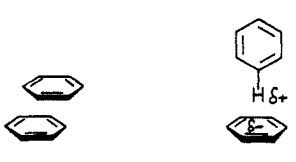
Interactions between aromatic rings play an important role in stabilizing protein structure.[1] A number of inter-ring geometries have been identified ranging from a parallel face-to-face stacking **1** to a perpendicular edge-to-face orientation **2** in which positively charged H atoms on one ring interact with negatively charged regions on a second.[1] A similar structural diversity can be seen in the protein recognition of nucleotide bases. The guanine-binding site of ribonuclease T_1 contains a tyrosine residue (Tyr 46) which stacks parallel to and at 3.4 Å from the purine plane.[3] In contrast, the human c-H-*ras* oncogene protein binds to guanine via a phenylalanine (Phe28) whose phenyl ring is positioned almost perpendicular to the nucleotide base.[4] As part of a study of general features of nucleotide base recognition[5] we sought to investigate the structural basis of these two geometries by incorporating them into artificial receptors. In this paper we report the synthesis and structural characterization of a class of thymine receptors which show either face-to-face or edge-to-face orientations, depending on the electronic properties of the stacking group.



1 **2**

The receptors are based on the two-site binding strategy (hydrogen bonding and stacking) introduced previously.[5a] Incorpo-

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