Self-Assembled Monolayers of 4-Mercaptobiphenyls

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FIGURE 1. 4-Mercaptobiphenyls and 4-(4′-mercaptophenyl)pyridine.

ABSTRACT

This Account focuses on our systematic studies of the formation and properties of self-assembled monolayers (SAMs) of 4-mercaptobiphenyls on gold surfaces. The key difference between alkanethiolate and biphenyl thiolate SAMs is the rigid π-character of the latter. The π-conjugation between the adsorbing thiolate and the substituent at the 4′-position results in a molecular dipole moment that affects the adsorption kinetics as well as the equilibrium structure of mixed SAMs. Due to the lack of conformational disorder in the assembling molecules, these SAMs can serve as stable molecularly engineered model surfaces. Infrared spectroscopy and scanning tunneling microscopy, as well as X-ray and helium diffraction studies, suggest that biphenyl moieties in the SAMs have small tilt angles with respect to the surfaces normal. Finally, the morphology of glycine crystals nucleated and grown on these SAM surfaces depends on the structure of the nucleating glycine layer, which, in turn, depends on the H-bonding of these molecules with the SAM surface.

Introduction

The idea that ordered monomolecular layers can be prepared by the self-assembly of synthetic molecules was first demonstrated by Zisman and co-workers.[1] Major steps forward were the preparation of stable self-assembled monolayers (SAMs)[2,3] from octadecyltrichlorosilane (OTS) on silicon oxide[4] and from alkanethiols on gold.[5] Later it was demonstrated that robust monolayers could be prepared with alkyl chains covalently bound to a silicon substrate by C–Si bonds,[6] and that multilayers can be prepared simply by alternating adsorption of Zr^{4+} ions and α,ω-alkylidenediphosphate.[7]

Self-assembled monolayers allow the formation of a variety of surfaces with specific interactions and with fine structural control.[8] The energies of SAM surfaces might span the range from "Teflon-like" surfaces (surface CF_3 groups) to very high-energy surfaces (surface OH or COOH groups), e.g., surface tensions of 10–70 dyn cm^{-1}. De-
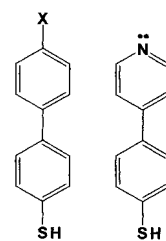
signed SAM surfaces have been shown useful in studies of molecular recognition,[9] biomaterial interfaces,[10] cell growth,[11] crystallization,[12] and many other systems.[13] In many cases, applications require stable molecularly engineered surfaces. However, in the case of alkyl derivative SAMs, it was found early on[14] that, due to the flexible nature of the chains, thermal disorder results in surface-gauche defects, and thus surface disorder.[15] This is an especially noteworthy process for chains containing very polar surface groups, such as OH, at their termini, where the introduced disorder may be significant[16] and not confined to the surface. Thus, stable surfaces cannot be based on flexible alkyl SAMs, where chain dynamics controls surface composition, and other systems should be developed to accomplish this goal. Such systems should be free of conformational freedom, so that functional groups are "stuck" at the surface, providing long-term stability. There are a number of possibilities to achieve rigidity. For example, Bard and co-workers[17] described SAMs made of rigid thiols; however, these molecules exhibit a large cross-sectional area that results in a sizable mismatch with the size of many substituents. It was postulated by Scaringe[18] that if the bulk crystal of a molecule can be viewed as a commensurate assembly of two-dimensional layers, this molecule might be a good candidate for SAM formation. Liquid crystals are an example of layered materials, and thus we studied 4,4′-dioctylbiphenyl, which spontaneously forms stable suspended liquid crystal (SLC) films.[19] The results showed that 4′-substituted-4-mercapto-biphenyl derivatives (Figure 1) might form ordered SAMs on Au(111) surfaces.[20]

The question then was, What do mercaptobiphenyls offer except for their rigidity to warrant extensive investigations? In fact, these aromatic thiols might have a number of advantages. First is the conjugation between the adsorbing thiolate and the 4′-substituent. This substitution affects the acidity of the thiol proton, making the thiolate a softer or a harder ligand, which should influence its bonding with different metallic surfaces. Second, since the thiolate is an electron-donating group, an electron-attracting substituent at the 4′-position may result in a significant molecular dipole moment, which might alter adsorption kinetics and the composition of mixed SAMs in equilibrium. Third, changing the electron density on the adsorbing thiolate may result in altered packing and ordering in SAMs on gold. For example, if the thiolate is stabilized by an electron-attracting group at the 4′-position, the driving force for adsorption at the hollow

FIGURE 2. Synthesis of 4′-substituted-4-mercaptobiphenyls. (a) $(CH_3)_2C=CH_2/H^+$, (b) Mg/THF/ N_2, (c) $X-C_6H_4-I(Br)/[(Ph_3P)_4Pd]/THF/ \Delta/N_2$, (d) $Hg(ClO_4)_2/CHCl_3/CH_3OH$.

site of the gold (111) lattice might be reduced, allowing adsorption in alternative sites. This is similar to the differences in adsorption of alkanethiolates on gold and silver surfaces.[21] Finally, the lack of conjugation between the adsorbing thiolate and the ω-substituent in alkanethiols does not allow the systematic investigation of how substitution affects the adsorption, composition, and structure of SAMs and mixed SAMs, making such studies using mercaptobiphenyl valuable.

A number of researchers developed elegant synthetic routes for rigid aromatic thiols,[22−25] measured the rates of interfacial electron transfer,[26] and applied cyclic voltammetry (CV) to study the structure of aromatic-derivatized thiol monolayer on gold.[27] Rubinstein and co-workers were the first to assemble 4-mercaptobiphenyl SAMs onto gold, and using molecular mechanics calculations they predicted a herringbone structure, with molecules oriented close to the surface normal.[22] However, there have been no studies where rigid aromatic thiols were used for the preparation of model, molecularly engineered surfaces. In this Account we review systematic studies of the formation and properties of SAMs of 4-mercaptobiphenyls on gold surfaces carried out in our group and with our collaborators.

Synthesis of 4-Mercaptobiphenyl Derivatives

The synthesis of mercaptobiphenyl derivatives is different from that of ω-substituted alkanethiols in that in almost all cases molecules must be prepared by aromatic coupling reactions. We developed two synthetic routes for the synthesis of 4′-substituted-4-mercaptobiphenyls.[28] In the first, methylthiophenylmagnesium bromide was coupled with 4-substituted iodobenzenes using $[(Ph_3P)_4Ph]$ as the catalyst, and the methyl protecting group was removed using potassium ethanethiolate in DMF. In the second (Figure 2), 4-*tert*-butylthiophenylmagnesium bromide was used for the coupling, and the protecting group was removed by $Hg(ClO_4)_2$, followed by decomposition of the Hg(II) salt using H_2S. The choice of the synthetic route depends on the nature of the substituent at the 4′-position and its sensitivity to the reagents used.

Adsorption Kinetics

The adsorption kinetics in the case of non-interacting adsorbates is proportional to the number of available sites, and thus follows the Langmuir growth curve, $d\Theta/dt = R(1 - \Theta)$, and Karpovich and Blanchard applied it successfully to fit the adsorption kinetics of alkanethiols on gold.[29] In some cases, however, SAM growth started after some delay time, and it was suggested that different
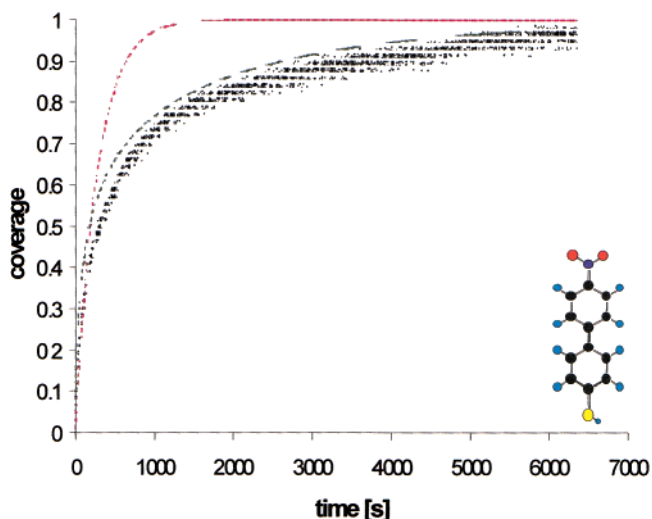

FIGURE 3. Fitting comparison using two different models for adsorption of 4′-nitro-4′-mercaptobiphenyl on gold.

sticking coefficients exist for areas already covered and for those still free.[30]

The adsorption kinetics of biphenyl thiols with different substituents at the 4-position (X = SCH_3, $N(CH_3)_2$, CH_3, CF_3, and NO_2) were studied using quartz crystal microbalance (QCM).[31] These substituents can be divided into electron acceptor (NO_2, CF_3) and electron donor ($N(CH_3)_2$, SCH_3 CH_3) groups; hence, the electron density on the adsorbing thiol S atom should be smaller for the 4′-NO_2 than, for example, for the 4′-$N(CH_3)_2$ substituent. It was observed that mass equilibrium for $CH_3S-Ph-Ph-SH$ was reached after a period of few minutes, clearly *slower* than reported adsorption kinetics for *n*-alkanethiols.[32]

More significantly, it was found that the adsorption of mercaptobiphenyl derivatives is fundamentally different from the corresponding process of alkanethiols, since the kinetics data could not be fitted to the Langmuir isotherm (Figure 3, red line). This is reasonable since the Langmuir isotherm is strictly valid only if the adsorbate molecules do not interact with each other, and cannot be appropriate for the polar 4-mercaptobiphenyl molecules. Therefore, a new chemisorption model that takes interadsorbate interactions into consideration explicitly was developed.[31] This model gave greatly improved fits (Figure 3, blue line).

Most researchers agree that the adsorption of alkanethiols onto gold is a process with multiple time scales.[32−34] The first step, which describes the adsorption of the thiol headgroups at the gold surface, is fast ($2500-3000$ L mol^{-1} s^{-1}) and results in $\sim 80-90\%$ coverage. The following step ($3-4$ times slower than the first step) can be described as a surface crystallization process, where alkyl chains get out of the disordered state and into unit cells, thus forming a two-dimensional crystal.[35] The last step ($35-70$ slower than the rate of chain stretching) encompasses the reorientation of the terminal methyl end groups.[36]

Mercaptobiphenyls are stiff molecules which do not have conformational excited states that allow facile lateral migration at room temperature before irreversible chemisorption occurs. Moreover, while for alkanethiols the interaction of the SH group with the metallic surface

should be the same, regardless of ω-substitution, the conjugation between the 4'-substituent and the thiol group affects the acidity of the SH proton and hence the basicity of the conjugate thiolate. These attributes, as well as the molecular dipole, affect the adsorption kinetics of mercaptobiphenyls. The QCM studies presented here provide information only on the first step. Sum frequency generation studies are required for determining time-dependent changes of packing and ordering in the SAM. These studies are underway.

Monolayer Structure

Phenyl rings introduce stronger interactions (molecule–substrate and molecule–molecule), and hence affect the nucleation and growth of phenyl-containing SAMs. For example, Creager and Steiger studied monolayers of 4-mercaptobenzoic acid on gold and concluded that the rigidity of the phenyl rings prevented intermolecular H-bonding and the dimerization of the carboxylic groups.[37] Oligo(phenylethynyl)benzenethiols of different lengths (with one, two, and three phenyl rings) were studied by STM. It was found that the degree of order in that series increased with the number of phenyl rings.[23]

Biphenylthiolate SAMs are expected to exhibit higher surface free energies than the corresponding alkanethiolate SAMs because of the aromatic benzene rings. In addition, the conjugation with the 4'-functionality results in a significant molecular dipole. Consequently, it was found that contact angle measurements are not a useful analytical tool for mercaptobiphenyl SAMs, because of the coupling between the wetting properties of the surface group and its effect on the underlying molecular dipoles. For example, the advancing water contact angles for SAMs having CH_3 and CF_3 surfaces are identical (85°),[28] because the dipole moment of the latter has an important effect of the surface free energy of the SAM. Also, because of difference in cross-sectional area between the biphenyl moiety and the substituents, the wetting liquid can penetrate the surface and sample the underlying benzene ring. For example, the advancing contact angle of 4'-hydroxy-4-mercaptobiphenyl SAMs is 30°, while that of ω-hydroxyalkanethiolate SAM on gold is ≤15°, although in both cases the surface is composed of OH groups.

Fourier transform infrared (FTIR) spectroscopy is a better analytical tool for structural studies of mercaptobiphenyl SAM. Figure 4 presents the external reflection FTIR spectrum of 4'-trifluoromethyl-4-mercaptobiphenyl in a SAM on gold, and for comparison the spectra in transmission mode of the solid thiol in KBr and as a 5 mM solution in CCl_4. The simplification of the spectrum in the SAM environment reflects the perpendicular orientation of the biphenyl moiety. This suggests that the surface–S–C angle should be ≤180°, which is in agreement with theoretical calculations.[34,38] There, it was suggested that the hybridization of the S atom might be either sp or sp^3, depending on molecular interactions.[39] Further support for this structure comes from helium and X-ray diffractions studies.
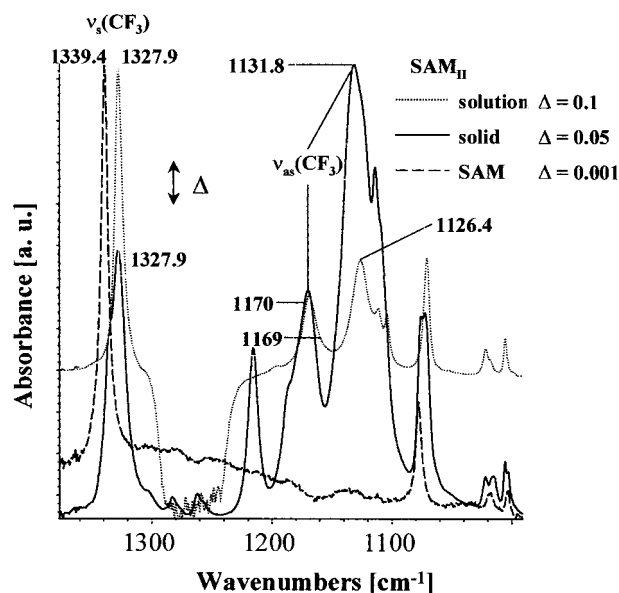

FIGURE 4. ERFTIR spectra of 4'-trifluoromethyl-4-mercaptobiphenyl in KBr, in CCl_4 solution (5 mM), and in a SAM on gold prepared in ethanol.

Methyl-4'-mercaptobiphenyl was selected for grazing incidence X-ray diffraction (GIXD) and low-energy atom diffraction (LEAD) investigation since it has both the same methyl "end group" and about the same length as decanethiol, so that possible differences in the structure could be attributed to the difference in the backbone. The structure and growth of the SAMs were studied by GIXD and LEAD.[40] Similar to alkanethiols, a low-coverage "lying-down" or "striped" phase and a high-coverage "standing-up" or hexagonal phase were found.

For the "lying-down" phase, an $(8 \times 2\sqrt{3})$ unit cell (corresponding to 23.08 Å × 10 Å) with four molecules per unit cell and a packing density of 57.7 Å^2 per molecule was found. The structure proposed in Figure 5 is characterized by a centered rectangular unit cell with the molecules lying in a head-to-head configuration. The resulting S–S distance is 2.1 ± 0.2 Å. To fully accommodate the molecules, it was suggested that the molecules tilt partly away from the surface. Interestingly, in contrast to alkanethiolate SAMs, the "lying-down" phase did not transfer to the hexagonal phase upon the addition of more methyl-4'-mercaptobiphenyl molecules.

The hexagonal phase was found to have a commensurate $(\sqrt{3} \times \sqrt{3})R30°$ structure, which implies that all sulfur atoms are in the same binding sites. The proposed upper limit value for the tilt angle of the biphenyl moiety was ≤19°, consistent with results reported by Kang and co-workers.[28] This smaller tilt angle of mercaptobiphenyls reflects the fact that the molecules do not need to tilt strongly in order to maximize their van der Waals (vdW) interactions when their spacing is constrained to 5 Å, as a small adjustment of the dihedral angle is sufficient. Comparing the vdW dimensions of the molecule (with a cross-sectional area of 21.1 Å^2 for the phenyl rings) to the area per molecule in the $(\sqrt{3} \times \sqrt{3})R30°$ structure (21.6 Å^2) supports this conclu-
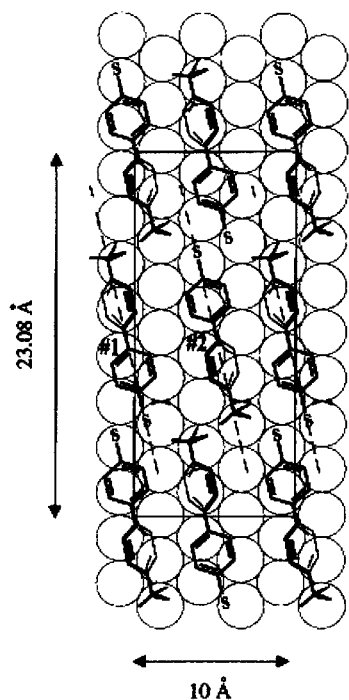
FIGURE 5. Proposed structure of lying-down phase of MMB after [110]. The dimensions of the rectangular unit mesh (23.08 Å × 10 Å) are consistent with an (8 × 2√3) lattice. From ref 40.
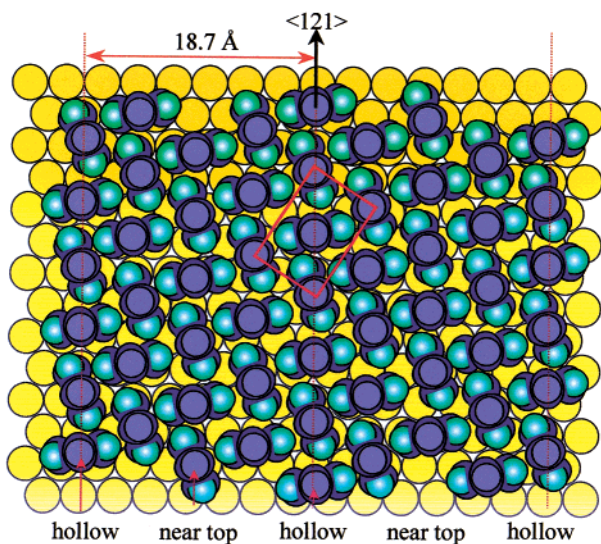

FIGURE 6. Schematic diagram of the proposed structural model for 4′-chloro-4-mercaptobiphenyl SAMs on Au(111).

sion, since the tilt angle deduced from this comparison is expected to be only about 14°.

The structure of the 4′-chloro-4-mercaptobiphenyl SAM was studied using scanning tunneling microscopy (STM).[28] The observed periodicity for 4′-chloro-4-mercaptobi-phenyl SAM is very similar to the crystalline structure of biphenyl[41] and 4-[4′-(phenylethynyl)-phenylethynyl]ben-zenethiol SAMs on Au(111).[42] The proposed structural model is shown in Figure 6, in which the phenyl planes along the ⟨121⟩ direction are most closely packed and orientated in a herringbone fashion based upon the crystalline structure of biphenyl. The molecular rows of

mercaptobiphenyls are oriented 55° instead of 60° from the ⟨121⟩ direction. As a result, six instead of three domains are present. This model can also successfully explain the periodicity and other detailed structural features of the superlattice. For instance, the interstripe spacing is 18.7 Å.

The emergence of a new structure for the 4′-chloro-4-mercaptobiphenyl SAM may be the result of the molecular dipole moment (intermolecular repulsion) and the elec-tron density (basicity) at the thiolate anion. In addition, Cl⋯Cl interactions may also contribute to packing mol-ecules more closely. Evidence for the existence of various adsorption sites of the sulfur headgroups on the Au(111) surface, such as triple-hollow, bridge, and top sites, etc., comes from the corrugation of the superlattice. Thus, for every four molecules along the row, sulfur atoms adsorb on the same surface sites, such as the triple-hollow site of Au(111). Preliminary high-resolution XPS data provide support for the various adsorption sites of the thiolates,[43] and hence the resulting incommensurate structure of the SAM. Determining whether thiolate−substrate or inter-molecular interactions among 4′-chloro-4-mercaptobi-phenyl molecules are the dominating factor determining the final SAM structure requires further studies. However, the experimental evidence already at hand strongly sup-ports the idea that the substituent at the 4′-position affects the packing and ordering of the SAM.

Mixed SAMs

The kinetics studies and FTIR data suggested that dipolar interactions play an important role in the adsorption process. This is reasonable given that the size of the molecular dipole moment and its direction are functions of the 4′-substituent. The first mixed SAMs we investigated were those of 4′-trifluoromethyl-4-mercaptobiphenyl and 4′-methyl-4-mercaptobiphenyl from ethanol (Figure 7). We observed a linear relationship of the positions of both the symmetric CF_3 vibration ($\nu_s(CF_3)$) and the b_{1u} biphenyl skeletal modes with surface CF_3 group concentration. The $\nu_s(CF_3)$ peak shift was explained by a classical electromag-netic theory, and an excellent agreement between theory and experiments was obtained.[44]

However, when the same mixed SAMs were prepared from toluene, the maximum shift in the $\nu_s(CF_3)$ peak position was smaller (5.2 vs 8.9 cm^{-1}), and the peak intensities revealed a clear development of a plateau, suggesting that there is a significant driving force for mixing.[45] This could be explained by the fact that the two components have molecular dipoles in opposite directions with respect to the surface. The question then was if the driving force for mixing is strong enough to facilitate thiol exchange. If this is the case, experiments starting from the two SAMs should show the same surface composition under equilibrium. In fact, experimental results show that when either SAM was placed in a 10 μM solution of the other component, equilibrium was established after 43 h, resulting in mixed SAMs with approximately the same composition (Figure 8).
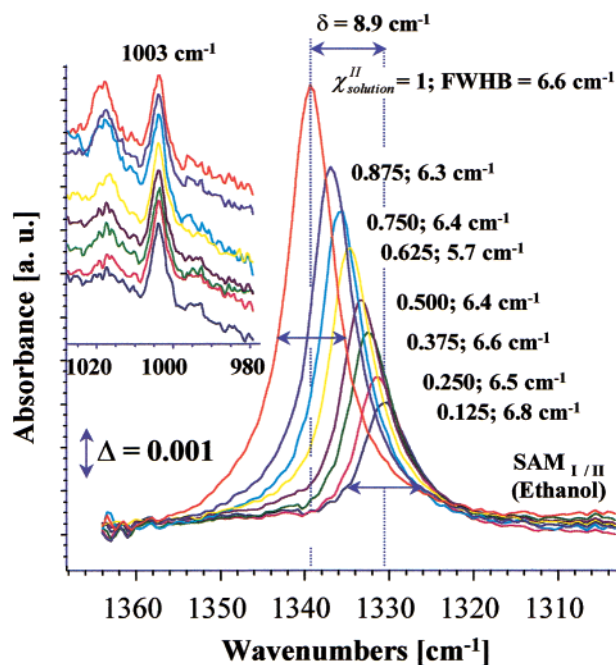
FIGURE 7. ERFTIR spectra of SAMs and mixed SAMs of 4′-trifluoromethyl-4-mercaptobiphenyl and 4′-methyl-4-mercaptobiphenyl prepared from ethanol.
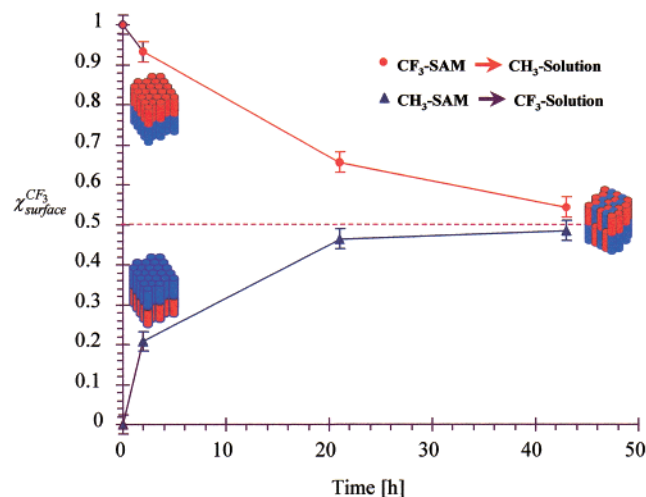

FIGURE 8. Integrated area under the $\nu_s(CF_3)$ band for exchange experiments.

The above experiments can be viewed, in principle, as self-assembly of dipoles, where the molecular dipoles of the components control the composition of the resulting mixture, in a given solvent polarity. The driving force for mixing should depend on the dipole moments of the two components and should increase with the increasing dipole, due to the increased intermolecular repulsion in the pure SAMs and the intermolecular attraction in the mixed SAM. To examine this hypothesis, we selected biphenyl thiols with strong electron acceptor (NO₂) and electron donor (N(CH₃)₂) substituents.[46] Figure 9 shows that intermolecular repulsion in a SAM of 4′-nitro-4-mercaptobiphenyl is so significant that there is a driving force for dilution with 4′-methylmercapto-4-mercaptobiphenyl, which for all practical purposes does not have a molecular dipole. Even when mixed SAMs were prepared
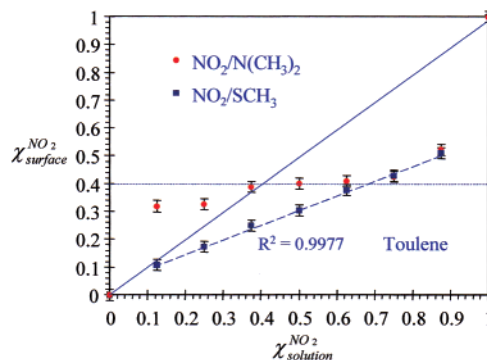

FIGURE 9. Integrated area under the $\nu_s(NO_2)$ band for mixed SAMs [NO₂/SCH₃] and SAMs [NO₂/N(CH₃)₂] made in toluene versus the molar fraction of NO₂ in solution.

in toluene solutions with a 9:1 ratio of 4′-nitro-4-mercaptobiphenyl to 4′-methylmercapto-4-mercaptobiphenyl, the surface concentration of NO₂ groups was only ∼50%. These mixed SAMs allow, for the first time, a systematic control of surface dipole concentration.

When mixed SAMs of 4′-nitro-4-mercaptobiphenyl and 4′-dimethylamino-4-mercaptobiphenyl were prepared in toluene, the surface NO₂ concentration, as determined by external reflection FTIR spectroscopy, showed a plateau at 40% (Figure 9). If one assumes that the equilibrium concentration of the two components in the mixed SAM, in a nonpolar solvent, is driven by the formation of a two-dimensional assembly with zero net dipole moment, one could explain the results by using the idea that the Hammett equation might be applicable in these systems. The dipole moment of the mixed SAM could then be expressed as a sum of contributions from the two components,

$$(1 - X)(\Delta\sigma(NO_2)) + X(\Delta\sigma(N(CH_3)_2)) = 0 \qquad (1)$$

where $\Delta\sigma = \sigma_p(NO_2 \text{ or } N(CH_3)_2) - \sigma_p(S-Au)$, assuming that the molecular dipole of the two thiols results primarily from the substituents at the 4- and 4′-positions. To account for the contribution of the S−Au to the dipole moment, the σ_p^+ value for SCH₃ (−0.164) was selected. If the effect of electronic state on dipole moment of the para-substituted compound is considered to be simply additive,[47] then $\Delta\sigma(NO_2) = 0.942$ and $\Delta\sigma(N(CH_3)_2) = -0.666$, and eq 1 gives $X = 0.4$, well within the experimental result. This control level of surface functionalities, surface chemical potential, and surface dipole has become possible only because of the unique properties of 4′-substituted-4-mercaptobiphenyls. Such control is not possible in mixed alkanethiolate SAMs, since dipolar interaction of surface functionalities will result in surface reorganization. The issue of long-term stability of molecularly engineered surfaces is described next.

Stable Model Surfaces

Model molecularly engineered surfaces may be useful only if they have significant stability. If surfaces reorganization is significant, one might find that a model surface has changed during an experiment, making systematic studies
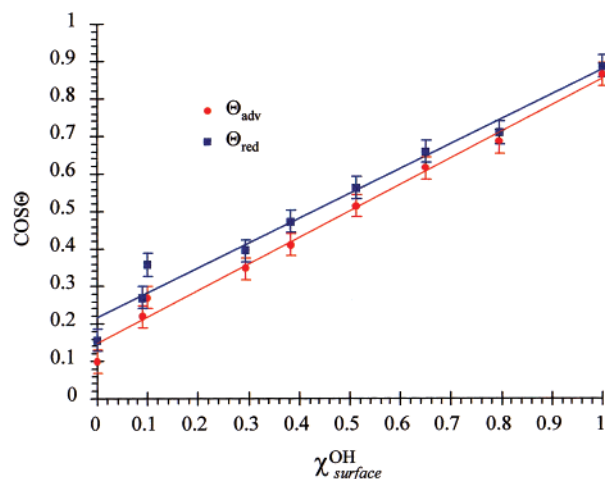
FIGURE 10. Cos θ of advancing and receding water contact angles on mixed CH_3/OH surfaces.

difficult. Therefore, we investigated the long-term stability of SAMs and mixed SAMs of 4-mercaptobiphenyls.

Mixed SAMs of 4′-methyl-4-mercaptobiphenyl and 4′-hydroxy-4-mercaptobiphenyl on gold exhibit an unusually small contact angle hysteresis (=5°). This is attributed to the high quality of the annealed gold surfaces.[48] It is important to note that such contact angle hysteresis values have not been observed for alkanethiolate mixed SAMs on gold. Figure 10 shows a plot of cos θ of advancing and receding water contact angles on mixed CH_3/OH surfaces. Such a linear relationship has been observed previously in mixed SAMs of alkanethiolate SAMs.[8] However, in that

case the surfaces reorganized, exposing the lower energy methylene groups.[15] For example, the advancing water contact angle measured on the surface of 11-hydroxyundecanethiolate SAM on gold increased from 20° to 60° within 1 h of exposure to ambient atmosphere. In contrast, when the samples used for the studies summarized in Figure 10 were investigated after 1 month storage under nitrogen, the same contact angles were recorded. This stability makes these surfaces ideal for studies of surface and interfacial phenomena, such as nucleation and growth of organic and inorganic materials.

Nucleation and Growth of Glycine Crystals

Crystallization from solution is a two-step process: nucleation, which is the birth of new crystals, and crystal growth, which is the growth of existing crystals to larger sizes. In this process, individual molecules form very small prenucleation aggregates (or embryos), which upon reaching a critical size become stable nuclei that grow into macroscopic crystals. In the absence of any foreign surface, homogeneous nucleation is rare and requires high supersaturation to surmount the activation barrier. However, for a fixed supersaturation, the activation barrier, ΔG_{crit}, can be lowered by decreasing the surface energy of the embryo, for instance by introducing a foreign surface. This foreign surface might be a Langmuir layer floating at the air−water interface of the solution or a SAM immersed in the solution.

Indeed, organic monolayer films[49] have been used as an interface[50] across which the geometric matching[51] and
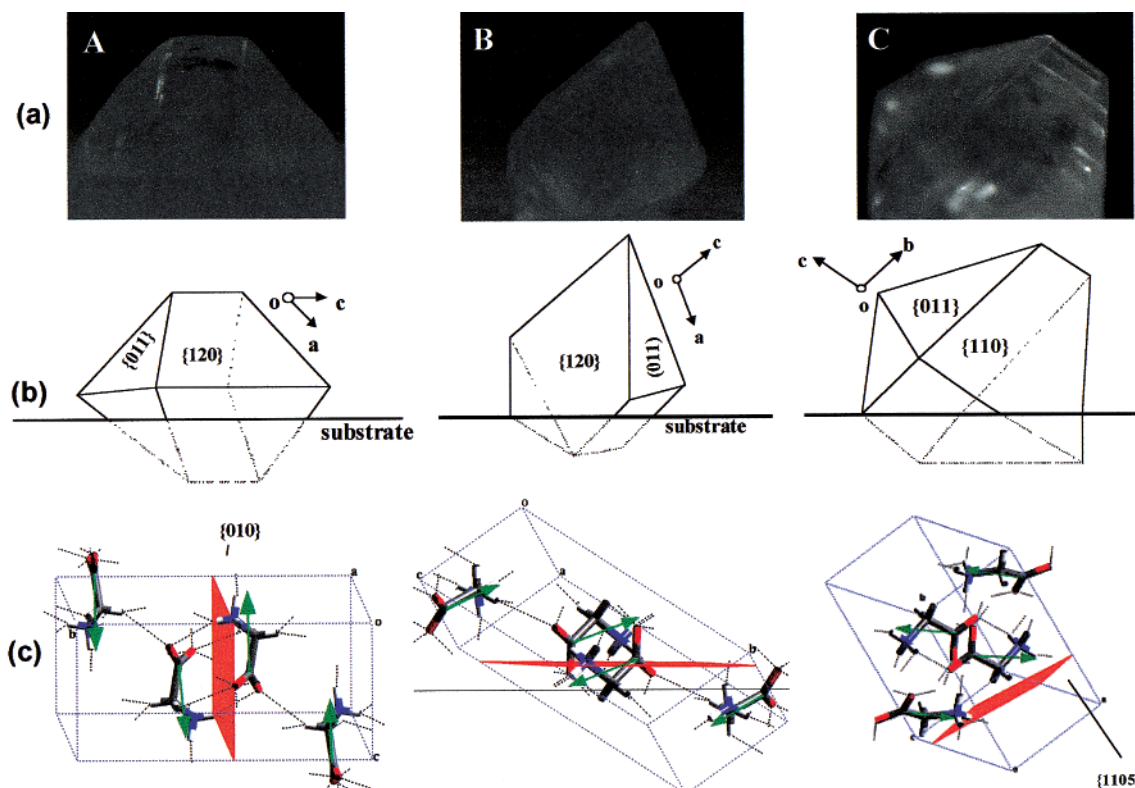

FIGURE 11. Crystallographic image (a), sketched structure (b), and proposed unit cell (c) of glycine crystal nucleated on 25% (A), 50% (B), and 100% pyridine (C).

interactions such as vdW forces and hydrogen bonding[52] can transfer order and symmetry from the monolayer surface to a growing crystal. In all the above examples, monolayers at the air−water interfaces were used as nucleating surfaces. In contrast, SAMs and mixed SAMs lack the mobility of molecules at an air−water interface and hence the possibility to adjust lateral positions to match a face of a nucleating crystal. This is especially true for SAMs of rigid thiols, where even conformational adjustment is not possible. Therefore, SAMs and mixed SAMs of 4-mercaptobiphenyls provide excellent model nucleation surfaces.

Silane SAMs have been used to promote heterogeneous nucleation and growth of iron hydroxide crystals[53] and to study the effect of surface chemistry on calcite nucleation, attachment, and growth.[54] The crystallization of $CaCO_3$ was investigated on surfaces of alkanethiolate SAMs on gold,[55] and recently it was reported that SAMs of functionalized alkanethiols could control the oriented growth of calcite.[56] The heterogeneous nucleation and growth of malonic acid ($HOOCCH_2COOH$) was investigated using alkanethiolate SAMs on gold that terminated with carboxylic acid and with methyl groups.[57]

SAMs and mixed SAMs of 4′-hydroxy-4-mercaptobiphenyl and 4′-methyl-4-mercaptobiphenyl on gold surfaces were used as templates for the nucleation and growth of glycine crystals.[12] The hypothesis was that H-bonding between surface OH groups and glycine molecules might affect the packing and ordering of the glycine-nucleating layer. It was found that glycine nucleates in the α-glycine structure independent of OH surface concentration, but that crystal morphology depends on the composition of the nucleating SAM surface.

Since the OH groups are both H-bond donor and acceptor, we examined mixed SAMs and mixed monolayers of 4-(4-mercaptophenyl)pyridine and 4′-methyl-4-mercaptobiphenyl on planar gold, since the pyridine group can serve only as H-bond acceptor. Again, glycine nucleates in the α-glycine structure independent of pyridine surface concentration, but in this case three different crystal morphologies were formed (Figure 11).

The crystallographic planes corresponding to the nucleation surfaces, for the different surface pyridine concentration studied, were determined by interfacial angle measurements. The difference between the three morphologies is attributed to an evolution of interfacial interactions between the glycine molecules and the SAM surfaces, where the direction of the dipoles of glycine molecules within the crystal is tilted farther away from the nucleation plane as the surface pyridine concentration increases. Additionally, the direction of dipoles of glycine molecules that nucleated on a pyridine surface is not as close to the surface normal as that of the molecules that nucleated on hydroxyl surface. It implies that the overall H-bonding interactions between the CO_2^- and NH_3^+ groups of the glycine and the hydroxyl groups of the SAMs surface are stronger than those between the NH_3^+ and the pyridine group, which is in agreement of the latter being only H-bond acceptor.

Conclusions

In this Account, we reviewed the preparation, structure, properties, and applications of SAMs of rigid 4-mercaptobiphenyls, a unique family of monolayers. These studies highlight the significant differences between SAMs of long-chain aliphatic thiols and aromatic mercaptobiphenyls. The conjugation between the thiolate group and the 4′-substituent through the biphenyl π-system results in a molecular dipole moment that affects the adsorption kinetics on gold surfaces, as well as the equilibrium structure of mixed SAMs. This allows the preparation of surfaces with controlled dipolar interactions, and work is under way to examine the potential applications of such surfaces. The substituent at the 4′-position affects the electron density on the adsorbing thiolate, which defines the structure of the adlayer. Wetting studies shows that SAMs and mixed SAMs of mercaptobiphenyls provide stable model surfaces that can be engineered at the molecular level. Such molecular engineering is important for nucleation and growth studies. The morphology of glycine crystals grown on such surfaces depends on the chemical composition of the SAM, which defines the H-bonding with glycine molecules in the nucleating layer. Studies using other amino acids are in progress.

References

(1) Bigelow, W. C.; Pickett, D. L.; Zisman, W. A. Oleophobic Monolayers: 1. Films Adsorbed from Solution in Non-polar Liquids. *J. Colloid Sci.* **1946**, *1*, 513−538.

(2) (a) Ulman, A. *An Introduction to Ultrathin Organic Films;* Academic Press: Boston, 1991. (b) Ulman, A. Formation and Structure of Self-Assembled Monolayers. *Chem. Rev.* **1996**, *96*, 1533−1554.

(3) See: *Thin Films;* Ulman, A., Ed.; Academic Press: Boston, 1999; Vol. 23.

(4) Sagiv, J. Organized Monolayers by Adsorption 1. Formation and Structure of Oleophobic Monolayers on Solid Surfaces. *J. Am. Chem. Soc.* **1980**, *102*, 92−98.

(5) Nuzzo, R. G.; Allara, D. L. Adsorption of Bifunctional Organic Disulfides on Gold Surfaces. *J. Am. Chem. Soc.* **1983**, *105*, 4481−4483.

(6) Linford, M. R.; Chidsey, C. E. D. Alkyl Monolayers Covalently Bonded to Silicon Surfaces. *J. Am. Chem. Soc.* **1993**, *115*, 12631−12632.

(7) Lee, H.; Kepley, L. J.; Hong, H.-G.; Mallouk, T. E. Inorganic Analogs of Langmuir Blodgett Films−Adsorption of Ordered Zirconium 1,10-Decanebiphosphonate Multilayers on Silicon Surfaces. *J. Am. Chem. Soc.* **1988**, *110*, 618−620.

(8) Ulman, A.; Evans, S. D.; Shnidman, Y.; Sharma, R.; Eilers, J. E.; Chang, J. C. A Concentration-Driven Surface Transition in the Wetting of Mixed Alkanethiol Monolayers on Gold. *J. Am. Chem. Soc.* **1991**, *113*, 1499−1506.

(9) Mrksich, M.; Grunwell, J. R.; Whitesides, G. M. Biospecific Adsorption of Carbonic-Anhydrase to Self-Assembled Monolayers of Alkanethiolates that Present Benzenesulfonamide Groups on Gold. *J. Am. Chem. Soc.* **1995**, *117*, 12009−12010.

(10) Mrksich, M.; Whitesides, G. M. Using self-assembled monolayers to understand the interactions of man-made surfaces with proteins and cells. *Annu. Rev. Biophys. Biomol. Struct.* **1996**, *25*, 55−78.

(11) (a) Tidwell, C. D.; Ertel, S. I.; Ratner, B. D.; Tarasevich, B. J.; Atre, S.; Allara, D. L. Endothelial Cell Growth and Protein Adsorption on Terminally Functionalized, Self-Assembled Monolayers of Alkanethiolates on Gold. *Langmuir* **1997**, *13*, 3404−3413.

(12) Zaccaro, J.; Kang, J. F.; Ulman, A.; Myerson, A. Control of Crystal Morphology in the Crystallization of Glycine on Self-Assembled Monolayer Surfaces. *Langmuir* **2000**, *16*, 3791−3796.

(13) Bishop, A. R.; Nuzzo, R. G. Self-assembled monolayers: Recent developments and applications. *Curr. Opin. Colloid Interface Sci.* **1996**, *1*, 127−136.

(14) Tillman, N.; Ulman, A.; Penner, T. L. Formation of Multilayers by Self-Assembly. *Langmuir* **1989**, *5*, 101−111.

(15) Evans, S. D.; Sharma, R.; Ulman, A. Contact Angle Stability: Reorganization of Monolayer Surfaces? *Langmuir* **1991**, *7*, 156−161.

(16) Kacker, N.; Kuman, S. K.; Allara, D. L. Wetting-Induced Reconstruction in Molecular Surfaces. *Langmuir* **1997**, *13*, 6366−6369.

(17) (a) Kim, Y.-T.; McCarley, R. L.; Bard, A. J. Scanning Tunneling Microscopy Studies Of Au(111) Derivatized with Organothiols. *J. Phys. Chem.* **1992**, *96*, 7416−7422. (b) Obeng, Y. S.; Laing, M. E.; Friedli, A. C.; Yang, H. C.; Wang, D.; Thulstrup, E. W.; Bard, A. J.; Michl, J. Self-Assembled Monolayers of Parent and Derivatized[n] Staffane-3,3(n-1)-dithiols on Polycrystalline Gold Electrodes. *J. Am. Chem. Soc.* **1992**, *114*, 9943−9952.

(18) Scaringe, R. P. In *Electron Crystallography of Organic Molecules*; Fryer, J. R., Dorset, D. L., Eds.; Kluwer: Dordrecht, 1990; pp 85−113.

(19) Young, C. Y.; Pindak, R.; Clark, N. A.; Meyer, R. B. Light Scattering Study of 2-Dimensional Molecular-Orientation Fluctuations in a Freely Suspended Ferroelectric Liquid Crystal Film. *Phys. Rev. Lett.* **1978**, *40*, 773−776.

(20) Ulman A.; Scaringe, R. On the Formation of Two-Dimensional Assemblies. *Langmuir* **1992**, *8*, 894−897.

(21) Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. Structure and Binding of Alkylthiolates on Gold and Silver Surface: Implications for Self-Assembly. *J. Am. Chem. Soc.* **1993**, *115*, 9389−9401.

(22) Sabatani, E.; Cohen-Boulakia, J.; Bruening, M.; Rubinstein, I. Thioaromatic Monolayers on Gold−A New Family of Self-Assembled Monolayers. *Langmuir* **1993**, *9*, 2974−2981.

(23) Dhirani, A.-A.; Zehner, R. W.; Hsung, R. P.; Guyot-Sionnest, P.; Sita, L. R. Self-assembly of conjugated molecular rods: A high-resolution STM study. *J. Am. Chem. Soc.* **1996**, *118*, 3319−3320.

(24) Jones, L., II; Schumm, J. S.; Tour, J. M. Rapid Solution and Solid-Phase Syntheses of Oligo(1,4-phenylene ethynylene)s with Thioester Termini: Molecular Scale Wires with Alligator Clips. Derivation of Iterative Reaction Efficiencies on a Polymer Support. *J. Org. Chem.* **1997**, *62*, 1388−1410.

(25) Hsung, R. P.; Babcock, J. R.; Chidsey, C. E. D.; Sita, L. R. Thiophenol Protecting groups for the Palladium-Catalyzed Heck Reaction−Efficient Synthesis of Conjugated Arylthiols. *Tetrahedron Lett.* **1995**, *36*, 4525−4528.

(26) Sachs, S. B.; Dudek, S. P.; Chidsey, C. E. D. Rates of Interfacial Electron Transfer through π-Conjugated Spacers. *J. Am. Chem. Soc.* **1997**, *119*, 10563−10564.

(27) Tao, Y. T.; Wu, C. C.; Eu, J. Y.; Lin, W. L. Structure Evolution of Aromatic-Derivatized Thiol Monolayers on Evaporated Gold. *Langmuir* **1997**, *13*, 4018−4023.

(28) Kang, J. F.; Ulman, A.; Liao, S.; Jordan, Yang, G.; Liu, G.-Y. Self-Assembled Rigid Monolayers of 4′-Substituted-4-mercaptobiphenyls on Gold and Silver Surfaces. *Langmuir* **2001**, *17*, 95−106.

(29) Karpovich, D. S.; Blanchard, G. J. Direct Measurements of the Adsorption Kinetics of Alkanethiolate Self-Assembled Monolayers on a Microcrystalline Gold Surface. *Langmuir* **1994**, *10*, 3315−3322.

(30) Dannenberger, O.; Buck, M.; Grunze, M. Self-Assembly of *n*-Alkanethiols: A Kinetic Study by Second Harmonic Generation. *J. Phys. Chem. B* **1999**, *103*, 2202−2213.

(31) Liao, S.; Ulman, A.; Shnidman, Y. The Effect of Molecular Dipoles on the Adsorption Kinetics of Rigid Thiols on Gold. *J. Am. Chem. Soc.* **2000**, *122*, 3688−3694.

(32) Bain, C. D.; Troughton, E. B.; Tao, Y.-T.; Evall, J.; Whitesides, G. M.; Nuzzo, R. G. Formation of monolayer films by the spontaneous assembly of organic thiols from solution onto gold. *J. Am. Chem. Soc.* **1989**, *111*, 321−335.

(33) Peterlinz, K. A.; Georgiadis, R. In Situ Kinetics of Self-Assembly by Surface Plasmon Resonance Spectroscopy. *Langmuir* **1996**, *12*, 4731−4740.

(34) DeBono, R. F.; Loucks, G. D.; Manna, D. D.; Krull, U. Self-assembly of short and long-chain *n*-alkyl thiols onto gold surfaces: a real-time study using surface plasmon resonance technique. *Can. J. Chem.* **1996**, *74*, 677.

(35) Hähner, G.; Wöll, Ch.; Buck, M.; Grunze, M. Investigation of Intermediate Steps in the Self-Assembly of *n*-Alkanethiols on Gold Surfaces by Soft X-ray Spectroscopy. *Langmuir* **1993**, *9*, 1955−1958.

(36) Himmelhaus, M.; Eisert, F.; Buck, M.; Grunze, M. Self-Assembly of *n*-Alkanethiol Monolayers. A Study by IR−Visible Sum Frequency Spectroscopy (SFG). *J. Phys. Chem. B* **2000**, *104*, 576−584.

(37) Creager, S. E.; Steiger, C. M. Conformational Rigidity in a Self-Assembled Monolayer of 4-Mercaptobenzoic Acid on Gold. *Langmuir* **1995**, *11*, 1852−1854.

(38) Buck, M.; Grunze, M.; Eiser, F.; Fiser, J.; Träger, F. Adsorption Kinetics of *n*-Alkanethiols on Gold studied by 2nd-Harmonic Generation and X-ray Photoelectron Spectroscopy. *J. Vac. Sci. Technol. A* **1992**, *10*, 926−929.

(39) Sellers, H.; Ulman, A.; Shnidman, Y.; Eilers, J. E. Structure and Binding of Alkylthiolates on Gold and Silver Surface: Implications for Self-Assembly. *J. Am. Chem. Soc.* **1993**, *115*, 9389−9401.

(40) Leung, T. Y. B.; Schwartz, P.; Scoles, G.; Schreiber, F.; Ulman, A. Structure and growth of 4-methyl-4′-mercaptobiphenyl monolayers on Au(111): a surface diffraction study. *Surf. Sci.* **2000**, *458*, 34−52.

(41) Charbonneau, G.-P.; Delugear, Y. Structural Transitions in Polyphenyls. 5. Biphenyl−3-Dimensional Data and new Refinement at 293 K. *Acta Crystallogr., Sect. B* **1977**, *33*, 1586−1588.

(42) Yang, G.; Qian, Y.; Engtrakul, C.; Sita, L. R.; Liu, G.-Y. Arenethiols Form Ordered and Incommensurate Self-Assembled Monolayers on Au(111) Surfaces. *J. Phys. Chem. B* **2000**, *104*, 9059−9062.

(43) Heister, K.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O.; Ulman, A., to be published.

(44) Kang, J. F.; Jordan, R.; Kurth, D. G.; Ulman, A. Optically Induced Peak Shifts in Infrared Spectra of Mixed Self-Assembled Monolayers. *Langmuir* **1999**, *15*, 5555−5559.

(45) Kang, J. F.; Liao, S.; Jordan, R.; Ulman, A. Mixed Self-Assembled Monolayers of Rigid Biphenyl Thiols: Impact of Solvent and Dipole Moment. *J. Am. Chem. Soc.* **1998**, *120*, 9662−9667.

(46) Kang, J. F.; Ulman, A.; Liao, S.; Jordan, R. Self-Assembled Monolayers of Highly Polar Rigid Thiols. *Langmuir* **1999**, *15*, 2095−2098.

(47) Debye, P. *The Dipole Moment and Chemical Structure;* Blackie & Son Limited: London and Glasgow, 1931.

(48) Kang, J. F.; Jordan, R.; Ulman, A. Wetting and Fourier Transform Infrared Spectroscopy Studies of Mixed Self-Assembled Monolayers of 4′-Methyl-4-mercaptobiphenyl and 4′-Hydroxy-4-mercaptobiphenyl. *Langmuir* **1998**, *14*, 3983−3985.

(49) Mann, S.; Heywood, B. R.; Rajam, S.; Birchall, J. D. Controlled crystallization of CaCO₃ Under Stearic Acid Monolayers. *Nature* **1988**, *334*, 692−695.

(50) Mann, S.; Archibald, D. D.; Didymus, J. M.; Douglas, T.; Heywood, B. R.; Meldrum, F. C.; Reeves, N. J. Crystallization at Inorganic−Organic Interfaces−Biominerals and Biomimetic Synthesis. *Science* **1993**, *261*, 1286−1292.

(51) Weissbuch, I.; Berfeld, M.; Bouwman, W.; Kjaer, K.; Als, J.; Lahav, M.; Leiserowitz, L. Separation of Enantiomers and Racemate Formation in Two-Dimensional Crystals at the Water Surface from Racemic α-Amino Acid Amphiphiles: Design and Structure. *J. Am. Chem. Soc.* **1997**, *119*, 933−942.

(52) Weissbuch, I.; Popvitz, R.; Lahav, M.; Leiserowitz, L. Understanding and control of Nucleation, Growth, habit, Dissolution and Structure of 2-Dimensional and 3-Dimensional Crystals Using Tailor-Made Auxiliaries. *Acta Crystallogr.* **1995**, *B51*, 115−148.

(53) Tarasevich, B. J.; Rieke, P. C.; Liu, J. Nucleation and Growth of Oriented Ceramic Films onto Organic Interfaces. *Chem. Mater.* **1996**, *8*, 292−300.

(54) Archibald, D. D.; Qadri, S. B.; Gaber, B. P. Modified calcite deposition due to ultrathin organic films on silicon substrates. *Langmuir* **1996**, *12*, 538−546.

(55) Kuther, J.; Tremel, W. Stabilization of aragonite on thiol-modified gold surfaces: effect of temperature. *Chem. Commun.* **1997**, 2029−2030.

(56) Aizenberg, J.; Black, A. J.; Whitesides, G. M. Oriented Growth of Calcite Controlled by Self-Assembled Monolayers of Functionalized Alkanethiols Supported on Gold and Silver. *J. Am. Chem. Soc.* **1999**, *121*, 4500−4509.

(57) Frostman, L. M.; Bader, M. M.; Ward, M. D. Nucleation and Growth of molecular-Crystals on Self-Assembled Monolayers. *Langmuir* **1994**, *10*, 576−582.