

Enhanced Chain Densities of *n*-Alkanethiolate Self-Assembled Monolayers on Gold from Aqueous Micellar Solutions

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This Letter reports that *n*-alkanethiolate self-assembled monolayers (SAMs) formed onto gold from aqueous micellar solutions of hexaethylene glycol monododecyl ether ($C_{12}E_6$) exhibit greater overall chain densities and are more electrochemically blocking than those formed from traditional organic solvents such as ethanol. As determined by reflectance infrared spectroscopy, the alkyl chains in SAMs formed from 10 mM $C_{12}E_6$ (aq) are less canted on average than those in SAMs formed from ethanol. This greater overall chain density for the water-borne SAMs is attributed to hydrophobic interactions between alkyl chains during assembly. Consistent with a more defect-free structure, the water-borne SAMs exhibit greater resistances against the diffusion of redox probes than SAMs formed in ethanol.

Introduction

The most widely studied system of self-assembled monolayers (SAMs) is that of *n*-alkanethiols ($CH_3-(CH_2)_{n-1}SH$) on gold¹ due to the synthetic flexibility afforded by thiols, the electrochemical inertness of gold, and the ease of preparing highly crystalline molecular films by a simple immersion process.² These films have immense utility in the design of functional surfaces and have been used to study friction,³ wetting,⁴ biological adhesion,⁵ and electron transfer.⁶ Alkanethiolate SAMs on gold are most often formed by immersion or contact of the metal substrate with a dilute organic solution containing the alkanethiol typically at ~ 1 mM concentration. Although organic solvents such as ethanol and isooctane are often employed because they effectively solvate long-chain alkanethiols, these solvents introduce waste disposal problems and generate volatile organic compound (VOC) emissions. The use of organic solvents in the assembly process is a major drawback as the applications of SAMs extend to commercial products.

Another type of self-assembly—that of surfactants into micelles in an aqueous solution—can be used to generate hydrophobic cores that can solubilize nonpolar species.⁷ The solvating ability of these micellar solutions can be extremely sensitive to the molecular structure of the surfactant,⁸ the temperature of the solution,⁹ and addi-

tives¹⁰ that trigger changes in the structure and aggregation number of the micelles. In this Letter, we investigate the structural and electrochemical barrier properties of *n*-alkanethiolate SAMs formed from aqueous micellar solutions of hexaethylene glycol monododecyl ether ($CH_3-(CH_2)_{11}(OCH_2CH_2)_6OH$, $C_{12}E_6$). Micelles of $C_{12}E_6$ offer several advantages as solubilizing vehicles for the assembly of alkanethiols: (1) $C_{12}E_6$ has a low critical micelle concentration (cmc $\sim 8.7 \times 10^{-5}$ M) so that little added surfactant is required to form micelles; (2) $C_{12}E_6$ is nonionic and avoids the presence of counterions that may interfere with the monolayer assembly process; (3) $C_{12}E_6$ is biodegradable;⁷ (4) at room temperature, the average hydrodynamic radius for micelles of $C_{12}E_6$ is considerably greater than that for monodispersed spherical micelles of charged surfactants such as sodium dodecyl sulfate,¹⁰ thereby providing greater core volume⁷ for solubilizing long-chain thiols in $C_{12}E_6$ micelles; and (5) the structure and aggregation number of $C_{12}E_6$ micelles can be tuned by controlling the temperature.⁹

Previous work has demonstrated that alkanethiolate SAMs can be formed from aqueous micellar solutions. Miller and Graetzel¹¹ found that hydroxyl-terminated thiols ($HO(CH_2)_nSH$, $n > 9$) formed more readily from water if micelles of decyltrimethylammonium bromide were present. More recently, Liu and Kaifer¹² reported the preparation of primarily dodecanethiolate ($C_{12}S^-$) SAMs from aqueous micellar solutions of Triton X-100, sodium dodecyl sulfate, and hexadecyltrimethylammonium bromide. They determined that the kinetics of $C_{12}S^-$ SAM formation depends on the concentration of surfactant. Below the critical micelle concentration (cmc), the SAM does not form, but above the cmc, the kinetic rate increases with surfactant concentration as the greater number of micelles enhances the solubilization of the thiol adsorbate. At high surfactant concentration, the rate decreases due to a larger fraction of “empty” micelles. Our work compares the structural properties of *n*-alkanethiolate SAMs with chain lengths as long as 18 carbons formed from aqueous micellar solutions of $C_{12}E_6$ with those formed from ethanol. In addition to the environmental benefits of processing

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SAMs in aqueous solvents, our work shows that the aqueous environment enhances the hydrophobic interactions between the hydrocarbon chains of the alkanethiolates and drives the formation of higher quality monolayers than those formed in typical organic solvents.

Experimental Section

Materials. Gold shot (99.99%) and silicon (100) wafers were obtained from J&J Materials (Neptune City, NJ) and Silicon Sense (Nashua, NH), respectively. All chemicals, including *n*-alkanethiols (Aldrich), hexaethylene glycol monododecyl ether ($C_{12}E_6$, Fluka), potassium ferricyanide ($K_3Fe(CN)_6$, Aldrich), and potassium ferrocyanide trihydrate ($K_4Fe(CN)_6 \cdot 3H_2O$, Aldrich) were used as received. Pure ethanol (AAPER), hexanes (OmniSolv), and isooctane (Fisher) were used as received. Deionized water (16.7 M Ω) was purified with a Modu-Pure system.

Sample Preparation. Gold (1500 Å) was evaporated in a diffusion-pumped chamber (operating pressure of 4×10^{-6} Torr) onto silicon wafers that were pretreated in a two-step process. First, the wafers were placed in piranha solution (4:1 v:v $H_2SO_4/30\% H_2O_2(aq)$) for 20 min followed by rinsing with water and drying thoroughly in a stream of nitrogen. Next, the wafers were immersed in a 50 mM solution of (3-mercaptopropyl)-trimethoxysilane and 1 mM 3-indolepropionic acid in hexanes for 5 min followed by rinsing with hexanes and drying in a stream of nitrogen.

SAMs were prepared by immersing evaporated gold films into solutions containing 1 mM alkanethiol in 10 mM $C_{12}E_6(aq)$ or ethanol at room temperature for times ranging from 1 to 100 h. For SAMs formed from octadecanethiol ($C_{18}SH$), the solutions were first heated to 35 °C to melt the thiol and facilitate solubilization before cooling to room temperature for the assembly. Upon removal, the samples were rinsed with fresh solvent ($C_{12}E_6(aq)$ or ethanol) and dried under a stream of nitrogen.

Reflectance Infrared Spectroscopy. IR spectra were obtained in a single reflection mode with a Bio-Rad Excalibur infrared spectrometer containing a Universal Reflectance Attachment. The p-polarized light was incident at 80° from the surface normal. The reflected light was detected with a narrow-band MCT detector cooled with liquid nitrogen. Spectral resolution was 2 cm^{-1} after triangular apodization. Spectra were referenced to those of SAMs prepared on gold from octadecanethiol- d_{37} , and 1000 scans of both sample and reference were collected.

Electrochemical Impedance Spectroscopy (EIS). Electrochemical impedance measurements of SAM-coated gold samples were performed with a CMS300 electrochemical impedance system (Gamry Instruments) interfaced to a personal computer. A glass cell equipped with a gold-coated silicon counter electrode and a Ag/AgCl/saturated KCl reference electrode contained an aqueous solution of 0.1 M Na_2SO_4 , 1 mM $K_3Fe(CN)_6$, and 1 mM $K_4Fe(CN)_6 \cdot 3H_2O$. The measurements were made at the open circuit potential with a 5 mV ac perturbation that was controlled between 50 mHz and 20 kHz. Film resistance and capacitance values were determined by fitting the EIS data with an equivalent circuit using software provided by Gamry.

Results and Discussion

The quality of the monolayers prepared from ethanol and from aqueous solutions of $C_{12}E_6(aq)$ was assessed using reflectance infrared spectroscopy. The C–H stretching modes in the infrared spectra can be used to determine the relative crystallinity and estimate the average structural conformation for SAMs on metal supports.¹³ Figure 1 shows reflectance infrared spectra of the C–H stretching region for alkanethiolate SAMs on gold (C_nS/Au ; $n = 8, 10, 12, 16$, and 18) formed from 1 mM solutions of the thiol in 10 mM $C_{12}E_6(aq)$ (solid line) or ethanol (dotted line) at room temperature for 100 h. We have chosen ethanol as

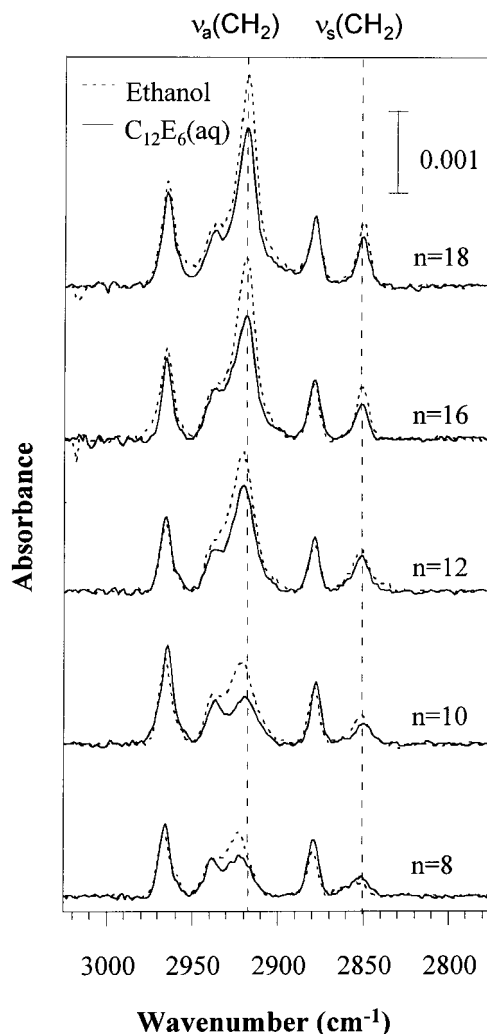


Figure 1. Reflectance infrared spectra of the C–H stretching region for SAMs of C_nSH on gold. The SAMs were formed by immersion in 1 mM thiol-containing solutions of ethanol (dotted line) or 10 mM $C_{12}E_6(aq)$ (solid line). The dashed lines indicate the positions of the primary methylene modes for a trans-extended monolayer with no defects: $\nu_a(CH_2) = 2918\text{ cm}^{-1}$ and $\nu_s(CH_2) = 2851\text{ cm}^{-1}$. The spectra for each chain length have been offset for clarity.

our organic control solvent since we obtain higher quality IR spectra for SAMs formed in ethanol than for SAMs formed in hydrocarbon solvents such as isooctane.¹⁴ From the spectra in Figure 1, the positions of the asymmetric methylene ($\nu_a(CH_2)$) stretching mode are $\sim 2923\text{ cm}^{-1}$ for $n = 8$, $\sim 2920\text{ cm}^{-1}$ for $n = 10$ and 12, and $\sim 2919\text{ cm}^{-1}$ for $n = 16$ and 18, indicating a decrease in the density of gauche conformers with increased chain length. For SAMs formed in 10 mM $C_{12}E_6(aq)$, the asymmetric methylene modes appear at similar ($n = 12, 16, 18$) or lower ($n = 8, 10$) wavenumbers than for the corresponding SAM formed in ethanol. The peak shifts for the SAMs formed from shorter-chained thiols suggest that these SAMs have a lower density of gauche defects when formed in $C_{12}E_6(aq)$, while the longer-chained thiols form SAMs with a relatively low density of gauche defects in either solvent.

The IR spectra for SAMs formed in $C_{12}E_6(aq)$ exhibit a markedly reduced asymmetric methylene intensity and (with the exception of $n = 8$) a reduced symmetric

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(14) On the basis of the positions and intensities of the asymmetric and symmetric methylene modes, spectra of SAMs formed from isooctane were of similar crystallinity but were more canted on average than SAMs formed from ethanol.

methylene ($\nu_s(\text{CH}_2)$) intensity in comparison with those formed in ethanol. The transition dipole moments of these methylene modes are perpendicular to the axis of the hydrocarbon chain, and their intensities in a reflectance infrared spectrum are a function of the molecular tilt (cant angle) and rotation of the chain axis (twist angle) relative to the surface normal.¹⁵ The reduced methylene intensities for the water-borne SAMs indicate a smaller average cant angle compared to those formed from ethanol. The differences in the spectra of the aqueous versus ethanolic SAMs shown in Figure 1 are highly reproducible based on several independent preparations and represent a measurably different average structure for the water-borne monolayer. For example, based on the best agreement for the methylene modes between simulated¹⁶ and measured spectra, the water-borne C_{18} -SAM exhibits a cant that is $\sim 5^\circ$ smaller than the C_{18} -SAM prepared from ethanol.¹⁷ The smaller cant for the water-borne SAM correlates to $\sim 4\%$ greater average chain density of the thiolate adsorbates.

To rationalize the differences in canted structures formed from the aqueous and ethanolic solutions, we must consider the factors that contribute to the average structure of a SAM. The structure that a SAM adopts on a particular metal surface is affected by the metal-adsorbate interaction and interchain contributions such as van der Waals and hydrophobic interactions. In situ AFM studies of SAM formation from 2-butanol onto Au(111) have shown that the thiols are initially physically adsorbed parallel to the gold surface before crystallizing into domains of oriented, chemisorbed thiolates with an interchain spacing of 5.0 Å.¹⁸ This spacing of the adsorbates suggests that the sulfur headgroups bind in the three-fold hollow sites on the gold surface and form a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ overlayer, which is consistent with the findings of others.¹⁹ Ab initio calculations have shown that the interaction between the sulfur and the three-fold hollow site of gold is more energetically favorable than other sulfur-Au interactions such as bridging or on-top sites that could lead to a denser packing of the alkyl chains.²⁰ Therefore, the level of packing for an alkanethiolate SAM on gold should have an upper limit based on the three-

fold hollows as metal-sulfur binding sites. Defects within the SAMs, such as domain boundaries, adsorbate vacancies, and missing-row structures, reduce overall chain density relative to a complete $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ layer.^{21,22}

The use of solvents that enable the thiolates to crystallize into large domains of a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ lattice will result in enhanced chain densities and fewer defects within the SAM. In general, the use of weaker solvents—those that interact weakly with the adsorbates—should provide less perturbation of interchain interactions of the thiolates during assembly than stronger solvents and thereby facilitate their crystallization into larger domains. That we¹⁴ and others^{23,24} observe higher quality films from ethanol than from stronger solvents such as isooctane supports the use of weaker solvents to form superior SAMs. In the case of adsorption from $\text{C}_{12}\text{E}_6(\text{aq})$, hydrophobic interactions likely enable the hydrocarbon chains of the adsorbing thiolates to displace water at or near the surface and crystallize into a film with fewer defects than that formed in ethanol. Stole and Porter²⁵ have used in situ IR spectroscopy to show that SAMs characterized in aqueous solvents are less prone to solvent-induced perturbations of the surface structure than SAMs characterized in less polar liquids. In addition, Hatchett et al. have shown that hydrophobic interactions contribute 1.02 kcal/mol per CH_2 group to the free energy of formation for electrochemically deposited thiolates (RS^-) onto silver electrodes from aqueous solutions.²⁶ Assuming this number to be roughly accurate for the assembly of thiols onto gold from $\text{C}_{12}\text{E}_6(\text{aq})$, the free energy corresponding to the hydrophobic effect for $n = 18$ (~ 20 kcal/mol) is comparable to the strength of interaction between sulfur and the gold surface.²⁷ The relative strength of these hydrophobic interactions should promote the crystallization of adsorbed thiolates into larger domains with fewer defects than would occur in organic solvents where weaker interchain van der Waals interactions are predominant.²⁸

If the SAMs formed from $\text{C}_{12}\text{E}_6(\text{aq})$ are indeed more defect-free than those formed in ethanol, then the water-borne SAMs should exhibit superior barrier properties. As a measure of the barrier properties of these aqueous SAMs, we used EIS to characterize the resistance and capacitance of SAMs in a solution of 1 mM $\text{K}_3\text{Fe}(\text{CN})_6$, 1

(15) On the basis of the surface selection rule, the integrated intensity for a given mode is proportional to the square of the component of its dynamic dipole moment along the surface normal. See: Greenler, R. G. *J. Chem. Phys.* **1966**, *44*, 310–314.

(16) Spectral simulations were performed using a computer program developed and provided by Atul Parikh and David L. Allara. See: Parikh, A.; Allara, D. L. *J. Chem. Phys.* **1992**, *96*, 927–945. The isotropic reference data required for the simulations were obtained by A. Parikh using $(\text{C}_{18}\text{S})_2$ in a KBr matrix.

(17) Using simulated spectra,¹⁶ we estimated that the C_{18}S -SAM from $\text{C}_{12}\text{E}_6(\text{aq})$ has an average cant of 22° and a twist of 54° whereas the ethanolic C_{18} -SAM exhibits a cant of 27° and a twist of 53° , in exact agreement with cant and twist values obtained by Laibinis et al.¹³ On the basis of a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ overlayer of thiolates on Au(111), we would expect the chains to cant $\sim 30^\circ$. That our measured cant values are less than 30° could be due to our use of a polycrystalline gold surface. While exhibiting a predominant (111) texture, the surface of polycrystalline gold often contains regions of other textures that can foster increased packing density of alkanethiols. For example, alkanethiolate SAMs are less canted on electroless gold that exhibits primarily (111) texture but also significant (200), (220), and (311) textures. See: Hou, Z.; Abbott, N. L.; Stroeve, P. *Langmuir* **1998**, *14*, 3287–3297. We emphasize that the cant and twist values reported here are merely estimates based on a single-chain model and should not be taken as exact values. Nevertheless, the difference in cant between the aqueous and ethanolic SAMs is useful to characterize relative differences in overall chain density.

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(28) A less plausible explanation for the smaller cant angle exhibited by the water-borne SAMs is that hydrophobic interactions could promote a greater level of packing than a complete $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ overlayer would allow. This denser packing would involve altering the sulfur-metal binding sites to reduce the interchain distances. However, similarities in the intensities of the methyl modes (Figure 1) between SAMs formed in $\text{C}_{12}\text{E}_6(\text{aq})$ and those formed in ethanol suggest that the metal-sulfur binding sites are independent of the solvent. When the S-S distance is shorter than that for a $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ layer, such as for SAMs on evaporated silver¹³ and silver-modified gold (see: Jennings, et al. *J. Am. Chem. Soc.* **1997**, *119*, 5208–5214), the intensities of the methyl modes are dramatically different than those for SAMs on gold. The different orientation of the terminal methyl groups in the more densely packed films likely results from a different S-C bond angle as the sulfurs occupy sites other than three-fold hollows. Since we observe no real differences in the methyl intensities (Figure 1) between SAMs formed in $\text{C}_{12}\text{E}_6(\text{aq})$ and those formed in ethanol, the increases in overall chain density that we observe are more likely due to SAMs with larger domains of $(\sqrt{3} \times \sqrt{3})\text{R}30^\circ$ structure and fewer defects.

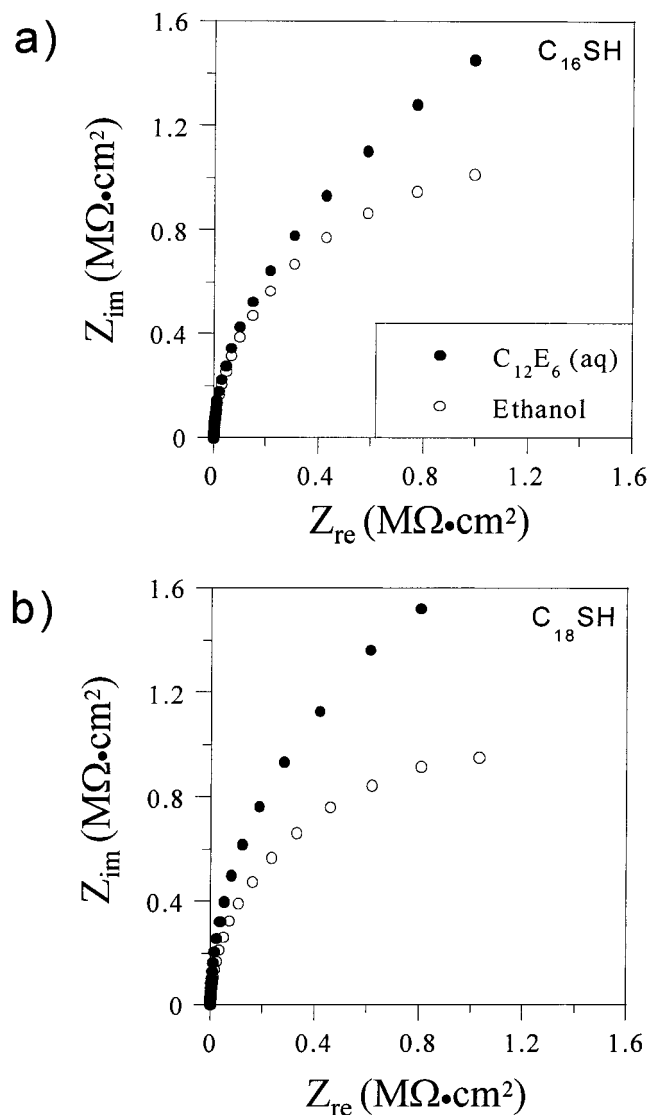


Figure 2. Electrochemical impedance spectra obtained in 1 mM $K_3Fe(CN)_6$, 1 mM $K_4Fe(CN)_6$, and 0.1 M $Na_2SO_4(aq)$ for SAMs formed onto gold from (a) $C_{16}SH$ and (b) $C_{18}SH$ in 10 mM $C_{12}E_6(aq)$ or ethanol for 100 h. The frequency range for these Nyquist plots is 20000 to 0.05 Hz.

mM $K_4Fe(CN)_6$, and 0.1 M $Na_2SO_4(aq)$. Figure 2 shows electrochemical impedance spectra in the form of Nyquist plots for SAMs formed from 100-h immersions in 1 mM solutions of $C_{16}SH$ (Figure 2a) and $C_{18}SH$ (Figure 2b) in either ethanol or 10 mM $C_{12}E_6(aq)$. The charge-transfer

resistance provided by the SAM scales with the radius of the partial semicircle displayed in the Nyquist plot and indicates that the aqueous SAMs exhibit greater resistances to charge transfer than the ethanolic SAMs do. Assuming a simple equivalent circuit containing a solution resistance in series with a parallel combination of interfacial capacitance and charge-transfer resistance, the capacitances from Figure 2a are 1.6 and $1.7 \mu F/cm^2$ and the resistances are 2.9 and $1.8 M\Omega \cdot cm^2$ for $C_{16}S$ -SAMs formed in $C_{12}E_6(aq)$ and ethanol, respectively. Similarly, the capacitances from Figure 2b are 1.5 and $1.6 \mu F/cm^2$ and the resistances are 3.4 and $1.2 M\Omega \cdot cm^2$ for $C_{18}S$ -SAMs formed in $C_{12}E_6(aq)$ and ethanol, respectively. While there are no strong differences in capacitance between the ethanolic and aqueous SAMs, the results are consistent with other reports^{29,30} that have demonstrated the sensitivity of resistance measurements to subtle differences in film structure and packing. The greater resistances for the SAMs formed in aqueous solution are consistent with a film containing larger domains and fewer defects as suggested by the lower average cant angle.

In summary, SAMs formed from $C_{12}E_6(aq)$ exhibit similar crystallinities but greater overall chain densities than SAMs formed from ethanol. These greater chain densities are consistent with increased hydrophobic interactions between the adsorbing thiols in the aqueous solvent that lead to the formation of larger crystalline domains with fewer defects. The greater overall chain density of the water-borne SAMs results in improved barrier properties, including increased resistance of the SAM against the diffusion of redox probes over that of SAMs formed from ethanol. Future efforts will explore the kinetic aspects of SAM formation from aqueous solutions where we report how the molecular composition of the surfactant, the size of the micelle, and the chain length of the alkanethiol affect the molecular structure of the film and the rate of forming SAMs in aqueous solutions.

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