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Supramolecular Ion-Pair Interactions To Control Monolayer Assembly

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Received September 17, 2008. Revised Manuscript Received November 21, 2008

We demonstrate that noncovalent ion-pair interactions in solution can be employed to control the molecular spacing of thiols in a self-assembled monolayer (SAM) on gold. Ion-pairs formed between the carboxylate tail-group of 16-mercaptohexadecanoic acid (MHA) and tetraalkylammonium (TAA⁺) hydroxide salts of various alkyl side-chain lengths remain intact during chemisorption of the thiol on gold. The resulting ion-pair SAMs exhibit a 1:1 molar ratio of MHA:TAA⁺ on the surface and are covalently bound to the gold surface through the thiol headgroup of MHA. We hypothesize that the incorporation of the bulky TAA⁺ group competes with the strong tendency of the thiols to organize into an ordered monolayer, which highlights the strength of the ion-pair complexes. The ion-pair films can be converted into a loosely packed MHA monolayer by rinsing the SAM with a solution of potassium perchlorate, which releases the TAA⁺ from the surface. Contact angle measurements and X-ray spectroscopy (XPS) confirm the stoichiometry and covalent attachment of the monolayers. XPS analysis and contact angle measurements indicate that the surface density of bound MHA decreases with increasing size of the TAA⁺ cation. These results suggest that steric hindrance created by the bulky side-chains of the TAA⁺ cation dictates the lateral spacing of MHA chains on the surface.

1. Introduction

Control of molecular assembly at the solid-liquid interface has the potential to impact micro- and nanoscale devices in areas as diverse as microelectronics and drug delivery, where precise control over interfacial chemistry has become an increasingly powerful tool for enhancing device functionality. 1,2 Physisorption of surfactant is a common method to reversibly alter surface chemistry. For example, surfactants have been shown to adsorb on solid surfaces as hemimicelles, bilayers, or interdigitated monolayers - supramolecular structures that parallel the association of the molecules in solution, but whose stability is highly dependent on the solution conditions.^{3,4} In contrast, chemisorption of self-assembled monolayers (SAMs) generally produces dense crystalline monolayers, stable over a range of solution conditions.² Although often a desired property, the crystalline nature obtained from SAMs limit their practical use in cases where mixed surface functionality or conformational freedom is desired. Motivation to control the packing density of SAMs lies in its potential to profoundly influence interfacial material properties such as wetting⁵ and ion transport.⁶ In addition, certain loosely packed SAMs undergo a reversible and stimuliresponsive conformational change, which could lead to innovation in chemical sensing and separation applications, whereby SAMs are used to trap and release analytes in solution.⁸

Systematic control over the molecular spacing between SAM chains on gold surfaces has been a challenge. SAM formation is known to proceed through a two-step process: rapid initial nucleation of domains (or tight clusters of adsorbates) on the surface, followed by union of the domains and gradual reordering of adsorbates into a crystalline monolayer. Thus, reducing the self-assembly time of a SAM does not result in uniform, lowdensity films. Introducing steric hindrance between neighboring thiol adsorbates during the self-assembly step has been shown to yield SAMs with increased lateral spacing between adsorbates. Various strategies, including the synthesis of dialkyl sulfides,^{5,10} chelating thiols, ¹¹ and thiols with a detachable, bulky terminus^{6,7} have been used to achieve SAMs with a disordered, more loosely packed assembly of thiols. However, all of these approaches rely upon covalent chemistry to chemically modify the structure of the alkane thiol, in order to generate the bulky adsorbate. A method for creating loosely packed monolayers using reversible chemistry, whereby broad variation in the thiol packing density can be readily achieved with minimal synthesis steps has yet to be developed.

We propose a versatile approach relying on noncovalent ion-pair interactions in solution to control the molecular packing density of SAMs at a solid—liquid interface. Ion-pairs are neutral complexes formed when two oppositely charged ions are drawn together by electrostatic attraction in solution. Although no chemical bond is formed between the two components, ion-pair formation between similarly sized organic ions in solution has been shown to produce a stable, nondissociating adduct, especially in low dielectric constant solvents. ^{12,13} The existence of stable ion-pairs has already been exploited in a variety of applications,

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⁽¹⁾ Chaki, N. K.; Vijayamohanan, K. *Biosens. Bioelectron.* **2002**, *17*, 1–12.

⁽²⁾ Love, J. C.; Estroff, L. A.; Kriebel, J. K.; Nuzzo, R. G.; Whitesides, G. M. Chem. Rev. 2005, 105, 1103–1170.

⁽³⁾ Tulpar, A., Ducker, W. A. J. Phys. Chem. B 2004, 108, 1667–1676.

⁽⁴⁾ Burgess, I.; Zamlynny, V.; Szymanski, G.; Lipkowski, J.; Majewski, J.; Smith, G.; Satija, S.; Ivkov, R. *Langmuir* **2001**, *17*, 3355–3367.

⁽⁵⁾ Troughton, E. B.; Bain, C. D.; Whitesides, G. M.; Nuzzo, R. G.; Allara, D. L.; Porter, M. D. *Langmuir* **1988**, *4*, 365–385.

⁽⁶⁾ Berron, B.; Jennings, G. K. Langmuir 2006, 22, 7235-7240.

⁽⁷⁾ Lahann, J.; Mitragotri, S.; Tran, T. N.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A.; Langer, R. *Science* **2003**, *299*, 371–374.

⁽⁸⁾ Huber, D. L.; Manginell, R. P.; Samara, M. A.; Kim, B. I.; Bunker, B. C. Science **2003**, *301*, 352–354.

⁽⁹⁾ Song, X.; Sylvain, J. N. C.-D.; Jayne, C. G.; Gang-Yu, L.; Jennings, G. K.; Tseh-Hwan, Y.; Paul, E. L. *J. Chem. Phys.* **1998**, *108*, 5002–5012.

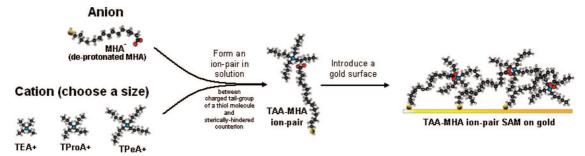
⁽¹⁰⁾ Zhang, S.; Jamison, A. C.; Schwartz, D. K.; Lee, T. R. Langmuir 2008, 24, 10204–10208.

⁽¹¹⁾ Park, J. S.; Vo, A. N.; Barriet, D.; Shon, Y. S.; Lee, T. R. Langmuir 2005, 21, 2902–2911.

⁽¹²⁾ Kraus, C. A. J. Phys. Chem. 1956, 60, 129-141.

⁽¹³⁾ Nagy, P. I.; Takacs-Novak, K. J. Am. Chem. Soc. 2000, 122, 6583–6593.

Scheme 1. Proposed Mechanism of Ion-Pair Assisted Self-Assembly on Gold^a



^a Orientation of ion-pairs within the SAM is not intended to be an accurate depiction of film; SAM image is merely meant to illustrate the experimentally observed chemisorption of sulfur on gold and loose-packing of MHA chains. Element color-code: carbon (black), hydrogen (white), nitrogen (blue), oxygen (red), sulfur (yellow).

including liquid—liquid extractions, ^{14,15} ion-exchange resins, ¹⁶ solubilizing lipophilic drug molecules, ^{17,18} and polymerization. ¹⁹ Ion-pairs have also been shown to influence molecular assembly at air—liquid interfaces ^{20–22} and at the solid—liquid interface of physisorbed Langmuir—Blodgett films. ²³

Here we combine ion-pair interactions with self-assembled monolayer formation at a solid—liquid interface. In doing so, we investigate the competition between supramolecular interactions in solution (which govern the formation of the ion-pairs) and intermolecular forces at the solid-liquid interface (which govern the self-assembly of the ion-pairs). Using X-ray photoelectron spectroscopy (XPS) and contact angle measurements we show that the formation of tight pairs between mercaptohexadecanoic acid (MHA) and tetraalkylammonium ions (TAA⁺) in solution leads to covalently bound monolayers that are composed of TAA-MHA pairs. Our results also indicate that the density of thiols on the surface can be varied with the size of the TAA⁺ ion employed. The TAA⁺ ion can be released from the film under the appropriate solution conditions and the resulting SAM exhibits a lower surface density of MHA chains compared to fully packed MHA SAMs. Lastly, the ion-pair SAMs are highly resistant to ion-exchange treatments in aqueous solution, in contrast to fully packed SAMs which were found to exhibit weak binding of TAA⁺ cations. These results support the conclusion that binding of quaternary ammonium groups is enhanced or stabilized by increased conformational freedom and lateral spacing between carboxylic acid moieties within a film, making ion-pair assisted self-assembly on gold a potential means for engineering robust molecular recognition devices.^{23,24}

2. Experimental Section

Materials. 16-mercaptohexadecanoic acid (90%), hexadecanethiol (92%), carbon tetrachloride (99.99%), and tetralkylammonium

hydroxide salts of increasing chain lengths: $[CH_3(CH_2)_n]_4N^+OH^-$ (hereafter referred to as TEA⁺ for n=1, TProA⁺ for n=2, and TPeA⁺ for n=4, purchased as 1 M aqueous solutions), were used as received from Sigma-Aldrich. KOH pellets, HClO₄, H₂SO₄, H₂O₂, and hexadecane were purchased from Fisher Scientific. Silicon wafers (100) were purchased from Montco Silicon. Gold wire (99.99%) was purchased from Kurt J. Lesker. Chromium (99.99%) was purchased from Alfa Aesar. Ethanol (200 Proof) was used as received from Warner-Graham Co. Purified water (18.3 M Ω -cm) was obtained from a Milli-Q Gradient system.

Preparation of Gold Substrates. The Au/Si(100) substrates were prepared by thermal evaporation of a 20 nm layer of Cr followed by 200 nm of gold, both at a rate of 0.2 nm/s, in a diffusion-pumped vacuum chamber (BOC Edwards) at 2×10^{-6} mbar. The gold films were cleaned prior to SAM deposition by sonication in acetone, followed by a 10-min immersion in piranha (4:1 H₂SO₄:H₂O₂) solution. The substrates were rinsed thoroughly with purified water and immersed in pure ethanol followed by pure carbon tetrachloride prior to immersion in the carbon tetrachloride-based SAM solution.

Formation of SAMs. TAA—MHA ion-pair SAMs were prepared by immersing the clean gold substrates in a 1 mM concentration of each TAA—MHA ion-pair in carbon tetrachloride for 24 h. Similarly, fully packed SAMs were prepared by immersing clean gold substrates in a 1 mM concentration of pure MHA in carbon tetrachloride for 24 h. All SAMs were rinsed with ethanol and dried with a stream of nitrogen gas upon removal from the SAM solution.

Characterization of SAMs. Static contact angle measurements were measured with a FTA125 apparatus from First Ten Angstroms using purified water and hexadecane. All measurements were taken at room temperature by the sessile drop method and averaging the results of 10 drops on at least three different samples. X-ray Photoelectron Spectroscopy (XPS) was performed using a Mg Kα (1253.6 eV) X-ray anode of a Physical Electronics 04-500 dualanode X-ray source and 10-360 precision energy analyzer. All spectra were acquired at 15 kV and 300 W, using a 45° takeoff angle and 44.75 eV pass energy. High resolution (with 0.125 eV/step) spectra were obtained for the Au4f, O1s, C1s, N1s, C12p, and S2p regions. A minimum number of scans were accumulated to try to minimize X-ray-induced damage to the monolayers. The binding energies were referenced to the Au4f(7/2) peak at 83.9 eV and background subtraction was effected following Shirley's method.²⁵ Peak areas, used to compute elemental ratios, ²⁶ were obtained from Gaussian functions after correction for photoionization cross section²⁷ in CasaXPS software.

3. Results and Discussion

3.1. Formation of Ion-Pair SAMs. The one-step approach for making ion-pairs (Scheme 1) is simple and relies on the

⁽¹⁴⁾ Choi, M. M. F.; Douglas, A. D.; Murray, R. W. Anal. Chem. **2006**, 78, 2779–2785.

⁽¹⁵⁾ Wu, J. M.; Lee, H. K. J. Chromatogr. A 2006, 1133, 13-20.

⁽¹⁶⁾ Kunio, K.; Okuwaki, A. Sep. Sci. Technol. 2006, 41, 379–390.

⁽¹⁷⁾ QuintanarGuerrero, D.; Allemann, E.; Fessi, H.; Doelker, E. *Pharm. Res.* 1997, 14, 119–127.

⁽¹⁸⁾ Fang, L.; Numajiri, S.; Kobayashi, D.; Ueda, H.; Nakayama, K.; Miyamae, H.; Morimoto, Y. *J. Pharm. Sci.* **2004**, *93*, 144–154.

⁽¹⁹⁾ Bordes, R.; Rbii, K.; Gonzalez-Perez, A.; Franceschi-Messant, S.; Perez, E.; Rico-Lattes, I. *Langmuir* **2007**, *23*, 7526–7530.

⁽²⁰⁾ Nakagawa, M.; Watase, R.; Ichimura, K. Chem. Lett. 1999, 28, 1209– 1210.

⁽²¹⁾ Panambur, G.; Zhang, Y.; Yesayan, A.; Galstian, T.; Bazuin, C. G.; Ritcey, A. M. *Langmuir* **2004**, *20*, 3606–3615.

⁽²²⁾ Panda, A. K.; Possmayer, F.; Petersen, N. O.; Nag, K.; Moulik, S. P. *Colloid Surface A* **2005**, *264*, 106–113.

⁽²³⁾ Kamino, A.; Koyano, H.; Ariga, K.; Kunitake, T. B. Chem. Soc. Jpn. 1996, 69, 3619–3631.

⁽²⁴⁾ Qune, L.; Makino, K.; Tamada, K.; Chen, W.; Wee, A. T. S. J. Phys. Chem. C 2008, 112, 3049–3053.

⁽²⁵⁾ Shirley, D. A. Phys. Rev. B 1972, 5, 4709-4714.

⁽²⁶⁾ Moulder, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D. In *Handbook of X-ray Photoelectron Spectroscopy*; Perkin-Elmer Corporation: Eden Prairie, MN, 1992.

⁽²⁷⁾ Scofield, J. H. J. Electron Spectrosc. Relat. Phenom. 1976, 8, 129-137.

Table 1. XPS Binding Energies (eV)

	МНА	MHA exposed to TEAOH	TEA- MHA pair	TProA- MHA pair	TPeA- MHA pair
C1s: COO O1s N1s	289.7 533.5	289.6 533.2 401.5	288.2 532.8 400.3	288.9 532.6 400.6	289.0 533.0 400.6

driving force for organic ions of opposite charge to associate into neutral complexes in low dielectric constant (ϵ_r) solvents. To this effect, we chose carbon tetrachloride as the solvent (ϵ_r = 2.2), MHA as the SAM precursor molecule (an organic anion upon deprotonation of the carboxylic acid group), and a tetraalkylammonium hydroxide salt as the source of cation. TAA-MHA ion-pairs were formed in solution by adding the tetralkylammonium hydroxide (TAAOH) aqueous solution to a 1 mM solution of MHA in carbon tetrachloride to obtain a molar ratio of 4:1 TAAOH:MHA. We chose to work with an excess of TAA⁺ to reduce the risk of incomplete pairing. Under these conditions, the TAAOH solution provides both the base to deprotonate the carboxylic acid tail-group of MHA and the cation for the subsequent formation of a TAA-MHA ion-pair. The mixture was sonicated for 5 min to facilitate transfer of the ionpair into the organic subphase, and then allowed to equilibrate for at least 48 h. Ion-pair SAMs were prepared by immersing clean gold substrates in an aliquot of the organic subphase for 24 h. The solution prepared from TPeA⁺ needed to be heated to 40 °C due to the low solubility of the pairs.

3.2. XPS Analysis. XPS was performed to determine the composition and coverage of the ion-pair monolayers. The following five spectral regions of interest were surveyed: O1s (526-538 eV), N1s (394-412 eV), C1s (280-300 eV), S2p $(158-170 \,\mathrm{eV})$, and Au4f $(80-95 \,\mathrm{eV})$. We looked for the presence of the ion-pairs on the surface, covalent attachment of the monolayer, and finally the film coverage (compared to a fully packed MHA film). Using the standard deviation of the peak area for each spectral region (C1s, O1s, N1s, S2p, and Au4f), we calculate the precision of our C/N and O/N ratios to be ± 1.1 and ± 1.5 , respectively. We note that this is considerably higher than the precision of our C/Au and C/O ratios, which are ± 0.09 and ± 0.5 , respectively. We have also analyzed the variation in the XPS ratios across multiple samples, for each type of SAM investigated in this study, and report the statistical mean \pm standard deviation for each XPS ratio in Table 2.

3.2.1. Presence of Ion-Pairs on the Surface. The presence of the TAA⁺ cation on the surface of all ion-pair SAMs is readily detected from the N1s signal (Figure 1). The position of the N1s peaks (BE between 400.3-400.6 eV, see Table 1) suggest that the TAA⁺ ions are present in the form of an ion-pair, rather than physisorbed within the film. Compact ion-pairs formed between tetra*methyl*ammonium cations (Me₄N⁺) and an inorganic anion, such as chlorine and bromine, have been known to appear at 402 and 401 eV, respectively.²⁸ The decrease in binding energy observed from the chloride to the bromide salt form (that is, with decreasing electronegativity of the anion) shows the strong influence that the electron affinity of the counterion has on the energy level of the N1s core electrons of the quaternary ammonium ion. The TAA⁺ cations used in this study are paired with a carboxylate anion, in which the negative charge is delocalized between two oxygen atoms. Because each oxygen atom in the carboxylate ion carries only a partial negative charge, it is likely that the valence shell of the nitrogen atom in a TAA⁺/ COO $^-$ ion-pair is less polarized than that of a Me₄N $^+$ /Cl $^-$ ion-pair, and consequently, the N1s core electrons in a TAA $^+$ /COO $^-$ ion-pair are less tightly bound to the nitrogen than those of the Me₄N $^+$ /Cl $^-$ ion-pair. Moreover, our data are consistent with that of ammonium paired with a carboxylate counterion (NH₄ $^+$ /CH $_3$ COO $^-$), which appears at 400.9 eV. 29 Thus, the presence and binding environment of the nitrogen photoelectrons confirms that TAA $^+$ ions are present within the monolayer and paired with the terminal carboxylate group of the MHA chain.

The peak positions for the C1s and O1s regions also confirm that the TAA⁺ ions are paired with the MHA chains (Figures 2-3). The carboxylic acid carbon of MHA in the ion-pair SAMs shifts to a lower binding energy compared to that of a monolayer of MHA made without TAA⁺ ions (Figure 2 and Table 1). This shift has been attributed to the deprotonation of MHA³⁰ and we have observed this shift (BE of 288.8 eV for COO) in monolayers prepared from a mixture of MHA and KOH in ethanol (data not shown). Similarly, the O1s region (Figure 3) of the ion-pair SAMs are consistently shifted to lower binding energy relative to the fully packed SAM made from MHA alone (Table 1). This small, but significant shift is in agreement with the loss of an acidic proton from the hydroxyl group of MHA, since converting the oxygen atoms at the terminus of MHA into a negatively charged carboxylate species would lower the binding energy of the O1s core electrons.

The stoichiometry obtained from XPS measurements is consistent with a molar ratio of MHA:TAA+ very close to 1:1 within the monolayers (Table 2). The C1s/N1s and O1s/N1s intensity ratios are in good agreement with an O1s/N1s ratio of 2 and the proper C1s/N1s ratios expected for all three of the TAA⁺ ions tested. It should be noted, however that ratios involving the N1s intensity (the C/N and O/N ratios) are particularly prone to a large uncertainty due the low signal-to-noise ratio measured for nitrogen. Water molecules are known to be part of ion-pairs¹³ and are difficult to remove from quaternary ammonium-containing films. 24,31 This could account for the higher O1s/N1s and lower C1s/Os ratios observed for the TPeA-MHA films. We also observe that the TPeA-MHA monolayer has the highest C1s/ Au4F ratio of the three ion-pair SAMs and is therefore more susceptible to attenuation of C1s photoelectrons with increasing depth of the film. This attenuation of C1s photoelectrons, with increasing distance from the film surface, also explains why the C1s/O1s ratios for TPeA-MHA and fully packed MHA SAMs are lower than the value predicted by stoichiometry.

3.2.2. Ion-Pairs Control the Coverage of MHA on Gold. The C1s/Au4f intensity ratios (Table 2) provide an estimate of the thickness of the three different ion-pair SAMs, relative to a fully packed MHA SAM.³² All three ion-pair SAMs have C1s/Au4f ratios less than 1.8 (the value obtained for the fully packed monolayer), indicating Au4f photoelectrons emitted from the underlying gold substrate are less attenuated in the ion-pair SAMs compared to the SAMs made from MHA alone. The ion-pair SAMs also exhibit a lower concentration of carboxylic acid groups, as seen from their lower O1s intensities, compared to the fully packed MHA SAM (Figure 3).

To a first approximation it appears that the number of MHA chains attached on the surface is dictated by the size of the TAA⁺ cation. The TAA⁺ cation is the only source of nitrogen within

⁽²⁸⁾ Wagner, C. D.; Riggs, W. M.; Davis, L. E.; Moulder, J. F.; Muilenberg, G. E. In *Handbook of X-ray Photoelectron Spectroscopy*. Perkin-Elmer Corp.: Eden Prairie. MN. 1979.

⁽²⁹⁾ Kelemen, S. R.; Afeworki, M.; Gorbaty, M. L.; Kwiatek, P. J.; Solum, M. S.; Hu, J. Z.; Pugmire, R. J. Energy Fuel 2002, 16, 1507–1515.

⁽³⁰⁾ Willey, T. M.; Vance, A. L.; van Buuren, T.; Bostedt, C.; Nelson, A. J.; Terminello, L. J.; Fadley, C. S. *Langmuir* **2004**, *20*, 2746–2752.

⁽³¹⁾ Azzaroni, O.; Moya, S.; Farhan, T.; Brown, A. A.; Huck, W. T. S. *Macromolecules* **2005**, *38*, 10192–10199.

⁽³²⁾ 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.

Table 2. Relevant Ratios of XPS Intensities for Fully-Packed (MHA) and Ion-Pair SAMs^a

	· · · · · · · · · · · · · · · · · · ·					
	MHA	MHA exposed to TEAOHb	TEA-MHA pair	TProA-MHA pair	TPeA-MHA pair	
C1s/Au4f	1.8 ± 0.2	2.3 ± 0.1	0.9 ± 0.4	0.7 ± 0.1	1.43 ± 0.01	
C1s/O1s	$7 \pm 1 \ (8)$	$5.8 \pm 0.2 (10.4)$	$10 \pm 1 \ (12)$	$12 \pm 3 (14)$	$9 \pm 1 (18)$	
O1s/N1s		$8.5 \pm 1.0 (3.3)$	2.4 ± 0.8	2.7 ± 0.7	3.5 ± 1.0	
C1s/N1s		$48.9 \pm 0.9 (34.4)$	$23.1 \pm 4.2 (24)$	$31.6 \pm 1.0 (28)$	31.9 ± 7.4 (36)	

 $[^]a$ Values are reported as the mean \pm standard deviation of several samples. Value in parentheses corresponds to the ratio based on stoichiometry of each TAA-MHA ion-pair or pure MHA adsorbate. b Number in parentheses corresponds to the ratio assuming MHA SAM adsorbs a monolayer of TEA+ cations that pack according to the steric size of TEA+ in solution (3.4 Å), e.g., a 1.65 molar ratio of MHA to TEA+.

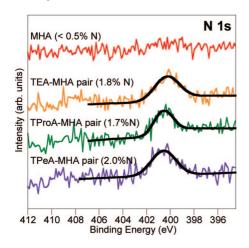


Figure 1. XP spectra of N 1s region for MHA and TAA—MHA ion-pair SAMs on gold.

the monolayers and the number of carbon atoms attached to each nitrogen atom is known from the chemical structures of the TPeA⁺, TProA⁺, and TEA⁺ shown in Scheme 1 (TPeA+ has 20 carbon atoms for every 1 nitrogen atom, TProA⁺ has 12, TEA⁺ has 8). The percentage of the total carbon on the surface coming from the TAA⁺ cation can be estimated for each ion-pair SAM. The remainder of the total carbon on the surface, after accounting for the quaternary ammonium carbon, is assigned to MHA molecules and taking the ratio of the remaining carbon to the carbon corresponding to a fully packed MHA monolayer allows us to approximate the MHA packing density of the three different ion-pair SAMs. The results of these calculations suggest that SAMs prepared from the TEA⁺, TProA⁺, and TPeA⁺ ionpairs contain 55 \pm 5, 43 \pm 3, and 31 \pm 11% of the amount of MHA present in a fully packed SAM, respectively (Table 3). This approach is only an approximation, as it does not take into account the attenuation of C1s photoelectrons and relies heavily upon the accurate detection of nitrogen within the monolayers. Nevertheless, the estimates of MHA packing density that we obtain through this calculation are not far from the theoretical packing limits of 61, 48, and 33% imposed by the size of the TEA^+ (3.4 Å radius), $TProA^+$ (3.8 Å), and $TPeA^+$ (4.6 Å) cations, respectively (assuming that each TAA-MHA ion-pair occupies a spherical cross-sectional area of radius approximately equal to the radius of the TAA⁺ cation in solution). ^{33,34} Additionally, the amount of MHA bound to the surface remains the same after the TEA⁺ cation has been removed (while the oxygen content remains at 5%, data not shown), which confirms both the loosely packed nature of the MHA films and the rough estimate of surface coverage. Alternatively, the packing density of MHA can also be estimated by comparing the amount of oxygen in an ion-pair film to the amount present in a fully packed MHA film (Table 3). Using this method we see that the surface coverage calculated for SAMs prepared using TEA⁺ and TProA⁺ is consistent with

Figure 2. XP spectra of C 1s region for MHA and TAA—MHA ion-pair SAMs on gold.

our previous estimates. Films prepared from TPeA⁺, however, have higher oxygen content than what we would expect based on the size of the ion. This discrepancy leads us to suspect that the lower charge density of the TPeA⁺ cation (longer alkyl sidechain length) may cause it to form loose (more hydrated)^{13,17} ion-pairs with MHA. As noted by Osakai et al.,35 anions are known to carry up to four water molecules during transfer from the aqueous to the organic phase, and according to Nagy et al. 13 the tendency to form solvent-separated ion-pairs becomes more favorable with increasing size of the organic ions. The synthesis of the ion-pair complexes made from TPeA⁺ is also more sensitive to the experimental conditions due to the lower solubility of the TPeA-MHA pairs in CCl₄. Finally, the crystal lattice and surface roughness might impose a lower limit on surface coverage and prevent us from achieving the packing density predicted by the radius of the TPeA⁺ cation.

The S2p intensity of a SAM is not a straightforward measure of thiol packing density, especially when considering SAMs

TProA-MHA pair

TPeA-MHA pair

TPeA-MHA pair

TPeA-MHA pair

292 290 288 286 284

Binding Energy (eV)

⁽³³⁾ Osakai, T.; Ebina, K. J. Phys. Chem. B. 1998, 102, 5691–5698.

⁽³⁴⁾ Samec, Z. Pure Appl. Chem. 2004, 76, 2147-2180.

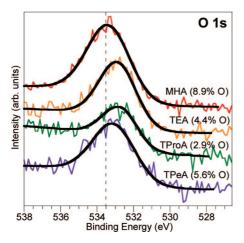


Figure 3. XP spectra of O 1s region for MHA and TAA—MHA ion-pair SAMs on gold.

composed of loosely packed or disordered thiol chains. ¹¹ Sulfur atoms are located furthest from the surface of the film and have a low atomic sensitivity factor, making the S2p intensity level particularly prone to attenuation by the overlying organic layer. For this reason, sulfur was not used to enumerate the number of MHA molecules bound to the surface. The ion-pair SAMs have approximately the same intensity of S2p photoelectrons (1.1–1.3% of total atoms on the surface) as the fully packed MHA monolayer (0.9%). The similarity in S2p intensities could be due to the fact that the ion-pair SAMs may have fewer, but more exposed (less attenuated) sulfur atoms on the surface than a fully packed MHA film.

The lower surface coverages of MHA observed in the ion-pair SAMs is not due to electrostatic repulsion arising from the deprotonation of MHA. SAMs prepared from MHA-K⁺ ionpairs resulted in the same coverage as that of a fully packed MHA monolayer. The presence of the TAA⁺ cation in solution by itself, and possibly physisorbed at the gold-solution interface, also does not account for the loose-packing of thiol observed with the ion-pairs, as we obtain defect-free SAMs when we expose gold substrates to a solution of 4:1 molar ratio of TProAOH: Hexadecane thiol in carbon tetrachloride. Only when a TAA⁺ cation is bound to the negatively charged carboxylate group at the terminus of MHA do we observe lower surface coverages of the thiol on gold. Taken together, these findings lead us to conclude that loosely packed MHA films result from TAA-MHA ion-pairs due to the steric hindrance created by the large size of the TAA⁺ cation, which is adsorbed at the surface in the form of a tightly bound ion-pair with MHA. The presence of the TAA⁺ cation, bound to every MHA tail-group, prevents the MHA molecules from achieving the same packing density as MHA alone. The orientation with which the TAA⁺ cation aligns itself with the tail-group of the MHA molecule, 36 as well as other intermolecular interactions, such as solvation of the ion-pairs, may be responsible for determining how the three TAA-MHA ion-pairs are arranged at the gold surface.

3.2.3. Covalent Attachment at the Gold Surface. All of the SAMs exhibited an S2p doublet with a maximum at 162 eV (Figure 4), which is characteristic of covalently bound thiols.³⁷ The SAMs also did not contain an appreciable amount of oxidized sulfur (S2p binding energy > 168 eV). A few of the ion-pair SAMs (TEA— and TProA—MHA pairs) needed to be fit with

an additional doublet, in order to account for a low level of S2p intensity at 163.5 eV that has been shown to arise from either X-ray induced damage 38,39 or a small amount of physisorbed thiol. 37 Chlorine, due to carbon tetrachloride molecules trapped within the monolayer, was not detected on any of the films (spectra not shown). These observations confirm that the thiol headgroup of MHA chemisorbs to the gold substrate in the form of unoxidzed sulfur, for both fully packed and ion-pair SAMs prepared in carbon tetrachloride. As expected, the thiol group does not chemically react with carbon tetrachloride, water, TAA^+ , and OH^- species present in solution.

3.2.4. Ion Exchange. In addition, we note that the ion-pairs assembled on the surface exhibit remarkably strong binding interactions with the TAA⁺ cations. The C1s/N1s and O1s/N1s ratios remain unchanged from the values presented in Table 2, even for ion-pair SAMs characterized by XPS after exposure to aqueous acid (0.5 M HClO₄) or base (0.5 M KOH) ion-exchange steps—demonstrating the strength and stability of the supramolecular TAA⁺/COO⁻ interactions. The TAA⁺ cation is successfully removed from the film using a solution of potassium perchlorate prepared in dimethyl sulfoxide (DMSO); Figure 5 shows the N1s and S2p spectra of a film prepared from TEA-MHA pairs, after the film has been exposed to the DMSO solution. Perchlorate anions are known to form strong pairs with TAA⁺ cations, ^{31,40} while the high dielectric constant of DMSO $(\epsilon_r = 48)$ likely weakens the stability of the TAA-MHA pair and facilitates the ion-exchange process.

In contrast to the tight TAA-MHA pairs observed in the ion-pair SAMs, XPS results indicate that fully packed MHA SAMs, exposed to a 1 mM solution of TEAOH in ethanol, bind fewer TEA⁺ cations on the surface than is predicted by the steric size (3.4 Å ionic radius in solution^{33,34}) of the TEA⁺ cation (Table 2). Furthermore, the binding energies of the carboxylic acid and oxygen photoelectrons emitted from the fully packed MHA film exposed to TEAOH appear at 289.6 and 533.2 eV, respectively, which suggests that the majority of MHA molecules within the fully packed monolayer are protonated, rather than paired with a TEA+ cation. In view of these results, it appears that the increased lateral spacing and conformation freedom of carboxylic acid moieties within films assembled from TAA-MHA ion-pairs in solution is beneficial for achieving tight, stable binding interactions with TAA+ cations, compared to the dense-packing of COOH groups present within traditional fully packed SAMs made from MHA alone. These findings are in agreement with what has previously been shown by Qune et al., with regards to the enhancement of binding interactions between quaternary ammonium and carboxylic acid functional groups achieved through tailoring the interatomic spacing of receptor moieties within a SAM.²⁴

3.3. Contact Angle Measurements. Contact angle measurements were performed on ion-pair SAMs and compared to fully packed SAMs made in carbon tetrachloride. The advancing water contact angles (Table 3) of fully packed SAMs made from pure MHA and pure hexadecanethiol (HDT) were consistent with what we have observed with the same SAMs prepared in ethanol, as well as previous reports of MHA and HDT films prepared in ethanol and carbon tetrachloride.³² The water contact angles of the ion-pair SAMs (~75°) are significantly higher than that of a fully packed MHA surface, and less than that of a pure methyl-

⁽³⁶⁾ Pradines, V.; Poteau, R.; Pimienta, V. Chem. Phys. Chem. 2007, 8, 1524–1533.

⁽³⁷⁾ Castner, D. G.; Hinds, K.; Grainger, D. W. *Langmuir* **1996**, *12*, 5083-5086.

⁽³⁸⁾ Laibinis, P. E.; Graham, R. L.; Biebuyck, H. A.; Whitesides, G. M. Science 1991, 254, 981–983.

⁽³⁹⁾ Heister, K.; Zharnikov, M.; Grunze, M.; Johansson, L. S. O.; Ulman, A. Langmuir 2001, 17, 8-11.

⁽⁴⁰⁾ Greving, J. E.; Bouman, H.; Jonkman, J. H. G.; Westenberg, H. G. M.; de Zeeuw, R. A. *J. Chromatogr.* **1979**, *186*, 683–690.

Table 3. Advancing Water Contact Angle (θ_{adv}) and Packing Density of MHA (%MHA) for Fully-Packed and Ion-Pair SAMs^a

	$\theta_{\rm adv}~({ m deg})$		% MHA			
	unrinsed SAM	after KClO ₄ / DMSO rinse	Cassie-Baxter equation	XPS (% O)	XPS (% C and % N)	estimated size of TAA ⁺ cation
MHA	15 ± 1	16 ± 1	99 ± 1	100	100	
HDT	104 ± 2		0	0	0	
TEA-MHA pair	79 ± 4	71 ± 3	47 ± 4	50 ± 6	55 ± 5	61
TProA-MHA pair	80 ± 6	74 ± 1	44 ± 1	37 ± 6	43 ± 3	48
TPeA-MHA pair	69 ± 8	77 ± 6	38 ± 8	66 ± 6	31 ± 11	33

^a Percentage of MHA was calculated relative to a fully-packed MHA SAM.

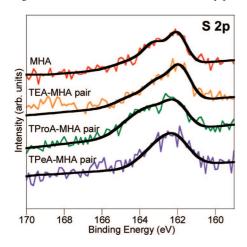


Figure 4. XP spectra of S 2p region for MHA and TAA-MHA ion-pair SAMs on gold.

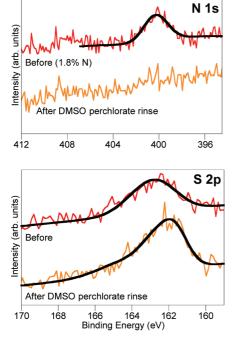


Figure 5. XP spectra of TEA-MHA ion-pair SAM before and after removal of the TEA+ ion.

suggests that the TAA⁺ ions may be present at the surface of these films, since TPeA⁺, TProA⁺, and TEA⁺ have four, longer aliphatic side-chains than the trimethylammonium group and could therefore be expected to contribute additional oleophilic methylene and methyl groups to the surface of the film. In an effort to verify the presence of TAA⁺ cations at the surface of the ion-pair films, we performed contact angle measurements using hexadecane. The contact angle of hexadecane was 0° for all three types of ion-pair SAMs—no different than that of a fully packed COOH-terminated SAM.

Contact angle measurements, performed on the ion-pair films after the TAA⁺ cation was removed in a DMSO-KClO₄ solution, corroborate the estimates of MHA packing density obtained with XPS. To determine the surface coverage, we used the Cassie-Baxter equation

$$\cos \theta_{mix} = f_{MHA} \cos \theta_{MHA} + f_{HDT} \theta_{HDT}$$

to estimate the packing fraction of carboxylic acid groups present on the surface. 42 As seen in Table 3, the fraction of MHA calculated with Cassie-Baxter analysis is very close to that obtained from the analysis of the X-ray photoelectron spectra and also shows the higher variability observed for TPeA-MHA pairs. These measurements confirm that the packing is dictated by the size of the ion and that the self-assembly of the TAA-MHA ion-pairs on gold results in a loosely packed MHA film.

4. Conclusions

Ion-pair interactions between MHA and TAA⁺ in an apolar solvent can be exploited at the solid-liquid interface to form loosely packed MHA monolayers. The ion-pair SAMs were found to be covalently bound to the gold substrate and consist of deprotonated MHA molecules paired with a TAA⁺ cation in a 1:1 stoichiometric ratio. The ion-pair interactions are reversible, meaning the TAA⁺ cation can be removed from the surface after covalent attachment of the thiols, using appropriate solvent conditions. The surface density of MHA molecules, as measured by XPS and water contact angle measurements, appears to be determined by the size of the TAA⁺ cation investigated, making ion-pair assisted self-assembly a versatile approach to engineer monolayers with a range of intermolecular spacing, simply by changing the size of the ions involved in the ion-pair. The results obtained in this study of ion-pair interactions suggest that other noncovalent interactions, such as hydrogen bonding, could be harnessed to control molecular packing.

The fact that the ion-pairs cannot be broken through aqueous ion-exchange and vigorous rinsing is in marked contrast to the weak binding interactions observed between fully packed carboxylic acid-terminated SAMs and quaternary ammonium ions. These results suggest that the increased lateral spacing of COO- groups and conformational freedom of the loosely packed thiol chains on the surface of the ion-pair SAMs facilitate superior binding of the TAA⁺ cation. These findings may be useful in understanding the stability of ion-pairs formed within polyelec-

terminated HDT surface. Holmlin et al. report a water contact angle of 52 \pm 8° on a trimethylammonium-terminated SAM prepared from HS(CH₂)₁₁N(CH₃)₃+Cl.⁴¹ The fact that the ionpair SAMs exhibit significantly higher water contact angles

⁽⁴¹⁾ Holmlin, R. E.; Chen, X. X.; Chapman, R. G.; Takayama, S.; Whitesides, G. M. Langmuir 2001, 17, 2841-2850.

trolyte films.^{31,43,44} With this in mind, SAMs made from ionpairs may have the potential to serve as highly selective molecular recognition devices, as these films exhibit remarkably stronger binding between the carboxylate group and the quaternary ammonium ions compared to traditional densely packed MHA. We are currently investigating the molecular recognition capabilities of these films and also seek to elucidate differences

in the orientation of the three forms of ion-pairs on the surface.

Acknowledgment. This work was supported by the NSF (CMMI-0748094), the U.S. Department of Homeland Security graduate fellowship to G.K.O., and 3M Corp. The use of the surface analysis laboratory at JHU was funded as part of the MRSEC, through the NSF. The authors extend their thanks to Dilip Asthagiri for useful discussion, Kevin Wepasnick and Jeffrey Braun for assistance with XPS experiments, and Sam Olivier for creation of the artwork shown in Scheme 1.

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⁽⁴³⁾ Moya, S. E.; Azzaroni, O.; Kelby, T.; Donath, E.; Huck, W. T. S. J. Phys. Chem. B 2007, 111, 7034–7040.

⁽⁴⁴⁾ Moya, S.; Azzaroni, O.; Farhan, T.; Osborne, V. L.; Huck, W. T. S. Angew. Chem., Int. Ed. 2005, 44, 4578–4581.