The adhesive properties of pyridine-terminated self-assembled monolayers

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The atomic force microscopy (AFM) adhesion force behaviour and contact angle titration behaviour of self-assembled monolayers (SAMs) presenting surface pyridine and substituted pyridine moieties has been investigated as a function of pH and electrolyte concentration. The pKa s of the pyridine moieties were modified through the incorporation of fluorine, chlorine and bromine substituents in the pyridyl ring. Contact angle titration and AFM adhesion force measurements were performed using aqueous phosphate buffered saline solutions over the pH range 3–9, and at concentrations of 150 mM and 0.1 mM. AFM adhesion force measurements were performed using a clean Si3N4 pyramidal-tipped AFM cantilever.

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1. Introduction

Since it was invented by Binnig, Quate and Gerber [1] the atomic force microscope (AFM) has been used to analyse the interactions which exist between surfaces of interest. The AFM has provided the modern researcher with the ability to perform repeated, accurate force measurements between a probe and a surface [2]. The data obtained has been used in the research and development of biosensors [3], surfactants [4], and materials with enhanced properties [5] to name only a few examples. AFM can be employed in the analysis of forces such as adhesion [6,7] and friction [8,9] between surfaces of interest. The tips of AFM cantilevers can be modified through chemical functionalisation [10] or by the attachment of a colloidal particle such as silica [2,11,12].

The measurement of forces using AFM is a rapidly growing research area, and surface chemistry is often an important consideration during AFM adhesion force measurements [13] as the attractive or repulsive forces between two surfaces will be influenced by the chemistry of the surfaces. One particular area of interest is that of chemical force microscopy (CFM) measurements, where a surface and an AFM cantilever tip with well-defined surface chemistries are presented to each other, perhaps involving the modification of the AFM cantilever tip and the surface with self-assembled monolayers [10] [10] CFM measurements are often made in aqueous environments [10] and typical variables are environmental ionic strength and pH, which can affect the adhesion between two surfaces by changing their ionisation state. Understanding the effect of surface chemistry on the interactions between surfaces in aqueous solution may impact upon research areas such as the development of microelectromechanical systems devices, biosensors, colloid science and drug development. Upon their incorporation into the terminal moiety of a self-assembled monolayer (SAM), protonatable chemical species such as amines, carboxylic acids and phosphate groups have been shown to exhibit a shift in their pKa when present at a surface, relative to their pKa as measured in free solution [14–16]. This shift in pKa has been attributed to the reduced availability and hindered orientation of the groups when present at the SAM surface. The use of contact angle measurements to estimate surface pKa values has previously been reported by Creager and Clarke [17] for mixed SAMs incorporating carboxylic acid-terminated alkanethiols. This work reports the synthesis of four disulfide species and the characterisation of the SAMs they form on Au thin films. Each SAM presents a surface pyridine or substituted pyridine moiety with a different predicted pKa. The pKa s of the pyridine moieties were altered through the incorporation of fluorine, chlorine and bromine substituents in the pyridyl ring, providing a range of protonatable SAMs. The adhesive properties of the SAMs were investigated as a function of electrolyte pH and electrolyte concentration.

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2. Experimental details

2.1. Chemical reagents

Four different dialkyl disulfides containing pyridine or substituted pyridine moieties were synthesised as described in Appendix A. The SAM structures, contact angle behaviour and the predicted pK\textsubscript{a}s (in aqueous solution) of their terminal pyridine moieties are listed in Table 1.

Predictions were made using the Hammett and Taft equations for heteroaromatic acids and bases [18]. The organic solvents used for SAM formation were HPLC grade ethanol (EtOH, Fisher Scientific, UK) and analytical grade CH\textsubscript{3}Cl\textsubscript{3} (Fisher Scientific, UK). Piranha solution was used for glassware cleaning and for cleaning Au slides prior to SAM formation.

Piranha solution was made as a 3:7 mixture of 30% laboratory reagent grade hydrogen peroxide (Fisher Scientific, UK) and analytical reagent grade concentrated sulfuric acid (Fisher Scientific, UK). Piranha solution is a very strong oxidising agent and has been known to detonate spontaneously upon contact with organic material. Therefore, eye protection (Fisher Scientific, UK) and nitrile gloves (Bodyguards, UK) were worn at all times, and as a precaution H\textsubscript{2}O ice was used as a quenching agent.

When required for pH adjustments, NaOH solutions were made by dissolving NaOH pellets (Fisher Scientific, UK) in 18 MΩ ultra-high purity H\textsubscript{2}O (Elga) at room temperature, followed by dilution as required. HCl solutions were made by diluting 11.65 M HCl solution (Fisher Scientific, UK) with 18 MΩ H\textsubscript{2}O at room temperature. All pH measurements were performed using an IQ150 pH meter (IQ Scientific Instruments) operating at room temperature. A 150 mM phosphate-buffered saline (PBS) solution (pH 7.4) was prepared by dissolving a PBS tablet (Sigma, UK) in 18 MΩ H\textsubscript{2}O at room temperature. The solution was adjusted to pH 3, 5, 7 and 9 through the addition of either EtOH or CHCl\textsubscript{3}, before being blown dry.

A 0.1 mM PBS solution was prepared by diluting a 150 mM PBS solution with 18 MΩ H\textsubscript{2}O. The 0.1 mM PBS solution was adjusted to pH 3, 5, 7 and 9 through the addition of HCl solution or NaOH solution as necessary. A 0.1 mM PBS solution was prepared by diluting 150 mM PBS solution with 18 MΩ H\textsubscript{2}O. The 0.1 mM PBS solution was adjusted to pH 3, 5, 7 and 9 through the addition of HCl solution or NaOH solution as necessary. The pH values of the adjusted 150 mM PBS solutions were all on the order of 100 mV, while the pH values of the adjusted 0.1 mM PBS solutions were all on the order of 1–5 mV.

2.2. Deposition of Au thin films and formation of SAMs

Au was deposited onto clean glass microscope slides (BDH, UK) by thermal evaporation using an Auto 306 vacuum evaporation chamber (Edwards, UK), using Cr as an adhesion promoter. The chamber pressure was reduced to ~10\textsuperscript{−7} Pa using a two-stage pumping system. Cr pieces of 99.99% purity (Agar Scientific, UK) were heated by electrical resistance using a voltage of 30 V and a current of 3 A until ~5 nm of Cr had been deposited onto the glass surface. Au wire of 99.99% purity (Advent Research Materials, UK) of 0.5 mm diameter was placed into a Mo boat (Agar Scientific, UK) and was heated by electrical resistance using a voltage of 10 V and a current of 3 A until ~100 nm of Au had been deposited onto the desired surface. Deposition was monitored using a quartz crystal microbalance (QCM) thickness monitor. The deposition rate for both Cr and Au was in the range 0.05–0.10 nm s\textsuperscript{−1}. Nitrile gloves (Bodyguards, UK) were worn during all handling procedures and Dumostar tweezers (Agar Scientific, UK) were employed to minimise contact with the samples whenever it was practical to do so. Where Au substrates were required to be cut up into smaller pieces, a diamond-tipped scriber (Agar Scientific, UK) was used. Any dust produced was blown away with Ar gas.

All glassware used in SAM formation was cleaned prior to use by immersion in piranha solution at room temperature for ~1 h. Cleaning with piranha solution was followed by rinsing with copious amounts of 18 MΩ H\textsubscript{2}O (Elga) and drying in an oven at 140 °C. SAMs were prepared by immersing Cr-primed, Au-coated glass microscope slides in 1 mM solutions of the SAM compounds for 48 h, using either EtOH or CHCl\textsubscript{3} as a solvent. All Au substrates were cleaned prior to SAM formation by immersion in piranha solution at room temperature for 10 min. Cleaning with piranha solution was followed by rinsing with copious amounts of 18 MΩ H\textsubscript{2}O (Elga) and rinsing with copious amounts of EtOH or CHCl\textsubscript{3} as was appropriate to the SAM solution.

Characterisation of SAMs formed on Au substrates involved assessing their wetting behaviour, elemental composition and thickness, employing dynamic H\textsubscript{2}O contact angle measurements, X-ray photoelectron spectroscopy and ellipsometry, respectively. Full descriptions of the SAM characterisation results can be found in the Appendix A. Dynamic H\textsubscript{2}O contact angles were measured using a home-made stage apparatus, employing a Charge-Coupled Device (CCD) KP-M1E/K camera (Hitachi) and FTA Video Analysis software.

<table>
<thead>
<tr>
<th>Table 1</th>
<th>Chemical structures of SAM compounds 1–4, their H\textsubscript{2}O contact angle behaviour and predicted pK\textsubscript{a}s in aqueous solution</th>
</tr>
</thead>
<tbody>
<tr>
<td>Compound structure</td>
<td>θ\textsubscript{H\textsubscript{2}O (°)}</td>
</tr>
<tr>
<td>1</td>
<td>88±2</td>
</tr>
<tr>
<td>2</td>
<td>92±1</td>
</tr>
<tr>
<td>3</td>
<td>59±2</td>
</tr>
<tr>
<td>4</td>
<td>62±1</td>
</tr>
</tbody>
</table>

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onto stainless steel sample holders, using both double-sided carbon employed throughout all measurements. Samples were immobilised with a pressure of ∼10 eV to 1200 eV, obtained using 1 eV increments. Recorded low resolution spectra would typically be an average of 5 scans. All high resolution spectra were obtained using a pass energy of 20 eV over a binding energy range of 20–30 eV, centred around a chosen photoelectron binding energy, obtained using 0.1 eV increments. A dwell time of 20 ms was employed when collecting data from each binding energy increment for all measurements. Recorded high resolution spectra would typically be an average of at least 10 scans.

2.4. AFM adhesion force measurement procedure

AFM adhesion force measurements were performed using a MultiMode AFM (Veeco, UK) operating in a liquid environment. The MultiMode AFM operated an E scanner, with a maximum lateral range of 1 µm×14 µm and a maximum vertical range of 3.8 µm. The AFM was housed on a vibration isolation table to minimise the effect of ambient noise on measurement quality. Nanoscope v5.12 software (Veeco, UK) was used throughout for both real-time analysis and post-capture results processing. Samples were immobilised onto steel SPM specimen disks (Agar Scientific, UK) using double-sided sticky tape (3M, UK) prior to AFM analysis. All sample handling was carried out using Dumostar tweezers (Agar Scientific, UK) to minimise the risk of sample contamination.

A glass fluid cell (Veeco, UK) with a silicone O-ring (Veeco, UK) was employed for all force measurements. For each tip/sample/electrolyte combination, the electrolyte was housed in a 5 mL capacity Luer-Lok plastic syringe (Fisher Scientific, UK) prior to introducing the liquid to the fluid cell through clean silicone tubing (Veeco, UK). Prior to performing each measurement, the fluid cell was rinsed thoroughly with 18 MΩ H₂O and dried through absorption of H₂O using a small 256 piece of paper towel (Kimberly Clark, UK). The fluid cell was subsequently irradiated with long-wave UV light (366 nm) for 20 min using a UV lamp (BDH, UK) positioned approximately 5 mm above the fluid cell. Upon being filled with electrolyte solution, the fluid cell was sealed off using tubing clips and the system was allowed to thermally equilibrate. Equilibration was deemed to have occurred once the vertical and horizontal deflection of the cantilever had stopped fluctuating.

Adhesion force measurements on SAMs were performed using triangular thick-legged Au-coated pyramid-tipped Si₃N₄ cantilevers.
Contact angle titration involves measuring the contact angle behaviour of a solid surface over a range of pH, generally performed using droplets of aqueous electrolyte adjusted to the desired pH. In this case, the contact angle behaviour of SAMs 1–4 was assessed using 150 mM and 0.1 mM PBS solutions adjusted to pH 3, 5, 7 and 9, affording analysis of the effect of pH and electrolyte concentration. The measured contact angle titration behaviour of SAMs 1–4 using 150 mM and 0.1 mM PBS solutions, shown in Figs. 1 and 2, respectively, reveal that the contact angle behaviour of SAMs 1–4 is similar to their contact angle behaviour measured using 18 MΩ H2O. Furthermore, there is little variation in the contact angle behaviour of each SAM with either pH or electrolyte concentration. Interestingly, however, the contact angle behaviour of SAM 4 is 25–30° lower than the contact angle behaviour of SAMs 1–3. Such an effect could be attributable to the lower predicted pKₐs of the terminal pyridine moieties of SAMs 1–3, 8.14–6.14 and 0.88 respectively, as shown in Table 1, relative to that of SAM 1, which is 5.60, given the hydrophobic nature of the halogen substituents incorporated into their terminal moieties. As the pH range studied is lower than the predicted pKₐs of the terminal pyridine moieties of SAMs 1–3, a change in contact angle behaviour would not reasonably be expected with pH. In comparison, as the pyridine moiety of SAM compound 4 has a predicted pKₐ in aqueous solution of 5.60, a change in the protonation state of this moiety in the SAM formed from compound 4 between pH 5 and 7 might be expected, were the moiety present in free solution. However, the effect of surface confinement on the pKₐ of the pyridine moieties appears to have altered the pKₐ of these moieties such that a change in protonation state, and hence the contact angle behaviour of the SAM, does not occur between pH 5–7. The change in pKₐ of moieties when present as the terminal moiety in SAMs has previously been reported for amino [14,15], carboxylic acid [16] and sulfonic acid [14] moieties, amongst others. Therefore, a change in the pKₐ of the pyridine moieties of SAMs 1–4 could reasonably be expected here also.

Inspection of the results for SAM 4 reveals no consistent trend in contact angle behaviour with pH for the two electrolyte concentrations studied. There is a slight decrease in contact angle behaviour for those measurements performed using 150 mM PBS solution between pH 3 and pH 5, but contact angle measurement is a relatively coarse method for examining subtle changes in surface character. Therefore, it is expected that the AFM force measurements will prove more sensitive to any change in the protonation state of the SAM terminal moieties. Interestingly, it has recently been reported that smoother Au surfaces produce greater shifts in the apparent surface pKₐ of mercapto carboxylic acid SAMs [24] and it may be that the roughness of the Au thin films employed here, which were found to have an Rₐ of 312 ± 1 nm when imaged by AFM, has influenced the behaviour of these SAMs.

3. Results and discussion

3.1. Contact angle titration behaviour of SAMs

AFM adhesion measurements were performed on SAMs 1–4 using a pyramidal-tipped Si₃N₄ AFM cantilever. Measurements were performed in 150 mM and 0.1 mM PBS solutions adjusted to pH 3, 5, 7 and 9. The jump-to forces exhibited by SAMs 1–4 measured in 150 mM and 0.1 mM PBS solutions are shown in Figs. 3 and 4 respectively. These results show that SAM 4 exhibited a greater jump-to force than SAMs 1–3, which all exhibited approximately similar jump-to forces. Therefore, the jump-to force as measured by AFM for each of the four SAMs follows the same trend as the contact angle behaviour, in that the SAMs with higher H₂O contact angle behaviour, and therefore less surface energy, exhibit smaller jump-to-forces. It is interesting that the jump-to forces do not vary significantly with pH, which suggests that there is no electrostatic interaction occurring between SAM 4 and the AFM cantilever tip. Additionally, there is no significant change in the magnitude of the jump-to force between the two different electrolyte concentrations studied, which also suggests that the jump-to force is not electrostatic in nature. Upon the approach of the AFM cantilever tip to the SAMs in 0.1 mM PBS solution but not in 150 mM PBS solution, a non-contact repulsive force was observed at pH 7 and pH 9 for all SAMs. The repulsive force, which did not vary significantly in magnitude between SAMs or with pH, probably occurred due to the increasing deprotonation of the SiO₂ surface of the AFM cantilever tip with increasing pH. It should be noted that the pull-off forces measured during the AFM measurement were approximately one order of magnitude greater than the measured jump-to forces, and displayed no apparent trend between SAMs or with pH and electrolyte concentration. The pull-off force is a result of a number of complex interactions at the AFM cantilever tip/SAM interface, with the possibility for rearrangement of SAM molecules and variations in contact area between tip and SAM, given the geometry of interaction in these systems. Indeed, given the large terminal moieties of SAMs 1 and 2, for example, there may be greater spacing between these molecules on the surface, allowing large terminal moieties of SAMs 1 and 2, for example, there may be greater spacing between these molecules on the surface, allowing...
greater penetration of the AFM cantilever tip into the SAM, therefore increasing the contact area. Additionally, the roughness of the Au surface and the exact point of contact between the AFM cantilever tip and the SAM will also affect the results, as there will not be an idealised sphere-on-flat contact geometry at all locations. Fears et al. [25] recently described the analysis of the surface pK$s_{a}$s of COOH-and NH$_2$-terminated alkanethiols on Au surfaces using surface plasmon resonance (SPR), and this would seem to be a suitably sensitive technique with which to analyse the SAMs investigated here. SPR allows the solution pH local to the SAM surface to be analysed, at sub-nanometre resolution, and therefore the type and concentration of ion present adjacent to the SAM surface can be assessed, which would afford further insight into the protonation state of these pyridine-terminated SAMs.

4. Conclusions

The effect of electrolyte pH and electrolyte concentration on four pyridine-terminated SAMs has been investigated using contact angle titration and AFM adhesion measurements. Measurements performed either using or while immersed in 150 mM and 0.1 mM PBS solutions studied the adhesion behaviour of the SAMs. It was found that both the pH and concentration of the aqueous electrolyte have little effect on the contact angle titration behaviour and the adhesion force behaviour of the SAMs, with the exhibited forces being due to van der Waals forces, rather than electrostatic interactions between the tip and the SAM. Such behaviour suggests that the protonation state of the terminal pyridine moieties of the SAMs does not change over the pH range studied here, due to a shift in the pK$_{a}$ of the pyridine moiety when present as the terminal group in a SAM. Similarly, the change in pK$_{a}$ of amino [14,15], carboxylic acid [16] and sulfonic acid [14] moieties when present as the terminal moieties in SAMs has previously been reported. For the systems studied here, it does not appear that pK$_{a}$ alone is a sufficient indicator of the adhesion behaviour of the system, whereas the presence of hydrophobic elements, such as the halogen substituents in the terminal moieties of SAMs 1–3, proved very influential on the results.

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Appendix A

The following information is presented in the appendix.

(i) Synthesis and characterisation data for SAM compounds 1–4.

(ii) Characterisation results for SAMs 1.

A.1. Synthesis and characterisation data for SAM compounds 1–4

Schemes A1 and A2 show the synthetic route employed in order to obtain SAM compounds 1–4. Compounds 5–9 are the intermediates synthesized prior to obtaining SAM compounds 1–4, and all molecules are introduced in order of their synthesis beginning with the SAM compound with the simplest head group (4), with SAM compounds 1–4 having previously been numbered in the main text.

• Compound 8

To a solution of 11-mercaptoundecanoic acid 7 (7.0 g, 32.1 mM) in C2H5OH (100 mL) heated under reflux was added a solution of iodine (4.07 g, 16.03 mM) in C2H5OH (50 mL). Heating was continued for 12 h after which the reaction was allowed to cool to room temperature and washed with a saturated aqueous solution of Na2S2O3 (50 mL). The products were extracted into CH2Cl2 (3×50 mL) and dried (MgSO4), filtered and the solvent was removed in vacuo affording 8 (6.47 g, 82%). m/z (ES) 513 [M+Na]+, δH (500 MHz, CD3)SO) 4.09 (4H, q, J=7.3, 14.3 Hz), 2.65 (4H, t, J=7.3 Hz), 2.26 (4H, t, J=7.3 Hz), 1.61 (8H, m), 1.34 (30H, m). δC (400 MHz, CDCl3) 173.9, 60.1, 39.1, 34.4, 29.3, 29.2, 28.5, 24.9, 14.2. Elemental analysis found C 60.78%, H 9.97%. Elemental analysis of C22H42O4S2 requires C 60.82%, H 9.88%.

• Compound 9

To a vigorously stirred solution of 8 (4.75 g, 9.68 mM) in THF (100 mL) was added a solution of potassium hydroxide (1.63 g, 29.0 mM) in H2O (100 mL) and dried in vacuo affording 9 as white plate-like crystals (4.20 g, 99%). m/z (ES) 457 [M+Na]+.

• Compound 10

To a solution of 9 (0.100 g, 0.23 mM) in dry THF (10 mL) cooled to 0 °C under an N2 atmosphere was added 1-(3-dimethylaminopropyl)-3-ethyl-carbodiimide hydrochloride (0.272 g, 1.38 mM) and a catalytic amount of 4-dimethyl-aminopyridine. The mixture was stirred for 30 min and 3-pyridinepropanol (0.094 g, 0.69 mM) was added over 10 min, followed by further stirring for 24 h under an N2 atmosphere at room temperature. The white precipitate was filtered off, washed with H2O (100 mL), cold C2H5OH (1:1, 20 mL). The reaction was stirred for 12 h, and acidified with HCl (aq, 2M, 20 mL) upon which a white solid precipitated. The solid was filtered off, washed with H2O (100 mL), cold C2H5OH (100 mL) and dried. m/z (ES) 493 [M+Na]+.

• Compound 11

A.2. XPS survey spectrum for SAMs 1–4

The following XPS survey spectra were acquired for SAMs 1–4:

- XPS survey spectrum for SAM 1.
- XPS survey spectrum for SAM 2.
- XPS survey spectrum for SAM 3.
- XPS survey spectrum for SAM 4.

We also acknowledge the assistance for production of Cr-primed Au-coated glass microscope slides given by Professor G.J. Leggett and Dr. S. Sun at the University of Sheffield, School of Chemistry.
Elemental analysis of C34H48O4 N2S2Cl4 requires C 54.15%, H 6.39%, N 3.61%. Elemental analysis found C 52.55%, H 6.39%, N 3.55%.

**Compound 4**

The same procedure was followed as described for the preparation of compound 4, using 2,6-dichloronicotinic acid (0.29 mg, 1.48 mM), EDC (0.71 g, 3.69 mM) in dry CH2Cl2 (25 mL). This yielded a white solid (150 mg, 41%). m/z (ES) 778 [M]+.

540

**Compound 6**

The same procedure was followed as described for the preparation of compound 6, using 11-mercaptop-1-undecan-1-ol (5.0 g, 4.89 mM), and iodine (0.75 g, 2.94 mM) in CH2OH (50 mL). This yielded a white solid (600 mg, 31%). m/z (ES) 801 [M]+. δH (400 MHz, CD3OD) 6.45%, N 3.64%. Elemental analysis found C 67.80%, H 8.82%, N 4.07%.

541

**Table A1**

<table>
<thead>
<tr>
<th>SAM</th>
<th>Calculated thickness range (nm)</th>
<th>Measured thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>1.64–1.89</td>
<td>0.87±0.15</td>
</tr>
<tr>
<td>2</td>
<td>1.64–1.89</td>
<td>1.30±0.13</td>
</tr>
<tr>
<td>3</td>
<td>1.64–1.89</td>
<td>1.69±0.19</td>
</tr>
<tr>
<td>4</td>
<td>1.94–2.24</td>
<td>1.42±0.31</td>
</tr>
</tbody>
</table>

123.2, 63.1, 39.0, 34.2, 29.8, 29.3, 29.1, 28.4, 24.9. Elemental analysis of C38H60O4N2S2 requires C 67.75%, H 8.91%, N 4.16%. Elemental analysis found C 65.44%, H 10.83%.

**A.2. Characterisation results for SAMs 1–4**

**XPS**

Figs. A1–A4 show the survey spectra obtained for SAMs 1–4, respectively, as well as the percentage compositions of the SAMs as calculated from XPS data. These results show that the SAMs all exhibited the correct element photoelectrons for the molecules from which the SAMs were formed. Additionally, no unexpected elements were found to be present in the SAMs, all of which suggests that the SAMs had formed successfully.

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**Ellipsometry**

A thickness range for each SAM was calculated by estimating the maximum lengths of the molecular structures of compounds 1–4 using ChemDraw Ultra (v7.0.1, CambridgeSoft, UK) and Chem3D Ultra (v7.0.0, CambridgeSoft, UK) software. The upper limit of the range of the full length of the SAM molecule was determined by the height of the SAM molecule at a tilt angle of 30° to the surface normal. These values are given in Table A1. The results indicate that the SAMs had all formed, although their thicknesses tended to be lower than the lower value of the calculated thickness range, with the exception of SAM 3. Given that the SAM molecules all exhibit sterically bulky pyridine head groups, it is probable that the size of the head groups decreased the maximum achievable packing density of the molecules on the surface, leading to a lower than expected SAM thicknesses.

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**References**