

Formation of Azide Self-Assembled Monolayers as a Reactive Foundation for Micro-Architecture

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Background

Self assembled monolayers (SAMs) form when a layer of molecules (surfactants) adsorb onto a surface in a well-defined way. In our case, the surface is gold, and the surfactants are thiol-terminated molecules. S-Au bonds arrange in a pattern defined by the underlying gold lattice.

To build a reactive SAM substrate, we needed to attach an azide group to the gold surface with a sulfur bond. For the azide, we had the option of using 11-Azido-1-undecane thiol, which would immediately attach to the gold surface and save us time. However, this chemical costs \$296.50/100 mg. Therefore, we began the reaction with S-(4-bromobutyl) thioacetate instead. This costs about thirty times less. To convert this thioacetate into a thiol, I performed three different deprotection reactions in order to remove the acetate and be left with the thiol. Reacting one of these mixtures with sodium azide will then give us the azide functional group at the surface, which serves as a reactive substrate for further coupling reactions.

Cost Comparison

	NaOH Reaction	HCl Reaction	Hydroxylamine Reaction	11-Azido-1-undecane thiol
	\$1.29 ethanol	\$0.98 methanol	\$1.29 ethanol	
	\$7.92 thioacetate	\$7.92 thioacetate	\$7.92 thioacetate	
	\$0.01 NaOH	\$0.49 HCl	\$0.0028 hydroxylamine	
Total	\$9.22	\$9.39	\$9.21	\$296.50

Thioacetate Deprotection

NaOH Reaction

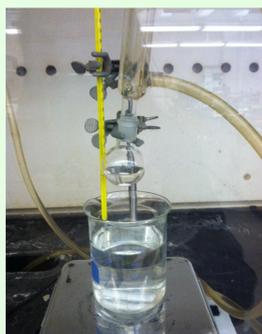
1. Dissolve S-(4-bromobutyl) thioacetate in ethanol
2. Add NaOH solution
3. Reflux reaction mixture for two hours before cooling to room temperature
4. Add concentrated HCl solution to neutralize mixture
5. Add hexane and water to mixture to separate the organic layer
6. Wash layer with water and then dry over Na_2SO_4

HCl Reaction

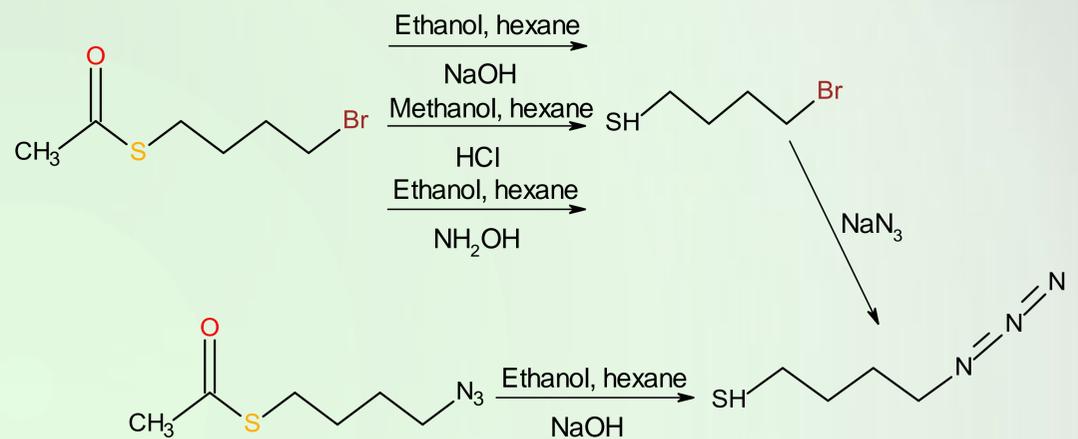
1. Add methanol to S-(4-bromobutyl) thioacetate
2. Add HCl solution
3. Reflux the reaction mixture for five hours
4. Quench mixture with water and extract twice with diethyl ether
5. Wash organic phase with water
6. Dry over Na_2SO_4

Hydroxylamine Reaction

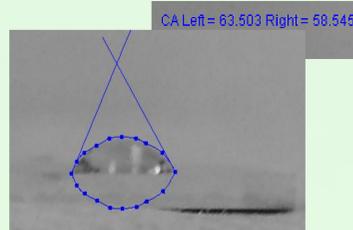
1. Put S-(4-bromobutyl) thioacetate in flask
2. Mix in ethanol
3. Put in 2 equivalents hydroxylamine
4. React for two hours at room temperature
5. Wash layer with water and extract with hexane
6. Dry over Na_2SO_4



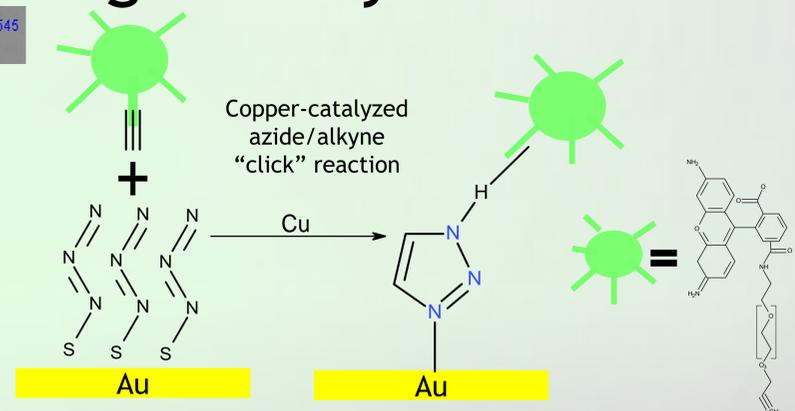
Reactions



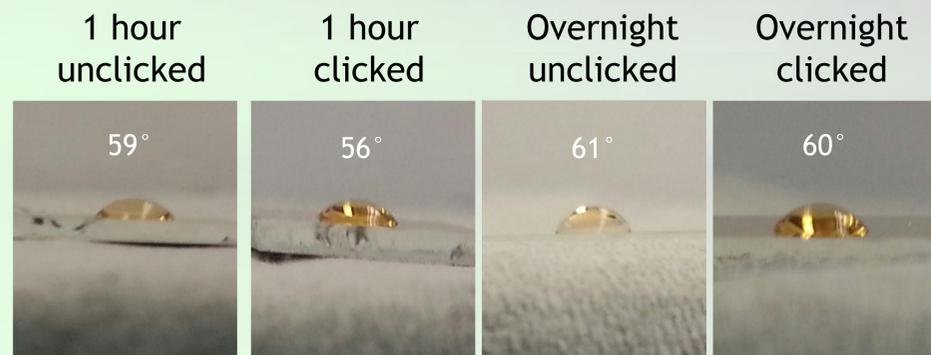
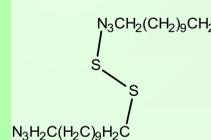
Contact Angle Analysis of SAMs



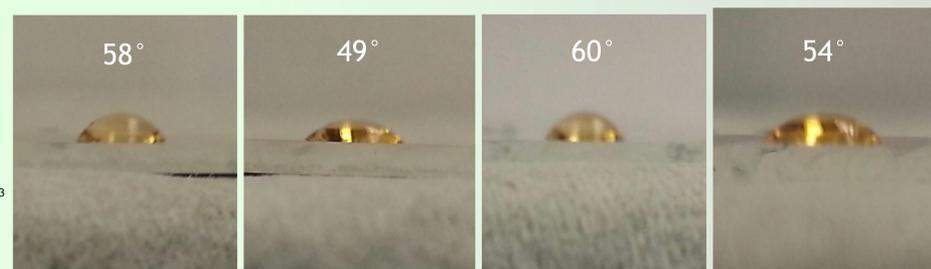
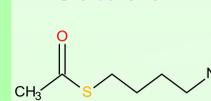
The water/surface contact angle is a reporter of the surface characteristics.



Disulfide Solution



Thioacetate Solution



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Concluding Remarks

Deprotecting thioacetates is an inexpensive way to arrive at more costly self-assembly materials. Results of the three reactions we used to deacetylate the thioacetate were similar. However, the hydroxylamine reaction was the best at converting the thioacetate to the thiol, with an overall yield of 89%. When using both the thioacetate and the disulfide solution, it appeared that they produced similar SAMs. A thiol is supposed to be the best way to build a SAM; therefore, upon further research, we will be able to see which solution works best.