PRF # 56993-UN15

Molecular Interactions of Alkanethiols, Aryl thiols, and C_{60} Fullerenes in Multi-component Self-Assembled Monolayers as Probed by Scanning Tunneling Microscopy

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Research

The everyday world does not exist in isolated compartments, but in mixtures. From contaminants to naturally occurring blends, chemical compounds are, more often than not, found intermingled with a multitude of other compounds. Furthermore, the existence of our world in non-vacuum conditions and the resulting exposure of a surface to over a mole of particles at standard temperature and pressure conditions introduces an entirely new set of variables that can alter the surface structures of compounds. Add to this the fact that the majority of chemical processes occur at interfaces and you have created a surface scientist's dilemma: **how is the surface structure and functionality of a compound impacted by its presence in a mixture in ambient conditions?**

Self-assembled monolayers (SAMs) of organothiol molecules are model systems through which to study the interaction of compounds on a surface. These molecules spontaneously order on surfaces (self-assemble) in order to reach energetically favorable configurations. Due to the dynamic nature of a SAM, there are several forces at play in the self-assembly process: the sulfur head groups covalently bond to and dramatically change the gold surface, while the tail groups interact through intermolecular interactions unique to their chemical nature. The delicate interplay of these forces guides the formation of the final structure of the monolayer. As a result, there is an abundance of information that can be distilled from the surface array of the compounds. To date, single-component SAMs have demonstrated applications in fields such as surface passivation and tribology. Due to the myriad of available compounds, the complete characterization of these SAMs is still an emerging phenomenon.

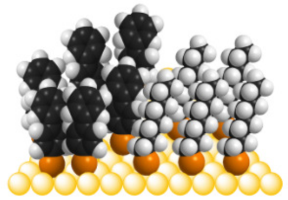

Figure 1: Schematic of a multi-component organothiol monolayer

Multi-component SAMs of aliphatic and aromatic components allow a surface chemist with a rare lens into the intermolecular forces that govern the structure of a mixed array. Studies have shown that the structure of a mixed monolayer is dependent on factors such as the method of deposition employed to deposit both species, the concentration of species used, and the chemical identity of the species used. Furthermore, each mixed SAM has been shown to demonstrate properties that are different from their single-component counterparts. Multi-component SAMs have found applications in nanotechnology and biology. It is clear that these complex self-organizing structures are of fundamental interest. To date, there has been a concerted effort from a number of groups contributing to the knowledgebase of mixed SAMs. However, the majority of studies on similar systems are conducted in ultra-pristine environmental conditions. There exists a pressing need to investigate these technologically relevant compounds in ambient conditions in order to simulate applications in realistic environments. Of course, investigating multi-component SAMs at ambient pressures and temperatures presents its own set of challenges to overcome. The great variability of these systems has made it clear to our research group that a *library* of these systems is necessary to identify trends present in mixed systems.

The ultimate goal of my research program is to characterize multi-component monolayers of organothiol compounds that are relevant to applications in nanotechnology, and to be able to make a large enough portfolio of these mixed systems such that we can identify trends in the resulting monolayer structures and use these trends to predict what surface structures a new system will form.

During the past calendar year, I was able to complete a multi-component SAM research project and submit a manuscript for publication in a peer-reviewed journal. This manuscript was accepted and will be published in the coming months in the journal *Surface Science*. This paper was published with student co-authors: Suhasini Aravinthan ’18, Keegan McCabe ’18, Hawar Haddadi ’19, Caroline Roy ’19, James Gould IV ’20, Christy Mangiacotti ’19, and Matthew Cummings ’20. This paper describes the creation of four distinct multi-component monolayers that resulted from varying the sequence of deposition and the concentration of the aromatic compound used. We plan to continue these studies in order to create a library of multi-component monolayers composed of aromatic and aliphatic organothiols by varying the fusion of the phenyl rings and the length of the molecules.

In addition to this publication, I presented two invited talks on my work at Trinity College (October 2017), Fordham University (November 2017), and Columbia University’s Summer High School Program (July 2018). I also attended and presented an oral presentation at the American Vacuum Society’s annual meeting in Tampa, FL in November 2017.