

4-Mercaptobenzoic acid
(4-MBA)

STM and STS Investigation of pH Effects on the Electronic Structure of 4-Mercaptobenzoic Acid, and 4-Aminothiophenol Monolayers on Au(111)

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4-Aminothiophenol
(4-ATP)

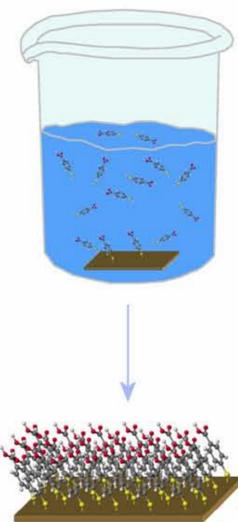
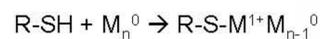
Introduction

Self-assembled monolayers (SAMs) are technologically significant systems for a number of reasons. Examples of potential applications include corrosion inhibition, chemical sensors, microelectronics fabrication, and biocompatibility. In addition to these practical uses, monolayers are also of interest as a system in which to study fundamental surface science because they allow the researcher to more thoroughly control the chemical properties of the surface on which an experiment may be conducted. However, in order to fully realize the possibilities open to these systems, it is necessary to thoroughly characterize their properties and how they react to different environments. The overarching purpose of this study is to elucidate the effect of pH on the electronic structure of acid and base terminated organothiol SAMs

SAM Formation

Formation of organothiol SAMs is a facile process of immersion. The process, while not fully understood, is a dissociative chemisorption. The reaction scheme is shown below, where M is typically a coinage metal such as Cu, Ag, Pt, or Au.

The thiol adsorbate spontaneously orders itself on the surface through intermolecular van der Waals forces.



Methods

Topographic information was obtained through Scanning Tunneling Microscopy (STM) using mechanically cut Pt/Ir (80/20) tips. Typical operating conditions consisted of a set point of ~ 0.08 nA @ +1V. Spectroscopic data was obtained through scanning tunneling spectroscopy (STS), with a scan rate of 4 sweeps per second and a 10 ms wait time between sweeps. The tip-surface separation was maintained by a set point of 0.10 nA and a tip bias of 1.0 V. Each individual spectra represents the average of 100 sweeps.

SAMs were prepared from 10mM ethanolic solutions of p-mercaptobenzoic acid (aldrich 97%), with an immersion time of ~ 24 h. Upon removal from the SAM solution the samples were rinsed vigorously with, and stored under, ultra pure (18.2 M Ω) H₂O.

Neutral samples were prepared through a rinse in ultra pure H₂O and blown dry with N₂. Protonated and Deprotonated samples were prepared in an analogous way using 0.1 M HCl (pH \sim 2), and 0.006 M NH₄OH (pH \sim 8) respectively.

Computational data was obtained using CAChe WorkSystem Pro. All calculations were done using PM5 geometry and wavefunction parameters.

Hypothesis

The hypothesized effects of deprotonating 4-MBA are illustrated in Figure-1. 4-MBA is expected to form dimer pairs on the surface when protonated. Upon deprotonation all capacity for hydrogen bonding will be lost and dimerization will no longer be possible, resulting in a significant structural shift. 4-ATP is not expected to form dimers due to the relative weakness of nitrogen hydrogen bonding, but it is still expected to exhibit some significant structural change upon protonation.

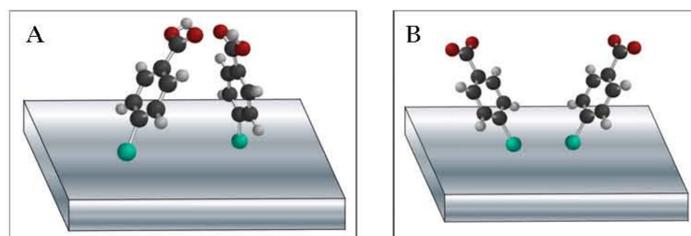


Fig. 1) The expected effects of pH. A) Protonated species experience attractive interactions due to hydrogen bonding. B) Deprotonated species experience repulsive coulombic interactions.

Results II

The requisite STM resolution for observing the hypothesized structural change was never reached. Figure 4 is representative of the images which were obtained. It is important to note that figure 4-C was obtained *in situ* unlike the other images displayed here. Images of the base treated SAM were never obtained in air. Ideally, all data should have been collected *in situ* however the technique proved to be prohibitively problematic.

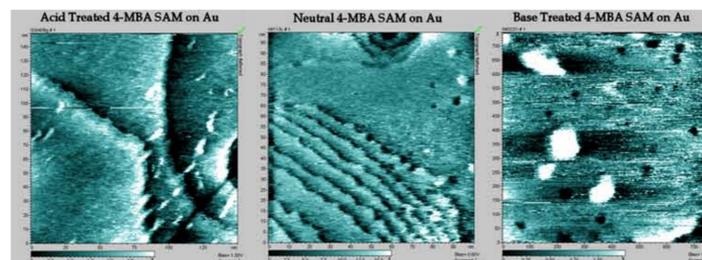


Fig. 4) A, B, and C, from left to right. The resolution of the instrument was adequate for imaging the bulk layer. Atomic stepping of the substrate, and defects in the SAM are apparent. However, individual molecules are indistinguishable

4-MBA Frontier Orbital Energy Diagram

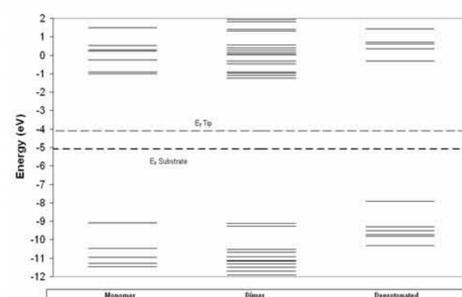


Fig. 7) This modeling was conducted using Hg atoms as the closest surrogate for Ag, and a capped bond to simulate an extended metal lattice. Only individual or dimer pairs of molecules were used. No attempt at simulating the extended SAM was made.

Results IV
Molecular modeling was conducted for three cases in an attempt to understand the variation in conductivity. By mapping the frontier orbitals of the monomer, dimer, and deprotonated species, it was expected that a change in the local density of electronic states would occur. However, the observed shift in MO energies does not fit with the experimental data. There is no distinct widening of an energy gap.

Experimental Design

In order to test our hypothesis, the samples were scanned at three pH steps: 2, 7, & 8, corresponding to dips in HCl, H₂O, and NH₄OH respectively. Details including concentrations can be found in the methods section.

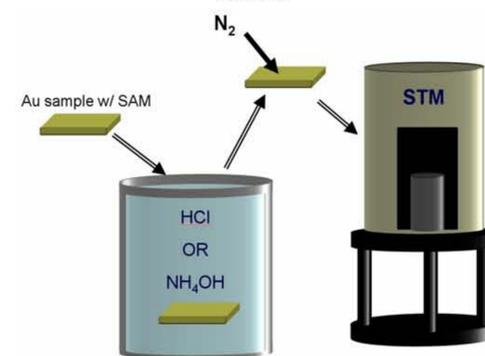


Fig. 2) The experimental setup. The sample is immersed in the appropriate solution, and blown dry with nitrogen before imaging, or taking spectra.

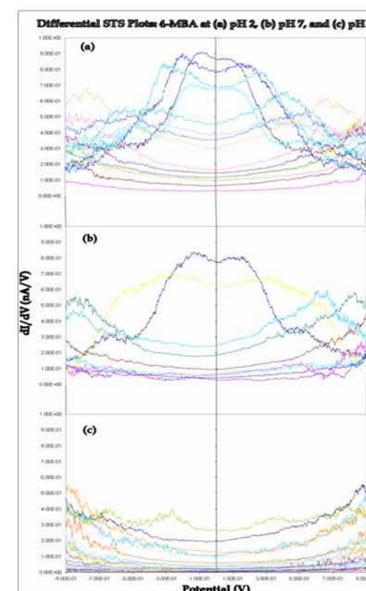


Fig. 5) pH mediation of conductivity through 4-MBA is very significant. A pH greater than 8 eliminated tunneling.

Results

A structural change in the film was expected. However, what was observed in the 4-MBA SAM was an electronic shift. It was observed that a reversible change in the conductivity of the film was caused by immersion in the basic solution. Figure 3 shows the distinct variation in tunneling current with the pH of the solution with which the sample was treated.

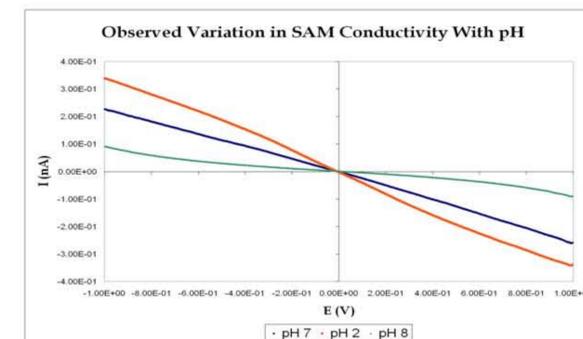


Fig. 3) STS spectra at three sample pH values. All spectra are the result of averaging 15-scans.

Results III

Plotting individual scans of the STS data as dI/dV vs. V in Figures 5 and 6, provides a profile of electronic surface structure. Peaks indicate the position of the energy levels involved in tunneling. There is a clear trend of decreasing conductivity with increasing pH for 4-MBA. In addition, the conductivity peaks shift from low to high potentials, indicating an increase in the energy gap between the relevant states in the surface and tip. 4-ATP on the other hand, shows random behavior, with no discernible regular structure. Conductivity switching was not observed in the amine terminated film.

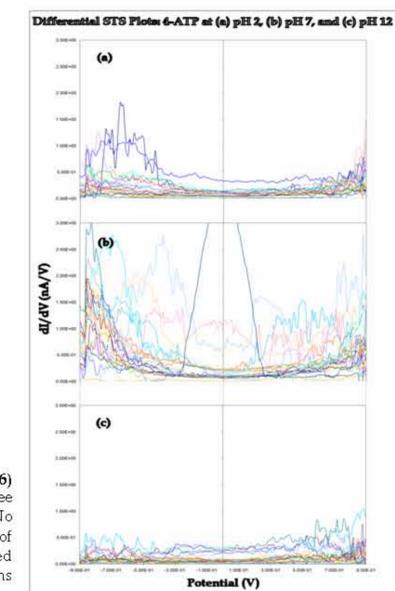


Fig. 6) Note that the scale is three times that of figure 5. No significant pH mediation of conductivity was observed in 4-ATP films

Conclusion and Future Directions

Figure 5 clearly shows a non-quantized response to changing pH. There is a progression of the conductivity peak, from low potential to high, as the pH is increased. An implication of this observation is that the observed STS spectra are the result of probing a relatively large number of molecules on the surface. A single molecule cannot be partially protonated.

Were this continuous behavior to be interpreted as simply the result of averaging some protonated, and some deprotonated domains, it would not explain the shift in the position of the conductivity peaks. In this situation only a shift in magnitude would be expected.

The conclusion which must be drawn from this data is that the energetic state through which tunneling occurs is not simply the HOMO or LUMO of the adsorbate. We propose that there exists a delocalized surface wavefunction, which has contributions from a relatively large number of surrounding molecules. The state of protonation of individual molecules alters their contribution to this wavefunction, causing shifts in its energy.

Several different experiments would be very helpful in discovering the exact nature of pH mediated conductivity variation. The fact that the carbonyl terminated film displays this behavior while the amine does not, suggest that it is in some measure dependant on the hypothesized dimerization of the 4-MBA film. Vibrational spectroscopy (RAIRS) might be used to determine the whether dimerization does in fact occur, and to compare the structures (tilt angles) of the 4-ATP and 4-MBA films. In addition other carbonyl and amine terminated SAMs must be investigated to see if they exhibit similar properties.

More accurate modeling would be a great help. For instance, an array of thiols bound to a gold cluster would provide a much better approximation of the actual surface environment than the methods which were used in this study.

Ultra violet photoelectron spectroscopy might be used effectively to elucidate the electronic structure of the surface, providing another way to characterize this novel behavior. This would provide an experimental map of the frontier orbitals within the SAM which could be compared to the modeling results.