PRECISE NANO-SCALE ASSEMBLIES:
UNDECAGOLD CLUSTERS AND SELF-ASSEMBLED MONOLAYERS

A Thesis in
Chemistry
by
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Abstract

Self-assembly has emerged to reach towards future device scales of several or tens of nanometers, and will directly compete with or will complement existing ‘top down’ fabrication schemes. Self-assembly techniques have created new materials from the ‘bottom up,’ connecting the length scales of synthetic chemistry and microfabrication. Extensive knowledge of the chemical, physical, and electronic properties of the constituents of ‘bottom up’ architectures is required to develop new materials rapidly. This thesis describes the development of precise, nanometer-scale assemblies derived from \( n \)-alkanethiolate self-assembled monolayers (SAMs): the phase behavior of multi-component SAMs containing internally substituted \( n \)-alkanethiolates, the electronic spectra of atomically precise gold clusters and larger nanoparticles immobilized atop \( n \)-alkanethiolate SAMs via \( \alpha,\omega \)-alkanedithiolate tethers, and the structure and order of single- and multi-component SAMs containing \( \alpha,\omega \)-alkanedithiols.

Replacement of methylene units of the \( n \)-alkanethiolate backbone with an amide bond buried near the sulfur headgroup begins to tune intermolecular interactions with precision in order to control the spatial distributions of the adsorbates on the surface. Solvent–solute interactions heavily contribute to determining film structure. The tunability of these interactions may be used to advantage when patterning molecules on surfaces; the strengths and types of these intermolecular interactions have a profound effect on the structure and quality of the structure of the nano-scale assembly.

The electronic properties of undecagold clusters and larger gold nanoparticles were investigated using STM, using \( n \)-alkanethiolate SAMs as supports that electrically isolated the particles from the substrate. The particles were immobilized using \( \alpha,\omega \)-alkanedithiolate tethers; significant
spectral diffusion was observed across single and multiple particles and was closely coupled to the particle's chemical and physical environment.

SAMs were created containing $\alpha,\omega$-alkanedithiolates, both single-component SAMs as well as dithiols inserted into host $n$-alkanethiolate SAMs (supports for the gold particles, *vide supra*). The intramolecular competition for the thiol to the surface as well as the propensity for aggregation due to short-range van der Waals forces led to SAMs with a distribution of complex structures and reactivities. A combination of scanning probe and ensemble measurements characterized the properties of these films across multiple length scales, showing that the SAM order was highly dependent on film preparation conditions. The structure and function of these $\alpha,\omega$-alkanedithiols cannot be substituted for their $n$-alkanethiol counterparts.

The creation of nano-scale assemblies from self-assembly techniques is deceptively simple; the structural properties of these assemblies are highly dependent upon the preparation conditions, and special care must be taken to keep the environments of these nano-scale assemblies controlled with high precision.
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List of Abbreviations

$\alpha, \omega$–AkDT $\alpha, \omega$–alkanedithiol(s), $\alpha, \omega$–alkanedithiolate(s)
1ATC9 3–mercapto–N–nonylpropionamide
1,8–ODT 1,8–octanethiol, 1,8–octanethiolate
1,10–DDT 1,10–decanethiol, 1,10–decanethiolate
1,16–HDDT 1,16–hexadecanethiol, 1,16–hexadecanethiolate
3×fpt 3 freeze–pump–thaw cycles
AFM atomic force microscopy (microscope)
BPD 4,4′–biphenyldithiol, 4,4′–biphenyldithiolate
C8 $n$–octanethiol, $n$–octanethiolate
C10 $n$–decanethiol, $n$–decanethiolate
C12 $n$–dodecanethiol, $n$–dodecanethiolate
C16 $n$–hexadecanethiol, $n$–hexadecanethiolate
CAG contact angle goniometry
CP–AFM conductive probe atomic force microscopy (microscope)
d–SAMs perdeuterated SAMs
D8 perdeuterated $n$–octanethiol, $n$–octanethiolate
D12 perdeuterated $n$–dodecanethiol, $n$–dodecanethiolate
D16 perdeuterated $n$–hexadecanethiol, $n$–hexadecanethiolate
DTT dithiothreitol
FT–IR Fourier transform infrared spectroscopy
Gdn·HCl guanidinium hydrochloride
$h$–PDMS hard PDMS
$h$–SAMs protiated SAMs, perhydrogenated SAMs
HD $n$–hexadecane
L–B Langmuir–Blodgett
LDOS local density of states
LFM lateral force microscopy (microscope)
MUDA 11–mercaptoundecanoic acid
oEG oligo(ethylene glycol)
OPE oligo(phenylene–ethynylene)
PDMS polydimethylsiloxane
$s$–PDMS soft PDMS
SAM self-assembled monolayer
SEM  scanning electron microscopy (microscope)
SET  single electron transport, single electron tunneling
SPM  scanning probe microscopy (microscope)
STM  scanning tunneling microscopy (microscope)
STS  scanning tunneling spectroscopy
TMU  1,1,3,3-tetramethylurea
TPP  triphenylphosphine
µCP  microcontact printing, microcontact printed
UHV  ultra-high vacuum
XPS  X–ray photoelectron spectroscopy
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“So – did you ever think about applying to Penn State?” Bob asked me as I was poring over chemistry department webpages and occupying valuable real estate in our computer office. As I shook my head, not really interested in loading yet another webpage, he continued, “You know, you should check out Paul Weiss’ webpage. That guy does some pretty cool work on STM of SAMs…” Curious as to what an ‘STM’ might possibly be and driven by a serious emotional investment in SAMs, the rest is history.

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Chapter 1

Introduction

Self-assembly opens the possibility of extending beyond the traditional length scales of synthetic chemistry and microfabrication, reaching into the future device scales of several or even tens of nanometers. In many instances, fabrication schemes have shifted focus from the time- and cost-intensive ‘top down’ methods (starting with large-scale materials and paring them down using lithographic tools) to ‘bottom up’ approaches, where features are constructed from the building blocks of atoms and molecules. To this end, extensive knowledge of materials fabricated via ‘bottom up’ approaches becomes imperative. In this thesis, studies of the phase behavior, structural properties and interfacial chemistry and reactivity of several self-assembled monolayers (SAMs) are presented. Also, the electronic properties of metal clusters and nanoparticles immobilized upon these SAM supports are measured.

Chapter 2 describes \( n \)-alkanethiolate SAMs, which provide the foundation for the research described in this thesis. This chapter also presents many of the measurement techniques used for characterization of these nano-scale assemblies and their intermediates. While the majority of the measurements presented in this thesis are acquired using the scanning tunneling microscope (STM), ensemble techniques including Fourier–transform infrared spectroscopy (FT–IR) along with wettability and optical characterizations of these SAMs have been used in concert to present a comprehensive view of the systems of interest.

Chapter 3 describes the phase behavior of a structural derivative of the \( n \)-alkanethiolate SAM, where an amide group has been substituted into the alkyl backbone of the \( n \)-alkanethiol.
These amide groups, buried down near the sulfur–gold interface, can hydrogen bond to neighboring amide-containing adsorbates, thus controlling film structure by strengthening the self-interactions of the assembly. While intermolecular hydrogen bonding in single-component, amide-containing SAMs has been verified using FT–IR spectroscopy [3, 4], we offer further evidence with STM studies. Scanning tunneling microscope images show that when coadsorbed with homologous, unfunctionalized $n$–alkanethiols, the amide-containing adsorbates aggregate together to exclude dissimilar adsorbates. Additionally, when diluted in low concentration on the surface within an unsubstituted $n$–alkanethiolate matrix, the intermolecular hydrogen bonding directs the alignment of these adsorbates on the surface to rows of molecules as thin as one molecule wide. This study was the first to demonstrate phase separation on the nanometer scale of alkanethiolate adsorbates with molecular resolution.

Chapter 4 describes the use of these amide-containing SAMs in novel soft lithography experiments, outlining design strategies for improving the patterning of SAMs by using intermolecular interactions of known and variable strengths. The self-directing alignment of these amide-containing molecules demonstrates great promise for improving the precision of placing and organizing molecules on surfaces. As the use of microcontact printing ($\mu$CP, a method of self-assembling molecules on surfaces in predetermined patterns) is rapidly expanding across many scientific communities, it is important to elucidate the issues of how to create high quality SAMs created using $\mu$CP, and to improve upon these SAMs using tunable intermolecular interaction strengths. Here, several fundamental studies of the $\mu$CP process are presented, including the incorporation of the amide-containing adsorbates into the final SAM structures. Armed with a thorough understanding of the interaction strengths of the molecules to be placed on the surface, one can more effectively understand and design surface structures of interest.
Chapter 5 presents STM measurements of the electronic properties of undecagold clusters and nanoparticles immobilized atop alkanethiolate SAMs using $\alpha,\omega$–alkanedithiolate tethers. The single-electron transport properties of nano-scale metal particles has led to great interest in using them as interconnects and points of attachment in ‘bottom-up’-based molecular-scale circuitry. The results of these experiments show that charge transport through these metal clusters immobilized on SAMs is not straightforward. Spectral diffusion is often observed in their conductance spectra; in particular, diffusion within the spectra is observed over a single cluster or nanoparticle. This diffusion, closely coupled to the particle’s chemical and physical environment, is of significant importance when considering integrating materials of this kind into molecular-scale circuitry applications. Several hypotheses for this spectral diffusion are described and tested.

Chapter 6 reports on the surface chemistry of SAMs containing $\alpha,\omega$–alkanedithiols ($\alpha,\omega$–AkDT). These experiments describe attempts to form high-quality SAMs of single-component $\alpha,\omega$–AkDT, as well as ordered SAMs of $\alpha,\omega$–AkDT inserted into $n$–alkanethiolate host SAMs. In addition to STM, several ensemble surface science techniques (including FT–IR, wettability, and optical characterization, all described in Chapter 2) are used to elucidate a more complete chemical picture of these thiol-terminated SAMs. The impetus for the research described in this chapter is to understand fully the surface chemistry of the thiol-terminated SAM for proper attachment of the gold clusters (vide infra) and nanoparticles. The combined reactivity and flexibility of the $\alpha,\omega$–AkDT leads to the creation of films with very complicated structures and kinetics of formation.

Chapter 7 presents the conclusions and the future prospects of the research undertaken in this thesis. Two themes are described in this thesis: the first describes control of the placement and organization of molecules at the smallest scales as exemplified in the adsorption and patterning experiments of the amide-containing alkanethiolate adsorbate presented in Chapters 3 and 4. The
second theme describes the spectroscopic measurements of atomically precise complex assemblies, here undecagold clusters and larger nanoparticles supported and immobilized atop \(n\)-alkanethiolate SAMs. Both of these projects are tied together through fundamental characterization of complex nano-scale assemblies that will assist in the creation of novel materials from the bottom up.
Chapter 2

Alkanethiolate Self-Assembled Monolayers: An Introduction to Self-Assembly and Applied Characterization Techniques

The interactions between molecules and surfaces are some of the most exciting and widely studied aspects of modern surface science. The strengths of the interactions between molecules and substrates are highly dependent upon their chemical natures, ranging from very weak (e.g., \( n \)-alkanes adsorbed on gold or graphite [5]) to strong enough to break chemical bonds within the molecule (e.g., ethylene on platinum [6]). One of the most remarkable molecule–substrate interactions is the spontaneous self-organization of atoms and molecules on surfaces into well-ordered arrays; the supramolecular assemblies that form often possess both short- and long-range order. In particular, the self-assembly of surfactant molecules adsorbed on transition metal surfaces has been of growing importance over the past two decades. The field of self-assembly has grown rapidly since the discovery of these structures and their ability to modify the physical and chemical properties of surfaces (Figure 2.1) [7–9]. Studies of these ultra-thin films have ranged from the very fundamental, studying the organizations and chemistries of the systems, to the applied, examining the robustness and chemical utilities of these assemblies once formed and placed in desired environments.

The concept of molecules organized into higher order structures has been explored in the past [10]. Examples of the ordering of atoms and molecules into both short- and long-range assemblies have been shown throughout biology, chemistry, and physics. However, in the context of surface chemistry, it is important to mention that amphiphilic molecules spontaneously organizing into assemblies on metal surfaces are only a subset of self-assembled films that have been reported and
Figure 2.1. Schematic of an $n$-dodecanethiolate monolayer self-assembled on an atomically flat gold substrate. The assembly is held together by the bonds between the S headgroups (shown in green) and the Au surface (yellow) as well as van der Waals interactions between neighboring hydrocarbon chains ($C =$ blue, $H =$ white).
characterized. Molecules that are amphiphilic can organize themselves at a variety of interfaces (liquid–liquid, gas–liquid, solid–liquid, and solid–air interfaces); of particular relevance to this type of surface chemistry are Langmuir–Blodgett (L–B) films, in which amphiphilic molecules organize at one interface (typically air–solution) and are transferred to another (air–solid). However, L–B films are known to suffer both in chemical and mechanical stabilities, and thus the trend of research has pointed to the creation of the more chemically stable systems of assemblies chemically bound to solid surfaces, which can be placed in many different environments. These systems can possess order at the nanometer scale, as well as higher degrees of order imposed upon their assembled structure and will be a focus of this thesis.

Many different mechanisms for the adsorption of amphiphiles on surfaces have been studied over the past 20 years, encompassing a range of substrates and an even greater variety of adsorbates. Self-assembled monolayers (SAMs) are typically formed from the exposure of a surface to molecules with chemical groups that possess strong affinities for the substrate or a material patterned on it. How well these assemblies order is a function of the nature of the chemical interaction between substrate and adsorbate, as well as the types and strengths of intermolecular interactions between the adsorbates that are necessary to hold the assembly together. Molecules ‘binding to’ surfaces are either described in terms of physisorption, in which the enthalpies of interactions are rather low (considered to be $\Delta H < 0.5$ eV, typically from van der Waals forces), or in terms of chemisorption with $\Delta H > 0.5$ eV. Stronger interactions between molecules and substrates and between molecules themselves include phenomena such as hydrogen bonding, donor–acceptor and/or ion pairing, and the formation of covalent bonds, rendering the assemblies more stable than their physisorbed counterparts. Other studies have focused upon directly ‘grafting’ molecules to surfaces, such as the
attachment of aryl-functionalized molecules to silicon [11], alkyl-functionalized molecules to germanium via Grignard reactions [12], and molecules to metal surfaces through diazonium salts [13,14], all of which indicate the formation of surface–carbon bonds.

Chemisorbing systems have included the assembly of trialkyl-, trichloro-, or trialkoxysilanes on silicon dioxide surfaces [9, 15–17], carboxylic acids adsorbed onto aluminum oxide and silver surfaces [18–20], and $n$–alkanethiols chemisorbed to gold surfaces [7, 21, 22], to name merely a few. As noted above, particularly well-studied SAMs are those formed on transition metal surfaces (e.g. Au, Ag) and surfactants with electron-rich headgroups (e.g. S, O, N) and $n$–alkyl tails. The affinities between the surfaces and headgroups are strong enough to form either polar covalent or ionic bonds, and favorable lateral interactions between adjacent molecules are sufficient to draw and hold the assembly together. A schematic of a SAM of $n$–alkanethiolate molecules chemisorbed to a gold surface is shown in Figure 2.1.

SAMs are of prime technological interest, as the presence of molecules chemically bound to the surface renders the properties of the modified interface (i.e., wetting, conductivity, adhesion, and chemistry) to be entirely different than those of the bare substrate. The exposed terminal groups of the SAM can be further modified to enhance or to alter the film properties. Changing the terminal groups exposed at the air–film surface is critical for controlling and designing the interaction strengths of proximal molecules or analytes (e.g. sensing, electron transfer, cell adhesion, polymer adsorption) or for post-assembly modification of the film. Molecules that are confined to the air–film interface can undergo selective chemistry, as they are confined to two dimensions; unlike three-dimensional solution-phase chemistry, the molecules are pinned at specific locations. The incorporation of functional moieties such as chromophores, electroactive groups, or molecules that can bond within the SAM (e.g. covalent cross-linking between adjacent molecules or non-covalent
hydrogen bonding) enable capabilities in sensing, electron transfer, molecular recognition, and other areas. Many technologically relevant materials possess well-defined surface chemistries, including metals, semiconductors, oxides, and other complex materials such as superconductors; a variety of heteroatom-containing molecules have been shown to self-assemble on such substrates (Table 2.1). The nature of interactions between molecules and substrates range from hard acid–base interactions to soft donor–acceptor charge transfer interactions. However, there are a number of materials that possess complex surface chemistry. Complex materials (e.g. some oxides, ferroelectric materials such as LiNbO$_3$ and others) possess crystal structures with a number of atomic constituents; certain areas of a material may be able to be selectively protected so as to create a distribution of chemical compositions within the same material, or for the purpose of further growth or etching.

When the first reports of self-assembled thin films emerged in the literature [7, 18], the chemical character of the molecules included a polar headgroup such as a thiol or carboxylic acid as well as a hydrophobic overlayer (generally linear and aliphatic). Today, the molecules used can possess a number of functional groups in addition to the moiety responsible for the molecule’s chemisorption. These functional groups can be buried near the film–substrate interface, distributed within the film interior, and/or located at the terminus of the molecule that presents itself to the film–air interface (Table 2.2). Variation in the chemical contact between the molecule and the substrate controls the strength of the interactions (and thus stability) of the assembly and also how easily electrons are transmitted from the molecule to the substrate under an applied potential [46–48]; manipulation of the film interior affects its innate ability to order and how easily electrons are conducted through the film [49–53].

The terminal functional group of a SAM is critical to its interfacial properties – the surface’s general hydrophobic/hydrophilic character, adhesive characteristics, and reactivity; especially
Table 2.1. Different chemical systems of adsorbates and substrates that form SAMs.

<table>
<thead>
<tr>
<th>Surface</th>
<th>Substrate</th>
<th>Adsorbate(s)</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Ag</td>
<td>R–COOH, R–SH</td>
<td>[22,27]</td>
</tr>
<tr>
<td></td>
<td>Pt</td>
<td>R–NC, R–SH</td>
<td>[28–30]</td>
</tr>
<tr>
<td></td>
<td>Pd</td>
<td>R–SH</td>
<td>[31]</td>
</tr>
<tr>
<td></td>
<td>Cu</td>
<td>R–SH</td>
<td>[32]</td>
</tr>
<tr>
<td></td>
<td>Hg</td>
<td>R–SH</td>
<td>[33]</td>
</tr>
<tr>
<td>Semiconductor</td>
<td>GaAs (III–V)</td>
<td>R–SH</td>
<td>[34,35]</td>
</tr>
<tr>
<td></td>
<td>InP (III–V)</td>
<td>R–SH</td>
<td>[36]</td>
</tr>
<tr>
<td></td>
<td>CdSe (II–VI)</td>
<td>R–SH</td>
<td>[37]</td>
</tr>
<tr>
<td></td>
<td>ZnSe (II–VI)</td>
<td>R–SH</td>
<td>[38]</td>
</tr>
<tr>
<td>Oxide</td>
<td>Al₂O₃</td>
<td>R–COOH</td>
<td>[18]</td>
</tr>
<tr>
<td></td>
<td>TiO₂</td>
<td>R–COOH, R–PO₃H</td>
<td>[39,40]</td>
</tr>
<tr>
<td></td>
<td>YBa₂Cu₃O₇−δ</td>
<td>R–NH₂</td>
<td>[41,42]</td>
</tr>
<tr>
<td></td>
<td>Tl-Ba-Ca-Cu-O</td>
<td>R–SH</td>
<td>[43]</td>
</tr>
<tr>
<td></td>
<td>ITO</td>
<td>R–COOH, R–SH, R–Si(x)₃</td>
<td>[44,45]</td>
</tr>
<tr>
<td></td>
<td>SiO₂</td>
<td>R–Si(x)₃</td>
<td>[9], etc.</td>
</tr>
</tbody>
</table>
noteworthy is the ability to perform chemical reactions using the pendant functional groups (e.g. carboxylic acids, quinones, amines, anhydrides). Meanwhile, the nature of the lateral interactions holding together the supramolecular assembly has varied, now expanding beyond the all trans (fully extended, minimal disorder) aliphatic chains that were reported in initial studies. Several examples of well ordered SAMs have been reported from linear phenylene [54–56], phenylene–ethynylene [53, 57], and phenylene–vinylene oligomers [52] with sulfur headgroups. Both covalent and non-covalent interactions between adsorbates have assisted in producing well ordered SAMs, such as those with crosslinked interiors [58–61] or by those with hydrogen bonding groups to impart stability [3, 62, 63]. SAMs can also have terminal groups with switchable conformations, such as those terminated with oligo(ethylene glycol) (oEG) groups; electric fields on the order of 1 V/Å can cause coiling of the terminal methoxy groups, which may ultimately affect the assembly’s ability to resist protein adsorption [64–66]. Self-assembled monolayers can also be designed to have extremely poor cross-interactions, such as in the case of 1–adamantanethiolate monolayers. The adamantane moiety, comprised of four fused cyclohexane rings all in the chair conformations, has such poor cross-interactions (low van der Waals as well as occupying a larger molecular volume than is comfortably allowed by the adsorption sites on the Au substrate lattice) that is easily displaced off of the surface by alkanethiols even as short as n–hexanethiol [67]. Although the structural elements within a SAM can vary, the important factor for its stability is the strength of the attractive interactions between neighboring molecules.

The physical and chemical properties of SAMs leave them amenable to further manipulation, thus creating patterns within the film. In this chapter, the nature of n–alkanethiolate SAMs is described, as are the techniques used in this thesis employed to study their formation and their
Table 2.2. Various functional groups that have been incorporated into thiol-based SAMs, whether within the interior (I) of the film or at the terminus (T). Substituents have been omitted for clarity, and sites of attachment to the remainder(s) of the thiol-based molecule are indicated by a ‘—’ off of the listed moiety.

<table>
<thead>
<tr>
<th>Functional Group</th>
<th>Name</th>
<th>I</th>
<th>T</th>
<th>Reference(s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>–CH₃, –CH₂⁻</td>
<td>alkyl</td>
<td>✓</td>
<td>[21,68,69]</td>
<td></td>
</tr>
<tr>
<td>–CF₃, –CF₂⁻</td>
<td>(tri)fluoro</td>
<td>✓</td>
<td>[70,71]</td>
<td></td>
</tr>
<tr>
<td>–CH₂OH, –CH₂OCH₂⁻</td>
<td>hydroxyl, ether</td>
<td>✓</td>
<td>[68,69,72–77]</td>
<td></td>
</tr>
<tr>
<td>–COOH, –COO⁻</td>
<td>carboxylic acid</td>
<td>✓</td>
<td>[68,78,79]</td>
<td></td>
</tr>
<tr>
<td>–CO₂CH₃, –CO₂CH₂⁻</td>
<td>ester</td>
<td>✓</td>
<td>[80]</td>
<td></td>
</tr>
<tr>
<td>–CONH₂, –CONH⁻</td>
<td>amide</td>
<td>✓</td>
<td>[3,4,62,81]</td>
<td></td>
</tr>
<tr>
<td>–Cl, –Br</td>
<td>halogen</td>
<td>✓</td>
<td>[21,68,79]</td>
<td></td>
</tr>
<tr>
<td>–CN</td>
<td>nitrile</td>
<td>✓</td>
<td>[21,79,82]</td>
<td></td>
</tr>
<tr>
<td>–NH₂, –NH₃⁺</td>
<td>amine</td>
<td>✓</td>
<td>[76,83]</td>
<td></td>
</tr>
<tr>
<td>–B(OH)₂</td>
<td>borate</td>
<td>✓</td>
<td>[84]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>alkene</td>
<td>✓</td>
<td>[21,77]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>alkyne</td>
<td>✓</td>
<td>[77]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>diacetylene</td>
<td>✓</td>
<td>[58,59,61,85,86]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>aryl</td>
<td>✓</td>
<td>[54,87]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>oligo(phenylene–ethynylene) (OPE)</td>
<td>✓</td>
<td>[56,88–91]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>quinone</td>
<td>✓</td>
<td>[92]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>oligo(ethylene glycol), oEG</td>
<td>✓</td>
<td>[65,93–95]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>sulfone</td>
<td>✓</td>
<td>[96]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>epoxide</td>
<td>✓</td>
<td>[97]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>pyrene</td>
<td>✓</td>
<td>[98,99]</td>
<td></td>
</tr>
<tr>
<td></td>
<td>azobenzene</td>
<td>✓</td>
<td>[88,100,101]</td>
<td></td>
</tr>
</tbody>
</table>
structures. As SAMs are of such technological importance, there is a great desire to control their features, or the features of the substrates supporting them, down to the nanometer scale as technology continues to shrink in size and dimension. Self-assembly has been a useful method with which to isolate and to study molecules and assemblies at the nanometer scale. The invention and development of scanning probe microscopes (vide infra) have greatly enhanced our ability to understand and to optimize the assembly and final structures of SAMs.

2.1 \( n \)-Alkanethiolate Self-Assembled Monolayers

Much research has been focused on the self-assembly of \( n \)-alkanethiolate and related molecules on gold substrates. Thiol-based SAMs are attractive structures for several reasons. Well-ordered SAMs can be formed from a variety of sulfur-containing species (i.e. thiol, sulfide, alkyldisulfide [7]), yet experiments show that thiol molecules kinetically outcompete the disulfide molecules for available surface sites when the two species are coadsorbed from solution [69]. The gold surface is relatively chemically inert; it does not readily form a surface oxide nor keep a strong hold of adventitiously adsorbed material, and therefore SAMs can easily be prepared in ambient conditions. Self-assembled monolayers render an ordinarily conductive metal surface to be relatively insulating, yet electrons can be moved controllably through the film through applied potentials when integrated into electrochemical cells (vide infra). Additionally, the molecules are stable once adsorbed on the surface, yet they are mobile enough such that they can be selectively processed after adsorption. Many different chemical functional groups have been incorporated into \( n \)-alkanethiolate SAMs (Table 2.2). Much research has focused on the incorporation of differing terminal groups into SAMs, for interfacial properties such as hydrophobicity and reactivity to be manipulated and controlled. Recognition factors can be incorporated into the exposed interface of a SAM for either cell adhesion [95], selective protein interactions [94], or for inhibiting the non-specific binding of
proteins [102]. The structures of SAMs as well as the dynamics of their formation will be discussed presently, as alkanethiolate SAMs have often provided the foundation for increasingly complex and functional nano-scale architectures. It is through such fundamental studies of SAMs that the most efficient and effective applied systems can be created and developed.

The surface structures formed by the adsorption of \( n \)-alkanethiols on gold surfaces are generally well ordered and crystalline. Upon exposure of a gold substrate to such a thiol in solution or in the gas phase, a bond between gold and sulfur (\( \sim 1.2 \) eV [103]) forms rapidly, typically within seconds to minutes. Following over the next few hours, contributing a significant amount of order to the assembly, is the close-packing of the hydrocarbon tails into a primarily all \textit{trans} configuration. The adsorption of the molecules extends laterally to accessible substrate, if the exposed thiol is in high enough concentration (with the occupation of \( \sim 10^{15} \) molecules/cm\(^2\)). However, the film is restricted from growth normal to the surface because of the molecule’s non-reactive, methyl-terminated tail, resulting in a chemically passivating film of monomolecular thickness. At low surface coverage, the alkanethiolate molecules lie flat with their hydrocarbon backbones parallel to the gold surface; at higher surface coverages, the molecules begin to stand up, with the hydrocarbon tails tilting approximately 30\(^\circ\) from the surface normal and in an extended configuration so as to maximize van der Waals interactions [104]. In ambient conditions, \( n \)-alkanethiolate SAMs with \( n \geq 6 \) methylene groups will order; studies in ultrahigh vacuum (UHV) have shown that \( n \)-alkanethiols as short as ethanethiol (\( n = 2 \)) will produce ordered SAMs [105]. Self-assembled monolayers of \( n \)-alkanethiylates on silver surfaces, for example, are more densely packed and have less of a tilt angle than those on gold [106]; this is of importance in terms of how the density of the packed SAM can affect the overall utility of the assembly. The tilt angle is determined by the packing density of the headgroups and the optimizing of van der Waals interactions between
chains. Exchange of adsorbates within the solution phase will occur in order to form a locally energetically favorable, though kinetically trapped, surface structure. It is possible to move these structures towards equilibrium by exchanging weakly bound molecules and to anneal film defects (e.g. increasing domain coherence length) by inserting additional adsorbates from the vapor phase at elevated temperatures [107].

The physical structures and chemical properties of \( n \)-alkanethiolate SAMs adsorbed onto gold surfaces have been studied by many ensemble averaging techniques to determine the macroscopic characteristics of the monolayer; complementary local probe techniques yield a comprehensive picture of the SAM. Such experimental methods to determine SAM properties include ellipsometry to measure film thickness [49,103,106]; Fourier transform infrared spectroscopy (FT–IR) to examine tilt and order [49,103,106]; contact angle goniometry (CAG) to measure the film’s wettability and surface energy [21]; electrochemistry to probe electron transport through the SAM and to examine structural defects such as pinholes [49,108]; quartz crystal microgravimetry to determine the kinetics of monolayer assembly [109–111]; X–ray photoelectron spectroscopy (XPS) to evaluate the composition of the bound species [103]; diffraction techniques (electron/He/X–ray) to investigate the structures of assemblies [112]; and temperature-programmed desorption to probe the thermodynamic aspects of adsorption and desorption and to determine bond strengths within the assembly [8]. From the early 1990s, STM studies of \( n \)-alkanethiolate SAMs on gold have shown their organization on the nanometer scale [104,113–116]. Other scanning probes including the atomic force microscope (AFM [117–119]) and the lateral force microscope (LFM [120]) are continuing these studies as well as demonstrating the manipulation of assembled films to make patterned surface structures from multiple adsorbates.
Self-assembled monolayers formed at room temperature are governed by a complex mixture of thermodynamics and kinetics. As described previously, SAMs are typically kinetically trapped at local thermodynamic minima. When imaged with local probes such as the STM (vide infra), a variety of local defects are observed. Such defects include substrate vacancies, ‘holes’ that are one atomic layer deep of gold have been formed during the adsorption process. One possible mechanism for the formation of these are from the ejection of individual gold atoms from the surface layer and subsequent rearrangement of the remaining gold adatoms. There is precedence for an adsorbate-mediated corrosion, whereby S–Au bond formations weaken the surrounding Au–Au bonds [121]. Another mechanism for their formation is from the reconstruction of the gold surface (compressed from extra surface atoms) upon adsorbate binding, where ∼2 Au atoms per unit cell are released upon lifting the surface reconstruction and the vacancies coalesce into islands [122,123]. Monatomic step edges, where one atomic layer of gold separates the gold terraces from each other with a height difference of ∼2.38 Å, are also present. Defects of the molecular lattice include domain boundaries of the SAM (mismatches in the tilts of the individual n–alkanethiolate adsorbates), vacancies within the crystalline lattice of the molecules, and larger grain boundaries.

Several structural features typical of chemisorption of n–alkanethiolates on Au{111} can be seen using the STM as a local probe [116] (Figure 2.2). Domain boundaries, regions where the alkyl tails may possess either opposite tilt vectors and/or rotations with those of neighboring adsorbates, stacking faults, or differing sulfur headgroup–lattice registry, can be found. The hexagonal packing of the alkanethiolates in the (√3×√3)R30° overlayer structure is also visible. The molecules are separated by 4.99 Å, the distance in between the sulfur headgroups bound to the gold substrate. Superlattice structures such as the c(4×2) are also formed [122,124]. Additional defects of the self-assembled film include vacancies in the molecular lattice itself. The structural features and
Figure 2.2. (A) Scanning tunneling microscope image of a 220 Å × 220 Å area of an n-decanethiolate (C10) SAM. The molecular lattice was resolved, and the hexagonal close packing of the adsorbates was readily visible. A step edge along with several film defects can be seen, including domain boundaries (protruding and depressed ridged lines) and substrate vacancy islands (dark, circular depressions). Tunneling conditions: \( V_{\text{sample}} = -1 \) V, \( I_{\text{tunnel}} = 10 \) pA. (B) Inset of (A) as marked by the red box, showing the \( c(4\times2) \) superlattice as well as the unit cell of the SAM.
defects shown by scanning probe microscopes such as the STM have shed light on the ability to pattern SAMs in specific locations. While alkanethiolate SAMs are stable surface structures, the adsorption process is highly dynamic and molecules can continue to exchange with other thiol species in solution or in the vapor phase, with many exchange events occurring at structural defect sites. The Au–S bond is strong enough to weaken proximal Au–Au bonds in the lattice beneath the assembly [125], and gold has been found dissolved in solution after desorption [121]. In SAM formation, equilibrium processes that are highly kinetically limited exist between species bound to the surface and free adsorbates (when in the solution phase, these free adsorbates are solvated, and additional energetic factors such as the enthalpy and entropy of solvation play critical roles in the dynamics of adsorption). Substrate vacancy islands, adsorbate vacancies in the molecular lattice, and domain boundaries are critical sites in the monolayer that will enhance and differentiate the effects of post-adsorption processing of the film [126].

The degree of disorder at these sites is increased relative to the rest of the close-packed monolayer, and thus molecules adsorbed at these defect sites are postulated to be less constrained than the surrounding matrix and may have greater conformational mobility. It is highly likely that the solution has increased access to these defect sites, and the presence of solvent may promote the exchange of adsorbed molecules for new species of interest [126]. Step edges are also likely accessible to the solvent and present substrate atoms with low coordination number and thus are sites of high probability for adsorption, and molecules that adsorb here may be comparatively more accessible by solvent than their neighbors in the close-packed film. These defect sites within the ‘host’ SAM are postulated to be the most susceptible to exchange to new ‘guest’ adsorbates exposed to the films (*vide infra*).
Alkanethiolate SAMs have been studied in extensive detail by a variety of methods, and with the knowledge obtained we are able to control the types, densities, and distributions of defects of the final monolayer product. The overall quality of the film allows the possibility for further patterning, manipulation and post-adsorption processing, including thermal annealing and backfilling of defects with new adsorbates, which will allow for the characterization (and manipulation) of single molecules with the STM. Exchange of \( n \)-alkanethiolate molecules for guest adsorbates will occur at defect sites within the SAM, with both host and guest molecules participating in individual and collective exchange events. Infrared spectroscopy studies have shown that multiple exchange events occur, with a rapid exchange first occurring at defect sites such as at grain boundaries, domain boundaries, or at the peripheries of substrate vacancy islands and then with a second, slow exchange, presumably occurring within the domains themselves [105]. We have demonstrated that molecules can be selectively inserted into SAMs at defect sites, domain boundaries, and step edges, and we use this molecular positioning ability to advantage [89,90,107,126,127]. By capitalizing on the dynamic exchange processes with thiol species in solution, we have started to characterize isolated molecules that are candidates for nanoelectronic interconnects and functional components with the STM through the positional assembly of these molecules into a surrounding, pre-formed alkanethiolate matrix [89,90]. Molecules can be brought into the well-defined and understood matrix in extremely low concentrations, and we can elucidate perturbative effects that such molecules introduce when they are studied individually and systematically.

The mobility of adsorbates at surface defect sites is increased as the molecules may not be strongly bound (e.g. sitting on a bridge or on-top site of the Au lattice rather than a three-fold hollow site), they may be located at the edges of large adsorbate domains and thus have a lower interaction energy than their fully-surrounded counterparts, or the molecules may be disordered
such that they are susceptible to more interactions with solvent, and thus more prone to exchange or desorption. The ability to reduce the mobility of molecules once they are placed on a surface allows these assemblies to be useful nano-scale structures.

The structure as well as the placement of alkanethiolate films on surfaces other than gold has been studied and reported. These systems have included alkanethiolates adsorbed on platinum [30, 128], palladium [129, 130], silver [106, 131], and copper [106, 132]. This area has not yet been explored extensively, but will no doubt prove to be useful in balancing order and placement of molecules with an ability to create stable and functional nanostructures.

2.2 Methods of SAM Characterization: Ensemble and Local Measurements

A variety of experimental methods have been used to probe the quality and chemical nature of SAMs, from techniques that are macroscopic and that average the signal across the entire film, to local probes such as the STM or the AFM, which can examine the structure of the SAM down to molecular resolution and better. Several techniques that have been typically used to characterize SAMs on the macroscopic level (ensemble averaging measurements) are described below. Although local probes provide the most detailed information regarding the structure and order of self-assembled films, by nature they cannot analyze more than hundreds to thousands of square nanometers at a time. Many different measurements used in concert present a comprehensive analysis of film properties. Listed here are the characterization methods that were used in this thesis, including techniques that measure the macroscopic film order as well as local probes that examine the local composition and structure. Additionally, scanning tunneling spectroscopy (STS) will be described for the experiments measuring the conductance of metal nanoparticles as well as the SAM supports beneath them.
2.2.1 Local Probes: Scanning Probe Microscopy

Scanning probe microscopes (SPMs) have greatly assisted in the assembly of high-quality SAMs and nanostructures by analyzing the structures and spatial distributions of adsorbates across surfaces. For comprehensive reviews of the mathematical and physical treatments of the STM, related SPMs and their capabilities, the reader is referred to several outstanding texts [133–135].

2.2.1.1 Scanning Tunneling Microscopy

The development of SPMs, in particular STM, has allowed the detailed study of the electronic features of clean surfaces, individual atoms and molecules adsorbed on surfaces, as well as those of supramolecular assemblies including SAMs [48,104,112,113,126,136] and nanoparticles [137–143]. Since its invention just over 20 years ago, the STM has revolutionized many sectors of scientific research by providing real-space imaging of features on the nanometer scale and below. STM was invented in the early 1980s by Drs. Heinrich Rohrer and Gerd Binnig at the IBM Zürich Research Laboratory, and was designed to probe the local electronic and physical structures of thin insulating layers [144]. STM can image the topographic and electronic structures of both metallic and semiconducting surfaces, and the single and networks of molecules adsorbed upon them whose activity is restricted to two dimensions. Therefore, STM serves unequivocally as a tool for the systematic analysis of novel materials and structures one at a time in emerging fields such as molecular electronics and chemical patterning. For example, it can provide simultaneous topographic and electronic profiles of a surface with subÅ resolution [144]; it can be used to measure the electrical conductance of molecules and their assemblies [145–148]; it can be used to perform single-molecule or single-nanoparticle spectroscopy examining the dynamics of single molecules and particles [149–151], it can be used to construct novel electronic or magnetic assemblies and features that ordinarily would not exist off of surfaces [152–155] as well as to direct and to mediate chemical
reactions and motion [156–159]. Tunneling electrons can be used to excite surface plasmons in metals, yielding photons that can be collected and analyzed [142, 160, 161].

The above examples illustrate the ability of STM to enable both fabrication and measurements of novel electronic devices from the ‘bottom up’ through detailed investigation and characterization of both the electronic and physical structures of innovative materials. In this thesis, STM has been used to probe the electronic states, motion, and other properties of molecules and assemblies that are candidates for such nanoelectronic materials, as well as to understand the phase behavior of \( n \)-alkanethiolates once adsorbed to a surface to further advance chemical patterning strategies. In particular, since the early 1990s, STM has been used to image SAMs of \( n \)-alkanethiolates adsorbed on gold surfaces. STM has been able to provide insight into the mechanism of SAM formation as well as to elucidate important structural features that lend SAMs their integrity as surface-stable entities.

In a STM, an atomically sharp metal wire (either mechanically cut or electrochemically etched) serves as the probe tip and is brought within nanometers or less of a surface. The principle of the STM’s operation is described by quantum mechanics and is based on an electron’s non-zero probability of tunneling through a classically forbidden potential barrier. This barrier is due to the work functions \( \phi \) of the tip and sample. When an external bias voltage \( V \) is applied between the tip and sample, an offset of the same potential occurs between their Fermi levels (Figure 2.3); this causes a net flow of electrons traveling with an energy \( eV \) from the filled states in the tip to the empty states in the sample. Reversing the bias polarity allows for the filled states of the sample to be examined.

The STM consists of three essential parts: scanning, feedback, and recording. Two photographs of the STM used for experiments operated at ambient conditions in this thesis are shown
Figure 2.3. Energy level diagram for a tunneling junction of a STM. The Fermi energy levels ($E_F$) of the tip and sample are offset by the applied bias voltage, $V$. LDOS = local density of states, $z =$ tip–sample separation.
in Figure 2.4 [162–164]. The important parts of the STM are labeled, including the preamplifier that detects the tunneling current from the back of the sample, the Macor® (ceramic) base in which the piezoelectric tubes responsible for walking and scanning are mounted, as well as the environment in which the STM is located. The STM rests on a series of vibration dampening stacks that eliminate low-frequency vibrations, and is placed in housing that contains acoustical foam to eliminate the coupling of acoustical noise. The entire assembly rests on a vibration isolation table, also for eliminating low-frequency vibrations. A thermometer–hygrometer constantly monitors the temperature and relative humidity inside the housing.

Designed in the “beetle” style, three piezoelectric actuators (labeled as ‘3’ in Figure 2.4) serve to support the sample and to advance it coarsely towards the probe tip. The tip is located centrally to the other three tubes (“legs”), and is housed in a fourth identical piezoactuator used to control its motion in three dimensions; the application of a voltage to these piezoelectric materials causes them to distend in extremely small increments (0.1–10 nm/V), and they are used to control both the highly precise motion of the STM tip as well as the coarse approach of the sample. The STM can record images in either constant-height mode or constant-current mode. In the former, the tip–sample separation (z) is held fixed, and the fluctuations in tunneling current due to features of the sample are measured; in the latter, the tunneling current is held constant, and the voltage applied to the z piezoactuator needed to maintain the set current via extension or retraction of the tip is monitored (Figure 2.5). Rastering the tip across the sample surface generates an image of electronic features, and the resulting image is a convolution of both the topographic and electronic features of tip and sample [165].

The tunneling current drops exponentially upon moving the probe tip away from the surface, typically with a decay constant of 1–2 Å⁻¹, describing how the wavefunction of the electron falls off
Figure 2.4. Close-up photographs of the STM scanner head. 1: second stage of the preamplifier; 2: Macor® base; 3: piezoelectric tubes for walking and scanning; 4: vibration dampening stacks; 5: first stage of the preamplifier; 6: acoustic dampening foam; 7: vibrational isolation table.
as a function of distance. Thus, the STM possesses high lateral resolution of features as the majority of tunneling occurs from the endmost atom of the tip, and proximal atoms or other tip features capable of tunneling contribute much less to the total tunneling current due to their increased distance from the surface. Depending upon the geometry of the probe tip, it is not uncommon for unwanted metal features (microtips) to be present that participate in the tunneling current. They often convolute artifactual features with the electronic and topographic information that constitute a STM image.

When an electron tunnels from a metal tip, through an alkanethiolate SAM and to the metal substrate underneath, it is traveling through two different regions; the first is through the gap from the end of the tip to the film interface (whether air or vacuum), and the second is through the film to the Au substrate. Each region has its own thickness and its own impedance, with particular decay constants and exponential prefactors to the tunneling processes. These decay constants change as per the chemical nature of the adsorbates, leading to different tunneling characteristics (and thus electronic contrast) between multiple adsorbates present on a surface [48]. When operating at low tunneling currents and when imaging adsorbates of sufficiently short lengths [136], an STM can resolve the molecular lattice of an $n$–alkanethiolate SAM, imaging the terminal methyl groups and showing their hexagonal close packing. A typical image of an $n$–decanethiolate SAM on Au{111} shows the individual molecules resolved in their superlattice configuration, as well as several film and substrate defects, shown in Figure 2.2.

An additional capability of the STM is that images can be acquired while concomitantly collecting other useful information through separate (i.e. spectroscopic) data channels. STS is used to examine the current–voltage spectrum, conductance, or other electronic properties of a material, and additionally can assist in mapping the local density of states (LDOS) by measuring both filled
Figure 2.5. Schematic of an STM tip rastering across the surface of an $n$–alkanethiolate SAM. (A) The STM is operating in constant height mode, maintaining a constant tip–sample separation. (B) The STM is operating in constant-current mode, where the STM tip extends and retracts in order to maintain a constant amount of tunneling current between tip and sample.
and empty states. Current–voltage spectroscopy, or I(V) spectroscopy, is often used to measure electronic structure [166–168]. Specifically, the tunneling current through the material of interest is measured as a function of changing the bias voltage of the sample. STS can be used to demonstrate the enhanced conductivity of electroactive molecules either fully composing or embedded in a ‘host’ self-assembled monolayer [53,148], or to examine the single-electron charging events of small metal particles [140, 169]. STM was used to demonstrate the utility of a fullerene (C\textsubscript{60}) molecule as an electromechanical amplifier, as a distinct change in the electronic spectrum occurs upon its physical compression with an STM tip in a tunneling junction [170, 171]. The I(V) characteristics of the fullerene become more linear (showing more metallic character) upon deforming the fullerene’s spherical shape, and gain was demonstrated as the current increased at lower applied voltages.

The LDOS is often recorded by measuring the first derivative of the I(V) spectrum, the differential conductance (dI/dV), typically acquired with a lock-in amplifier. The LDOS is proportional to this quantity when normalized for changes in gap impedance during the acquisition of the spectrum by dividing by the quantity (I/V), i.e., to (dI/dV)/(I/V) [168]. Briefly, I(V) spectra are acquired by monitoring the tunneling current through a sample or in a surface site of interest as a function of sweeping the sample bias across a range of voltages. While imaging, the feedback loop is set to measure a constant tunneling current, and the \( z \) piezoactuator adjusts to keep the current constant by either moving the tip closer to or away from the sample. Instead, while acquiring spectra, the tip–sample separation control feedback loop is temporarily turned off so that a variety of tunneling currents can be measured and the piezoactuator will not compete to hold the tip steady. The bias voltage is then swept across a range (\( i.e., \) from \(-2 \) V to \(+2 \) V), and the tunneling current is measured at each sampling point). It is imperative that the STM be both vibrationally and thermally isolated so that the tip neither drifts out of tunneling range nor makes contact with
the sample surface when the feedback loop is disabled. Proper acoustic isolation additionally en-
sures that superfluous noise does not couple into the electronic signal through the scanning probe
microscope’s relatively large mechanical loop.

2.2.1.2 Atomic Force Microscopy

While STM is a powerful tool that examines the electronic and physical properties of
molecules and their assemblies on the nanometer scale, it is only one of many SPM techniques that
are rapidly changing our understanding of molecular-scale behavior and that will ultimately design
and shape the research and structures in fields including chemical patterning, biomolecule-based
assembly and molecular nanoscience. The atomic force microscope (AFM) has greatly enriched
the analysis of surfaces and surface-bound assemblies [172,173]. Whereas the STM requires that a
sample be conducting, semiconducting, or at least conducting enough to dissipate charge quickly
and avoid changing the potential difference between tip and substrate, the AFM has no such re-
quirement. The principles of the AFM’s operation have led to the instrument’s many permutations
to obtain much more than merely topographic information. Briefly, the AFM typically operates
by rastering a sample against a sharp tip that is connected to the end of an oscillating cantilever
(Figure 2.6). Attractive and repulsive forces between the tip and the chemical environment of the
sample will cause the cantilever to deflect to a certain degree.

Feedback mechanisms and thus measurement sensitivity for the AFM include forces due to
magnetism, friction, surface charge or potential, capacitance, etc. This enables the development
of scanning probes that are specific to molecular-scale properties; there are several modes of AFM
operation that have been chosen to create and to characterize patterned SAMs at the nano-scale,
including the lateral force microscope (LFM), which can distinguish between different chemical
functionalities on a patterned surface due to tribological differences [120,174]; conducting probe
Figure 2.6. Schematic of an AFM's operation. A sharp tip resides at the end of a cantilever, rastering along a surface, detecting differences in features (illustrated here as dark stripes). The deflection of the AFM tip as a function of surface properties is recorded by shining a laser beam upon the cantilever's back, which is then sent to a position-sensitive photodiode (shown with four quadrants).
AFM, where the tip has been coated with a metal that can send current through a SAM to measure either its conductance or to desorb adsorbates reductively in particular patterns, magnetic force microscope, which has probed the magnetic properties of atomic-scale structures and ultrathin films [155, 175]; the electrostatic force microscope, which has been used to probe the local domain structure of ferroelectric crystals as well as study the structures and charges of semiconductor surfaces [176–179]; the scanning capacitance microscope, which has been used to examine two-dimensional dopant profiling in semiconductors for integrated circuits [180, 181]; and the chemical force microscope to examine the adhesive and frictional forces of surfaces [182, 183].

### 2.2.1.3 Lateral Force Microscopy

The LFM is a variant of the AFM, differing in that the feedback mechanism is tuned to respond to tribological differences of the surface. This has been useful for determining the spatial distributions of multiple adsorbates on a surface that differ in terminal groups in order to predispose a portion of the surface to a particular reactivity. In addition to topographic features that change the position of the cantilever, the cantilever can also experience twist (torsion) from changes in the tip-sample interaction. This torsion also affects the position of the cantilever, and thus the signal of the laser on the photodiode. For LFM operation, the difference between the signals from the left and right sides of the photodetector is registered as a lateral force, and a relatively larger positive difference between the left and right sides of the photodetector corresponds to greater lateral force [120]. For example, within an \( n \)-alkanethiolate SAM, the LFM can easily distinguish between adsorbates terminated with polar groups (here, \(-\text{NH}_3^+\)) that have been patterned amongst \(-\text{CH}_3\)-terminated alkanethiolates (Figure 2.7). The friction between the tip and sample will be higher in the \(-\text{NH}_3^+\)-terminated regions, and the tip will glide easily in the relatively low friction \(-\text{CH}_3\)-terminated regions; the differences in lateral forces exerted on the probe tip in these regions
are recorded. The LFM can provide excellent chemical contrast between such differing molecules, and can show with nanometer-scale precision the placement of different molecules on a surface.

## 2.2.2 Ensemble Measurements

While SPMs can provide extensive information about a surface or SAM’s properties at the smallest of scales, the principal disadvantage is that the information is highly localized. By nature, SPMs cannot provide information about the properties of a SAM across its entire surface. It is especially important to augment the information gained using local probes with ensemble techniques that average and sample information over a much larger area of the surface.

### 2.2.2.1 Contact Angle Goniometry

Contact angle goniometry (CAG) is used to measurement the general wettability (hydrophilicity, hydrophobicity) of surfaces [184, 185], and it has been applied to SAMs as well [21, 72, 75]. CAG is the angle at which a liquid–vapor interface meets a solid surface, and this angle is sensitive to the particular interfacial forces present. A variety of methods exist to measure these contact angles, including a ‘dragging’ method, the Wilhemy balance technique, or by adding volumes of liquid to the existing droplet from either its top or bottom. For static CAG, a $\mu$L-sized droplet of H$_2$O, $n$–hexadecane (HD) or other liquid of interest is placed into contact with the surface, and the angle tangent to where the surface and the liquid droplet intersect is measured (Figure 2.8). To gain information about surface roughness and heterogeneity, the advancing and receding (dynamic) contact angles are measured [186]. The techniques used for measuring static, advancing, and receding contact angles using the dragging method are described schematically in Figure 2.8. The measured angle reflects the degree of surface order, and can indicate the incorporation of particular functional groups, as the contact angle changes with varying film composition. CAG can indicate the relative order in a $n$–alkanethiolate SAM as the contact angle will be slightly
Figure 2.7. A LFM image contrasting the individual domains of $-\text{NH}_3^+$- and $-\text{CH}_3$-terminated alkanethiol adsorbates patterned on a gold surface. The $-\text{NH}_3^+$-terminated regions are shown as brighter due to stronger tip-sample interactions, as a greater voltage is being required to balance the lateral force of the cantilever.
different from a H\textsubscript{2}O droplet resting upon a close-packed, –CH\textsubscript{3}-terminated surface versus a droplet resting upon the disordered and thus exposed –CH\textsubscript{2}– groups and interior of the film. Additionally, the terminal groups serve to shield the chemical forces of the substrate that cause the change in contact angle for terminal groups such as –CH\textsubscript{3} that have little polarizability (a decrease in contact angle with decreasing \textit{n}-alkyl chain length). For more hydrophilic surfaces (\textit{i.e.}, –OH, –COOH, or –CO\textsubscript{2}CH\textsubscript{3}-terminated surfaces), the water droplet will make a smaller contact angle as the water more effectively wets the hydrophilic surface, even probing through the surface to depths up to 5 Å [75]. Conversely, a drop of neat HD placed atop the surface of a SAM will have a low contact angle, as the hydrocarbon liquid spreads across the surface of the film. Solvents such as H\textsubscript{2}O are expected to probe acid–base interactions present at the interface, while solvents such as HD probe short-range dispersion forces, the polarizability of the functional groups at the SAM surface, and the general disorder of the film [21]. While CAG cannot determine the exact molecular composition of a SAM, it can provide an estimate of both film order and heterogeneity. Many groups have used CAG to analyze and to estimate the relative mole fractions of the adsorbates composing mixed SAMs, as the contact angle will change with varying film composition, although the contact angle can be highly nonlinear when polar terminal groups are present [68]. The spatial resolution of the technique is in the many tens of microns range, so submicron patterns are not readily observed.

### 2.2.2.2 Ellipsometry

Ellipsometry is used to measure the thicknesses of SAMs chemisorbed to Au surfaces based on measuring the changes in polarization and intensity of linearly polarized light when reflected off the surfaces. Light is linearly polarized when all of the photons in a beam of light have their electric field vectors oriented in the same direction, or when two linearly polarized waves with the same wavelength are combined in phase [187]. If two linearly polarized beams are combined and
Figure 2.8. Schematic of CAG techniques using the dragging method. (A) A static contact angle measured from a sessile drop on the surface. (B) Advancing and receding contact angles measured from when the drop is in motion.
are slightly out of phase with each other, elliptically polarized light results. In particular, when linearly polarized light is reflected from a metal surface, it changes its state to elliptically polarized, as there is a shift of the phases of both the components that are parallel and perpendicular to the plane of incidence; $p$- and $s$-polarized light will be reflected differently. $s$-polarized light is (field vector) perpendicular to the direction of propagation and is parallel to the plane of the surface, and $p$-polarized light is perpendicular to the direction of propagation, contained in the plane of incidence.

The amount of ellipticity induced depends on factors including the optical properties of the substrate as well as thickness and optical properties of the adsorbed films. Molecules such as $n$-alkanethiols adsorbed onto SAMs have well defined optical constants, with known indices of refraction ($n$), and extinction coefficients ($k$). For thin dielectric layers such as these, $k = 0$ as none of the light is absorbed. The measured values are $\Psi$ and $\Delta$, which are related to the ratio of Fresnel reflection coefficients $R_p$ and $R_s$ (the ratios of the amplitudes of the reflected wave to the amplitudes of the incident waves, for $p$- and $s$-polarized light, respectively):

$$\tan \Psi e^{i\Delta} = \frac{R_p}{R_s},$$

where $\Delta$ is the phase shift of the polarized light upon reflection; it can be described as $\delta_1 - \delta_2$, where $\delta_1$ is the phase difference between the parallel and perpendicular components of the incident wave, and $\delta_2$ is the phase difference between the parallel and perpendicular components of the reflected wave [187]. $\tan \Psi$ is the change in amplitude upon reflection. The ratio of these two values is measured, which is accurate, reproducible, and not susceptible to scatter. With the $\Delta$ and $\Psi$ values calculated from these treatments of the polarized light, monolayer thicknesses can be determined using computational models and fits.
2.2.2.3 Fourier Transform Infrared Spectroscopy (External Reflective)

Fourier transform infrared spectroscopy (FT–IR) has long been used to measure the vibrational frequencies of bonds within molecules. The vibrational modes of molecules attached to metal surfaces can also be detected using $p$-polarized light at a grazing angle [188]. In the case of SAMs (and not just for $n$–alkanethiolates SAMs), particular functional groups can be identified with ease and several structural features of the SAM can be measured. For such molecules attached to surfaces, specific selection rules exist and can be used to advantage. Only chemical bonds whose vibrations are perpendicular to the surface will be detected with $p$-polarized light, as the oscillations running parallel to the surface are effectively cancelled out by the dipole symmetry between the molecules in the film and the metal substrate. Infrared spectroscopy has been used to characterize the vibrational modes of many types of SAMs, including $n$–alkanethiolates and arylthiolates on metal substrates [57, 103], $n$–alkanethiolates on semiconductor surfaces such as GaAs, and for $n$–alkanoic acids on $\text{Al}_2\text{O}_3$ supports. FT–IR is often used to characterize the general order within the alkyl matrix of the SAM [49,189]. The alkyl tails vibrate at characteristic frequencies (in the region of $\sim 2800–3000 \text{ cm}^{-1}$ [49]); both the breadth of these peaks as well as the frequencies of the vibrations themselves yield a picture of the relative order and fraction of chain defects within the SAM. Should the chains be disordered, the vibrational spectra show a decrease in peak intensity (highly dependent upon the tilt and twist of the molecule), the breadth of the peaks (a lack of a constraining environment imposed by neighboring alkyl chains will allow a distribution of vibrational frequencies), as well as a slight blueshift in vibrational frequency. FT–IR can identify the presence of particular functional groups by measuring their characteristic vibrational frequencies (i.e. those of carbonyls, amides, hydroxyls, etc.). Thus, the progress of reactions at SAM surfaces can be followed using FT–IR. Raman spectroscopy has also been used to study...
SAMs [190,191]; it provides important information about adsorbate orientation through measured vibrations in the $\nu$(C–S), $\nu$(C–C), $\nu$(C–H), and $\nu$(S–H) regions, which are often too weak to be detected in IR spectra.

2.3 Conclusions

The $n$–alkanethiolate SAM is used in many of the experiments within this thesis to create precision nano-scale structures, from serving as an insulating support for tethered metal clusters to modifying a Au surface with a particular chemical pattern of adsorbates upon it. In order to obtain the most complete chemical and physical picture of these SAM systems, one must use both local probe and ensemble measurements. Although the techniques described are just a fraction of techniques used to study SAMs, they provide detailed information for how to improve upon the design and fabrication of these assemblies.
Chapter 3

Self-Assembled Monolayers with a Buried Functional Group: 
Phase Behavior of an Amide-Containing Alkanethiolate

The goal of the research covered in this chapter is to gain a fundamental understanding of the formation of bi-component, alkanethiolate SAMs through traditional solution-phase techniques using molecules with functionality buried near the sulfur headgroup. A particular emphasis is placed upon an n-alkanethiol with an amide group (–CONH–) that has been substituted into the hydrocarbon backbone; most importantly, the presence of this buried functional group does not disrupt the order of the monolayer, but rather, strengthens the intermolecular interactions [3, 62]. Previous studies on the formation of bi-component SAMs will be reviewed in the context of the work presented here; often times, these bi-component SAMs are found in near-homogeneous phases from separation of the two adsorbates as a result of their relative intermolecular interaction strengths. Here, the phase separation of n-decanethiolate from an amide-containing alkanethiolate adsorbate is reported. The hydrogen bonding ability of this buried amide group is particularly enhanced when buried in an apolar environment, such as what the hydrocarbon matrix provides. These high-strength intermolecular interactions can be of significant utility when patterning SAMs by soft lithography techniques including microcontact printing (µCP), as described in Chapter 4.

3.1 Introduction: Formation of Multicomponent Self-Assembled Monolayers

Although SAMs created from just one adsorbate are interesting on their own merits, there is a significant attraction to SAMs made of multiple components. There is a great interest in multicomponent SAMs, as it becomes possible to impart functionality or reactivity to the interface from
the properties of the individual adsorbates. An overarching goal in the self-assembly community is to gain tight control of the spatial distributions of these different components on surfaces such that desired patterns can be created. Different adsorbates often separate into domains through the adsorption process, by spontaneous assembly governed by thermodynamics and kinetics at the local scale, by their direct placement in a stepwise fashion, or by post-adsorption processing of the individual adsorbates. Changing the relative mole fractions of adsorbates on the surface may necessitate changing patterning schemes in order to yield the desired structure. Similarly, patterning strategies may need modification to avoid the inevitable processes of adsorbate diffusion and exchange. This chapter discusses our efforts to pattern alkanethiols (in particular an amide-containing alkanethiol) on a gold substrate, starting with understanding solution-phase adsorption, from which it can be determined how molecules interact with both similar and dissimilar adsorbates on the surface at the local level. Chapter 4 further explores how to pattern these molecules through their positive placement on the surface (microcontact printing) using the information gained from STM studies of their behavior on surfaces. In these studies, a higher level of control is obtained at the expense of feature boundary resolution. As these kinetically trapped systems are not at equilibrium, they are susceptible to further manipulation by a variety of methods. SAMs that preferentially self-assemble into discrete domains are of marked importance in the future design of nanoscale structures. By selectively tuning the interaction strengths between molecules deposited on a surface, it is possible to direct their assembly with very high precision.

3.1.1 Spontaneous Phase Separation

Generally, when two different adsorbates are mixed in solution and then exposed to a substrate, both species will adsorb on the surface. If the species differ moderately in molecular composition, they will separate into homogeneous domains on the surface so as to maximize self–self
interactions through van der Waals, hydrogen bonding, or other interactions. As these SAMs are kinetically trapped structures, it is difficult to estimate the number and sizes of individual domains formed as these are strong functions of preparation and processing conditions. If the adsorbates differ drastically in molecular composition, it can be assumed that the domains will be mostly single-component; however, there is a statistical likelihood that molecular entanglement will occur. Inter-adsorbate exchange may also affect the domain homogeneity; adsorbates can somewhat freely exchange into defect sites of the monolayer, and mixing of the adsorbates may occur. Although the exchange process can occur readily, the process reaches a limit where adsorbate distributions remain constant [128]. As a result, it is difficult to pattern molecules on a surface by solution-phase coadsorption alone, as many complex factors arise.

It is important to note that the relative fractional surface coverages of the molecules will not necessarily reflect the coadsorption solution; for example, a 1:1 mole ratio of adsorbate $A$ and adsorbate $B$ in solution will not necessarily yield a surface composition of 1:1 $A:B$. This observation is supported by CAG, SPM, and electrochemical studies [68, 79, 192–195]. Factors that affect the competition for adsorption sites include the relative solvation of the adsorbates by the solution, the sticking probability of each molecule, and the degree of interaction between the molecules once they are adsorbed. Molecules that are preferentially solvated may not adsorb as quickly to the surface, while relatively less soluble molecules may either aggregate in solution or aggregate together on the surface, both possible situations where the molecules’ self-interactions are maximized. The enthalpies of these intermolecular interactions as well as the minimization of poor cross-interactions provide driving forces for the separation of multiple adsorbates into their homogeneous domains.

STM has greatly assisted in understanding the distribution of molecules coadsorbed on surfaces, as well as how surfaces can be manipulated once the adsorbates are placed on the surface.
From information at the nanometer scale that STM has provided, more complicated nanostructures have been created. Previously, numerous spontaneously-separating, multicomponent SAM systems have been studied, using both local probes as well as ensemble-averaging measurements. Such systems include the coadsorption of short- and long-chain alkanethiols [192,196,197], molecules that differ both in chain length and functional groups (e.g., 3-mercaptopropanol and n-tetradecanethiol [198]), molecules of similar length but with differing terminal groups (e.g., n-hexadecanethiol and its –CO₂CH₃-terminated analog [115], n-undecanethiol and 11-mercaptopoundecanoic acid [78]) and molecules of similar length but with differing, buried functional groups (e.g., 3-mercapto-N-nonylpropionamide and n-decanethiol [194,195]). However, molecules of sufficiently similar composition will not phase separate if formed at room temperature from the same solution (e.g., n-decanethiol and n-dodecanethiol [126]). In this case, the likelihood of preferential exchange is decreased, as the energies of solvation and exchange will be similar between the two adsorbates. Energetically similar van der Waals interactions prevent them from moving great distances, though if the substrate is still immersed in solution, they are free to exchange off of the surface and then back on again. The following sections describe previous studies of the phase separation of bi-component SAMs from adsorbates differing in alkyl chain length and terminal functional group.

3.1.1.1 Variation of the Alkyl Chain

Some of the first phase-separated SAMs reported were formed from the coadsorption of n-alkanethiols that differed only in the lengths of their alkyl chains [22,196,199]. Whitesides and coworkers reported CAG measurements, ellipsometry, and XPS data of SAMs formed from different concentration ratios of adsorbates; they showed that SAMs of particular adsorbate coverages could be formed reproducibly. Using their ensemble measurements and modeling the adsorption events and the relevant intermolecular interactions, they inferred that single-component SAMs were the
lowest energy structure of a SAM exposed to a solution of two alkanethiols. Scanning probe microscopy data, however, show the presence of nanometer-scale domains of each type of adsorbate and mixtures of the two components [115]. Nevertheless, both local probe and ensemble-averaging measurements agree that the adsorbate domains existing on the surface tend towards homogeneity. These experiments of Whitesides and coworkers provided the first portion of evidence for the fact that the solution composition does not mirror the final film structure.

3.1.1.2 Variation of the Terminal Functional Group

The surface composition of multicomponent SAMs can be varied from completely mixed to completely separated depending on the terminal group. Separation of two adsorbates into single-component domains on surfaces has been observed when the components’ tail groups are vastly different in polarity. Unsubstituted alkanethiolates have been shown to be essentially miscible with hydroxyl-terminated (–OH) alkanethiolates when the chain lengths are similar [22]. Many of the early phase separation studies by Whitesides and coworkers were performed using –OH-terminated and methyl-terminated (–CH₃) adsorbates in order to probe molecular cross-interactions as well as to analyze how each adsorbate’s terminal groups responded to hydrophilic and hydrophobic contact angle measurements. SAMs composed of –CH₃- and carboxylic acid-terminated (–CO₂H) alkanethiolates have been shown to be miscible (undecanethiolate and 11–mercaptopoundecanoic acid), although domains of each molecule are readily observed [200]. Scanning tunneling microscopy studies have shown that coadsorbed SAMs of n–hexadecanethiol and its methyl ester analog phase separate into single component domains [115]. Scanning tunneling microscopy has also confirmed that molecules with vastly different functionality (i.e., both terminal group as well as chain length) will separate on the surface, such as short-chain, CO₂H-terminated thiols from long-chain, hydrophobic n–alkanethiolates [201].
3.1.1.3 Variation of the Buried Functional Group

There are many instances in which phase separation can be driven in binary-component SAMs by changing the terminal functional group between the two adsorbates. However, phase separation can also occur if the molecules possess different functional groups that are buried near the film–substrate interface. This chapter describes the phase separation of a binary-component SAM where the adsorbates are a mixture of \( n \)-alkanethiolate and an adsorbate containing an amide bond buried near the sulfur headgroup [194, 195]. These amide-containing molecules are capable of hydrogen bonding to their nearest neighbors, providing a high enthalpic driving force for phase separation when adsorbed on the surface. The increasing interaction enthalpies with molecules containing multiple amide groups further assists in imparting order (and thermal stability as well) to the assembly, as the directionality of the hydrogen bond can assist in aligning molecules. These hydrogen bonds can assist in forming the sharpest of boundaries between domains of molecules, even those that are only one molecule wide. This propensity may be useful in exploiting intermolecular interactions for the precise placement of molecules in films.

3.1.2 Phase Separation of Alkanethiolate Adsorbates with a Buried Functional Group

While SAMs have been proposed for uses in diverse applications [15, 202, 203], few methods of generating stable molecular-scale patterns have been demonstrated [119]. Recent studies have shown evidence of directed assembly and patterning of binary mixtures of adsorbed alkanethiols, either by partial thermal desorption or by selective electrochemical desorption with subsequent deposition of a new adsorbate [48, 193, 204]. Here we demonstrate phase separation driven by intermolecular interactions buried within the film, showing that it is possible to induce phase separation of SAM components by methods that do not change the general reactivity of the molecular film.
surface. This strategy provides additional tools for the design of nanostructured monolayer assemblies. Our objective is to control and to manipulate the molecular-scale structures of SAMs en route to the design of new and functional devices.

Scanning tunneling microscopy measurements of the phase separation of a SAM formed from a binary mixture of adsorbates, \( n \)-decanethiolate (C10) and an amide-containing alkanethiol of similar length, namely 3-mercapto-\( N \)-nonylpropionamide (1ATC9), a molecule with an amide group, a thiol, and a \( n \)-nonyl C9 overlayer) are reported here (Figure 3.1). While mixtures of \( n \)-alkanethiols of similar length (i.e., \( n \)-decanethiol and \( n \)-dodecanethiol) show no phase separation, the introduction of a hydrogen-bonding functionality buried deep within the film induces the formation of single-component domains on the nanometer scale. Phase separation occurs at all relative compositions studied, and for these molecules maintains the same exposed terminal functionality across the entire film. In nonequimolar concentrations of adsorbates in the deposition solution, we observe that the component present in greater concentration will generally dominate the composition of the adsorbed monolayer, consistent with enthalpic contributions from both the solvent and intermolecular interactions of adsorbates. The STM provides valuable information about the spatial distribution of adsorbates on the nanometer scale.

Thus, the STM is the tool of choice to study the molecular-scale phase separation of this internally-functionalized, amide-containing alkanethiol 1ATC9 from an \( n \)-alkanethiol C10 on Au\{111\} under ambient conditions without post-assembly treatment. We hypothesize that intermolecular hydrogen bonding of the buried amide functionality (shown in Figure 3.1) is the primary driving force for the spontaneous formation of nanometer-scale, phase-separated domains upon coadsorption. The long-range structures of the films described here are most likely kinetically
Figure 3.1. Schematic of a phase-separated SAM composed of \( n \)-decanethiolate (C10) and 3-mercapto-\( N \)-nonylpropionamide (1ATC9). In this cartoon (of limited scale), there is no mixing of the components.
trapped rather than equilibrium structures (typical of SAMs in general), yet the observed short-range structure is due to thermodynamic interactions between species adsorbed on the surface. As in our previous work, the STM images are single snapshots of the overlayer structures [205]. The formation of phase-separated domains is indicative of adsorbate assemblies and conformations that are both energetically favorable and accessible at ambient temperature [205].

3.2 Experimental Procedures

Mixed monolayers were prepared by coadsorption from solutions of 1ATC9 and C10 in N2-sparged, absolute ethanol (Pharmco) onto flame-annealed, mica-supported gold substrates (deposition solutions were always 1 mM in total thiol). n-Decanethiol (C10) was used as received from Lancaster Synthesis (Windham, NH). 3-Mercapto-N-nonylpropionamide (1ATC9) was prepared from previously described methods [3]. Substrates were typically exposed to thiol solution for 40 h, after which they were rinsed with absolute ethanol and blown dry with N2. All STM experiments were performed under ambient conditions using a custom-built STM as described previously [126]. Images were recorded with a sample bias of +1.0 V, and tunneling currents of either 1.0 or 2.0 pA.

3.3 Results and Discussion

Well ordered, phase-separated domains of both the 1ATC9 and C10 species on the gold terraces were resolved on the molecular scale (Figure 3.2). The two adsorbates are similar in length, with 1ATC9 being only three carbon atoms longer, containing one additional methylene and an amide group. The 1ATC9 molecules correspond to the topographically higher (displayed as brighter) regions in the images, confirmed by studies in which the relative concentrations of the components were varied. The rows of protrusions within some of the 1ATC9 regions are characteristic of how the STM images molecules at specific types of structural domain boundaries
Figure 3.2. Scanning tunneling microscope image of a phase-separated SAM formed from an equimolar solution of C10 and 1ÅTC9. The white arrow points to a single-molecule-wide row of 1ÅTC9, consistent with their aligning to maximize intermolecular hydrogen bonding interactions. A monatomic step edge separates the two terraces in the lower right hand corner of the image. Tunneling conditions: $V_{\text{sample}} = +1 \text{ V}$; $I_{\text{tunnel}} = 1 \text{ pA}$; 220 Å × 220 Å.
Figure 3.3. (A) Scanning tunneling microscope image of a phase-separated SAM formed from an equimolar solution of C10 and 1ATC9. (B) Scanning tunneling microscope image, a central inset of (A) (dashed square). Tunneling conditions: $V_{\text{sample}} = +1 \text{ V}$, $I_{\text{tunnel}} = 1 \text{ pA}$; (A) 2000 Å × 2000 Å; (B) 1000 Å × 1000 Å.
(as commonly observed for \(n\)-alkanethiolate monolayers, shown in Chapter 2) [116]. The measured STM topographic height difference between the molecules is \(~1.9\) Å (about half of the physical height difference), consistent with our understanding of the convolution of physical and electronic properties of these molecular films when imaged by STM [89]. In Figure 3.2 a monatomic gold step runs through the lower right-hand corner, creating what might otherwise appear to be two separate domains of differing adsorbates; the Au substrate steps may be seen more clearly in an image of larger area, Figure 3.3 Substrate vacancy islands in the gold (typically seen in STM images of SAMs prepared at room temperature [116]) are similarly visible. Substrate vacancies can be distinguished from the adsorbate domains as they tend to be roughly circular in shape and of a characteristic depth, that of one Au atom).

Phase separation of these molecules is also found in SAMs for which the deposition solutions are not equimolar in the two adsorbates. Figure 3.4 is an STM image of a monolayer formed by exposing a gold substrate to an adsorbate solution composed of a 1:3 mole ratio of \(1\text{ATC9}\) and \(\text{C10}\) (1 mM in total thiol). The \(1\text{ATC9}\) adsorbates are visible on the surface, but are present in significantly lower concentration (as compared to the corresponding deposition solution). In both this figure and images for even lower \(1\text{ATC9}\) concentrations, the \(1\text{ATC9}\) molecules bind to the surface at the edge of these vacancies and at grain boundaries in the \(\text{C10}\) matrix. The most likely reason for such directed nucleation of the \(1\text{ATC9}\) molecules in the SAM is that it would be energetically unfavorable for the polar amide moiety to be buried within the crystalline matrix of the apolar \(\text{C10}\) molecules; therefore, adsorption may occur at sites of minimal van der Waals contact from the surrounding molecules, and also at sites where there may be additional contact with the weakly hydrogen bonding ethanol solvent (\textit{vide infra}). Flipping of molecules between adjacent domains observed for alkanethiolate monolayers and flow of substrate steps through these
films can also result in isolating included molecules such as the amides at domain boundaries of the alkanethiolate matrix [89,115]. In the upper left-hand corner of Figure 3.4, 1ATC9 molecules are adsorbed at a Au vacancy island (the protruding molecular features are the 1ATC9, examples are indicated by arrows). Two additional 1ATC9 islands can be seen within the image located around surface defects (also indicated by arrows). In monolayers formed from an adsorbate solution of a 1:3 mole ratio of C10 and 1ATC9 (Figure 3.5), the relative surface coverages also do not reflect the solution ratio.

The observed phase segregation in the SAM is presumably the result of enthalpic contributions, as entropy favors mixing of the constituents within the monolayer. Hydrogen bonding driving the spontaneous phase separation is consistent with observed spectroscopic evidence of hydrogen bonding in undiluted monolayers of 1ATC9 [4] and the expectation that hydrogen bonding in the SAM will be enhanced by the apolar C10 diluent [206]. The enthalpic stabilization due to hydrogen bonding and van der Waals interactions can be approximated from the heats of sublimation of homologous compounds. The van der Waals interaction energy of a methylene group with its neighbors within a SAM is derived from the heat of sublimation (\(\Delta H_{\text{sub}}\)) of \(n\)-alkanes versus chain length (taken from the NIST Webbook database [207]). Plotting \(\Delta H_{\text{sub}}\) as a function of \(n\)-alkane chain length yields a slope whose value is the van der Waals interaction energy per methylene unit (Figure 3.6). An estimate for the stabilization due to individual van der Waals interactions of the methylene matrix is 8.3 kJ/mol per methylene. While these values are referenced to the gas phase, they do provide a reasonable estimate for the relative energetic values of this system. The interaction energies of the –CONH– group in a series of \(N\)-methylamides of the formula \(C_nH_{2n+1}CONHCH_3\) \((n = 9, 11, 13, 15)\) were reported in Reference [208] to be \(\sim 33.5\) kJ/mol.
Figure 3.4. Scanning tunneling microscope image of a SAM formed from a 1:3 mole ratio 1ATC9:C10. The arrows point to areas of 1ATC9 adsorption in the C10 matrix. Tunneling conditions: $V_{\text{sample}} = +1 \text{ V}$, $I_{\text{tunnel}} = 2 \text{ pA}$; 580 Å × 580 Å.
Figure 3.5. Scanning tunneling microscope image of a SAM formed from a 1:3 mole ratio C10:1ATC9. The arrows point to areas of C10 adsorption in the 1ATC9 matrix. Tunneling conditions: $V_{\text{sample}} = +1$ V, $I_{\text{tunnel}} = 1$ pA; 515 Å × 475 Å.
Figure 3.6. Plot of the heat of sublimation versus carbon chain length for a homologous series of \( n \)-alkanes. The slope of the line is the van der Waals interaction energy per methylene group, \( \sim 8.3 \text{ kJ/mol} \). An onset of even–odd chain length dependence emerges in the longer chains, \( n \geq 13 \). Data were extracted from Reference [207].
The enhanced stabilization of the 1ATC9 phase is approximately \([(8.3 \text{ kJ/mol methylene}) + (33.5 \text{ kJ/mol amide H-bond})]\), or 41.8 kJ/mol greater than the interactions between the non-hydrogen bonding constituents of the film. By way of comparison, the total enthalpic contribution of the 10 methylene groups in C10 is \(~83 \text{ kJ/mol adsorbate}\) versus our estimate of \(~125 \text{ kJ/mol}\) for 1ATC9. Such differing energetics most likely drive the composition of the final SAM to be different than that of the deposition solution. We expect that the ordered 1ATC9 domains are more stable than the C10 domains from previous evidence of closely packed films [3,4,62]. Also, we have not yet observed intercomponent diffusion on the limited time scales of our measurements.

Substrate–adsorbate exchange or mobility may be highly limited in the 1ATC9 due to the steric limitations imposed by the domain having to move in a concerted manner (the hydrogen bonding and the van der Waals interactions being greater than the barrier to diffusion).

As shown in Figures 3.4 and 3.5, if the relative concentrations of adsorbates in the deposition solution are reversed, the relative surface coverages do not reflect the concentration differences. The 1ATC9 molecules are significantly underrepresented in the monolayer when present in low mole fraction, \(\chi\), in the deposition solutions \((\chi \leq 0.25)\), and they are overrepresented when on the surface in greater mole fraction relative than the C10 adsorbates. However, the domains of the C10 molecules within the 1ATC9 matrix are larger and irregularly shaped (Figure 3.5 arrow) as compared to the 1ATC9 domains within the C10 matrix (Figure 3.4 arrows). Although in the gas phase the molecules’ affinities for the surface \([\Delta H_{ads}(1ATC9) \text{ and } \Delta H_{ads}(C10)]\) are roughly equal, the enthalpy of solvation of 1ATC9 in ethanol is greater than that for C10, effecting a more energetically favorable surface adsorption for C10 than for 1ATC9. However, once on the surface, the 1ATC9–1ATC9 intermolecular interactions predominate. As in our earlier work, we
infer from the minimized interface length between the different surface components that the cross-
interactions between the C10 molecules and the 1ATC9 molecules are lower than the attraction
between like molecules of either type [205].

Still, the kinetics of monolayer assembly are certainly a factor in determining the final surface
composition, especially with regard to adsorbate solubility in the deposition solvent. At low relative
concentrations of 1ATC9, the solvation energy of 1ATC9 molecules in ethanol may be greater
than that required to adsorb to the surface within an apolar matrix. As the 1ATC9 is well solvated
by the ethanol, C10 may adsorb at higher concentrations and/or at a faster rate; the small amount
of 1ATC9 adsorption that may occur is located at naturally occurring defects within the SAM,
where solvent molecules may still be present, or is later isolated there via film motion. At higher
relative concentrations of 1ATC9, solvent may partially disrupt the nascent monolayer or interfere
with hydrogen bonding between adjacent 1ATC9 molecules, allowing an increased opportunity for
C10 molecules to chemisorb to the surface.

3.4 Conclusions and Future Prospects

These results show great promise for controlling the patterning and structure of thin films
by using buried functionalities of adsorbates. Self-assembled monolayer formation is a complex
interplay between kinetics and thermodynamics; the observation of short-range phase separation
is evidence that enthalpic interactions are also important in determining film structure. However,
we do not know how close these structures are to thermodynamic equilibrium. Further experi-
ments studying the monolayer structures formed as a function of systematically varying adsorption
solvents and deposition times will provide us with a greater understanding of the complicated
processes of SAM formation. Elucidating the mechanisms that govern phase separation and the in-
termolecular interactions of adsorbates may ultimately lead to the creation of nanoscale structures
using knowledge gained from the results of these experiments. Additionally, manipulation of the mechanisms of SAM formation as a result of intermolecular interactions may be useful to create patterns within these thin films.
Chapter 4

Positive Placement of n-Alkanethiolates and 1ATC9:
Exploring Alternative Lithographies

4.1 Introduction: Patterning SAMs Using Soft Lithography

In 1993, Whitesides and coworkers introduced the field of ‘soft lithography’ [209]. Since that time, there have been numerous studies demonstrating this family of techniques and its versatility in constructing architectures at the nanometer to micrometer scales [210–213]. Soft lithography refers to the use of soft materials such as flexible, elastomeric polymers as the primary means of transferring and fabricating features into and onto substrates without the assistance of energetic beams (i.e., photons, ions, electrons). The chemical systems generated by soft lithography are not damaged by the tools used to create them, and thus can be integrated easily into systems where tools such as energetic beams would be too destructive. In particular, these methods have found considerable usage in patterning SAMs; initially, such SAM patterning served as a means to an end, in which the patterned SAMs served as sacrificial resists to pattern the substrates underneath them. There is a vast body of literature available that describes in detail the various soft lithography techniques, namely microcontact printing (μCP), micromolding in capillaries, solvent-assisted micromolding, replica molding, and microtransfer molding (see Reference [210] for a thorough review on each of these topics and the variety of materials, surfaces, and chemical systems that can be employed).

While commonly used to create patterned SAMs, the soft lithography process and in particular μCP, is not straightforward. In the work described in this chapter, simple model systems were
studied in order to understand how common processes in SAM formation such as diffusion and exchange come to play in μCP. The STM is an excellent tool to analyze these fundamental processes of μCP, providing valuable information at the nanometer scale. For example, how ordered are the molecules that have been printed? How do particular adsorbates diffuse during the printing process? What truly occurs in the ‘backfilling’ process? How susceptible are these films to exchange, and thus, how homogeneous are these printed regions? Is it possible to observe and to measure the boundaries between printed and backfilled regions on the nanometer scale? The phase behavior of 1ATC9, as described in Chapter 3, was integrated into the μCP experiments to attempt to improve the quality of the printed structures. An introduction to μCP is presented in this chapter; the results of STM and LFM studies of both n–alkanethiolate SAMs and 1ATC9-containing SAMs patterned using μCP are presented and discussed.

4.1.1 Microcontact Printing

Microcontact printing (μCP) as a method to pattern SAMs has grown in popularity due to the ease of fabricating the printing tools, the relatively high spatial resolution of features produced (linewidths of <100 nm [212]), and large printing capacity (up to tens of cm² of sub-micron-sized features can be printed in parallel). Microcontact printing is a technique that creates bicomponent SAMs arranged in simple spatial patterns for the purpose of organized attachment of molecules, colloids, or cells, or to use such printed SAMs as sacrificial layers for complex fabrication of nanoscale materials, to name merely a few applications. Microcontact printing uses the concept of positive placement to transfer adsorbates to a surface. The patterning of SAMs by μCP works by first creating a flexible, polymeric stamp with patterned reliefs (typically fashioned from polydimethylsiloxane, PDMS) followed by applying a solution of molecules (‘ink,’ typically n–alkanethiols) directly to the stamp. Once the stamp has been inked and dried, the stamp is then briefly pressed against a
gold substrate (or any other substrate whose surface chemistry is compatible with the ink used) via mechanical contact (‘stamping’), and the alkanethiolate molecules transfer from the polymer to the substrate beneath, where they self-assemble into patterns pre-determined by the relief patterns of the stamp (Figure 4.1) [210]. Bi-component SAMs are then formed by backfilling the non-patterned areas with a different adsorbate. The μCP technique is attractive because it is inherently rapid and can be performed in parallel, for many features can be printed simultaneously with one stamp application. In addition, it is generally cost-effective and can be applied to many substrates and desired patterns. However, the resolution of the resulting patterns is limited by the material and dimensions of the elastomeric stamp. Furthermore, the reproducibility of the process is dependent on the stamp’s resistance to degradation, the replication accuracy of the contact pressure that is applied to the substrate, and registration with other surface features and the surface itself. Typical features that have been constructed are on the order of hundreds of nanometers to micrometers, although structures with dimensions as low as 30–50 nm have been reported [214].

4.1.2 Elastomer Stamp Fabrication

The first step in μCP and other soft lithography techniques is the fabrication of the elastomeric stamp or mold. Generally, the elastomer is cast onto a silicon master that has been patterned and etched by electron beam lithography to contain the desired relief structure on its surface (first structure in Figure 4.1), followed by a surface functionalization procedure to prevent the PDMS from directly bonding to the Si master when the polymer is poured atop it [211]. The surface of the wafer can be coated with photoresist, wax, metals, Si3N4, or even a perfluorinated silane monolayer formed at the wafer’s surface. Additionally, pre-fabricated, commercially available structures such as transmission electron microscopy grids or diffraction gratings can be used
Figure 4.1. Scheme of the $\mu$CP process. The relief patterns of the silicon master are transferred as negatives to the PDMS stamp; the dimensions of post width ‘$l$’, post separation ‘$d$’, and post height ‘$h$’ are critical for proper transfer of molecules and pattern fidelity across multiple transfers. Elements are not drawn to scale.
as masters. The elastomer is cast onto the master, and then thermally cured and peeled off; this master can be reused many times in further replications.

It is important to stress that although soft lithography techniques capitalize upon low cost and simplicity, the most common practice to construct the master from which the stamps are formed remains traditional energetic beam lithography techniques, which are typically expensive and time-consuming. Whitesides and coworkers have improved upon this by developing alternative methods to create masters that do not rely on such these lithographic techniques; rather, the basic ideas used in soft lithography are implemented in order to produce the masters themselves [215]. For example, masters have been produced by $\mu$CP of a $n$–hexadecanethiol SAM onto silver substrates. In this case, the printed SAM is used as an etch resist and the surrounding Ag can be selectively etched away, creating a silver substrate with relief features etched into it. This pattern can then be used to cast additional PDMS stamps for microcontact printing [215]. While these examples are encouraging steps toward the replacement of lithographic techniques for the production of master structures, the resolution of the features generated using non-lithographically patterned masks is greatly compromised and is typically not less than one $\mu$m.

The elastomer that is used in these techniques is most commonly PDMS, although other polymeric materials such as phenolformaldehyde polymer (Novolac resin), polyurethanes, and polyimides have also been used. PDMS is chosen as it is a chemically inert material that can be reused many times. The material cures under moderate conditions (65 °C for 12–24 h or 100 °C for 1 h) and is easily removed from surfaces, making it amenable to patterning complex structures on delicate or nonplanar surfaces [210]. As illustrated in Figure 4.1, the dimensions of $d$, $h$, and $l$ are of critical importance, for it has been shown that the ratios of these dimensions must be optimized to afford the most reproducible pattern transfer [216]. The resolution, reproducibility and stability
of features produced using soft lithography are often dictated by the properties of the elastomeric stamp or mold. Therefore, it is crucial that the material properties of the elastomer are appropriate for the desired structure. Challenges associated with using an elastomer such as PDMS include capillary forces that cause the pattern to spread after conformal contact, gravitational or adhesion forces that can cause unintentional contact between the stamp and the substrate, and features either buckling upon contact with the surface, sticking together, or being drawn together through capillary action when inked with solvent (Figure 4.2).

To this end, the conformal and adhesion properties of elastomeric materials have been extensively investigated [217]. It is important to note that increasing stiffness of the elastomeric material produces patterns that are more stable and reproducible; however, stiffer materials decrease the conformability of the stamp or mold, thereby reducing the contact between the stamp and the substrate and causing defects in the pattern. In addition, stiffer materials limit the versatility of the patterning technique since these cannot be used with non-planar substrates. Therefore, an acceptable balance must be achieved between the conformability and stiffness of the material in order to produce stable patterns.

Similarly, one must consider the fidelity of pattern transfer. Even though a stamp may be laid across a substrate to transfer the pattern, the stamp may not lie across the surface in the same way at all points. Figure 4.3 shows that when a stamp with a particular relief pattern is laid across a surface, here a glass microscope slide in order to image the features with optical microscopy, the features on the stamp do not make conformal contact uniformly to the substrate. Factors such as the size and thickness (and thus flexibility) of the stamp, as well as the relative size of the substrate to the stamp can make a significant difference in the degree of pattern transfer.
Figure 4.2. (A) Optical micrograph of a PDMS stamp made from a master whose pattern is square posts of 500 nm in size and with a pitch of 1 µm (Ref. [1]). (B) Optical micrograph of the same stamp, where several regions of the posts have buckled together.
Irreproducible pattern transfer may make it increasingly difficult to find a boundary between two molecular domains of a particular pattern, should the pattern not transfer faithfully at all points.

Schmid and Michel have manipulated the chemical composition of the PDMS elastomer to increase its stiffness somewhat, resulting in sharper feature edges with less of the adverse spreading that occurs as a result of mechanical contact transfer. They have worked toward creating polymers of increasing stiffness by starting with PDMS precursors and adding more crosslinking functional groups; a slightly stiffer polymer improves upon pattern transfer, yet still maintains the physical properties of PDMS (i.e., flexibility, low surface free energy) that make it such a desirable material for a reusable stamp, Figure 4.4 [2]. In most cases, the size of the desired feature can help determine the proper hardness of the material, i.e., the smaller the pattern, the more rigid the elastomer [217]. Whitesides and coworkers improved upon the design of this new ‘hard’ PDMS (h–PDMS) by creating a composite (bilayer) stamp that had a very thin layer of the stiffer PDMS directly bonded to a thicker layer of the softer, typical formulation of ‘soft’ PDMS (s–PDMS) [214]. The bilayer stamp has both the properties of a lower compressibility when stamping, as well as the mechanical flexibility afforded by the s–PDMS formulation. These factors all contribute to the final resolution and precision of the pattern and must be considered when using elastomeric stamps or molds.

4.1.3 The Quality of SAMs Printed by μCP

There have been several studies comparing the quality of a SAM formed by soft lithography techniques with traditional solution- or vapor-deposited SAMs [218–224]. The majority of these studies involve SAMs produced using μCP compared to solution-deposited films studied by a variety of techniques, including scanning probe microscopy [218, 220, 221, 224], FT–IR [218, 221], near edge X–ray absorption fine structure spectroscopy [219], CAG [220], scanning electron microscopy (SEM) [222, 223], and X–ray diffraction methods [224]. In general, it was shown that the quality
Figure 4.3. Optical micrographs of different areas of the same PDMS stamp prepared from a 600 grooves/mm diffraction grating master laid against a glass surface akin to the stamping process (areas ∼mm apart); features are spaced ∼1.67 µm apart. Micrographs (A) through (D) show a significant distribution of pattern transfer to the substrate, from complete transfer (A) to hardly any at all (D).
Figure 4.4. Scanning electron microscope images show that the sharpness of features produced by µCP can be increased by changing the stiffness (composition) of the elastomeric stamp, adapted from Ref. [2]. (A) Features replicated using a PDMS stamp made from the typical formulation of Sylgard 184. (B) Features replicated using the h-PDMS formulation, where the density of the crosslinking functional groups has been increased. Scale bar = 1 µm for both (A) and (B).
of the \( \mu \)CP SAM is similar to (or better than) that of a solution- or vapor-deposited SAM [221]; however, there are minor disparities between these studies that suggest the order of the system is somewhat dependent on the formation process. Possible dissimilarities between SAMs made with the two processes include differences in packing density [218], tilt angle of the alkyl chains [219], and domain size [224]. Figure 4.5 shows that both types of SAMs, those formed from the solution phase and those formed by \( \mu \)CP, are similarly well-ordered at the nanometer scale when imaged with the STM. The concentration of the inking solution was found to be critical in the resulting order of monolayers formed by \( \mu \)CP. For \( \mu \)CP alkanethiol SAMs from solutions with concentrations less than 10 mM, it was shown that the printed SAM was relatively disordered, even though the solution-deposited SAMs remained well-ordered [220]. STM images of microcontact-printed \( n \)-dodecanethiolate SAMs revealed the familiar \((\sqrt{3} \times \sqrt{3})R30^\circ\) packing structure and showed that the domain size increased with increasing concentration [220]. In the case of organosilane monolayers, printed SAMs of octadecyltrichlorosilane on SiO\(_2\) were shown to be more complete at an inking solution concentration of 10 mM, even though monolayers formed from solution were disordered at this concentration [221].

Diffusion processes that occur during and after the printing process can also compromise the order observed in \( \mu \)CP SAMs [222, 223]. Biebuyck and coworkers have described several different diffusion pathways for the molecules in a \( \mu \)CP SAM [222]. For instance, the inking solution can spread from the surface of the stamp to areas of the substrate not intended for patterning. This process can be circumvented by using a dry stamp to allow printing of the vapor-phase molecules trapped in the stamp. There is also the possibility of ink transfer from the stamp to the substrate in non-contacting areas by the vapor phase, which is directly related to the vapor pressure of the inking molecule (i.e., molecules having a high vapor pressure such as \( n \)-alkanethiols will have a
Figure 4.5. Scanning tunneling microscope images comparing the quality of \( n \)-alkanethiol SAMs prepared from solution-phase deposition and from \( \mu \)CP. Both types of SAMs are well-ordered on the nanometer scale, and typical SAM features such as domain boundaries and substrate vacancy islands are seen faithfully across both types of SAMs (arrowheads). Images A, B, and C are from solution-phase grown SAMs, and images D, E, and F are from SAMs created by \( \mu \)CP. Adapted from Reference [220].
higher chance of this type of diffusion). In addition, the molecules can diffuse along the substrate after the stamping procedure, forming areas of moderately ordered monolayers. These effects can be reduced by using a lower concentration inking solution, thereby reducing the number of molecules available for diffusion. In order to form a complete monolayer, it is then necessary to increase the printing time (>1 second). Delamarche et al. found that the optimal printing process involves a 0.2 mM solution of eicosanethiol (CH$_3$(CH$_2$)$_{19}$SH) printed for 3 seconds [222]. These conditions are not always possible given the desired experiment; however, this study served to demonstrate that it is necessary to find the proper balance between alkanethiol length, solution concentration, and printing time.

The aforementioned studies show that the quality of the SAM after soft lithography patterning depends on a number of factors, including chemical and physical properties of the inking molecule, concentration of the inking solution, duration of contact, and printing method. In order to produce high-quality SAMs using soft lithography, it is necessary to attain a balance between these factors. Often, this can only be achieved empirically, which can make optimizing the patterning method a laborious and time-consuming process. Ratner and coworkers have analyzed the degree of contamination in the printing process using electron spectroscopy for chemical analysis; they showed that uncured, low molecular weight PDMS was being transferred to the substrate during the stamping process along with the thiol of interest. The presence of these small, protopolymeric molecules could certainly disrupt the local order of μCP films [225]. To eliminate the problems of contamination, they recommended several cycles of extraction, rinsing, and sonication in order to remove all small fragments of the stamp. The purity of the monolayers was found to increase if an inking solution of sufficiently high concentration was used (10–50 mM).
4.2 Scanning Tunneling Microscopy Studies of $n$–Alkanethiolates Patterned by $\mu$CP

To probe several of the fundamental processes of $\mu$CP described at the beginning of this section, STM was used to examine the structure and quality of $\mu$CP SAMs. The success of this type of experiment hinges on several conditions. First, to measure the structures and properties of $\mu$CP SAMs using the STM, a system of molecules must be chosen such that they both print well and are short enough in length to image with STM. Second, these molecules should preferably be –CH$_3$-terminated, so as to minimize adverse tip–sample reactions (the STM does not resolve individual molecules with polar terminal groups, as they have a tightly bound shell of H$_2$O that interacts with the probe tip). However, if a pattern or molecular boundary of a pattern cannot be found using the STM alone, a system of molecules whose contrast can be determined by LFM should be employed. Third, the printing must be done on a substrate of very low surface roughness such that is amenable to imaging with STM; in particular, Au thermally evaporated onto freshly cleaved mica sheets has been used in these studies. These substrates have a large number of \{111\} and thus atomically flat terraces.

The phase separation found for 1ATC9 with $n$–alkanethiol SAMs as discussed in Chapter 3 specifically their ability to form single-molecule-wide rows, potentially makes them of great use in $\mu$CP. The directionality of the adsorbates as a result of their intermolecular hydrogen bonding may assist in the annealing and straightening of edges printed by $\mu$CP, with dispersive edges resulting from both local diffusion of the printed adsorbate as well as from the inherent compressibility of the PDMS stamp. These molecules could also serve as barriers to adsorbate diffusion; the 1ATC9 molecules would have to move in concert either to diffuse across the surface or to allow another adsorbate to move past it. In the remainder of this chapter, several experiments describe the fundamental processes of $\mu$CP using both amide-containing adsorbates as well as $n$–alkanethiols.
The strategic goal of these experiments is to create a simple pattern of \(n\)-alkanethiolate adsorbates on a Au surface using \(\mu\)CP, and to analyze the edge resolution of the printed features using STM, integrating the 1ATC9 as necessary to align and to heal the edges of printed features. Systems of molecules were investigated with both LFM as well as STM.

4.2.1 Experimental Procedures

For the experiments described in this thesis, PDMS stamps were prepared either with no relief pattern, or were fabricated from diffraction grating masters, resulting in an array of lines. PDMS replicas without relief patterns (‘flat stamps’) were prepared by combining a 1:10 mixture of curing agent to the prepolymer ‘base’ as per the manufacturer’s recommendation (Sylgard 184, Dow Corning). After vigorously stirring to mix the two, the polymer was poured into a flat polystyrene Petri dish (VWR) and placed into a vacuum dessicator. The dessicator was evacuated to de-aerate the polymer and eliminate any air bubbles that may be trapped in the PDMS and more importantly, any air bubbles that may trapped at the interface of the polymer and the Petri dish. After evacuation for 20–30 min, the PDMS was removed from the dessicator and placed in a 55 \(^\circ\)C oven to cure for 24 h. The PDMS was then peeled away from the Petri dish and a stamp of arbitrary size was excised using a razor blade.

The PDMS stamps with lines as features were fabricated using a diffraction grating as the master. Diffraction gratings (replicated ruled gratings with Al coatings over an epoxy resin) were purchased from Optometrics LLC (Ayers, MA) with a variety of grating constants: 600, 830, 1200, and 1800 grooves/mm, each grating with features spaced every 1.7, 1.2, 0.8, and 0.6 \(\mu\)m, respectively. The diffraction grating was placed feature-side-up in the Petri dish; freshly mixed PDMS prepolymer was poured directly over the grating, the dish was transferred to the vacuum dessicator and de-aerated, and the assembly was cured in the oven. The PDMS and grating were
removed from the Petri dish, and the stamp was excised from around the grating with a razor blade. Although the PDMS peels away nearly effortlessly from the diffraction grating, the gratings could be removed of PDMS residue by cleaning in a dilute solution of soap and water or rinsed with most solvents and gently scrubbing until clean.

Bilayer stamps of s–PDMS with a thin layer of h–PDMS at the transfer interface were prepared using the formulation described by Schmid and Michel, and Whitesides and coworkers [2,226]. The HMS–301 (25–30% methylhydrosiloxane–dimethylsiloxane copolymers), VDT–731 (7–8% vinylmethysiloxane–dimethylsiloxane copolymer, trimethylsiloxy-terminated), and SIP6831.1 (platinum–divinyltetramethylsiloxane complex in xylene, 2.1–2.4% Pt) were purchased from Gelest, Inc. (Morrisville, PA) and used as received. 2,4,6,8–tetramethyl–2,4,6,8–tetravinylcycloctetrasiloxane (TMTVCTS) was purchased from Sigma–Aldrich and used as received. Briefly, 3.4 g of VDT–731 was stirred with 0.1% w/w of TMTVCTS (∼4.4 µL) and 10 ppm w/w of the Pt catalyst (∼10–20 µL). 1.0 g of the HMS–301 was directly pipetted into the mixture, and stirred briefly but thoroughly as it began to cure instantly and became sticky. Once the polymer components were stirred together, the h–PDMS was poured atop the diffraction grating immediately and gently distributed before polymer solidification. Alternately, the h–PDMS could be spincoated onto the diffraction grating; typical parameters were a 5 s spin at 500 rpm, followed by 30 s at 1000 rpm (Model KW–4, SPI Supplies, West Chester, PA), although it was difficult to get reproducible thicknesses as a result of the immediate curing of the polymer. Spinning too quickly, for instance, resulted in no h–PDMS at the center of the grating; not spinning quickly enough resulted in an uneven distribution of the polymer. After a brief cure (10–15 min) of the h–PDMS, s–PDMS was poured atop the coated grating and then fully cured. In the course of the experiments presented here, there was little to no improvement with the bilayer of PDMS.
To remove any uncured or low molecular weight PDMS, once excised, the stamps were cleaned using a procedure adapted from Reference [225]. The stamps were sonicated in \( n \)-hexane for 30 min, dried with inert gas, heated at 90 °C until the stamp returned to its original size, and sonicated for 5 min in 2:1 EtOH:H\(_2\)O and dried with inert gas (3×). The entire procedure was cycled three times, and the stamps were dried again for 15 min.

In order to improve the reproducibility of the stamping process, particularly with regards to applied pressure to the stamp as well as the ability to controllably remove the stamp from the sample without compromising the pattern, various ‘backplanes’ were investigated [212]. The backplanes were either glass coverslips, glass microscope slides, or pieces of Invar (0.005" thickness, Eagle Alloys, Inc.), all of which could be directly bonded to the PDMS. An effort to make the stamps all the same size and thickness was made in order to control the applied pressure. Generally, there was little to no improvement with the presence of the backplane.

For all STM experiments, the Au substrates used were thermally evaporated Au onto freshly cleaved mica sheets (Molecular Imaging, Tempe, AZ). The Au\{111\}/mica substrates used were cut into quarters after receipt, using sharp scissors. The cutting may not appear to cause delamination of the Au from the mica substrate, but it was especially easy to strip away the entire thin film of Au (1500 Å) when removing the PDMS stamp after the stamping process. Particular care was taken when removing the PDMS stamp off of the quartered Au, starting the removal process from the native boundary of Au and mica from the initial evaporation process, rather than one of the freshly cut edges.

All solutions of thiol were prepared from 200 proof EtOH (Pharmco). A few drops of the solution (typically 1–10 mM, depending on the particular experiment) were pipetted directly onto the PDMS stamp, and then the stamp was blown dry with either ultra-high purity N\(_2\) or Ar. The
dried stamp was gently laid across the substrate and held with a gentle hand pressure for a small amount of time (s–min), and then was gently peeled away. As the Au{111}/mica substrates were so small (0.5 cm × 0.5 cm, and smaller than the size of the stamp), the substrates were affixed to the flat underside of a Petri dish with adhesive (3M Scotch double stick tape) to hold it steady. The tape was consistently smaller than the size of the substrate to avoid contamination of the PDMS stamp with adhesive. The substrates were peeled off the tape with clean tweezers, taking care to avoid delamination of the mica sheets.

Backfilling of either patterned or non-patterned samples was performed by immersing the substrate into a 2-mL V–vial (Wheaton Scientific) filled with an ethanolic solution of thiol (1 mM, unless otherwise stated). V–vials were cleaned using piranha solution (1:3 30% H₂O₂:H₂SO₄ — *highly oxidizing!* ) and rinsed with water (Water Pro Plus, LabConco, minimum resistivity of 18.2 MΩ·cm) followed by absolute EtOH. Samples were rinsed with EtOH, dried with ultra-high purity Ar or N₂, and imaged directly.

4.3 Results and Discussion

An effort was made to prepare well ordered SAMs of 1ATC9 by µCP. A 9.4 mM solution of 1ATC9 was prepared and applied to a flat PDMS stamp. After drying, the stamp was laid flat against a piece of Au{111}/mica with a gentle hand pressure for 30 s, and then carefully peeled away from the substrate. The attempts to form a well-ordered SAM of 1ATC9 by µCP were unsuccessful (Figure 4.6). The image of larger size, Figure 4.6A, somewhat resembles the 1ATC9 SAMs formed from the solution phase (although with many fewer substrate vacancies), but the higher resolution images (e.g. Figure 4.6B) failed to yield any kind of reproducible order.

As the printing of 1ATC9 was not a straightforward process, several control experiments were performed to elucidate further the mechanisms of the µCP process. It was proposed that the
Figure 4.6. (A) Scanning tunneling microscope image of a 1ATC9 SAM formed by μCP. (B) Higher resolution STM image of the same 1ATC9 SAM. While some molecules were resolved, there appeared to be no long- or short-range order. Tunneling conditions: $V_{\text{sample}} = -1\text{V}$, $I_{\text{tunnel}} = 4$ pA (A) and 5 pA (B); (A) 1540 Å $\times$ 1540 Å, (B) 190 Å $\times$ 190 Å.
**1ATC9** might be hydrogen bonding too well to itself in the solid phase (i.e., once the solution was dried on the stamp) in order to form a well ordered SAM upon transfer to the substrate. In order to obtain such a well ordered SAM, a step back was taken to understand how a short \( n \)-alkanethiol would print. Control experiments were performed using methods described by Michel and coworkers [220]; \textbf{C10} was chosen as a starting point (Figure 4.7). In these sets of experiments, a 25 mM inking solution of \textbf{C10} was prepared and applied to a stamp that had been subjected to three cleaning cycles; this was followed by stamping under an Ar environment.

Since a flat stamp was used, the \textbf{C10} was expected to diffuse uniformly across the substrate; the higher diffusion rate of \textbf{C10} relative to longer chain, \( \omega \)-functionalized \( n \)-alkanethiols would cause it to diffuse rapidly from a stamp with a pattern, a problematic scenario. As can be seen in Figure 4.7 when using a flat stamp, a well ordered SAM was formed on the Au substrate, although the film was not pristine on the molecular scale. Defects that are typically found in SAMs were present here, including domain boundaries and substrate vacancies, although the substrate vacancies did not seem as pronounced as compared to adsorption experiments, where solvent is present. It was found that the PDMS stamp needed to go through the cleaning process, as the SAMs formed from stamps that had not gone through the cleaning cycles were significantly disordered.

To examine the susceptibility of this \textbf{C10} SAM to exchange with a backfilling adsorbate, after its analysis with STM, the \( \mu \)CP SAM was then exposed to a 1 mM solution of \textbf{1ATC9} for 5 min, Figure 4.8A. Although in this instance there were no bare areas of Au for the \textbf{1ATC9} into which to backfill, it was possible to observe the extent of the \textbf{1ATC9} exchange and insertion into the natural defects in the \textbf{C10} monolayer, as well as how the presence of solvent may assist in the ordering of the printed SAM. Upon exposure of the \( \mu \)CP \textbf{C10} SAM to the backfilling solution of \textbf{1ATC9}, the quality of the SAM markedly improved. As can be seen in Figure 4.8A, there
Figure 4.7. (A) Scanning tunneling microscope image of a C10 SAM formed by μCP (flat stamp). (B) Higher resolution STM image of the same C10 SAM. The SAM is ordered, although some defects were present. Tunneling conditions: $V_{\text{sample}} = -1$ V, $I_{\text{tunnel}} = 5$ pA; (A) 1150 Å × 1150 Å; (B) (385 Å × 385 Å).
appeared to be very little insertion of the 1ATC9 into the C10 host matrix, consistent with the fact that it is energetically unfavorable to insert a polar functional group, here the amide, into an apolar matrix (as discussed in Chapter 3).

In Figure 4.8A, isolated 1ATC9 have inserted into the well ordered C10 matrix (arrow). The presence of the ethanol may assist in the reorganization of the C10 SAM by allowing for the removal of weakly bound molecules and for the general improvement of the SAM by permitting adsorbate exchange and exclusion of impurities from the μCP printing process. However, it is most likely that the order of the C10 SAM arises from the shortness of the chains allowing the SAM to organize into an array of minimal energy, even when printed in the absence of solvent; longer chains would be kinetically trapped, forming more domains of much smaller size (supported by STM measurements from SAMs deposited from the solution phase).

The delay for analysis proved to be important, as the fractional surface coverage of 1ATC9 increases upon backfilling immediately after μCP. Backfilling immediately after printing is common throughout most μCP experiments. As shown in Figure 4.8B, the sample showed a significant increase in the fractional surface coverage of 1ATC9 as well as a decrease in film order. The sample in Figure 4.8A was analyzed for ~3 days before proceeding to backfill with 1ATC9. Such delay allows for significant film reorganization before the introduction of a second adsorbate, affecting the amount of exchange and its kinetics.

To examine the stability of the μCP 1ATC9 SAMs to backfilling, a SAM of 1ATC9 was formed by μCP using a flat stamp. With the flat stamp leaving no bare areas of gold remaining, the SAM was exposed to a backfilling solution of n-octanethiol (C8). Figure 4.9 shows that almost the entire 1ATC9 film has lifted off the surface, and a C8 SAM was observed across the majority of the Au surface. The C8 has all but completely displaced the μCP 1ATC9 SAM, and what
Figure 4.8. (A) Scanning tunneling microscope image of a C10 SAM formed by µCP (flat stamp) that was exposed to a backfilling solution of 1 mM 1ATC9 for 5 min after 3 days; a small amount of the 1ATC9 molecules was inserted (arrow). Inset: Fourier transform of the STM image, showing the SAM’s hexagonal structure. (B) Scanning tunneling microscope image of a C10 SAM formed by µCP (flat stamp) that was exposed to a backfilling solution of 1 mM 1ATC9 for 5 min immediately after printing. Tunneling conditions: $V_{\text{sample}} = -1\text{V}$, $I_{\text{tunnel}} = 5\text{ pA}$; (A) 330 Å × 330 Å; (B) 330 Å × 330 Å.
1ATC9 remained was sparsely included in the C8 diluent. The 1ATC9 protruded from the C8 matrix with a measured apparent height of 0.96 ± 0.15 Å, consistent with previous data from a 1ATC9:C8 adsorbate system [195]. What was remarkable about the inclusion of the 1ATC9 in the C8 matrix was that there appeared to be a correlated distance and directionality between the 1ATC9 adsorbates. The reason for this correlation may lie in how the μCP 1ATC9 SAM nucleated and aligned across a particular distance when initially placed on the surface, or from a pre-association of the molecules in solution before adsorption, either with themselves or in combination with the weakly hydrogen bonding ethanol.

As the 1ATC9 molecules appeared to be hydrogen bonding too well to one another in the solid phase to form a well-ordered SAM when printed by μCP, experiments were done to assess the ability to disrupt in part the hydrogen bonding network of the 1ATC9 adsorbates. Figure 4.10 shows two different hydrogen bond competitors used, guanidinium hydrochloride (Gdn-HCl) and 1,1,3,3–tetramethylurea (TMU). STM experiments were performed on SAMs of 1ATC9 formed from the solution phase (i.e., not by μCP) with a particular mole fraction of hydrogen bonding competitor included in the deposition solution.

Figures 4.11A and 4.11B show SAMs of 1ATC9 formed from a deposition solution with differing mole fractions of Gdn-HCl, χ=0.2 (A) and χ=0.8 (B). There appeared to be minimal disruption to the 1ATC9 domains, although regions of disorder connecting the domains were more frequently observed here than in SAMs formed from solutions of pure 1ATC9. Even when χ_{Gdn-HCl}=0.8, the SAM showed many small yet well ordered domains of 1ATC9. STM measurements showed that 1ATC9 when deposited from the solution phase from a mixture of 1ATC9 and TMU did not yield an ordered film.
Figure 4.9. (A) Scanning tunneling microscope image of a SAM that was formed by μCP of 1ATC9 using a flat stamp followed by exposure to a backfilling solution of C8. (B) Higher resolution STM image of the same SAM. Here, the 1ATC9 lifted entirely off of the surface and was replaced by the C8. Tunneling conditions: $V_{\text{sample}} = -1\text{V}$, $I_{\text{tunnel}} = 5\text{ pA}$; (A) 770 Å × 770 Å; (B) 310 Å × 310 Å.
Figure 4.10. Molecules coadsorbed with 1ATC9 for the purpose of disrupting the hydrogen bonding network either on the surface or in solution prior to adsorption. (A) Gdn-HCl = guanidinium hydrochloride; (B) TMU = 1,1,3,3-tetramethylurea.

Although generally ordered SAMs of 1ATC9 could be formed with substantial $\chi_{Gdn\cdot HCl}$, this did not extend to form ordered SAMs of 1ATC9 when formed by $\mu$CP. No detectable improvement was observed when using ‘inking’ solutions of mixtures of 1ATC9 and Gdn-HCl.

4.3.1 Lateral Force Microscope Studies of $n$–Alkanethiolates Patterned by $\mu$CP

Lateral force microscopy was a very helpful tool to assess both the fidelity of the printing process as well as to give insight into the quality of the SAM formed by $\mu$CP and backfilling. The LFM was employed for the samples whose patterns were replicated from diffraction gratings, resulting in striped patterns of the printed and backfilled molecules. Lateral force microscopy detects a difference in the frictional forces at the termini of the adsorbates; thus, 11–mercaptoundecanoic acid (MUDA) was chosen as one adsorbate of the two-component system, as LFM contrast between it and its CH$_3$-terminated counterpart would be evident. Also, it was of the appropriate length to be imaged using the STM, although its polar terminus prevents resolution of the individual MUDA adsorbates.

An LFM image of a SAM formed by $\mu$CP of MUDA and backfilled with 1ATC9 is shown in Figure 4.12. There was a fairly weak contrast in between the two domains; here, the stripes that were higher friction (displayed as brighter) were the MUDA molecules transferred to the Au, and
Figure 4.11. (A) Scanning tunneling microscope image of a SAM from an adsorption solution of 4:1 1ATC9:Gdn-HCl. (B) Scanning tunneling microscope image of a SAM from an adsorption solution of 1:4 1ATC9:Gdn-HCl. Tunneling conditions: \( V_{\text{sample}} = -1 \text{V}, I_{\text{tunnel}} = 5 \text{ pA} \) (A) and 2 pA (B); (A) 310 Å \( \times \) 310 Å; (B) 310 Å \( \times \) 310 Å.
the lower friction stripes (displayed as darker) were the CH$_3$-terminated 1ATC9 backfilled in the bare areas from the solution phase. The contrast between the two domains decreased with repeated imaging.

If the LFM images show that the striped pattern of molecules transferred to the surface, it would be ideal to image the same sample using STM and to measure the sharpness of the boundaries in between the printed and backfilled features. Figures 4.13, 4.14, and 4.15 are STM images of the same sample that had been measured with the LFM in Figure 4.12. Unfortunately, no ‘striped’ patterns were found using the STM. However, it was possible to infer if the STM was imaging in a printed or a backfilled region. For example, it is most likely that the tip was in a printed region in Figure 4.14A, as there appeared to be an even distribution of the two adsorbates, organized into homogeneous domains (the MUDA imaged as the more protruding of the two molecules). In Figure 4.14B, the tip was most likely in a region of backfilled 1ATC9, as that component was present in extremely high fractional surface coverage. However, MUDA was sparsely included in this 1ATC9 matrix, which is to be expected from the backfilling process. Any MUDA in the solid phase that was transferred to the substrate without directly bonding, physisorbed to the top of the layer of MUDA already adsorbed to the Au substrate, had a likelihood of being removed by the solvent and readsorbing to the bare Au destined to be covered by the backfilling adsorbate. Figure 4.15 is a high resolution STM image of this region, showing the 1ATC9 array with a small fraction of MUDA inserted into the 1ATC9. These molecules were included into the matrix and did not necessarily reside at defect sites, similar to the included 1ATC9 in the C8 matrix and consistent with being pinned in place by backfilling adsorbates (i.e., Figure 4.9).
Figure 4.12. (A) Lateral force microscope image of a SAM formed by μCP of MUDA and backfilling with 1ATC9 (MUDA: brighter stripes, 1ATC9: darker stripes). The tip interacted with a surface contaminant that was removed upon repeated imaging. (B) Lateral force microscope image of the same SAM; the topography of the sample was also visible. Imaging conditions: scan rate: 3 Hz, setpoint: (A) 0.8 nN, (B) 0.9 nN.; (A) 5 µm × 5 µm; (B) 3 µm × 3 µm.
Figure 4.13. (A) and (B): Scanning tunneling microscope images of a SAM formed on Au\{111\}/mica from \( \mu \)CP of MUDA and backfilling with 1ATC9; no ‘stripes’ of molecules are visible. In (A), a small impurity is present on the surface. Tunneling conditions: \( V_{\text{sample}} = -1V \), \( I_{\text{tunnel}} = 5 \text{ pA} \); \( 1\mu m \times 1 \mu m \).
Figure 4.14. (A) Scanning tunneling microscope image of a SAM formed on Au\{111\}/mica by \(\mu\)CP of MUDA and backfilling with 1ATC9; here, there was mixing of domains of both adsorbates on the molecular scale (MUDA: brighter regions, 1ATC9: darker regions). (B) Scanning tunneling microscope image of the same SAM; here, it appears that the sample was mostly 1ATC9, with a small amount of MUDA located at the defect sites. Tunneling conditions: \(V_{\text{sample}} = -1V\), \(I_{\text{tunnel}} = 5\) pA; 1150 Å × 1150 Å.
Figure 4.15. Scanning tunneling microscope image of a SAM formed by $\mu$CP of MUDA and backfilling with 1ATC9. Here, individual molecules of 1ATC9 were resolved, with MUDA molecules interspersed in the 1ATC9 matrix. Tunneling conditions: $V_{\text{sample}} = -1\text{V}$, $I_{\text{tunnel}} = 5\text{ pA}$; $385\text{ Å} \times 385\text{ Å}$. 
4.4 Conclusions and Future Prospects

The first steps have been made in the patterning of SAMs by designing their structures through the known and well documented intermolecular interactions of their adsorbates. To date, most of the SAMs created by μCP have been formed from alkanethiol adsorbates with simple functional groups at the terminus (i.e., COOH- or NH$_3^+$-terminated) to be building blocks for future steps; the information that is presented here in the design and ‘healing’ of these SAMs will be of great utility to control the final self-assembled structures tightly. It is important to be able to tune and to understand the intermolecular interactions so as to place the 1ATC9 on the surface in a more controlled fashion than at present (i.e., ensuring proper adsorption of the 1ATC9 during the μCP stamping process). If it is the hydrogen bonding that is disrupting the ability of the 1ATC9 to order, a different series of molecules could be used in the hydrogen bond competition experiments; for example, an amine with a short n–alkyl chain might be useful for both disrupting the hydrogen bonding network as well as perturbing the aggregation of the alkyl tails of the 1ATC9. Understanding how to control the edge resolution of the molecular boundaries, as well as how to avoid or to control the amount of exchange and diffusion between the printed and backfilled regions will be of significant utility in the development of patterned self-assembled monolayers and structures.
Chapter 5

Measuring the Electronic Properties of Precise, Ligand-Stabilized Undecagold Clusters

The single electron transport (SET) properties of metal nanoparticles have led to great interest in their potential integration into nanoscale electronics. In this chapter, the electronic properties of isolated, solution-derived, and ligand-stabilized undecagold clusters (\(\text{Au}_{11}\)) and nanoparticles (\(\text{Au}_{101}\)) are presented and discussed. The electronic properties of clusters with two different ligand shells were measured, \(\text{Au}_{11}\) with a mixed triphenylphosphine (TPP) and chloride ligand shell (\(\text{Au}_{11}(\text{PPh}_3)_7\text{Cl}_3\), henceforth \(\text{Au}_{11}–\text{TPP}\)) and \(\text{Au}_{11}\) with a \(n\)-octanethiol ligand shell (\(\text{Au}_{11}(\text{S}(\text{CH}_2)_7\text{CH}_3)_{10}\), henceforth \(\text{Au}_{11}–\text{C8}\)). The electronic properties of TPP-stabilized nanoparticles, \(\text{Au}_{101}–\text{TPP}\), were measured for comparison to understand how the electronic spectra changed as a function of size. Data were acquired in both cryogenic (4 K, UHV) and ambient conditions using STM and STS. The clusters, with a core diameter of 8 Å, were immobilized on alkanethiolate SAMs with inserted \(\alpha,\omega\)–dithiolate molecules; the nanoparticles, with a core diameter of 1.5 ± 0.4 nm, were tethered similarly. At 4 K, spectral hopping and diffusion was observed throughout the conductance (\([d\text{I}/d\text{V}(\text{V})]\)) spectra for both cluster and nanoparticle species. The electronic spectra of these \(\text{Au}_{11}–\text{TPP}\) clusters were compared to their larger nanoparticle counterparts, \(\text{Au}_{101}–\text{TPP}\).

5.1 Introduction to Nanoparticles

Over the past decade, interest in nanoparticles has grown due to easily accessible synthetic routes, the variety of materials from which they can be prepared, and the increasingly improved
analytical tools available. Of interest to many scientific communities, their optical and electronic properties can be tailored as a result of the facile manipulation of the particles’ sizes and well-defined surface chemistries. In the mid-1800s, Faraday was studying both the chemistry and optical scattering properties of gold colloidal solutions [227]. With an electronic band structure that is neither that of a single atom nor with the continuous band structure of bulk material, nanoparticles are particularly subject to quantum confinement effects, leading to exploitable optoelectronic properties [228]. For example, the ability of metallic nanoparticles to suppress current flow at low bias voltages as well as accept single electrons at room temperature [229]) has led to their proposed use as single electron transistors [140, 169, 230]. Moreover, the tunable excitation and emission spectra of nanoparticles (especially those composed of semiconducting material or with insulating components) coupled with their photostability have led to considerable interest in their use in both near-field and infrared communications as well as for fluorophore replacements [228, 231–235]. Arrays of nanoparticles can be organized to order across long length scales, leading to their proposed use as artificial lattices and photonic materials [236–238].

By definition, nanoparticles are clusters of atoms whose sizes range from sub-nanometer to hundreds of nanometers in diameter. A key aspect of the application of nanoparticles as novel nanoelectronic materials is due to our ability to control and to tune their properties via synthesis and manipulation in the solution phase. The synthesis of nanoparticles has been studied and reviewed extensively [239–241], and they have been rigorously characterized with the assistance of techniques including electron microscopy [242], optical spectroscopy [243–246], electrochemistry [247–249], and scanning probes [139, 140, 169, 230]. They can be synthesized from a number of materials with characteristics of insulators (SiO₂), semiconductors (II–VI, III–V), or metals (including the noble transition metals and others such as Co, Ni, and Fe). They can be made to be either homogeneous
or heterogeneous in composition, with shell–core structures or with their cores as mixed alloys (i.e., Ag–Au) or oxides (i.e., Fe₂O₃); moreover, they can be synthesized in a variety of shapes (from spheres to cubes to anisotropic rods [250–254]) and sizes (from sub-nanometer to over 100 nm [255–259]). They can be fabricated onto substrates by lithography or electrodeposition, as opposed to via traditional wet chemistry methods [260–265]. Nanoparticles are often stabilized by passivating layers that prevent their aggregation and coalescence back to bulk material, either by repulsive electrostatic forces or by the presence of large bulky molecules presenting steric barriers that render the surfaces of the nanoparticles inaccessible. Such passivating molecules possess headgroups that will chemisorb to the nanoparticle surface, and are often similar to adsorbates found on two-dimensional monolayers, including \( n \)-alkanethiols and \( n \)-alkanoic acids (see Chapter 2). Through changing the chemical moieties of the ligand shell, it is possible to aggregate particles reversibly through noncovalent interactions [266, 267], as well as aggregate particles deliberately through bridging molecules such as \( \alpha,\omega \)-alkyl- or \( \alpha,\omega \)-aryldithiolates as well as \( \alpha,\omega \)-aryldiisonitriles [141, 237]; such changes in the density of nanoparticles bring about distinct changes in both optical and electronic properties [266–269].

5.1.1 Measuring the Charge Transport Properties of Nanoparticles with SPM

The two main scanning probes used to study nanoparticles adsorbed on surfaces are the STM and the AFM; nanoparticles have been studied both in groups and in isolation. The small sizes and finite band structures of nanoparticles impart many properties that make them interesting components for novel nanoelectronic devices. Nanoparticles demonstrating SET when in tunneling junctions have been modeled as \( RC \) circuits in series (Figure 5.1). Each tunneling barrier, the first between the probe tip and the cluster, and the second between the cluster and the substrate, has its own resistance and capacitance. It is the ratio of these resistances and capacitances (i.e.
that dominate transport through the junction. The STM provides the external potential and electrons necessary to charge the nanoparticle as well as measures the current moving through the assembly when the particle is placed in a tunneling junction.

The energy required to charge a metallic nanoparticle core with a single electron is inversely proportional to the particle’s capacitance,

\[ E_{\text{charge}} = \frac{e^2}{2C} \]  

where \( e = 1.602 \times 10^{-19} \text{ C} \). The smaller the nanoparticle and thus the smaller its capacitance, the more energy is required to overcome the electrostatic barrier to placing an extra electron on the core. The particle’s capacitance can be calculated as

\[ C = 4\pi\varepsilon\varepsilon_0 r \]  

where \( \varepsilon \) is the dielectric constant of the surrounding ligand shell, \( \varepsilon_0 \) is the dielectric constant of vacuum, and \( r \) is the particle radius. Even though an external bias can be applied to move electrons onto the particle, a region of current suppression exists where the driving force to charge the particle is increased yet no electrons move onto nor off the particle. This region is referred to as ‘Coulomb blockade,’ and the potential at which current begins to flow as the ‘threshold voltage.’ Although nanoparticle capacitances are directly proportional to both the particle radius and the dielectric constant of the surrounding ligand shell when placed in a tunneling junction, the particle’s capacitance is modified by an additional term that causes the capacitance to be inversely proportional to the thickness \( L \) of the tunneling junction as well [229, 270]

\[ C = 4\pi\varepsilon\varepsilon_0 r \left(1 + \frac{r}{2L}\right). \]
Figure 5.1. Schematic of the double barrier tunneling junction formed with a ligand-stabilized Au$_{11}$ cluster immobilized atop a C$_8$ SAM via an inserted tether (here, 1,10-DDT). Each tunneling barrier (tip$\leftrightarrow$cluster, and cluster$\leftrightarrow$substrate) has its own resistance $R$ and capacitance $C$. L = ligand.
For SET to occur, the energy required to charge the nanoparticle must be greater than the thermal energy $k_B T$. Typically, STM and other experiments that have examined the Coulomb blockade and electronic spectra of metal particles have been performed at cryogenic temperatures in order to lower the thermal energy and observe a large blockade region experimentally. However, if the nanoparticle is small enough, with a core diameter of $\leq 10$ nm, Coulomb blockade will persist up to room temperature as long as additional capacitances are not introduced into the system (such as the presence of proximal nanoparticles). When the nanoparticles are assembled into arrays, Coulomb blockade will dominate electron transport between particles that are surrounded by a dielectric medium whose resistance to tunneling is greater than that of the quantum unit of resistance, $\frac{h}{e^2}$ [271]. ‘Coulomb staircases’ result from quantized electron charging onto a nanoparticle.

The STM is a well-matched tool for studying the electronic properties of nanoparticles adsorbed on surfaces as it can measure the electronic spectra of individual nanoparticles, readily acquiring their I(V) properties as a function of size and chemical environment. As the STM locally probes distinct and separate nanoparticles, there is monodispersity in each measurement, important for elucidating how the electronic spectra change upon varying individual nanoparticle characteristics including composition and size. The STM often cannot however, directly determine with precision the morphological features of the nanoparticle, as STM images are a convolution of the electronic structures of both tip and sample. Sizes of nanoparticles measured solely with a scanning probe are not always dependable due to the convolutions of the topography with the geometric and electronic structures of both tip and sample. For example, if the tip radius exceeds that of the nanoparticle or other surface feature of interest, the apparent feature size will resemble that of the larger object (the tip), as it continues to send tunneling electrons into the smaller feature when it is rastered over the sample.
Using the STM, I(V) spectra are acquired by positioning the probe tip over the nanoparticle of interest, blanking the feedback loop, and recording the change in tunneling current as a function of changing the applied bias voltage. The conductance spectrum, dI/dV(V), of the nanoparticle is acquired using lock-in amplification. This quantity, when normalized to eliminate variations in gap impedance, is proportional to the LDOS of the nanoparticle.

5.2 Previous Studies of Coulomb Blockade and Nanoparticles in Tunneling Junctions

Several groups have reported Coulomb blockade in nanoparticles adsorbed on substrates [140, 169, 272, 273]. Dorogi et al. and Andres et al. reported observations of Coulomb blockade at room temperature in STM tunneling junctions composed of naked gold nanoparticles (diameter of 2 nm). These nanoparticles were synthesized in a gas-phase cluster beam and were affixed to a Au{111} substrate through a 1,4-xylyldithiolate (henceforth, XYL) SAM on a gold substrate, and the STM tip was used as a local electrical contact [140, 169]. The dithiolate was presumed to form well-ordered SAMs with one thiol chemisorbed to the Au{111} substrate, and the other directly bound to a (ligandless) Au particle. They described the electronic spectra acquired over the XYL SAM at room temperature as nearly linear at moderately high tunneling currents, while I(V) spectra acquired over the nanoparticles displayed Coulomb blockade. They were able to estimate the resistance of a gold nanocluster as well as a single XYL molecule by acquiring I(V,z) data showing single-electron tunneling and weak electronic coupling between the gold nanocluster and the Au{111} substrate beneath. Using the double-barrier tunneling junction as a model for the nanoparticle tethered to a gold substrate through a SAM, they estimated the resistances and capacitances of both the tip–nanoparticle barrier as well as the nanoparticle–substrate barrier through a best fit routine of their I(V,z) data acquired over a variety of tip–sample distances. Their
data showed that the resistance and capacitance of the nanoparticle–substrate barrier remained relatively constant, while the tip–nanoparticle resistance decayed upon moving the STM probe tip further away from the sample holding a constant tip–nanoparticle capacitance. From the data and geometrical considerations of cluster size and the lattice spacing of the monolayer beneath, they were able to estimate the resistance of a single XYL molecule to be approximately 9 MΩ. Further refinement of the calculations including the presence of a fractional charge on the nanoparticle in the fitting routine estimated the resistance of a single XYL molecule to be on the order of 18 MΩ.

Nanoparticles have also been imaged with the STM when the nanoparticles were adsorbed on atomically flat surfaces that had been functionalized with \( n \)-alkanethiolate SAMs, as opposed to when a second thiolate is covalently attached to the particles [139, 274–276]. The alkyl chains of the SAM stabilized the clusters that were themselves passivated with \( n \)-alkanethiols, with the mechanism of stabilization most likely including the interdigitation of the tails to some degree. Although the particular molecule that passivates the substrate may vary, it is generally agreed that a stabilizing layer is indeed necessary in order to perform STM imaging and spectroscopic measurements reliably. However, particles are particularly stable to imaging when tethered directly. Nanoparticles deposited on unfunctionalized atomically flat surfaces, such as highly ordered pyrolytic graphite and bare Au\{111\}, are easily moved across the surface from the large electric fields of the STM tip [277].

In addition to using scanning probes to characterize the nanoparticles themselves, nanoparticles have facilitated probing the conductance properties of both single and groups of molecules by serving as nanoscale electrical contacts. Using a gold nanoparticle as a single-point probe, Lindsay and coworkers have been able to determine the conductance of a single molecule, 1,8–octanedithiol (1,8–ODT), using a conductive probe AFM (CP–AFM) tip to make a contact with
the nanoparticle [278]. A SAM of 1,8–ODT was formed and gold nanoparticles (≤2 nm diameter) were deposited upon the SAM surface (see Chapter 6 for further discussion on the formation of α,ω–alkanedithiolate SAMs). Single molecules were presumed to span the distance between the gold substrate and the gold nanoparticle, each sulfur moiety of the dithiolate chemically connected to each contact. Upon the CP–AFM tip’s contacting the nanoparticle and measuring the current moving through the assembly, they found that the I(V) spectra were integer multiples of one fundamental spectrum, indicating that the electronic properties of the particle changed as a function of how many molecular contacts the nanoparticle was making to the surface (i.e., if either one, two, or more 1,8–ODT were chemisorbed to the particles).

Several experimental and theoretical studies of nanoparticles in tunneling junctions are beginning to reveal how quantum mechanics are coupling into the electrostatically gated charge transport commonly observed for these systems. Hou and coworkers have demonstrated that fine structure exists within their Coulomb blockade measurements of alkanethiolate-stabilized Pd nanoparticles deposited on Au(111) surfaces [279]. They attributed this fine structure, observed as a splitting of the conductance (dI/dV) resonances, to the interplay of the SET events on the particle with the effects of discrete energy levels existing within a particle of this size (d ∼ 2 nm). They showed how the transport characteristics of these particles can be manipulated by controlling the tip–particle distance, which selectively tunes that junction’s capacitance [280]. They have also demonstrated that the crystallinity of the particle can significantly affect the transport [281], where the degeneracy of energy states and electron relaxation dynamics play large roles in the transport.

Theoretical treatments of nanoparticles connected to dithiol linkers are also beginning to emerge. Ratner and coworkers have placed a nanoparticle connected to a (rigid) α,ω–alkanedithiol angstroms away from a resonating metallic tip, designed to simulate a probe tip attached to a
resonating CP–AFM cantilever. Using the Landauer formalism delineating scattering through barriers, they have described much of the barrier within the transport through the particle and molecules as a mismatch of their energy levels when they are chemically connected [282, 283]. They report that the transport through these types of junctions is not simply a function of how electrostatic transport proceeds through a junction of a particular geometry, but is also affected by the junction’s electrochemical potentials.

5.3 Transport Properties of Precise Gold Clusters

This chapter describes the study and measurement of the fundamental transport properties of structurally precise undecagold (Au$_{11}$) clusters. We use a UHV STM at 4 K to measure the conductance of these Au$_{11}$ clusters, stabilized by triphenylphosphine (TPP) ligands (Au$_{11}$(PPh$_3$)$_7$Cl$_3$, Au$_{11}$–TPP). We acquire measurements at 4 K because of the minimal thermal broadening of energy states, the low mobility of the clusters on the substrate, and the stability of the tunneling junction. The charge transport through these clusters are of particular interest as they may be more ‘molecular’ in nature than their larger nanoparticle counterparts (particles with diameters $\geq$ 1 nm); their conductance spectra may show resolvable and discrete electronic states mixed with classical Coulomb blockade behavior. This hypothesis is supported by both electrochemical and electron relaxation dynamic studies [123, 284]. Often, nanoparticles prepared in the solution phase possess a distribution of sizes, which will ultimately affect their transport properties as the capacitance of the nanoparticle is inversely proportional to particle size. These Au$_{11}$ clusters may demonstrate enhanced transport properties as compared to their larger nanoparticle counterparts, as their precise size and well defined ligand shells may result in reduced dispersion in electronic behavior. The STM was used to measure the conductance of these undecagold clusters immobilized atop alkanethiolate
SAMs using $\alpha,\omega$-alkanedithiol $\alpha,\omega$-AkDT tethers (Figure 5.2). Tunneling spectra have been previously acquired on $\text{Au}_{55}\text{–TPP}$ nanoparticles deposited on weakly interacting graphite; the data indicate that the charging states of the particles are convoluted with quantum confinement effects as well as ‘impurity’ states from the ligand shell [285]. The electronic spectra of the $\text{Au}_{11}\text{–TPP}$ were compared to the spectra of $\text{Au}_{101}\text{–TPP}$ that were immobilized atop an $n$-octanethiolate $\text{C}_8$) SAM with an identical tethering scheme using 1,10-decanedithiol (1,10-DDT).

$\text{Au}_{11}\text{–TPP}$ was synthesized in the solution phase [255], and the clusters tethered to $\text{C}_8$ SAMs through inserted 1,10-DDT at low fractional surface coverage, Figure 5.3. We acquired the differential conductance spectra ($[dI/dV(V)]$) that when normalized for variations in gap impedance, is proportional to the tunneling junction’s LDOS. We acquired the $[dI/dV(V)]$ simultaneously as the $I(V)$ using phase-sensitive detection. Our ultrastable cryogenic STM takes high quality spectra and images simultaneously; thus, we may understand how the physical environment of the clusters affects their conductance.

5.4 Materials and Methods

$n$-Octanethiol ($\text{C}_8$) and 1,10-decanedithiol (1,10-DDT) were used as received from Lancaster Synthesis (Alfa Aesar, Windham, NH). 4,4’-biphenyldithiol was used as received from TCI America (Portland, OR). All ethanol used (Mallinckrodt, Pharmco) was 200 proof. CH$_2$Cl$_2$ (J. T. Baker) was used as received (spectrophotometric grade). All H$_2$O used was purified using a Water Pro Plus System (LabConco), and had a minimum resistivity of 18 MΩ·cm. All solutions were prepared from solvents that had been subjected to three freeze–pump–thaw cycles ($3 \times$ fpt). Gold substrates were predominantly Au{111} surfaces, and were epitaxially grown (1500 Å thick) onto cleaved mica substrates (Molecular Imaging, Tempe, AZ). Substrates were annealed in a H$_2$ flame prior to deposition. All glassware used was cleaned with freshly prepared piranha solution
Figure 5.2. Schematic of a ligand-stabilized $\text{Au}_{11}$ cluster immobilized atop an alkanethiolate SAM (here, $\text{C}_8$) with an inserted $\alpha,\omega$–alkanedithiolate tether (here, 1,10–DDT). These schematics show possible insertion sites for the 1,10–DDT tether, at a step edge (left) and at a domain boundary (right). L = ligand.
Figure 5.3. Scanning tunneling microscope images of $\text{Au}_{11}$ clusters immobilized atop a C8 SAM tethered via 1,10-DDT molecules. The physical environment of these clusters is known with high precision; the clusters are anchored at film defect sites (Au step edges) supported atop a crystalline C8 matrix. (A) $\text{Au}_{11}–\text{TPP}$, $V_{\text{sample}} = +1.5$ V, $I_{\text{tunnel}} = 18$ pA, $134 \, \text{Å} \times 134 \, \text{Å}$; (B) $\text{Au}_{11}–\text{C8}$, $V_{\text{sample}} = +1.0$ V, $I_{\text{tunnel}} = 5$ pA, $166 \, \text{Å} \times 166 \, \text{Å}$. 
(caution: highly oxidizing!, 1:3 30% H₂O₂:H₂SO₄), following by rinsing with copious H₂O and absolute EtOH. All glassware that was exposed to gold clusters or nanoparticles was cleaned with aqua regia (caution: highly corrosive, fumes NO₂ gas!), 1:3 HCl:HNO₃, to dissolve any trace metal, followed by rinsing with copious H₂O.

Triphenylphosphine-stabilized undecagold clusters were prepared by our collaborators at the University of Oregon according to published procedures [255, 286]. Briefly, Au₁₁−TPP were prepared by the reduction of AuCl(PPh₃) with the slow addition of NaBH₄ and stirring at room temperature for 2 h; the mixture was then poured into 1 L hexanes and allowed to precipitate overnight (~20 h). The brown solid was collected and subjected to a series of washes: hexanes (4×15 mL), CH₂Cl₂:hexanes (1:1, 4×15 mL), and CH₂Cl₂:hexanes (3:1, 4×15 mL). The remaining solid was dissolved in CH₂Cl₂ (15 mL) and filtered a second time to remove a colorless, insoluble powder. Crystallization from CH₂Cl₂:hexanes gave the Au₁₁−TPP cluster (~140 mg, 18% yield) as deep red plates. Transmission electron microscopy measured the core diameter of the cluster as 8 ± 2 Å.

Larger, triphenylphosphine-stabilized nanoparticles were prepared by our collaborators at the University of Oregon according to published procedures [256]. Briefly, HAuCl₄·3H₂O (1.00 g, 2.54 mmol) and tetraoctylammonium bromide (1.60 g, 2.93 mmol) were dissolved in a N₂-sparged H₂O:toluene mixture (50 mL:65 mL). When the golden color had transferred into the organic phase, TPP (2.32 g, 8.85 mmol) was added and the solution was stirred vigorously for at least 10 min until the organic phase was white and cloudy. Aqueous NaBH₄ (1.41 g, 37.3 mmol, dissolved in 10 mL H₂O immediately prior to use) was rapidly added. The organic phase immediately turned dark purple after which it was stirred for 3 h under nitrogen. The toluene layer was separated and washed with water (2×100 mL). The solvent was removed in vacuo or with a stream of N₂ to yield
a black solid. The resulting solid was washed with a series of solvents (hexanes, saturated aqueous NaNO₂, and 2:3 CH₃OH:H₂O) to remove the phase transfer catalyst, byproducts, and unreacted starting materials. Further purification by precipitation from CHCl₃ upon slow addition of pentane (typically 2–3 precipitations) removed Au salts such as AuCl(PPh₃). After purification, the yield was 170 mg of purified nanoparticle from 1 g of HAuCl₄. Transmission electron micrographs measured the core diameters of the nanoparticles to be 1.5 ± 0.4 nm. Ultraviolet–visible spectroscopy confirmed the size distributions, showing no significant plasmon resonance at 520 nm, indicative of gold nanoparticles that are <2 nm in diameter.

Cluster and nanoparticle assemblies were prepared in an inert environment; all self-assembly and Au₁₁ and Au₁₀₁ attachment was performed in a glovebag (Spiifyter, VWR) that had been evacuated and purged with Ar. Host matrices were formed for ~24 h from ~1 mM ethanolic solutions and rinsed with EtOH after adsorption (all 3×fpt-EtOH). Host matrices were then immediately immersed into ~1 mM ethanolic solutions of α,ω-dithiol for 30 min–2 h. SAMs were rinsed with 3×fpt-EtOH after adsorption and immersed into 3×fpt-CH₂Cl₂ solutions of Au₁₁. Cluster assemblies were rinsed with additional 3×fpt-CH₂Cl₂, dried with N₂ or Ar, and stored in an inert environment until analysis. Assemblies were imaged with STM in ambient conditions before transfer to the cryogenic STM for imaging and spectroscopy.

Data at ambient conditions were acquired using a ‘beetle’-style STM using custom-built hardware and custom software [287]. After analyses, samples were transferred to an extremely high vacuum STM operating at cryogenic temperatures (4.2 K) and in constant current mode [288]. Pt/Ir tips (90:10, annealed, Alfa Aesar) were prepared in situ by field emission on a Cu{111} single crystal. All measurements were acquired at 4–5 K and at chamber pressures of ≤10⁻¹⁴ Torr. Differential conductance measurements were acquired simultaneously with the I(V) using
phase-sensitive detection of the first harmonic of the tunneling current from a lock-in amplifier with an 8 mV modulation at 1000 Hz applied to the sample bias. Lock-in amplifier settings were typically at 20 mV full-scale sensitivity and a time constant of 30 ms. Both I(V) and conductance spectra \([dI/dV(V)]\) over the insulating C8 matrix were always acquired before (and occasionally after) acquiring spectra over a cluster of interest in order to ascertain the cleanliness of the probe tip. All STM images presented are unfiltered.

5.5 Results and Discussion

Unexpectedly, the precise Au\(_{11}\) cluster does not show a precise electronic spectrum. Upon repeated probing of the Au\(_{11}\)–TPP, significant hopping in the conductance \((dI/dV(V))\) spectra is observed. Not only is spectral diffusion observed across multiple Au\(_{11}\)–TPP, it is also observed in single clusters as well. The dI/dV resonances vary widely in both spacing and energy. Generally, four spectral ‘families’ were observed, as illustrated in Figure 5.4. The observed results were independent of tunneling conditions; widely varying spectra were obtained for identical setpoint conditions (i.e. tunnel currents, bias voltages). Figure 5.5 is a histogram of the magnitudes of the Coulomb blockade regions (where there is zero current before the first charging steps). There were several values occurring at high relative frequency, including at \(\sim 0.5\) V, at \(\sim 1.0\) V, and \(\geq 2.0\) V. The sizes of the blockade regions were independent of tunneling setpoints including sample bias voltage and tunneling current.

A compilation of 24 representative tunneling spectra for the Au\(_{11}\)–TPP is presented in Figure 5.6; the spectra are labeled ‘a’ through ‘x,’ with every other letter omitted for clarity. Two spectra (‘o’ and ‘s’) are shown in detail, illustrating the color-scale correspondence of the compiled spectra to the intensities of the dI/dV resonances \((dI/dV \geq 1\) is saturated). While Figure 5.6 is particular to one cluster, diffusion was observed for other Au\(_{11}\)–TPP.
Figure 5.4. Representative tunneling spectra acquired over Au$_{11}$–TPP clusters immobilized on a C$_8$ SAM via 1,10–DDT tether(s). Generally, four families of I(V) and [dI/dV(V)] spectra were observed. Spectra are plotted on the same scale for clarity. Spectral families were independent of tunneling conditions (V$_{sample}$ = ±1.5 V, I$_{tunnel}$ = 5–20 pA.)
Figure 5.5. Histogram of the magnitudes of the Coulomb blockade regions of Au$_{11}$–TPP immobilized on a C8 SAM via 1,10–DDT tether(s), across all tunneling conditions. This magnitude is the width of the zero-current region, shown by the arrow in the tunneling spectrum (inset). Magnitudes of $\sim$0.5 V, $\sim$1.0 V, and $\geq$2 V were prevalent. Bin size = 50 mV.
Figure 5.6. Compilation of 24 representative tunneling spectra (dI/dV(V)) for Au$_{11}$–TPP on a C8 SAM with a 1,10–DDT tether, spectra ‘a’ through ‘x’ (alternate letters omitted for clarity). The colorscale corresponds to the dI/dV intensity (any dI/dV ≥ 1 is saturated). For clarity, two spectra ‘o’ and ‘s’ are shown to illustrate more clearly how the conductance spectra and the colorscale correspond.
Reversible spectral diffusion and hopping were observed (Figure 5.7). Spectra with small, intermediate, and large regions of zero-conductance interchanging reversibly were observed, indicating no irreversible damage or perturbation to the \( \text{Au}_{11} \text{–TPP} \). The magnitudes of the region of zero-conductance (before the first charging steps) fully spanned an order of magnitude, from as small as 0.2 V (spectrum ‘v’) to greater than 2.5 V (spectrum ‘c’); a variety of plateau widths between charging steps also was observed. Based on geometric models of the cluster and the junction thickness, we expect the capacitance of the \( \text{Au}_{11} \text{–TPP} \) to be \( \sim 0.15 \) aF, for the zero-conductance width to be \( \sim 1.3 \) V, and charging step widths to be \( \sim 1 \) V. This system, with a monodisperse particle size distribution, should exhibit a uniform spectral response, but in the limit of isolated, chemically anchored particles, different behavior was observed. Additional observations include some spatial dependence for the conductance spectra, but there is no obvious correlation between the spectral diffusion and the acquisition location on the cluster (\textit{vide infra}). Fluctuations of the asymmetry of the dI/dV resonances around 0 V were observed, consistent with a fluctuating background charge residing on \( \text{Au}_{11} \text{–TPP} \). The spectral hopping rates exceeded the timescale of STM measurements, and were not thermally activated.

Several mechanisms may be responsible for the observed diffusion in the conductance spectra. Significant electrostatic forces are present in the tip–sample junction. The high electric field of the STM tip exerts a force on the cluster that may distort the connection to its thiol tether and change the transmission characteristics of the assembly. It is well known that the STM tip ‘pushes’ particles around if they are not chemically attached to the substrate [139]. Even though the SAM has very low corrugation, it too is susceptible to compression by the probe tip even though low tunneling currents are used to avoid adverse tip–sample interactions (5–20 pA) [117,289]. The SAM compresses elastically under forces of these magnitudes (\( \sim 100 \) pN), and the particle can oscillate
Figure 5.7. Representative tunneling spectra acquired over Au$_{11}$–TPP clusters immobilized on a C8 SAM via 1,10-DDT tether(s). Many different blockade behaviors are measured for this single cluster. Measured spectra are independent of tunneling conditions ($V_{\text{sample}} = +1.5$ V, $I_{\text{tunnel}} = 7–24$ pA.)
in concert with charge transfer events when connected to the substrate by ‘soft’ mechanical linkers such as alkanethiolates [290]. Assuming that the capacitive coupling to the cluster with the tip is constant, there may be shifts in the charging steps if the cluster–substrate distance changes with distortion in the SAM or tether underneath the \(\text{Au}_{11}–\text{TPP}\) when the cluster is probed. Any geometrical changes of the particle near the Au surface due to mobility or tether compression would induce changes in the junction’s behavior. The locations of the \(\text{Au}_{11}–\text{TPP}\) are dictated by the dithiol tethers, which preferentially adsorb at defect sites in the SAM; thus, the clusters are not immobilized with a crystalline SAM matrix underneath for electrical isolation. Notably, we see no measurable change in the apparent height of the \(\text{Au}_{11}–\text{TPP}\) relative to the SAM across the tunneling spectra. We are currently testing the mechanism of conductance change as a function of tether flexibility using an aromatic (rigid) tether.

Many studies have demonstrated reproducible Coulomb blockade over particles, often measuring blockade as a function of particle size. These studies have been on either dense arrays of nanoparticles directly deposited onto surfaces with no decoupling electrical barrier, or affixed to short or ill-defined SAMs with little potential for mobility [140, 141]. Particle arrays have often been chemically crosslinked, and thus are coupled electrically [237, 291]. Invasive tunneling conditions (~nA) are used in most studies. However, quantum mechanical effects dominating many aspects of the charge transport through particles in tunneling junctions are just beginning to be understood [280–283].

Great care was taken in the preparation of the cluster assemblies so as to optimize cluster attachment to the tethers; careful assembly keeps the –SH reduced, important for both optimal immobilization of the clusters and ensuring that the transport is not convoluted with pathways other than S–Au contacts. The charge transport of the S–Au contact has been modeled extensively
[292–297]; thus, these studies may bring experimental data and theory closer together to understand more fully these types of charge transport. All self-assembly was performed using 3×fpt solvents to reduce film defects and impart greater stability to the assemblies when exposed to air (see Chapter 6 for further discussion on the use of fpt solvents). Figure 5.8 shows the characterization of the cluster assemblies at each step. Figure 5.8A is a representative STM image of the host C8 SAM. Defects that are typical of n–alkanethiolate SAMs formed on gold surfaces are present, including domain boundaries, substrate vacancies, and step edges. The SAMs are then exposed to α,ω–dithiol to serve as tethers for cluster attachment; Figure 5.8B shows that the dithiols (here, 1,10–DDT) have inserted at film defect sites. The dithiols appeared as protrusions from the C8 host SAM. These SAMs that presented thiol groups at the interface were exposed to clusters for adsorption (Figure 5.8C, here Au11–TPP). The immobilized clusters adsorbed at film defect sites and were stable to imaging (they are minimally perturbed by the STM tip). n–Octanethiol was chosen as the host matrix for the 1,10–DDT tether as the –SH could protrude a small distance from the surface of the SAM to allow for greater immobilization efficiency of the clusters. Data using C10 as the host SAM showed that the clusters did not readily attach, presumably as the ligand shell of the cluster presented a significant steric hindrance to cluster attachment. For the 1,10–DDT tether, once an estimate of fractional surface coverages had been ascertained for particular insertion conditions, the imaging of the SAM with inserted tethers alone was no longer performed, so as to avoid –SH oxidation. Clusters were attached directly after dithiol insertion.

Figure 5.9 shows molecular resolution of the C8 lattice as well as the particle’s location at a film defect site; an area of desorbed C8 is observed near this defect site, with initial desorption presumably occurring when the SAM was exposed to Au11–TPP deposition solution [128]. Over a period of 20 h, the C8 SAM has desorbed all the way up to and possibly underneath the cluster.
Figure 5.8. Scanning tunneling microscope images showing the progressive characterization of the SAM–cluster assemblies. Tunneling conditions: $V_{\text{sample}} = +1 \text{ V}$, $I_{\text{tunnel}} = 5 \text{ pA}$. 
While these particles are immobilized atop the SAM for measurement, we hypothesize that these assemblies may still be dynamic enough to affect their transport properties significantly.

Figure 5.10 shows a Au$_{101}$–TPP nanoparticle anchored to a C$_8$ SAM via 1,10–DDT tethers. The nature of the defect site is unclear, as the nanoparticle obscures the defect completely. We strive to correlate the spectral diffusion to tether location. We hypothesize that the fluctuations in the energies and intensities of conductance resonances are closely coupled to the molecular motion of the SAM matrix and tether. Figure 5.11 shows that from spectrum to spectrum, dI/dV resonances can fluctuate on the order of 100 mV. The resonances change in intensity from spectrum to spectrum as well (typically observed). It is noteworthy that in this particular location where the tether and nanoparticle are present, either in a very small C$_8$ domain boundary or within a full domain of C$_8$, that the spectral diffusion is small, with the overall tunneling spectrum remaining constant except for small and distinct fluctuations. This is in contrast to the more dramatic spectral diffusion observed at the large film defects at Au step edges.

The Au$_{101}$–TPP electronic spectra changed as generally expected, as a function of the particle size. Smaller particles typically showed larger regions of zero-conductance than particles with larger apparent diameters. Figure 5.12 shows that the region of zero-conductance for the Au$_{101}$–TPP in the upper right corner is smaller than the zero-conductance region of the Au$_{101}$–TPP in the lower left corner of the figure. Tunneling spectra acquired at the junction in between the two particles were less stable than those acquired over the center of the Au$_{101}$–TPP. The regions of zero-conductance are smallest here; this could be from the presence of multiple pathways for tunneling, or from enhanced motion of the particles or tethers underneath them from the tip probing the particles’ edges.
Figure 5.9. Scanning tunneling microscope images of a Au$_{11}$–TPP adsorbed at a step edge. Over 20 h of analysis (from A to B), the C8 host matrix has desorbed, including up to and perhaps underneath the cluster. Tunneling conditions: $V_{\text{sample}} = (A) +1.5$ V, (B) $-1.5$ V; $tunnel = (A)$ 20 pA; (B) 14 pA; 134 Å × 134 Å.
Figure 5.10. Scanning tunneling microscope image of $\text{Au}_{101}$–TPP nanoparticles tethered to a C8 SAM via 1,10–DDT tethers. The nature of the defect site where the particle on the left is anchored at is unclear. Tunneling conditions: $V_{\text{sample}} = +1.5$ V, $I_{\text{tunnel}} = 5$ pA; 210 Å $\times$ 210 Å.
Figure 5.11. (A) Scanning tunneling microscope image of a $\text{Au}_{101}^{-}\text{TPP}$ nanoparticle tethered to a C8 SAM via 1,10-DDT tethers. Nine spectra are acquired over the nanoparticle (3 each at points 1, 2, and 3). (B) The tunneling spectrum shows the average of the nine acquired spectra, yet the individual insets (C) show that the dI/dV resonance averaging to +1.10 eV fluctuates $\sim$100 mV in energy. Tunneling conditions: $V_{\text{sample}} = +1.5 \text{ V}$, $I_{\text{tunnel}} = 8–16 \text{ pA}$; 120 Å × 120 Å.
Figure 5.12. 400 Å × 400 Å STM image of two individual Au_{101}–TPP immobilized on a C8 SAM via 1,10–DDT tethers. The tunneling spectra show the spatial dependence upon the acquisition location over and between the two nanoparticles. Tunneling conditions: $V_{\text{sample}} = +1.5$ V, $I_{\text{tunnel}} = 8$ pA.
Figure 5.13 is a histogram of the ‘approximate’ LDOS of the Au$_{11}$–TPP and Au$_{101}$–TPP immobilized atop a C$_8$ SAM. The histogram plots the occurrences of dI/dV resonances at particular energies; the resonances were tabulated across all spectra at all tunneling setpoints. The histogram shows that the Au$_{11}$–TPP possess a more discrete set of energy levels than the Au$_{101}$–TPP, whose dI/dV resonances were more widely distributed in energy.

5.6 Conclusions and Future Directions

Significant spectral diffusion was observed for both Au$_{11}$–TPP and Au$_{101}$–TPP species immobilized on a C$_8$ SAM through α,ω–alkanedithiol tethers. At this stage of experiments, it is more important to understand the mechanism behind the spectral diffusion, rather than strive for a direct comparison between the two species. It is most likely the chemical and physical environment that the cluster or nanoparticle is in that is dominating the charge transport. This system, though carefully constructed and controlled, may be susceptible to diffusion due to the size of the metallic core and the flexibility of the alkanethiolate support underneath; this is especially important when considering the application of clusters of this sort for their charge transport properties, as their local environments may heavily dominate transport. Nanoscale structures created by self-assembly techniques, including the use of matrix-inserted tethers, have concomitant electronic and conformational dynamics that must be accounted for when further integrated into molecule-based architectures.

We are currently testing the hypothesis of motion of the dithiol tether coupling to charge transport by using an aromatic and rigid tether, 4,4’–biphenyldithiol (BPD) to tether Au$_{11}$–TPP. Although the BPD will alter the charge transport through the cluster by decreasing the resistance of the cluster–substrate junction, it will be interesting to observe to what extent the spectral diffusion persists in this system.
Figure 5.13. Histograms comparing the approximate LDOS for $\text{Au}_{11}$–TPP and $\text{Au}_{101}$–TPP immobilized atop a C8 SAM via 1,10–DDT tether(s). The histograms plot the occurrences of dI/dV resonances as a function of energy, measured across all clusters or particles at all tunneling setpoints. 50 mV bin for each species.
Chapter 6

Understanding Bifunctional Interfaces:
The Formation of Self-Assembled Monolayers
Containing $\alpha,\omega$-Alkanedithiols

While the formation of $n$-alkanethiolate SAMs has been extensively studied and characterized, this has only been the case for 1-alkanethiolates, or rather, using adsorbates with a single thiol terminus. While the surface chemistry and assembly of several $\alpha,\omega$-heterobifunctional alkanethiols has been documented (Table 2.2 in Chapter 2), this has not been the case for the homobifunctional $\alpha,\omega$-alkanedithiol ($\alpha,\omega$-AkDT). Significant intramolecular competition for adsorption to the metal substrate arises from the two terminal sulfur groups, leading to SAMs with complicated structures and interfaces. This chapter presents and discusses methods for forming SAMs containing $\alpha,\omega$-AkDT adsorbed on Au substrates; the characterization of these SAMs uses a multi-technique approach including both ensemble measurements and local probes. The driving force behind this project was to understand how to prepare high quality SAMs with thiol-terminated interfaces with reproducible reactivity for the attachment of gold clusters, nanoparticles, and even evaporated metal films. Several problems arose in the experiments of Chapter 5 when attaching gold clusters and nanoparticles to the inserted dithiol tethers; chiefly, the particles often would not immobilize with high efficiency on the monolayers. Also, increasing the fractional surface coverage of tether did not necessarily lead to an increased fractional surface coverage of particles. This chapter presents possible reasons behind this, and describes methods to prepare high-quality thiol-terminated SAMs with an understanding of the driving forces behind their self-assembly.
6.1 Introduction

α,ω–Alkanedithiols have found themselves in the foreground of many recent experiments involving single-molecule electronics and charge transport measurements [278, 298–301], as well as novel fabrication techniques such as ‘nanotransfer printing’ [302–304]. These molecules are particularly attractive as the free thiols at their ends can make contacts to many different kinds of materials (Table 2.1 in Chapter 2). However, unlike their 1–alkanethiol analogues, the structures of SAMs formed from α,ω–AkDT are not well known [305–307]; at length scales where defects can heavily dominate charge transport and device function, great care should be taken when attempting to substitute the structure and function of a 1–alkanethiol with an α,ω–AkDT. Due to the significant intramolecular competition of the –SH groups for the Au surface, the SAMs formed are rarely ordered; the α,ω–AkDT can exist in a multitude of conformations, ranging from lying flat on the surface with the axis of the hydrocarbon backbone parallel to the plane of the Au surface, to looping over, with both –SH groups attached to the Au and the flexible hydrocarbon chain looping around. These kinetically trapped films are highly disordered from the lack of van der Waals interactions between the individual adsorbates from the random ‘pinning’ of the –SH groups preventing the occupation of every available adsorption site, the sensitivity of the –SH group to oxidation, and the variability of conformations of the adsorbates. The structures of the α,ω–AkDT SAMs used in the aforementioned studies are not known, and in some of those experiments the attempts to do so are not made. Reports of the structures and properties of α,ω–aryldithiols are emerging [308–310]; the rigidity of these aromatic adsorbates restricts molecular motion such that there is less ambiguity in the final structures of the SAMs.
6.1.1 Previous Studies of the Structure of $\alpha,\omega$–Alkanedithiol SAMs

There is an existing debate on the structures of single component SAMs of $\alpha,\omega$–AkDT; some studies have reported that the molecules adsorbed in all trans geometries similar to their 1–alkanethiol counterparts with one –SH chemisorbed to the Au substrate and the other –SH at the opposite interface [304, 311, 312]. Other studies using techniques from X–ray diffraction to STM showed that the alkanedithiols laid flat on the gold surface, with their hydrocarbon backbones parallel to the plane of the Au surface (a ‘striped’ phase) [305–307]. While the existence of this striped phase is not disputed, it is mostly observed at low adsorbate density. The films prepared in these studies showing striped phases were prepared by controlled dosing in vacuo, rather than from the solution phase.

The data in this chapter show that the quality of SAMs containing $\alpha,\omega$–AkDT is heavily dependent upon their preparation conditions; STM, FT–IR, CAG, and ellipsometry were used to determine both the structure and order of films containing $\alpha,\omega$–AkDT. The structure and order of both single component SAMs of $\alpha,\omega$–AkDT as well as inserted $\alpha,\omega$–AkDT into n–alkanethiolate host SAMs were investigated and are presented here.

6.2 Experimental Procedures

Self-assembly containers were either glass or Teflon and were cleaned with piranha solution (1:3 30% H$_2$O$_2$:H$_2$SO$_4$ — highly oxidizing!) and rinsed with Nano-pure water (Barnstead or Lab-Conco, minimum resistivity of 18.2 MΩ·cm) followed by absolute EtOH. Containers were allowed to dry at least 12 h to remove all traces of piranha; containers not permitted this drying step showed significant oxidation of the sulfur moieties in the FT–IR spectra.

Perdeuterated alkanethiols ($d$–alkanethiols) were prepared according to previously described procedures [67]. Briefly, 1 eq. $d$–bromoalkane was reacted with 1 eq. thiourea by refluxing overnight
in degassed absolute EtOH overnight under inert atmosphere. The alkylthiouronium salt was hydrolyzed by adding degassed 3–4 eq. 4 N NaOH (aq.) and then quenched with degassed 6 N HCl. Column chromatography was performed on the d–alkanethiol to remove oxidized product and other impurities (eluent: degassed hexanes). A similar procedure was used for the preparation of 1,16–hexadecanediithiol (1,16–HDDT) from its 1,16–dibromohexadecane precursor. n–Octanethiol (C8) and n–hexadecanethiol (C16) were used as received from Sigma–Aldrich (St. Louis, MO). 1,8–octanediithiol (1,8–ODT) and 1,10–decanediithiol (1,10–DDT) were used as received from Lancaster Synthesis (Windham, NH). Solvents were subjected to 3 freeze–pump–thaw cycles for the FT–IR experiments; 3×fpt solvents were used for both α,ω–AkDT assembly and rinsing.

For FT–IR and ellipsometry experiments, self-assembly substrates were prepared by thermal evaporation of a ~100–200 Å chromium adhesion layer [chrome-plated tungsten rod, R. D. Mathis (Long Beach, CA)] followed immediately by thermal evaporation of ~1000–1500 Å Au [Au wire, Refining Systems, Inc. (Las Vegas, NV), 99.99% purity] onto 2” silicon wafers. Silicon wafers (Silicon Quest, Santa Clara, CA) were p-type and 10–20 Ω·cm resistivity; bare wafers were cleaned by immersion in fresh piranha solution, followed by rinsing copiously with Nano-pure H2O and absolute EtOH. Wafers were recycled by removing the previous monolayer and Au film by immersion in an etching solution, followed by copious rinsing with Nano-pure H2O, immersion into freshly prepared piranha solution, and then rinsing again with H2O and EtOH. After drying in a stream of N2, wafers were loaded in the deposition chamber and deposited at base pressures of 1×10−7 Torr. After the Au deposition, ellipsometry measurements were performed on the bare wafers and then they were immediately immersed into solutions of either α,ω–AkDT or n–alkanethiol.
Au\{111\}/mica substrates for STM experiments were cut into quarters after receipt from Molecular Imaging (Tempe, AZ). 1,8–octanedithiol (1,8–ODT) and 1,10–decanedithiol (1,10–DDT) were used as received from Lancaster Synthesis. Dithiothreitol (DTT) was used as received from Sigma–Aldrich (St. Louis, MO). For STM experiments, all solutions used were \(~1\) mM and were prepared from absolute EtOH (Pharmco). Host C8 SAMs adsorbed for \(~24\) h. For vapor-phase insertion experiments, a 2.0 mL V-Vial (Wheaton Scientific) and cap were heated in a 65 °C oven for 15–30 min; a drop of neat 1,10–DDT was placed in the bottom of the vial, and the Au substrate with C8 host SAM was suspended above it. After blanketing with N2 gas, the assembly was sealed and placed back in the oven for the deposition time. Samples were rinsed with absolute EtOH and dried with either N2 or Ar before imaging.

\(d\)–Alkanethiol host matrices were prepared from 1 mM ethanolic solutions; \(d\)–octanethiolate (D8) SAMs were allowed to form for at least 8 h, while \(d\)–dodecanethiolate (D12) and \(d\)–hexadecanethiolate (D16) SAMs were allowed to form for at least 18 h. All \(\alpha,\omega\)–AkDT self-assembly steps were performed in a controlled atmosphere (N2-filled glovebox) in order to minimize oxidation. EtOH used for deposition of the host matrices was 200 proof (Pharmco); solvents used for \(\alpha,\omega\)–AkDT assembly and rinsing were all air-free, either Pharmco EtOH subjected to 3×fpt cycles, or purchased from Aldrich (Sure/Seal®) and used without further purification; all air-free solvents were stored in the glovebox. Sure/Seal® solvents were transferred via cannula into adsorption containers. After preparation and rinsing, samples were placed in a sealed container and transferred to the dry air or N2 environment inside the FT–IR spectrometer. Samples subjected to thermal annealing were placed in an oven at 72 °C. Samples immersed in their insertion solutions were transferred directly from the glovebox in sealed containers to the oven and then back again without
exposure to the environment. If necessary, samples were taken from the oven to the sonicator and sonicated for 10 min, and then taken to the glovebox for sample rinsing, drying, and storage.

Figure 6.1 shows a scheme of the FT–IR spectrometer used in the experiments of this chapter. This spectrometer is in the Allara Laboratory, in the Department of Chemistry at The Pennsylvania State University. This setup employs a Digilab FTS–60A commercial spectrometer (Bio–Rad, Cambridge, MA) with custom-designed external optics. These optics are encased in Plexiglass housing with a constant purge of either N$_2$ or CO$_2$- and H$_2$O-free air; a mercury–cadmium–telluride detector (MCT, cooled with liquid N$_2$) is used to detect a variety of IR wavelengths. The $p$–polarized component of the IR beam is sent to the sample at a grazing angle of 86°.

Ellipsometry measurements were performed on a Gaertner Ellipsometer (model LSE, Gaertner Scientific Corporation, Skokie, IL) with a wavelength of 632.8 nm (HeNe source) and an angle of incidence of 70°. The AUTO-EL program (Allara Laboratory, The Pennsylvania State University) was used to estimate the thicknesses of the monolayers, using computational models and fits from the reflection data of the unmodified (bare) Au surface and estimated optical constants of the SAM ($n = 1.47–1.61$ and $k = 0$). Calculations assumed no contributions from the optically distinct interface of the S–Au bond [320]. Refractive indices of $\text{1,8–ODT}$ (1.57) and $\text{1,16–HDDT}$ (1.61) were calculated using quantitative structure–activity relationship methods described in Ref. [313].

Contact angle measurements were performed on a custom-built apparatus using video capturing of the droplets on the monolayer-modified surfaces. Advancing, receding, and sessile contact angles were recorded. Advancing and receding angles were created using the ‘dragging’ method, with the droplet moving out from under the needle at a rate of 50 µm/s. Contact angles were measured from the optical micrographs using ImageJ [314]. The intrinsic error associated with this ‘dragging’ technique is ± 5°.
Figure 6.1. Scheme of the FT–IR spectrometer of the Allara laboratory, The Pennsylvania State University. (1) Digilab IR spectrometer; (2) aperture; (3) mirror; (4) mirror; (5) polarizer; (6) rotating goniometer stage; (7) sample holder; (8) mirror; (9) MCT detector; (10) dry air purge inlet port; (11) Plexiglass housing; (12) vibrational isolation table. Scheme not drawn to scale.
6.3 Scanning Tunneling Microscopy Studies of $\alpha,\omega$–AkDT Inserted Into $n$–Alkanethiolate Host SAMs

Scanning tunneling microscopy was used to analyze the quality and order of SAMs containing $\alpha,\omega$–AkDT, as well as to measure the amount of $\alpha,\omega$–AkDT inserting into $n$–alkanethiolate host matrices as a function of time and temperature. Here, the system of 1,10–DDT inserted into C8 host SAMs was chosen as these molecules were the system of interest for the cluster and nanoparticle attachment as described in Chapter 5, and their length is compatible for measurement using STM.

Figure 6.2 shows the quality of the films formed from the insertion of 1,10–DDT into C8 host SAMs. Figure 6.2A and 6.2B are STM images of insertion of 1,10–DDT from 1 mM ethanolic solutions for 2 and 8 h, respectively. The 1,10–DDT imaged as protrusions from the C8 host SAM; the $\alpha,\omega$–AkDT inserted at SAM defect sites, including Au step edges and at the edges of substrate vacancies (arrows).

The molecules were easily visible at low fractional surface coverage (Figure 6.2A), but were more difficult to resolve at higher fractional coverage (inserted for longer periods of time, Figure 6.2B). Significant streakiness existed in the fast scan direction of Figure 6.2B, indicating a strong interaction of the –SH groups with the Pt/Ir STM tip. Further evidence supporting the strong interaction of the 1,10–DDT with the probe tip was the consistent degradation of image quality after several scans, as well as the progressive disappearance of dithiols that had once been resolved. Ordered domains of C8 were present, but regions of significant disorder existed, nucleating inward from film defect sites where the 1,10–DDT inserted. Figure 6.2C is an STM image where 1,10–DDT has been inserted from the (neat) vapor phase for 1 h at 65 °C. This method of insertion consistently yielded the highest fractional surface coverage of $\alpha,\omega$–AkDT, yet was not necessarily functional for particle attachment.
Figure 6.2. Scanning tunneling microscope images of 1,10–DDT inserted into a C8 SAM from the solution phase for (A) 2 h and (B) 8 h; the C8 host SAM can be resolved in images (A) and (B), and individual 1,10–DDT can be resolved in (A) as protrusions from the C8 matrix (arrows). Image (C) shows insertion from the vapor phase (1 h, 65 °C). Tunneling conditions: (A) $V_{\text{sample}} = -1 \text{ V}, I_{\text{tunnel}} = 5 \text{ pA}, 390 \text{ Å} \times 280 \text{ Å}$; (B) $V_{\text{sample}} = -1 \text{ V}, I_{\text{tunnel}} = 5 \text{ pA}, 800 \text{ Å} \times 800 \text{ Å}$; (C) $V_{\text{sample}} = -1 \text{ V}, I_{\text{tunnel}} = 5 \text{ pA}, 300 \text{ Å} \times 300 \text{ Å}$. 
As particles were not attaching with a surface coverage proportional to the fractional surface coverage of the 1,10–DDT tether, it was hypothesized that the terminal groups were no longer functional due to their oxidation over the time of the insertion process. The presence of residual O₂ and H₂O oxidizes thiols to sulfonates, sulfones, or other oxidized species (particularly when heated), rendering them much less reactive towards the attachment of gold particles. Another oxidized product of a –SH-terminated surface would be the formation of alkyldisulfides resulting from oxidative coupling of the tethers during the period of the insertion process. If this were the case, this interface would be ill-defined from the presence of flexible alkyldisulfide ‘ropes,’ unable to attach particles themselves or possibly obscuring other available, reduced –SH groups. The formation of these alkyldisulfides can be reversed by rinsing with a disulfide cleaving agent that reduces the disulfides to free –SH groups. Dithiothreitol (DTT, Figure 6.3), was chosen to reduce any disulfides present at the interface of the SAM [315–318]. It was observed that particle attachment improved when SAMs that had 1,10–DDT inserted for significant periods of time, particularly from the vapor phase, were rinsed with DTT (Figure 6.4).

Contact angle measurements were performed to test the hypothesis of DTT’s cleavage of alkyldisulfides at the –SH-terminated interface. Figures 6.5 and 6.6 show the sessile contact angles of H₂O droplets atop SAMs with inserted 1,10–DDT. Several trends persist across both vapor- and solution-phase insertion of 1,10–DDT. After a dramatic drop in contact angle after the insertion begins, the contact angle begins to rise again after longer insertion times (62 min in the vapor phase, and 8 h in the solution phase). This supports the hypothesis that the surface can regain some hydrophobic character from tether cross-coupling during the insertion process. Rinsing of these films with DTT reduces the contact angle by greater than 10°, as the alkyldisulfides were removed and free thiols remained. Incomplete alkyldisulfide cleavage by the DTT would explain
**Figure 6.3.** Structure of dithiothreitol (DTT), a common reagent for the reduction of disulfide groups to free thiols.

**Figure 6.4.** Scanning tunneling microscope images of a C8 SAM that has had Au$_{11}$–TPP adsorbed to it after the insertion of 1,10–DDT from the vapor phase for 1 h ($65 \, ^{\circ}C$); (A) shows poor cluster attachment without DTT treatment before cluster exposure, while (B) shows significant cluster attachment after rinsing with 10 mM DTT solution before cluster exposure. Tunneling conditions: (A) $V_{sample} = -1 \, V$, $I_{tunnel} = 10 \, pA$, 1500 Å × 1500 Å; (B) $V_{sample} = -1 \, V$, $I_{tunnel} = 5 \, pA$, 2000 Å × 2000 Å.
why the contact angle did not continue to decrease dramatically after the long insertion times (i.e.,
the post-DTT Au/SiO₂ case in Figure 6.5).

These insertion experiments were performed on two types of Au substrates, Au{111}/mica, and thermally evaporated Au on SiO₂ substrates through a Cr adhesion layer. Generally, the Au/mica substrate had higher contact angles than the Au/SiO₂, consistent with more ordered SAMs from flatter substrates and/or less insertion from the decreased fraction of Au grain boundaries. However, this system of a short-chain α,ω–AkDT tether and an even shorter-chain host matrix (C₈), may influence the CAG measurement somewhat with the interaction of the H₂O droplet with the Au surface. Also consistent across insertions from the vapor and solution phases was the decrease in the measurement errors of the contact angles after rinsing with DTT. The lack of variability in the measurement implied a lack of variability in surface character, which would follow from cleavage of disordered alkylidisulfide overlayers and the presentation of more uniform thiol-terminated interfaces.

It is entirely possible in principle that the decrease in the contact angle of the film would be from the formation of a DTT–tether adduct, a structure that occurs during the reduction process [315]. Infrared spectroscopy was used to test for the presence of –OH functional groups that would have been present if the adduct were to occur. No –OH were found to be present on the surface; little change was measured in the –CH₂– region of the FT–IR spectrum. Therefore, the consistent decrease in contact angle was not a result of the formation of a hydrophilic DTT adduct.

However, the experimental parameter found to be the most significant for the successful attachment of gold particles to thiol-terminated interfaces was the use of 3×fpt solvents followed by a short exposure of the tether solution to the host SAM (i.e., 30–60 min). Not only was the
Figure 6.5. $H_2O$ contact angles (sessile) of $1,10$–DDT inserted into C8 SAMs from the vapor phase (65 °C), onto both Au/mica and Au/SiO$_2$ substrates, before and after rinsing with DTT. For each substrate, the contact angles decreased after rinsing with DTT and the error in the measurement decreased as well.
Figure 6.6. H₂O contact angles (sessile) of 1,10–DDT inserted into C₈ SAMs from the solution phase onto both Au\{111\}/mica and Au/SiO₂ substrates, before and after rinsing with DTT. For each substrate, the contact angles decreased after rinsing with DTT and the error in the measurement decreased as well.
efficiency of particle attachment found to increase significantly, but the quality of the C8 host SAMs was markedly improved as well based on the decreased fraction of film defects and fewer disordered regions nucleating from these defects, leading to an overall enhanced stability of the assembly.

6.4 Infrared Spectroscopy Studies of Thiol-Terminated Interfaces

To increase our understanding of the structures and the kinetics of formation of films containing $\alpha,\omega$–AkDT, FT–IR was used to determine the order of $\alpha,\omega$–AkDT SAMs and to learn how to optimize their structures. Single component SAMs of $\alpha,\omega$–AkDT were formed using both short- and long-chain adsorbates (1,8–ODT and 1,16–HDDT) to probe the degree of interplay between intermolecular van der Waals forces and the pinning of the –SH head and tail groups to the Au surface. Also, both 1,8–ODT and 1,16–HDDT were inserted into perdeuterated $n$–alkanethiolate host SAMs of varying chain length (D8, D12, and D16) to understand the interplay and compromise between film order and fractional surface coverage of $\alpha,\omega$–AkDT. The variables of $\alpha,\omega$–AkDT chain length, host matrix chain length, time, solvent, and temperature were explored. Figure 6.7 shows the FT–IR spectra of a D16 SAM (left, pink trace) and an $n$–hexadecanethiolate C16 SAM (right, blue trace). Each of the vibrational modes particular to each sample has been assigned; for spectra containing $\alpha,\omega$–AkDT, no –CH$_3$ resonances are expected.

6.4.1 Infrared Spectroscopy Studies of Single Component SAMs of $\alpha,\omega$–AkDT

Infrared spectra were acquired on SAMs of solution-phase deposited 1,8–ODT and SAMs of 1,16–HDDT also formed from the solution phase; here, short- and long-chain $\alpha,\omega$–AkDT were used to understand how the van der Waals interactions between the molecules would compete with the thiol group adsorption in SAM assembly in each case. Figure 6.8 shows the FT–IR spectra for single component SAMs of 1,8–ODT and 1,16–HDDT formed from $\sim$1 mM solutions in
Figure 6.7. Infrared spectra of the C–D and C–H stretching regions for a D16 SAM (red trace) and a C16 SAM (blue trace). a: 2075 cm$^{-1}$, CD$_3$ sym. stretch; b: 2090 cm$^{-1}$, CD$_2$ sym. stretch; c: 2193 cm$^{-1}$, CD$_3$ asym. stretch; d: 2221 cm$^{-1}$, CD$_2$ sym. stretch; e: 2850 cm$^{-1}$, CH$_2$ sym. stretch; f: 2878 cm$^{-1}$, CH$_3$ sym. stretch; g: 2918 cm$^{-1}$, CH$_2$ asym. stretch; h: 2938 cm$^{-1}$, CH$_3$ resonance mode; i: 2965 cm$^{-1}$, CH$_3$ asym. stretch. Spectral mode assignments taken from Ref. [319] for D16 and Ref. [103] for C16.
3 × fpt-EtOH for 24 h. If adsorbed in an all *trans* geometry, vibrational frequencies of ∼2919 cm⁻¹ and ∼2851 cm⁻¹ would be expected for the −CH₂− asymmetric and −CH₂− symmetric stretches, respectively [103]. Figure 6.8 shows that single component SAMs of 1,8–ODT formed somewhat reproducibly, but not with any particular degree of order; the −CH₂− asymmetric stretch centered at ∼2928 cm⁻¹, and the −CH₂− symmetric stretch was at ∼2854 cm⁻¹. The higher vibrational frequencies are indicative of film disorder. On the other hand, the −CH₂− asymmetric stretch varied from 2918 to 2929 cm⁻¹ for single component SAMs of 1,16–HDDT, and the resonances possessed a variety of intensities as well. This is indicative of a large dispersion in adsorbate conformations or even differences in the amounts of 1,16–HDDT on the surfaces from the occlusion of available binding sites. Parameters to optimize the order and structure of these single component SAMs of α,ω–AkDT, including increased concentrations, different solvents, or thermal annealing treatments, have yet to be explored.

Ellipsometry of single component SAMs of 1,8–ODT gave measured film thicknesses of 9.7 ± 0.9 Å (n = 1.61); SAMs of 1,16–HDDT were measured to be 27.6 ± 1.7 Å (n = 1.57). Refractive indices were calculated from atom-fragment quantitative structure–activity relationships [313,320]. Expected film thicknesses for the all *trans* configurations bound to a surface are ∼14.2 Å and ∼24.9 Å for 1,8–ODT and 1,16–HDDT, respectively [320,321].

### 6.4.2 Infrared Spectroscopy Studies of the Insertion of α,ω–AkDT into Perdeuterated n–Alkanethiolate SAMs

Forming SAMs of α,ω–AkDT from direct deposition from the solution phase results in films where the adsorbates have no particular order, but rather a dispersion of conformations resulting from the interplay between van der Waals interactions and −SH adsorption to the Au surface. Alternatively, α,ω–AkDT can be attached to the surface in a predetermined orientation by inserting them into pre-existing n–alkanethiolate host SAMs. If a ‘host’ SAM is placed in a solution of a
Figure 6.8. Infrared spectra of single component SAMs of (A) 1,8–ODT and (B) 1,16–HDDT deposited from 1 mM solutions in 3×fpt-EtOH for 24 h. The 1,8–ODT SAMs generally form reproducibly, but are disordered; the 1,16–HDDT SAMs do not form reproducibly with identical preparation conditions, possessing a variety of adsorbate conformations.
thiolated molecule, the ‘guest’ adsorbate inserts into the defect sites of the host film, including Au grain boundaries, the edges of terraces, the substrate vacancies on the terraces, as well as domain boundaries and disordered regions of the host SAM [127]. In this instance, the presence of a host SAM will direct the $\alpha,\omega$-AkDT to insert in predominantly one orientation, where one –SH exchanges at the surface, and the other is at the top of the film, guided by the presence of host adsorbates in the $\text{trans}$ configuration.

Here, isotopic labeling experiments were performed to quantify the amount of $\alpha,\omega$-AkDT inserted into their host films by changing the host adsorbates to their perdeuterated forms. With the $d$-alkanethiolates as the host matrix, the kinetics $\alpha,\omega$-AkDT insertion could be followed using FT–IR spectroscopy; upon insertion of the protiated $\alpha,\omega$-AkDT, the decrease of C–D stretching modes was monitored with the concomitant increase of C–H stretching modes. The frequencies of the C–H (2800–3000 cm$^{-1}$) and the C–D (2000–2200 cm$^{-1}$) stretching modes do not overlap (Figure 6.7). As it is only the hydrogen atoms that are changed to deuterium atoms, one would expect minimal effects on the overall structure of the SAMs, as well expect minimal deviation from the behavior of the perhydroalkanethiolate SAMs ($\text{vide infra}$). Figure 6.9 shows a schematic of the insertion of $\alpha,\omega$-AkDT into different length $d$-SAMs, 1,8–ODT into a D8 SAM and 1,16–HDDT into a D16 SAM.

Figure 6.10 shows the C–H region of the IR spectra for both 1,8–ODT and 1,16–HDDT inserted into D8 host SAMs, as well as 1,16–HDDT inserted into a D16 matrix. Figure 6.10A shows the insertion of 1,8–ODT into D8 host SAMs for both 4 and 16 h (red and blue traces, respectively). The amount of 1,8–ODT inserted for 4 h varies within 9%, where as the variation between measurements for the 16 h case increased to 16%. The frequency of the –CH$_2$– asymmetric stretch was measured to be 2927 cm$^{-1}$, indicating that the inserted 1,8–ODT molecules are not
Figure 6.9. Schematic of $\alpha,\omega$-AkDT inserted into perdeuterated $n$-alkanethiolate host SAMs, (A) 1,8–ODT inserted into a D8 SAM, and (B) 1,16–HDDT inserted into a D16 SAM (C = purple, D = blue, H = white, S = green).
in an all \textit{trans} configuration, which would be expected for a short-chain host matrix and a flexible ‘guest’ molecule prone to disorder. The measured \(-\text{CH}_2\)– asymmetric stretching frequency for a \textbf{C8} SAM deposited from the solution phase for \(\sim 24\) h is \(2922.6 \pm 0.4\) cm\(^{-1}\). Shorter length alkanethiolate SAMs are more prone to \textit{gauche} defects, which increase the frequencies of the \(-\text{CH}_2\)– stretching modes; thus, a frequency of \(2927\) cm\(^{-1}\) would indicate that some order is retained in the host–guest assembly with inserted \textbf{1,8–ODT}.

Figure 6.10B shows the FT–IR spectrum for \textbf{1,16–HDDT} inserted into shorter-chain \textbf{D8} host matrices. The fractional surface coverage has increased, as indicated from the increase in the absorbance and which is expected from previous studies showing that longer-chain thiols outcompete shorter-chain thiols for the surface [21]. However, the frequency of the \(-\text{CH}_2\)– asymmetric stretching mode was measured to be \(2929\) cm\(^{-1}\), indicative of some disorder within the film. This is to be expected, as the remainder of the inserted \textbf{1,16–HDDT} adsorbates protruded from the host matrix and they may either be aggregated together to maximize van der Waals interactions, or they could be laying across the surface of the film in a variety of conformations.

Figure 6.10C shows the FT–IR spectrum of the insertion of \textbf{1,16–HDDT} into a host matrix of the same length, \textbf{D16}. In this instance, the fractional surface coverage was lowest compared to the other host–guest assemblies, as there is a large entropic barrier to insertion of 16 methylene units into a host matrix that is very well ordered and has few defects other than those from the Au substrate. The inserted \textbf{1,16–HDDT} retained the order of the \textbf{D16} matrix, showing a \(-\text{CH}_2\)– asymmetric stretching frequency of \(\sim 2919\) cm\(^{-1}\), which is comparable to the order of a \textbf{C16} SAM formed from the solution phase with few \textit{gauche} defects.

The effects of solvents were explored in the insertion processes to see if the amount of \(\alpha,\omega\)–\textbf{AkDT} insertion could be increased or if the order could be optimized. Ethanol, \(\text{CH}_2\text{Cl}_2\), and
Figure 6.10. Infrared spectra of (A) 1,8–ODT inserted into D8 host SAMs for 4 and 16 h, (B) 1,16–HDDT inserted into D8 host SAMs for 4 and 24 h, and (C) 1,16–HDDT inserted into D16 host SAMs for 4 and 24 h. Red traces: 4 h; blue traces: (A) 16 h, (B) and (C) 24 h.
2,2,4-trimethylpentane (isooctane) were all used as solvents for inserting the α,ω-AkDT. Figure 6.11 shows the FT-IR spectra for the insertion of α,ω-AkDT into D8 matrices. Generally, it was observed that insertion was facilitated using EtOH as the solvent; insertion was not as effective using CH$_2$Cl$_2$. Isooctane did not offer any improvement in the insertion process, and was even observed to include itself in the monolayer from observed −CH$_3$ resonances after the insertion process.

Consistently observed across all experiments was that final monolayer products became less reproducible with longer insertion times, regardless of the solvent used. The 4 h insertion experiments possessed less variation in the fractional surface coverage than their 16 or 24 h counterparts.

Figure 6.12 shows the average behavior for the insertion of 1,16-HDDT into D8 and D12 host matrices, using either EtOH or CH$_2$Cl$_2$. D12 was chosen here as a compromise between D8 and D16, where the 1,16-HDDT may adopt the order of the D12 and has less of a chance of laying prone across the surface, disordered. Figure 6.12 shows that on average, 1,16-HDDT inserted in greater fractional surface coverage when EtOH was used, even for times as short as 4 h. Figure 6.12B shows the average insertion behavior of 1,16-HDDT into D12 host matrices, for either 4 or 24 h in either EtOH or CH$_2$Cl$_2$. The frequency of the −CH$_2$– asymmetric stretch is ∼2928 cm$^{-1}$, reducing to 2926 cm$^{-1}$ when the insertion process continued for 24 h in EtOH.

Films were subjected to thermal annealing in a 72 °C oven in their adsorption solutions to ascertain if the inserted films could be ‘pushed’ to an ordered final product. Figure 6.13 shows the thermal annealing of the SAMs shown in Figure 6.12. After 6 h of annealing the D8 and 16 h of annealing the D12 SAMs, the spectra generally converged to one form, with a −CH$_2$– asymmetric stretch of 2929 cm$^{-1}$. The frequency of this vibrational mode was higher than expected; although the fractional surface coverage was pushed close to unity (89 ± 4%), defects may have
Figure 6.11. Infrared spectra showing the solvent dependence upon insertion of either 1,8–ODT ((A) and (B)) or 1,16–HDDT ((C) and (D)) into D8 host matrices for 4 and 24 h. Generally, there is less insertion from the CH$_2$Cl$_2$ solutions. Blue traces: insertions from EtOH; red traces: insertions from CH$_2$Cl$_2$. 

Blue traces: 4h, EtOH
Red traces: 4h, CH$_2$Cl$_2$ 

Blue traces: 24h, EtOH
Red traces: 24h, CH$_2$Cl$_2$
Figure 6.12. Infrared spectra showing the average insertion behavior of 1,16–HDDT into (A) D8 and (B) D12 host matrices, for either 4 or 24 h from either EtOH or CH₂Cl₂ as indicated. Fractional surface coverage is sacrificed for an improvement in film order.
been introduced to the assembly through side reactions or cross-coupling of the tethers from the elevated temperatures.

A control experiment was performed inserting C16, the 1–alkanethiol analog of 1,16–HDDT into host matrices of D12, Figure 6.14. Most of the trends observed in the α,ω–AkDT experiments – preferential insertion when EtOH was used as the insertion solvent, irreproducible insertion with longer insertion times (24 h vs. 4 h), and convergence of the FT–IR spectra with vigorous thermal annealing (72 °C, 16 h) – were observed except for the indicator of order in the –CH2– asymmetric stretching frequency. For the thermally annealed C16 samples, the –CH2– asymmetric stretch measured at 2919 cm\(^{-1}\) is expected for a C16 in the all trans configuration, unlike the frequency observed for the annealed 1,16–HDDT SAMs (2929 cm\(^{-1}\)). This deviation from an ordered geometry indicates the complexity in the assembly of α,ω–AkDT, even when inserted into d–SAM host matrices, where a particular insertion geometry can be imposed.

6.4.3 Using Deuterated Alkanethiolates as Host Matrices

There has been a question as to the chemical and structural similarities between protiated and deuterated SAMs. Isotope effects have been reported to be distinguishable in the hydrophobic interactions between molecules [322–324]. Our preliminary data indicate that there are slight differences in the wettability of the surfaces, with d–SAMs having slightly lower advancing contact angles than for h–SAMs. The FT–IR spectra are different between the C–D and C–H stretching modes, with the C–D modes being relatively lower in intensity and significantly more broadened. The question arises if these subtle differences between the two types of SAMs has an effect on the insertion kinetics into h–SAMs vs. d–SAMs. Figure 6.15 is a series of STM images showing that there are only a few structural differences between C8 and D8 SAMs. Figure 6.15A is an STM image of a C8 SAM, and typical features such as step edges, substrate vacancies, and domain
Figure 6.13. Infrared spectra of thermally annealed SAMs where 1,16–HDDT has been inserted into either D8 or D12 host SAMs. The films generally converged to one spectrum, independent of host matrix chain length or annealing time.
Figure 6.14. Infrared spectra of the control experiment of inserting C16 into D16 host matrices: (A) and (B) show the amount of fractional surface coverage as a function of time and solvent; (C) and (D) show the fractional surface coverage and order after thermally annealing the samples in their insertion solutions for 16 h at 72 °C. Both sets of annealed samples converge to the same spectrum with a –CH₂– asymmetric stretching frequency of 2919 cm⁻¹, expected for a C16 in a mostly trans configuration.
boundaries are present; a few SAM domain boundaries were observed. It was observed across the experiments in both Chapters 5 and 6 that the number of domain boundaries in the monolayers decreased significantly when 3×fpt-EtOH was used as the deposition solvent.

Figure 6.15B is an STM image of a D8 SAM; few to no domain boundaries are present in this d–SAM. Also, ‘mottled’ areas of film disorder were more prevalent in the D8 SAMs than in their protiated analogs. These structural differences are of minimal concern as domain boundaries and terraces are not the main locations of adsorbate exchange; major structural defects such as grain boundaries dominate the exchange processes.

6.5 Conclusions and Future Directions

The formation of well ordered SAMs of α,ω–AkDT is of critical importance for their integration into structures and devices that would require reproducible and defect-free structures. This chapter has explored the preparation of α,ω–AkDT SAMs, ranging from SAMs of α,ω–AkDT deposited from the solution phase, to inserting α,ω–AkDT into n–alkanethiolate host matrices of varying chain length. Different solvents, temperatures, and chain lengths of α,ω–AkDT and host n–alkanethiolate host matrices were explored. It was found that α,ω–AkDT insertion was most effective when EtOH was used as the insertion solvent. Fractional surface coverage of the α,ω–AkDT decreased with increasing chain length of the n–alkanethiolate host matrix, but the order of the inserted α,ω–AkDT adsorbates increased or was preserved with the order of the host matrix. Fractional surface coverage was found to be less reproducible with longer insertion times. Thermal annealing appeared to push the α,ω–AkDT SAMs to one convergent structure, but the frequency of the –CH2– asymmetric vibration indicated that the film was not entirely ordered.
Figure 6.15. Scanning tunneling microscope images of a (A) C8 SAM, (B) D8 SAM, and (C) and (D) a C8:D8 SAM formed from an ethanolic equimolar deposition solution. There were few to no domain boundaries in the D8 SAM, and a decreased number in the codeposited SAM relative to a single component SAM of C8. Although the films appear to be different on the scale of tens to hundreds of nanometers, images of molecular resolution cannot distinguish between the two adsorbates (C). Tunneling conditions: (A) $V_{\text{sample}} = -1$ V, $I_{\text{tunnel}} = 5$ pA, 1200 Å × 1200 Å; (B) $V_{\text{sample}} = -1$ V, $I_{\text{tunnel}} = 5$ pA, 900 Å × 900 Å; (C) $V_{\text{sample}} = 1$ V, $I_{\text{tunnel}} = 10$ pA, 350 Å × 350 Å; (D) $V_{\text{sample}} = -1$ V, $I_{\text{tunnel}} = 5$ pA; 1500 Å × 1500 Å.
To continue to optimize the preparation of these $\alpha,\omega$-AkDT-containing SAMs, parameters including adsorbate concentration and less dramatic thermal annealing treatments should be explored. The increased concentration of $\alpha,\omega$-AkDT could drive the films to greater order and to continue to increase the fractional surface coverage. Gentle thermal annealing treatments may allow for the pathways of ordering to be more observable.
Chapter 7

Conclusions and Future Outlook

This thesis has described the precise control of the structure, placement, and measurement of nano-scale structures. These chapters have discussed experiments that test the boundaries of controlling the environment and organization of molecules on surfaces, and measuring the electronic spectra of precisely constructed gold clusters attached to such molecules.

7.1 Phase Behavior and Controlled Placement of Amide-Containing Alkanethiolate Adsorbates

Chapters \([3]\) and \([4]\) described how tightly controlled intermolecular interactions within \(n\)-alkanethiolate SAMs have been used to manipulate film structure and properties. Substitution of an amide bond for two methylene groups in the hydrocarbon chain of the \(n\)-alkanethiol adsorbates of a SAM increased the interaction energy of the film, as short-range van der Waals forces were replaced by higher energy, directional hydrogen bonds. These amide-containing adsorbates were found to phase separate from their \(n\)-alkanethiol homologs when codeposited on a surface from the solution phase. Varying the mole fractions of the adsorbates in the deposition solution showed that the amide-containing molecules aggregate on the surface together in geometries directed by the orientation of the amide groups; however, when in low mole fraction in an \(n\)-alkanethiol diluent, they tended to remain in solution with the weakly hydrogen bonding solvent.

With an understanding of how tuning the intermolecular interactions of single adsorbates from high (inclusion of hydrogen bonds) to low (van der Waals only) can be used to control the organization of molecules on surfaces, these amide-containing molecules were integrated into \(\mu\)CP
experiments. The directionality imposed by inter-adsorbate hydrogen bonding may assist in increasing the sharpness of the boundaries between groups of molecules placed on surfaces. Scanning tunneling microscopy was used to analyze the spatial distribution of these molecules at the nanometer scale, and to measure the sharpness of boundaries between groups of molecules placed on the surface. Scanning tunneling microscopy was also used to examine the quality of short-chain \( n \)-alkanethiolate SAMs (here, \( n \)-decanethiolate) formed by \( \mu \)CP; the amide-containing adsorbate was integrated into the \( \mu \)CP process as both a printing and a backfilling adsorbate. Printing full SAMs of the amide-containing adsorbate from the solid phase has been unsuccessful to this point, demonstrating the importance of the presence of solvent in forming high-quality monolayers. Not only do the amide-containing adsorbates not form well ordered SAMs when printed by \( \mu \)CP, but they lift off the surface almost completely to be solvated during backfilling processes.

The research described in Chapters 3 and 4 has resulted in the following publications:


Chapter 5 described the measurement of the electronic spectra of ligand-stabilized undecagold clusters \( \text{Au}_{11} \) and nanoparticles \( \text{Au}_{101} \) immobilized upon \( n \)-alkanethiolate SAMs (in particular, C8) via \( \alpha,\omega \)-alkanedithiol tethers (1,10-DDT). Significant and reversible spectral diffusion was observed within a single cluster or nanoparticle, as well as across several particles. The diffusion showed that the Coulomb blockade region varied across an order of magnitude, a much greater dispersion than would be expected for clusters and nanoparticles of these sizes, 0.8 nm and 1.4 ± 0.4 nm core diameters. The variations in the Coulomb blockade region were more than could be accounted for by changes in the junction geometries alone. Measurements on the \( \text{Au}_{101} \) nanoparticles showed an expected change in the zero-conductance region as a function of particle size distribution.

We hypothesize that the nature of the spectral diffusion stems from the close chemical and physical coupling between charge transport and the particles’ chemical and physical environment. This hypothesis is supported by the ‘hopping’ nature of the spectra, as certain ‘families’ of spectra consistently and reproducibly appear throughout the measurements; this would be consistent with molecular motion that is constrained along a few particular pathways. Although the transport is dictated by geometrical considerations of the junction (particle size, thickness and composition of the barriers separating the particles from their current source and drain), molecular motion of the tether underneath the particle of interest may be causing the electrochemical potentials of the junction to be modulating as well. This coupling of charge transport to the particles’ chemical and physical environment must be taken into consideration when using self-assembly techniques to integrate these materials into nano-scale devices.

The research described in Chapter 5 has resulted in the following manuscript:
7.3 Preparation of Thiol-Terminated Interfaces: Self-Assembled Monolayers of $\alpha,\omega$-Alkanedithiols

Chapter 6 described the preparation of $n$-alkanethiolate SAMs containing $\alpha,\omega$-AkDT adsorbates. It is extremely difficult to prepare SAMs of $\alpha,\omega$-AkDT, as significant intramolecular competition exists between the –SH groups at each end for the Au surface, as well as from the flexibility of the alkyl chain, enabling a distribution of conformations. This variability in alkyl chain structure coupled with the pinning of –SH groups to the surface independent of the overlayer packing leads to SAMs with variable and ill-defined structures. A combination of ensemble and local probe techniques including STM, FT–IR, ellipsometry, and CAG have been used to examine the structure and quality of SAMs containing alkanedithiols; a variety of conditions were used in film preparation, including single-component solution-phase deposition, and insertion of the $\alpha,\omega$-AkDT from the solution and vapor phases into $n$-alkanethiolate host matrices.

We observe a dependence on film order with chain length of the $\alpha,\omega$-AkDT; generally, single-component films of shorter dithiols form more reproducibly (i.e., 1,8–ODT), though not with any particular degree of order. SAMs composed of longer dithiol molecules (i.e., 1,16–HDDT) do not form reproducibly. While they insert into $n$-alkanethiolate host matrices of similar length in an ordered manner as dictated by the order of the host matrix, they insert at low fractional surface coverage from the large entropic barrier to assembling into the host matrix. The amount of dithiol surface coverage when inserted into $n$-alkanethiolate host matrices can be tuned by the length of the dithiol and the length of the host matrix; experiments used FT–IR to measure the amount of dithiol inserted into perdeuterated host matrices. A complex interplay exists between the fractional
surface coverage of inserted dithiol and its order within the film; generally, film order is sacrificed for surface coverage when inserting $\alpha,\omega$–AkDT into host matrices that are shorter in length. The insertion procedures appear to be generally independent of the solvent used. Annealing of the SAM as well as increasing the fractional surface coverage of inserted $\alpha,\omega$–AkDT can be performed by a gentle increase in temperature. These experiments show that the flexibility and reactivity of the $\alpha,\omega$–AkDT adsorbates lead to SAMs with complicated structures and interfaces. Much remains to be understood about the kinetics of formation of these bifunctional adsorbates; they cannot be directly substituted for their 1–alkanethiol analogues.

The research described in Chapter 6 has resulted in the following manuscript:


7.4 Conclusions

The creation of nano-scale structures from the ‘bottom up’ is not a straightforward task; this thesis has demonstrated that the new properties emerging at these specific length scales demand thorough measurement and understanding before structures and devices created from self-assembled materials can progress forward. Having precise control over the placement and organization of molecules on surfaces will ultimately enable the creation of new devices and sensors with highly desirable properties – ultra-small and with optimized feature densities. Additionally, understanding the electronic properties of precisely designed, ultra-small materials placed on surfaces and how those properties couple to their physical and chemical environments will expand the function of many rapidly developing materials.
References

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