Substrate and Head Group Modifications for Enhanced Stability in Molecular Electronic Devices

Michael-Anthony Ferrato
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Substrate and Head Group Modifications for Enhanced Stability in Molecular Electronic Devices

by

Michael-Anthony Ferrato

A Thesis

Submitted to the Faculty of Graduate Studies through Chemistry & Biochemistry

in Partial Fulfillment of the Requirements for the Degree of Master of Science at the

University of Windsor

Windsor, Ontario, Canada

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Substrate and Head Group Modifications for Enhanced Stability in Molecular Electronic Devices

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Declaration of Co-Authorship

I hereby declare that this thesis incorporates material that is result of joint research, as follows: This thesis incorporates the outcome of the research undertaken in Dr. Tricia Carmichael’s research group. I acknowledge my colleague Dr. Michael S. Miller for assistance with raw molecular electronics data acquisition in Chapter 3. I acknowledge Andrei Zaharia, Dalia Kashash, and Rana Abduelmula for their assistance with sample preparation and raw data collection in Chapters 2 and 3. I am aware of the University of Windsor Senate Policy on Authorship and I certify that I have properly acknowledged the contribution of other researchers to my thesis, and have obtained written permission from each of the co-author(s) to include the above material(s) in my thesis. I certify that, with the above qualification, this thesis, and the research to which it refers, is the product of my own work.

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Abstract

Poor Self-Assembled Monolayer (SAM) stability is a barrier which impedes the incorporation of molecular layers as functional components in electronic device architectures. Here we investigate the molecular electronic characteristics of two well established approaches to enhancing SAM stability. In Chapter 2 we investigate the electrochemical modification of Au substrates by the underpotential deposition of silver monolayers (Ag$_{UPD}$). In Chapter 3 we study chelating dithiophosphinic acid (DTPA) head groups to anchor SAM molecules to substrates. Based on molecular electronic characterization using EGaIn Tip testbeds, we observed that Ag$_{UPD}$ substrates maintained the inherent electronic character of n-alkanethiolate SAMs, but reduced charge transport by almost 1 order of magnitude as compared with the same SAMs on bulk Au substrates. Similar molecular electronic characterization of (diphenyl)dithiophosphinic acid SAMs on Au substrates revealed that the DTPA head group induced a ~3 order of magnitude drop in charge transport as compared with analogous thiophenol SAMs.
Dedication

This thesis is dedicated to the memory of my father,

Lorenzo Ferrato
Acknowledgments

I would like to start by thanking my father, Lorenzo Ferrato, who passed away during the early stages of this Master’s degree. Dad, you always taught me to have confidence in myself and my abilities, and to put forth an honest effort. You might not have taught me a single thing about molecular electronics but you taught me everything I ever needed to know to be successful in life.

I would like to thank my mom, Maureen Ferrato, and my sisters, Eileen and Yolanda Ferrato, for their endless support, love and encouragement throughout the course of this Master’s degree. Together, we have had to embrace many changes over the course of the past three years, but we always managed to do so as a family and I hope that we always will.

I would like to thank my advisor, Dr. Tricia Carmichael, for her many years of mentorship and supporting my numerous pursuits, both in and outside of the lab. Had she not been so understanding, the thesis might have been completed much sooner. I will also be eternally grateful to her for providing me with the incredible opportunity, to spend a portion of this degree as a visiting research scholar, with the Whitesides group at Harvard University.

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<tr>
<td>θ</td>
<td>used to represent an angle or work function</td>
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<tr>
<td>ϕ</td>
<td>electron tunneling barrier height</td>
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<td>hole tunneling barrier height</td>
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<td>metal work function</td>
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<td>UPD adlayer coverage</td>
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<td>used to indicate a van der Waals interface</td>
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<td>4-mercaptopyridine</td>
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<td>standard silver redox potential</td>
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<td>template-stripped silver</td>
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<tr>
<td>AgUPD/AuTS</td>
<td>underpotentially deposited silver on a template stripped gold substrate</td>
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<tr>
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<td>CA</td>
<td>contact angle</td>
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<td>centimeter</td>
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<td>cm-1</td>
<td>wavenumbers</td>
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<tr>
<td>Symbol</td>
<td>Definition</td>
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<tr>
<td>m&lt;sub&gt;e&lt;/sub&gt;</td>
<td>electron mass</td>
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<td>micro Coulomb</td>
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<td>minutes</td>
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<td>millivolt</td>
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<td>even number of carbons in an alkyl chain</td>
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<td>odd number of carbons in an alkyl chain</td>
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<td>nanometer</td>
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<td>number of carbon</td>
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<td>asymmetric stretching frequency</td>
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<tr>
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<td>symmetric stretching frequency</td>
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<td>NOA</td>
<td>norland optical adhesive</td>
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<tr>
<td>OA</td>
<td>optical adhesive</td>
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<tr>
<td>p</td>
<td>probability</td>
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<td>q</td>
<td>charge of an electron</td>
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<td>(diphenyl)dithiophosphinic acid</td>
</tr>
<tr>
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<td>thiophenol or benzethiol</td>
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<tr>
<td>ppm</td>
<td>parts per million</td>
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<tr>
<td>RAIRS</td>
<td>reflection absorption infrared spectroscopy</td>
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<tr>
<td>R</td>
<td>rotated with respect to underlying lattice</td>
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<tr>
<td>RMS</td>
<td>root mean squared</td>
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<td>s</td>
<td>second</td>
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<td>σ</td>
<td>standard deviation</td>
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<td>SAM</td>
<td>self-assembled monolayer</td>
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<tr>
<td>STM</td>
<td>Scanning Tunneling Microscopy</td>
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<tr>
<td>TS</td>
<td>template-stripped or through space</td>
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<td>TB</td>
<td>through bond</td>
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<td>UPD</td>
<td>underpotential deposition or underpotentially deposited</td>
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<td>transmission barrier</td>
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<td>ultraviolet</td>
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<td>V</td>
<td>volt</td>
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Chapter 1

Introduction
1.1. A Brief History of Molecular Electronics

At its most fundamental level molecular electronics is defined as a field which seeks to incorporate organic molecules as functioning components in electronic circuits and devices. Motivation for research in the field is twofold, being both out of necessity and general scientific curiosity. With the inevitable end of Moore’s Law - which for half a century guided the exponential growth rate of computing power - many believe organic molecules, with their small dimension and diverse properties, to be the preeminent candidate to replace conventional inorganic silicon based electronics.\(^1\) Theoretically, if incorporated into a functional devices these “molecular circuits” made up of individual molecules, acting as everything from wires to switches to memory cells, have the potential to increase computing power by a factor of \(10^6\), as compared with present day state of the art standards.\(^1\) Furthermore, the ability of molecules to selectively self-assemble on surfaces opens up prospects of being able to fabricate high density devices with complex architectures without the need for expensive and time consuming lithographic steps which are ubiquitous in the modern day semiconductor industry. As such, many feel fundamental research in this area is critical to the further advancement of high performance low cost electronics. Another appealing aspect of the field lies in the diverse properties of organic molecules over which we have good synthetic control. It is possible that certain molecules might also possess new functionalities unrivaled by their inorganic counterparts and therefore research in the field is also motivated by a desire to discover and manipulate such novel effects.\(^1,2,3,5,27-30\)

Many trace the origin of molecular electronics to the 1974 paper published by Aviram and Ratner, in which they conceptualized the notion of a molecular rectifier.\(^26\) In their visionary paper, the authors proposed that by incorporating an aromatic electron rich and an aromatic electron poor moiety into the same molecule one could effective achieve a molecule that would rectify charge transport between two electrodes, as shown in Figure 1.1.\(^26\)
Figure 1.1 (i) The conceptualized molecular rectifier proposed by Aviram and Ratner. (ii-iv) are the energy level diagrams for three different biases applied to the junction: (ii) $V=0$, (iii) $V>0$ on the right side of the junction and (iv) $V>0$ on the left side of the junction. The molecule consists of three subunits: a tetracyanoquinodimethane “acceptor” unit on the left, a tetrathiofulvalene “donor” unit on the right and a triplet of bridging methylene units linking the two. Rectification was explained in terms of the forward bias sense (iii) and reverse bias sense (iv). In the forward sense at a threshold bias the Fermi level of the left electrode would overlap with the lowest unoccupied orbitals on the acceptor unit (B), and the highest occupied orbitals on the donor unit (C) would overlap with the Fermi level of the right electrode leading to charge transfer and unpaired electron states on both acceptor and donor. Given their proximity, the final step in charge transport would occur via coherent intramolecular tunneling of an electron from the acceptor (B) to the donor(C). In the reverse bias sense (iv) the first step in charge transport would have to involve internal tunneling from (C) on the donor to (B) on the acceptor. The threshold voltage required for this step to occur would likely be higher than required for charge transport in the forward sense (iii) and therefore there would be a bias range where the molecule could rectify charge transport. Adapted from reference 26 Copyright (1974) with permission from Elsevier.
Although the rectifier proposed by Aviram and Ratner was based solely on semi-quantitative calculations and has thus far not been shown to rectify currents to any significant extent, the paper nonetheless introduced the concept of molecules acting as circuit components. Furthermore, it established what remains a core aspiration for the field: the facile manipulation of charge transport based on the rational design of synthetically achievable molecules.

While this objective is fairly straightforward, the scope of the field is rather broad in that the rational design and study of molecular junctions incorporates elements of materials science, surface chemistry, physical chemistry, supramolecular chemistry, quantum mechanics, organic chemistry, nanoelectronics and computational chemistry to name a few. In comparison to traditional semiconductor based electronics, progress in the field of molecular electronics has been relatively slow. Shortcomings of and incongruences between many of the testbeds used to study metal-molecule-metal junctions have left an incomplete understanding of the mechanisms and energy barriers that govern charge transport.\(^1,2,6,31\) For some time, differences in conductance observed between molecular junctions were routinely attributed to variations in molecular properties without sufficient statistical evidence to support the claim or without taking into consideration the electronic or physical properties of the junctions as a whole system (*both molecules and electrodes*). In fact, as recently as the start of this past decade it was not uncommon for prominent leaders in the field to issue statements along the lines of “it behooves one to heed a ‘know thy contact’ credo”\(^6\) and “It is therefore not meaningful to talk about the current-voltage characteristic of the molecule, but only the molecular junction.”\(^5\)

It has only been more recently, since the advent of more well-suited testbeds (discussed in greater detail in section 1.7. Molecular Junction Test Beds) and advancements in computational chemistry, that more emphasis has been placed on drawing conclusions from statistically robust data and treating molecular electronic junctions as a whole system rather than just as isolated molecules.\(^16,20,32,34\) Consequently, theoretical models of junctions and empirical evidence from
charge transport studies have begun to corroborate one another more frequently, indicating that, perhaps for the first time, significant progress is being made towards developing a comprehensive understanding of the governing parameters for charge transport across molecular junctions.  

1.2. Charge Transport across Molecular Junctions

Although there are many different types of junction geometries, it is convenient to describe molecular junctions as a metal-molecule-metal sandwich. Research in molecular electronics is differentiated from organic electronics – which seeks incorporates molecular layers as functioning components in devices such as organic photovoltaics and organic light-emitting diodes – in that the dimensions of the junctions investigated are small (≤ 10nm) and often only consist of one or two layers of molecules.¹ On account the small dimensions, charge transport across these types of junctions is dominated primarily by coherent non-resonant tunneling.¹⁴⁻⁶ Unlike conventional ohmic transport, charge tunnelling is non-dissipative (i.e. does not give off energy or heat), is independent of temperature and cannot be explained using classical mechanics. Tunneling is a purely quantum mechanical process which is often explained in terms of the wave-particle duality of matter. As shown in Figure 1.2., using classical mechanics if a particle finds itself on one side of an energy barrier and does not have the energy to get over said barrier, it will not. It might get reflected by the barrier or even absorbed by the barrier, but it is forbidden for the particle to cross to the other side of the barrier. Treating the same scenario using quantum mechanics, the wavefunction of the particle must be continuous at the barrier; it will decay exponentially inside the barrier; it will be vastly reduced on the other side of the barrier but it will still be continuous and it will still exist. Consequently, there will be a finite probability of finding the particle on the other side of the barrier.⁵¹² Applying the quantum mechanical barrier model to the molecular junction system we get the energy level diagram shown in Figure 1.3.
In the classical mechanical model a particle with energy $E_0$ approaches a barrier of height $U_0$. If $E_0 < U_0$, therefore the particle is reflected. If $E' = E_0$ the reflection is elastic, if $E' < E_0$ it is said to be inelastic. In the quantum mechanical model, the wavefunction of the particle with energy $E_0 < U_0$ approaches the barrier. The wavefunction stays continuous through the barrier but decays exponentially as it does so. On the right side of the barrier the amplitude of the wavefunction is significantly reduced but not zero. Therefore there remains a finite probability of finding the particles on the right side of the barrier and these particles are said to have “tunneled” through the barrier.

**Figure 1.2** In the classical mechanical model a particle with energy $E_0$ approaches a barrier of height $U_0$. $E_0 < U_0$ therefore the particle is reflected. If $E' = E_0$ the reflection is elastic, if $E' < E_0$ it is said to be inelastic. In the quantum mechanical model, the wavefunction of the particle with energy $E_0 < U_0$ approaches the barrier. The wavefunction stays continuous through the barrier but decays exponentially as it does so. On the right side of the barrier the amplitude of the wavefunction is significantly reduced but not zero. Therefore there remains a finite probability of finding the particles on the right side of the barrier and these particles are said to have “tunneled” through the barrier.
In the diagram a molecule is sandwiched between two bulk metal electrodes. When the junction is formed the Fermi levels—the highest occupied orbital of the valence electron band at 0K—of the bulk metals are situated between the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) of the molecule. If this is not the case initially (i.e., Fermi level is below the HOMO or above the LUMO), charge transfer will occur to or from the metal until this scenario is realized.\(^5\) When electrons (holes) to go from the Fermi level of one electrode to the other they travel along the LUMO (HOMO) and therefore must overcome a barrier height of \(\phi_e\) (\(\phi_h\)), which is the difference between the metal fermi level and the
LUMO (HOMO). Because the energy of the Fermi level is lower (higher) than the LUMO (HOMO), under classical mechanics the electron (hole) would not have sufficient energy to overcome the barrier and reach the LUMO (HOMO) and there would be no charge transport across the junction. However, on account of quantum mechanics and tunneling, charge transport does occur and the rate is determined by the Simmons approximation (eq 1):\[ J = \frac{q}{4\pi\hbar d^2} \left\{ \left( \phi - \frac{qV}{2} \right) \exp\left( -\frac{2d\sqrt{2m_e\phi}}{\hbar} \sqrt{\phi - \frac{qV}{2}} \right) - \left( \phi + \frac{qV}{2} \right) \exp\left( -\frac{2d\sqrt{2m_e\phi}}{\hbar} \sqrt{\phi + \frac{qV}{2}} \right) \right\} \] where \( J \) is the current density, \( q \) is the electronic charge, \( \hbar \) is the reduced Plank’s constant, \( m_e \) is the electron’s effective mass, \( V \) is the applied bias across the junction, \( \phi \) is the tunneling barrier height and \( d \) is the barrier width. In the low bias regime the barrier is assumed to be rectangular (as is shown in Figure 1.2.) and eq 1 can be reduced down to:

\[ J \propto V \exp\left( -\frac{2d\sqrt{2m_e\phi}}{\hbar} \right) \] (2)

Simplifying this even further for a given molecular system at a given bias, \( V \), we get the simple Simmons equation:\[ J = J_o \exp^{-\beta d} \] (3)

The \( \beta \) term is commonly referred to as the decay coefficient and describes the exponential rate of decay is current density across the junction in terms of molecular length, \( d \). The \( J_o \) term is a constant term and is representative of the effective contact/interfacial resistance within the junction. Alternatively, it can also be thought to be the theoretical current which would arise given a molecule of no length. The simplified Simmons equation is undoubtedly a generalized picture of a tunneling junction and fails to capture many junction intricacies, such as image potentials on the bulk metal that round tunneling barriers and reduce effective thickness, and
asymmetries in the barrier heights caused by the HOMO and/or LUMO not being delocalised over
the full extent of the molecule. Nevertheless, it does capture the quintessential exponential decay
of J with d, characteristic of the tunneling process, and reporting of the parameters J_o and β still
remains a common and useful method of describing charge transport across a molecular series in
literature.

It should also be noted at this point that although charge transport occurs via coherent non-
resonant tunneling – meaning that it is not coupled with any nuclear motions, never actually
resides in any molecular orbital, and electron spin and phase are conserved – it does follow a
“through bond” as opposed to “through space” path. This concept is particularly relevant in
studies involving ensemble junctions, which can comprise several to several thousand molecules
in parallel. As illustrated in Figure 1.4., the molecules within the junction are tilted and electron
transport can occur via three different paths: A “through bond” (TB) path along the σ- or Π-
bonding orbitals along the backbone of the molecule, a “through space” (TS) path directly from
one electrode to the other and an “interchain” (IC) path which is essentially a TB path with a
lateral TS hop. Experimental studies involving n-alkanethiolate monolayers tilted at various
angles have shown that charge transport occurs almost exclusively via the TB path, with minimal,
if not negligible, contributions from the IC path. Relating this to the energy level diagram in
Figure 1.3., the barrier height for electron transport via the TS path is equivalent to the metal work
function, $\phi_{wf}$; the difference between the Fermi level and the vacuum level. This is significantly
larger than the barrier for electron transport $\phi_e$; the difference between the electrode Fermi level
and the LUMO. Consequently, Slowinski et al. postulated that the β for the “through bond” path
across n-alkanethiolate molecules to be 0.91 Å⁻¹, as compared to 1.31 Å⁻¹ for the “through space”
path. Therefore, despite being the shortest path to charge transport the “through space” path
simply is not favoured. This should hold provided the tilt angle of the molecules is not too
extreme.
Figure 1.4 Schematic of the different possible path for charge transport. (a) The “through bond” path, (b) the interchain path and (c) the through space path. Reproduced from reference 6. Copyright (2003) with permission from John Wiley and Sons.

1.3. Factors Affecting $J_0$ and $\beta$

While we have yet to reach the level of control over molecular transport predicted by Aviram and Ratner, certain changes in molecular structure have been shown to significantly influence charge transport. In particular aromatic/conjugated molecules have been shown to conduct charge significantly better than their aliphatic/saturated counterparts.\textsuperscript{1,14,15,37,40-49} This can be understood in terms of the factors that influence $\beta$ within junctions, these being the effective electron mass, $m_e$, and the barrier height $\phi$. Conjugated molecules inherently have delocalised electronic structure and $\Pi$-orbitals tend to be spread over multiple atomic nuclei. This delocalised nature of the $\Pi$-electron density results in an effective electron masses of $\sim 0.3m_e$, which is significantly less than that observed for electrons in less delocalised $\sigma$-orbitals in aliphatic systems or for free electrons in vacuum, $m_e$.\textsuperscript{1,50} Furthermore, the HOMO-LUMO gap for conjugated systems (3-5eV) is much less than for aliphatic systems (7-9eV) and as such it is very likely that the distance between the metal fermi and the closest frontier orbital is smaller for
conjugated molecules (i.e. $\phi$ will be smaller for conjugated systems).\textsuperscript{6,24,51} These factors combined, explain why $\beta$ values for most aromatic systems are typically $0.2 - 0.61$ Å\(^{-1}\); significantly less than the accepted literature range for aliphatic systems, $0.73 - 0.89$ Å\(^{-1}\).\textsuperscript{15,16,24}

Even small disruptions in conjugation have been shown to have dramatic effects on charge transport across junctions.\textsuperscript{1,6,24,49,52-55} In their study Sedghi et al., found the beta value for an extensively conjugated system of porphyrin rings increased by an order of magnitude in going from the “fused tape” structure shown in Figure 1.5A, where conjugation was maintained throughout the entire structure of the molecule, to the “twisted ring” structure shown in Figure 1.5B.\textsuperscript{54}

\begin{figure}
\centering
\includegraphics[width=\textwidth]{molecular_structures.png}
\caption{Molecular structures of the (A) “fused tape” porphyrin molecules and the (B) “twisted” ring molecules. Adapted with permission from reference 56. Copyright (2012) John Wiley and Sons.}
\end{figure}
While \( \beta \) values for a particular molecular system are typically consistent across multiple test beds, \( J_o \) values have been shown to vary depending on the specific junction used and especially between single molecule and ensemble test beds.\(^{16}\) Factors which lead to subtle variations between these paradigms will be discussed in more detail in section 1.7 Molecular Junction Test Beds, but the largest discrepancies in \( J_o \) values typically arise due to differences in effective contact area.\(^{16}\) For single molecule test beds such as scanning tunneling microscopy (STM)\(^{21,53,56,57}\) and break junctions,\(^{20,58,59}\) effective contact area is fairly straightforward to decipher as it literally consists of a single molecule. For ensemble approaches such as vapour deposited top contact,\(^{50,60,61}\) polymer top contacts,\(^{62}\) cross wire junctions,\(^{14,63,64}\) and mercury\(^{65,69}\) and eutectic gallium indium (EGaIn)\(^{15,16,19,33,70-78}\) drop methods determining contact area is more complicated. For instance, in the case of the EGaIn drop technique, surface roughness of the EGaIn tip and underlying metal substrate upon which self-assembled monolayers (SAMs) were formed, were found to produce effective electrical contact areas which were only 0.01\% of the observed geometrical contact.\(^{16}\) Naturally, this led to reported \( J_o \) values for EGaIn tip studies which were \( \sim 10^{-4} \) smaller than those reported for STM studies for analogous systems.\(^{16,17}\)

Apart from effective contact area, the other junction parameter, that has a crucial influence on interfacial resistance, and thus \( J_o \), is the way in which molecules interact electronically with electrodes.\(^{5,7,79}\) Molecules that are chemically bound or electronically coupled to electrodes conduct charge significantly better than analogous molecules that are only in physical contact. In the case of alkanethiolate based systems, numerous paradigms (both ensemble and single molecule) have observed that current densities across alkanedithiolates, which can be chemically bound to both top and bottom electrodes, are up to three orders of magnitude higher than conventional alkanethiolates, which can only be chemically bond to a single electrode.\(^{2,12,80,81}\). For fully conjugated molecules, the presence of chemical contact is less significant than for aliphatic systems, but still results in a \( \sim 1-2 \) order of magnitude increase in conductivity.\(^{6,48,64,82}\) The reason
Introduction

for this is that, even without covalent bonding, \( \pi \)-electron density from conjugated molecules can overlap with electron density from metal electrodes, allowing the two to interact and couple. Both theoretical and experimental studies have shown that insertion of a single aliphatic carbon in-between electrodes and the conjugated portion of a molecule is sufficient to disrupt coupling between the two moieties, resulting in a significant decrease in \( J_o \).\textsuperscript{37,83}

1.4. Expanding the Molecular Junction Model: Asymmetric Barrier Heights

Controlling conjugation and electrode coupling have allowed researchers to tune molecular junction transport to a certain extent, but thus far, little else has emerged that provides a handle for fine tuning junction behavior to the extent initially envisioned by Aviram and Ratner. By and large, experimental and theoretical studies have shown subtle changes to molecular geometries and electronic structures simply do not significantly influence charge transport. Studies by Whitesides et al. have revealed that tunneling currents through Metal-Molecule//EGaIn junctions were insensitive to numerous tail groups,\textsuperscript{74} head groups,\textsuperscript{51,70} internal polar groups\textsuperscript{73} and even metal substrates possessing different work functions.\textsuperscript{72} Some of the molecules which were found to have tunneling currents indistinguishable from analogous n-alkanethiolate SAMs (Figure 1.6, #30) are summarized in Figure 1.6. and includes: n-alkanethiolate SAMs with various aromatic (Figure 1.6, #1-7), aliphatic (Figure 1.6, #8-12) and polar tail groups (Figure 1.6, #14-27); n-alkanethiolate SAMs with polar amide, R-NC(O)R, linkages inserted in the middle of alkyl chains (Figure 1.6, #1-13); and aliphatic SAMs with carboxylate, RCO\(_2\), and acetylene, RCCH, head group (Figure 1.6, #28-29).
Figure 1.6 Charge densities across SAMs of molecules #1-29 were measured using the EGaIn Tip test bed and were found to be indistinguishable to charge densities across analogous n-alkanethiolate SAMs (#30) of similar length. Figures 1.6. (1-13) Adapted with permission from reference 74. Copyright (2012) with permission from John Wiley and Sons. Figures 1.6. (#14-27). Adapted with permission from reference 73. Copyright (2013) American Chemical Society. Figure 1.6 (#27-30) Adapted with permission from reference 51. Copyright (2015) American Chemical Society. 51
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In order to understand the lack of influence of the various functional groups it is necessary to expand upon the schematic for molecular junctions initially presented in Figure 1.2. In reality, molecular junctions do not always present simple rectangular symmetric tunnelling barriers, but can also exist as asymmetric multi-barrier systems. In these instances, which typically arise for molecules that are neither fully aliphatic nor conjugated, the tunnelling barrier is not just the HOMO (LUMO), but the ensemble of highest occupied (lowest unoccupied) molecular orbitals which together cover the width of the junction, which we will refer to as HOMO* (LUMO*). This concept was well illustrated in a study by Liao et al., who observed that by combining aliphatic and aromatic subunits into a molecule with a carboxylate head group bound to Ag, the individual moieties contributed differently and independently to the tunnelling barrier. The schematic they proposed for the molecular junction and relative barrier heights for each subunit are shown in Figure 1.7. Based on this two barrier system, they were able to expand upon the simple Simmons equation and successfully described current densities across the junction using the relationship: \( J(V) = J_0(V) \exp \left( -\beta_1 d_1 - \beta_2 d_2 \right) \), where \( \beta_i \) and \( d_i \) were the tunnelling decay coefficients and lengths, respectively, for the aliphatic and aromatic portions of the molecule.
Figure 1.7  Schematic of the molecular junction and asymmetric tunneling barrier proposed by Liao et al., in their study on multi barrier junctions. They were able to describe current densities through junction using an expanded version of the simple Simmons equation: $J(V) = J_0(V) \exp \left( -\beta_1 d_1 - \beta_2 d_2 \right)$, where $\beta_i$ and $d_i$ are the tunneling decay coefficient and length for the aliphatic and aromatic portions of the molecule. Reproduced with permission from reference 24. Copyright (2015) American Chemical Society. 

With this view of multi-barrier junctions in mind, Mirjani et al. performed density functional theory (DFT) studies on molecules 1-13 from Figure 1.6. and standard n-alkanethiolate SAMs, in order to provide a theoretical explanation for the insensitivity of charge transport observed. They reached three important conclusions: 1) The HOMO/HOMO* energy levels were closer to the Fermi level of the electrode than those of the LUMO/LUMO*, therefore charge transmission occurred via hole tunneling. 2) Charge transport can be significantly influenced by coupling between molecule and electrode due to a broadening of the molecular levels, however for the cases studied there exist no large discrepancies in interfacial coupling interactions. 3) In all cases the HOMO was localised on the Metal-Head Group bond and the energy levels were relatively unchanged. Therefore charge transmission was mainly determined by tunneling through the rest of the molecule which consisted predominantly of long aliphatic carbon chains.
The first conclusion - that the charge transport occurs primarily through hole tunneling for n-alkanethiolate like molecules - has been corroborated by numerous other studies and stems from the fact that the HOMO* energy levels for aliphatic carbon chains (~ -7.8eV), the primary barrier element, is closer to the Ag Fermi level (~ -4.5eV) than the LUMO* for aliphatic chains (~ -2 eV).\textsuperscript{12,13,51,79,84}

The second conclusion is simply a reiteration of the point made earlier in this chapter, that coupling between molecules and electrodes significantly enhances charge transport across junctions. For molecules 1-27 in Figure 1.6, all have essentially the same coupling to the bottom electrode (all are bound via Ag-S). The fact that molecules 28 and 29, whose heads groups are vastly different both geometrically and electronically, were also indistinguishable from n-alkanethiolates based on electron transport studies, implies that, for the molecules tested, the exact nature of the metal-head group interaction has little effect on interfacial resistance; provided a covalent bond exists between molecule and substrate little modulation in current densities should be expected.\textsuperscript{51} With regards to coupling with the top contact, all molecules in the study were in van der Waals contact with the EGaIn tip electrodes.\textsuperscript{16} Theoretically, molecules with aromatic/conjugated tail groups that delocalise $\Pi$-electron density, could couple to the electron density of the EGaIn electrode, leading to better conductivity (higher $J_0$). However, a unique feature of EGaIn tips is that they possess a very thin (~0.7 nm) insulating $\text{Ga}_2\text{O}_3$ skin.\textsuperscript{16,33,34} As stated earlier, a single aliphatic methylene unit (<0.2 nm) is sufficient to decouple electrode electron density from conjugated molecular subunits,\textsuperscript{24,37,83,85} therefore coupling to the top electrode was also likely similar for all the molecules studied.

The final conclusion provides perhaps the best insight towards the insensitivity of charge tunneling. Given the relative length of the aliphatic carbon chains in the molecules studied as compared to the various aromatic and polar groups, and the fact that aliphatic barriers heights are typically larger than those associated with conjugated moieties, it seems reasonable that the
molecular orbitals along the carbon back-bone of the molecules would be the predominant element of HOMO* and the primary barrier to charge transport. A similar conclusion was drawn by Armstrong et al., who observed that for asymmetric tunneling barriers, if the length and/or height of one barrier became large relative to the other, transmission through the junction was essentially reduced to transmission through a single rectangular barrier.\textsuperscript{86} Sufficed to say, the insensitivity of charge transport through the molecules shown in Figure 1.6 was attributable to the overwhelming influence of the aliphatic chains, which masks any differences in tail, head and/or internal functional groups and causes junctions to behave like pseudo-single barrier systems.\textsuperscript{35}

1.5. Expanding the Molecular Junction Model: Fermi Level Pinning

In lieu of the insensitivity of long aliphatic molecules, some have speculated that modifications of conjugated systems - which have smaller barrier heights and MOs that are delocalised over the entire structure - might prove more effective for the purpose of manipulating charge densities.\textsuperscript{35,50,87} Indeed, studies of conjugated oligo(phenylene ethynylene)s (OPEs), discussed in more detail below, have shown that modification to the metal-head group interaction and configuration can influence junction conductivity.\textsuperscript{8-10,88} However, further studies of conjugated systems have also shown that attempts to modulate charge transport using functional groups, generally suffer from a “leveling effect”, due to a breakdown of the Schottky-Mott rule.\textsuperscript{1,48,50,87} The Schottky-Mott rule was initially developed to describe barrier heights in metal/semiconductor contacts and states that \( \phi_e = E_f - E_{\text{LUMO}^*} \) and \( \phi_h = E_f - E_{\text{HOMO}^*} \) (refer to the simplified version of the molecular junction shown in Figure 1.3). The rule holds for molecular junctions provided no changes occur to the energy levels of either the Fermi or HOMO*/LUMO*, when molecules and electrodes are brought into contact.\textsuperscript{1} However, this is generally not the case
for paradigms in which molecules exhibit strong coupling and/or form ordered 2D dipole layers as a result of the molecule-metal bond dipole and/or the inherent dipole moment of the molecules.\textsuperscript{1,89,90}

Figure 1.8 illustrates what happens when an attempt is made to modify $\phi_h$ and $\phi_e$ by functionalizing a conjugated molecule with an electron withdrawing group. As shown, in Figure 1.8A, the addition of the electron withdrawing nitro group has the effect of lowering the HOMO and LUMO of an aromatic molecule in the isolated gas phase. According to the Schottky-Mott rule this should alter $\phi_h$ and $\phi_e$, and thus modify current density across the junction. However, as shown in Figure 1.8B, when the molecules are actually brought into contact with the electrode, electronic interaction and charge transfer results in the creation of a 2D dipole layer, which has the effect of changing the vacuum energy level across the junction.\textsuperscript{1,89} The change in the vacuum level essentially negates the initial effect of the electron withdrawing group and hinders any significant modification of the current density. Similar effects are observed for the addition of electron donating groups (opposite case to Figure 1.8) and other modifications to conjugated systems. In their study, Sayed et al. prepared a series of conjugated molecules with various functional groups and geometries.\textsuperscript{50} Based on the Schottky-Mott rule and using isolated gas phase energy levels of the HOMOs and electrode Fermi, they predicted that $\phi_h$ values, across the series of molecules would range from 0.69 to 2.99 eV. When the molecular junctions were formed, however, both conductivity measurements and ultraviolet photoelectron spectroscopy, confirmed that $\phi_h$ values for the series only spanned from 1.1 to 1.5 eV.\textsuperscript{50}
Figure 1.8  (A) Shows the isolated gas phase Fermi level of the metal, as well as the relative HOMO and LUMO energies of a generic conjugated molecule (benzene) and the same molecule functionalized with an electron withdrawing group (nitro group). (B) Shows the leveling effect which occurs when the modified molecules and electrode are brought into contact. The vacuum levels on the two sides of the junction are offset due to charge transfer interactions and the creation of a 2D dipole layer. This essentially negates the influence of the nitro group on charge transport. The HOMO and LUMO are used in place of HOMO* and LUMO* because it is assumed that for fully conjugated systems they are one in the same. Adapted from reference 1 with permission of the PCCP Owner Societies

This compression of the tunneling barrier is frequently referred to as Fermi level pinning, as the effect also extends to attempts to modify the Fermi energy of the electrodes. Metal substrates, commonly used as electrodes in molecular electronic studies, such as Ag, Au and Pt
have different Fermi levels: ≈ -4.5, ≈ -5.1 and ≈ -5.6 eV, respectively. Therefore, if one metal were substituted for another, if the Schottky-Mott rule were to hold, the substitution would effectively alter $\phi_h$ and $\phi_e$, and thereby $\beta$ as well. In contrast, numerous theoretical and experimental studies on aliphatic and aromatic systems incorporated into various single molecule and ensemble junction paradigms, have found that $\beta$ values are virtually independent of metal work functions and has led to the conclusion that altering the metal substrate is simply not a feasible means of controlling the tunneling barrier. It must be noted, that while metal electrode choice has little impact on $\beta$, it can impact $J_0$, however this seems to depend a great deal on the junction paradigm used. For instance, using an EGaIn tip paradigm Baghbanzadeh et al. found that current densities through a series of n-alkanethiolates on Au and Ag were indistinguishable from one another, but using CP-AFM, Engelkes et al. observed that resistance across the series drop more than an order of magnitude in going from Ag to Au electrodes. Likewise, Kim et al., who studied oligoacenes using CP-AFM, observed a similar drop in resistance in going form Ag to Au. The authors rationalized this observation in terms of a multi-barrier system, much like the one shown in Figure 1.7. According to this model, lowering the work function of the metal effectively reduced the charge injection barrier (equivalent to lowering the Ag/CO2 barrier in Figure 1.7 and increasing $J_0$), but tunneling was still governed by the HOMO* of the molecule, which was subject to Fermi level pinning and hence $\beta$ and $\phi_h$ remained independent of the metal. The reasons for why $J_0$ is sensitive to the metal electrode in certain junction paradigms, but insensitive in others, are still not well understood.

1.6. Interesting Molecular Electronic Phenomena

While the insensitivity of the above mentioned systems might seem discouraging, researchers have discovered several systems which do show promising behavior for applications
in molecular electronics. Conjugated OPEs have shown potential as molecular circuitry components and have exhibited practical electronic properties such as negative differential resistance (increase resistance with increased applied voltage), bistable conductance states (a basis for molecular memory) and reversible switching. In a particularly elegant feat of molecular engineering, Lewis et al., demonstrated good control over the bias dependant switching of modified OPEs, while simultaneously improving the stability of the “On/Off” states of the molecule. In their study, OPEs were modified with various functional groups to provide molecules with a range of dipole moments (both positive and negative) and these molecules were then inserted into the defect sites of amide containing n-alkanethiolate SAMs, as shown in Figure 1.9. Biases were then applied between an STM tip and the substrate, creating an electric field which interacted with the dipole moment of the molecules. Repulsive interactions resulted in OPEs tilting to the side into the more resistive “Off” state, while attractive interactions led to the molecule standing erect in the more conductive “On” state. The authors attributed the difference in the conductance between states, to a change in the hybridization of the S-Au bond from sp, in the upright “On” state, to sp³ in the more tilted “Off” state. They went on to elaborate that the former resulted in a lower contact resistance than the latter. Furthermore, by incorporating functional groups which could hydrogen bond with the surrounding SAM matrix, both the “On” and “Off” states remained stable for extended periods of time and stochastic switching was dramatically reduced.
Figure 1.9 Interactions of the dipole moment of a functionalized OPE with the electric field generated from the STM tip. The image on the left is the “On” state and is more conductive as shown by the height difference in the STM images inset. The “Off” state is shown on the right and is stabilized by hydrogen bonding to the amide group incorporated into the SAM. Adapted with permission from reference 23. Copyright (2005) American Chemical Society.

Spiropyran, spiroxazine, diarylethene, azobene and quinone derivatives have also shown promise as potential molecular switches. Much like the study by Sedghi et al., presented in Figure 1.5, differences in conductivity between the “On” and “Off” state in these types of molecules depend critically on configurations and the extent of conjugation. However, unlike the Sedghi study, instead of forcing specific configurations through chemical modification, these molecular switches possess stable conformers or isomers which can be reversibly accessed via external stimuli. Using ultra-violet and visible light Kumar et al., demonstrated the reversible switching of azobenze-functionalized molecules which were isolated in SAM matrices, as shown in Figure 1.10. As one might expect, the trans conformation, where extended conjugation was maintained, was determined by STM analysis to be the more conductive (“On” state) of the two conformers. In addition to photoisomerization, studies have also demonstrated reversible
switching in conjugated system using other forms of external stimuli including electron injection and applied electric fields.

Moving beyond coherent non-resonant tunneling, molecular systems utilizing activated forms of transport such as charge “hopping” and resonant transport have also garnered interest. 11-(ferrocenyl)1-undecanethiol (SC\textsubscript{11}Fc) SAMs on Ag substrate have been reported by Nijhuis et al.,\textsuperscript{25,28,29} to show charge rectifying properties, with rectification ratios upwards of ~10\textsuperscript{2} observed using EGaIn test beds. While this ratio is significantly lower than those observed for standard inorganic based rectifiers (10\textsuperscript{5}), these small molecule rectifiers still represent a significant discovery and their self-assembly is compatible with current device architectures.\textsuperscript{86} A schematic of the junction, which was described in terms of a double barrier system comprising the ferrocene and alkyl moieties, and the proposed mechanism of rectification are illustrated in Figure 1.11. As shown, when a bias is applied to the junction, the HOMO, which is localised on the ferrocene group, shifts along with the Fermi energy level of the EGaIn top electrode on account of a week coupling interaction. When a negative bias is applied to the EGaIn electrode, the HOMO ends up in an energy window in-between the Fermi levels of the two electrodes and can therefore participate in active charge transport. Nijhuis and colleagues went on to postulate that, in this window, charge transport would proceeded initially via electron tunneling from the HOMO (creating a Fc\textsuperscript{+} ion) to the Ag electrode through the C11 aliphatic chain, followed by an electron hopping step from the EGaIn electrode to the Fc\textsuperscript{+} moiety. The rate limiting step in the process would be the tunneling step through the C11 chain. In contrast, when a positive bias is applied, the HOMO on the Fc moiety never falls in between the electrode Fermi levels. In this scenario, charge transport would only proceed via hole tunneling through the entire width of the molecule, resulting in the markedly lower currents observed experimentally.\textsuperscript{25,28,29}
Figure 1.10  Schematic of the study performed by Kumar et al., which demonstrated the reversible photoisomerization of azobenzene-functionlized molecules in n-alkanethiolate SAM matrices on A(111). STM analysis confirmed that the trans conformation of the molecule was the more conductive of the two isomers. Reprinted with permission from reference 22. Copyright (2008) American Chemical Society.

Figure 1.11 Schematic of the rectifying mechanism for 11-(ferrocenyl)1-undecanethiol (SC11Fc) on template stripped Ag (AgTS) substrates. The rectification ratio, J(-1V)/J(1V), observed experimentally was ~10^2. The dotted red line indicates the charge transport paths. Reprinted with permission from reference 25. Copyright (2010) American Chemical Society.
Molecular junctions incorporating redox/hopping events such as the ferrocene example, as well as other systems incorporating moieties capable of undergoing stable redox exchanges such as phthaocyamine and porphyrin derivatives, are of great interest to researchers as their mechanisms for charge transport represent a fundamental departure from those of conventional conductor and semiconductor based electronics, and may also be conducive towards applications in molecular memory and switching.\textsuperscript{1,54,96-98} This and other forms of transport currently being investigated, which also depart from conventional mechanisms, such as ballistic resonant transport and field emission, typically take place on scales in-between that of conventional organic electronics (~10 nm) and the limits of coherent non-resonant tunneling (< 6 nm).\textsuperscript{1} Given the lack of versatility in modulating non-resonant coherent tunneling, many believe that the future of molecular electronics ultimately resides in phenomena associated with these “hybrid” forms of transport, which will afford molecular electronics unique advantages over their semiconductor counterparts.\textsuperscript{1}

1.7. Molecular Junction Test Beds

Molecular junction test beds can be effectively classified into one of two paradigms: single molecule junctions and ensemble junctions. Both paradigms present their own set of advantages and disadvantages, and both have evolved over time as knowledge of the parameters influencing charge transport has grown. When experimental research in molecular electronics finally became accessible in the late 1990’s it was largely dominated by single molecular paradigms which relied primarily on well-established scanning probe techniques, in particular STM. As they consist of single isolated molecules, these types of junctions represent the very limit of molecular electronic device dimension.\textsuperscript{1} Furthermore, compared with ensemble paradigms, they are relatively easy to treat theoretically on account of there being no
contributions from intermolecular effects or effective electrode contact areas. The insertion of individual molecules into SAM matrices,\textsuperscript{22,23} as shown in Figures 1.9 and 1.10, and break junctions,\textsuperscript{20,58,59} shown in Figure 1.12, are two of the more popular methods which use atomically sharp STM tips to probe the conductance of isolated single molecules. In the insertion technique, molecules of interest chemisorb onto substrates at defect sites in an already formed SAM matrix (typically n-alkanethiolates).\textsuperscript{10,23,99} The resulting surface is probed by STM and the molecules of interest typically appear as protrusions in the STM image. Absolute conductance values from these images can be tricky to interpret, as protrusion can arise due to a convolution of both molecular height and conductivity. Break junctions are formed by crashing and withdrawing STM tips from a substrate in situ, surrounded by the molecule of interest. Upon withdrawal the molecule/s insert/s in between the substrate and the tip completing the junction. Conductivity measurements from these test beds are easier to interpret, but do suffer from a great deal of variance associated with random and stochastic thermal variations in binding configuration and orientation.\textsuperscript{20,58,59}

Single molecule test beds continue to provide an excellent platform with which to study molecular electronics and have helped advance the field to the point where experimental and theoretically studies based on these paradigms have begun to agree reasonable well with one another. Where they lack, however, is that they are not compatible with parallel fabrication techniques, which would be required for low-cost manufacturing, should molecular circuitry components ever prove desirable and/or feasible.\textsuperscript{1} Furthermore, from a research perspective, the high cost (measurements are typically performed under ultra-high vacuum) and high level of user expertise required to perform experiments using these paradigms, make them inaccessible to a large portion of the research community and hinders progress.\textsuperscript{16}

In contrast, ensemble junctions, which generally take advantage of well-established self-assembly methods, are very amenable to current microelectronics processing methods.\textsuperscript{1,100} Furthermore,
because the junctions consist of anywhere from several hundred to several thousand molecules, measurements are typically subject to less variation because they represent an aggregate response.

There exist numerous types of ensemble test beds, and as discussed above, current density interpretations from these can be complicated by effects such as Fermi level pinning, differences between geometric and electrical contact, and intermolecular interactions. In spite of this, perhaps the greatest pitfall associated with this paradigm has been a misinterpretation of electronic phenomena due to the assumed physical integrity of junctions. In particular, the selection of a “top-contact”, which is a characteristic feature for the specific types of testbeds, has proven particularly problematic.

Early attempts to form top contacts by evaporating metal films directly onto a SAM, resulted in degradation of the SAM structure, penetration of metal atoms through to the underlying substrates, and ultimately current density measurements which were dominated either by defect sites in SAMs or short circuits due to metal filaments. Since then, several methods have emerged, which have attempted to resolve the issue of junction integrity with varying degrees of success, including: conducting polymer junctions, cross-wire junctions, conductive probe AFM (CP-AFM) junctions, and liquid metal junctions.

The implementation of a conductive polymer buffer layers, in-between the SAM and evaporated top contact has proven to be a particular reliable and reproducible technique to maintain junction integrity. It was recently demonstrated that this method could be integrated seamlessly with current microelectronics fabrication techniques to produce 20000 molecular electronic junctions in parallel with 100% yield; a rather significant achievement for the field.

Cross-wire and CP-AFM test beds typically contain a few hundred molecules in their junctions and use a conductive nanowire or an AFM tip as top contacts (AFM tips are have larger radii than STM tips, but otherwise the techniques can be thought of as similar), respectively. Most other types of ensemble junctions are over a significantly larger area and comprise several thousands of
molecules. Liquid metal top-contacts have also gained in popularity and allow for soft non-damaging conformal contact to be made with SAMs.

While not practical for the purpose of device integration, liquid metal top contacts are an attractive option for researchers because non-damaging contact helps ensure junction integrity, the equipment and materials require minimal start-up capital, the technique requires limited expertise from users, measurements can take place in ambient lab conditions, and the technique is amenable to the rapid collection of robust and statistically significant data sets. Initially, mercury drops were the top contact of choice for liquid metal studies, but recently EGaIn tips have emerged as better candidates owning their more well defined contact areas and higher junction yields (mercury drops are round, which leads to ambiguous contact areas and the liquid mercury also tends to penetrate SAMs and amalgamate with underlying metals, causing shorts and low junction yields). In the next section we discuss the EGaIn technique in greater detail, as this was the exclusive test bed used for all molecular junction studies reported in this thesis.
Figure 1.12  (A) Schematic of a repetitive break junction and the time dependant conductance across the single molecule paradigm.  (B) Histogram of the conductance of bipyridine molecules from the repetitive break junction experiment.  Reprinted from reference 21 with permission from A.A.A.S.\textsuperscript{,21}

1.8.  EGaIn Tips

EGaIn tip top contacts (and their precursor mercury drops) were developed with the intention of affording scientists a low-cost method to probe molecular layers with assured junction integrity.\textsuperscript{,16,33} Furthermore, the simple and efficient nature of the measurements was also
intended to make it easy for researchers to compile statistically robust data sets (using this
technique several hundred current-voltage scans across multiple samples can be collected within a
day). Therefore, it was anticipated that EGaIn junctions would help spur experimental research in
molecular electronics by making it more accessible to non-specialized groups, while at the same
time reducing erroneous reporting of molecular electronic phenomena, which was a problem in
the field and was primarily caused by reliance on statistically insignificant data or an assumption
of junction integrity.\textsuperscript{1,2,5,6}

Studies of well-established molecular systems such as n-alkanethiolate SAMs using EGaIn tip
top-contacts compare favourably with results for analogous systems using both single molecule
and other ensemble molecule paradigms, suggesting that these types of contacts are a suitable
option for molecular electronics researchers.\textsuperscript{16,27,33,72} Having said this, the EGaIn tip method is not
without its own set of idiosyncrasies and, as has been stated before, it behooves one to consider
the entirety of junction when interpreting data collected using this (or any other) method.

What makes EGaIn unique from other liquid metals, such as mercury, is that its exterior is coated
by a thin (~0.7 nm) self-limiting Ga\textsubscript{2}O\textsubscript{3} “skin”.\textsuperscript{16,17,19} This “skin” affords EGaIn non-Newtonian
properties that allow it to be extruded into a conical shape. Additionally, the oxide layer also helps
prevent EGaIn from amalgamating with other metals, and thus helps to reduce short circuits when
contacting molecular layers. Studies have shown that the resistivity of the oxide layer is negligible
compared to that of the molecules and therefore charge transport within these type of junctions is
still dominated by the molecules.\textsuperscript{16,17,19,34} The oxide layer does, however, impart micro scale
roughness to EGaIn tips which dramatically reduce contact area. Taking into account the
roughness of the EGaIn as well as the roughness of the underlying substrate, Simeone et al.,
determined that the effective electrical contact area for EGaIn tip with SAMs on ultra-smooth
template stripped metal substrates, was 0.01% the geometric contact areas as observed by optical microscopy.\textsuperscript{16} Naturally, this means that the absolute current densities reported for EGaIn tip studies are several orders of magnitudes smaller than for analogous studies using more conformal contacts and has led to the conclusion that EGaIn tip studies are best used for comparative, self-consistent physical-organic studies.

In addition to influencing effective contact area, $\beta$ values determined from EGaIn tip studies have also been reported to be particularly sensitive to the roughness and topography of the underlying metal substrate. In their study, Nijhuis et al. found that the $\beta$ value for series of n-alkanethiolate SAMs dropped significantly with increased root-mean squared (RMS) roughness of the underlying metal substrate and even fell outside of the accepted literary range for the series, as determined using other testbeds (0.9 -1.1 nC\textsuperscript{-1}).\textsuperscript{18,102}

In order to avoid erroneous reporting of molecular phenomena several methods have been developed to prepare ultra-smooth metal substrate for molecular electronics characterisation including: template-stripping\textsuperscript{66,103-106}, cold-welding\textsuperscript{107} and chemical mechanical planarization.\textsuperscript{108} Figure 1.13A shows a schematic of EGaIn junctions formed on a rough as-deposited substrate (asdep) and an ultra-smooth substrate. On asdep substrates, defect sites in the SAM caused by large step heights and grain boundaries cause thin area defect sites where ohmic transport can occur leading to joule heating. These “hot spot” tend to dominate the overall charge transport within junction and mask molecular properties.\textsuperscript{17} Comparatively, SAMs on the ultra-smooth substrate are more well-ordered, and have fewer defects. Current densities are therefore dominated by transport through the molecules.\textsuperscript{17,18,66} It should be noted, however, that for n-alkanethiolate SAMs “hot spots” have been shown to develop when EGaIn contacts become large (>960 $\mu$m geometric contact area), even if ultra-smooth substrates are used.\textsuperscript{17}
Typically, EGaIn tip experiments are performed in ambient lab conditions, although a recent study by Barber et al., demonstrated that current densities are unaffected if measured in environments of O₂, Ar and N₂. For a given molecular system, it is recommended that users collect data from multiple samples, using multiple tips per sample and collecting multiple junctions per tips. This helps prevent biasing data sets due to any one particular sample, tip or junction. The exact number of scans collected is left up to the user but the minimum reported is usually around ~300 current-voltage scans from at least two samples. It is also recommended that data collection take place within a 2 hour window of removing samples from solutions, in order to limit the impact of physisorbed adventitious organic matter on both the EGaIn tip and sample surface.

With the scans complete, current densities at a given voltage are fit to a log normal Gaussian distribution. The log normal distribution is used because the length of the tunneling path, \( d \), is said to follow a normal distribution and hence current densities will be log normal distributed as described in the modified version of the simple Simmons equation:

\[
\log J(V) = \log J_0 - 0.4343 \beta d
\] (4)

As shown in Figure 1.13B, plotting the mean log J(V) values (as determined by the Gaussian fit), against length for a particular series of molecules, one can easily determine \( \beta \) and \( J_0 \) values for the series, from the slope and y-intercept of the line of best fit, respectively.

Taking all these factors into account are what make EGaIn a rather ideal choice for a liquid metal top-contact, as it allows for: non-damaging contact with SAMs, well defined contact areas, high junction yields, a high throughput of sample scans and relatively straightforward data interpretation.
Figure 1.13  (A) Schematic of what an EGaIn tip contact might look like for a generic SAM on rough (left) and smooth substrates (right). Rough substrates tend to led to higher variability in current densities and lower yields than their smooth counterparts. They can even result in erroneous reporting of β values for a series of molecules studied. (B) Schematic of typical data treatment and analysis for a molecular electronics study of a series of molecules. On the left Log J(V) values at a given junction bias are fit to a Gaussian distribution. The Gaussian mean and standard deviation, represent by the red triangle, are used as the log J(V) mean and standard deviation for a given molecule in the series at said bias. These data points are then plotted vs molecular length (on the right) and their line of best fit (dotted line in the plot on the bottom right) is used to extrapolate the β and log J₀ values for the molecular series.
1.9. Scope of this Thesis: Methods for Enhanced Stability

Recent advancements in testbed paradigms and computational methods, as well as general progress in our understanding of the parameters affecting charge transport and the discovery of novel molecular electronic phenomena, has led many experts in the field to believe, that the ultimate hurdle to the real world integration of molecular electronics, will be the lack of stability currently displayed by the molecular components.\textsuperscript{1,4,11,109} Thiolated head groups, for instance, are commonly used in many molecular electronic studies to anchor SAMs to underlying gold substrates. These SAMs, however, have been shown to desorb at temperatures $\sim 50\, ^\circ\text{C}$; well below the operating temperature of modern day central processing units ($70\, ^\circ\text{C}$).\textsuperscript{1,109} Despite the serious limitations that this problem poses, there are relatively few reports in literature focusing on the development of molecular junctions capable of performing in a reliable and reproducible manner at temperatures and within environments commonly encountered in operating electronic devices.\textsuperscript{11,62,110}

The task at hand is not unrealistic. McCreery et al., incorporated diazonium derivative layers into patterned devices using conventional semiconductor fabrication techniques and demonstrated that said devices showed negligible changes to current densities after $10^9$ voltage cycle and withheld operating temperatures of $150\, ^\circ\text{C}$.\textsuperscript{109,111,112} They achieved this via electrochemical reduction of diazonium ions, which led to formation of radical molecules and subsequently resulted in the formation of strong irreversible covalent C-C bonds between the diazonium reagent molecules and a pyrolyzed photoresist carbon electrode. A schematic of one of these molecular layers being fully integrated into a functioning Si chip in this manner is shown in Figure 1.14. While this shows great progress, and was a significant achievement for the field, the technique is somewhat limited in the sense that it is only conducive to stable diazonium reagents, and the radical growth mechanism is difficult to control and often results in disorganized multilayer films.
Penner et al., also recently reported on carbon nanomembranes (CNM) which were said to possess enhanced thermal stability and mechanical strength for application in molecular electronics.\textsuperscript{11} In this process, CNM were formed by preassembling SAMs on a gold electrode and subsequently inducing intermolecular crosslinking, via electron bombardment.\textsuperscript{11,113} While potentially well suited for applications as molecular dielectric layers, the scope of these carbon nanomembranes (CNM) is also limited by the facts that it is only applicable to polyaromatic SAMs, and that the cross-linking steps results in an amorphous organic layer whose internal structure is not fully known.

\textbf{Figure 1.14} Steps in the parallel fabrication of carbon/molecule/Cu/AU molecular junction. Molecular layers were assembled via diazonium reduction, followed by a subsequent radical growth mechanism. Resulting monolayer were robust enough to withstanding electron beam deposition of metal top contact and still produced good device yields. Pictured are: (A) A 100nm Si/SiO\textsubscript{2} wafer after photoresist patterning and pyrolysis; (B) an individual chip with 32 junction “pads” and contact areas; (C) schematic of a fluorine molecular junction bound to the underlying photoresist pyrolyzed film (PPF) electrode and with evaporate metal top contacts; (D) Completed chip after packaging. Reproduced reference 1 with permission of the PCCP Owner Societies.
Apart from these ex-situ approaches, the only molecular approach, of which we are aware, towards the enhancement of SAM stability explicitly for the purpose of molecular electronic applications, was reported by von Wrochem et al., who studied the electronic properties of SAMs incorporating a chelating dithiocarbamate head group.\textsuperscript{110} We will discuss this approach in greater detail in Chapter 3.

Herein, we report on two different approaches towards SAM stabilization, with the aim of paving a route to more robust and reliable molecular junctions, while preserving the synthetic versatility afforded by thiolate bonds and the convenience of the self-assembly process. The first method - the underpotential deposition of a silver monolayer - involves an electrochemical modification to the substrate prior to the self-assembly process, whereas the second method involves the use of a chelating dithiophosphinic acid (DTPA) head group, capable of bonding to metal substrates in a bidentate manner. Throughout the course of demonstrating the molecular electronic viability of these stabilization methods, we also discuss/analyse tunneling phenomena associated with underpotentially deposited monolayers and the DTPA head group, as well as idiosyncrasies related to the EGaIn tip test bed.
1.10. References


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Chapter 2

Underpotentially Deposited Silver as a Substrate for the Enhancement of Molecular Junction Stability
Underpotentially deposited (UPD) films of Ag on Au (Ag\textsuperscript{UPD}/Au) offer numerous benefits as a substrate for self-assembled monolayers. SAMs prepared on Ag\textsuperscript{UPD}/Au are more stable towards oxidation, and thermal and electrochemical desorption compared to analogous SAMs prepared on either bulk Au(111) or Ag(111).\textsuperscript{1-7} Furthermore, unlike its bulk counterpart, Ag\textsuperscript{UPD}/Au films are resistant to etching and surface reconstruction upon SAM formation, leading to high quality films with fewer pits and step heights.\textsuperscript{8,9} These properties make Ag\textsuperscript{UPD}/Au films an appealing substrate for applications in nanoscience and molecular electronics, which require components to be stable throughout a range of temperatures and conditions. However, to our knowledge, SAMs formed on Ag\textsuperscript{UPD}/Au have yet to be characterised explicitly for their electronic properties. Herein, we report on the charge transport properties of a series of SH-(CH\textsubscript{2})\textsubscript{n}-1·CH\textsubscript{3} SAMs (n = 8, 10, 12, 14 and 16) on Ag\textsuperscript{UPD}/Au films prepared at +60mV (vs. Ag\textsuperscript{+}/0), and compare them to well-established results for the same series on bulk Au(111) and Ag(111) substrates. Using the EGaIn tip method as our testbed, we found that the decay coefficient, β, for the series of n-alkanethiolates on Au(111), Ag(111) and Ag\textsuperscript{UPD}/Au were 1.02 ± 0.07 nC\textsuperscript{-1}, 1.02 ± 0.03 nC\textsuperscript{-1} and 0.94 ± 0.03 nC\textsuperscript{-1}, respectively, all of which are in agreement with the accepted literature range of 0.9-1.1 nC\textsuperscript{-1} as reported for other testbeds.\textsuperscript{11,12} Interestingly, while current densities measured on Au(111) and Ag(111) were practically identical, current densities on Ag\textsuperscript{UPD}/Au were on average, ΔLog J (A/cm\textsuperscript{2}) = 0.71 + 0.15 less than the series on Au(111). The magnitude of the drop in the current density is consistent with an elongation of the charge tunneling path by the width of a single Ag atom (0.25 nm),\textsuperscript{13,14} therefore, we attribute the lower current density to the presence of the Ag\textsuperscript{UPD} layer and propose that this has the effect of increasing the width of the tunneling barrier compared to analogous bulk substrate systems. We believe these results are significant for the field of molecular electronics as they contribute to the further understanding of factors that govern charge transport while demonstrating that UPD substrates - with their enhanced stability - are a
viable option as a substrate for molecular electronics and that current densities are dampened by this simple electrochemical modification of the substrate.

2.1. Background

2.1.1. Underpotentially Deposited Metal Films

Underpotential deposition (UPD) is an electrochemical process whereby up to a monolayer of metal is deposited on to a dissimilar metal substrate at potentials positive of bulk electrodeposition. The process is driven by an offset in the work functions of the adatom and the substrate atom which results in an adatom-substrate interaction that is more energetically favourable than adatom-adatom interactions. Theoretically, this makes the UPD process self-limiting to a single monolayer, however experimentally some bulk deposition, or multi-layer deposition, is typically observed prior to 100% coverage and adlayer films are only seen to approach full monolayer coverage, without incurring bulk deposition, on highly ordered monocrystalline substrates.

The UPD process has been studied extensively for many metal adatom-substrate combinations including: Cu, Ag, Pb and Hg on Au(111), Cu, Ag on Pt(111) and Pb and Ti on Ag(100). The one common aspect of all these systems is that the metal adatom is deposited onto a more noble metal substrate (i.e., the substrate has a higher work function than the adatom), resulting in UPD layers being inherently electron deficient as compared with their bulk analogues. This property has made UPD layers particularly attractive for use as substrate for self-assembled monolayers (SAMs) as the electron deficient nature of the adlayer makes it more stable towards oxidation, but also leads to a stronger molecule-substrate interaction and has been shown to enhance SAM stability towards thermal and electrochemical desorption. Furthermore, due to the strong nature of the adatom-substrate interaction, when SAMs are formed on UPD substrates, unlike
with bulk metal substrates, neither surface reconstruction nor metal etching is observed.\textsuperscript{8,10,18-20} As shown in Figure 2.1, this results in more homogeneous films with fewer step heights and pits.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure2.png}
\caption{STM images of the surface reconstruction from the formation of butanethiol SAMs on Au and Ag\textsuperscript{UPD}/Au substrates. (A) 340 x 300nm image of bare Au(111). The step heights shown are the equivalent of one atomic step (0.24nm). The inset is a 70 x 70nm showing the herringbone reconstruction. (B) 240 x 210nm image of a butanethiol monolayer on Au(111). The pits shown were found to have depths of 1 atomic step height. (C) Image of a butanethiol monolayer on a Ag\textsuperscript{UPD}/Au substrate prepared at a deposition bias of 460mV (vs Ag\textsuperscript{+}/0). The substrate was soaked in 1 mM butanethiol for 72 h, the 50 x 50nm inset was for the same SAM/substrate but with a soaking time of 120 h. Adapted with permission from reference 8. Copyright (2000) American Chemical Society.\textsuperscript{8}}
\end{figure}

UPD systems are unique in that numerous studies have shown that for a particular adatom-substrate combination, adatom coverage and adlattice structure are highly sensitive to various deposition parameters including: deposition bias, time the sample is held at the deposition bias, sweep rate of cathodic and anodic scans, substrate topography, ion concentration, and the counter ion involved in the deposition process.\textsuperscript{1-7,16-22} UPD processes are perhaps best described in terms of their cyclic voltammogram, where the peaks of the cathodic deposition scans and anodic stripping scans tend to correspond with specific coverages, adlattice structures or adlattice rearrangements/transition.
Ag\textsuperscript{UPD} on Au(111) is a system that has been studied extensively in the literature and is considered to be an “ideal” UPD system due to the fact that bulk Ag and Au adopt the same crystal structure and the nearest neighbour distances in the lattices of close packed Ag(111), 2.89Å, and Au(111), 2.88Å, are nearly identical.\textsuperscript{10,23} Given their similarity this should in theory allow for a commensurate Ag\textsuperscript{UPD} layer to be deposited on Au(111).\textsuperscript{5} CV of the deposition of Ag\textsuperscript{UPD} on Au(111) from a solution of 0.05M H\textsubscript{2}SO\textsubscript{4} and 1mM Ag\textsubscript{2}SO\textsubscript{4} is shown in Figure 2.2A.\textsuperscript{9} The first UPD peak, I, in the cathodic scan is found around ~480mV (vs Ag\textsuperscript{+/0}) and integrates to 70-75 µC/cm\textsuperscript{2}. This peak has been reported to correspond to the formation of an open √3 × √3 R30° Ag adlattice with 33% surface coverage on the Au (111) substrate.\textsuperscript{10,21} It is important to note that even at this early stage of the deposition no local Ag(111) or Au(111) structure are observed on the surface, indicating that the Ag\textsuperscript{UPD} adlayer is an extended layer across the film and not merely a mixture of islands of close packed Ag and Au.\textsuperscript{18,20}

As the bias approaches the second major UPD peak various studies report a transition to either a p(3 x 3) or p(5 x 5) adlattice, with the preferred structure depending on the concentration of the SO\textsubscript{4}\textsuperscript{2-} counter anion and potential.\textsuperscript{5,21} Chen et al., observed a very faint peak around ~420mV (vs Ag\textsuperscript{+/0}), which they attributed to p(3x3) adlattice reconstruction.\textsuperscript{10} They imaged films prepared at this potential by atomic force microscopy (AFM) as shown in Figure 2.3A alongside of a schematic of the adlattice with the underlying Au(111), Figure 2.3B. The coverage at this potential was determined to be ~44% by chronocoulometry and coverage was also found to slowly but steadily increase at more negative potentials approaching the next UPD peak.\textsuperscript{10}
Figure 2.2 CV (A) and coulometric curve (B) of Au (111) in 1 mM Ag₂SO₄ + 0.05 M H₂SO₄. The scan rate was 2 mV/s. The reference electrode was the reversible hydrogen electrode in 0.05 M H₂SO₄. Reprinted with permission from reference 9. Copyright (1995) Elsevier.
Figure 2.3 5 x 5 nm AFM image of the Ag$^{\text{UPP}}$ layer deposited on Au(111) at +420mV (vs Ag$^{+/0}$). Arrow indicates rows of atoms in alternating atop and bridging sites. (B) Schematic representation of the p(3x3) adlattice. Large circle represent Au, small circles shaded dark grey and light grey, represent Ag adatoms in the bridging and atop sites, respectively. Reprinted with permission from reference 10. Copyright (1992) American Chemical Society.

In between and including peaks II (50-70μC/cm$^2$) at ~100mV vs Ag$^{+/0}$ to III (140-160 μC/cm$^2$) ~20mV vs Ag$^{+/0}$, no discernible adlattice has been successfully resolved. STM studies reveal an aperiodic pattern with no local structures resembling either bulk Ag(111), Au(111) or any of the early UPD adlattices.$^{5,8}$ At these potentials it appears as though the adlayer is undergoing a transition from an open p(3x3) or p(5x5) structure to the closed packed (1x1) Ag adlattice with the Ag adatoms occupying the 3-hole interstitial sites of the underlying Au(111), which has been observed at potentials more cathodic than the third UPD peak.$^{5}$ Based on their study of Ag$^{\text{UPD}}$ deposited on Au(111) at +45 mV vs Ag$^{+/0}$, Hsieh et al, reported an adlattice coverage of greater than 85% with rows of adatoms alternatively occupying bridging sites and 3-hole interstitial sites of the Au(111) lattice.$^{14,20,21,24}$ The nearest neighbor distance of the Ag adatoms at this coverage was estimated to be 0.33nm, significantly less than the nearest neighbour distance of 0.5nm observed for the p(3x3) adlattice and approaching the 0.29 nm observed for a commensurate closed packed (1x1) Ag adlayer on Au (111).$^{10,24}$
Underpotentially Deposited Silver as a Substrate for the Enhancement of Molecular Junction Stability

The total charge integrated for the entire UPD process is typically found to be around 270-280 µC/cm², which is ~ 50 µC/cm² higher than predicted for a monolayer of Ag on Au(111) (222 µC/cm²) assuming 1 electron for every Ag atom deposited. The source of this additional charge is generally attributed to anion co-absorption and desorption throughout the course of the deposition, but could also be due to multilayer adsorption or unaccounted working electrode area due to surface roughness. Nevertheless, comparing the coulometric integration of the anodic and cathodic scans to the theoretical charge require for a full monolayer remains a popular method of estimating surface coverage. Other common methods used to determine surface coverage with more certainty include x-ray photoelectron spectroscopy, auger electron spectroscopy and using an electrochemical quartz crystal microbalance for depositions.

At this point it must be stated that there is no consensus in literature as far as adlayer coverage for a given deposition potential. Multiple studies conducted using slightly different deposition conditions report UPD peaks and coverages at potentials which are in general agreement, but are by no means identical. For instance, Hsieh et al. (asdep gold, 0.1M H₂SO₄, 1mM AgNO₃) reported a coverage of greater than 85% at a deposition potential of +45 mV vs Ag⁺/0, whereas Ogaki et al. (monocrystalline gold, 0.05 M H₂SO₄, 1mM Ag₂SO₄) and Jennings et al. (asdep gold, 0.1M H₂SO₄, 0.6 mM Ag₂SO₄), reported coverages of 93% and 64%, respectively, at +50mV vs Ag⁺/0. Adding even more discrepancy, Mrozek el al., who performed perhaps the most comprehensive studies of adlayer coverage as a function of deposition potential (see Figure 2.4), reported coverages greater than a monolayer at potentials more cathodic than +60mV.
2.1.2 Self-Assembled Monolayers (SAMs) on $\text{Ag}^{\text{UPD}}$/Au Substrates as Compared to Bulk Au and Ag

Modification of gold substrates with $\text{Ag}^{\text{UPD}}$ monolayers have been shown to improve the stability of SAMs prepared on these substrates against thermal and electrochemical desorption, and against molecular exchange with other thiol containing solutions, as compared with analogous SAMs on bulk Au.\textsuperscript{2,17,22} In their study, Jennings et al., observed that 1-docosanethiol SAMs (C22) on $\text{Ag}^{\text{UPD}}$/Au substrates were stable against thermal desorption at $>84$ °C for up to 3 hours and were $\sim$29 kJ/mol more stable than similar SAMs on unmodified gold substrates.$^1,2$ Furthermore, on account of their electron deficient nature, $\text{Ag}^{\text{UPD}}$ monolayers have also been shown to have a more noble redox potential as compared to bulk Ag making it more resistant to oxidation in ambient conditions.$^1$ These traits have allowed $\text{Ag}^{\text{UPD}}$ layers to emerge as an

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{coverage_vs_potential_plot.png}
\caption{Coverage vs potential plot of $\text{Ag}^{\text{UPD}}$ deposited on Au(111) as reported by Mrozek et al.\textsuperscript{21} Circles represent the silver adlayer coverage as determined by Auger electron transition, the dotted line represents the coverage as determined using coulometric data from the depositions after subtraction of $20\mu$F/cm$^2$ double layer charge. Reprinted from reference 21 with permission from Elsevier. Copyright (1995).}
\end{figure}
appealing substrate for thiolated SAMs, as its more robust properties circumvent many of the limitations associated with thiolated SAMs on either gold or silver.\textsuperscript{16,17,22,25}

On account of their relatively simple structure, n-alkanethiolate SAMs are good “baseline” molecules for probing subtle differences in SAM formation on different substrates. Comparing these molecules on Ag, Au and Ag\textsuperscript{UPD}/Au, one finds three unique SAMs in terms of their binding, lattice arrangement and electronic structure. The covalently bound sulfur headgroup in n-alkanethiolate SAMs is sp hybridized on Ag and Ag\textsuperscript{UPD}/Au, but sp\textsuperscript{3} hybridized on Au.\textsuperscript{1,2,8,13} With regards to lattice structure, n-alkanethiolates on Au(111) form a \(\sqrt{3} \times \sqrt{3} \) \(R30^\circ\) adlattice with nearest neighbor spacing of 5.0 Å resulting in an overall packing density of \(7.64 \times 10^{-10}\) mol cm\(^{-2}\).\textsuperscript{8,25-28} On Ag(111) the adlattice structure is \(\sqrt{7} \times \sqrt{7} \) \(R19.1^\circ\) with nearest neighbour spacing of 4.6 Å, resulting in a packing density of \(1.1 \times 10^{-9}\) mol cm\(^{-2}\), a 29\% increase as compared to Au(111).\textsuperscript{7,8,12,26,27,29} No adlattice structure has been conclusively determined for n-alkanethiols on Ag\textsuperscript{UPD}/Au; however, based on the periodic height modulation in their STM study Hseih et al., proposed that at Ag\textsuperscript{UPD} coverages of \(~75\%\) butanethiol monolayers adopted a distorted \(\sqrt{7} \times \sqrt{7} \) \(R19.1^\circ\) adlattice with nearest neighbor spacing of 5.0 Å, making it somewhat of a hybrid of the previous two bulk substrates, see Figure 2.5.\textsuperscript{5}
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Figure 2.5 (A) 280 x 280nm STM image of a butanethiol monolayer on Ag\textsuperscript{UPD}/Au prepared at 460mV (vs Ag\textsuperscript{+}/0). The underlying Ag adlattice was reported to be a 3x3 open structure. No periodic bonding scheme is observed for the butanethiol. (B) Molecularly resolved 10x 10 nm image of a butanethiol monolayer on Ag\textsuperscript{UPD}/Au prepared at 45 mV (vs Ag\textsuperscript{+}/0). Coverage of the Ag\textsuperscript{UPD} layer was ~85% and Ag-Ag nearest neighbour distances was 0.33nm. A distorted (\(\sqrt{7} \times \sqrt{7} \ R \ 19^\circ\)) structure for the butanethiol SAM was proposed to account for the modulation in the STM line scan shown below the image. (C) Proposed schematic for the butanethiol SAMs on the Ag\textsuperscript{UPD}/Au layers with adlayer coverage of ~75%. Reprinted with permission reference 5. Copyright (2000) American Chemical Society.

The different combinations of head group hybridization and nearest neighbour spacing results in n-alkanethiolate SAMs adopting different tilt angles on the three substrates in order to maximize their van der Waals interactions. As determined by reflectance absorption infrared spectroscopy (RAIRS), tilt angles of the n-alkanethiolate SAMs on Au(111), Ag(111) and Ag\textsuperscript{UPD}/Au, are 30°, 11° and ~20°, respectively\textsuperscript{1,2,17,23,27} The trend in tilt angles is reflected in the \(\text{I}_{\text{CH2asym}} / \text{I}_{\text{CH3asym}}\) dichroic ratios in the RAIRS spectra reported for the SAMs on the three substrates\textsuperscript{17,30} SAMs on Au were reported to have the highest dichroic ratios, whereas SAMs on Ag had the lowest ratios and SAMs on Ag\textsuperscript{UPD}/Au had ratios in between the previous two. These results are consistent with the surface selection rule which states that for RAIRS only vibrations
with a transition dipole moment component perpendicular to the plane of the substrate will be active (for the vibrations in question $I_{\text{CH}_2\text{asym}}$ increases with SAM tilt angle, $I_{\text{CH}_3\text{asym}}$ is less sensitive to changes in substrates).\textsuperscript{17}

$I_{\text{CH}_2\text{asym}} / I_{\text{CH}_2\text{sym}}$ dichroic ratios, for the SAMs on Au(111), Ag(111) and Ag\textsuperscript{UPD}/Au (with 60% Ag\textsuperscript{UPD} coverage), are $\sim 2.5$, $\sim 2$ and $\sim 1.5$, respectively, and are related to the average chain twist angles (the angle the CCC bond plane relative to the plane of the surface normal and the tilted chain) on the various substrates which are 52°, 49° and 45°, also respectively.\textsuperscript{1,30} This spectral feature is particularly significant as it establishes that n-alkanethiolate SAMs on Ag\textsuperscript{UPD}/Au are unique hybrids and not merely composites of SAMs on Au (111) and Ag (111) (otherwise a $I_{\text{CH}_2\text{asym}} / I_{\text{CH}_2\text{sym}}$ ratio and average twist in between that of Au and Ag would be expected).

The differences in SAM tilt, hybridization and twist also lead to different orientations the terminal methyl groups for odd, $n_{\text{odd}}$, and even, $n_{\text{even}}$, n-alkanethiolates on each substrate.\textsuperscript{12,27,31-34} As shown in Figure 2.6, this difference is particularly apparent for SAMs on Au. For $n_{\text{even}}$ SAMs the orientation of the methyl group is parallel to the surface normal but for $n_{\text{odd}}$ it is tilted away from the surface normal. Consequently, high resolution electron energy loss spectroscopy studies have revealed that the $n_{\text{odd}}$ SAM surface is composed of a mixture of methyl groups and underlying methylene groups, which translates into $n_{\text{odd}}$ and $n_{\text{even}}$ having different surface free energies and wetting properties.\textsuperscript{12,27} This phenomenon has been well documented for n-alkanethiolate SAMs on Au and Ag and is commonly referred to as the odd-even effect.\textsuperscript{31} While obvious on Au, the effect is much more subtle on Ag and Ag\textsuperscript{UPD} where sp hybridization and smaller tilt angles lead to terminal methyl orientations for $n_{\text{odd}}$ and $n_{\text{even}}$ which are only slightly different.\textsuperscript{12,27}

With regards to charge transport, both $n_{\text{odd}}$ and $n_{\text{even}}$ alkanethiolate SAMs have been tested on Ag and Au using the EGaIn tip method as a test. In their study Whitesides et al., reported that charge transport for $n_{\text{odd}}$ and $n_{\text{even}}$ SAMs on Ag\textsuperscript{TS} and $n_{\text{even}}$ SAMs on Au\textsuperscript{TS} were indistinguishable from
one another; $n_{\text{odd}}$ SAMs on Au$^{\text{TS}}$, the only system were the terminal methyl group points significantly away from the surface normal, were reported to have current densities roughly half an order of magnitude higher than the other systems.$^{12}$ This increase in current density was attributed to an increase in the effective electrical contact area of the EGaIn tip due to the increases wettability of the $n_{\text{odd}}$ SAMs on Au. Therefore, the discrepancy was related to a physical property of the test bed rather than any fundamental difference in the energetic properties of the molecular junction. Furthermore, based on the similarity of their charge transport results, it was concluded that $n_{\text{odd}}$ and $n_{\text{even}}$ on Ag and $n_{\text{even}}$ on Au present essentially the same interface or at least ones that are indistinguishable with respect to the EGaIn test bed.$^{12}$

Bearing this in mind in this study we chose to investigate $n_{\text{even}}$-alkanethiolate SAMs on Au, Ag and Ag$^{\text{UPD}}$/Au in order to demonstrate that Ag$^{\text{UPD}}$/Au, with their enhanced stability against oxidation and SAM desorption, are a viable substrate for molecular electronics applications. By selecting the even chain lengths, where methyl group orientations are similar, we avoid unnecessary ambiguities associated with the test bed and focus primarily on the barrier properties of the three systems.
Figure 2.6  Schematic illustrating the differences in tilt angle, S-atom hybridization and nearest-neighbour spacing of n-alkanethiolate SAMs on (A) Ag, (B) Ag\textsuperscript{UPD}/Au and (C) Au. On each substrate there is an even chain n-alkanethiolate on the left (C8) and an odd chain on the right (C9). The tilt angles on Ag, Ag\textsuperscript{UPD}/Au and Au are 11°, 20° and 30°, respectively.

2.2. Experimental

2.2.1. Chemicals

All chemicals used were purchased commercially and were used as received with the exception of the n-alkanethiols used for SAM formation. These were purchased from Sigma Aldrich and were purified prior to use by silica gel column chromatography using a gravity elution with 100% hexanes. Nuclear magnetic resonance (NMR) spectroscopic data of the isolated thiols were collected on a Bruker Ultrashield 300 MHz spectrometer at room temperature. The shifts reported are in parts per million (ppm) and are referenced to the residual proton peaks.
of CDCl₃ (δ = 7.27 ppm). The ¹H-NMR spectra of the purified n-alkanethiolates were checked periodically throughout the project in order to ensure the quality of the SAM being formed. We assigned ¹H NMR peaks as follows: δ = 2.5 ppm (quartet, 2 H, J = ~7.2 Hz), δ = ~ 1.6 ppm (multiplet, 2 H), δ = ~ 1.3 ppm (multiplet, 2n – 6 H, where n is the number of carbons in the n-alkanethiolate), δ = ~ 0.9 ppm (triplet, 3 H, J = ~7.0 Hz), δ = ~ 1.5 ppm (H₂O), δ = 7.27 ppm (CDCl₃).

2.2.2. Preparation of Template Stripped Metal Substrates

Template-stripped gold (Au⁴⁵) and silver (Ag⁴⁵) films were produced by first depositing a 500 nm layer of the metal, at a rate of ~3-4 Å/s, onto 75 mm diameter silicon wafers using an electron-beam evaporator. Next, a small drop of UV curable adhesive (NOA 83H, Norland Optical) was applied to the surface, followed by a clean glass slide (see cleaning procedure below). The size of the glass slides and the amount of adhesive applied varied depending on the intended use of the sample, but ranged from 1 cm x 1 cm slides, which required ~10 μL of adhesive, to 3 cm x 3 cm slides, which required ~45 μL of adhesive. After curing the adhesive under 365 nm light from a 126 W UV lamp (Spectroline model SB-100P, Spectronics Corporation) for 15 minutes, residual uncured adhesive was removed by immersing wafers in an ethanol bath for 1 hr and then blowing them dry under a stream of nitrogen. Finally, prior to use, glass samples were wiped with an ethanol soaked kimwipe (Kimtech Science), blown dry under nitrogen and stripped from the Si wafers using a scalpel. Samples were generally used within 2 weeks of preparation and as a means of limiting contamination due to adventitious organic matter and oxidation (especially in the case of Ag⁴⁵). Bare metal coated Si wafers were stored in a glove box under a nitrogen atmosphere until they were ready to undergo the subsequent steps.

Glass slides used as substrates for template-stripped (TS) and underpotentially deposited (UPD) films underwent a thorough cleaning procedure prior to adhesion to the metal. This consisted of
sonicating the glass slides for 15 minutes in both isopropyl alcohol and then acetone, blowing dry under a stream of nitrogen and then subjecting them to UV/Ozone exposure for 5 minutes to remove any residual organics from the surface.

2.2.3. Under Potential Deposition of Ag and Coulometric Calculations

Silver was underpotentially deposited on to AuTS substrates (1 cm x 3 cm for CA and MEC, 3 cm x 3 cm for RAIRS) in an glass cell with a Pt wire as the counter electrode, a freshly stripped AgTS sample as the reference electrode and a Zahner Model IM6ex electrochemical workstation (Zahner-elektrik) was used as the potentiostat. The electrodes were immersed in a 0.1M H₂SO₄(aq) solution of 0.6 mM Ag₂SO₄ and cycled at 20 mV/s between 60 mV and 600 mV (vs Ag reference) twice before being held at the UPD deposition potential of 60 mV (vs Ag reference) for 30 seconds. The AgUPD/Au electrode was then removed from solution under potential control, rinsed with distilled water followed by a copious amount of anhydrous ethanol, blown dry under N₂ and finally transferred to an n-alkanethiolate solution for SAM deposition. The 0.1 M H₂SO₄/0.6 mM Ag₂SO₄ solution was deoxygenated via nitrogen bubbling for 30 minutes prior to use and was kept deoxygenated with nitrogen bubbling throughout the course of depositions.

Coulometric analysis was performed using AuTS substrate with a defined geometric working area of 0.97 cm². After subtracting 20 μF/cm² to account for a double layer charging effect, the integrated charge over the anodic and cathodic scans of the UPD deposition were averaged and this was compared with the expected value for a close-packed monolayer of underpotentially deposited silver atoms on Au (111), 222 μC/cm², in order to estimate the surface coverage.

Samples used for coulometric analysis were also sent for XPS analysis (see below) allowing us to directly compare the surface coverages calculated from both techniques.
2.2.4. SAM Formation

SAMs were prepared by immersing metal substrates in 3 mM solutions of the appropriate n-alkanethiolate in anhydrous ethanol, under nitrogen, for 3 hours. Upon removal from solution, samples were rinsed under a stream of anhydrous ethanol and then sequentially transferred to three baths of anhydrous ethanol for 1 minute each. Samples were blown dry under a stream of nitrogen between each wash step. The extensive cleaning process post-SAM formation was intended to minimize the amount of physisorbed n-alkanethiolate present.

2.2.5. Atomic Force Microscopy and Roughness Analysis

AFM images were acquired using a Digital Instruments Multimode atomic force microscope run in contact mode. Bruker DNP-S10 silicon nitride cantilevers (Bruker Corporation) were used with a nominal tip radius of 10 nm. Images were collected using Nanoscope 6 software at a scan rate of 1.2 Hz and with a scanning resolution of 512 samples/line and processed using WSxM 5.0 Develop 4.3 software. In order to assess the impact of the UPD process on surface roughness, 9 randomly selected 2µm x 2µm areas on both AuTS and AgUPD/Au were imaged by AFM (3 samples/substrate, 3 images/sample) and their RMS roughness were determined using the WSxM software. The average RMS roughness for AuTS and AgUPD/AuTS were taken to represent the RMS roughness of a film pre- and post-UPD, respectively.

2.2.6. X-ray Photoelectron Spectroscopy and Coverage Calculations

Samples were analyzed by XPS using a Krato Axis Nova X-ray photoelectron spectrometer. Survey scan analyses were carried out with an analysis area of 300 x 700 µm and a pass energy of 160 eV. A 90 degree take-off angle was used for all samples. XPS measurements and peak fitting was performed by Surface Science Western (London, Ontario).
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All samples for UPD adlayer coverage ($\phi_{UPD}$) analysis consisted of UPD films which had been prepared on Au$^{TS}$ at a deposition potential of 60mV (vs Ag reference) and had been immersed in a dilute solution of 1-undecanethiol for at least 3 hrs to form a SAM. Coverages of the UPD adlayer were calculated, as per the literature, and based on the measured intensities of the Ag$^{UPD}$ adlayer ($I_{UPD}$) and the bulk Au$^{TS}$ substrate ($I_{AuTS}$) peaks in accordance with equation 1.\(^1\)

$$
\phi_{UPD} = \frac{I_{Au}}{I_{upd}} \left( \frac{I_{upd}}{I_{Au}} \right) C_{SAM} \left[ 1 - \exp \left( -\frac{a_{upd}}{\lambda_{upd}(KE_{Au})\cos \theta} \right) \right] + \left[ 1 - \exp \left( -\frac{a_{upd}}{\lambda_{upd}(KE_{Au})\cos \theta} \right) \right]^{-1}
$$

Where $a_{upd}$ is the diameter of the Ag adatom (2.56 Å), $\lambda_{upd}(KE_{Au})$ and $\lambda_{upd}(KE_{upd})$ are 18 and 15 Å, respectively, the inelastic mean free path through the Ag adlayer for electrons of kinetic energy (KE) emanating from Au(4f$^{7/2}$) and Ag(3d$^{5/2}$), also respectively. $\theta$ is the angle of the detector to the surface normal ($\theta = 0^\circ$), and $I_{Au}$ and $I_{upd}$ are the sensitivity factors for Au and Ag, respectively, which were 6.25 and 5.987, also respectively, for the XPS in question. It must also be noted that $C_{SAM}$ represents the attenuation of adlayer and bulk photoelectrons due to the presence of the overlying 1-undecanethiol SAM, which was treated as a generic layer of carbonaceous matter. The relationship for this attenuation is shown by equation 2.

$$
C_{SAM} = \frac{\exp \left( -\frac{d_{SAM}}{\lambda_{SAM}(KE_{upd})\cos \theta} \right)}{\exp \left( -\frac{d_{SAM}}{\lambda_{SAM}(KE_{Au})\cos \theta} \right)}
$$

Where $\lambda_{SAM}(KE_{upd})$ and $\lambda_{SAM}(KE_{Au})$ are 34 and 40 Å, respectively, the inelastic mean free path through the SAM for photoelectrons of kinetic energy (KE) from Ag(3d$^{5/2}$) and Au(4f$^{7/2}$), also
respectively. $d_{SAM}$ is the thickness of the SAM which was calculated based on the relationship, 

$$d_{SAM} = nd \cos \alpha,$$

where $n$ is the number of methylene group of the adsorbate, $d$ is the increase in thickness due to the contribution of an addition methylene group ($d=1.27 \, \text{Å}$), and $\alpha$ is the tilt angle of the hydrocarbon chain relative to the surface normal (for Ag$^{UPD}$ $\alpha = 20^\circ$).\(^1\)

2.2.7. Contact Angle Goniometry

Static contact angle, as well as the advancing and receding contact angles of hexadecane were measured with a Ramé-Hart contact angle goniometer equipped with a microliter syringe and tilting stage. A minimum of three drops were averaged for each SAM on each substrate. The hysteresis was calculated by taking the difference of the advancing and receding angles on a tilting stage right before the leading edge of the drop moved, indicated by a sudden drop in the advancing contact angle.

2.2.8. Reflection Absorption Infrared Spectroscopy (RAIRS)

RAIRS spectra were collected using a Bruker IFS 66/v spectrometer equipped with an MCT detector and Harrick Autoseagull accessory. The p-polarized light was incident at $80^\circ$ from the surface normal. A spot size with a diameter of 0.48 cm was used to collect 1024 scans at a resolution of 2 cm\(^{-1}\). Bare substrates of fresh stripped Ag$^{TS}$, Au$^{TS}$ and freshly prepared Ag$^{UPD}$/Au$^{TS}$ were used as background samples and were rinsed with anhydrous ethanol and blown dry under a stream of nitrogen prior to being loaded.

2.2.9. Molecular Electronic Characterisation (MEC) of n-alkanethiolate SAMs on Metal Substrates

2.2.9.1. Experimental Setup

MEC measurements were performed using a home-made eutectic gallium-indium (EGaIn) molecular junction system. Conical shaped EGaIn top electrodes are characteristic of
such setups and were fabricated by extruding a small drop of EGaIn from a 10 μL gas tight syringe (Hamilton Scientific LLC), allowing it to hang in ambient lab conditions for 1hr, and bifurcating the EGaIn drop into a conical shaped tip by slowing withdrawing the syringe from a sacrificial substrate (generally bare AuTS), as shown Figure 2.7. Allowing the drop to hang in the ambient conditions for an hour and withdrawing the syringe in a 2 steps forward, 1 step back manner, were seen to improve tip stability. Subsequent tips were formed by driving used tips into the sacrificial substrate and once again bifurcating the EGaIn into a conical shape by withdrawing the syringe. AuTS substrates served as the ground electrode by means of a micro hook test lead (E-Z Hook) that penetrated SAMs and connected the gold directly. Likewise, a second test lead bearing a micro hook was connected to the syringe bearing the EGaIn tip and both electrodes were connected via triaxial cable to an external amplifier, which was connected to a Keithley 6430 subfemtoamp remote source meter. A high resolution analytical CCD camera (Edmund Optics) was used to visualize the EGaIn tips and determine the diameter of their effective geometric contact area with SAMs, which were assumed to be circular. Finally, manipulation of the syringe, camera and sample (which was held in place by double sided tape on a platform) was accomplished with manual nanopositioning stages (Thorlabs) which provided us with fine control over the motions of the above mentioned.

Figure 2.7 Optical microscopy of the EGaIn tip extrusion and bifurcation process.
2.2.9.2. Tip Conditioning

Prior to being brought into contact with SAMs, newly formed EGaIn tips first underwent an additional conditioning step. This “flattening” step, introduced in a recent publication by Simeone et al., has been shown to increase the effective electrical contact area of tips with SAMs, while also improving junction yields and reducing the dispersion in measurements of \( \log |J(V)| \), where \( J \) is the current density in A/cm\(^2\).\(^{11}\) Immediately after bifurcation, tips were brought into contact with a clean p-type Si (100) chip which served as a ground electrode. Tips were tapped down gently three times before being brought into sustained contact on the Si chip. We then ran five current voltage (CV) scans between ±2V (0V \( \rightarrow \) 2V \( \rightarrow \) 0V \( \rightarrow \) -2V \( \rightarrow \) 0V). If the CV traces coincided well with one another the tip was deemed suitable to proceed for junction characterization. However, if the traces shifted significantly over the course of the scans, the “flattening” process was repeated at another spot of the Si chip.

2.2.9.3. Establishing Junction Contact

The image of the EGaIn tip, as well as its reflection on the substrate, could be seen as it approached SAMs via optical microscopy using the high resolution analytical camera. Previous protocols for junction formation called for the images of tip and its reflection to be gently brought into contact. The flattened tip protocol described by Simeone et al., however called for the tip to be brought into contact with the SAM until apex deformation was observed.\(^{11}\) As such, to form stable contacts, we first brought tips into light contact with the SAMs and then pushed down until buckling or “wrinkling” of the Ga\(_2\)O\(_3\) skin was observed by optical microscopy. The comparison between the two methods is shown in Figure 2.8.
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Figure 2.8 Optical microscopy images of the EGaIn tip and the process of forming a junction. (A) The tip approaches the surface and its reflection (bottom tip) is seen on the substrate. (B) The tip is brought in to contact with its reflection, this would be considered a “soft” contact. (C) The tip is brought further in to contact with the SAM and there is a deformation or “wrinkling” of the tip apex. This was the type of contact established “flattened” tip junctions which were used in this chapter (see Chapter 3 for further details on the difference between “soft” and “flattened” tips).

2.2.9.4. Junction Measurement Protocol

CV scans of molecular junctions were recorded between ±0.5V (0V → 0.5V → 0V → -0.5V → 0V). An initial CV scan was done for each junction tested, if this initial scan did not short, an addition 19 scans were run and thus 20 scans were recorded per working junction. We recorded a minimum of 18 junctions (360 scans) across at least 2 samples for each molecule/substrate combination, limiting the number of junctions collected per EGaIn tip to 3-5. Typically, the number of junctions per tip was kept consistent within a sample to not artificially give more statistical weight to any particular tip/s; however, there were exceptions made when a tip prematurely shorted (shorting occasionally caused the EGaIn to stick to the underlying metal substrate at which point a new tip would be fabricated). We defined a working junction as one where the CV scans had a sigmoidal shape, characteristic of a charge tunnelling mechanism, and remained stable for all 20 scans. Shorts were defined as any junction tested which either reached the compliance current of the Keithley (105 mA) or displayed linear CV scans, characteristic of
ohmic charge transport, at any point throughout the standard 20 scans. The yield was calculated as
the percentage of working junctions over the total number of junctions tested (i.e. the number of
working junctions added to the number of shorts). All scans were recorded within 2 hrs of
removing the sample from solution to limit the influence of adventitious organic matter which
could physisorb on either the sample or EGaIn tip.

2.2.9.5. Junction Data Treatment

The logarithm of all current densities, Log J (A/cm²), measured were fit to a unimodal
Gaussian distribution for each system (molecule/substrate combination). Current densities
through n-alkanethiolate SAMs are known to have a log normal distribution and therefore the
mean and standard deviation of the Gaussian fit were taken as the mean and standard deviation for
each particular system.¹¹

2.2.9.6. Side by Side MEC of CₙS-AuTS and CₙS-AgUPD/AuTS

Side by side comparisons of n-alkanethiolate SAMs on AuTS and AgUPD/AuTS were done
using AuTS substrates from the same Si wafer. Substrates were placed simultaneously in the same
n-alkanethiolate solution during SAMs formation and were removed from said solution at the
same time before undergoing identical washing steps. The samples were placed alongside one
another on a platform in our home-made EGaIn junction station and junction measurements
proceeded in the following manner: tip 1 (CₙS-AuTS → CₙS-AgUPD/AuTS → CₙS-AuTS → CₙS-AgUPD/AuTS), tip 2 (CₙS-AgUPD/AuTS → CₙS-AuTS → CₙS-AgUPD/AuTS → CₙS-AuTS), tips 3 and 4
repeated the pattern of tips 1 and 2, respectively.
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Figure 2.9 Schematic of the experimental procedure. A) Preparation of AuTS substrates; B) electrochemical deposition of a AgUPD layer; C) SAM formation; D) molecular electronic characterisation of SAMs with an EGaIn tip as top contact. The experimental procedure for AgTS is similar to that of AuTS, with Ag being evaporated on to the Si wafer in place of Au.
2.3. Results & Discussion

2.3.1. Atomic Force Microscopy of Ag\textsuperscript{UPD}/Au\textsuperscript{TS} Surfaces

While Ag\textsuperscript{UPD}/Au substrates have been studied on various polycrystalline and monocrystalline Au templates, to our knowledge the process has yet to be applied to Au\textsuperscript{TS} substrates. TS films incorporate a glue adhesive layer; therefore it was necessary to check that this interlayer was stable throughout the UPD process and did not induce any significant changes in surface topography due to swelling or delamination (both can occur if the interlayer is exposed to harsh conditions such as being immersed in halogenated solvents).\textsuperscript{36} Therefore, to assure the integrity of our Ag\textsuperscript{UPD}/Au\textsuperscript{TS} films samples were characterized prior to and following the UPD process by AFM. AFM images collected are shown in Figure 2.10, and reveal no significant changes to topography due to the UPD process. The average RMS roughness of the films prior to and post-UPD were 4.2 ± 0.5 Å and 3.8 ± 0.5 Å, respectively, implying that from a strictly topographical standpoint Au\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS} films are indistinguishable.

\textbf{Figure 2.10} 2 x 2 μm AFM images of (A) Au\textsuperscript{TS} and (B) Ag\textsuperscript{UPD}/Au\textsuperscript{TS} prepared at +60mV (vs Ag\textsuperscript{+0}). The average RMS roughness determined for the two substrates were 4.2 ± 0.5 Å and 3.8 ± 0.5 Å, respectively.
2.3.2. Adlayer Coverage as Determined by XPS and Coulometry

Average coverage of the Ag^{UPD}/Au^TS adlayer prepared at +60 mV (vs Ag^{+}/0) were determined by coulometry and XPS analysis to be 79 ± 5 % and 80 ± 7%, respectively, and were therefore in very good agreement with one another. In fact, as shown in Table 2.1, even coverages determined by both methods for individual samples were in good agreement with one another, with the largest difference in reported surface coverage by the two methods being only 4%. XPS spectra, as well as the CV scans and integrations of the cathodic and anodic sweeps are provided in the supplemental section of this chapter.

Table 2.1 Surface coverages of Ag^{UPD}/Au prepared at 60mV (vs Ag^{+}/0) as determined by Coulometry and XPS analysis.

<table>
<thead>
<tr>
<th>UPD Samples prepared @ +60MV</th>
<th>Surface Coverage from Coulometry</th>
<th>Surface Coverage from XPS</th>
<th>Coverage</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sample 1</td>
<td>74.7%</td>
<td>72.2%</td>
<td></td>
</tr>
<tr>
<td>Sample 2</td>
<td>79.3%</td>
<td>83.3%</td>
<td></td>
</tr>
<tr>
<td>Sample 3</td>
<td>84.1%</td>
<td>85.2%</td>
<td></td>
</tr>
<tr>
<td><strong>Average</strong></td>
<td><strong>79 ± 5 %</strong></td>
<td><strong>80 ± 7 %</strong></td>
<td></td>
</tr>
</tbody>
</table>

The coverages we reported are in general agreement to those reported in similar Ag^{UPD}/Au studies, but discrepancies can be attributed to subtle differences in the substrate topography of Au templates and deposition conditions. For instance, using an identical deposition solution as in the present study, Jennings et al. reported surface coverages of only 64% at 50 mV.
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(vs Ag⁰) prior to seeing bulk deposition, using as-deposited Au (Au_{asdep}) films as opposed to Au_{TS}. In contrast, Ogaki et al., were able to achieve a commensurate close-packed (1x1) Ag adlattice prior to observing bulk deposition at ~15mV (vs Ag⁰) using a highly ordered monocrystalline Au (111) beads as a substrates.

Given that Au_{TS} can be considered a smoother version of Au_{asdep}, with fewer defect sites, it is not surprising that we were able to achieve higher coverages than Jennings et al., however full a characterisation of Ag_{UPD} coverage on Au_{TS} as a function of deposition potential is beyond the scope of this study. The deposition potential used in this study, +60mV, was selected primarily to avoid the onset of bulk deposition. It is possible that with further optimization of both the deposition potential and environment, Ag_{UPD}/Au films similar to those observed by Ogaki et al., could be achieved using Au_{TS} templates.

Of the Ag_{UPD}/Au studies reported in literature one in particular seems to most closely mimic our own. Using polycrystalline Au_{asdep} templates, Hsieh et al. prepared Ag_{UPD}/Au films that were subsequently used as substrates for butanethiol SAMs. They reported an Ag surface coverage greater than 85% at a deposition potential of +45mV and butanethiol nearest neighbour spacing of 5.0Å (see Figure 2.5). Without STM analysis of our own system, we presume n-alkanethiolate SAMs prepared on Ag_{UPD}/Au_{TS} in this study to adopt similar spacing and hence have similar packing densities to n-alkanethiolate SAMs on Au_{TS} which also have nearest neighbour spacing of ~5.0 Å.
2.3.3. SAM Characterization on Au\textsuperscript{TS}, Ag\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS}

In order to assure the integrity of the junctions measured on Au\textsuperscript{TS}, Ag\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS}, SAMs were probed using RAIRS and contact angle (CA) goniometry prior to being measured on the EGaIn tip test bed.

2.3.3.1. RAIRS of n-Alkanethiolate SAMs

RAIRS spectra collected for the series of n-alkanethiolates on all substrates agreed well with literature reports with regards to wavenumbers of characteristic CH\textsubscript{2} and CH\textsubscript{3} vibrations and dichroic ratios (Table 2.2).\textsuperscript{1,17,30,32} The asymmetric, CH\textsubscript{2}\text{asym}, and symmetric, CH\textsubscript{2}\text{sym}, methylene stretches for the longer (n \( \geq 12 \)) chains on all substrates were generally around \( \sim 2918 \) cm\textsuperscript{-1} and \( \sim 2850 \) cm\textsuperscript{-1}, respectively, indicating crystalline SAM were formed.\textsuperscript{1} These stretching frequencies tended to shift towards more liquid-like values (liquid n-alkanethiolate vCH\textsubscript{2}\text{asym} vCH\textsubscript{2}\text{sym} are reported to be 2925 cm\textsuperscript{-1} and 2855, respectively) for C8 and C10, which was to be expected for shorter chains with fewer stabilizing van der Waals interactions.\textsuperscript{37-39} The more liquid-like nature of the shorter SAMs has been shown by Simeone et al. to have no influence on tunnelling currents.\textsuperscript{11} If anything, work by Nijhuis et al. has demonstrated that the liquid-like nature of chains in the SAMs helps cover-up pinholes and other defects in SAMs which can lead to better junction yields.\textsuperscript{40}

Concentrating on the dichroic ratios for the longer well-ordered crystalline chain lengths (C \( \geq 12 \)) the \( \frac{I_{\text{CH}_2\text{asym}}}{I_{\text{CH}_2\text{sym}}} \) ratios on Au\textsuperscript{TS} and Ag\textsuperscript{TS} agree relatively well with those reported in literature of \( \sim 2.5 \) and \( \sim 2 \) respectively.\textsuperscript{1} The \( \frac{I_{\text{CH}_2\text{asym}}}{I_{\text{CH}_2\text{sym}}} \) ratios reported on Ag\textsuperscript{UPD}/Au\textsuperscript{TS} for C12, C14 and C16 were 1.15, 1.05 and 1.00, respectively, which were all well below their respective ratios on Au\textsuperscript{TS} and Ag\textsuperscript{TS}. This is a critical result, as it is as evidence that the SAMs formed on Ag\textsuperscript{UPD}/Au\textsuperscript{TS} substrates in the present study were in fact unique and not simply combinations of SAMs on Au\textsuperscript{TS}.
and Ag\textsuperscript{TS}. Therefore we also conclude that the Ag\textsuperscript{UPD} films prepared were in fact an extended adlattice and did not constitute a mixture of Au and Ag close packed islands.

We note that the $I_{\text{CH2asym}}/I_{\text{CH2sym}}$ dichroic ratios we report are smaller than Jennings et al. reported for C18 on Ag\textsuperscript{UPD}/Au\textsuperscript{TS}.\textsuperscript{1} However, the Jennings study was done using Ag\textsuperscript{UPD} coverages of ~60% and therefore the slight discrepancy between our values is not necessarily a concern. As stated in the introduction of to this chapter the $I_{\text{CH2asym}}/I_{\text{CH2sym}}$ ratio is related to the twist angle, $\beta$, of the chains and this relationship is given by: $\tan \beta = \tan \beta_0 \left( \frac{I_{\text{CH2 asym}}}{I_{\text{CH2 sym}}} \right)^{\frac{1}{2}}$ where $\beta_0$ is the twist angle of a known standard SAM such as n-alkanethiolates on Au or Ag, and $I_{\text{o CH2 asym}}$ and $I_{\text{o CH2 sym}}$ are the intensities of the asymmetric and symmetric methylene stretches, respectively, in the RAIRS spectra of the selected standard SAM.\textsuperscript{30} Based on this relationship the twist angles calculated for the n-alkanethiolate SAMs on our Ag\textsuperscript{UPD}/Au\textsuperscript{TS} were ~41° and this agrees reasonably well with the twist angle of 45° reported by Jennings et al. their study.\textsuperscript{1}

Finally, for all chain lengths studied (with the exception of C8) the $I_{\text{CH2asym}}/I_{\text{CH3asym}}$ dichroic ratio was largest on Au\textsuperscript{TS}, smallest on Ag\textsuperscript{TS} and intermediate on Ag\textsuperscript{UPD}/Au\textsuperscript{TS}. This ratio is known to increase with SAM tilt\textsuperscript{17} and as such these results are directly in line with literature reports of n-alkanethiolate SAMs having tilt angles of 30°, 11° and 20° on Au, Ag and Ag\textsuperscript{UPD}/Au, respectively.\textsuperscript{1,2,17,23,27}
Table 2.2 RAIRS wavelengths for the asymmetric and symmetric methylene stretch of the n-alkanethiolate SAMs on Au\textsuperscript{TS}, Ag\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS}. I\textsubscript{CH2asym}/I\textsubscript{CH3asym} and I\textsubscript{CH2sym}/I\textsubscript{CH2asym} dichroic ratios are also reported. *C10 and C8 Ag\textsuperscript{TS} RAIRS spectra could not be collected at an incidence angle of 80° and had to be collected instead using an incidence angle of 85°. Therefore the dichroic ratios of from these spectra should not be directly compared with those from the other spectra.

<table>
<thead>
<tr>
<th>SAM</th>
<th>Metal</th>
<th>CH\textsubscript{2asym} (cm\textsuperscript{-1})</th>
<th>CH\textsubscript{2sym} (cm\textsuperscript{-1})</th>
<th>Dichroic ratio</th>
<th>Dichroic ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td></td>
<td>I\textsubscript{CH2asym} / I\textsubscript{CH3asym}</td>
<td>I\textsubscript{CH2sym} / I\textsubscript{CH2asym}</td>
</tr>
<tr>
<td>C16SH</td>
<td>Au\textsuperscript{TS}</td>
<td>2919</td>
<td>2851</td>
<td>3.22</td>
<td>2.41</td>
</tr>
<tr>
<td></td>
<td>Ag\textsuperscript{UPD}/Au\textsuperscript{TS}</td>
<td>2918</td>
<td>2850</td>
<td>1.11</td>
<td>1.00</td>
</tr>
<tr>
<td></td>
<td>Ag\textsuperscript{TS}</td>
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<td>2848</td>
<td>0.60</td>
<td>2.21</td>
</tr>
<tr>
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<td>Au\textsuperscript{TS}</td>
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<td>2851</td>
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<td>2.41</td>
</tr>
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<td>1.05</td>
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<td>Au\textsuperscript{TS}</td>
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<td>2851</td>
<td>2.24</td>
<td>3.11</td>
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<td></td>
<td>Ag\textsuperscript{UPD}/Au\textsuperscript{TS}</td>
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<td>2851</td>
<td>0.42</td>
<td>0.93</td>
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<tr>
<td></td>
<td>Ag\textsuperscript{TS}</td>
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<td>1.19</td>
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<tr>
<td>C8SH</td>
<td>Au\textsuperscript{TS}</td>
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<td>2851</td>
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<td>2.04</td>
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<tr>
<td></td>
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<td>2851</td>
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<td>1.03</td>
</tr>
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<td>Ag\textsuperscript{TS}</td>
<td>2917</td>
<td>2851</td>
<td>0.13</td>
<td>1.85</td>
</tr>
</tbody>
</table>
2.3.3.2. Contact Angle Analysis of n-Alkanethiolate SAMs

CA is a simple and effective way of probing SAM quality, as the contact angle of various probe liquids such as water and hexadecane are sensitive to SAM defects and subtle changes in terminal groups. Grain boundaries and step heights on the substrate, misalignments in SAM domains, surface impurities and gauche defects in carbon backbone are all potential defects which, in the case of n-alkanethiolate SAMs, expose interior methylene groups and increase the number of interactions available per unit area between SAM and probe liquid. More interactions decrease the surface free energy of the liquid/SAM interface, $\gamma_{SL}$, and reduces the contact angle of the probe liquid in accordance with Young’s equation, illustrated in Figure 2.11. Additionally, SAMs with higher packing densities and/or terminal groups tilted significantly away from the surface normal are also known to have increased interactions with probe liquid. In the case of the former, it is inherently because there are more molecules per unit area to interact with; in the case of the latter, terminal groups orient away from the surface normal expose underlying methylene groups such that there are more atomic contacts per unit available.

**Young’s Equation**

$$\gamma = \gamma_{SV} + \gamma_{LV} \cos \theta$$

**Figure 2.11** Schematic of contact angle goniometry. $\gamma_{SV}$ is the solid/vapor surface free energy, $\gamma_{LV}$ is the liquid/vapor surface free energy and $\gamma_{SL}$ is the solid/liquid surface free energy. $\theta$ is the contact angle between the probe liquid surface and air.
Table 2.3 lists the static hexadecane contact angles as well as the hysteresis value for the various chain lengths tested on the three different substrates. For all chain lengths, on all substrates (with the exception of C8 on Ag^TS), hexadecane static contact angles are above 40°. This is in line with literature reports for high quality n-alkanethiolate SAMs on these substrates.\textsuperscript{17,42,46,47} The few results close to or below 40° reported for the shorter chains are still in-line with literature values and are simply a reflection of the trend observed across all substrates whereby contact angles decrease with shorter chain lengths. This is due to the fact that, as chain lengths decrease there fewer stabilizing van der Waals interactions within SAMs, leading to less rigid, less well-defined structures, allowing probe liquids to sense underlying metal substrates.\textsuperscript{27}

Comparing contact angles across substrates, static angles on Ag^TS were generally smaller than those on Au^TS or Ag^{UPD}/Au^TS. This was to be expected and is inherently caused by the higher packing densities of n-alkanethiolate SAMs on Ag^TS relative to the other substrates. Contact angles on Au^TS and Ag^{UPD}/Au^TS were generally within error of one another. Assuming similar packing densities of SAMs on the two substrates, this implies that there was not a significant difference in the orientation of the SAMs’ terminal methyl group on the two substrates.\textsuperscript{17,27,44,46}

Hysteresis values, $\Delta\theta_{\text{hys}}$, are defined as the difference between the advancing and receding contact angle of the probe liquid on a SAM and are used to gauge SAM homogeneity and uniformity. For well-ordered densely packed n-alkanethiolate SAMs on atomically smooth mica substrates, hysteresis has been shown to be virtually non-existent,\textsuperscript{41,42} but tends to increase for heterogeneous SAMs and for rough substrates where there exists a higher density of step heights, grain boundaries, lattice misalignments, impurities and other miscellaneous defects.\textsuperscript{44} Hysteresis values reported for n-alkanethiolate SAMs on as-deposited substrates are typically ~5-8°.\textsuperscript{44} The majority of the hysteresis values we report are ~2-4°, which is reasonable for relatively smooth template stripped substrates, and is in-line with the complete lack of hysteresis, that Ulman et al. observed for n-alkanethiolate SAMs on ultra-smooth gold substrates.\textsuperscript{49}
Therefore, based on AFM, XPS, RAIRS and CA analysis we concluded that the SAMs prepared on all substrate were well-ordered, crystalline, smooth and relatively defect free and that it was suitable to proceed with molecular electronic characterizations.

### Table 2.3  Summary of hexadecane contact angles and hysteresis on n-alkanethiolate SAMs on Au\textsuperscript{TS}, Ag\textsuperscript{TS} and Ag\textsuperscript{UPD/Au}

<table>
<thead>
<tr>
<th>SAM</th>
<th>(\text{Static}) Contact Angle (°)</th>
<th>(\Delta \theta_{\text{hys}}) (°)</th>
<th>(\text{Static}) Contact Angle (°)</th>
<th>(\Delta \theta_{\text{hys}}) (°)</th>
<th>(\text{Static}) Contact Angle (°)</th>
<th>(\Delta \theta_{\text{hys}}) (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>C8SH</td>
<td>41.7 ± 1.4</td>
<td>3.8 ± 1.3</td>
<td>37.6 ± 0.6</td>
<td>2.8 ± 0.6</td>
<td>40.4 ± 1.6</td>
<td>2.3 ± 1.3</td>
</tr>
<tr>
<td>C10SH</td>
<td>45.0 ± 0.9</td>
<td>2.6 ± 1.8</td>
<td>40.5 ± 1.5</td>
<td>2.3 ± 1.0</td>
<td>42.7 ± 1.1</td>
<td>1.3 ± 1.2</td>
</tr>
<tr>
<td>C12SH</td>
<td>45.4 ± 1.2</td>
<td>3.2 ± 3.0</td>
<td>42.0 ± 0.2</td>
<td>1.9 ± 1.2</td>
<td>45.8 ± 0.7</td>
<td>2.0 ± 1.0</td>
</tr>
<tr>
<td>C14SH</td>
<td>46.2 ± 1.5</td>
<td>2.5 ± 1.7</td>
<td>43.7 ± 1.8</td>
<td>2.3 ± 0.8</td>
<td>44.4 ± 3.1</td>
<td>2.6 ± 0.6</td>
</tr>
<tr>
<td>C16SH</td>
<td>47.7 ± 0.5</td>
<td>3.9 ± 1.5</td>
<td>44.9 ± 0.6</td>
<td>1.5 ± 0.3</td>
<td>46.0 ± 1.7</td>
<td>4.7 ± 2.1</td>
</tr>
</tbody>
</table>

#### 2.3.4. Molecular Electronic Characterisation

Figure 2.12 shows the current densities measured at junction bias of +0.5V as a function of chain length on all three substrates. Based on the linear least squares best fits the tunneling decay coefficient, \(\beta\), for the series on Au, Ag and Ag\textsuperscript{UPD/Au}\textsuperscript{TS} were 1.02 ± 0.07 nC\(^{-1}\), 1.02 ± 0.03 nC\(^{-1}\) and 0.94 ± 0.03 nC\(^{-1}\), respectively. All of these values fall within accepted the literature range determined for \(\beta\) for n-alkanethiolate SAMs using numerous test beds (0.9 – 1.1 nC\(^{-1}\)).\textsuperscript{11,12,50,51}
Furthermore, in addition to being indistinguishable from each other, current densities for the series on Au\textsuperscript{TS} and Ag\textsuperscript{TS} were also indistinguishable from those observed by Whitesides et al., who studied the same SAM series, on the same substrates, using the same test bed\textsuperscript{12}. This result is rather significant for the EGaIn tip community as recently there have been concerns expressed with regards to the reproducibility of data collected using this testbed. Our ability to reproduce the results of Whitesides et al., in a different lab, using a different EGaIn Tip set up, helps to assuage concerns associated with the reproducibility of data collected using EGaIn tips (at least in the case of n-alkanethiolate SAMs). A full breakdown of the data collected for each chain length on each substrate can be seen in Figure 2.13 (and Table S2.1) and a full comparison of the tunneling currents we observed for the n-alkanethiolate on Au\textsuperscript{TS} and Ag\textsuperscript{TS} and those reported by the Whitesides’ group at Harvard, can be seen in the supplemental section of this chapter.

\textbf{Figure 2.12} Current densities measured at a junction bias of +0.5V for C8, C10, C12, C14 and C16 n-alkanethiolate SAMs on Au\textsuperscript{TS} (blue square), Ag\textsuperscript{TS} (grey diamond) and Ag\textsuperscript{UPD}/Au\textsuperscript{TS} (red triangle). The least squared lines of best fit for each series are also included. The least square fits for the series on Au\textsuperscript{TS} and Ag\textsuperscript{TS} are difficult to distinguish because they are in fact identical.
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Figure 2.12 Shown on the left are histograms and Gaussian fit for n-alkanethiolate SAMs at junction bias of +0.5V on (A) Au\textsuperscript{TS}, (B) Ag\textsuperscript{TS} and (C) Ag\textsuperscript{UPD}/Au\textsuperscript{TS}. Shown on the right are the average current voltage traces for the series on (F) Au\textsuperscript{TS} (B) Ag\textsuperscript{TS} and (C) Ag\textsuperscript{UPD}/Au\textsuperscript{TS}. 
While the charge transport results on $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{TS}}$ are expected, the results observed on the $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ substrate are far more surprising. Table 2.4 summarizes the key tunneling parameters for the n-alkanethiolate series on $\text{Au}^{\text{TS}}$, $\text{Ag}^{\text{TS}}$ and $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$. While the log $J_o$ values determined from the least square fits are nearly identical for the SAM series on $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{TS}}$, $3.9 \pm 0.4$ and $3.9 \pm 0.2$, respectively, the value for the series on $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ is more than an order of magnitude smaller, $2.7 \pm 0.2$. The difference in log $J_o$ is somewhat exaggerated by the smaller $\beta$ value determined for $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$, but is still significant. Comparing only the data that we directly measured for the SAM series on $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ we still find an average drop in current densities of $\Delta \log J = -0.71 \pm 0.15$, in going from $\text{Au}^{\text{TS}}$ to $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ (see Table S2.1). In order to verify that this trend was in fact real and not due to systematic error caused by some aspect of the SAM or substrate preparation, or the EGaIn tip test bed, C16SH SAMs on $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ were prepared and tested alongside one another. The $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ substrates were taken from the same wafer, both samples were immersed in the same C16SH deposition solution, for the same length of time, and junction data was collected intermittently (i.e., a tip was used to form a junction on the $\text{Au}^{\text{TS}}$ sample and then was used for form a junction on the $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ sample.

Table 2.4 Summary of the charge transport parameters $\beta$ (the decay coefficient) and log $J_o$ for the series of n-alkanethiolate SAMs on $\text{Au}^{\text{TS}}$, $\text{Ag}^{\text{TS}}$ and $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$

<table>
<thead>
<tr>
<th>Substrate</th>
<th>$\beta$ (nC^{-1})</th>
<th>Log $J_o$</th>
</tr>
</thead>
<tbody>
<tr>
<td>$\text{Ag}^{\text{TS}}$</td>
<td>$1.02 \pm 0.03$</td>
<td>$3.9 \pm 0.2$</td>
</tr>
<tr>
<td>$\text{Au}^{\text{TS}}$</td>
<td>$1.02 \pm 0.07$</td>
<td>$3.9 \pm 0.4$</td>
</tr>
<tr>
<td>$\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$</td>
<td>$0.94 \pm 0.03$</td>
<td>$2.7 \pm 0.2$</td>
</tr>
</tbody>
</table>
and vice versa) on both samples, using the same EGaIn tips. In this manner, any systematic error which would have contributed to the results observed for Ag\textsuperscript{UPD}/Au\textsuperscript{TS} would also be observed for the C16SH Au\textsuperscript{TS} sample. The results for the experiment are shown in Figure 2.14. Analysing the data as a paired t-test yielded a $t$-stat = 7.6, ($p < 0.0001$, $df = 7$), and hence we can reject the null hypothesis, that current density across C16SH SAMs on Au\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS} are the same, with more than 99.9\% confidence.
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Figure 2.14 Side by side MEC of C16SH and C15SH SAMs on Au\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS} Shown on the left are the (A) paired test results, (B) histogram and Gaussian fits and (C) the average cyclic voltammetry scans measured for C16SH on the two substrates. Shown on the right are the (D) paired test results, (E) histogram and Gaussian fits and (F) the average cyclic voltammetry scans measured for C15SH on the two substrates.
2.3.5. Cause of $\Delta \log J$ on $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ Substrates

Although n-alkanethiolate SAMs have unique properties on each of the three substrate studied, there are certain properties that can be eliminated as potential causes for the discrepancy in current densities. Charge transport is known to occur via non-resonant coherent hole tunneling which follows a through bond path; therefore, the different tilt angles of the carbons chains has no influence on charge transport (evidenced by the fact that current densities across SAMs on $\text{Au}^{\text{TS}}$, which have tilts of $\sim 30^\circ$, and SAMs on $\text{Ag}^{\text{TS}}$, which have tilts of $\sim 11^\circ$, were indistinguishable). Different packing densities likely do influence charge transport to some extent, but the effects should be negligible given that the densities on $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ are assumed to be similar (the different packing densities on $\text{Ag}^{\text{TS}}$ and $\text{Au}^{\text{TS}}$ would theoretically only translate to a $\Delta \log J = 0.1$, see supplemental section 2.6.1 for explanation). This leaves four possible causes for the drop in current densities on $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$: 1. Differences in terminal methyl group orientation lead to different interactions with EGaIn tips and different effective electrical contact areas, as was observed for $n_{\text{even}}$ and $n_{\text{odd}}$ n-alkanethiolate SAMs on $\text{Au}^{\text{TS}}$. 2. Different injection barriers/resistance at the top and/or bottom interfaces. 3. The barrier height to charge transport is larger for n-alkanethiolate SAMs on $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ than it is on $\text{Au}^{\text{TS}}$ or $\text{Ag}^{\text{TS}}$. 4. The length of the tunneling path for hole transport is longer on $\text{Ag}^{\text{UPD}}/\text{Au}$ as compared to $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{TS}}$.

Based on our contact angle study, which found that n-alkanethiolate SAMs on $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ had similar static hexadecane contact angles, the first scenario seems fairly unlikely. Nevertheless, in order to ensure that this was not the case, we tested an odd chain n-alkanethiolate SAM, C15SH, on both $\text{Au}^{\text{TS}}$ and $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$, in the same side by side method used for C16SH, see Figure 2.14. If the drop in current density was due simply to terminal group orientation we might expect that the trend observed for C16SH to be reversed for C15SH on account of the odd-
even effect. This did not turn out to be the case; current densities were once again consistently lower for C15SH on Ag\textsuperscript{UPD}/Au\textsuperscript{TS}, Δlog J = -0.9 ± 0.4 (see Table S2.3). The results for the paired t-test yielded a t-stat = 6.14, (p<0.0005, df=7), allowing us to once again reject null hypothesis that charge transport is the same for C15SH on the two substrate with greater than 99.9% confidence. We therefore conclude that orientation had little to no effect on charge transport.

The SAMs on all substrates are in van der Waals contact with the top EGaIn tip contact, therefore it is unlikely that the drop in current densities on Ag\textsuperscript{UPD}/Au\textsuperscript{TS} would arise due to different injection barrier heights at this interface. Metal-S hybridization likely does not affect Log J\textsubscript{o} for the SAMs here because current densities on Ag\textsuperscript{TS} and Au\textsuperscript{TS} were indistinguishable. This leaves only the Ag\textsuperscript{UPD}/Au\textsuperscript{TS} interface as a potential contributor to the increased resistivity of Ag\textsuperscript{UPD}/Au\textsuperscript{TS} junctions. Based on the current study, we cannot conclusively confirm or deny that this contributed to the lower J\textsubscript{o} values observed for SAMs on Ag\textsuperscript{UPD}/Au\textsuperscript{TS} substrates, but we do point out that if the Ag\textsuperscript{UPD}/Au interface acted as an additional resistor in series with the tunneling barrier (i.e. charges tunneled to the Ag\textsuperscript{UPD} layer and then continued on to underlying Au via ohmic transport) it would not have the consistent influence on current densities across all chains lengths that was observed experimentally. Put another way, currents drop ~3 orders of magnitude in going from C8 to C16 on all substrates. Theoretically, even if a resistor in series with the tunneling junctions were to cause a 1 order drop in current density between C8 SAMs on Au\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS}, its impact would be practically negligible for C16 SAMs whose resistance is comparatively much larger. Hence, we do not attribute the lower current densities observed on Ag\textsuperscript{UPD}/Au substrates to any interfacial barrier effects.

With regards to barrier height as a potential cause: For n-alkanethiolates charge transport is dominated by hole tunneling along the HOMO\textsuperscript{*} along the aliphatic backbone; therefore, the primary barrier height for the tunneling process is the energy gap between the metal Fermi level and this HOMO\textsuperscript{*}\textsuperscript{,54} Based on this it would seem logical that molecular junctions using higher
work function metals (i.e. metals with lower Fermi levels) would have smaller a tunneling barrier and be more conductive. In practice, however, Fermi level pinning, caused by misalignment in vacuum levels across junctions, significantly mitigates potential differences in barrier heights caused by different metal electrodes. This has led many to conclude that changing the work function of said metal simply does not provide a handle for tuning junction properties. In a study relevant to our own system, Tognalli et al., compared the Raman spectra of 4-mercaptopyridine on Au, Ag and Ag\textsuperscript{UPD}/Au surfaces and determined that the Fermi-HOMO energy gap for molecules on all three substrates varied by only ~0.1eV. Subsequent DFT calculations corroborated their observation, as have similar studies done for other molecules. Even if we were to assume, for the sake of discussion, that the Schottky-Mott rule held and Fermi level pinning was not a factor, the work functions of Ag\textsuperscript{UPD}/Au and Au are essentially the same (~5.1 eV) and, what is more, they are higher than that of Ag (~4.5 eV). If the Schottky-Mott rule were to hold and there truly were significant differences in barrier heights in the junctions, theory would predict tunneling currents on Au and Ag\textsuperscript{UPD}/Au to be similar, and tunneling current across Ag to be smaller. In contrast, the present study, and others, have observed similar tunneling currents for n-alkanethiolate SAMs on Au and Ag, and therefore we dismiss barrier heights as a significant contributor to the drop in current observed on Ag\textsuperscript{UPD}/Au.

Returning to the Raman study performed by Tognalli et al., they observed a significant chemical enhancement in their Raman spectra of 4-mercaptopyridine (4MP) on Ag\textsuperscript{UPD}/Au as compared with the spectra for the molecule on either bulk Au or Ag. Chemical enhancement are a common feature observed in Surface Enhanced Raman Spectroscopy (SERS) and are caused by metal-molecule charge transfer involving brief (5 fs) electron transfers between either the metal Fermi and molecular LUMO, or the metal Fermi and the molecular HOMO. The enhancement to Raman scattering as a result of these transfers is dependent on a number of factors, but one of them is the physical distance between the centre of charge density of the molecular frontier orbital.
involved in the transition and the metal image plane. Based on their experimental data and subsequent DFT modelling, Tognalli et al. reported that the chemical enhancement to the SERS spectra observed on all three substrates was due primarily to a charge transition between the molecular HOMO and Fermi level of the respective metals. Furthermore, they reported that the additional enhancement to Raman scattering observed for the molecule on Ag\textsuperscript{UPD}/Au, as compared with bulk Au and Ag, was due primarily to an increase in the physical distance between the molecular HOMO and metal Fermi level by 2.5 Å, which correlates to the width of a single layer of Ag atoms. Figure 2.15 shows the projected charge density of the HOMO of 4MP SAM and Fermi levels for all three substrates.
Figure 2.13 Projected charge densities for the HOMO (Left) and Fermi (right) levels of 4MP molecules on Au (top), Ag\textsuperscript{UPD}/Au (centre) and Ag (bottom). The d values shown in the central column are the effective distance for charge transfer between the molecular HOMO and metallic Fermi. Reprinted with permission from reference 13. Copyright (2011) American Chemical Society.
Surprisingly, unlike the topmost layers of bulk Au and Ag, the top Ag\textsuperscript{UPD} layer of the Ag\textsuperscript{UPD}/Au substrate has virtually no contribution to the metal Fermi level. It does, however, show some contribution to the molecular HOMO. Applying these parameters to our Ag\textsuperscript{UPD}/Au\textsuperscript{TS} system, if charge transfer were to occur between the EGaIn tip and substrate, a hole would have to tunnel across the length of the molecule, as well as the Ag\textsuperscript{UPD} layer, in order reach the underlying Fermi level of the substrate (which would technically start at the first Au layer of atoms). Based on the literature accepted $\beta = 0.73 - 0.89$ Å\textsuperscript{-1}, the additional 2.5 Å added to the length of the tunneling path due to the Ag\textsuperscript{UPD} layer would theoretically result in a drop in current density of $\Delta\log J = -(0.79 - 0.97)$. This agrees very well with $\Delta\log J = -0.71 \pm 0.15$ we observed experimentally. Therefore, we propose that the higher resistance observed for n-alkanethiolate SAMs on Ag\textsuperscript{UPD}/Au is due to a lengthening of the tunneling path caused by the presence of the Ag\textsuperscript{UPD}. A schematic model of the proposed tunnelling barrier for the bulk metal and UPD substrates is shown in Figure 2.16.

While the Ag\textsuperscript{UPD} layer likely does contribute to the molecular HOMO for the n-alkanethiolates systems, since the primary junction barrier is the HOMO* (the density of states that spread along the backbone of the alkyl chain) this contribution likely does not affect the primary tunneling barrier height in any significant way, as evidenced by the fact that the $\beta$ value (which is sensitive to barrier height) was relatively the same for the SAM series all three substrates. What does matter is that the Ag\textsuperscript{UPD} does not appear to be part of the metal Fermi level and therefore charges must tunnel through it as well as molecules to span the full width of the junction. Based on our results for the aliphatic n-alkanethiolate system and Tognalli et al., results for an aromatic system we predict that the UPD layer effect will hold for other molecular systems as well.
Figure 2.14  Schematic of the simplified energetic structure for n-alkanethiolate SAMs on bulk metal and Ag$^{\text{UPD}}$/Au substrates. The tunneling distance is increased by $d'$, the length of an Ag atom (2.5Å), for the Ag$^{\text{UPD}}$/Au system (bottom image) relative to the bulk metal system (top image) that has tunneling distance, $d$. $\theta_{\text{M-SAM}}$ and $\theta_{\text{M-AgUPD-SAM}}$ are the work functions of the metal substrates after modification by the SAM, while $\Delta\theta_{\text{M-SAM}}$ and $\Delta\theta_{\text{M-AgUPD-SAM}}$ are the changes to the substrate work functions upon modification by the SAM. $\phi_h$ and $\phi_e$ are the hole and electron
tunneling barriers. HOMO* and LUMO* is the highest occupied molecular orbitals and lowest unoccupied molecular orbitals that run along the backbone of the alkyl chain, respectively. VDW is the van der Waals contact between the EGaIn tip and terminal end of the SAM and acts as a barrier to transmission in the junctions.

2.4. Conclusion

Here in we have demonstrated the viability of the Ag\textsuperscript{UPD}/Au\textsuperscript{TS} substrates for the purposes of molecular electronics. Molecular electronic characterisation of n-alkanethiolate SAMs on Au\textsuperscript{TS}, Ag\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS} substrates with EGaIn tip top contacts revealed that the inherent electronic properties of SAMs were not dramatically altered by Ag\textsuperscript{UPD} adlayer. We did however observe that the Ag\textsuperscript{UPD}/Au\textsuperscript{TS} systems had comparatively lower tunneling currents, as compared with Au\textsuperscript{TS} and Ag\textsuperscript{TS} systems. We attribute this phenomenon to the Ag\textsuperscript{UPD} layer adding length to the tunneling barrier and not contributing to the underlying bulk metal Fermi level. We propose this based on reported Raman studies of SAMs on Ag\textsuperscript{UPD}/Au substrates\textsuperscript{13} and based on the fact that the calculated impact on current densities of lengthening tunneling barriers by a single Ag atom, agreed well with experimental observations. We do acknowledge that a comprehensive DFT study of the systems reported here would augment the current study and would likely be of great benefit to the field and would help to conclusively elucidate the impact of certain molecular junction parameters on charge transport. Although we have only demonstrated its viability for n-alkanethiolate SAMs, Ag\textsuperscript{UPD} substrates are compatible with a variety of molecular systems making it an attractive option for a wide range of molecular electronic application where greater thermal and electrochemical stability are desired. Furthermore, although we chose to focus our study exclusively on Ag\textsuperscript{UPD} layers, there are numerous other well-established UPD systems available for investigation. Amongst the many parameters that might prove interesting to study for their electronic impact are: UPD systems with different adlayer coverages and adlattices, UPD systems involving different metals,\textsuperscript{5} and multilayer (three of more metals) UPD systems.\textsuperscript{5,16}
2.5. References


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2.6. Supplemental

2.6.1. Impact of Packing Density of n-alkanethiolate SAMs on Au and Ag on Tunneling Currents

In this chapter we mentioned the difference in the packing density of n-alkanethiolate SAMs on AuTS and AuTS would result in only a $\Delta \log J = \sim 0.1$. Here we walk through the calculation to arrive at that number. Thuo et al.\textsuperscript{56} report that the packing density of n-alkanethiolate SAMs is 29% higher on AgTS than it is on AuTS. Consider the equation for the resistance of a film with $x$ parallel wires, where $R_Au$ is the total resistance of a SAMs on Au and $R_1$ is the resistance through an individual molecular wire:

$$\frac{1}{R_{Au}} = x \left( \frac{1}{R_1} \right)$$  \hspace{1cm} (1)

If we adjust this for the packing density of the SAM on Ag we get equation 2, where $R_{Ag}$ is the resistance of the SAM on Ag:

$$\frac{1}{R_{Ag}} = 1.29x \left( \frac{1}{R_1} \right)$$  \hspace{1cm} (2)

Because we know $R \propto 1/J$ at a given applied bias, equations 1 and 2 are equivalent to 3 and 4, respectively, where $J_{Au}$ is the current density across the SAM on Au, $J_{Ag}$ is the current density across the SAM on Ag and $J_1$ is the current density across an individual molecule at a given bias.

$$J_{Au} = x \left( J_1 \right)$$  \hspace{1cm} (3)

$$J_{Ag} = 1.29x \left( J_1 \right)$$  \hspace{1cm} (4)

Next, dividing $J_{Ag}$ by $J_{Au}$ we get equation 5 and by applying the log function we get equation 6:

$$\frac{J_{Ag}}{J_{Au}} = 1.29$$  \hspace{1cm} (5)

$$\Delta \log J = \log J_{Ag} - \log J_{Au} = \log 1.29 = 0.11$$  \hspace{1cm} (6)
2.6.2. XPS Survey Scans of Ag$^{UPD}$/Au$^{TS}$ Substrates

**Figure S2.1.** XPS survey scan of Ag$^{UPD}$/Au$^{TS}$ sample 1 in Table 2.1.
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**Figure S2.** XPS survey scan of $\text{Ag}^{\text{UPD}}/\text{Au}^{\text{TS}}$ sample 2 in Table 2.1
Figure S2.3. XPS survey spectra of Ag\textsuperscript{UPD}/Au\textsuperscript{TS} sample 3 in Table 2.1
2.6.3. Cyclic Voltammetry Scans of Ag\textsuperscript{UPD} Depositions

**Figure S2.4** (A) CV scan, (B) the Coulometric integration of the anodic sweep and (C) the Coulometric integration of the cathodic scan of the UPD process for sample 1 in Table 2.1
Figure S2.5 (A) CV scan, (B) the Coulometric integration of the anodic sweep and (C) the Coulometric integration of the cathodic scan of the UPD process for sample 2 in Table 2.1
Figure S2.6 (A) CV scan, (B) the Coulometric integration of the anodic sweep and (C) the Coulometric integration of the cathodic scan of the UPD process for sample 3 in table 2.1
2.6.4. RAIRS Spectra of n-alkanethiolates SAMs on Au\textsuperscript{TS}, Ag\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS}

**Figure S2.7** RAIRS spectra of C8, C10, C12, C14, C16 n-alkanethiolate SAMs on (A) Au\textsuperscript{TS}, (B) Ag\textsuperscript{TS}, and (C) Ag\textsuperscript{UPD}/Au\textsuperscript{TS}.
2.6.5. Comparing Tunneling Currents with Whitesides et al.

Figure S2.8  Comparison of the tunneling currents observed for even n-alkanethiolate SAMs on (A) Au_{TS} and (B) Ag_{TS}. The data points reported in this study are blue squares, whereas the data reported by Whitesides et al. in reference 12 are red diamonds. Data reported was adapted with permission from reference 12. Copyright (2014) American Chemical Society.
2.6.6. Summary of MEC Data

Table S2.1  Summary of MEC data collected for n-alkanethiolate SAMs on Au\textsuperscript{TS}, Ag\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS}. Current densities J are reported for an applied bias potential of +0.5V.

| SAM  | Substrate | Log $|J(0.5V)|$ (A/cm\textsuperscript{2}) | Yield (%) | Junc. | Scans |
|------|-----------|-------------------------------------|-----------|-------|-------|
| C8SH | Ag\textsuperscript{TS} | 0.3 ± 0.4                          | 93        | 26    | 520   |
|      | Au\textsuperscript{TS} | 0.2 ± 0.5                          | 40        | 21    | 420   |
|      | Ag\textsuperscript{UPD}/Au\textsuperscript{TS} | -0.6 ± 0.2                        | 94        | 34    | 680   |
| C10SH| Ag\textsuperscript{TS} | -0.5 ± 0.1                         | 97        | 33    | 660   |
|      | Au\textsuperscript{TS} | -0.3 ± 0.4                         | 59        | 20    | 400   |
|      | Ag\textsuperscript{UPD}/Au\textsuperscript{TS} | -1.2 ± 0.2                        | 52        | 33    | 660   |
| C12SH| Ag\textsuperscript{TS} | -1.3 ± 0.4                         | 69        | 29    | 580   |
|      | Au\textsuperscript{TS} | -1.5 ± 0.2                         | 68        | 21    | 420   |
|      | Ag\textsuperscript{UPD}/Au\textsuperscript{TS} | -2.2 ± 0.1                        | 65        | 41    | 820   |
| C14SH| Ag\textsuperscript{TS} | -2.4 ± 0.3                         | 100       | 28    | 560   |
|      | Au\textsuperscript{TS} | -2.4 ± 0.2                         | 76        | 28    | 560   |
|      | Ag\textsuperscript{UPD}/Au\textsuperscript{TS} | -3.0 ± 0.2                        | 91        | 30    | 600   |
| C16SH| Ag\textsuperscript{TS} | -3.2 ± 0.3                         | 100       | 39    | 780   |
|      | Au\textsuperscript{TS} | -3.2 ± 0.4                         | 80        | 39    | 780   |
|      | Ag\textsuperscript{UPD}/Au\textsuperscript{TS} | -3.8 ± 0.5                        | 91        | 39    | 780   |
Underpotentially Deposited Silver as a Substrate for the Enhancement of Molecular Junction Stability

Table S2.2 Summary of MEC data for the side-by-side (paired T-test) measurements of C16 n-alkanethiolate SAMs on Au\textsuperscript{TS} and Ag\textsuperscript{UPD}/Au\textsuperscript{TS}. Current densities J are reported for an applied bias potential of +0.5V.

| Junction # | \( \log |J(0.5V)| \) (A/cm\(^2\)) | \( \Delta \log J = \log J_{\text{AuTS}} - \log J_{\text{AgUPD/AuTS}} \) |
|------------|---------------------------------|--------------------------------------------------|
| 1          | -3.41 ± 0.03                    | -3.74 ± 0.06                                     | 0.33 |
| 2          | -3.85 ± 0.08                    | -4.47 ± 0.05                                     | 0.62 |
| 3          | -2.86 ± 0.10                    | -3.52 ± 0.03                                     | 0.67 |
| 4          | -3.65 ± 0.07                    | -4.02 ± 0.09                                     | 0.37 |
| 5          | -3.14 ± 0.06                    | -4.02 ± 0.09                                     | 0.88 |
| 6          | -3.00 ± 0.04                    | -3.40 ± 0.06                                     | 0.40 |
| 7          | -2.32 ± 0.03                    | -2.82 ± 0.05                                     | 0.50 |
| 8          | -3.18 ± 0.04                    | -3.64 ± 0.09                                     | 0.46 |
| **Average**|                                | **0.53 ± 0.18**                                  |
Table S2.3  Summary of MEC data for the side-by-side (paired T-test) measurements of C15 n-alkanethiolate SAMs on Au<sup>T</sup>S and Ag<sup>UPD</sup>/Au<sup>T</sup>S. Current densities J are reported for an applied bias potential of +0.5V.

| Junction # | Log |J(0.5V)|<sub>T</sub>S (A/cm<sup>2</sup>) | Log |J(0.5V)|<sub>Ag</sub><sup>UPD</sup>/Au<sup>T</sup>S (A/cm<sup>2</sup>) | ∆Log J = Log J<sub>Au</sub>TTS - Log J<sub>Ag</sub>UPD/TTS |
|------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|-------------------------------|
| 1          | -3.08 ± 0.07                  | -3.76 ± 0.02                  | 0.68                          |
| 2          | -2.70 ± 0.10                  | -4.00 ± 0.10                  | 1.31                          |
| 3          | -3.57 ± 0.09                  | -3.74 ± 0.18                  | 0.17                          |
| 4          | -3.47 ± 0.07                  | -4.19 ± 0.35                  | 0.72                          |
| 5          | -2.75 ± 0.16                  | -3.86 ± 0.08                  | 1.10                          |
| 6          | -2.54 ± 0.07                  | -3.92 ± 0.06                  | 1.39                          |
| 7          | -2.63 ± 0.04                  | -3.51 ± 0.05                  | 0.88                          |
| 8          | -2.74 ± 0.06                  | -3.77 ± 0.06                  | 1.03                          |

Average 0.91 ± 0.39
Chapter 3

The Influence of Head Group, Substrate Topography and EGaIn Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions
Au-S bonds are amongst the most common head-group substrate interactions used in molecular self-assemblies and are commonly featured in both single and ensemble molecular junction studies. This bond, however, has been shown to degrade at ~50-60°C and therefore does not meet threshold requirement to be incorporated into modern central processing units which can operate at temperatures upwards of ~70°C.\textsuperscript{1,2} In previous work, our group showed that SAMs incorporating a chelating dithiophosphinic acid (DTPA) head group demonstrated improved stability against thermal desorption compared to analogous thiolate SAMs.\textsuperscript{3-6} Furthermore, much like the thiolate molecule, the DTPA head group can be easily functionalized to anchor a variety of substituent groups. This combination of enhanced stability and chemical versatility make DTPA derivative SAMs an appealing candidate for molecular electronic applications. Recent studies have revealed that the influence of the head group on charge transport is more sensitive in conjugated systems than it is for systems incorporating long aliphatic chains.\textsuperscript{7,8} Therefore, we chose to characterize the charge transport properties of DTPA SAMs functionalized with two pendant phenyl rings, (diphenyl)dithiophosphinic acid (Ph\textsubscript{2}DTPA), and compare them with those of the well characterized analogous thiolate SAM, thiophenol (PhSH) using an EGaIn tip test bed. We show that the current densities across PhSH and Ph\textsubscript{2}DTPA SAMs were $\log J(+0.5V) = 0.0 \pm 0.3$ and $\log J(+0.5V) = -2.8 \pm 0.5$, respectively. The value of $\log J(+0.5V) = 0.0 \pm 0.3$ for PhSH is in relatively good agreement with conductance trends for thiolated aromatic SAMs reported in literature;\textsuperscript{9,10} however, the drop in current density of nearly three orders of magnitude of Ph\textsubscript{2}DTPA SAMs is surprising, and cannot be reconciled with the PhSH value by taking into account a slightly longer through bond tunneling path (~2Å). We therefore attribute the drop in current density to a decoupling of the phenyl pendant groups from underlying gold electrode and disruption in conjugation, due to the additional spacing and tetrahedral geometry induced by the P atom. Furthermore, throughout the course of this study we paid careful attention to the quality of the junctions and found that using “flattened” EGaIn tip (which formed larger contacts) and/or as-deposited (asdep) substrates resulted in the increased prominence of ohmic transport through thin
area SAM defects. In contrast, when “soft” tips and smooth template stripped surface were used, fewer thin area defects were available to probe and charge transport was predominantly dependent upon molecular properties.

3.1. Background

3.1.1. PhSH SAMs: a Baseline Aromatic SAM Structure

Conjugated aromatic systems have garnered great interest in the field of molecular electronics. In addition to being relatively conductive, these systems are also amongst the few systems in which researchers have successfully altered charge transport by manipulating subtle features such as head group hybridization, as well as molecular conformations and configurations. Furthermore, these systems have also demonstrated interesting electronic properties such as negative differential resistance, reversible switching, and bistable conductance states. These properties could serve as a basis for the development of useful electronic components such as molecular memory, molecular diodes and molecular dielectric layers and make aromatic/conjugated systems appealing candidates for integration into circuitry and microelectronic devices. Hence, given their potential, researchers have been motivated to study monolayers of such systems, with goal of improving their thermal stability, while simultaneously elucidating the factors that govern their organization and conductance on metal electrodes.

Much like n-alkanethiolates can be considered a baseline aliphatic series, thiolated oligoacenes can be viewed as a baseline conjugated series and at the very base of this series is thiophenol (PhSH), which consists solely of a thiol group coordinated to a single phenyl ring. Unlike n-alkanethiolate SAMs - which have extensively been shown to self-assemble in a $\sqrt{3} \times \sqrt{3} \ R30^\circ$ adlattice on Au(111) substrates - PhSH SAMs on Au(111) form disorganized monolayers and display a mix of randomly dispersed islands, pit and step edges, as shown in Figure 3.1(i). In
their DFT analysis, Nara et al. presented compelling evidence that the lack of molecular periodicity observed for PhSH SAMs was the result of multiple Au(111) binding sites and adlattices being essentially degenerate.\(^2\) They concluded that the SAM consisted predominantly of a \(2\sqrt{3} \times \sqrt{3} \) R 30° herringbone structure (with molecules bound to the fcc-bridging sites of Au(111) and phenyl rings tilted \( \sim 21° \) from the surface normal), stabilized against a \(\sqrt{3} \times \sqrt{3} \) R30° structure (for which the fcc-bridging and –hollow sites were degenerate, resulting in phenyl rings either tilted \( \sim 33° \) relative to the surface normal or being nearly upright, respectively). The proposed adlattice structures as well as the potential binding sites for the PhSH molecules on Au(111) are shown in Figures 3.1(ii-iv).
Figure 3.1  i) STM image taken by Dhirani et al., of a PhSH SAM on Au(111). The vertical scale ranges 6.4Å from dark to bright. ii) Top view of the Au(111) surface. Large, medium and small circles denote the top, second and third layers of Au atoms, respectively. Dots labelled (a)-(e) denote the different adsorption sites probed by Nara et al., for PhSH SAM formation. (a) hcp-bridge, (b) fcc-bridge, (c) hcp-hollow, (d) fcc-hollow and (e) on-top site. Dotted line denotes the (1x1) Au surface unit cell. iii) Optimized $\sqrt{3} \times \sqrt{3}$ R 30° PhSH SAM structure on Au(111). iv) Optimized $2\sqrt{3} \times \sqrt{3}$ R 30° herringbone PhSH SAM structure on Au(111). Figure3.1i) Adapted with permission reference 18. Copyright (1996) American Chemical Society. Figures 3.1ii-iv) Reprinted with permission from reference 22. Copyright (2004), AIP Publishing LLC.
3.1.2. Improving Stability by Engineering Molecular Structure

Unfortunately, much like other thiolate SAMs, PhSH SAMs tend to desorb from Au substrate at temperature < 70 °C, and therefore these baseline aromatic SAMs are ill-suited to applications in real world electronic devices.\(^{1,24}\) In Chapter 1 we touched on a few ex-situ approaches aimed at circumventing this problem. These included the carbon nanomembrane approach proposed by Penner et al.\(^{25}\), and the radical growth mechanism for diazonium based molecular layer proposed by McCreery et al.\(^{2}\) In Chapter 2, we also reported on the use of underpotential deposited monolayers of Ag on Au\(^{TS}\) to enhance SAM stability for molecular electronic applications. In addition to these ex-situ approaches, SAM stability can also be enhanced from the inside out. In-situ approaches focus on engineering molecular structures to improve SAM stability either by enhancing intermolecular interactions, enhancing substrate-molecule interactions or some combination of the two. We report on such approaches next.

3.1.2.1. PhSH Derivatives

Interestingly, DFT studies of the PhSH SAMs have revealed that intermolecular interactions have relatively little influence on their overall stability.\(^{22}\) This can be attributed to the fact that the short rigid nature of the PhSH molecule limits its ability to engage in favourable van der Waals interactions with neighbouring molecules on surfaces. In fact, related studies on derivatives of PhSH molecules incorporating either short aliphatic chains and/or additional aromatic rings have been shown to significantly improve the stability of SAMs.\(^{18,24,26,27}\) In a STM study correlated with the above mentioned DFT report, Dhirani et al. observed that extending the number of aromatic units eventually led to the formation of well-ordered SAMs with \(2\sqrt{3} \times \sqrt{3}\) herringbone adlattices on Au(111), implying that intermolecular interactions and hence SAM stability were enhanced in this structure.\(^{18}\) Furthermore, in their study, Noh et al., found that the addition of a single methylene unit in-between the phenyl ring and thiol head group granted...
enough conformational flexibility to allow for favourable Π-Π stacking intermolecular interactions to take place and improved the thermal stability of benzenemethanethiol SAMs relative to PhSH SAMs as shown in Figure 3.2.\textsuperscript{24}

**Figure 3.2** Thermal desorption spectroscopy of (a) Benzenethiol (aka PhSH) and (b) Benzenemethanethiol SAMs on Au(111). Filled circles, are the parent mass species (R-SH\(^+\)) and would correspond to the desorption of physisorbed molecules; open circles correlate with the chemisorbed mass species (R-S\(^+\)); and the solid lines, correspond to molecular fragments species formed via C-S bond cleavage during heating (R\(^+\)). Reprinted with permission from reference 24. Copyright (2010) Elsevier.
3.1.2.2. Chelating Head Groups

In addition to enhancing intermolecular interaction, another in-situ approach for improving SAM stability has been the incorporation of chelating head groups. These types of head groups tend to form multiple bonds per molecule with substrates and have been shown to lead to more robust SAMs, with enhanced stability against thermal and electrochemical desorption as a result of the chelate effect.\(^3\) Another interesting feature of this class of molecules is that their architectures can vary greatly from that archetypical n-alkanethiolate SAMs, as they can incorporate multiple different pendant groups.\(^8,28\) Some common examples of chelating head groups are shown in Figure 3.3, and include: spiroalkanedithiols,\(^29\) carboxylic acids,\(^9,30\) dithiocarboxylic acids,\(^31\) xanthic acids\(^32\) and dithiocarbamates.\(^8,33,34\)

![Figure 3.3](image)

**Figure 3.3** A schematic of various chelating head groups and their bonding configuration on metal substrates. The head groups shown are: A) spirokanedithiol, B) dithiocarboxylic acid, C) xanthic acid, D) carboxylic acid and E) dithiocarbamate.
3.1.3 The Influence of Chelating Head Groups on Charge Transport Across SAMs

While there exists a large body of literature on thermal stability and organization of molecules incorporating chelating head groups, there are relatively few reports regarding their impact on molecular conductance. Studies that have been reported, however, seem to suggest that individual systems are unique and that no general trend exists amongst chelating groups in terms of their influence on charge transport. Based on their recent studies, Whitesides et al. concluded that current densities across molecules incorporating carboxylic acid head groups were indistinguishable from those across analogous alkanethiolate SAMs and that the presence of the lone C atom on the carboxylic acid head group was sufficient to decouple pendant aromatic rings from underlying electrodes.\(^9,35\) In contrast, in their study on dithiocarbamate based molecular junctions, von Wrochem et al., observed that the chelated head group significantly lowered the barrier to charge injection, leading to \(~2\) orders of magnitude increase in \(J_o\) as compared with thiolated analogues. This was despite the aromatic backbone of the SAMs having similar orientations to the surface with both head groups.\(^8\) The authors concluded that the increase in junction conductivity was the result of the electronically delocalised nature of the chelated head group (see Figure 3.3E), enhancing/maintaining coupling between the molecule’s aromatic backbone and the metal electrode. As mentioned before, another particularly interesting aspect of head groups such as dithiocarbamates, which can present multiple pendant groups, is that they open the door for a wide range of chemical versatility. In the von Wrochem study an aromatic pendant group was paired with a relatively short aliphatic group. It is not unreasonable to presume, however, that different combinations of different pendant groups might induce different packing structures and molecular orientations, which might in turn also influence molecular electronic properties.
3.1.4 Dithiophosphinic Acid (DTPA) Head Groups

In this chapter we focus our study on aromatic Ph$_2$DTPA SAMs which incorporate a chelating head group. The DTPA head group has been explored by our group in the past for its impact on SAM organization and thermal stability,$^{3-6, 28}$ but has yet to be characterized explicitly for its effect on molecular electronic structure. This head group is particularly appealing for molecular electronics applications not only on account of its enhancement to SAM stabilities, but also because it can be readily prepared from stable secondary phosphines, and therefore offers a wide range of chemical versatility. The structural architecture of DTPA molecules, shown in Figure 3.4, with its two pendant groups and chelating sulfurs, is reminiscent to that of the dithiocarbamates discussed earlier. There are, however, a few distinguishing features between the two. First and foremost, while the dithiocarbamates generally adopt planar stereochemistry,$^{34}$ the DTPA molecules are generally tetrahedral.$^6$ This tends to induce some interesting and unique structural effects in DTPA SAMs. As we reported previously, short chain dialkyl(DTPA) SAMs on Au$^{TS}$ possess crystalline alkyl chains, which become progressively more liquid-like with increasing chain lengths.$^6$ This is contrary to the trend observed for standard n-alkanethiolate SAMs, in which short alkyl chains are liquid-like and become more crystalline as chain lengths increase due to an increased number of van der Waals interactions.$^4$ The odd trend in crystallinity for the dialkyl(DTPA) SAMs was rationalized by a model in which the tetrahedral geometry of the molecules allowed short to chains interdigitate with one another, leading to stabilizing van der Waals interactions, whereas bulkier long chains forced larger nearest neighbor distances, leading to fewer van der Waals interactions and more liquid-like behaviour.$^{3, 6}$
The Influence of Head Group, Substrate Topography and EGaIn Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions

Another unusual feature of DTPA SAMs is that their binding configuration has been shown to be highly dependent on substrate morphology.\(^5\) As we showed in a previous study (Figure 3.5) dialkylDTPA SAMs bind exclusively in a bidentate manner on smooth Au\(^{TS}\), but roughly 40% of molecules are monodentate on rougher as-deposited gold (Au\(^{asdep}\)) substrates. This finding was a fairly substantial discovery for the field of surface science, as it marked the first reported instance of substrate morphology having a pronounced influence on SAM organization. DFT investigation revealed the pragmatic reason for this was that the bidentate species was only 13-20 kJ/mol more stable than its monodentate counterpart. This is a relatively small chelate effect enhancement and only represent a 1.7-2.3 % improvement to the overall stability of the system;\(^3\) in comparison, the enhancement for dithiocarbamates was determined to be \(\sim 30\) kJ/mol.\(^8\) Consequently, on rough Au\(^{asdep}\) substrates, where there are more defect sites (smaller grains, deeper grain boundaries, and more step heights), bidentate bonding becomes even less favourable, and molecules bind in a monodentate fashion, as it grants them more

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Figure 3.4  A) Schematic of the DTPA head group and its chelated binding configuration on metal substrate. B) Schematic of diphenylDTPA (Ph\(_2\)DTPA) investigated in this study.
conformational flexibility, allowing for greater packing densities and more interchain van der Waals interactions.\textsuperscript{3-5} Most intriguing of all, the change from a SAM structure dictated by head group-metal interaction on Au\textsuperscript{TS}, to a SAM structure which favoured intermolecular interactions and higher packing density on Au\textsuperscript{asdep}, resulted in a complete reversal in the trend in crystallinity observed for dialkylDTPA SAMs on the two substrates (short chain dialkylDTPA SAMs on Au\textsuperscript{asdep} start off as liquid like and get progressively more crystalline with chain length). Hence, DTPA derivative SAMs are exemplary illustrations of how SAM structure is governed by a delicate balance between the steric demands of molecules, molecule-substrate binding interactions, intermolecular interactions, and substrate morphology.\textsuperscript{3-6,28,36}
Figure 3.5  A) and B) AFM images (left) of 200 nm Au\textsuperscript{asdep} and Au\textsuperscript{TS}, respectively. The vertical scale of the AFM images is 20 nm. The white lines correspond to the cross-sectional profiles shown next to each image (right). The Au\textsuperscript{asdep} surface consisted of ~50nm grains with grain boundaries as deep as 10nm and an RMS roughness of ~27Å. The Au\textsuperscript{TS} surfaces consisted of grains with sizes >200nm and had grain boundaries depths 2 nm along with an RMS roughness of ~4 Å.  C) Schematic of the monodentate binding configuration of dialkylDTPA SAMs on Au\textsuperscript{asdep} (left) and the bidentate binding configuration on Au\textsuperscript{TS} (right). Adapted with permission reference 5. Copyright (2011) American Chemical Society.
Our initial foray into the molecular electronic properties of the DTPA head group focuses specifically on Ph₂DTPA SAMs (see Figure 3.5C) on Au<sup>TS</sup> and Au<sup>asdep</sup>, and a comparison with PhSH SAMs for the following reasons: 1. Current densities have been shown to be particularly sensitive to head group modification when molecules are predominantly aromatic. Therefore we selected a molecule where both pendant groups of the DTPA were aromatic with the hope it would allow for the unambiguous interpretation of the DTPA head group’s influence on charge transport. 2. Ph₂DTPA is commercially available so it was a convenient choice that fit the first criteria. 3. Given the behavior we have observed for dialkylDTPA SAMs on Au<sup>TS</sup> and Au<sup>asdep</sup>, we felt it would be interesting to see if the Ph₂DTPA responded in a similar fashion and bound partially monodentate on Au<sup>asdep</sup> and were curious to investigate what effect this might have on charge transport. We chose to do this despite the known pitfalls associated with trying to measure current densities on rough substrates, as discussed in the introduction.⁴⁰,⁴⁹ 4. The EGaIn tip method was used for molecular electronics characterisation and as mentioned previously, absolute values collected with this paradigm do not always compare well with those from other testbeds. Therefore, an internal standard was needed to compare results collected for Ph₂DTPA with, and PhSH was selected because it was the closest thiolated analogue.

3.1.5 EGaIn Tip Junction Development

As touched on early in 1.8 EGaIn Tips in Chapter 1, EGaIn metal tips were developed as a replacement for Hg drop top-contact in the late 2000’s.³⁷,³⁸ The Ga₂O₃ “skin” on the EGaIn grants it non-Newtonian fluid dynamics and enables conical shaped tips (see Figure 2.7) to be extruded from drops of the liquid metal, which lends itself to more well-defined geometric contact areas. Furthermore, the oxide skin also helps prevent amalgamation with underlying metal electrodes leading to higher yields compared with Hg drop junctions. In spite of these
improvements, however, researchers still grappled with sporadic reproducibility, large standard deviations and user to user variations associated with this test bed. Researchers also struggled to determine the reasons why current densities measured using EGaIn tip top contacts were several orders of magnitude lower than those reported by analogous studies using single molecule and other ensemble test beds.\textsuperscript{39} A great deal of time and effort has been invested by numerous groups into both understanding the idiosyncrasies of this junction paradigm and refining data collection methods.

Nijhuis et al., have been proponents of the need to systematically study the influence of various EGaIn junction parameters and have contributed to understanding the influence substrate roughness and contact area size have on charge transport. In particular, in independent studies, they reported that rougher substrates and large EGaIn contact areas ($A_{\text{geometric}} > 960 \ \mu \text{m}^2$) cause more SAM defects (at grain boundaries, step heights, phase boundaries, etc.) to be contacted, which translates into electrical currents that are predominantly governed by ohmic (active) transport across these thin area defects, as shown in Figure 3.6.\textsuperscript{40,41,49}

**Figure 3.6** Illustration of thin area defects site in SAM based EGaIn molecular junctions, as proposed by Nijhuis et al. Arrows indicated the direction of current flow, the red areas are meant to indicate areas where Joule heating would be likely to occur. Reprinted with permission reference 40. Copyright (2015) American Chemical Society.
These ohmic transport sites effectively act like pseudo-shorts, as charges pass from one electrode to the other unencumbered by the molecular layers. According to Nijhuis et al., the net effect of thin area defects can result in current densities up to 5 orders of magnitude higher than would otherwise be reported for a “proper working” junction and, if left unchecked, can lead to erroneous $\beta$ and $J_0$ tunneling parameters and false interpretations of molecular electronic properties.\textsuperscript{40} Unfortunately, such “pseudo-shorts” do not manifest in the form of lower junction yields, as one might expect, and therefore researchers must be vigilant in assessing whether ohmic transport plays a significant role and/or minor role in measured current densities. One method, readily available to researchers, involves plotting normalized differential conductance, $\delta J/\delta V$ ($J$ is current density in, A/cm\textsuperscript{2}, and $V$ is applied bias in, V), as a function of applied bias, $V$. Due to Joule heating, which is the conversion of electrical energy to thermal energy during activated forms of charge transport, as higher biases are applied to a junction more and more heat gets dissipated at thin area defect sites, impeding ohmic charge transport. Consequently, in junctions where ohmic transport is dominant, the curvature of the $\delta J/\delta V$ vs $V$ plot becomes flat or even negative with increasing applied bias.\textsuperscript{40,41} In contrast, charge transport via tunneling is independent of temperature and tends to increase exponentially with applied bias in accordance with the Simmons equation (see eq 1 in the Introduction chapter). Consequently, differential conductance plots for junctions where tunneling is dominant, and where charge transport is governed by molecular electronic properties, will tend to have more positive curves. This concept was well illustrated by Rabson et al., who modelled the effect of charge transport through a dielectric layer with various conductive pinhole sizes. As shown in Figure 3.7, as the size of the pinholes increased, currents became increasing ohmic in character and the shape of the differential conductance plot shifts from positive (upwards) to negative (downwards).\textsuperscript{41}
Figure 3.7  A) Modelling of normalized differential conductance across a dielectric layer with a conductive pinhole with varying size, done by Rabson et al. The solid lines trace differential conductance from no pinhole, to a pinhole of size 1.5 nm, in 0.1 nm increments. The plot on the right (B) shows percentage of current that flows through the pinhole as a function of its size. The main graph was modelled for a temperature of 77 K, the insert is for modelling at 300 K. The input voltage in both cases was 0.3 V. Reprinted with permission from reference 41. Copyright (2004), AIP Publishing LLC.

Whitesides et al. have also been strong advocates for the EGaIn Tip paradigm since its inception and have taken a lead role in both studying and refining the technique. Amongst their many contributions, the group pioneered the use of smooth template stripped metals as a substrate for SAM formation, which has led to more reproducible results and been critical for the overall advancement of molecular electronics.42,43 Recent studies of theirs more specific to the EGaIn tip paradigm have also revealed that currents measured using this technique are largely insensitive to the environment they are collected in,44 are consistent across a range of SAM formation time45 – currents measured across n-alkanethiolate SAMs formed in solution for times ranging from 3 hrs up to a week were indistinguishable – and that the resistance of the Ga2O3 skin on EGaIn tips does not influence charge transport across SAMs to any significant extent.39,46 Recently, they also
published a report on a new method of fabricating/pre-treating EGaIn tips, aimed at addressing concerns over the variance of measurements, reproducibility, and relatively low current densities observed using the technique. The so called “flattened” tip method involves pre-treating a freshly formed EGaIn tip, prior to bringing it into contact with a SAM, by tapping it down on clean ultrasmooth SiO\textsubscript{2} wafers and applying a bias sweep between 2V to -2V across the SiO\textsubscript{2}/Ga\textsubscript{2}O\textsubscript{3}/EGaIn junction.\textsuperscript{39} These conditioning steps are thought to flatten tip asperities and lead to more stable robust contacts, although no specific tip parameters are reported pre or post conditioning step. In the initial “flattened” tip report, specific emphasis was also placed on the manner in which to contact SAMs. Previous reports, which used freshly extruded unmodified tips for contacts (referred to as “soft” tips), stressed that contact be established by gently touching the EGaIn tip to its reflection on the metal substrate.\textsuperscript{46-48} In comparison, the “flattened” tip method, perhaps on account of the increased robustness of the pre-treated tips, emphasised that contact be established by applying pressure until “wrinkling” of the Ga\textsubscript{2}O\textsubscript{3} skin or tip apex deformation is observed. Naturally, the method of contact for “flattened” tips results in larger contact areas and it is fair to speculate that the force applied to the SAM by “flattened” tips is also likely greater than that applied by “soft” tips. Images of both “soft” and “flattened” tips and their junction contact are shown in Figure 2.8 in the Chapter 2.

The result is that “flattened” EGaIn tips reduce the variance in measurements of current densities for a series of n-alkanethiolate SAMs, from log $\sigma = 0.5 - 1.1$ ($\sigma$ is the standard deviation of current density measurement in A/cm\textsuperscript{2}) with standard “soft” tips, to log $\sigma = \sim 0.3$, while still achieving junction yields of $\sim 90\%$.\textsuperscript{39} Furthermore, current densities recorded using the “flattened” tip were $\sim 2$ orders of magnitude higher than previous studies of the same SAM system with “soft” tips, likely due to an increase in the effective electrical contact area for the former.\textsuperscript{39} Best of all, the “flattened” tips and the manner in which contact is established seem to minimize the amount of user to user variation in the test bed that was common-place using “soft” tips. For
example, in Chapter 2 using “flattened” tips we were able to effectively replicate current density measurements reported by Whitesides et al. for n-alkanethiolate SAMs on Au\textsuperscript{TS} and Ag\textsuperscript{TS}.

While there are numerous appealing aspects to the “flattened” EGaIn tip, its use has only been reported for well-established, densely packed n-alkanethiolate SAMs on template stripped substrates at the time of this study. Given the novelty of the SAM/substrate systems we chose to study here, and the pitfalls in assuming junction integrity, we characterised the electronic properties of each system using both “flattened” and “soft” EGaIn tips.\textsuperscript{40,49} Therefore, herein we report on the electrical characterisation of eight different molecular electronic junctions: PhSH and Ph\textsubscript{2}DTPA SAMs on Au\textsuperscript{TS} and Au\textsuperscript{asdep} substrates, with “flattened” and “soft” EGaIn top contacts.

\section*{3.2. Experimental}

All chemicals used were purchased commercially. PhSH was used as received, while Ph\textsubscript{2}DTPA was recrystallized in anhydrous ethanol prior use for SAM formation. \textsuperscript{1}H and \textsuperscript{31}P-NMR (only in the case of Ph\textsubscript{2}DTPA) spectra of the compounds were checked periodically to ensure purity. Spectra were collected on a Bruker Ultrashield 300 MHz spectrometer at room temperature. The shifts reported are in ppm and where reference to the residual proton peaks of CDCl\textsubscript{3} (δ = 7.27 ppm) for \textsuperscript{1}H spectra, while those for the \textsuperscript{31}P spectra were reference to an external 85\% H\textsubscript{3}PO\textsubscript{4} standard (δ = 0 ppm).
3.2.1 Preparation of Metal Substrates

Au⁹⁸ gold substrates were prepared using the same methods as described in Chapter 2 and had RMS roughness of ~4 Å.⁵,⁶ Au⁹⁸ films were prepared by first evaporating a 3 nm seed-layer of Ti, followed by a 200 nm layer of Au, at a rate of ~2 Å/s, onto 75 mm diameter silicon wafers using an electron-beam evaporator. Au⁹⁸ samples were generally used within a couple days of being evaporated and had a nominal RMS roughness of 27 Å.⁵,⁶ As the substrate surface was exposed to ambient atmosphere, samples were cleaned prior to use by sonication in acetone and methanol, each for 5 minutes, followed by a rinse step with either anhydrous ethanol or anhydrous toluene (depending on what solvent was intended for the SAM deposition solution) and were finally blown dry under a stream of nitrogen.

3.2.2 SAM Formation

PhSH and Ph₂DTPA SAMs were formed by immersing substrates in 3 mM solutions of the molecules in anhydrous ethanol and anhydrous toluene, respectively, under nitrogen, for 3 hours at room temperature. Aromatic thiolated SAMs formed from 1mM solutions, with exposure times longer than 1 hour, do not exhibit any changes to binding motif, based on XPS analysis.²⁴ We therefore selected our deposition parameters to ensure SAMs were fully formed, while simultaneously minimizing potential surface defects, resulting from prolonged exposure of the OA glue, used in the fabrication of template stripped substrates, to the solvents used.³⁶
3.2.3 Molecular Electronic Characterisation

EGaIn Tip top contacts were used as top contacts for molecular electronics characterisation. The measurement protocols and methods used to treat junction data were as reported in 2.2.9. Molecular Electronic Characterisation (MEC) of n-alkanethiolate SAMs on Metal Substrates in Chapter 2, as were the methods for fabricating and establishing electrical contact with the so-called “flattened” tip. In this chapter, however, we make the distinction between “flattened” and “soft” EGaIn tips based on the steps used to fabricate them and the manner in which they were used to establish electrical contact. The primary distinction, in terms of the preparation of “flattened” vs “soft” tips, was that “soft” tips were extruded into a conical shape, as were “flattened” tips, but were not subjected to subsequent conditioning steps on Si substrates. Instead, in order to mimic the time lapse due to these conditioning steps, “soft” tips were allowed to sit in ambient lab conditions for 5 minutes prior to being brought into contact with SAMs. Much like the conditioning steps, we believe this wait time allowed for the formation of a more robust Ga$_2$O$_3$ layer and observed that it improved junction yields compared with tips where the wait period was not observed. The primary distinction, in terms of contact with SAMs, can be seen in Figure 2.8 in Chapter 2. Junction contact for “flattened” tips (Figure 2.8C) was characterised by applying pressure until a deformation or “wrinkling” of the tip apex was observed. In contrast, for “soft” tips, junction contact was said to be established when the tip was brought into gentle contact with its reflection of the metal substrate (Figure 2.8B). Generally speaking, this resulted in geometric contact areas of ~200 $\mu$m$^2$ and ~700 $\mu$m$^2$, for “soft” and “flattened” tips, respectively.

Differential conductance values were calculated for each system based on the average traces we determined experimentally. These values were then normalized against their respective conductance values at an applied bias of -0.05V, G(-0.05V), as per published methods.$^{26,40}$
3.2.4 X-ray Photoelectron Spectroscopy

Samples for XPS were analyzed using a Kratos Axis Nova X-ray photoelectron spectrometer. Survey and high resolution analyses scan analyses were carried out with an analysis area of 300 x 700 μm and a 90 degree take-off angle. The pass energy for survey and high resolution scans were 160 eV and 20 eV, respectively. XPS measurements and peak fitting was performed by Surface Science Western (London, Ontario).

3.2.5 Contact Angle

Contact angle measurements were measured using the same experimental setup and equipment as described in section 2.2.7 Contact Angle Goniometry Chapter 2, with the exception that reagent grade water was used as the probe liquid in place of hexadecane (which was found to wet both Ph$_2$DTPA and PhSH SAMs). Static contact angles reported here represent an average of at least 8 measurements recorded on at least 2 samples.

3.3 Results & Discussion

3.3.1 XPS Characterisation of PhSH and Ph$_2$DTPA SAMs

PhSH and Ph$_2$DTPA SAMs on Au$^{TS}$ and Au$^{asdep}$ substrates were characterised by high resolution x-ray photoelectron spectroscopy (HR-XPS) to determine the binding configuration of the DTPA head group. Survey scans for all the systems studied are shown in the supplemental section of this chapter (see Figures S3.1-4) and the HR-XPS spectra of the S 2p region are shown in Figure 3.8. We fit the S 2p region using either one or two pairs of S 2p$_{3/2}$ and S 2p$_{1/2}$ spin-orbit split components, assuming a Gaussian/Lorentzian (70%/30%) line shape and a splitting energy
fixed at $1.18 \text{ eV}$. The specific binding energies and relative percentages of the spin-orbit split components determined for the systems are summarized in Table 3.1, while the relative packing densities based on the atom% from XPS survey scans are summarized in Table 3.2.

**Figure 3.8** HR-XPS of the S 2p binding region for a PhSH SAM on Au$_{asdep}$ (top left), a PhSH SAM on Au$^{TS}$ (top right), a Ph$_2$DTPA SAM on Au$_{asdep}$ (bottom left) and a Ph$_2$DTPA SAM on Au$^{TS}$ (bottom right). The black line is the raw spectral data, the red and blue lines correspond to different S 2p$_{1/2}$ and S 2p$_{3/2}$ spin orbit pairs. The specific binding energies and relative % of the spin orbit pairs are summarized for each system in Table 3.1.
Table 3.1 Summary of the binding energies, areas and percentage of total sulfur species, for the spin orbit pairs observed in S 2p region of the HR-XPS of the various SAM/substrate systems investigated in this study. The red and blue rows in the table correlate with the red and blue line fits for the respective HR-XPS plots shown in Figure 3.8.

<table>
<thead>
<tr>
<th>SAM</th>
<th>S 2p species</th>
<th>Au\textsuperscript{asdep}</th>
<th>Au\textsuperscript{TS}</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>B.E. (eV)</td>
<td>Area (a.u.)</td>
<td>Rel. %</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B.E. (eV)</td>
<td>Area (a.u.)</td>
</tr>
<tr>
<td>PhSH</td>
<td>S 2p\textsubscript{1/2}</td>
<td>163.15</td>
<td>74.9</td>
</tr>
<tr>
<td></td>
<td>S 2p\textsubscript{3/2}</td>
<td>161.97</td>
<td>149.8</td>
</tr>
<tr>
<td></td>
<td></td>
<td>163.19</td>
<td>81.5</td>
</tr>
<tr>
<td></td>
<td>S 2p\textsubscript{1/2}</td>
<td>162.42</td>
<td>122.1</td>
</tr>
<tr>
<td></td>
<td>S 2p\textsubscript{3/2}</td>
<td>161.24</td>
<td>244.2</td>
</tr>
<tr>
<td></td>
<td></td>
<td>162.31</td>
<td>42.6</td>
</tr>
<tr>
<td></td>
<td>S 2p\textsubscript{1/2}</td>
<td>162.45</td>
<td>163.6</td>
</tr>
<tr>
<td></td>
<td>S 2p\textsubscript{3/2}</td>
<td>161.27</td>
<td>327.1</td>
</tr>
<tr>
<td>Ph\textsubscript{2}DTPA</td>
<td>S 2p\textsubscript{1/2}</td>
<td>163.22</td>
<td>62.8</td>
</tr>
<tr>
<td></td>
<td>S 2p\textsubscript{3/2}</td>
<td>162.04</td>
<td>125.6</td>
</tr>
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<td></td>
<td></td>
<td>162.78</td>
<td>81.5</td>
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<td></td>
<td>S 2p\textsubscript{1/2}</td>
<td>162.45</td>
<td>163.6</td>
</tr>
<tr>
<td></td>
<td>S 2p\textsubscript{3/2}</td>
<td>161.27</td>
<td>327.1</td>
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</table>
The Influence of Head Group, Substrate Topography and EGaIn Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions

Table 3.2 Summary of packing densities based on %atom from XPS survey scans. Relative packing densities are normalized against the %S/%Au ratio for Ph$_2$DTPA on Au$^{TS}$. The fact that there are two S atoms for every one Ph$_2$DTPA molecule is taken into account when determining relative packing density for PhSH SAMs.

<table>
<thead>
<tr>
<th>SAM</th>
<th>Substrate</th>
<th>S %atom</th>
<th>Au %atom</th>
<th>%S/%Au</th>
<th>Rel. Packing Density</th>
</tr>
</thead>
<tbody>
<tr>
<td>PhSH</td>
<td>Au$^{asdep}$</td>
<td>3.1</td>
<td>62.6</td>
<td>0.050</td>
<td>2.6</td>
</tr>
<tr>
<td></td>
<td>Au$^{TS}$</td>
<td>2.5</td>
<td>68</td>
<td>0.037</td>
<td>1.9</td>
</tr>
<tr>
<td>Ph$_2$DTPA</td>
<td>Au$^{asdep}$</td>
<td>3.0</td>
<td>55.9</td>
<td>0.054</td>
<td>1.4</td>
</tr>
<tr>
<td></td>
<td>Au$^{TS}$</td>
<td>2.5</td>
<td>65.8</td>
<td>0.038</td>
<td>1.0</td>
</tr>
</tbody>
</table>

Previous literature studies of the S 2p region in HR-XPS spectra have established that the binding energy of S 2p$_{3/2}$ peak is quite sensitive to the environment of the S atom and appears at: ~161-162 eV when bound to Au, ~163-165 eV when non-interacting/unbound and >166 eV when oxidized.$^{3,19,20,51}$ However, studies of PhSH SAMs on Au reveal a more complex interpretation of XPS data for this aromatic system. PhSH SAMs form disorganized monolayers, therefore, it is not uncommon to find multiple sulfur species present in their HR-XPS spectra. PhSH SAMs adsorbed onto Au(111) films on atomically smooth Mica exhibit 75% bound S species and 25% unbound (physisorbed) S species based on fitting the HR-XPS S 2p region with two spin orbit pairs with S 2p$_{3/2}$ binding energies of 162.0 eV (bound) and 163.1 eV (physisorbed).$^{24}$ Binding S 2p$_{3/2}$ peaks around 162.0 eV and 161.1 eV have also been reported for various PhSH derivative SAMs on Au(111).$^{18-20,24}$ Interestingly, in their study Ishida et al., found that the peak at 161.1 eV became gradually smaller as the number of aromatic units in thiolated molecules increased, eventually leading to a single sulfur species on surfaces with S 2p$_{3/2}$ binding energy of ~162.0
The Influence of Head Group, Substrate Topography and EGaIn Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions

eV.\textsuperscript{20} Multiple studies have confirmed this finding and led to the conclusion that that this single binding energy corresponds to well-ordered SAM structures.\textsuperscript{18,22,24} In a further study, Ishida et al., also observed the peak at \(\sim 161.1\) eV for n-alkanethiolate SAMs on Au(111), but this was only found for SAMs with low coverage, after annealing steps or during initial SAM growth. Fully formed n-alkanethiolate SAMs are very well ordered on Au(111) and HR-XPS spectra of the S 2p region typically reveal only a single sulfur species with S 2p\textsubscript{3/2} binding energy of \(\sim 162\) eV.\textsuperscript{19} They therefore concluded that the S 2p\textsubscript{3/2} peak at 161.1 eV on Au(111) was likely the result of contributions from three different sources: 1. S atoms bound to Au (111) with different hybridizations; specifically sp\textsuperscript{3} hybridizations corresponding to S 2p\textsubscript{3/2} binding energies of \(\sim 162.0\) eV and sp hybridization corresponding to S 2p\textsubscript{3/2} binding energies 161.1 eV. 2. Different energies associated with the hcp-bridge, fcc-bridge, hcp-hollow, fcc-hollow and on-top bonding sites of the Au(111) surface.\textsuperscript{22} 3. S atoms bound to various defect sites such as grain boundaries and step heights.\textsuperscript{19,20}

Our XPS analysis of PhSH SAMs on Au\textsuperscript{TS} and Au\textsuperscript{asdep} – both are Au (111) surfaces – is consistent with the above mentioned sources as the likely contributors to the S 2p\textsubscript{3/2} peaks observed at 161.1 and 162.0 eV. On account of the disorganized nature of PhSH SAMs, PhSH molecules are likely bound to multiple Au(111) bonding sites and have different tilt angles. In fact, in their DFT study Nara et al., proposed that PhSH on Au(111) likely consisted of \(2\sqrt{3} \times \sqrt{3} R 30^\circ\) and \(\sqrt{3} \times \sqrt{3} R30^\circ\) adlattices stabilized against each other in multiple surface bonding sites and in which molecular tilts could range from 33\(^\circ\) (implying sp\textsuperscript{3} S hybridization) to \(-0^\circ\) (implying sp S hybridization).\textsuperscript{22} As a result, we observe S 2p\textsubscript{3/2} species at \(\sim 162.0\) eV and \(\sim 161.1\) eV on both substrates as a result of contributing factors #1 and #2 proposed by Ishida. Furthermore, given the higher density of defect sites and grain boundaries on Au\textsuperscript{asdep} we find a relatively higher percentage of sulfur species with S 2p\textsubscript{3/2} energy of 161.1 eV on Au\textsuperscript{asdep}, 62.0\%, compared with 34.3\% on Au\textsuperscript{TS}, on account of contributing factor #3.\textsuperscript{49}
In contrast, \( \text{Ph}_2\text{DTPA} \) SAMs on Au\(^{\text{TS}}\) show only a single S species with S 2\( p_{3/2} \) energy of 161.6 eV. This value corresponds well with the binding energies observed previously for fully bidentate dialkylDTPA SAMs on Au\(^{\text{TS}}\) of 161.5 eV. \( \text{Ph}_2\text{DTPA} \) SAMs on Au\(^{\text{asdep}}\), on the other hand, exhibited two S 2\( p_{3/2} \) species at 162.0 eV and 161.3 eV, with relative percentages of 27.3 % and 72.3 %, respectively. Both unbound PhSH molecules and the non-interacting S atom of monodentate bound dialkylDTPA molecules on Au\(^{\text{asdep}}\) are reported to have S 2\( p_{3/2} \) binding energies of >163 eV,\(^{24,50}\) therefore we are reluctant to attribute the S 2\( p_{3/2} \) peak at ~162.0 eV for \( \text{Ph}_2\text{DTPA} \) SAMs on Au\(^{\text{asdep}}\) to an unbound S species. Instead, much like was observed for the disorganized PhSH SAMs, we attribute it to the presence of two S species to different S-substrates interaction which result from the increased density of defect sites on the Au\(^{\text{asdep}}\) substrate. The fact that \( \text{Ph}_2\text{DTPA} \) molecules did not bind in a monodentate manner on Au\(^{\text{asdep}}\), unlike their dialkylDTPA counterparts, implies that doing so likely offers very little to the SAM in terms of additional intermolecular stability from increased van der Waals interactions. This is not surprising given the results for the relative packing densities of SAMs on the two substrates (see Table 3.2). XPS survey scans revealed that \( \text{Ph}_2\text{DTPA} \) systems had packing densities that are half that of the analogous PhSH systems. This is likely due to a combination of the tetrahedral geometry of the DTPA head group requiring a bigger footprint and the short, rigid nature of the pendent phenyl rings inhibiting favourable \( \Pi-\Pi \) intermolecular interactions.

### 3.3.2 Contact Angle Analysis of PhSH and \( \text{Ph}_2\text{DTPA} \) SAMs

In addition to XPS analysis, SAMs were also characterised by water CA analysis. Water contact angles are sensitive to surface composition, structure, packing density and substrate
roughness, and hence offer a simple and effective means of probing both SAM surface interface and SAM quality.\textsuperscript{52-57} For instance, densely packed, highly ordered, crystalline, hydrophobic SAMs, such as long chain n-alkanethiolates on smooth Au(111) substrates, exhibit water contact angles >110°.\textsuperscript{54-57} In comparison, contact angles for high quality aromatic SAMs, which are less densely packed and intrinsically more polarizable, range from ~70-90° depending on the specific nature of the SAM.\textsuperscript{18,58,59} Furthermore, they are also highly sensitive to the orientation terminal of aromatic rings. A recent study by Toledano et al., reported that static water contact angles varied by as much as 9° between n=odd and n=even numbered (C\textsubscript{6}H\textsubscript{5})(CH\textsubscript{2})\textit{n} SAMs on Si(111) substrates, primarily due to the orientation of the terminal phenyl ring. In particular, contact angles were observed to be higher on the n-even SAMs, where the aromatic ring was nearly upright and the surface consisted mainly of terminal C-H units.\textsuperscript{26} Contact angle were lower on n-odd SAMs for which the aromatic ring was nearly parallel to the substrate, exposing the highly polarizable face of the benzene ring.

In our study, we observed static water contact angles for both PhSH and Ph\textsubscript{2}DTPA SAMs on Au\textsuperscript{TS} substrates to be ~70° (Table 3.3). These values are similar to those reported by Tao et al. in their study on PhSH and other derivative SAMs on smooth Au(111) substrates.\textsuperscript{59} In their study Tao et al. also observed that contact angles increased to \(\geq 80°\) when an additional phenyl group was added to PhSH molecules.\textsuperscript{59} Additional aromatic units beyond this, however, had only minor influence on contact angles. Based on this observation, the authors proposed that the lower contact angles on PhSH SAMs were likely the result of the probe liquid being able to sense the underlying substrate through the short SAM. Beyond a certain distance, however, probe liquids no longer sense the underlying substrate and contact angles became independent of SAM thickness.

One might expect static contact angles on the slightly thicker (by a single P atom) and more well-ordered, Ph\textsubscript{2}DTPA SAMs on Au\textsuperscript{TS} to be higher than those of the PhSH SAMs. The fact that they
are the same, however, is likely the result of Ph\textsubscript{3}DTPA SAMs being relatively less densely packed. A short, rigid, non-densely packed, aromatic SAM would almost certainly expose more of the polarizable face of the aromatic rings, as well as a portion of the underlying substrate to probe liquids, lowering contact angles. Our group’s previous characterization of these two SAMs on Au\textsuperscript{TS} by electrochemical impedance spectroscopy (EIS) showed just as much.\textsuperscript{60} EIS analysis revealed that while PhSH SAMs acted as an effective molecular dielectric layer, Ph\textsubscript{2}DTPA SAMs allowed electrolyte ions to penetrate across the SAM to the underlying gold electrode, resulting in charge transport that was mediated by a diffusion process.\textsuperscript{60} Therefore it is very likely that Ph\textsubscript{2}DTPA SAMs organise in non-densely packed, partially open adlattices on Au\textsuperscript{TS} substrates. This porous nature may offset any potential increase in contact angle compared to PhSH SAMs due to either thickness or being more well-ordered.

While an investigation of the orientation of the phenyl rings in Ph\textsubscript{2}DTPA SAMs is beyond the scope of this study, we note that the rigid nature and steric demands of the two pendant phenyl rings make it unrealistic that these would be oriented upright. Therefore the polarizable face of the phenyl rings is probably more exposed in these SAMs than it would be for comparable single chain PhSH derivative SAMs, and this would also likely contribute to the \(\sim70^\circ\) contact angles observed.

Contact angles for both PhSH and Ph\textsubscript{2}DTPA SAMs on Au\textsuperscript{asdep} substrates were lower than for their analogous Au\textsuperscript{TS} systems. This is in direct agreement with expected behavior stipulated by the Wenzel equation: \(\cos \theta_{\text{ex}} = r \cos \theta_{\text{th}}\), where \(\theta_{\text{ex}}\) is the observed contact angle, \(\theta_{\text{th}}\) is the theoretical contact angle based on Young’s equation (see Figure 2.11 in Chapter 2) and, \(r\), is the coefficient of roughness of the surface.\textsuperscript{61,62} According to this relationship, contact angles that are \(<90^\circ\) become smaller with increased surface roughness. The drop in contact angle for SAMs on Au\textsuperscript{TS} and Au\textsuperscript{asdep} was noticeably larger in the case of Ph\textsubscript{2}DTPA SAMs. This may imply that Ph\textsubscript{2}DTPA molecules had more trouble compensating for the higher defect density of Au\textsuperscript{asdep} than did less
bulky PhSH molecules, and allowed more sensing of the underlying substrate by probe liquids.

Finally, hysteresis measurements corroborate our XPS results, as the hysteresis values were smallest for Ph$_2$DTPA SAMs on Au$_{TS}$, which based on HR-XPS analysis was the only well-ordered system with a single S species.

Table 3.3 Static water contact angles and contact angle hysteresis of PhSH and Ph$_2$DTPA SAMs on Au$_{asdep}$ and Au$_{TS}$ substrates.

<table>
<thead>
<tr>
<th>SAM</th>
<th>Au$_{asdep}$</th>
<th></th>
<th>Au$_{TS}$</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Static CA (°)</td>
<td>CA Hysteresis(°)</td>
<td>Static CA (°)</td>
<td>CA Hysteresis(°)</td>
</tr>
<tr>
<td>PhSH</td>
<td>64.9 ± 1.2</td>
<td>8.1 ± 2.0</td>
<td>70.1 ± 1.3</td>
<td>10.8 ± 2.8</td>
</tr>
<tr>
<td>Ph$_2$DTPA</td>
<td>57.2 ± 1.1</td>
<td>9.0 ± 5.8</td>
<td>70.8 ± 2.2</td>
<td>5.4 ± 1.7</td>
</tr>
</tbody>
</table>

3.3.3. Molecular Electronic Characterisation of PhSH and Ph$_2$DTPA SAMs

The molecular electronic systems reported here constitute a 2x2x2 matrix (2 SAMs, 2 substrates, 2 top contacts). Interpreting the electrical data collectively can be challenging; hence, although we present our electrical characterisation results collectively below, we will focus our discussion on the isolated influence of the three parameters (EGaIn top contact, the substrate, and the SAM layer itself) on molecular electronic properties. Figure 3.9 shows the average traces for each SAM/substrate system tested with both “soft” and “flattened” EGaIn tips. Additionally, this figure shows the histograms and associated Gaussian fits for the current densities for each of the molecular junctions characterised, at an applied bias of +0.5 V, which are also summarized in Table 3.4.
Based on XPS and CA analysis, we were conscious of the fact that the SAMs investigated were not necessarily very well organised (except perhaps Ph\textsubscript{2}DTPA on Au\textsuperscript{TS}) and that thin area defects site might have a substantial role in charge transport. Therefore, after a sufficient number of junctions were collected for each system investigated, we calculated and plotted the differential conductance for each of these systems based on the average traces shown in Figure 3.9. The plots of differential conductance vs applied bias are shown for PhSH and Ph\textsubscript{2}DTPA SAMs, on both substrates and characterized using both tips in Figure 3.10.

Table 3.4 Summary of molecular electronic junction data collected using EGaIn tip top contacts. Data for PhSH SAMs on Au\textsuperscript{TS} collected with a “soft” tip is reproduced with permission from reference 60.
Figure 3.9  Histograms and corresponding Gaussian fits (left plots) of current densities collected at an applied junction bias of 0.5V for A) PhSH SAMs on Au$^{\text{TS}}$, B) PhSH SAMs on Au$^{\text{asdep}}$, C) Ph$_2$DTPA SAMs on Au$^{\text{TS}}$ and D) Ph$_2$DTPA SAMs on Au$^{\text{asdep}}$. The average traces (right plot) for each molecular junction are shown next to their corresponding histogram plot. Current densities collected with a “flattened” EGaIn top contact are red and those collect with a “soft” EGaIn top contact are blue. Note “soft” tip data for PhSH SAMs on Au$^{\text{TS}}$ is reproduced with permission from reference 60.
Figure 3.10 Plotted are calculated normalized differential conductance values for the experimental applied bias range of -0.5 V to 0.5V for A) PhSH SAMs on Au\textsuperscript{TS}, B) PhSH SAMs on Au\textsuperscript{asdep}, C) Ph\textsubscript{2}DTPA SAMs on Au\textsuperscript{TS} and D) Ph\textsubscript{2}DTPA SAMs on Au\textsuperscript{asdep}. The solid red line corresponds to junction data collected using a “flattened” EGaIn top contact, the dashed blue line corresponds to data collected using a “soft” EGaIn top contact.
3.3.3.1 “Soft” vs “Flattened” EGaIn Top Contacts

Several features emerge when directly comparing data collected using “soft” and “flattened” EGaIn tips. The most obvious is that current density for Ph$_2$DTPA SAMs varies significantly depending on which tip was used. For Ph$_2$DTPA SAMs on Au$^{TS}$, current densities dropped two orders of magnitude in going from “flattened”, log $J(0.5V) = -0.8 \pm 0.8$, to “soft”, log $J(0.5V) = -2.8 \pm 0.5$, tips. On Au$^{asdep}$, the difference was smaller but still significant: log $J(0.5V) = -0.5 \pm 0.6$ and log $J(0.5V) = -1.4 \pm 0.7$, for “flattened” and “soft” tips, respectively. For Ph$_2$DTPA SAMs on Au$^{TS}$, Figure 3.10 reveals that junctions collected with the “flattened” tips produce consistently flatter differential conductance plots than the analogous junctions collected using “soft” tips. This indicates that ohmic transport, caused by thin area defects as Nijhuis et al. and Toledano et al. described, likely plays a significant role in the charge transport measurement across Ph$_2$DTPA SAMs collected using “flattened” tips.

Furthermore, this result implies that, although they are well suited to study densely packed systems like n-alkanethiolate SAMs, “flattened” EGaIn tips are not ideally suited to study more porous SAMs such as Ph$_2$DTPA. We speculate that the reason for this might be due to the fact that junction contacts formed using “flattened” tips generally have diameters that are roughly twice as large, and apply more pressure to SAMs, as compared with “soft” contacts. Although it was not systematically tracked throughout the course of the experiment, the larger geometric contact area and increased pressure for “flattened” tips is an inherent by-product of the conditioning step (which blunts tips to a certain extent) and the manner in which contact is established with the SAM (we look for apex deformation with flattened tips, as opposed to simply touching the tip to its reflection on the substrate for soft tips).

In contrast, the type of tip had no measurable impact on current densities across PhSH SAMs, as log $J(0.5V)$ values were indistinguishable for every PhSH system investigated. Furthermore, differential conductance plots are nearly identical for PhSH molecular junctions collected using
both tips on both substrates. We therefore attribute the similarity in current densities for PhSH SAMs collected using “flattened” and “soft” tip to two potential and somewhat contradictory sources. If we assume that charge transport is governed by molecular properties and that thin area defects had no discernable impact on charge transport, this implies that PhSH SAMs are robust enough to be characterized using “flattened” EGaIn tips. One explanation for this may be that PhSH SAMs are more densely packed than Ph$_2$DTPA SAMs, which results in fewer porous areas and hence fewer shorts and thin area defects. Alternatively, we could also assume that thin area defects are dominant in all the PhSH systems characterised, including those with “soft” EGaIn top contacts. This too could be rationalized by the fact that PhSH SAMs are short and rigid, both of which tend to decrease yield and hence might also make thin area defects more prominent and probable to contact. 49

Both scenarios have evidence to support them. An argument for current transport being dominated primarily by molecular properties is that the log $\frac{\text{J}(0.5\text{V})}{\text{values}}$ we report for the PhSH SAMs are in relatively good agreement with the current densities others have reported for more robust well-ordered PhSH derivative systems. 9,10,26 An argument for thin area defects playing the dominant role in all the PhSH systems investigated is that the differential conductance plots are significantly flatter than those of analogous the Ph$_2$DTPA system (this will be discussed in more detail in section 3.3.3.3 Ph$_2$DTPA vs PhSH SAMs). Unfortunately, answering this question conclusively is beyond the scope of this study; however, we propose that plotting differential conductance at higher applied bias might help to resolve the issue (at higher bias the effects of Joule heating become more prominent and therefore become more obvious in differential conductance plots). 41

For the time being, however, based on the results for the Ph$_2$DTPA system, we presume that “soft” EGaIn top contacts offer the best insight into the molecular electronic properties for the specific systems studied. Therefore, from here on, we focus our discussion exclusively on systems
using “soft” EGaIn top contacts, because drawing conclusions based on comparisons between systems where ohmic transport is known to occur would be counterproductive.

3.3.3.2 Au$^{TS}$ vs Au$^{asdep}$ Substrates

Our initial objective in studying SAMs on Au$^{asdep}$ surfaces, in spite of the known pitfalls which have been reported, was to resolve the potential impact of the monodentate binding configuration of the DTPA head group on charge transport. Our HR-XPS analysis of the S region, however, revealed that no such configuration exist in Ph$_2$DTPA SAMs on either Au$^{asdep}$ or Au$^{TS}$. Hence we cannot attribute the substantial difference in log $J(+0.5\,\text{V})$ values for this SAM on Au$^{asdep}$ and Au$^{TS}$ substrates (with “soft” EGaIn top contacts), which were $-1.4 \pm 0.7$ and $-2.8 \pm 0.5$, respectively, to any fundamental difference in binding configurations of the molecules. Turning to the differential conductance plots for the systems in question, shown in Figure 3.11; the plot for Ph$_2$DTPA SAMs on Au$^{asdep}$ was slightly flatter in comparison to that of the analogous Au$^{TS}$. This result might suggest some additional contributions from ohmic transport, but, once again, without data for higher applied biases (which would enhance contribution from Joule heating and make ohmic contribution more obvious) it is difficult to attribute the ~1 order of magnitude increase in current density in going from Au$^{TS}$ to Au$^{asdep}$ substrates exclusively to an increased density of thin area defects, based solely on the minor discrepancies in conductance.
Nijhuis et al. reported that rougher substrates tended to produce β values for SAMs series that were comparatively lower than with ultrasmooth substrates. The reason was attributed to increased contribution from ohmic transports from thin area defects, but also points to the possibility that grain boundaries tend to induce deviations from assumed SAMs thicknesses. It is certainly possible that the higher density of defects and grain boundaries might induce different molecular orientation which would allow SAMs to be contacted in a different manner. For example, in a recent molecular electronic study on PhSH derivative SAMs, Toledano et al. reported that placing odd and even length alkyl spacers placed in between phenyl tail groups and...
thiol head groups resulted in different orientations of the phenyl ring and that the parallel orientation lead to better coupling with evaporated top-contact and produced a ~1 order increase in conductivity. Although a comprehensive study of pendant phenyl ring orientations for Ph$_2$DTPA SAMs on Au$^{TS}$ and Au$^{asdep}$ is beyond the scope of this study, we certainly acknowledge that this might have played some role in the discrepancy between charge transports for Ph$_2$DTPA SAMs on the two substrates.

For the purpose of comparing the electronic properties of SAMs in the next section, however, we chose to focus on Ph$_2$DTPA SAMs on Au$^{TS}$ substrates as the truest representation of the SAM’s molecular electronic properties based on several points: 1. Differential conductance plots for the Au$^{TS}$ substrate were slightly more positive than those for the Au$^{asdep}$ substrate, therefore charge transport was more likely to be dominated by molecular properties on this substrate. 2. Contact angles drop more in going from Ph$_2$DTPA on Au$^{TS}$ to Au$^{asdep}$ then they did in going from PhSH on Au$^{TS}$ to Au$^{asdep}$. This implies the Ph$_2$DTPA on Au$^{asdep}$ might be especially porous. 3. HR-XPS analysis of the S region for the SAM on both substrates revealed a single S species on Au$^{TS}$, but multiple S species on Au$^{asdep}$. 4. Variance of the current densities measured for the SAM were much smaller on Au$^{TS}$ indicating a more well-ordered system (see Table 3.4), this is corroborated by HR-XPS analysis, as well as by CA hysteresis.

Finally we must also acknowledge the fact that current densities across PhSH SAMs were indistinguishable on the two substrates and that, if anything, the differential conductance plots shown in Figure 3.11, seem to suggest charge transport on the Au$^{asdep}$ substrate might have somehow been subject to fewer thin area defects than it was on Au$^{TS}$ substrates. Nevertheless for the purpose of comparing the molecular electronic properties of the SAMs in the next section, we still choose to do so using the results for the PhSH Au$^{TS}$ system for the following reasons: 1. CA analysis suggests the Au$^{TS}$ surface has fewer defects. 2. Variance in measured current densities was significantly lower on Au$^{TS}$ than it was on Au$^{asdep}$. 3. We have established that Au$^{TS}$
substrates provided us with the best representation of the molecular electronic properties of Ph₂DTPA SAMs, therefore to properly compare the electronic properties of PhSH SAMs the current densities collected on the Au

3.3.3.3 Ph₂DTPA vs PhSH SAMs

The ~3 orders difference in log \( J(+0.5\text{V}) \) values for Ph₂DTPA and PhSH SAMs on Au

The higher packing density of PhSH SAMs (roughly twice that of Ph₂DTPA SAMs) would also only have a minor effect on charge transport, on the order of \( \Delta \log J = \sim 0.3 \) (see supplemental section 3.6.2 for detailed calculation).

Furthermore, based on a previous DFT study of PhSH and Ph₂DTPA molecules bound to Au atoms, the relative energy levels of the frontier orbitals cannot explain the low currents through Ph₂DTPA SAMs observed experimentally. The aforementioned DFT study is summarized in Figure 3.12, and shows that the HOMO level of the Ph₂DTPA molecule (-5.70 eV) is closer in energy to the Fermi level of the gold electrode (-5.1 eV), than the HOMO of the PhSH SAM (-6.36 eV), which would predict better conductivity across Ph₂DTPA SAMs, the opposite of what we observed experimentally. We note that the LUMO for PhSH (-3.33 eV) is closer to the Au Fermi level than the LUMO of Ph₂DTPA (-2.91 eV), which might contribute to the lower conductivity of Ph₂DTPA SAMs. However, we reject this argument for the following reasons: 1.
Both LUMOs are further away from the Au Fermi than their respective HOMOs, therefore the LUMOs would only find themselves closer to the Fermi level of Au if Fermi level pinning, which was unaccounted for in the DFT study, had a significant effect. 2. Even if Fermi level pinning did have a significant effect, the band gap (gap between HOMO and LUMO) for the Ph$_2$DTPA system (2.80 eV) is smaller than the band gap for PhSH (3.03 eV). In all likelihood this would result in one of the frontier orbitals of Ph$_2$DTPA still being closer to the Au Fermi level, regardless of the specific effect of Fermi Level pinning. 3. The difference in energies of the frontier orbitals for PhSH and Ph$_2$DTPA are relatively insignificant compared to their differences with the frontier orbitals of an aliphatic system and likely would not account for a ~3 orders of magnitude discrepancy in charge transport.
Figure 3.12  Summary of the key finding of the DFT study carried out by Miller et al. Shown are the schematics of PhSH and Ph₃DTPA bound to Au atoms (top images), follow by MO diagrams of the respective LUMOs (middle images) and HOMOs (bottom image). The energy levels of the respective HOMOs and LUMOs are also listed. Adapted with permission from reference 60.
Instead, in order to rationalize the experimental results we observed, we turn our attention to the molecular orbital diagrams of the HOMOs and LUMOs, shown in Figure 3.12. For the PhSH system, both the HOMO and LUMO have contributions from the aromatic phenyl ring. This implies that it is effectively coupled with the underlying electrode and that charge transport likely occurs across a single symmetric barrier consisting of either the HOMO or LUMO, as shown in the diagram in Figure 3.13. In contrast, both the HOMO and LUMO for the \( \text{Ph}_2\text{DTPA} \) molecule bound to Au are localised on the DTPA headgroup, implying that the pendant aromatic rings are effectively decoupled from the underlying substrate. We believe this decoupling stems primarily from the tetrahedral nature of the P atom and the steric demands of the phenyl rings, making it unfavourable to maintain conjugation throughout the molecule. Additionally, studies have shown that the spacing provided by a single methylene unit (or even a single carbon as in the case of carboxylic acid head groups) is sufficient to decouple aromatic subunits from underlying electrodes.\(^9,23\) Therefore, we propose that the tunneling barrier for \( \text{Ph}_2\text{DTPA} \) is an asymmetric barrier consisting of independent conjugated/aromatic subunits: The DTPA head group bound to the underlying gold and the pendant phenyl rings.

This is a similar concept to what was discussed in 1.4. Expanding the Molecular Junction Model: Asymmetric Barrier Heights, in Chapter 1, for molecules that incorporated both aliphatic and aromatic subunits, but here we make the distinction that both independent tunneling barriers would likely have similar heights, as they are both conjugated (see Figure 3.13). We therefore do not attribute the unusually low current observed for \( \text{Ph}_2\text{DTPA} \) SAMs to an increase in tunneling barrier height. We do not attribute it exclusively to a decrease in the injection current, \( J_0 \), at the junction interfaces. Both SAMs are in van der Waals contact with the top EGaIn electrodes and based on previous studies, an odd-even like behavior between \( \text{Ph}_2\text{DTPA} \) and PhSH SAMs at this interface would likely alter charge transport by \(< 1\) order of magnitude.\(^{26,45}\)
Instead, we attribute the lower conductivity of the Ph$_2$DTPA molecule to a large transmission barrier between the independent conjugated units. In their theoretical study of asymmetric barriers involving aliphatic and aromatic units, Mirjani et al., described the use of a tunneling parameter, $\tau$, to specifically account for the barrier to transmission between independent subunits.$^{64}$ In this manner, they describe the gateway from a saturated orbital to a conjugated subunit as being “a narrow passage leading to an easily traversable track.”$^{64}$ Therefore, in much the same manner, we proposed that the unusually low currents observed experimental for the Ph$_2$DTPA SAMs, stems from narrow transmission window which exists in-between its independent subunits, resulting from the disruption in conjugation induced by the P atom in the DTPA head group. For all intents and purposes, incorporating this parameter into the simple Simmons equation would look identical to a decrease in the $J_0$ parameter, although as we have pointed out it likely does not stem from a difference in injection barriers at the interfaces. Other molecular electronics studies have also reported significant decreases in conductivity due to the disruptions in conjugation between aromatic subunits and we believe this “transmission” parameter, $\tau$, would have likely played a role in these systems as well.$^{12-16}$ We also point out that while decoupling does lower transmission through the molecular layer, the ability to decouple pendant aromatic units from electrodes might actually prove to be a useful molecular electronic property as it may partially mitigate the effects of Fermi level pinning as Penner et al. recently showed for their decoupled and amorphous, aromatic carbon nanomembranes.$^{25}$
Figure 3.13  (Top Image) Schematic of the symmetric tunneling barrier for Au-S-Ph\(//\)Ga\(_2\)O\(_3\)/EGaIn molecular junctions. Energy levels are indicated by solid line, red lines indicate levels that we propose to be coupled with one another. The vacuum energy level is denoted by \(E_{\text{vac}}\). \(\theta_{M-\text{SAM}}\) is the work functions of the metal substrates after modification by the SAM, while \(\Delta \theta_{M-\text{SAM}}\) is the changes to the substrate work functions upon modification by the SAM. \(\phi_h\) and \(\phi_e\)
are the hole and electron tunneling barriers, respectively. The transmission barrier due to van der Waals contact with the top EGaIn electrode is denoted by the dashed curved lines. The HOMO* and LUMO* are the highest occupied molecular orbitals and lowest unoccupied molecular orbitals that span the width of the junction, respectively. Based on DFT studies for PhSH SAMs on Au these might consist exclusively of the actual HOMO and LUMO. (Bottom Image) Schematic of the asymmetric tunneling barrier proposed for Au-DTPA-Ph₂//Ga₂O₃/EGaIn molecular junctions. ϕ₁ and θ₂ denotes the hole tunneling barrier heights for the independent subunits of the asymmetric barrier. Likewise ϕₑ₁ and ϕₑ₂ denote the electron tunneling barriers. Both the transmission barriers due to the van der Waals contact with the top EGaIn contact and due to transmission between subunits, τ, are denoted by the dashed curved lines. We note that the MOs along the DTPA head group portion are shown in red indicating that they are coupled to the underlying Au electrode, while those along the aromatic phenyl rings are shown in black as we believe these to be decoupled from the electrode.

Before proceeding to the conclusion, it is important that we address the apparent difference between the differential conductance plots for the two SAMs (Figure 3.14). Earlier we placed great emphasis on how comparing these between analogous systems might provide us with an indication of whether or not ohmic transport played a significant role in charge transport. Based on the differential conductance plots shown in Figure 3.14, it would seem obvious that thin area defects likely played a significant role in charge transport across PhSH SAMs making our comparison of the molecular electronic properties of PhSH and Ph₂DTPA SAMs somewhat in vain. Although it might very well be the case that ohmic transport did have additional contribution to charge transport across PhSH SAMs - they are relatively thin and poorly organized - we cannot presume this solely based on the differential conductance plots.

The reason for this is that PhSH and Ph₂DTPA, as we have shown, do not belong to the same molecular series and their responses to applied bias would likely be inherently different. If we are to assume that PhSH SAMs act as single rectangular barriers that are strongly coupled to
electrodes, their response to applied bias would be entirely different from that of the Ph$_2$DTPA SAMs which are multi barrier systems and have a decoupled subunit. Figure 3.15 shows a schematic of the effect of an applied bias on both coupled and decoupled subunits in a molecular junction. In the top image the frontier orbital (in this case the HOMO) is coupled with the left electrode and therefore moves with the left Fermi level as a bias is applied across the junction. Consequently the barrier height, before and after applied bias, is not much different, and conductance would be relatively insensitive to applied bias. In contrast, in the bottom image the frontier orbital is decoupled from the substrate and remains relatively stagnant when a bias is applied across the junction. This would effectively reduce the tunneling barrier (at least through this subunit) and results in a relatively larger positive response in conductance with increased applied bias. We therefore cannot assume that the discrepancy in the differential conductance plots of Ph$_2$DTPA and PhSH SAMs stems from increased contributions from thin area defects in the latter. Furthermore, as mentioned previously, current density measurements for PhSH SAMs in this study were in relatively good agreement with other EGaIn studies on PhSH derivative SAMs, which leads us to believe that the result we obtained, as well as the conclusion we drew from them, to be reasonable. 

\[ \text{Normalized Differential Conductance (}\delta\mathcal{J}/\delta V) \]

**Figure 3.14** Differential conductance plot for PhSH (red solid line) and Ph$_2$DTPA (blue dashed line) SAMs on Au$^{TS}$ substrates with “soft” EGaIn top contacts.
Figure 3.15 Schematic of the response of a coupled (top image) and decoupled (bottom image) molecular orbital (MO) to applied bias within a molecular junction. $\phi$ and $\phi'$ are the barrier heights to tunneling before and after applied bias, respectively. The thick black line corresponds to the energy level of the MO. The thin black line denotes the vacuum energy level. The grey rectangles represent the valence bands of the electrode and $\Delta V$ is the bias applied to the system. As shown in the top image, the coupled MO shifts with the electrode when bias is applied to the system and as a result $\phi \approx \phi'$. In the bottom image the decoupled MO energy level remains fairly stagnant when a bias is applied, which leads to $\phi' < \phi$. 
3.4 Conclusion

Herein we have reported on the electronic properties of the DTPA head group, substrate morphology, and the nature of EGaIn top-contact based on an internal comparison between Ph$_2$DTPA SAMs and analogous thiolated PhSH SAMs on Au$^{TS}$ and Au$^{asdep}$ substrates, contacted with “soft” and “flattened” EGaIn tips. CA, XPS and differential conductance analysis revealed that for the SAMs investigated both Au$^{asdep}$ substrates and “flattened” EGaIn tip were ill suited for molecular electronics characterisation studies. Instead Au$^{TS}$ substrates with “soft” EGaIn top-contacts were determined to offer the best insight into the molecular electronic properties of the SAMs investigated. Electronic characterizations using this paradigm, and previous DFT analysis, indicate that, unlike its thiolated counterpart, the DTPA head group effectively decouples its pendant aromatic rings from the underlying substrate. Furthermore, we also propose that the disruption in conjugation within the molecule itself, results in an additional barrier to transmission in between independent subunits of an asymmetric tunnelling barrier. We attribute the ~3 orders of magnitude drop in current across Ph$_2$DTPA SAMs as compared with PhSH SAMs to the combined effect of the decoupling of pendant rings from the bottom electrode and the intramolecular disruption in conjugation. Although the decoupling of the pendant aromatic rings in the Ph$_2$DTPA molecule results in significantly larger impedance, we point out that this might in fact prove to be a useful molecular electronic property; allowing for some degree of molecular electronic tunability by mitigating the effects of Fermi level pinning as others have shown for similarly decoupled aromatic systems.$^{25}$

We acknowledge that, based on electronic and SAM characterisation, neither PhSH nor Ph$_2$DTPA SAMs proved to be particularly well-ordered or robust for the purposes of molecular electronic applications. This can be attributed to the fact that both molecules had relatively short pendant chains which limited their ability to engage in intermolecular interaction and form high quality
densely packed SAMs. We also acknowledge that the reported enhancement to SAMs stability afforded by the DTPA head group for dialkylDTPA SAMs may, or may not, be the same for the SAMs study here and that our current study would be augmented by a thermal desorption study and a more comprehensive DFT investigation.

Looking forward, others have previously shown that additional aromatic units can induce PhSH derivative SAMs to become more well-ordered and grant increased SAMs stability due to favourable van der Waals interactions. Therefore, a comparison between longer PhSH derivatives and longer Ph₂DTPA derivatives would not only constitute a natural progression of our present work, but might also prove a rather compelling study into the role of intermolecular interactions on charge transport. SAMs would likely be more robust and such a study might avoid many of the ambiguities we encountered here. Perhaps the most compelling feature of the DTPA head group - perhaps even more so than the potential enhancement to SAM stability - is that it is amenable to a wide variety of pendant group combinations. Molecular characterization of dialkylDTPA on Au⁵⁸ and Au⁻¹⁰¹ might still prove a viable option, as the dialkylDTPAs are more densely packed on Au⁻¹⁰¹.⁵ If feasible, this would provide an ideal system to directly evaluate the influence of SAM crystallinity on charge transport, which has been done in the past, but never directly using the same SAM with different crystallinities. Even more intriguing would be the investigation of asymmetric DTPAs with different pendant chains. This could open the door to a host of SAMs with specific and useful molecular electronic properties. For instance, DTPA head groups with aliphatic and aromatic pendant chains, as have been reported by San Juan et al. (see Figure 3.16),⁶⁸ would almost certainly prove to be more robust than the Ph₂DTPA SAMs investigated here, as liquid like aliphatic chains have been shown to compensate for large nearest neighbour distances, substrate roughness, and other common defects, leading to SAMs which are not as porous and higher yield molecular junctions.⁴⁹ Although it would certainly be much further down the line, it is also not hard to envision that one might be able to equip a DTPA head group
with two reversibly isomerizable pendant chains, which respond to different external stimuli, yielding SAMs with quadrastable conductance states. We emphasize that the present study constituted an initial foray into the molecular electronic characteristic of the DTPA head group; the possibilities for further expansion of this investigation are virtually endless.

**Figure 3.16** Molecular structures of a) PhC6DTPA, b) PhC10DTPA and c) PhC16DTPA. Reproduced with permission from reference 68.
3.5 References


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The Influence of Head Group, Substrate Topography and EGaIn Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions

The Influence of Head Group, Substrate Topography and EGaIn Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions


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The Influence of Head Group, Substrate Topography and EGaIn Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions


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The Influence of Head Group, Substrate Topography and EGaln Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions

3.6 Supplemental

3.6.1 XPS Survey Scans

Figure S3.1 XPS survey scan of a PhSH SAM on Au\textsuperscript{asdep}

The Influence of Head Group, Substrate Topography and EGaIn Tip Fabrication on Charge Transport across (Diphenyl)dithiophosphinic Acid Molecular Junctions
Figure S3.2 XPS survey scan of a PhSH SAM on AuTS
Figure S3.3 XPS survey scan of a Ph₂DTPA SAM on Au^{TS}. 
Figure S3.4 XPS Survey scan of a Ph₂DTPA SAM on Au⁻dep
3.6.2 Packing Density Impact on Tunneling Currents Across PhSH and Ph$_2$DTPA SAMs

In this chapter we mentioned that doubling the packing density of a SAM would result in only a $\Delta \log J \approx 0.3$. Here we walk through the calculation to arrive at that number.

Consider the equation for the resistance of a Ph$_2$DTPA SAM with $x$ parallel molecular wires, where $R_{Ph2DTPA}$ is the total resistance of the SAM and $R_1$ is the resistance of an individual wire:

$$\frac{1}{R_{Ph2DTPA}} = x \left( \frac{1}{R_1} \right) \quad (1)$$

To model the PhSH SAM we will double the packing density and get equation 2 where $R_{PhSH}$ is resistance of the PhSH SAM:

$$\frac{1}{R_{PhSH}} = 2x \left( \frac{1}{R_1} \right) \quad (2)$$

Because we know $R \propto 1/J$ at a given applied bias, equations 1 and 2 are equivalent to 3 and 4, respectively, where $J_{SAMS}$ is the current density across the SAMs and $J_1$ is the current density across an individual molecular wire at a given bias.

$$J_{Ph2DTPA} = x (J_1) \quad (3)$$

$$J_{PhSH} = 2x (J_1) \quad (4)$$

Next, dividing $J_{PhSH}$ and $J_{Ph2DTPA}$ we get equation 5 and by applying the log function we get equation 6:

$$\frac{J_{PhSH}}{J_{Ph2DTPA}} = 2 \quad (5)$$

$$\Delta \log J = \log J_{PhSH} - \log J_{Ph2DTPA} = \log 2 = 0.30 \quad (6)$$
Chapter 4

Conclusion
4.1 Outlook

While advancements in the field of molecular electronics were initially few and far between, recent improvements to experimental studies, coupled with more robust theoretical studies, has led to a surge in the knowledge base of what physical organic properties do, and do not, influence charge transport in molecular junctions.\textsuperscript{1-3} We may never reach the level of control predicted by Aviram and Ratner, but recent progress has been encouraging.\textsuperscript{4} Within the past decade experimental and theoretical transmission studies have started to corroborate one another to the point where theoretical investigation might even prove to be the more economical and practical of the two research methods.\textsuperscript{3} A greater awareness of the perils of assuming junction integrity has also led to the development of practical low cost techniques for research, as well as methods for the seamless integration of molecular components into electronic devices which are compatible with current semiconductor industry fabrication methods.\textsuperscript{5-9} The need for stable, uniform and ultra-smooth substrates for molecular electronic characterization has sparked innovation in the materials field and led to the development new methods aimed at meeting these needs.\textsuperscript{10-14} Furthermore, the recent discovery of molecular systems utilising transport mechanisms beyond non-resonant tunneling has demonstrated that molecular electronics could indeed possess desirable functionalities unrivaled by current state-of-the-art semiconductor based electronics.\textsuperscript{1,15}

Herein, we have reported on molecular electronic phenomena associated with two techniques - one ex-situ and one in-situ - aimed at helping to resolve what many feel will be the preeminent challenge faced by molecular electronics: the lack of stability of the molecular components. Our ex-situ approach involved the electrochemical modification of Au\textsuperscript{TS} substrates with an underpotentially deposited monolayer of Ag, prior to SAM formation. Our molecular electronic characterisation of n-alkanethiolate SAMs on these substrate revealed the inherent molecular
The electronic characteristics of n-alkanethiolate SAMs remained unchanged on Ag\textsuperscript{UPD}/Au\textsuperscript{TS}, however current densities were significantly lower on this substrate as compared with either Au\textsuperscript{TS} or Ag\textsuperscript{TS} bulk substrates. We proposed that the reason for this is that the Ag\textsuperscript{UPD} layer added additional length to the tunneling path. In our in-situ approach we studied the influence of the chelating DTPA head group by comparing charge transport across aromatic Ph\textsubscript{2}DTPA and PhSH SAMs. Current densities were found to drop ~3 orders of magnitude in going from PhSH SAMs to Ph\textsubscript{2}DTPA SAMs on Au\textsuperscript{TS} substrates, and based on a previous DFT study\textsuperscript{18} of these systems, we attributed the significant drop in charge transport to the decoupling of the pendant phenyl rings in Ph\textsubscript{2}DTPA from the underlying gold electrode. We also proposed that the Ph\textsubscript{2}DTPA molecule likely constituted an asymmetric tunneling barrier, with independent subunits and an additional barrier to transmission within the molecule itself, and that this also contributed to the reduction of conductivity observed.

Both methods for the enhancement of SAM stability are relatively straightforward, are compatible with current device fabrications techniques and offer a great deal of versatility in that they could be incorporated with a wide variety of molecular electronic systems. We note that neither of these approaches offers an outright solution to the problem of molecular electronic stability, as the stability they provide to SAMs (~29 kJ/mol for Ag\textsuperscript{UPD} and ~13-20 kJ/mol for DTPA),\textsuperscript{19,20} is only slightly better than high-end van der Waals interactions, and is smaller than enhancements observed from other ex-situ which take advantage of the strength of covalent C-C bonds.\textsuperscript{5,7} The advantages that these techniques offer is primarily associated with their simplicity, the chemical versatility they afford, and the fact that they might be readily combined with other approaches towards enhancing SAM stability – including each other – and in this manner the potential net enhancement to stability might be sufficient for real world applications.

Finally, we would be remiss to close our discussion without providing some additional commentary on the EGaIn Tip test bed, which was as much a focus in this thesis as any SAM.
Conclusion

Having had the opportunity to collaborate with many of the leading forebears of this junction paradigm (Whitesides et al., and Nijhuis et al.) we have been especially privy to many of the trials and progressions associated with this technology, especially the development of the aforementioned “flattened” EGaIn tip. The fact that we were able to essentially reproduce the data for n-alkanethiolate SAMs on AuTS and AgTS, collected by Whitesides the group at Harvard University, on our own experimental set-up at the University of Windsor, marks a significant step forward in being able to directly compare absolute value from EGaIn tip studies and not limiting the technique solely to internal comparisons. Recent studies by Nijhuis et al. on the influence of EGaIn tip contact size and substrate roughness on charge transport also mark a significant contribution to furthering our understanding the impact of various parameters within these junctions. As can be inferred from our study of Ph2DTPA SAMs, however, the technique is still not infallible and many questions regarding these junctions still need conclusive answers, including: Why certain minor effects, observed by other testbeds, are obscured in EGaIn tip studies? Why do different types of EGaIn junctions produce different odd-even effects for n-alkanethiolate SAMs? What effect does the preconditioning step on Si actually have on EGaIn tips? In spite of these questions, we still believe this junction paradigm to be well positioned for future molecular electronic studies, especially given the recent shift in the fields focus towards molecular systems that incorporate additional forms of activated transport, other than coherent non-resonant tunneling. In such systems, the effects under investigation typically modulate current densities over >2 orders of magnitude, with the ultimate goal being to mimic or surpass the behavior of Si based electronics where “On” and “Off” currents vary by as much as 5 orders of magnitude. On this scale, the minor discrepancies in EGaIn tip studies, which are generally <1 order of magnitude, would be rendered irrelevant, making EGaIn junctions a convenient and perfectly suitable testbed for the investigation of pronounced molecular electronic phenomena.
4.2 References


Appendices

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Self-Assembled Monolayers of Dithiophosphinic Acids on Gold

Ronan Roca San Juan, University of Windsor

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Abstract
This dissertation reports the synthesis of derivatives of dithiophosphinic acids (R 1 R 2 DTPAs), and the formation and characterization of DTPA SAMs on gold to build a
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