

Fabrication, Assembly, and Characterization of Molecular Electronic Components

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Invited Paper

One of the ultimate miniaturizations in nanotechnology is molecular electronics, where devices will consist of individual molecules. There are many complications associated with the use of molecules in electronic devices, such as the electronic perturbations in the molecule associated with being bonded to an electrode, how electrons traverse the metal–molecule junction, and the difficulty of macroscopically addressing single to very few molecules. Whether fabricating a test structure or a usable device, the use of self-assembly is fundamental to the fabrication of molecular electronic devices. We will discuss how to fabricate self-assembled monolayers into test assemblies and how to use intermolecular interactions to direct molecules into desired positions to create nanostructures and to connect functional molecules to the outside world. These assemblies serve as test structures for measurements on single or bundled molecules. The development of several experimental techniques, including various scanning probes, mercury drop junctions, break junctions, nanopores, crossed wires, and other techniques using nanoparticles have enabled the ability to test these structures and make reproducible measurements on single molecules. Many of these methods have been developed to test molecules with potential for integration into devices such as oligo (phenylene–ethynylene) molecules and other π -conjugated molecules, in ensemble or single-molecule measurements.

Keywords—Break junctions, mercury drop junctions, molecular conductance, molecular electronics, nanopores, nanorods, scanning probe microscopy, self-assembled monolayers (SAMs), single-molecule measurements.

I. INTRODUCTION

The field of nanotechnology is being approached from two directions: the drive to retain macroscopic/bulk properties from ever diminishing geometries (extending the “top-down” methodology of fabrication) and the attempt to

control individual molecules or other quantum structures for device applications (the “bottom-up” methodology of fabrication). The latter, when applied to individual molecules, or assemblies thereof, has been given the name molecular electronics. As defined by the conceptual creators Aviram and Ratner [1], molecular electronics is the “study of molecular properties that may lead to signal processing” [2]. However, making molecular electronics into a functioning, manufacturable technology will require revolutions in circuit architecture, fabrication, and design philosophy in addition to gaining a fundamental understanding of conduction and electronic interactions in single molecules. Many of these broad and critical issues are discussed in this special issue. The focus of this paper is to highlight a selection of molecules that have displayed functional electronic behavior, how they have been assembled into test structures, and the methods used to probe from ensemble assemblies down to individual molecules.

Even with the development of ever-improving lithographic tools, silicon is approaching fundamental physical limitations of operation. As gate widths decrease below 100 nm, bulk properties yield to quantum phenomena and leakage currents from electron tunneling prevent proper device operation. For further device miniaturization to occur new device operating principles and materials must evolve [3]–[5]. Chemistry, by its very nature, operates at the nanometer scale by controlling the placement of individual atoms and functional groups on molecules through synthetic chemistry, allowing macroscopic properties from rigidity to optical and electronic behavior to be engineered. Molecules have already been designed and synthesized that have electronic characteristics tailored for applications in bulk devices such as organic light-emitting diodes [6], semiconducting polymers [7], and numerous other applications. The approach of molecular electronics is to progress from using the ensemble averaged response of molecules to addressing the properties and/or state of individual molecules for information storage or processing.

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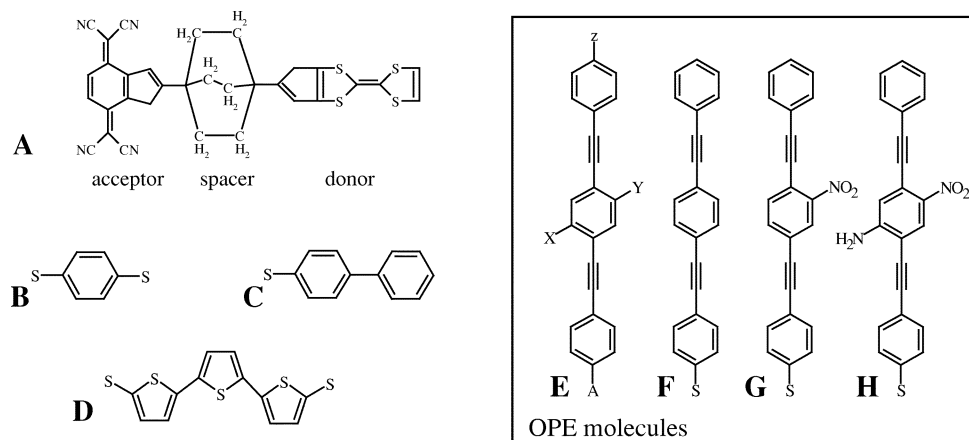


Fig. 1. The molecules described in the text. (A) Donor–spacer–acceptor rectifier proposed by Aviram and Ratner. (B) Benzene-1,4-dithiol. (C) Biphenyl-4-thiol; example of a polyphenylene. (D) 2,2';5',2''terthiophene-5,5''-dithiol; example of a polythiophene. (E) 4,4'-di(ethynylphenyl)-1-benzenethiol, the base unit for most of the OPE molecules. (F) The base OPE molecule with the various substituents where X and Y can be any of H, NO₂, or NH₂, and A and Z can be H or S (or any other linker group). (G) 4,4'-di(ethynylphenyl)-2'-nitro-1-benzenethiol, the OPE molecule that has shown room temperature NDR. (H) 2'-amino-4,4'-di(ethynylphenyl)-5'-nitro-1-benzenethiolate, another OPE molecule that has shown NDR. Note that these molecules are shown in their surface-bound thiolate form, rather than the solution phase thiol (SH).

Many molecules have been proposed for use in molecular electronics [8]. Among the proposed molecules, there are several mechanisms for controlling molecules, including electric fields, electromechanical and photochromic actuation, and electrochemistry [4] (and references therein). This paper will focus on molecules that are controlled by an electric field. These molecules are related to solid-state electronics in function and have the potential to be produced at the highest device densities [4], [9]. The concept of molecular electronic structure is analogous to that of semiconductors; the molecule's highest occupied molecular orbital (HOMO) and lowest unoccupied molecular orbital (LUMO) are the equivalent of filled and empty levels in solid-state systems, respectively. By adjusting the chemical functionalization of the molecule with electron-donating or electron-withdrawing substituents, thus altering the energy and geometry of the molecular orbitals, one can "dope" the molecule.

Using the concept of molecular doping, Aviram and Ratner first proposed a rectifying molecule (molecule 1A) based on the use of electron-donating, spacer, and electron-accepting functionalities [1]. In this system, the electron donor is a low ionization potential substituent separated from a high electron affinity acceptor by a saturated alkyl chain, which acts as a tunneling barrier. Under forward bias, the electrons can tunnel from the donor to the acceptor through the spacer at an energy near the ground state of the molecule. The complementary reverse bias conduction scheme would lie several electronvolts higher and thus be inaccessible [1]. In the terms of solid-state physics, this is an asymmetric, multilevel resonant tunneling structure [10]. Experiments have demonstrated the operation of a molecule very similar to the one proposed by Aviram and Ratner [1], [11]. While this molecule demonstrates that electronic functions can be implemented on the molecular level, issues

such as how to connect a probe to address the device, the effect of adsorption on the molecule, how to assemble molecules and devices in high yield, and how to design suitable architectures to exploit the advantages of molecular electronics still exist before molecules can be implemented as functioning devices.

Fig. 1 provides an abbreviated list of molecules that have been proposed for use in devices. One of the common features of these candidate molecules for use in nanoscale devices is extended π -conjugation (overlap and delocalization of electron orbitals); such as polyporphyrins, polythiophenes, polyphenylenes, and oligo(phenylene–ethynylene)s (OPEs). The π -conjugation provides electron delocalization along the length of the molecule, providing a low barrier path for electron transport [12], [13]. Conjugated OPE molecules, such as molecules 1E–H, have been identified as possessing favorable characteristics for molecular electronics; they have low HOMO–LUMO gaps (relative to saturated alkyl-based, σ -bonded molecules), they are fully conjugated (providing delocalized π -electrons for improved conduction [14], [15]), the terminal groups are easily functionalized to allow covalent bonding to metal surfaces, and substituents can be added to the molecule that modify its electronic properties to be electron donating (NH₂), electron withdrawing (NO₂), or to possess substituents that aid in the solubility of the molecule and, thus, ease of processing [9], [16]–[18]. By manipulating these components of the molecule, properties ranging from high-conductivity wires [19], [20], rectification [21], [22], negative differential resistance (NDR) [21], and bistable conductance [23], [24] have been demonstrated.

While silicon microelectronics is based largely on three-terminal devices such as transistors, molecular electronics will most likely remain limited to two-terminal devices because the alignment and contact of two points of a molecule

is already difficult to attain. The lack of a third terminal complicates circuit design because there are no gain elements for amplification or signal restoration. Although limited to two terminals, useful devices such as mixers, multipliers, and logic can be made from two-terminal devices that exhibit NDR [25]. It has also been proposed that molecular NDR devices can be used for digital signal restoration and latching [26], [27]. Others have shown that full logic systems can be developed from diode-based logic [28]. To implement molecular electronics, methods must be developed to contend with the complications of addressing individual or small numbers of molecules such as fault tolerance, resilience to withstand repeated cycling, and the ability to map/address individual molecules to the macroscopic world. To address these issues we must find ways to assemble molecules in a reproducible manner, and develop methods to test these molecules.

II. SELF-ASSEMBLY AND DIRECTED ASSEMBLY

To probe individual molecules electronically, one of the first issues that arises is how to attach the probe electrodes to either side of a *molecule*. All of the methods discussed here use some form of self-assembly to adsorb the molecules on an electrode. For both the test structures discussed here and for future devices to be fabricated, the ability to position and to pattern molecules selectively on a surface with molecular precision is vital. Self-assembly offers a selective chemistry where the covalent attachment of the molecule's linking group (i.e., S, O, N) can be used to bind the molecule selectively to specific transition metals [29]–[33]. Because the linking group enables the molecule to bind to the metal for electrical contact, the linking group has become known as a molecular “alligator clip” [18]. While there are many potential alligator clip groups such as isonitriles (R-N≡C), disulfides (R-S-S-R), or carboxylic acid (R-COOH), one of the most common and well characterized self-assembling alligator clips uses the sulfur headgroup of thioliates (R-S⁻) (e.g., *n*-alkanethiols) adsorbed to Au{111} to form self-assembled monolayers (SAMs). A SAM is a nominally complete one molecule thick layer of adsorbates where a nonreactive “tail” functionality prevents further growth normal to the surface. One advantage of SAMs is that the linking group can be made chemically specific. For example, the commonly used thiol chemistry will adsorb molecules to a Au electrode, but not to a Si substrate; conversely, using various silane chemistries, a SAM can be formed specifically on SiO₂ surfaces [34]–[37].

When an Au{111} surface is exposed to an organothiols, either in solution or the gas phase, a strong covalent bond (1.9 eV or 45 kcal/mol) forms between sulfur and gold. Often, the thiol is protected with an acetyl group (RSCOCH₃) to prevent the formation of a disulfide. If present, the acetate can be removed *in situ* by the addition of NH₄OH to the adsorption solution to allow the formation of the surface-bound thiolate. In the case of *n*-alkanethiols, such as dodecanethiolate, a well ordered and crystalline SAM is formed (Fig. 2). The SAM is formed by two driving

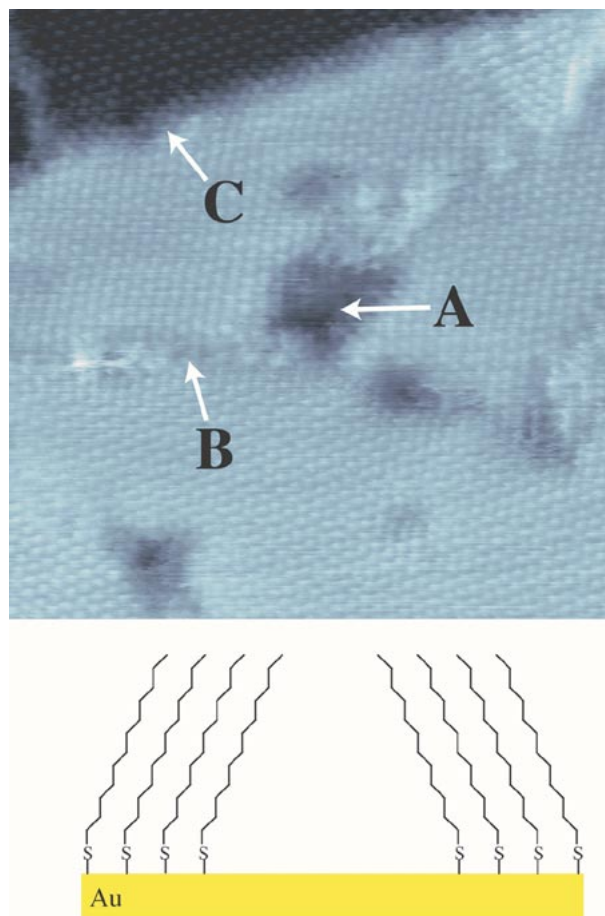


Fig. 2. Top: Topographic STM image of a decanethiolate self-assembled monolayer on Au{111}, imaging conditions $V_{\text{sample}} = 500 \text{ mV}$, $I = 10.0 \text{ pA}$, $250 \text{ \AA} \times 250 \text{ \AA}$. Several of the inherent defects are seen in this image including: (A) substrate vacancies; (B) domain boundaries; and (C) step edges. Bottom: Representation of a domain boundary in a self-assembled monolayer.

forces: the formation of a strong covalent bond between the metal substrate (Au) and the linking group (S) that binds the molecule to the surface, and the close packing of the hydrocarbon chains as a result of van der Waals interactions between adjacent hydrocarbon tails. These interactions form a well-ordered, energetically favorable, though kinetically trapped, $(\sqrt{3} \times \sqrt{3})R30^\circ$ overlayer structure and related superlattices.

Alkanethiolates form excellent host matrices because of their ability to self-assemble, the dynamics of formation allow control of film quality and postadsorption processing are well understood, they are chemically inert, and they have low electrical conductivity. Experiments using scanning tunneling microscopy (STM) and conductive probe-atomic force microscopy (CP-AFM) have characterized the electron transport, current–voltage (I – V) properties, and breakdown voltages of insulating SAMs [38]–[46]. For example, an I – V curve of decanethiol measured by STM is shown in Fig. 3, displaying a sigmoidal trend with linear behavior at low bias voltage and a large current onset above $\sim 0.7 \text{ V}$. Because alkanethiols are easily assembled and chain length and chemical functionality can be selected or modified,

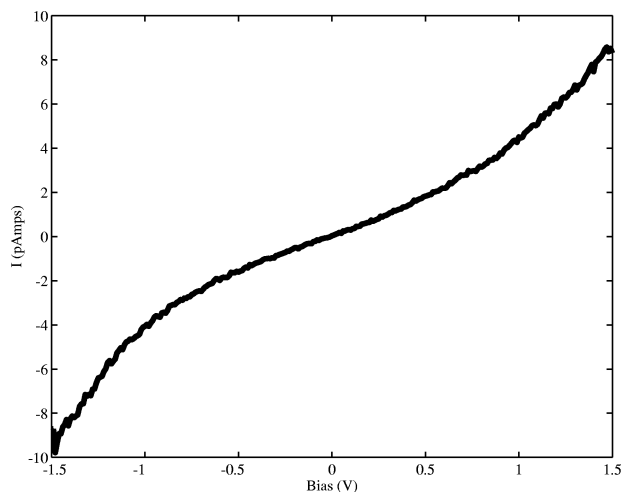


Fig. 3. I - V characteristics of decanethiol acquired by STM where the gap conditions were $+1.0 V_{\text{sample}}$ and 5-pA tunneling current.

they have been used as model systems for measurements of electron transport through molecules. As alkanethiolates are often used as an insulating host matrix, their electronic characteristics establish the background/threshold currents for many of the techniques used to characterize other molecules. Thus, by knowing the electronic properties and electron transport mechanisms of alkanethiolate SAMs, we can isolate and explore the electronic properties of embedded molecules.

Molecules can be measured from either pure monolayers or from a mixed monolayer formed by the simultaneous coadsorption of a host matrix and the molecule of interest. When forming a mixed monolayer by coadsorption, the surface coverage can be modified to dilute either of the adsorbates by adjusting the ratio of the constituents in solution. However, some molecules have different sticking probabilities resulting from more stable surface bonds or intermolecular interactions resulting in the possibility that the surface composition of either of the molecules may not reflect the solution composition [47].

SAM order is usually determined by the packing efficiency of the adsorbates. For a mixed monolayer, the molecules may not pack as well around the “impurity” of a second adsorbate, which can lead to greater disorder in the overall SAM [48]. We have observed by STM that the coadsorption of the OPE molecules will disrupt the order of an alkanethiolate SAM [49]. However, molecules that do not form ordered monolayers can be coadsorbed at low concentration with SAMs that do form ordered monolayers. The disadvantages of using coadsorption to form a mixed monolayer include the lack of control over the placement of either of the molecules and the possibility of disrupting the order and/or quality of the film.

Pure n -alkanethiol SAM surfaces tend to be well ordered; however, there are defects inherent to SAMs, several of which are noted in Fig. 2. Substrate vacancies are one atomic layer deep, resulting from the ejection of individual surface layer gold atoms and the subsequent rearrangement of the remaining gold adatoms during SAM adsorption [50]. These vacancies appear as depressions in the image

[Fig. 2(A)]. Domain boundaries [Fig. 2(B)], are created where regions of the alkyl tails may possess differing tilts (the optimized van der Waals interactions result in a chain tilt of about 30° for alkanethiols) and/or rotations with those of neighboring adsorbates, stacking faults, or differing sulfur headgroup-lattice registry. Finally, monatomic substrate step edges are present at the edge of atomic terraces [Fig. 2(C)].

While alkanethiolate SAMs are stable surface structures, the adsorption process is highly dynamic, allowing molecules to exchange continuously on and off of the surface with other thiol species in solution or in the vapor phase [51]. It is expected that exchange is most active at SAM defect sites, substrate vacancy islands, and substrate step edges as the molecules are less constrained than the surrounding matrix and may have greater accessibility to the solvent. Thus, exchange processes can be moderated by controlling the types and densities of defects. Using an exchange process to insert molecules into SAM defects, a dodecanethiolate film can be used as an insulating host to support and to isolate molecules of interest for analysis, a process referred to as directed self-assembly [52]. Using directed self-assembly, a surface with a “host” SAM is placed in a solution or exposed to the vapor of a “guest” molecule. Due to the enhanced exchange kinetics, the guest will selectively insert or exchange into the host at defect sites or at step edges. Because of the restricted space available in most defect sites a guest molecule such as the rigid OPE molecules that insert into the film are forced to stand up nearly normal to the gold surface, leaving the terminal end of the molecule slightly protruding from the SAM host [53]. We have demonstrated that molecules can be selectively inserted into SAMs using this procedure at defect sites, domain boundaries, and step edges [19], [52]–[55]. Directed self-assembly has the advantage that guest molecules can be inserted into a host SAM with minimal disruption to the order or quality of the overall SAM. However, insertion is favored at defect sites and step edges; therefore, it can be difficult to get high surface coverages of guest molecules using directed assembly.

Similar to the n -alkanethiolates, some OPE molecules, specifically molecule 1E, form well-ordered monolayers [56]–[58]. However, we have found that other OPE molecules with various substituents do not seem to form well-ordered monolayers by STM analysis [49]. The presence of a substituent can induce a dipole on the molecule and steric hindrance associated with the substituent disrupts the ability of the molecules to order and to form stable surface structures. Other systems such as oligophenylene-dithiols have also been shown to form disordered monolayers or even multilayer films [59]. However, by using either coadsorption or insertion, these molecules can be controllably embedded in a host SAM for analysis by ensemble or single-molecule techniques. As discussed below, the order of these monolayers and how a second electrode interfaces to each of the molecules can influence the behavior of the device. As a final caution on self-assembly, often the “cartoons” we draw to describe these systems, such as Fig. 4, may not properly represent reality as many of these molecules may not actually form well-oriented or ordered films. Unless the

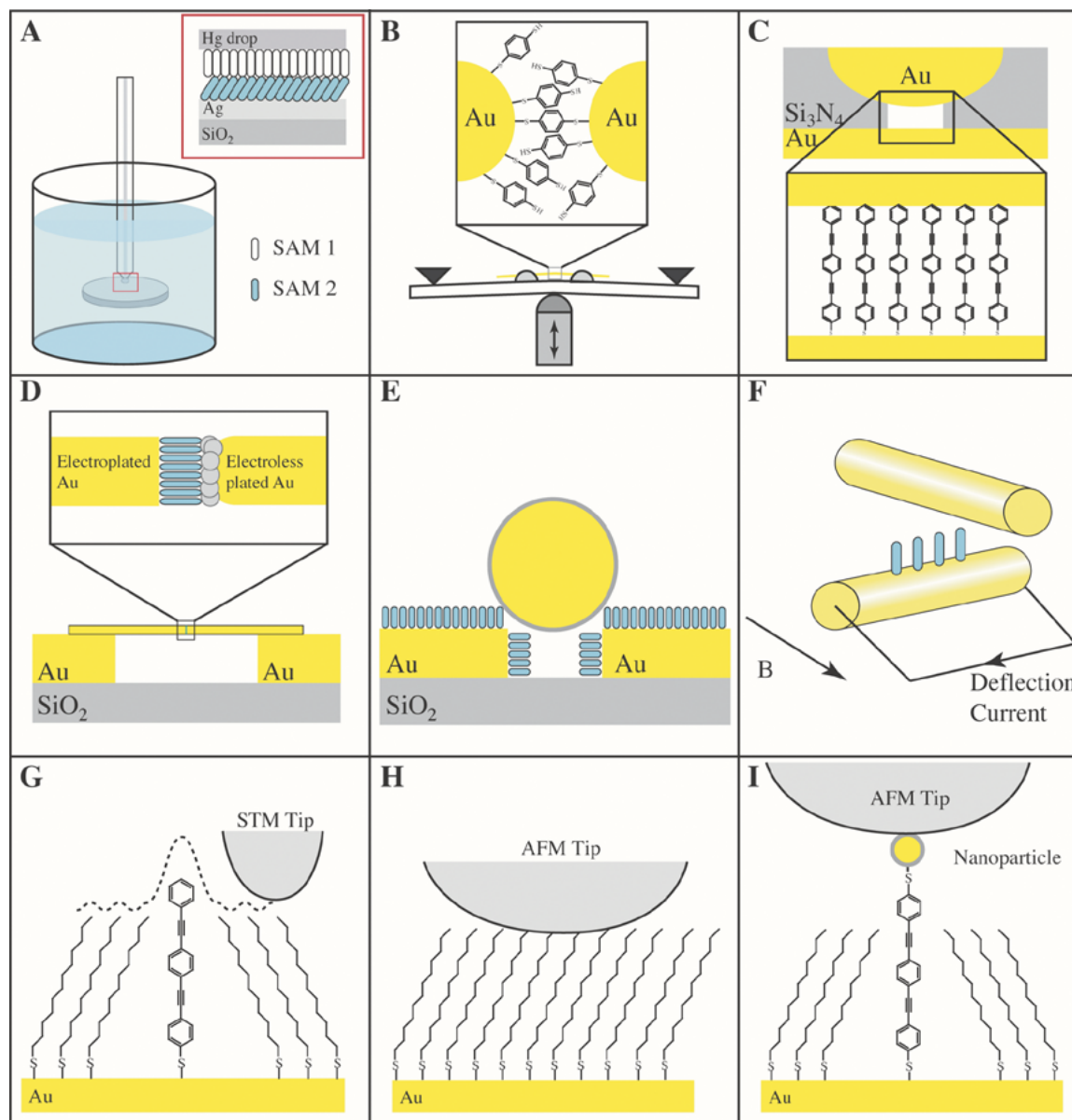


Fig. 4. The various techniques discussed in the text used to measure electronic properties of molecules. Note that images are not to scale. (A) Hg drop junction. (B) Mechanically controlled break junctions. (C) Nanopore. (d) Nanowire. (E) Nanoparticle bridge. (F) Crossed wires. (G) STM. (H) Contact CP-AFM. (I) Nanoparticle coupled CP-AFM.

system has been specifically investigated, the formation of an ordered monolayer is not a safe assumption.

III. MOLECULAR CONDUCTIVITY

As we now have methods to fabricate structures for analyzing single and bundled molecules, we begin to ask, What makes any given molecule more conductive than another, and how do electrons traverse a metal–molecule–metal interface? Electron transfer for the majority of systems discussed here can be described either by coherent nonresonant tunneling or coherent resonant tunneling. Coherent nonresonant tunneling occurs when the electronic states of the molecule are far from the energy of the tunneling electrons (e.g., transport in *n*-alkanethiols); the rate of electron transport is exponentially dependent on the length of the molecule. Coherent

resonant tunneling occurs when the energy of the tunneling electrons is resonant with the energy of the molecular orbitals; the rate of electron transport is dominated by contact scattering, is essentially independent of length, and increases with the number of available modes [60].

The components of the system that determine how electrons traverse metal–molecule–metal junctions include the nature of the molecular orbitals in the molecule, the interaction and energy alignment of molecular orbital levels with the continuum of states in the metal, and the type of bonding in the metal–molecule junctions and the effects of these bonds on the molecule [61]. Starting with the electronic structure of the molecular orbitals, extended π -conjugation aids in providing delocalized orbitals that can span the length of a molecule, such as the π -conjugation present in the OPE molecules. A highly conducting channel

is a molecular orbital that is fully delocalized along the molecule; conversely, a nonconducting channel has localized molecular orbitals that do not span the molecule [62]. It may be that a molecule can be in a conductive state (low impedance) if the molecular orbitals around the Fermi level are delocalized across the molecule (resonant transfer), and in a nonconducting state (high impedance) when the molecular orbitals around the Fermi level are localized to specific parts of the molecule (nonresonant transfer) [62]. Electrons can travel through the LUMOs [63] and in specific cases, hole transport can occur through HOMOs [62], [64], [65].

In most cases, the Fermi level of the metallic contact does not align with the HOMO or LUMO levels of the molecule [40], [61]. Charge transfer from the metal electrodes to the molecule, as a result of the metal–molecule bond, increases the electrostatic potential within the molecule and creates a potential barrier at the metal–molecule interface, reducing the transmission of electrons through the junction [61], [66]. Electron transmission is regulated by the alignment of molecular HOMO–LUMO levels relative to the metal Fermi level, the molecular equivalent to the Schottky barrier formed at metal–semiconductor interfaces [61], [67]. The properties of this barrier (i.e., height and effective barrier thickness) determine the transport mechanisms such as thermionic emission, direct tunneling, or defect-mediated transport [67]. Changes in the electrostatic potential of molecular systems, such as that induced by the Schottky barrier or an applied bias, can raise the energy of some molecular orbitals and lower the energy of others [61]. Di Ventra *et al.* found that the electronic structure of molecules changes substantially as a function of applied bias voltage [68], [69]. Thus, for any theoretical analysis of a molecule under a bias, the molecular Hamiltonian must be recalculated as a function of applied bias.

When analyzing a molecule for its potential application as a device component, the electronic characteristics of the molecule play a significant role in the behavior of the device; however, it is the characteristics of the full system, including the metal–molecule contact, that determine the device performance. Recent experiments and calculations [38], [61], [67], [69], [70] have shown that the metal–molecule interface plays a vital role in the overall conductivity of the system, and in some cases the overall behavior of the system [71]. For thiolate-gold SAMs, the interfacial electronic structure is dominated by σ^* (sigma antibonding) orbitals localized to the C–S–Au system, a $p\pi - \sigma$ system. The delocalized π -orbitals responsible for the enhanced conductivity of the conjugated molecule cannot couple strongly to the localized σ states at the interface because of the symmetry of the orbitals [67], thus decreasing the conductivity of the molecule. Use of other molecular alligator clips and different metals with better coupling is being explored, specifically, the use of isonitrile (metal–C \equiv N–R) and Group 10 metals [13]. When isonitrile binds to Group 10 metals, the metals' d orbitals overlap with the isonitriles' π^* orbitals, allowing electron density to transfer across the metal–molecule interface through a $d\pi - p\pi$ system [67], offering greater conductivity than the S–Au ($p\pi - \sigma$) system. Thus, while the OPE molecules with thiol alligator clips may

have full π -conjugation to enhance electron conduction, the lack of π -orbital overlap with the metal–molecule interface ($p\pi - \sigma$) greatly decreases the overall conductivity of the molecule. In addition, the bond angle of the molecule to the surface (and, thus, the degree of $p\pi$ orbital overlap with the metal) can also play a role in the conductivity of a molecule [72], [73].



Theoretical [13] and experimental [38] efforts have been executed to determine the optimal linker–metal combination. Theory, based on the alignment of the local density of states (LDOS) in the molecule with the Fermi energy of the electrode has predicted that a S–Pd system should have the highest conductivity, followed by an NC–Pd system [13]. However, using contact CP-AFM, Beebe *et al.* systematically tested different substrate/tip metal combinations with thiol and isonitrile linking groups to find the optimal linker–metal combination [38]. From these experiments, the NC–Au linker provided about 10% less contact resistance than S–Au junctions. However, for the same linker molecules, it was found that different metals could influence the contact resistance of the junction by more than two orders of magnitude. It was found that the contact resistance decreases with increasing metal work function. This indicates that there is a smaller barrier to charge transport in the junction for higher work function metals, implying that the Fermi level lies closer to the HOMO than the LUMO. This could indicate that charge transport for these systems is actually hole rather than electron tunneling [38].

One commonly used method to determine the characteristics of a molecule and its electron transfer mechanism is to measure the structure-dependent tunneling attenuation factor β . As previously mentioned, coherent nonresonant electron tunneling current shows an exponential dependence to length and, thus, junction resistance R , as given by $R = R_0 \exp(\beta l)$ (sometimes measured in terms of current as $I = I_0 \exp(-\beta l)$), where l is the length of the molecule and R_0 is the effective contact resistance [12], [39], [46]. Often, β is reported in terms of oligomer units (β_N), yielding a junction resistance $R = R_0 \exp(\beta_N N)$, such as the number of methylenes or phenyl rings in the molecule. The β term is usually obtained by measuring the junction resistance as a function of the number of oligomers in the molecule. The β term yields information on the conductivity of the molecule, whereas the contact resistance yields information on the coupling of the metal–molecule junction; thus, these two terms can be used to characterize the effect of the molecule and its linking group on the behavior of the device (for coherent, nonresonant tunneling). Different types of electron transport will show varying dependences on distance; for example, coherent resonant transport will show only a weak coupling to variation of distance and the resistance should vary linearly for diffusive transport.

IV. MEASURING MOLECULAR ELECTRONIC COMPONENTS

Most molecules of interest are two-terminal devices where the ideal measurement would be to attach a probe at each terminal and measure the conductance or I – V characteristic of an individual molecule. However, the difficulties associated

Table 1
Various β Values Expressed in \AA^{-1}

Method		
CP-AFM	1.1 [45], 0.94 [46], 0.8 [74], 0.57[†] [127]	0.42 [46]
STM	1.2 [39]	
Hg junction	0.87 [75,77], 0.89 [80], 0.65[‡] [64]	0.61 [75,77]

[†] β for a dithiol using nanoparticle coupling CP-AFM.

[‡] β for hole tunneling only.

$\beta_{\text{vacuum}} = 2$

with addressing an individual molecule greatly complicate the measurement. The envisioned implementation for these molecules is a metal–molecule–metal junction. Especially because of the influence of the junction on the device behavior, the test structures will have tremendous influence on the resulting behavior. Only through recent progress in scanning probe microscopes and developments in nanofabrication have we been able to probe small bundles down to individual molecules. Unfortunately, the results can be as varied as the techniques used to measure these systems, as seen by the distribution of β values in Table 1; experimental values for conductivity can differ by many orders of magnitude for the same molecule [45], [74], [75], with the same order of magnitude disagreement with theory [69]. Below, we discuss the methods used to measure these metal–molecule–metal junctions and some of the results from these techniques.

A. Mercury Drop Junctions

One of the limiting factors of any method to probe a two-terminal molecule is the difficulty associated with fabricating a structure that can reproducibly connect to both ends of a molecule. However, using a mercury drop as an electrode allows for a reasonably easy method to form a metal–molecule–metal junction. Similar to gold, mercury can form thiol-based SAMs [76]. The junction is created by forming a mechanical contact of a SAM supported on a solid substrate and a SAM supported on a suspended mercury drop [75] [Fig. 4(A)]. The resulting metal–SAM–SAM–metal junction allows for the ensemble measurement of pure and mixed monolayers.

The junction is formed with a SAM on a Si-supported Ag surface that is immersed in a solution containing the second SAM that will adsorb to the Hg. A Hg drop is formed on the end of a Hg column electrode while immersed in the solution allowing the formation of the Hg-side SAM. The Hg is lowered until mechanical contact is established forming the metal–SAM–SAM–metal junction. There are other variations of this system where both metal contacts can be Hg [77], or Hg–SAM–semiconductor structures can be formed [64], [65], [78]. These junctions are fast and easy to construct, allowing multiple SAM and metal combinations to be analyzed; however, this method is limited to ensemble measurements and cannot be performed at cryogenic temperatures [48], [77].

Using these junctions, the breakdown voltages and tunneling characteristics of alkanethiols and polyphenylenes have been characterized [75], [77], [79]–[81]. One significant difference in this technique is the unique junction formed at the SAM–SAM interface. The terminal functionality of the SAMs can be controlled such that the electron transport between the two SAMs can be monitored as a function of SAM–SAM interactions. Holmlin *et al.* found that the interaction of covalent, hydrogen, or van der Waals-like bonds could modify conductivity by more than four orders of magnitude [82]. Junctions of mixed monolayers have also been formed with molecules of tetracyanoquinodimethane-functionalized decyldisulfide that display rectification [48].

Selzer *et al.* was able to modify the junction in a different manner using a Hg–SAM–semiconductor interface [64], [65]. For this system, there is only one SAM in the junction, and it is bound either to the Hg drop using a thiolate bond or to the oxidized surface of a p-doped Si substrate using an alkyltrichlorosilane to form a siloxane bond to the surface. The use of p-doped Si and analysis at low bias ensures a hole tunneling transfer mechanism, which was found to produce β values for alkylsilanes on the same order as conjugated polyphenylenes [64], [65], as seen in Table 1.

B. Break Junctions

Some of the first single-molecule conductivity measurements were executed using mechanically controllable break (MCB) junctions [Fig. 4(B)]. This method uses a notched Au metal wire attached to a flexible substrate. The substrate is bent by a piezoelectric actuator until the notch fractures, producing a gap whose separation can be adjusted by the actuator, enabling an adjustable tunneling junction [83]–[86]. After fracturing, benzene-1,4-dithiol (molecule 1B), one of the simplest molecules proposed for use in characterizing molecular conductance, was deposited on the electrodes from a solution of tetrahydrofuran (THF), forming a SAM of the molecules on each of the electrodes. The THF was evaporated and the electrodes were brought together until one molecule bridged both electrodes. While this system yields reproducible information on these small and rigid molecules, this system is not easily adapted for longer or more flexible molecules as the exact structure of the tunneling junction is unknown, and multiple contacts between other molecules in the junction could lead to the creation of unwanted parallel currents.

The benzene-1,4-dithiol system displayed a symmetric I – V curve with an apparent bandgap of about 0.7 V, and a threshold resistance of a single molecule was found to be about 22 M Ω [85], [86]. The bandgap is thought to arise as a result of the alignment of the HOMO–LUMO levels with the Fermi level of the electrodes; thus, the onset of current is a result of resonant states of the molecule at various probe biases. Further theoretical interpretation of this data revealed that the origin of these properties could be the result of two molecules each bound to only one electrode where the overlap of the molecules provides electron transport if there

is a high density of SAMs in the area of the junction or single-molecule conduction for dilute SAMs [87].

Using a junction created by electromigration rather than a mechanical break, others have analyzed oligothiophene molecules [88] and derivatives of OPE molecules [89], [90]. In both cases, several stable junctions with different I - V properties for the same molecule could be obtained. The changes in I - V characteristics were attributed to changes in the metal-molecule junction [88]. This emphasizes the difficulty of defining the environment and geometry of the molecules in this junction, making it difficult to fully understand the behavior of the molecule.

C. Nanopores

In another system used to characterize molecular electronics, Reed and coworkers fabricated a structure, referred to as a nanopore [Fig. 4(C)], to measure the conduction directly through a small number (thousands) of organic molecules [20]–[22], [24], [85], [91]. The nanopore consists of a SAM of conjugated molecules (e.g., molecules 1E–H) sandwiched between two electrodes. The devices are fabricated using a combination of electron-beam lithography, plasma etching, and use of an anisotropic etchant to create a suspended silicon nitride membrane with a 30–50 nm aperture [20]. An Au contact is evaporated on the top of the aperture and the device is immersed in a solution of the molecule of interest to form a SAM. After deposition, the bottom electrode is formed by evaporating 200 nm of Au onto the sample, which is held at 77 K to minimize damage to the SAM [21]; however, this deposition can still be quite harsh on the organic layer [92]–[96]. Once the structure is sealed by the evaporated electrode, it is impossible to know the structure or status of the sandwiched organic layer. In addition, due to the geometry of the nanopore, it is not possible to determine the order or orientation of the SAM even before the top electrode is evaporated in place.

Using the nanopore device, Reed and coworkers have measured the properties of biphenyl-4-thiol (molecule 1C) [10], [20]. This molecule exhibited strong rectifying behavior arising from the asymmetry of the molecule. There are two sources of asymmetry in this molecule. First, only one side of the molecule has a thiol for covalent bonding to the Au electrode. Second, for this particular experiment, a Ti adhesion layer was evaporated on the phenyl end group of the SAM before the Au layer was evaporated, likely reacting with the organic layer [95], [96]. This is also the likely case for the crossed wire systems developed by Collier *et al.* [97]–[99]. This Ti layer presents a different metal-molecule interface than the Au–S barrier (the workfunction of Au > Ti) and, thus, allowed electrons to flow only from the Au/Ti electrode to the S–Au surface [85].

In other experiments, Reed and coworkers have demonstrated that the nitro and nitro-amino substituted OPE (molecule 1G and H) exhibit NDR at cryogenic [21] and room temperatures [22]. NDR is a characteristic of the device where increased driving voltage results in less current (negative resistance), as shown in Fig. 5. This type of behavior is very similar to resonant tunneling diodes (RTD) where there

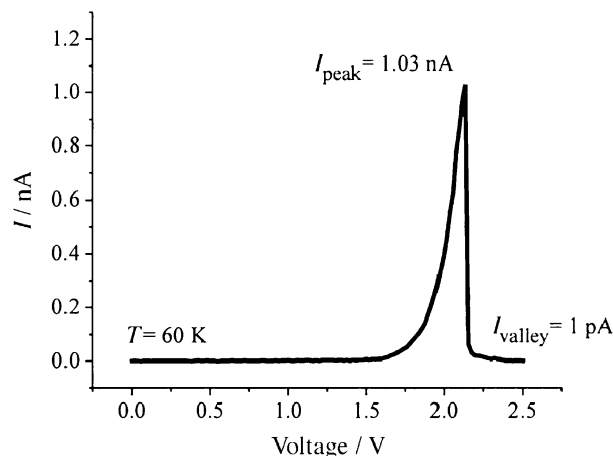


Fig. 5. I - V characteristics from a nanopore with the molecule H at 60 K that exhibits negative differential resistance with a peak to valley ratio of 1030:1. Copied with permission from [21].

is enhanced conduction present only while the device is in an energetically resonant state. Such devices can be used for electronic applications such as logic [100]. Seminario *et al.* have proposed that the NDR displayed by these molecules is a function of the electronic charge state of the molecule and the resulting change in molecular conformation [63]. In this proposed mechanism, the molecule can be neutral, singly, or doubly reduced. In the singly reduced state, the LUMO becomes fully delocalized, allowing enhanced conduction, thus creating the onset of the NDR peak. As the bias voltage is increased the molecule becomes doubly reduced, the LUMO becomes localized across the molecule and decreases the conductivity of the molecule, reducing the current passed through the molecule [63].

The conductance state of the molecule has shown retention times of greater than 10 min [24]. The ability to retain various conductivity states allows for these molecules to store information similar to a RAM cell [24]. To set the molecular “bit,” a negative voltage is applied, placing the molecule in its neutral charge state and, thus, its lower conductivity state. A positive voltage pulse (or no pulse) writes the bit to an ON (or OFF) state. The bit can then be read by a small positive voltage where the presence or lack of current indicates the value of the stored bit [24]. However, it is difficult to conceive of how different charge states could be stable for a molecule in chemical and electronic contact with a metal electrode surface without some simultaneous change such as a conformational motion of the molecule or system [73].

D. Metal Nanowires

Rather than sandwich the molecule of interest in a vertical structure, Mallouk and coworkers have developed a method to incorporate molecular junctions in metallic nanowires grown by template replication [101] [Fig. 4(D)]. Using template replication [102], metallic wires can be grown with nanometer-scale diameters but micrometers in length. This provides a nanoscopic interface to the molecules while the microscopic length of the nanowire allows for connection to the outside world. One very different aspect of this

configuration is that the top of the metal–molecule–metal junction is not evaporated, but rather uses a more gentle electroless plating deposition.

The functionalized wires were grown in track-etched polycarbonate membranes where the bottom portion of the wire was electrochemically deposited in the membrane pores. For an initial test structure a SAM of 16-mercaptohexadecanoic acid ($\text{HS}(\text{CH}_2)_{15}\text{COOH}$) was deposited on the wire using standard thiol adsorption. The second layer of metal was grown by electroless plating using a seed layer of Sn(II) ions that adsorb to the carboxyl tail group of the SAM. The seed layer of Sn(II) promotes the subsequent formation of Ag nanoparticles from a solution of ammonia and AgNO_3 . The remaining portion of the nanowire was then electrolessly plated from a Au(I) solution using formaldehyde as a reducing agent [101]. This electroless plating method is more gentle than the evaporation used in other methods, reducing the possibility of damaging the organic layer during deposition. Similar to the nanopore, it is still difficult to know the structure or quality of the SAM during the formation of this junction. One complication of using the carboxylic acid terminal functionality to promote the Sn(II) ionic layer is that the different electronic coupling of the carboxylic group could be responsible for the observed reduced current density [82].

To test the electronic properties of this system, a method was developed to align the nanowires across two metallic contact pads using an ac electric field [103]. Once in contact, the metal–molecule–metal junction can be easily addressed. The 16-mercaptohexadecanoic acid functionalized nanowires were found to exhibit nonlinear behavior at biases above 2.0 V, and breakdown voltages of about 3.5 V, comparable to CP-AFM measurements, discussed below. Upon repeated cycling at high voltages, the breakdown voltage was found to decrease, indicating degradation of the SAM. More recently these nanowires have been functionalized with molecule 1G and have demonstrated room temperature NDR for this system [104].

One possible complication with this method involves the strain exerted on the SAM. As shown by CP-AFM, the force on the SAM can greatly influence the breakdown bias [45], [74], [105]. It is possible that the SAM is under tensile or compressive strain in the nanowire, which could influence the behavior of the system [101]. Finally, while mixed monolayers can be used in this system to decrease the number of active molecules being probed, this technique is used mostly for ensemble measurements.

E. Bridging Nanoparticles

In a technique similar to the metal nanowires, Amlani *et al.* have used metallic nanoparticles to bridge the gap between two electrodes functionalized by candidate molecules [106] [Fig. 4(E)]. The assembly is fabricated using a combination of photolithography and electron-beam lithography to grow Au electrode contacts with a gap of 40–100 nm. Using an ac electric field across the contacts a nanoparticle becomes trapped over the gap between the electrodes and closes

the circuit. If a SAM is formed on the Au electrodes before the nanoparticle is trapped, a metal–molecule–nanoparticle–molecule–metal interface is formed.

Initial molecules analyzed with this system include the molecules 1F and 1G [106]. When functionalized with the molecule 1F, the device shows only linear behavior. However, when functionalized with molecule 1G, two NDR peaks were observed [106]. Although this circuit is more complicated than a simple metal–molecule–metal interface, when functionalized with a NDR molecule the system can be thought of as two resonant tunneling diodes in series, which are known to show this type of behavior [100]. While this new technique has been used to characterize only these two molecules, it should aid in the rapid assembly and analysis of many molecules in the future. It also proves a unique method to demonstrate how these molecules may behave when connected in series.

F. Crossed Wires

Similar to the Hg tunnel junctions, crossed-wire tunnel junctions take advantage of eliminating the difficulty associated with fabricating metal electrodes with extremely small gaps by having “mobile” electrodes. Crossed-wire tunnel junctions are formed by placing two wires, one of which is functionalized with a SAM, in a crossed geometry where one of the wires is perpendicular to an applied magnetic field [71] [Fig. 4(F)]. The wire spacing is controlled by the Lorentz force (the deflection controlled by the dc current in the wire perpendicular to the magnetic field). This method has the advantage of forming a metal–molecule–metal contact without using an evaporated layer to form the second metal–molecule contact, decreasing the chance of damaging the organic layer, and increasing the ease of varying the identity of the metal contacts.

Using this technique, Kushmerick *et al.* have demonstrated the influence of symmetry in the metal–molecule junction [71]. Here, symmetry is determined by the functionality of the “head” and “tail” groups on the molecule. To focus on the influence of the tail functionality, molecule 1F (the simplest of the OPE molecules) was analyzed for cases where the X substituent is a thioacetyl group (which leads to thiolate coupling) and the Z substituent is either a hydrogen (in the asymmetric case) or a second thioacetyl group (in the symmetric case). It was found that when the Au–molecule–Au contact was established, the symmetric molecule exhibited a symmetric I – V curve with a large current onset after ± 0.5 V, and the asymmetric molecule exhibited an asymmetric I – V curve, possessing a large current onset only at positive bias voltage [71]. In comparison to previous nanopore measurements where rectification was observed [20], the nanopore interface used a Au–molecule–Ti/Au layer in contact with the molecules, which was believed to generate a Schottky barrier and possibly damage the organic layer. However, for the crossed-wire measurement, the rectification in the system is isolated to the chemical contact of one of the metal–molecule junctions. Under the assumption that all of the voltage is dropped at the junctions,

the asymmetry arises because the LDOS at the Fermi energy for the different metal–molecule interfaces causes different voltage drops across the junctions [40], [71]. Thus, the rectification observed for the asymmetric system is a function of the different voltage drops at each of the junctions.

Similar to exchanging the linking group to find the most conductive system, this technique has also been used to measure how the bond length of a molecule can influence its overall conductance [107]. Under the initial assumption that the planarity of oligo(phenylene–vinylene) (OPV) molecules would yield a higher conductance as a result of better π -conjugation, an OPV molecule was compared to the OPE wire molecule. It was found that the OPV molecule was about three times more conductive, in agreement with previous electrochemical [108], [109] and theoretical work [12]. From theoretical modeling it was found that the enhanced conductivity for these molecules was not a result of the planarity of the molecule but that the regular periodicity of the molecule resulted in a smaller HOMO–LUMO gap, lowering the contact potential at the junctions, thus increasing the conductivity of the molecule [107].

G. Scanning Tunneling Microscopy

The previous techniques have focused mostly on measurements of ensembles of molecules. Use of a scanning probe microscope (SPM) allows the analysis of a few or even individual molecules. Much of the initial work done with scanning probes used STM [Fig. 4(G)], where the topography is measured by monitoring a feedback loop that maintains a constant tunneling current. This technique has the advantage of being able to image and to measure the transport properties of individual molecules; however, the interpretation of the I – V characteristics are complicated by the tunneling barrier inherent to the feedback mechanism of the STM tip.

Some of the initial quantitative measurements using the STM were performed on SAMs of *p*-xylene- α,α' -dithiol ($\text{HS-CH}_2\text{-C}_6\text{H}_4\text{-CH}_2\text{-SH}$) [110]–[112]. Using a geometry similar to nanoparticle coupled conductive probe AFM [Fig. 4(I); see below], one thiol of the molecule forms a SAM on the substrate leaving the other thiol to bind to a vacuum deposited Au cluster, forming a metal–molecule–metal junction. When probed by STM this structure creates a double barrier tunnel junction that produces Coulomb blockade, where each barrier can be modeled as a resistor and capacitor in parallel [112]. The first barrier represents the tunneling junction of the STM tip to the Au cluster and the second barrier represents the cluster–molecule–substrate junction. By fitting the Coulomb blockade I – V data to the model, the resistance of the cluster–molecule–substrate system was estimated, yielding single-molecule resistance on the order of $\sim 9 \text{ M}\Omega$ [110]–[112].

STM has also been used to characterize full monolayers of various molecules, including molecule 1E [56]–[58], which has displayed rectification attributed to charge transfer from the substrate to the sulfur and into the molecule, forming a Schottky-like barrier [57]. In other experiments, alkanethiols were inserted into a monolayer of molecule

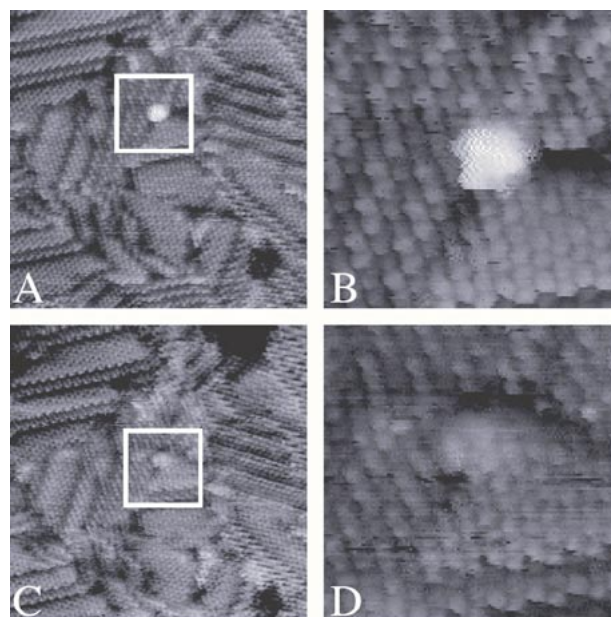


Fig. 6. Topographic STM images of a molecular switch, molecule 1H, inserted in a dodecanethiol self-assembled monolayer. The vertical scale on all images is 8.5 Å. All images are acquired at a sample bias of -1.0 V and 1.0 pA tunneling current. (A) $200 \text{ Å} \times 200 \text{ Å}$ image of the switch molecule in the ON state and the surrounding dodecanethiol SAM. (B) Higher resolution image from the highlighted area in (A), showing a $50 \text{ Å} \times 50 \text{ Å}$ area. The switch molecule is adsorbed in the domain boundary that separates the tightly packed dodecanethiol domains in the upper left and lower right of the image. (C) and (D) are low- and high-resolution images, respectively, showing the same molecule in the OFF state.

1E to dilute the local concentration of active molecules [113]. By varying the insertion time they controlled the size of the islands of molecule 1E and, thus, the number of molecules in an island. These measurements yield information on the collective behavior of the molecules. Using the directed self-assembly technique discussed earlier, individual molecules can be isolated either as individual molecules or in small bundles in an insulating SAM matrix and addressed by STM for characterization [19], [23], [54], [60], [114]. As the inserted molecule is in a defect site, defining the exact environment of the molecule is quite difficult, therefore analytical measurements comparing different molecules cannot be made [39]. The STM is well suited to measure electron transfer through single molecules due to the localized nature of electron tunneling and the high spatial resolution associated with this technique [19], [23], [52], [54], [115]. However, use of the STM to characterize these molecules leads to an inherently asymmetric junction as the tunneling feedback forms a metal–molecule–gap–tip junction. In contrast to the sandwich-style configurations such as the nanopore measurements, here the molecules are bound to one electrode and the STM tip acts as the second electrode, capable of imaging and addressing individual molecules [Fig. 4(G)]. Because topographic STM images are a convolution of the geometric and electronic structure of the tip and surface, it can be difficult to distinguish individual from bundled molecules. However, in certain cases we can infer that most of the protruding features are

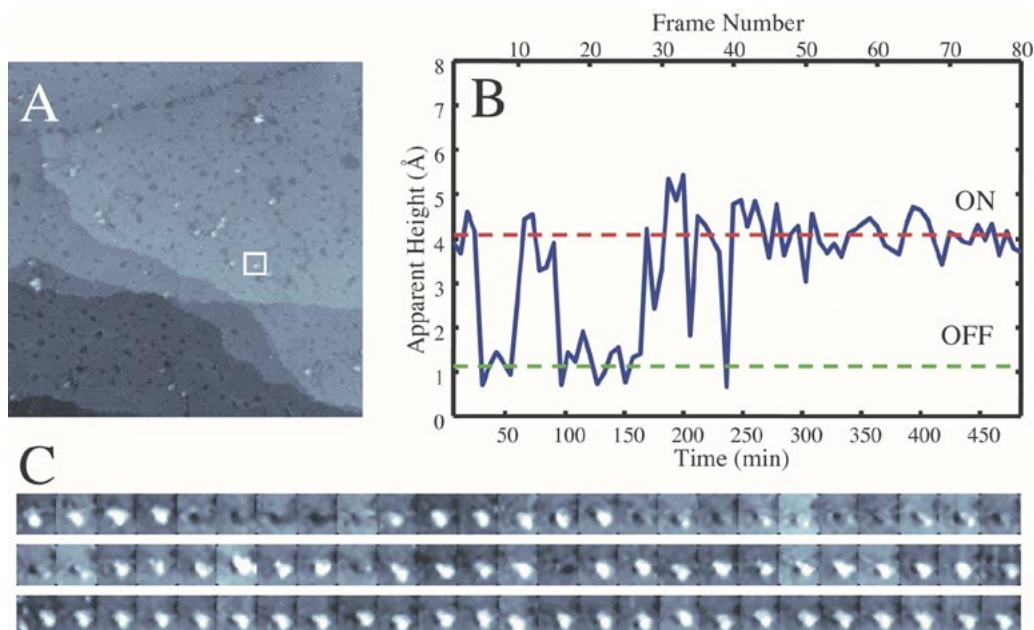


Fig. 7. (A) 1500 Å × 1500 Å topographic STM image acquired at a sample bias of -1.4 V and tunneling current of 0.2 pA. The vertical scale is 30 Å. Several switch molecules are inserted at self-assembled monolayer defect sites. The area in the white square is extracted from the sequential series of images to calculate height of the molecule over time. (B) The calculated apparent height versus time for the molecule in the extracted area. The red and green lines are guides to the eye in discerning the ON versus OFF states. (C) The extracted area for one molecule from the sequential series of images. The time interval between each frame is about 6 min.

individual molecules because of the limited access available during the insertion process [19], [54]. For instances where more than one molecule seems to be inserted, we have observed collective effects consistent with the behavior seen in nanopores.

This method was initially used to study the conductivity of molecule 1F [19]. Using a SAM of decanethiol and the inserted molecule 1F, we could identify the molecule by direct imaging and by measuring the apparent tunneling barrier height (ATBH). ATBH is acquired by monitoring the tunneling current (I) while oscillating the STM tip-sample distance (z) to acquire (dI/dz) images [116]. The ATBH images revealed that the ATBH over the wire was at least two times higher than the surrounding decanethiol SAM matrix. This higher relative ATBH, when concurrent with greater tip-substrate separation, indicates that the junction contains regions of higher conductivity when over a wire; this is a result of the existence of surface states available for tunneling that extend significantly past the molecule-air/vacuum interface [54]. In addition, the differences in the topographic height in STM images between the SAM and the wire increase with decreasing junction impedance (decreasing tip-substrate separation), also indicating the presence of frontier orbitals extending from the molecule.

After molecule 1H exhibited NDR and bistable conductance when bundled in nanopores, it was of interest to determine if individual, isolated molecules behaved similarly. Using the same insertion technique, Donhauser *et al.* observed that upon repeated scanning the inserted molecule (molecule 1H) exhibited stochastic conductance switching [23]. Because topographic STM images are a convolution

of the geometric and electronic structure of the surface and the tip, a change in the apparent height could be the result of a change in conductance, a change in the physical height of the molecule, or both. When a molecule is in the higher conductance state, referred to as the ON state, it appears as a ~ 3 -Å protrusion above the SAM surface; when in the lower conductance OFF state, it appears as only a slight protrusion (Fig. 6). The presence of the protrusion in the OFF state in the same location and the reversible switching back to the ON state indicates that the molecule is still present in the same defect site. We define “switching” as a molecule’s ability to occupy two or more stable conductance states as detected by STM topography.

Time-lapse series of images were acquired, each for several hours (up to 30) to monitor the temporal behavior of the molecules. Using large scan areas, we monitor multiple molecules and compile statistics on the switching behavior. To obtain this information, each molecule is digitally extracted from each image of the sequence [Fig. 7(C)], and the apparent height of the molecule relative to the SAM is calculated [Fig. 7(B)] [117]. For the molecule highlighted in Fig. 7(A), reversible switching occurred for the first 250 min of acquisition (40 frames). One factor of note on this observation is that no external perturbations were applied to the switching molecules aside from imaging. Because STM uses raster-based image acquisition, the time scale to acquire images is quite slow, on the order of 6 min between images, for this image sequence. It is possible that the molecules could switch multiple times between images, and this bias to our data must be considered. Some information is contained in multiple scan lines, as our resolution is such that we

typically measure each molecule on several consecutive line scans through the course of imaging. Thus, if rapid switching were occurring, it would be observed as topographic changes between lines.

We have observed this type of switching for molecule 1H [23], [73], molecule 1F [23], [73], and oligothiophenes [118]. This shows that the chemical functionality of the OPE molecule may not play a significant role in the stochastic switching observed by STM. Instead, we found that the order of the surrounding matrix plays a dominant role in the switching of the molecules, leading us to conclude that the switching observed here is a result of a change in molecular orientation or position. By controlling the deposition time of the initial host SAM we can control the degree of order and packing on the surface, thus allowing us to control the placement, orientation, and local environment of the inserted single molecules. Although initial monolayer formation occurs rapidly, exchange processes allow the film to restructure and to order further over long periods. By varying deposition times from 5 min to 24 h, we can create host SAMs with less order and higher defect densities or more order and fewer defect densities, respectively.

After a molecule is inserted into a defect site, it is possible that the molecule may not be well constrained. We have developed a vapor phase annealing process to “backfill” the defect sites and further increase SAM order and packing around inserted molecules [53]. Vapor phase annealing is carried out by placing the preformed host/guest monolayer in a sealed vial with a small amount of the molecule to be used for backfilling. The system is then placed in an oven at 80 °C for 2 h. During this time, the vapor phase molecules are introduced to the host/guest monolayer; however, insertion occurs with significantly less exchange than occurs in the solution phase. By vapor phase annealing a decanethiolate SAM with a dodecanethiol vapor, we observed that the inserted dodecanethiol molecules formed domains with a high degree of connectivity, lining the substrate step edges and surrounding substrate vacancies [53]. This indicates that the vapor phase molecules are inserting at the domain boundaries and defect sites in the SAM. When vapor phase annealing is used on a sample with a previously inserted molecule, the chemical nature of the surroundings remains the same, but the conformational freedom of the inserted molecule may be hindered as the newly inserted molecules pack tightly into lattice sites that could have been previously unoccupied by the host matrix [53]. By preparing SAMs of varying packing order and using the vapor phase annealing process to further order the system, we have shown that the switching rate is highly dependent on the conformational freedom of the molecule [23], [73].

In addition to stochastic switching, we have had limited success in controllably switching these molecules [23]. Molecules of 1G can be switched from the ON state to the OFF state using a controlled 4.0-V pulse when the probe tip is located above the molecule. Molecules have been switched OFF when the tip was in tunneling range of the sample and when retracted by 2 nm, suggesting that controlled switching is due to the applied electric field, rather than

direct oxidation state changes. Unfortunately, the higher voltages used for inducing switching tend to degrade image quality, seemingly because of structural changes in the host matrix, the molecule, and/or the tip. Because of the induced structural changes, the controllable switching we observed is likely caused by conformational changes [23]. We have had less success controllably switching a molecule from the OFF to ON state, though we have observed molecules that have been controllably turned OFF stochastically return to the ON state [23].

Several mechanisms have been proposed for the change in conductivity. Seminario and coworkers postulated that switching may arise from the rotation of a phenyl ring relative to the alkyne spacers, creating a discontinuity in the π -orbital overlap and, thus, breaking the conjugation of the system [63], [119]. Others have suggested that similar ring twisting can lead to NDR as a result of a resonant tunneling process where the rotating ring acts as a tunneling barrier [120], [121]. However, theoretical calculations indicate that the rotational barrier for one of the phenyl rings relative to the other two is 0.86 kcal/mol (0.037 eV) for an isolated molecule, low enough for the rings to rotate even at cryogenic temperatures [63], [119], [122]. More recent calculations show that when the oligomer is complexed with undecane (modeling a very tightly packed system) the same rotational barrier increases to 38 kcal/mol (1.6 eV) [123]. While the molecules may not be this tightly packed in our experiments, this model shows that the packing density of the SAM may affect the rotational barrier and, thus, the probability and lifetime of a given conductivity state. In contrast, Di Ventra *et al.* propose that ring rotation plays little role in changing the electronic structure near the HOMO and LUMO, but rather the rotation of the NO₂ substituent on the benzene ring can change the electronic structure and energy of the system [68].

Other proposed conformation-based mechanisms include molecular tilting of the inserted molecule or a change in the orientation of the molecule with respect to the surface and/or the STM tip. This type of molecular motion can result from varying the hybridization of the sulfur atom (sp versus sp^3) [124], [125]. This transition has an energy barrier as low as 2.5 kcal/mol (0.11 eV) [125], allowing the molecule to change orientation at room temperature. Theoretical calculations have shown that the molecular tilt can influence the overlap of the π -conjugated molecular orbitals with the orbitals of the metal electrodes, modulating the conductivity of a molecule by up to two orders of magnitude [72], [126]. If the switching observed by STM is related to a molecular tilt, the molecule must be located in a defect site large enough to allow for reorientation. Finally, as two conductivity states were observed independent of the defect site, this would imply that there are two preferred tilt angles associated with the inserted molecules that are irrespective of the insertion site [73].

Seminario has proposed that the switching observed in nanopores for the molecule 1H was the result of changes in the charge state of the molecule [62], [63]. For some charge states the frontier molecular orbitals become localized, re-

sulting in lower conductivity. Because our previous results were obtained under ambient conditions, we were unable to apply the higher voltage (± 2 V) necessary to induce a charge on a molecule [21]. However, we did vary the bias voltage from -1.4 V to $+1.4$ V (with magnitudes as low as 250 mV), and tunneling currents from 0.1 to 4.0 pA, and found no correlation with switching activity. Experiments now being done in ultrahigh vacuum (UHV) are enabling us to probe larger bias voltage magnitudes where charging may occur.

Finally, initial experiments done in UHV eliminate the possibility that switching results from complexation of the molecule with residuals in the air or in the film or charge transfer with ambient, unidentified species [73]. It is possible that the forces and high electric field exerted by the STM tip during imaging could be the driving force for switching. However, if the tip were responsible for inducing the change in conductance, we would expect to see more molecules switch while being imaged; therefore, we would image only a small part of a molecule before it changed conductance states. We have seen molecules switch while being imaged by the probe tip for only a small fraction of the many hundreds of molecules that we have observed over long periods.

H. Contact Conductive Probe AFM

In addition to the STM, CP-AFM has been used to probe electron transport in metal–molecule systems [Fig. 4(H)]. In CP-AFM, a metal-coated AFM tip is placed in direct contact with the SAM under a controlled load, typically 2 nN [38], [44]–[46]. The tip-SAM contact area is estimated to be about 15 nm^2 , resulting in a junction of about 75 molecules [45]. This technique differs from STM in that it cannot measure the I – V characteristic across single molecules, but has the advantage that interpretation of the I – V curve is in some sense simplified because the probe is in direct and controllable contact with the SAM [44]. Thus, CP-AFM is a good technique to measure electron transport properties such as β and contact resistance of thin films.

The controllable aspect of the contact is the force exerted on the sample by the tip. By applying larger forces, the tip will progress from contact (1 nN), to deformation of the SAM, to contact with the substrate metal (>150 nN) [45]. As the force of the tip on an alkanethiolate SAM is increased, there is an exponential increase in the current [74]. The type of contact between the metallic tip and the SAM determines some of the behavior of the junction. In contrast to the previous force measurement where the metallic tip contacted the methyl group of the SAM [45], Cui *et al.* found that when measuring dithiol SAMs with a Au-coated tip (possibly allowing the formation of a S–Au bond), this junction produced larger currents (higher conductivity) and showed little to no variation with force [74]. For small forces (2 nN) and bias voltages in the range of ± 1.5 V, the current for alkanethiolate SAMs displayed sigmoidal characteristics, similar to that displayed in Fig. 3. Alkanethiolate films also display chain length dependent breakdown voltages as indicated by large increases in current, which resulted in an irreversible change in the SAM. The breakdown process is associated

with a constant field strength (2×10^7 V/cm) rather than a voltage-dependent process [45].




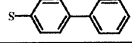
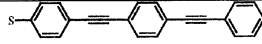
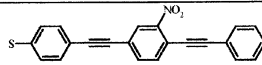
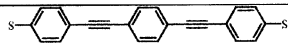
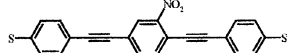
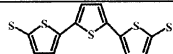
The β values were determined as a function of molecular length for alkanethiols (0.94 \AA^{-1}) and oligophenylene thiolates (0.42 \AA^{-1}) [46] in the low bias voltage regime (± 0.3 V). The significantly lower β value for the oligophenylene molecules indicates a junction through which it is easier to tunnel (higher conductivity) [46]. While the β value yields information on the properties of the molecule, the contact resistance yields information on the conductivity of the metal–molecule interface. By varying the metal used as the substrate and the chemistry of the linking group, the nature of the metal–molecule contact can be investigated. Using Au, Ag, Pd, and Pt surfaces, the contact resistance of S and CN linking groups were measured [38]. It was found that Au–CN–R–Au systems yielded junction resistances about 10% lower than similar Au–S–R–Au junctions. However, varying the metal could influence the contact resistance for metal–thiolate–metal junctions by more than two orders of magnitude [38]. The contact resistance was shown to decrease with increasing metal work function, indicating that “hole transport” is the likely transport mechanism for this system [38].

I. Nanoparticle Coupled CP-AFM

A second CP-AFM approach utilizes an inserted bifunctional molecule to anchor Au nanoparticles to the surface by the formation of a covalent bond, forming a metal–molecule–nanoparticle structure with the potential for addressing single molecules [105], [127], [128] [Fig. 4(I)]. Because the CP-AFM tips used here have an effective area of about 15 nm^2 , any attempt to address a single molecule with an AFM tip in contact mode would result in measuring the molecule of interest and its surrounding host matrix. Using directed assembly, isolated molecules with thiols on each end of the molecule can be inserted into insulating SAMs, leaving the terminal end of the molecule with a thiol exposed. The SAM is then exposed to triphenylphosphine-passivated gold nanoparticles allowing the terminal thiol to serve as an anchor that binds the nanoparticle to the surface, creating a metal–molecule–metal junction that can be probed by CP-AFM. To control the adhesive force between the sample and the CP-AFM tip, the sample is imaged under toluene (or other inert fluids or gasses). The most significant advantage of this technique is the ability to measure single molecules without a tunneling junction. However, one complication is that the nanoparticle may be in contact with more than one molecule. It was found that where more than one molecule was believed to be in contact with the nanoparticle there were quantitative increases in current, i.e., each molecule independently and equally contributed to the observed current [105].

Using this technique, Lindsay and coworkers have measured the conductivity of alkanedithiols on Au. Unlike the previous contact CP-AFM measurements where an increase in the force of the tip exerted on the SAM resulted in an exponential increase in current and lower breakdown voltages [74], when the force was increased over the nanoparticle

Table 2
Experimental Characteristics of Several Molecules and Selected Papers That Address These Properties

molecule	symmetric I-V	asymmetric I-V	other properties
	[40, 41, 43–45, 74, 75, 105, 127, 133]		
	with bandgap [46, 57, 75, 85]		
	[85, 86]		
		[75, 85, 134]	
	[9, 21]	[57, 71]	stochastic conductance switching of isolated molecules observed by STM [23, 73]
		NDR [21, 22, 24, 67, 106]	stochastic conductance switching of isolated molecules observed by STM [23, 73]
	[71, 106, 130]		
		NDR [22, 24, 106, 130]	
	[88]	[88]	

there was little change in the I - V characteristic [105]. This indicates that the interatomic distances within a molecule undergo little change when stressed and that the bond between the molecule and the metal do not change under stress. Similar to the Hg junctions discussed earlier [65], [129], there is also a strong dependence on the presence of a chemical bond at the metal–molecule interface. I - V curves were obtained for monolayers without the dithiolate present such that the nanoparticle was in contact with the terminal methyl group in the monolayer. This resulted in currents several orders of magnitude lower than the dithiolate molecule and voltage dependences dominated by the contact rather than molecular properties [105].

Rawlett *et al.* have employed this method to test dithiol forms of the OPE molecules 1E and 1G [130]. Similar to other techniques, the unfunctionalized molecule 1E displayed characteristics similar to alkanethiols. However, the nitro-functionalized molecule 1G displayed NDR at 1 V and ohmic characteristics at low bias. Unlike the similar experiments of Cui *et al.* [74], [105], these data did not produce integer multiples of resistance. The lack of integer multiples in the calculated resistances implies that only single molecules were bonded to the nanoparticle and that single molecules can produce NDR [130].

V. CONCLUSION AND FUTURE OUTLOOK

While the properties of molecules play a significant role in the behavior of molecular devices, the nature of the metal–molecule junctions can greatly influence the overall

behavior of the device. As seen in Table 2, subtle differences in the molecular configuration or in the metal–molecule junction can change the characteristics of the device. One of the complications with these measurements is the difficulty associated with knowing the chemical nature and order of the contacts that are being measured. As with many analytical techniques, there are advantages and disadvantages to each type of measurement. Ensemble measurements usually provide simple, rapid analyses of the system, while single-molecule techniques tend to yield more information on the local structure, identity, and electronic characteristics of the system, but are usually more difficult to fabricate and to analyze.

While various architectures using the NDR peak and diode logic have been proposed, the physical requirements for the devices must still be established. Berg *et al.* has performed modeling calculations to derive the electronic parameters required for operating a dynamic RAM (DRAM) cell using an NDR molecule [131]. It was determined that some of the key factors for the functionality of a device using an NDR latch in a DRAM cell are the peak-to-valley-current ratio, and more importantly that the valley current be very small. Unfortunately, all of the published data for molecular NDR producing devices does not meet the requirements (especially for a minimal valley current) established by the International Technology Roadmap for Semiconductors for implementation into DRAM devices in 2008 [131]. However, it is expected that by reducing the number of molecules in the device and finding other molecules, the minimal valley currents may be achieved [131].

We have discussed self-assembly and how SAMs can be used to test potential molecular electronic devices. Important factors in molecular electronic device behavior include the electronic characteristic of the molecule, the type of linking group used to bind a molecule to an electrode, the metals used for either of the electrodes, the type of electronic coupling to the surface, and the electronic symmetry of the junction. A number of creative experimental methods have been developed to probe these systems and found a variety of results. Many of the ensemble techniques have shown interesting electronic behavior; however, single-molecule techniques such as STM have shown that the local environment of the molecule can strongly influence the behavior of the molecule.

Eventually, these devices will be well characterized and understood at which point they will need to be implemented into functioning devices. However, just as fabricating devices for characterization has proven difficult, producing a high density of devices that provides fault tolerance, resilience to repeated cycling, and the ability to address few or individual molecules will be quite challenging. Among the many complications in using two-terminal molecular electronic devices is the lack of a gain component (such as a transistor) at the molecular level. The lack of transistors complicates signal restoration, latching, and inverting components. However, two-terminal logic can be implemented using diode-resistor logic [26], [28], and NDR can be used for signal restoration and latching [26], [27].

Incorporating these concepts, Goldstein *et al.* have proposed a reconfigurable architecture system, similar to a field-programmable gate array (FPGA), that employs self-assembled molecular electronic devices to be used for digital logic [26], [27]. In this proposed case, self-assembled crossed wires form junctions where molecular electronic rectifiers can be configured in ON or OFF states and NDR latches are used maintain signal levels [27]. Because the devices use a reconfigurable architecture, it can compensate for faults in fabrication and assembly of the device. These and related ideas may guide the way to the implementation of molecular electronics.

Since the submission of this paper, another review of molecular electronics has been published [132].

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