

Progress with Molecular Electronic Junctions: Meeting Experimental Challenges in Design and Fabrication

By Richard L. McCreery* and Adam Johan Bergren

Molecular electronics seeks to incorporate molecular components as functional elements in electronic devices. There are numerous strategies reported to date for the fabrication, design, and characterization of such devices, but a broadly accepted example showing structure-dependent conductance behavior has not yet emerged. This progress report focuses on experimental methods for making both single-molecule and ensemble molecular junctions, and highlights key results from these efforts. Based on some general objectives of the field, particular experiments are presented to show progress in several important areas, and also to define those areas that still need attention. Some of the variable behavior of ostensibly similar junctions reported in the literature is attributable to differences in the way the junctions are fabricated. These differences are due, in part, to the multitude of methods for supporting the molecular layer on the substrate, including methods that utilize physical adsorption and covalent bonds, and to the numerous strategies for making top contacts. After discussing recent experimental progress in molecular electronics, an assessment of the current state of the field is presented, along with a proposed road map that can be used to assess progress in the future.

1. Introduction

The origin of molecular electronics is generally correlated to the 1974 paper by Aviram and Ratner entitled "Molecular Rectifiers."^[1] Although conducting polymers and rudimentary organic electronics were emerging at that time, the Aviram and Ratner paper generated significant excitement by outlining a theoretical model indicating that a single molecule could exhibit preferential electronic conduction in one direction along its molecular axis. This early theoretical model showed that molecules may possess unique electrical properties that could be exploited in order to accomplish important electronic functions. The subsequent development of self-assembled monolayers (SAMs) and scanning probe microscopies (SPMs) in the 1980's provided the initial

experimental tools for investigating electron transport across molecules. Reports of intriguing electronic behavior began to appear in the late 1990's in studies using single molecules and molecular monolayers. Some early examples which generated significant "press" were negative differential resistance in Au/thiolate/Ti structures,^[2] molecular memory based on rotaxanes,^[3] and a unimolecular rectifier based on the Aviram and Ratner postulate.^[4] The field of molecular electronics underwent very rapid growth following these initial reports. These efforts are and were motivated, in part, by a multitude of advances that might be possible when incorporating molecular components into microelectronic devices. For example, the potentially diverse electronic functions arising from the numerous degrees of freedom inherent in molecular structure may present new, previously unattainable functions; the promise of lower cost compared to crystalline semiconductors is

attractive in manufacturing; and the much smaller size of molecules compared to current microelectronic components may enable heightened capacities and faster performance. Several recent reviews of the active field of molecular electronics are available.^[5–12]

Because several closely related areas underwent rapid parallel growth, it is important to distinguish molecular electronics from other fields, such as organic and/or polymer electronics. Many investigators differentiate molecular electronics from organic electronics by the small size of molecular components, often in reference to the familiar Moore's Law of the semiconductor industry. For example, if a single molecule can indeed perform a useful electronic function (e.g., rectification or memory), then the resulting device density has the potential to be orders of magnitude higher than today's state of the art, extending Moore's Law to the dimensions of a single molecule. Other researchers consider molecular electronics to encompass devices based on molecular monolayers, where charge carriers travel across molecule-scale distances in only one dimension. However, it is useful here to consider molecular electronics in a broader context.

Figure 1 shows a triangular representation of the three primary areas where molecular devices can be distinguished from conventional electronics. Although size (blue corner) is a valuable attribute of a molecular device, function (red corner) and integration (green corner) are considerations for commercially

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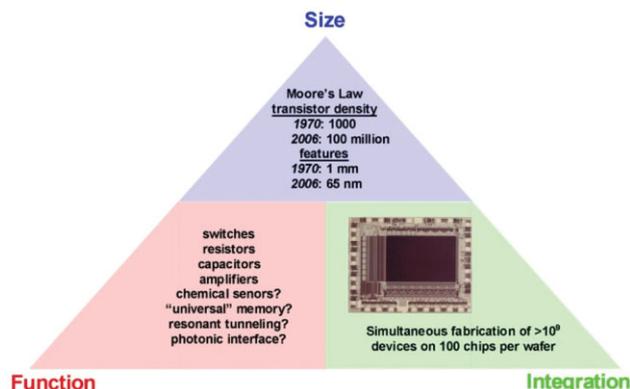
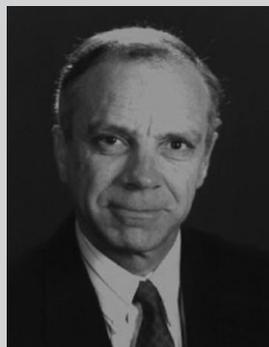


Figure 1. Molecular electronics' "triangle of targets," illustrating three related objectives for the realization of practical molecular electronic devices. In addition to the commonly cited motivation of decreased feature size (top), molecular electronics could have important implications in realizing new functions (bottom left). In order to realize the potential of decreased size, better performance, or new functions, molecular devices must be integrated into functional packages that can be fabricated in a massively parallel fashion (bottom right).

interesting devices. As stated above, the size of a molecular electronic device can potentially be as small as a single molecule. However, the power of modern fabrication techniques lies not only in the ability to make devices with small features (<100 nm), but also in the remarkable facility to make $>10^9$ devices simultaneously on possibly hundreds of chips per wafer. From an economic perspective, massively parallel fabrication is at least as important as feature size. The more general concept of integrating components into practical structures is prominent in industry analyses, such as the International Technology Roadmap for Semiconductors (ITRS, <http://www.itrs.net/>, last accessed May, 2009). The third corner (function, red) is a particularly promising sector that may distinguish molecular devices from conventional electronics. The great diversity of molecular structures, with their associated energy levels and possible interactions with chemical or biological agents, may permit tuning electronic properties through structural effects on orbital energies, modification of energy gaps over a wide range, and incorporation of sensors into microelectronic circuits.

It is important to consider all aspects of the triangle (Fig. 1) when evaluating molecular electronic devices for commercial applications. For example, it is our opinion that the greatest promise for molecular electronics in the foreseeable future is augmentation of the already sophisticated microelectronics industry by adding molecular components that enhance function (red corner). However, this can only be facilitated by maintaining massively parallel fabrication (green corner) and by continuing increases in device density (blue corner). In the near term, it is much more likely that molecular electronic components will be integrated with silicon-based addressing and support electronics,^[13] rather than replacing silicon, with its excellently established industrial and scientific base.

This progress report focuses primarily on experimental results for the molecular junction, a basic building block of molecular electronics that consists of one or more molecules suspended



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between two contacts, usually metals or metallic conductors. Figure 2 shows several examples of molecular junctions taken from the literature of the past decade. Section 2, "Targets and Objectives," will introduce some motivations and goals that drive the field of molecular electronics. As is apparent in Figure 2, junctions differ greatly in size and construction; this is discussed in Section 3, "Experimental Paradigms." Section 4 will cover the progress that has been made in working toward the goals outlined in Section 2. Finally, a summary of where the field stands will be followed by a proposed "Molecular Junction Road Map." This progress report is not intended to be a comprehensive review of molecular junctions, but will cite a variety of experimental investigations and reviews as illustrations.

A particularly strong attribute of research in molecular electronics is the highly interdisciplinary nature that results from the diverse chemical, physical, and electronic phenomena involved. Contributions from physicists, chemists, materials scientists and engineers, electrical engineers, etc. are all invaluable to progress. For example, from the perspective of a physicist, a molecular junction might be considered a parallel plate capacitor with an unusual dielectric layer, while a chemist may focus on the structure of the molecule between the plates. Depending on the structure and thickness of the "dielectric," the device may have a variety of current–voltage (i – V) signatures, and may operate under large electric fields ($>10^6$ V cm⁻¹). A molecular junction may also be considered an organic electronic

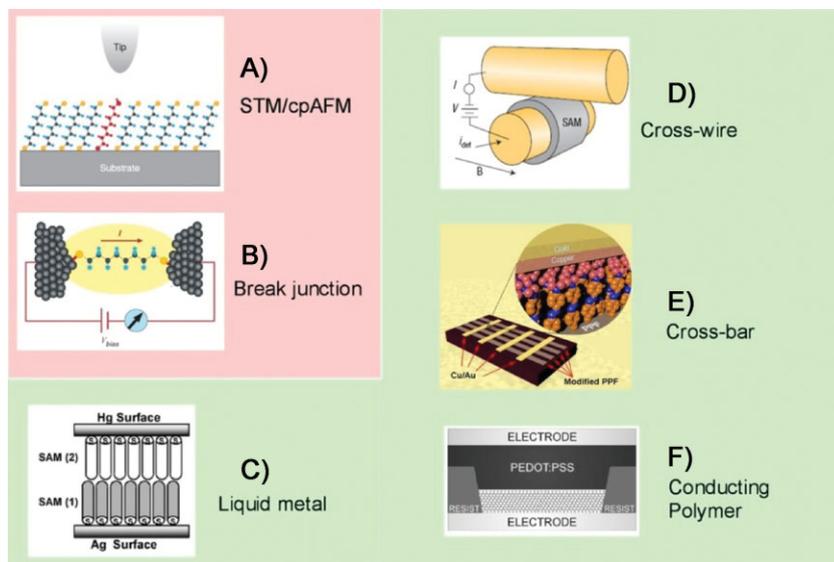


Figure 2. Examples of single-molecule (red) and ensemble (green) molecular junctions. A) Single molecule interrogated using an scanning tunneling microscopy (STM) or conducting probe atomic force microscopy (cpAFM) tip. Often, the molecule of interest is dispersed in a less conducting molecular layer; red molecule is “active.” B) Mechanical break junction formed by withdrawal of a sharp metal tip (e.g., STM tip) from a metallic surface. A molecule from solution fills the gap. C) Example of a liquid–metal junction formed by suspending an Hg drop over a metal surface (e.g., Ag) in a solution of thiol molecules, which adsorb to form monolayers at both surfaces. Alternatively, a dithiol can be used to form a junction containing a single molecular layer. D) Cross-wire junction formed at the intersection of two metallic wires, one of which is coated with a monolayer. E) Planar cross-bar junction made by evaporating a metal onto a molecular layer covalently bonded to a carbon substrate. F) A junction made using a conducting polymer as the top contact. Reproduced with permission: (A) and (B) from [11], copyright 2007 Annual Reviews; (C) from [68], copyright 2004 Elsevier; (D) from [113], copyright 2005 Nature Publishing Group; (E) from [81] and (F) from [64], copyright 2008, Institute of Physics.

device in which the critical dimension between the “contacts” is short enough for electron tunneling to occur, or for electron transport to occur without the thermally activated “hopping” between sites, which normally accompanies conduction in thicker organic films. Alternatively, an electrochemist might view a molecular junction as a very thin electrochemical cell, possibly with redox active components or even mobile ions. Changes in the oxidation state of molecules within junctions can accompany electron conduction and also result in the bistability important to memory devices.^[10,14,15] As described in later sections, the concepts from these various disciplines are important for understanding the behavior and functions of molecular junctions, all of which are needed to meet key objectives in the field.

2. Targets and Objectives

In order to establish how research in molecular electronics has progressed to date, it is useful to describe the initial goals of the field. A general objective was establishing the behavior of molecular components in electronic circuits and the eventual integration of molecules into conventional semiconductor microelectronic devices. A National Science Foundation (NSF) workshop entitled “Building Electronic Function into Nanoscale

Molecular Architectures” in June, 2007^[16] defined six Research Targets, some of which are paraphrased here. First: “Create accessible, easily transportable, standard molecule-based measurement platforms with detailed calibration standards. . .” Although one might consider reproducibility to lie at the base of the “scientific food chain,” this goal has proven elusive in molecular electronics. Second: “Develop measurement techniques and platforms to probe the details of molecular structure/function for ensembles and single molecules under multiple stimuli.” This objective is often referred to as a “molecular signature” of an electronic device, meaning that at least part of the electronic behavior of a junction is controlled by the structure of the molecule. This goal also provides a basis for measuring the potential to obtain large changes in the electronic signature of the device from small changes in molecular structure. Third: “Develop time-resolved optical spectroscopies and imaging schemes to probe molecular structure in operating devices.” One could argue that a major impediment to developing standard and reproducible molecular electronic devices is the difficulty of the structural characterization of a single molecule or a molecular monolayer, often buried between two conducting contacts, which may be opaque to ultraviolet, visible, and infrared light.^[17] Finally, the NSF workshop targets finish with the biggest challenge: “Demonstrate technologically innovative, commercially viable mole-

cular-based electronic function.” These goals comprise an excellent framework for evaluating the progress of molecular electronics in the context of the molecular junction, and might be stated briefly as: “Make a robust molecular junction with reproducible electronic behavior; determine the relationship between molecular structure and current–voltage characteristics; exploit new functions enabled by molecular components by integrating with commercially viable microelectronics.” A tall order to be sure, but one that provides some milestones for assessing progress to date.

3. Experimental Paradigms

As described in a previous review,^[18] molecular junctions are readily divided into two types: single molecule and ensemble. They may be further categorized by the method of making the electrical contact between the conductors and molecule(s) since the conductor–molecule bonds have major effects on the electronic properties and stability of the finished junction. Figure 2 shows examples of each type, with single-molecule devices in the red area, and ensemble junctions in the green section. Significant progress has occurred in recent years with various combinations of junction configuration and binding mode, and no one approach has emerged as being dominant. A

brief review of several paradigms is useful for evaluating progress and predicting future trends.

The single-molecule approach was enabled by the development of scanning probe microscopy (SPM) in the 1980's. This collection of techniques made it possible to image individual molecules on surfaces, or rather the electronic structure of the molecules, and further characterize molecular behavior using scanning tunneling spectroscopy (STS).^[19–33] The experiment is depicted generally in Figure 2A, which shows an alkanethiolate monolayer adsorbed at a solid support (e.g., Au) and interrogated with a scanning tunneling microscopy (STM) or conducting probe atomic force microscopy (AFM) tip. The red molecule in Figure 2A is active, and in practice can be a single molecule or a small ensemble of molecules. One of the earliest papers on this approach to molecular electronics appeared in 1996,^[28] for the case of isolated phenylethynyl thiolate molecules diluted in a less conducting dodecanethiolate monolayer. An apparent increase in height when the STM tip was over the conjugated thiolate was correlated with the greater electronic conductance of the phenylethynyl moieties. Later reports noted that the conductance was stochastic, implying a “conductance switching” mechanism.^[27,34] In addition to SPM studies of thioliates on Au,^[35] elegant experiments have been reported using SPM to observe single molecules suspended between two nanoscale contacts in “break junctions,” as depicted in Figure 2B.^[22,25,32,33,36] These junctions are formed when a molecule in solution bridges a newly formed gap in a metal conductor^[2,37–43] or on molecules bonded to silicon.^[20,23,24,44] SPM applied to single-molecule devices at low temperature have enabled visualization of molecular orbitals and observation of molecular charging.^[25,45–48]

Some physical insights and concepts derived from specific single-molecule experiments will be discussed below, but some general comments about the paradigm are appropriate. First, the ability to image molecules and even molecular orbitals provides atomic level detail of the specific bonding and conformation of the molecular junction. Insight into how orbitals are affected by bonding to contacts and the degree of electronic coupling between contact and molecule are available in some cases.^[5,23,25] Second, isolation of a single molecule on a surface or in a break junction should eliminate possible electronic coupling between molecules, which is likely to broaden the orbital energies of the molecules. At least in principle, the path of the charge carriers is known precisely, and the influence of molecular structure on conduction can be probed directly. Third, the use of SPM or nanogap techniques to make single-molecule junctions avoids metal vapor deposition on molecules, with the attendant risk of thermal damage to the molecule.^[6,49] Fourth, a single molecule may be surrounded by a solution or gas to investigate interactions of the molecule with its environment. Of particular note is a single molecule in an electrolyte solution, which permits adjustment of the electrochemical potential.^[12,50–52] Most molecular junctions are solid state and lack the well-defined reference to a potential provided by a reference electrode in solution. Fifth, single-molecule junctions can be probed with inelastic electron tunneling spectroscopy (IETS), which simultaneously provides a current–voltage curve and a vibrational spectrum of the molecule.^[53] Although IETS is most useful at liquid helium temperatures, it is the only method available providing both structural and electronic information about a

single-molecule device, for the particular conformation and contact geometry of the molecular junction present at low temperature. Sixth, theoretical modeling of a single molecule and its associated contacts is more tractable than that of large collections of possibly interacting molecules.^[54,55] As has been pointed out for single-molecule studies using repetitive break junctions, theory and experiment are in reasonable agreement for the case of a single alkane and conjugated molecules between metallic contacts.^[56] The analogous first-principles theory for a large number of molecules with a variety of contact geometries in an ensemble junction would be difficult indeed.

Single-molecule experiments have provided important insights into how electron transport occurs within molecules and their contacts. However, there are some limitations imposed by the nature of the paradigm. It is generally recognized that the details of contact geometry and conformation are critical to the electronic behavior of the junction, and these may vary significantly for each molecule studied.^[55] Except for the special cases of IETS and tip-enhanced Raman, single-molecule devices are not amenable to spectroscopic characterization of working junctions, so it is difficult to determine the precise conformation and contact geometry. In addition, thermal fluctuations of molecular conformation can create stochastic variations in electron transport,^[57] resulting in noise in the i - V curves, or even in apparent conductance switching, noted above. Finally, it is not clear how single-molecule junctions might be integrated with commercially viable microelectronics. Even if a useful single-molecule junction could be made reliably, there would remain the problem of “wiring up” and addressing a large number of such devices into a commercially viable product. Although studies of single-molecule devices have yielded important fundamental information, many of the goals outlined in Section 2 have not been satisfied using single-molecular experiments. Perhaps most disturbing is the continued large variations of conductance measured for ostensibly the same molecule. This irreproducible response must be understood and controlled if single-molecule devices are to meet the goal of providing a reliable junction design.

The main alternative to the single-molecule paradigm is the ensemble approach, in which $\sim 10^3$ to 10^{12} molecules are aligned in parallel between two conducting contacts. Several common ensemble devices are shown in the green area of Figure 2. Some of the earliest molecular junctions made with Langmuir–Blodgett (L–B) and SAM chemistry were composed of ensembles of $>10^3$ molecules assembled in parallel between two conductors.^[3,14,58] Ensemble junctions may be nanopores with diameters of ~ 30 nm,^[59] molecules bridging nanowires with diameters of 40–400 nm,^[60,61] lithographically fabricated structures with dimensions of a few micrometers up to several hundred micrometers,^[10,62–67] and molecular layers between a mercury drop and a planar contact or two mercury drops (Fig. 2C).^[68–73] For typical monolayer densities of 5×10^{-10} mol cm⁻², the range of areas reported for ensemble junctions corresponds to ~ 2000 molecules for a 30 nm diameter nanopore to $>10^{12}$ molecules for a 1 mm diameter Hg drop.

While the number of molecules certainly increases the complexity of the junction compared to a single-molecule device, the ensemble approach also brings certain advantages. First, ensemble junctions are often large enough to probe with optical

spectroscopy, and in some cases, even while a bias is applied and the junction is electronically active.^[67,74–78] Raman, Fourier transform IR (FTIR), and UV–Vis absorption spectroscopy cannot only help to confirm junction structure after fabrication, but in some cases can be used to monitor bias-induced structural changes that may reflect a fundamental aspect of electronic function. Second, the observed electronic behavior represents an average over many molecules, with presumably several different conformations and contact geometries. Until the advent of SPM, virtually all chemical experiments involved large ensembles of molecules, with 1 ng of a typical organic compound corresponding to $\sim 10^{12}$ molecules. It was, and remains, difficult to monitor individual molecules, but the measured properties of an ensemble are reliable, provided a statistically significant number of molecules is monitored. Third, lithographically fabricated molecular junctions are readily amenable to integration with conventional microelectronics.^[13,79] If a single ensemble junction with a useful electronic function can be made reliably with high yield, then adding a large number of such junctions to an existing complementary-metal-oxide-semiconductor (CMOS) circuit is feasible without major technological innovations. An important recent demonstration of massively parallel fabrication of ensemble molecular junctions reported preparation of 20 000 alkane-based junctions with 5 μm diameter on a 150 mm wafer with high yield.^[80] Two hundred such junctions connected in series had the expected series resistance extrapolated from the resistance of a single junction, with no observable defective junctions.

One could reasonably argue that the ensemble molecular junction is merely an example of the broad area of organic electronics, and not conceptually distinguishable from conducting polymer devices, organic light-emitting diodes (OLED), and organic thin-film transistors (OTFT). However, ensemble molecular junctions have at least one dimension in the nanometer scale, resulting in fundamentally different electron transport behavior. Transport in organic electronic devices is almost exclusively by “hopping,” an activated charge exchange that results in relatively low carrier mobility. On the other hand, a molecular junction is often thin enough to permit tunneling, and temperature-independent conduction incompatible with hopping has been reported.^[71,81,82] A second important distinction between molecular junctions and organic electronics that arises from the nanometer scale dimensions of the molecular layers is that very high electric fields, often above 10^6 V cm^{-1} , can result in unusual effects, such as field emission at low applied bias. Finally, the small dimension of a molecular layer across which charge flows can lead to anisotropy, especially in highly ordered materials. Thus, the molecules in an ensemble molecular junction usually have a well-defined orientation with respect to the contacts, unlike most organic electronic devices. As will be discussed below for both mesoscale and ensemble molecular junctions, the differences between organic electronic devices, with generally much thicker molecular layers, distinguishes their behavior from molecular junctions in many important ways.

In comparison to single-molecule paradigms, the ensemble approach has the added problems associated with possible defects

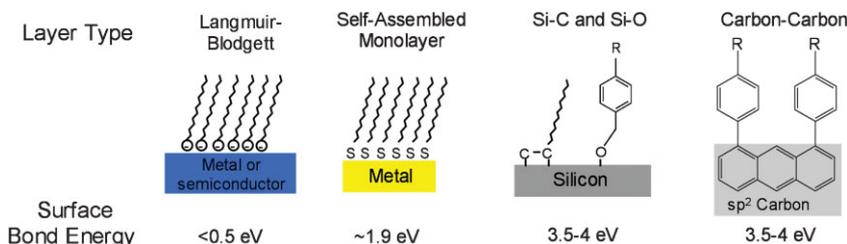


Figure 3. Examples of surface attachment schemes. The method used to anchor the molecular layer to the substrate largely determines the stability of the layer, which is important when considering the method for making the top contact in fabricating the molecular junction.

and with interactions between molecules. Metal deposition of the top contact onto a molecular layer composed of at least thousands of molecules has proven difficult, due to penetration of the metal through the molecular layer to yield metal filaments and short circuits.^[6,49] Even well-ordered self-assembled monolayers have domains of finite size, typically less than 1 μm , such that metal penetration at grain boundaries or other defects is likely for macroscale junctions. A densely packed monolayer of molecules may have substantial intermolecular interactions, possibly resulting in significant changes to the energies and shapes of orbitals involved in conduction. Thus, it is not at all clear that an ensemble behaves electronically like individual molecules in parallel, and the issue of scaling remains an open question. It is not surprising that both single-molecule and ensemble approaches are valuable to understanding conduction in molecules, and it is likely they both will continue to be useful in the future in order to determine the importance of issues such as molecular conformation and intermolecular interactions in determining the electronic signature of a particular device. However, it is important to recognize the advantages and pitfalls of each approach when evaluating and comparing results.

Several methods for bonding molecules to conducting substrates used in both single-molecule and ensemble junctions are shown in Figure 3. The method for bonding molecule(s) to conducting contacts is a critical aspect of the experimental paradigm for at least two distinct reasons. First, the nature of the contact–molecule bond determines the degree of electronic coupling between the molecule and conductor(s). This interaction is fundamental in determining the importance of injection barriers in the overall electronic properties of the device. Moreover, the broadening of molecular orbitals through mixing with metallic orbitals in the contact depends on the molecule–contact bonding. Ultimately, the transport of electrons from the contact into the molecule can be controlled in large part by the type of bond formed between them. If molecular electronics is ever to be realized in practical devices, the electronic coupling between the contacts and the molecules must be understood or at least controlled reproducibly. If, for example, there is a large injection barrier between the contact and molecule, the overall electronic behavior may be interface-dominated, and lead to frustrated attempts to modify device characteristics by changes in molecular structure. Although the nature and strength of electronic coupling are actively under investigation, there is general agreement that the commonly used metal/sulfur, Langmuir–Blodgett, and covalent metal–carbon or silicon–carbon bonds should differ significantly in this respect. As an illustrative

example, Figure 3 lists the strengths of several surface bonds for different molecular layers. The second important aspect of contact–molecule bonding is more practical, dealing with device fabrication and stability. Metal/thiolate SAMs and metal/L–B structures have been the preferred approach for making molecular junctions largely because they result in well-ordered molecular layers, and these monolayers have been thoroughly characterized with spectroscopy, SPM, etc. The ordering results from "assembling" into a low energy state, which is enabled by the molecular motion permitted by surface diffusion and/or forming and breaking the metal/sulfur bond in SAMs or on the surface of water in L–B films. However, a requirement for ordering is a relatively weak metal–thiolate or electrostatic bond which allows surface diffusion to occur, with bond strengths of ~ 1.9 eV for Au–thiolate and < 0.5 eV for the various interactions that anchor L–B films (i.e., electrostatic, van der Waals, etc.). The less commonly studied silicon–carbon^[44,66,67,83,84] and carbon–carbon^[10,85] binding modes have the attraction of much stronger bonds (3–4 eV), but as a consequence they are generally less ordered. Once the surface bond is formed, usually by a radical or photochemical route, the molecules cannot move, and therefore cannot assemble into a low energy, ordered arrangement. There are a few examples of short-range ordering of molecules on single-crystal silicon,^[21,44,86–88] but generally for < 100 molecules in ultrahigh vacuum (UHV). For the case of C–C surface bonds, bonded layers have been shown to be stable on sp^2 hybridized graphitic carbon to > 500 °C in UHV.^[10,89] For the majority of techniques for bonding molecules to carbon and silicon surfaces, there is a trade-off between order and stability, with the most thermally stable structures being the least ordered. It may transpire that a strong surface bond is a requirement for practical devices, since current microelectronic packaging with polyimide coatings requires process temperatures of ~ 400 °C.^[13] For this reason, an irreversible covalent attachment scheme seems the most likely candidate for realizing reproducible ensemble junctions that are capable of being integrated into commercial technologies. Furthermore, covalent bonds which produce strong electronic coupling between contacts and molecules are likely more advantageous for useful devices.

4. Experimental Progress with Molecular Junctions

4.1. Single-Molecule Junctions

The substantial recent progress in understanding electronic conduction through single organic molecules is apparent from several excellent review articles written in 2003,^[90] 2006,^[91] 2007,^[56] and 2008.^[5] In the earliest of these reviews, Salomon et al. point out that the currents observed through a given molecule (e.g., a C_{14} alkane with a 0.2 V bias) reported by several laboratories varied across four orders of magnitude. Some of the disparities can be attributed to the use of different contact materials and experimental arrangements, as

well as the small number of molecules examined in many cases using demanding conditions. A very significant step toward narrowing this unacceptable experimental variation was made possible starting in 2003 with a repetitive break junction method which generated a histogram of the conductivity observed for thousands of Au–molecule–Au junctions formed in a solution of alkanethiol or pyridine molecules.^[41,92–94] In addition to providing a statistically significant data set, the method also generated a variety of contact geometries, some of which could be resolved in the histograms. The Lindsay and Ratner review in 2007^[56] compiled single-molecule conductance results primarily using this technique, and concluded that not only were the experimental results fairly consistent for a series of dithiol molecules, but also that the observations agreed with theoretical predictions based on nonequilibrium Green's function calculations to within an order of magnitude in most cases.

A clear molecular signature for conductance was reported for the case of a photochromic molecule, which could be switched between a more and less conjugated configuration by exposure to light.^[95] The two forms had an observed conductance ratio of 131, and the theoretically predicted value was 178. Not only was there a large difference in conductance with a relatively small change in molecular structure, but the agreement with theory was also very good. Venkataraman et al.^[96] used amine linkers with the break junction technique to observe a strong dependence of the conductance of diaminobiphenyl derivatives with substituents which forced the phenyl rings to be nonplanar. Figure 4 shows the strong effect of conjugation on the observed conductance, as well as a linear dependence on the square of the cosine of the dihedral angle between phenyl rings. These observations agreed well with theory, and a subsequent theoretical treatment pointed out significant differences between the thiolate and amine linkers.^[97] This study represents significant progress toward understanding fundamental aspects of molecular conduction since it meets the initial goals outlined in Section 2 of obtaining a molecular signature. However, it also illustrates the potential problems in obtaining a reproducible response in a manufactured single-molecule device. Since conductance is so sensitive to molecular conformation, a method to fabricate single molecules in a "locked-in" configuration is needed in order to ensure conductance stability over any length of time. This may hinder the

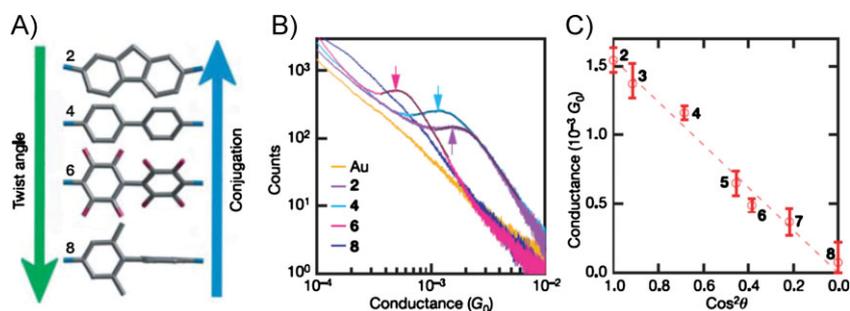


Figure 4. A) Geometric models of biphenyl derivatives showing the correlation between the twist angle between the phenyl rings and electronic conjugation. B) Conductance histograms for molecular junctions containing each of the molecules shown in (A) and for a control experiment with no molecules (yellow line). C) Plot of the conductance histogram peaks for several molecules as a function of $\cos^2\theta$, where θ is the phenyl–phenyl ring twist angle. Reproduced with permission from [96]. Copyright 2006 Nature Publishing Group.

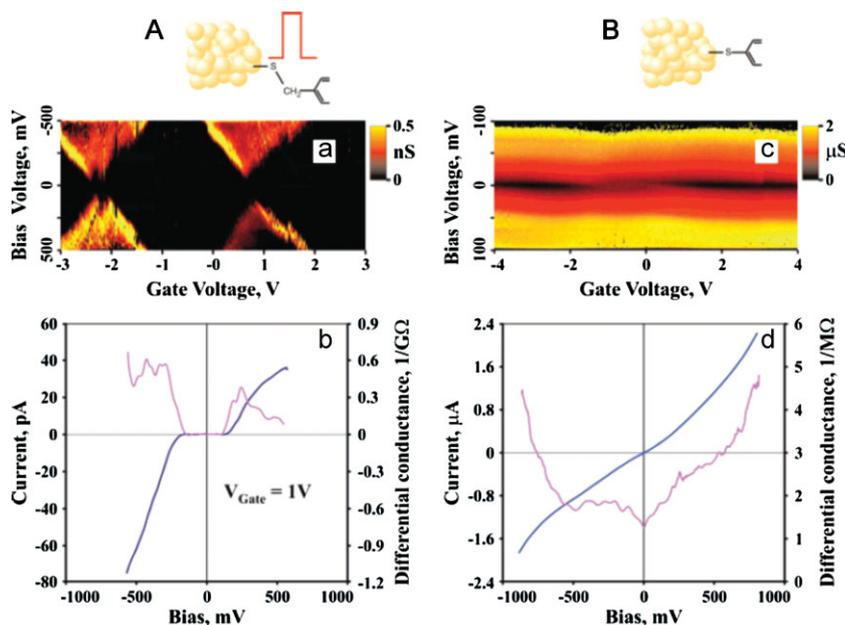


Figure 5. Comparison of the transport characteristics for electronic junctions made using two structurally distinct molecules, **A** and **B**. a) Differential conductance (color scale) as a function of gate and bias voltages and b) i - V (blue) and di/dV (magenta) curves for a device containing molecule **A**. The corresponding plots for a device containing molecule **B** are shown in (c) and (d). Reproduced with permission from [33]. Copyright 2008 American Chemical Society.

development and operation of independent single-molecule circuit elements, limiting the device density to far lower values than the theoretical limit for single-molecule components.

While the repetitive break junction paradigm yields statistical support for the mean conductance values observed, some elegant results have been reported by studying a few single-molecule devices in detail. As noted in general terms earlier, such experiments are subject to sampling error, but they can nevertheless illustrate fascinating phenomena when the single-molecule device can be adequately characterized. Figure 5 illustrates the transport characteristics for three terminal devices made by bonding a dithiol molecule between two gold contacts supported on a thin oxide layer over aluminum, which serves as the gate electrode.^[33,36,98,99] Of particular note in this case is the change induced by the insertion of a methylene group between the conjugated molecule and the gold contacts, which results in a stronger barrier for tunneling. The conjugated molecules lacking the CH_2 group are strongly coupled to the contacts, resulting in a linear i - V curve at low voltage (Fig. 5d). However, the presence of the methylene group drastically decreases conductance (Fig. 5b), and even changes the transport mechanism.^[33] In a different STM investigation, it was demonstrated using a three-terminal single-molecule device that the electric field from a charged surface atom could modulate the conductance of nearby molecules bonded to a silicon surface.^[23] Unique behavior, such as negative differential resistance, has been reported for single molecules on silicon,^[87,100] consistent with a theoretical model based on alignment of the molecular orbital energies with those of the semiconductor.^[101] In addition to a strong Si-C bond in many of the single-molecule experiments on Si, the interactions of the molecular energy levels with the semiconductor bands in Si

can be exploited to achieve useful electronic effects.^[19,24] Again, these studies illustrate important aspects of molecular conduction, but they also show that progress toward reproducible and stable single-molecule devices has many obstacles to overcome based on the high sensitivity of conductance to the details of molecular geometry, contact methods, and the surrounding environment.

An important parameter in both single-molecule and ensemble junctions is β , which describes the attenuation of current through the junction as a function of the distance between the contacts:

$$J = Be^{-\beta d} \quad (1)$$

where J is current density, B is a constant, and d is the contact-contact separation distance. Generally, the length of the molecule is used to approximate d since the space between the contacts contains the molecule of interest. Although changes in molecular length with added methylene groups are predictable, the absolute value of d may be affected by contact geometry and composition. Extensive investigations of electron transport through alkane

monolayers in electrochemical experiments has resulted in a consensus that $\beta = 1.0$ per CH_2 group (0.8 \AA^{-1}), meaning that the current decreases by a factor of e^{-1} for each additional CH_2 group.^[102] As noted in past reviews^[18,56,90] and recent reports,^[103] single-molecule junctions containing alkane molecules of increasing length also yield β values in a range of ~ 0.8 to 1.0 per CH_2 group ($1\text{--}1.2 \text{ \AA}^{-1}$), although good statistical support for this finding was reported relatively recently.^[56,93] An advantage of comparing β values across experimental platforms is that β does not, in principle, depend on the number of molecules or the junction area, so direct correlations of single-molecule and ensemble paradigms can be made. Theoretical support for a $\beta \approx 1 \text{ \AA}^{-1}$ for alkanes has been somewhat elusive, although as noted in the Lindsay and Ratner review,^[56] the nonequilibrium Green's function approach has resulted in good agreement between theory and experiment for single molecules with a range of lengths.

Measurements of the conductance of single *conjugated* molecules result in much lower values of β , in the range of $0.04\text{--}0.3 \text{ \AA}^{-1}$. An example is shown in Figure 6 for porphyrin centers connected to a thiol-containing aromatic group via ethynyl linkages.^[104] The plot of $\ln(\text{conductivity})$ versus the S...S spacing yields a slope of 0.04 \AA^{-1} , implying that electron transport can occur over significant distances through these molecules. Additional examples include carotenoid polyenes^[105] ($\beta = 0.22 \text{ \AA}^{-1}$), oligothiophenes^[106] (0.1 \AA^{-1}), phenylene ethynylene^[107] (0.21 \AA^{-1}), and oligophenyleneimines^[82] (0.3 \AA^{-1}). Such low values of β are important for both fundamental and practical reasons, since they not only indicate a possibly quite different mode for electron transport compared to alkanes, but because they also imply that

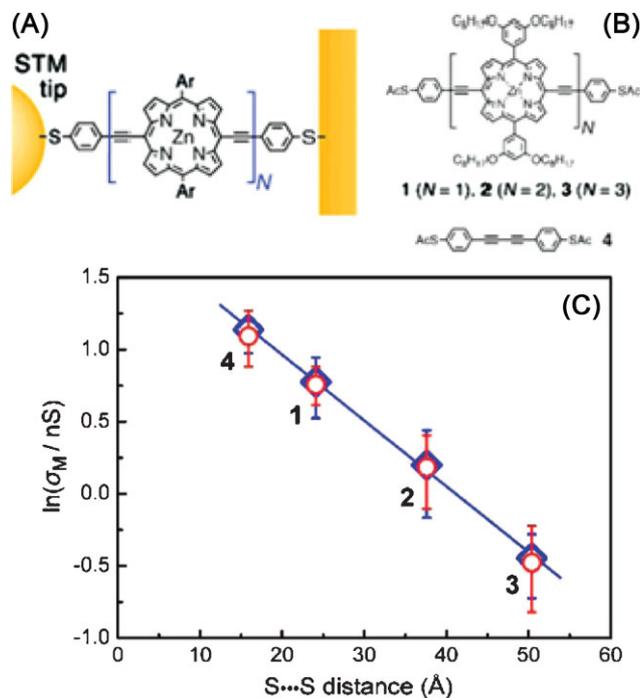


Figure 6. A) Experimental schematic for measuring the conductance of single molecules with porphyrin moieties linked to gold electrodes through an aromatic thiolate linkage. B) The structures used in the study consisted of an increasing number of porphyrin units (1–3), and a reference molecule that does not have a porphyrin structure (4). C) Conductance at 0.6 V as a function of molecular length for 1–4. Reproduced with permission from [104]. Copyright 2008 American Chemical Society.

electron transport across many molecules may occur. As noted by recent authors,^[104,106] a low β is required for molecular “circuits” in which the active molecular device is large relative to typical tunneling distances. Observed values of β significantly below 1.0 \AA^{-1} present some theoretical difficulty, since such values are not expected for classical tunneling. The β for alkanes is considered consistent with coherent tunneling coupled to superexchange, with the lower attenuation factor in an alkane compared to a vacuum attributed to the presence of molecular orbitals with the molecule present. β values less than $0.2\text{--}0.3 \text{ \AA}^{-1}$ are not consistent with coherent tunneling, even for conjugated

molecules, and are generally considered an indication of “hopping” mechanisms, including redox exchange.^[82,108,109] For comparative purposes, Table 1 presents a selection of results for experimental measurements of β using a variety of platforms and methods.

4.2. Progress with Mesoscale Molecular Junctions

Before considering recent ensemble junctions with lateral dimensions in the range of $1\text{--}500 \mu\text{m}$, it is useful to describe some mesoscale paradigms which bridge the gap between single-molecule and ensemble devices. These include conducting probe AFM (cpAFM) of molecular monolayers on flat surfaces and a crossed-wire junction formed when molecules bridge a gap between two cylindrical metal fibers, as illustrated in Figure 2D. Recent reports^[82,110–112] using these paradigms are informative about conduction mechanisms in both single-molecule and ensemble junctions, and will be used here as illustrations of mesoscale devices.

The crossed-wire experiment shown in Figure 2D uses the magnetic Lorentz force to tune the gap between two cylindrical gold wires in order to contact dithiol molecules suspended between the wires.^[110,111,113,114] A comparison of $i\text{--}V$ curves using the crossed-wire geometry were compared to those from STM using the same molecules adsorbed on a flat surface.^[114] Figure 7 shows that the $i\text{--}V$ curves from the two paradigms are in qualitative agreement. The number of conducting molecules in the crossed-wire junctions is uncertain; however, multiplying the original STM current data by 1000 brings the crossed-wire and STM data into quantitative agreement.^[114] This observation implies that a set of 1000 molecules conducting in parallel act as a linear combination of the conductance from each molecule, and also that lateral interactions may not be important in conduction. However these conclusions are tentative given the uncertainty about the actual number of molecules involved in the crossed-wire experiment.

Crossed-wire junctions have also been compared to cpAFM devices, with interesting results.^[110,111] Because both cpAFM and crossed-wire geometries lead to uncertainty in the number of molecules involved in transport, comparisons were made using experimental observations that are independent of area (e.g., temperature effects and curve shape). The inset in Figure 8 shows

Table 1. Comparison of β for a variety of molecules using different platforms.

Molecule type	Method	System	β [\AA^{-1}]	Reference
Alkane	Electrochemistry [a]	Au/alkanethiolate	0.8	[102]
Alkane	Single-molecule junction	Au/alkanedithiol/Au	0.84	[93]
Alkane	Ensemble junction	Au/alkandithiol/PEDOT:PSS [c]	0.57–0.66 [b]	[62]
Alkane	Ensemble junction	Ag/alkanethiolate/eGaln [d]	0.43	[139]
Aromatic	Electrochemistry [a]	Carbon/phenylene	0.22	[178]
Phenylene ethynylene	Electrochemistry [a]	Au/thiolate	0.33	[179]
Oligothiophene (OTP)	STM Break	Au/OTP/Au	0.1	[106]
Carotenoid polyenes (CP)	STM Break	Au/CP/Au	0.22	[105]
Phenylene ethynylene (PE)	cpAFM	Au/PE/Au	0.21	[107]
Oligophenyleneimines (OPI)	cpAFM	Au/OPI/Au	0.3	[82]

[a] Charge transport through a monolayer to a redox center in electrolyte solution. [b] Bias dependent. [c] PEDOT:PSS = polyethylenedioxythiophene/polystyrene sulfonate. [d] eGaln = eutectic Ga/In.

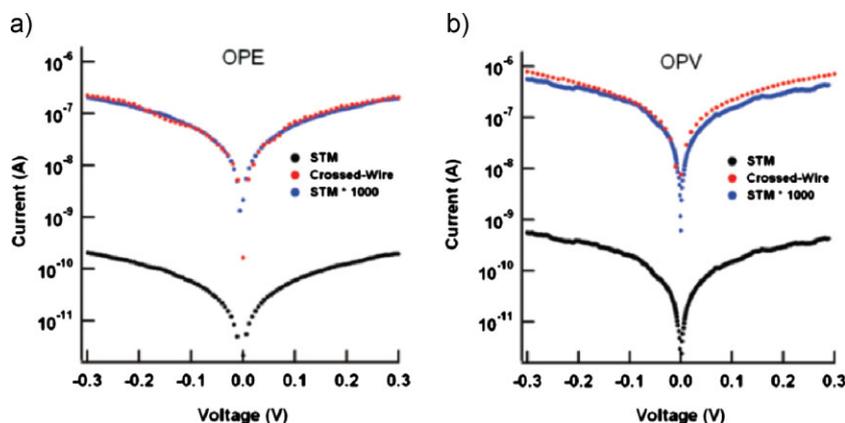


Figure 7. Comparison of i - V curves for crossed-wire and STM-based junctions for two different molecules, a) oligophenylene-ethynylendithiol (OPE) and b) oligophenylene-vinylendithiol (OPV). The black and red curves are the original data from STM and crossed-wire junctions, respectively. The blue curve shows that when the current from the STM experiment is multiplied by 1000, both data sets match closely. Reproduced with permission from [114]. Copyright 2004 American Chemical Society.

a current-voltage curve representing the average of 100 cpAFM junctions, while the main plot is appropriate for testing field emission (also known as Fowler-Nordheim tunneling).^[111] As indicated in the upper right portion of Figure 8, low bias should result in coherent tunneling, yielding a linear increase in current and corresponding to the Simmons equation for a rectangular tunneling barrier. As the bias increases in Figure 8, a transition occurs to the case where the barrier becomes triangular, and field emission occurs. The vertical dashed line indicates the transition voltage, V_{trans} , where the mechanism changes from tunneling to field emission. As such, V_{trans} is conceptually a rough estimate of the tunneling barrier height. V_{trans} determined from both the crossed-wire and cpAFM measurements agreed well for a series of molecules, and is independent of uncertainties in junction area. Subsequent investigation^[115] showed that V_{trans} is molecule specific; i.e., it correlates with molecular structure, providing useful insights into electron transport mechanisms. As will be

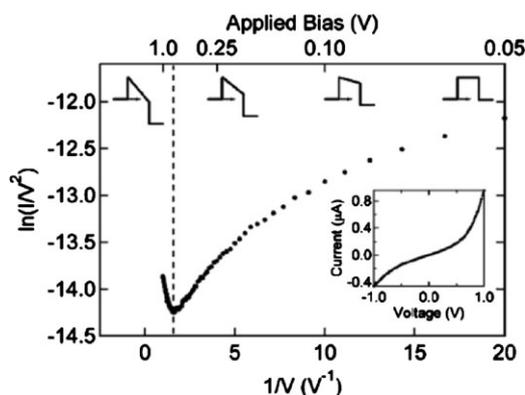


Figure 8. Main plot: Fowler-Nordheim plot for the average of 100 Au-anthracenethiol-Au junctions measured using cpAFM, showing a transition from direct tunneling to field emission. The dashed line shows the voltage at which the transition occurs, where the bias is sufficient to create a triangular tunneling barrier. Inset: corresponding i - V curve for the same data. Reproduced with permission from [111]. Copyright 2006 American Physical Society.

discussed below, a field emission plot for a large-area carbon/molecule/copper junction also showed a transition voltage, for both positive and negative bias.^[81] In addition, examination of molecules on conductors with photoelectron spectroscopy has shown that the orbital energies and tunneling barrier derived from them can be significantly modified by broadening and electronic coupling with the contacts.^[7,116]

An elegant application of a mesoscale cpAFM experiment appeared recently, for the case of conjugated molecules of variable length.^[82] A layer by layer synthesis produced oligophenyleneimine (OPI) molecules of various lengths bonded to Au through a thiolate linkage (Fig. 9A).^[82] Reflectance FTIR was used to confirm the monolayer structure, as shown in Figure 9B. Figure 10 shows current-voltage curves obtained with cpAFM in semilog format for different OPI lengths

(Fig. 10A), and in field emission format (Fig. 10C,D). The transition from tunneling to field emission is apparent in Figure 10C and D, for both short (OPI 4) and long (OPI 10) molecules. Figure 11A is a semilog plot of resistance versus molecule length, the slope of which is β . The pronounced change in slope from 0.3 \AA^{-1} for short molecules to 0.09 \AA^{-1} for molecules with four or more subunits indicates a change in conduction mechanism with molecular length; this was one of the first direct observations of such in the literature. Figure 11B shows a clear dependence on length of the measured resistance versus temperature plots, with the short OPI 4 molecule exhibiting transport that is independent of temperature and the longer OPI 6 and 10 molecules showing significant thermal activation, where the activation energy E_a is given by the slope of the Arrhenius plot and equals 0.28 eV for OPI 6 and OPI 10. These results provide experimental support for a theoretically predicted transition from tunneling for short molecules to activated "hopping" for longer molecules.^[117-119]

From the perspective of a progress report on molecular junctions, the mesoscale cpAFM and crossed-wire results illustrate important characteristics of scientifically informative junction experiments. The experiments are adequately repeatable such that sufficiently large data sets can be collected, helping to ensure that the observed behavior is statistically meaningful. They permit comparisons of conductance across platforms, leading to correlations between STM, cpAFM, and crossed-wire paradigms for similar molecules. In addition, several parameters that should impact conductance have been varied over a wide range, including temperature, bias, and molecule length. Since a mechanism deduced from these results must be consistent with the effects of varying several parameters, the range of possible mechanisms is narrowed considerably.

4.3. Progress with Ensemble Molecular Junctions

As noted earlier, ensemble junctions containing $>10^3$ molecules are more complex than single-molecule devices, but they are also

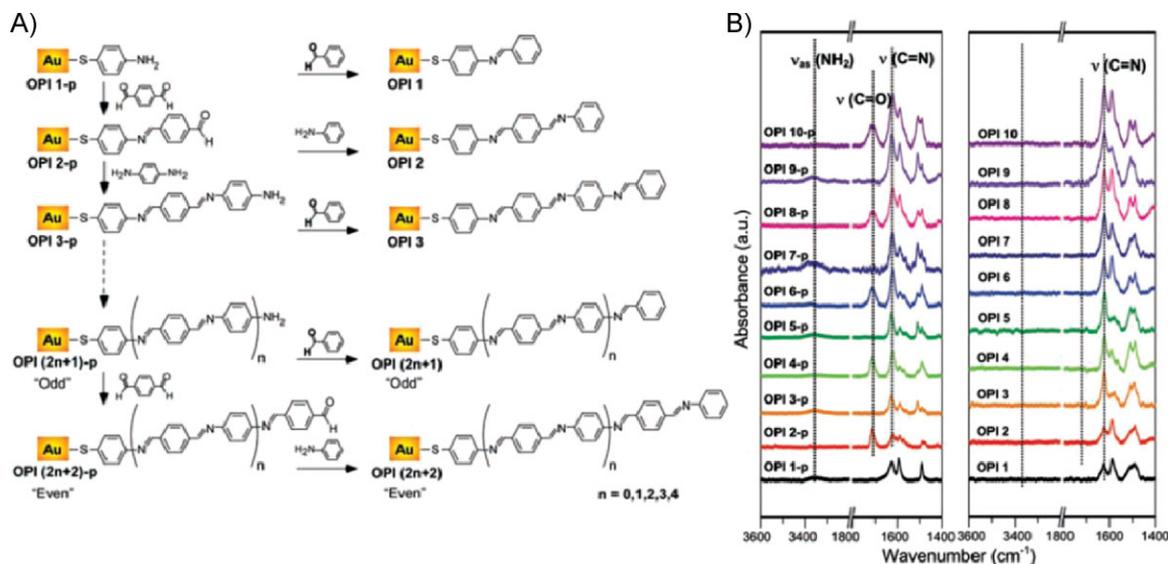


Figure 9. A) Synthesis and fabrication of OPI molecular layers on Au. B) Reflectance IR spectra of the molecules at Au confirming various structural aspects. Reproduced from [82] with permission from the American Association for the Advancement of Science, AAAS (copyright 2008).

more amenable to mass production and integration with conventional electronics. A rather wide range of experimental conditions and junction structures have been investigated by various research groups, and a consensus about the electronic behavior of molecules in ensemble junctions has not yet

emerged. While there are examples of good consistency for a given junction structure in a single laboratory, agreement between laboratories has been elusive, even for a nominally identical set of conditions. Difficulty in comparing results from different laboratories is due to several factors that will be

discussed briefly here, including differences in the substrate and top contact, a variety of different molecular structures and surface bonding motifs, and variations in the degree of structural order in the completed junction.

When considering molecular junctions larger than a few nanometers in lateral dimension, some requirements are imposed on the substrate. First, the substrate surface should be flat with respect to the thickness of the molecular layer. For typical adlayers having thicknesses of 1–3 nm, the root-mean-squared (rms) roughness of the substrate should be less than approximately 0.5 nm. Second, the substrate and molecular layer must be free of defects (e.g., pinholes that could result in metallic filaments) over the entire area of the junction. For a 1 nm thick layer used in a 50 μm × 50 μm junction, the aspect ratio is 50 000, so the requirement of defect-free flatness over a very wide and very thin junction is indeed demanding. Some techniques for achieving sub-nanometer substrate flatness include the Au deposition on a thiol primer on silicon^[120] and the pyrolysis of photoresist in a reducing atmosphere, resulting in a substrate dubbed “pyrolyzed photoresist film,” or PPF.^[121,122] Both substrate flatness and defect occurrence favor the use of small junction areas where possible.^[59,60,63,66]

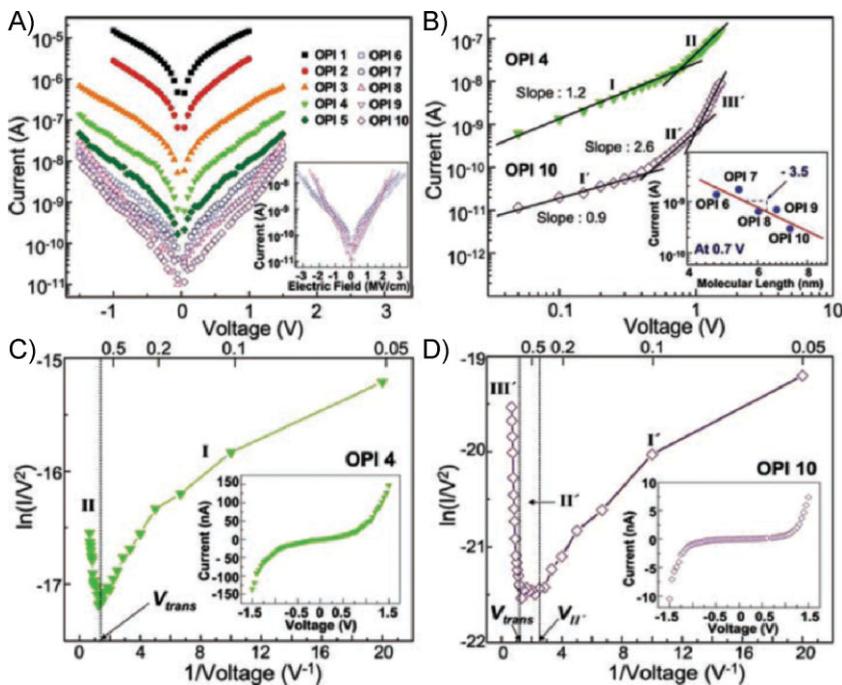


Figure 10. A) *i*-*V* curves (semilog) for the average of 10 junctions with different molecules. The inset is re-plotted using the electric field as the abscissa. B) Log-log for two junctions containing short (OPI 4) and long (OPI 10) molecules; the inset shows the current at 0.7 V versus molecular length for several OPI molecules. C, D) Fowler-Nordheim plots for the short (OPI 4) and long (OPI 10) molecules; insets: *i*-*V* curves. Reproduced from [82] with permission from AAAS (copyright 2008).

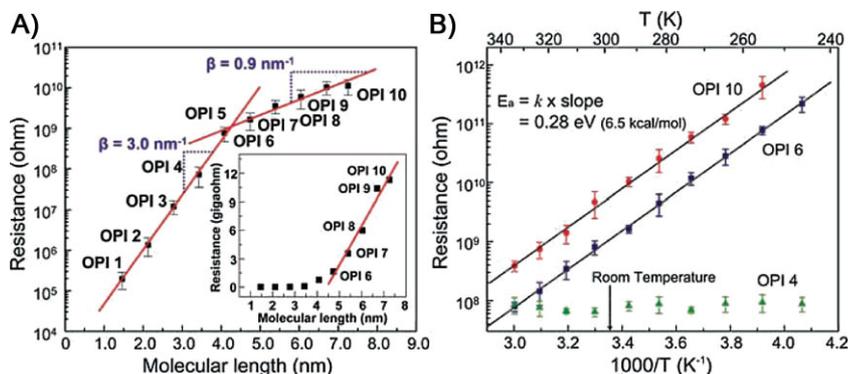


Figure 11. Resistance of OPI molecular wires versus length (A) and temperature (B). Reproduced from [82] with permission from AAAS (copyright 2008).

Making a second, or top, contact between a conductor (usually metallic) and a molecular monolayer over an area covering at least thousands of molecules has proven challenging. The main obstacles are the formation of metallic filaments from metals penetrating the molecular layer; they contact the bottom conductor directly, resulting in a short-circuit junction and potential damage or disruption of the monolayer during top contact formation. Early devices utilized vapor-deposited titanium as an adhesion layer for further metal deposition, in part to form a Ti-C bond which prevented penetration of metals into the monolayer.^[14,59,123] Later work reported that Ti reacts with a SAM^[124] or L-B film,^[125] with possibly severe structural changes. In addition, Ti can oxidize during deposition, resulting in a molecule/TiOx/Ti (TiOx = titanium oxide) structure with different properties from that of a molecule/metal device.^[126,127] While TiO₂ has proven to be a useful component of molecular junctions used for memory applications,^[10,74,121,128,129] any user of Ti for fabrication should be aware of possible artifacts from the high reactivity of vapor-deposited Ti atoms. Several other metals have been vapor-deposited on molecular mono- and multilayers, including Au, Ag, Al, and Cu, and in many cases the metal penetrates the monolayer to form metallic “shorts.”^[6,49] A detailed study of metal deposition on SAMs revealed that penetration channels were formed through lateral motion of the thiolate molecules such that after deposition, the vapor-deposited metal was observed to be located on the substrate, with thiolate molecules re-adsorbing on top of the deposited metal.^[124,130,131] Unfortunately, the same lateral restructuring of a thiolate SAM that permits a high degree of ordering to be obtained during assembly also permits metal penetration and causes relatively low thermal stability. Au readily penetrates L-B structures as well, although a soft deposition technique involving a cooled sample and an Ar backpressure to thermalize evaporated atoms has proven successful for Au,^[132–134] Pb, and Al top contacts.^[135] Collectively, these issues indicate that vapor deposition of metallic top contacts on molecular layers must be done with care: it often results in low yield and poor reproducibility, or even behavior that is not directly related to the molecule (as with TiO₂). Two approaches for avoiding these problems are noted here: avoiding metal vapor deposition completely and using adlayers with stronger bonds to the substrate.

As reviewed previously,^[18] some early ensemble junction designs involved a top contact consisting of a mercury drop lowered onto a metal/SAM substrate, or by establishing contact between two Hg drops each with associated thiolate monolayers (see Fig. 2C).^[69,136–138] Related paradigms involve using eutectic Ga/In (eGaIn, melting point $\sim 16^\circ\text{C}$) on SAMs at Ag,^[139] Hg on adlayers bonded to flat carbon,^[71,72,140] and Hg on a molecular layer at silicon.^[141] A liquid metal top contact circumvents the use of vapor phase atoms, so metal incursion into the molecular layer is less likely. Recent results using eGaIn are shown in Figure 12 for C₁₀ to C₁₆ alkanethiolates on a thin film of Ag on glass.^[139] The trend with alkane length is clear ($\beta \sim 0.43 \text{ \AA}^{-1}$), and although the yield was >90%, the relative standard deviation of the observed current was fairly high. A detailed comparison^[142] of Hg junctions of the type Hg/SAM/Hg and Ag/SAM/Hg with 24 carbon atoms between electrodes revealed a range of current values spanning a factor of 40, and β values for a range of alkane lengths of 0.57–1.0 \AA^{-1} . For Ag substrates prepared by two different methods, the results were shown to depend strongly on the flatness of the substrate, as shown visually in Figure 13. Defects associated with SAM ordering and also doping induced by radiation have also been considered for Si/molecule/Hg junctions.^[143] While Hg and eGaIn top contacts are attractive from the standpoint of simplicity and minimal effects on the molecular layer, their limited reproducibility hinders widespread use. Furthermore, it is

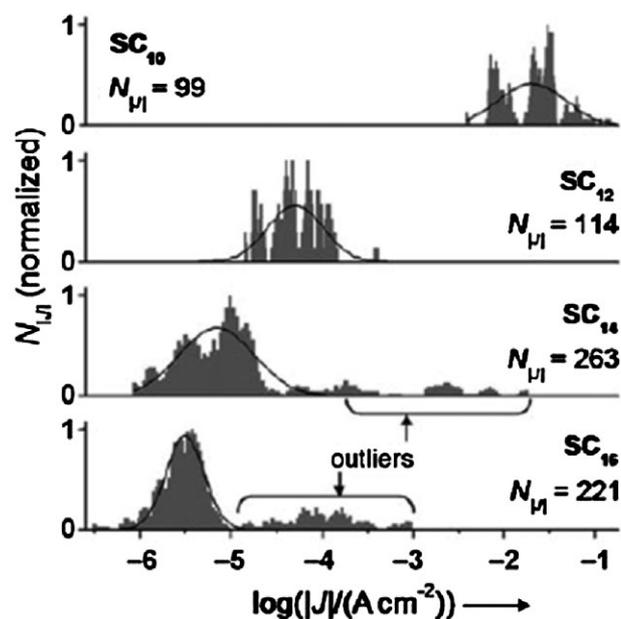


Figure 12. Histograms for molecular junctions formed using eGaIn as a top contact on C₁₀ to C₁₆ thiolate monolayers adsorbed at template-stripped Ag. $N_{|J|}$ represents the number of times J was measured. The average current decreases as the chain length increases. Reproduced from [139]. Copyright 2008 Wiley-VCH Verlag GmbH & Co. KGaA.

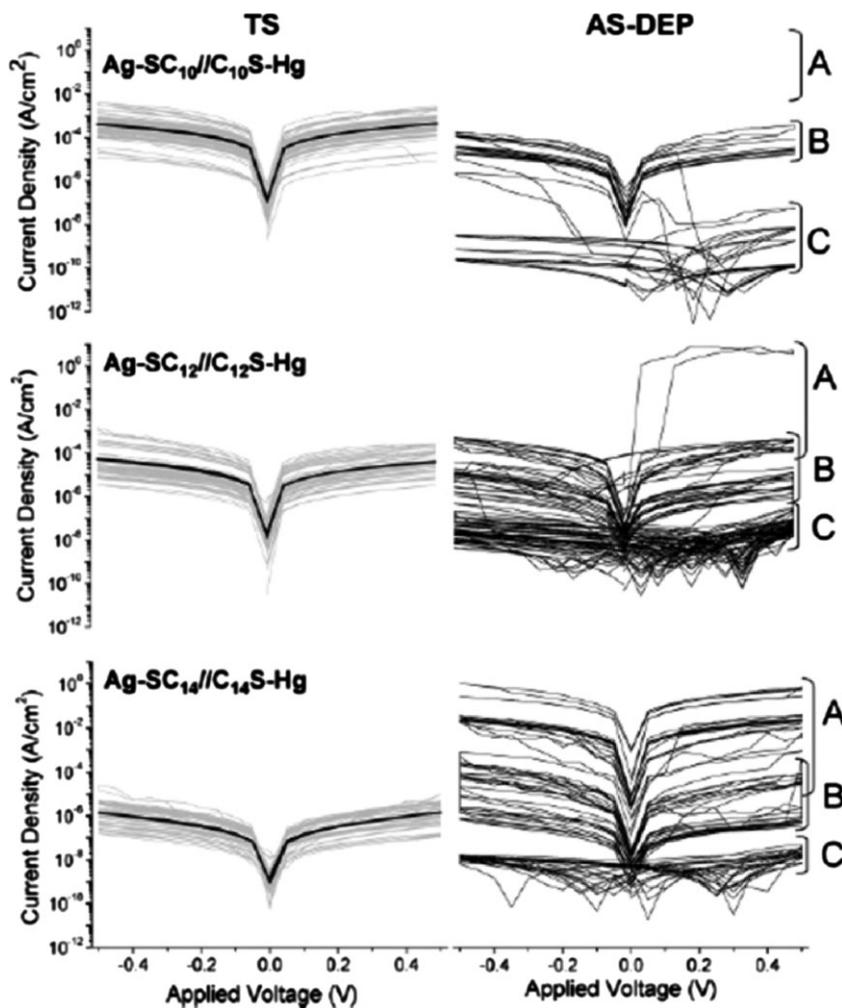


Figure 13. The effect of substrate flatness on Ag/thiolate/thiolate/Hg junctions shows that when a smooth substrate (template stripped Ag, left) is used, a less sporadic result is obtained when compared to a more rough substrate (as-deposited, AS-DEP, right). Reproduced with permission from [142]. Copyright 2007 American Chemical Society.

difficult to imagine liquid metal contacts outside the research laboratory, particularly in massively parallel integrated circuits.

A recent alternative to liquid metals is the use of a commercially available conducting polymer based on poly-(3,4-ethylenedioxythiophene)/poly(styrenesulfonate), abbreviated PEDOT:PSS. Akkerman et al. used the polymer as a top contact on alkanethiolate monolayers at Au.^[62–64,144] A variable junction diameter ranging from 10 to 100 μm , with the geometry shown in Figure 14A, was used. The PEDOT:PSS was spin-coated from a water-based suspension on top of the SAM/Au, followed by drying and vapor deposition of Au. Given the polymeric nature of the PEDOT layer, it is unlikely to penetrate the SAM, and the high conductivity of the polymer (30 S cm^{-1}) yields negligible resistance. As indicated by the error bars on the J - V curves of Figure 14B, the reproducibility of the devices was excellent, and the current decreased exponentially with molecule length. The value of β determined as shown in Figure 14C was somewhat bias-dependent, ranging from 0.66 \AA^{-1} at 0.1 V to 0.57 \AA^{-1} at

0.3 V.^[62] The current was directly proportional to device area, and was stable for at least 75 days in air. Analysis of the current–voltage curves with a Simmons relationship modified for image charge showed a good fit of theory with experiment, provided the electron mass was adjusted to $0.28m_e$, a value which proved consistent over a range of molecular lengths from C_8 to C_{14} .^[63] A detailed cross-platform comparison of the results with STM, cpAFM, nanopore, and evaporated metal results is shown in Figure 15, with the results stated as the resistance per molecule calculated from the junction area and surface concentration.^[64] While the various platforms all show a trend of conductance with molecular length, there is a variation of several orders of magnitude in the absolute values of the current densities for a given molecular length. The authors attribute this variation to the nature of the contacts, as indicated in Figure 15. The Au/SAM/PEDOT/Au junctions exhibit several hallmarks of very informative molecular electronic results: excellent yield (>95%) and reproducibility, scaling with device area, and dependence on molecular length. Not only are the results consistent within the set of SAM/PEDOT junctions, but they were compared in detail with several other paradigms, both single-molecule and ensemble methods.^[64] If the variables that control electron transport through molecular junctions are well-understood, it should be possible to readily predict how a given molecular structure will behave across several different paradigms.

A major reason for the difficulty of making viable molecular junctions by depositing metallic contacts on SAM and L–B monolayers is the weak molecule/substrate bond. An obvious alternative is the use of bonding schemes that result in stronger, less labile surface bonds to provide a stable template for the junction. Examples include Si–C bonds resulting from alkene attachment to H-terminated silicon^[84,145] and the use of aromatic diazonium reagents to result in Si–C^[66,67] and C–C^[10,72,121] bonds after electrochemical reduction of the diazonium ion. Si–C and C–C bond strengths are ~ 4 eV, compared to ~ 1.6 eV for Au–S, making lateral motion of the molecules on the Si or C surface impossible at temperatures commonly experienced in top contact deposition. Although these methods lead to molecular layers that are bonded to the bottom contacts, deposition of top contacts still leaves the layer vulnerable to attack by impinging metal atoms during top contact evaporation. Thus, in many cases spectroscopic characterization is carried out in order to validate the structure of the molecular layer after top contact deposition.

There have been several reports of spectroscopic studies carried out after deposition of various metals onto molecular layers anchored using a covalent bond on Si or carbon surfaces. A detailed set of spectroscopic studies of monolayers bonded to Si

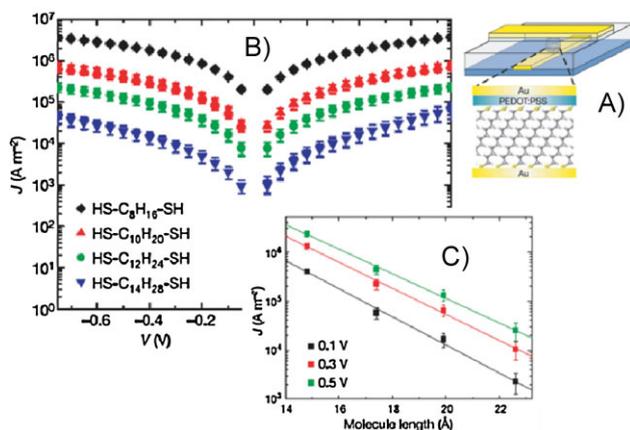


Figure 14. A) Schematic illustration of junctions made using PEDOT:PSS top contacts. B) J - V curves for junctions made using a series of alkanethiolate molecules at Au showing a decrease in conductance as a function of increasing chain length and excellent reproducibility (error bars are the standard deviation from at least 17 junctions). C) Plot of J versus molecule length used to determine β . Reproduced with permission from [62]. Copyright 2006 Nature Publishing Group.

showed that the molecular structure was unaffected by deposition of thin layers of Cu, Ag, and Au.^[84,146] An earlier study of monolayers bonded to Si with organosilane reagents showed disruption of the surface bonds by Au and damage to the molecules by Al and Ti.^[77] For the case of C–C surface bonds, the substrate is the flat PPF surface noted earlier, and the surface bond is between a phenyl ring in the molecule and the edge of a graphitic plane in the surface.^[10] Raman and X-ray photoelectron spectroscopy (XPS) showed that molecules bonded to PPF were unaffected by direct electron-beam (e-beam) deposition of Cu or Au, except for the case of a covalent interaction between Cu and a terminal NO₂ group on the molecular layer.^[10,75] Interactions

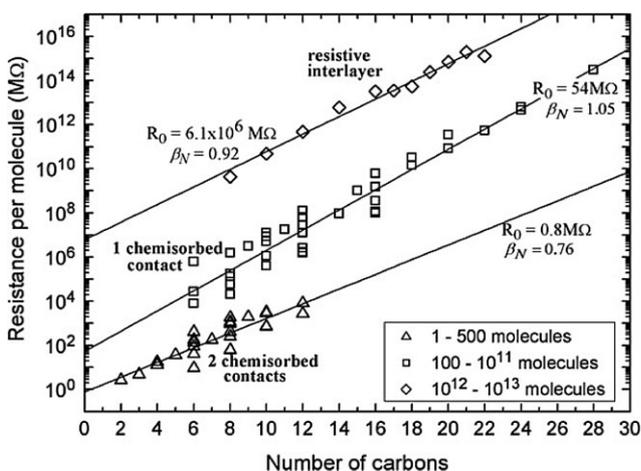


Figure 15. Resistance per molecule as a function of the number of carbon atoms in the alkane used to make the junction. Several junction platforms are represented, showing that the method of making contacts is critical in determining the magnitude of the measured resistance. R_0 is the value of the intercept and represents the contact resistance, while β_N is the decay factor for each series of molecules. Reproduced with permission from [64]. Copyright 2008 Institute of Physics.

between end groups of the molecular layer and deposited metals have also been reported for Cu on porphyrin monolayers^[84,147] and on SAMs.^[130,148–151] Notably, particular end-group/top contact metal combinations can yield a chemical association that reduces metal penetration into the monolayer.^[150,151] An FTIR study of aromatic monolayers bonded to Si via Si–C bonds derived from diazonium reduction reported that soft deposition of 100 nm of Au produced minor perturbations of the IR spectrum, while direct e-beam deposition of the same thickness caused serious degradation of the aromatic structure of the monolayer.^[152] However, e-beam deposition of thinner layers (3–10 nm) of Cu, Ag, or Au did not significantly perturb the FTIR^[84] or Raman^[74,75] spectra of similar molecular layers on carbon substrates. For the Raman study, reversible bias-induced structural changes were observable in a working junction, which indicated dynamic reduction of the molecular layer.^[74] The damage observed with e-beam deposition for the thicker metal films is likely due to thermal degradation caused by the condensing metal atoms, as well as radiation from the e-beam source.^[6,49] The sensitivity of the molecular layer to deposition conditions is a strong motivation for independent structural verification of the finished devices, usually by optical spectroscopy.

A particularly important aspect of the robust template provided by irreversible bonding of molecular layers to flat bottom contacts is the production of devices free from short circuits caused by metal filaments bridging between the substrate and the metallic top contact that can potentially form during vapor deposition.^[10,65,66,81,84] Examples from three different laboratories where vapor deposition was carried out successfully onto covalently bonded molecular layers are shown in Figure 16 and 17. Figure 16 shows results for molecular junctions made using diazonium-derived aromatic molecular layers on carbon with e-beam-deposited Cu top contacts.^[65,81] Figure 17A–C show J - V curves for porphyrin layers bonded to Si with Cu, Ag, and Au

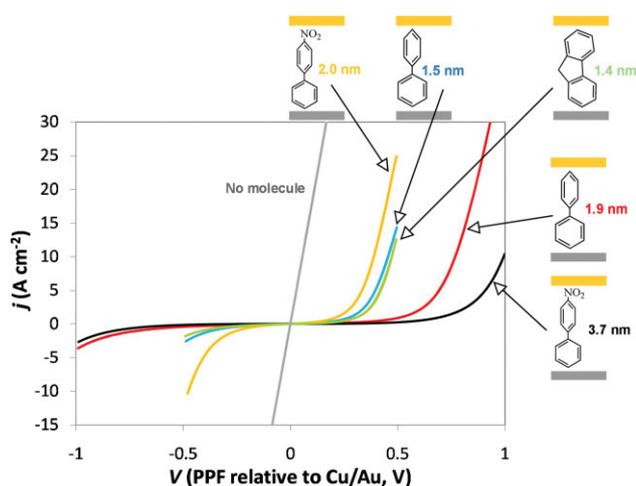


Figure 16. Overlay of J - V curves for molecular junctions fabricated from diazonium-derived adlayers at carbon (PPF). The molecular structure and thickness of the layer are given for each curve. The top contact is 30 nm Cu followed by 15 nm Au, deposited by electron beam evaporation. Adapted with permission from [81]. Copyright 2008 Institute of Physics.

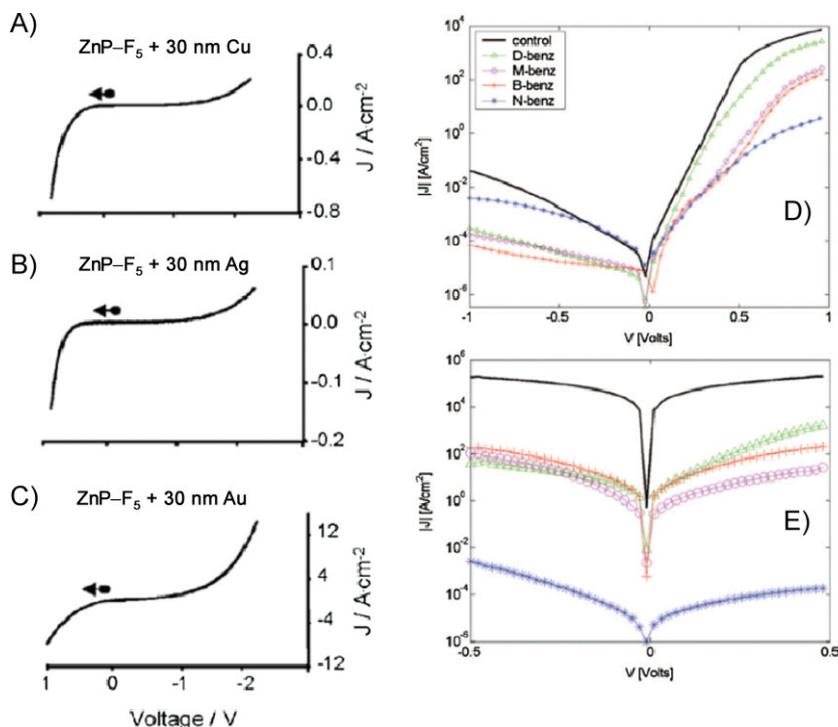


Figure 17. A–C) J – V curves for junctions containing porphyrin moieties covalently bonded to Si with Cu (A), Ag (B), and Au (C) top contacts deposited using electron beam evaporation. J – V curves for D) n-doped and E) p-doped Si with covalently bonded molecular layers (diazonium reduction) using a soft-deposited Au top contact. Reproduced with permission: (A–C) from [84]. Copyright 2008 American Chemical Society and (D–E) from [66]. Copyright 2007 American Institute of Physics.

top contacts made by e-beam deposition.^[84,147] Finally, Figure 17D–E shows results from diazonium-derived aromatic layers on Si with soft Au deposition used for the top contact.^[66,152] The high device yield and good reproducibility reported in these studies is due in part to the strong C–C and Si–C surface bonds, implying that damage and penetration during metal deposition is significantly reduced. The J – V curves of such devices are strongly dependent on molecular structure, indicating that the observed electronic behavior is unlikely to originate from an artifact of junction fabrication. An additional argument against the possibility that metal filaments could account for the electronic signature of carbon/molecule/Cu junctions is the fact that such filaments would be required to carry $>10^{11}$ A cm^{–2} in order to account for the observed junction resistance and current, and would likely burn out in a few nanoseconds due to local heating.^[81]

Although individual laboratories have achieved good yield and reproducibility with ensemble junctions, there is not yet a consensus on the correct current–voltage behavior for a given molecular layer. Much of the difficulty of comparing results from different laboratories is due to differences in paradigm, notably the type of contact (including the presence or absence of bonding to the molecular layer) as well as the molecular structure. Although the majority of studies have utilized alkanes as the molecular component, aromatic species are more likely to have useful electronic functions due to their higher conductivity. As

noted above, ensemble molecular junctions made by molecule and metal deposition on microfabricated substrates are amenable to massively parallel lithographic fabrication, and are therefore of possible commercial interest.

4.4. Progress with Conductance Switching

As noted briefly in Section 3, the term “conductance switching” has been used to describe changes in the conductance of a molecular junction, often induced by a voltage pulse or exposure to light. In addition to being one of the earliest reported phenomena in molecular electronics,^[3,123] switching has been the focus of numerous subsequent reports. Efforts to understand switching mechanisms is motivated, in part, by the potential commercial applications of molecular memory devices. Single devices can often be switched repeatedly, and such conductance changes do not rely on yield and reproducibility as heavily as comparisons of junction current between devices. Although switching often attributed to structural changes in the molecules rather than plasticity in the metal or semiconductor components of the junction, many nonmolecular mechanisms for conductance switching have been reported for organic electronic devices,^[15] including the formation and breaking of metallic filaments and motion

of ions and defects. The prevalence of switching phenomena in the literature stimulates a review of some prominent examples along with some mechanisms and pitfalls for both single-molecule and ensemble junctions.

Several experimental and theoretical studies have addressed conductance switching in single-molecule devices. STM studies of oligophenylene-ethynylene (OPE) molecules diluted in an alkanethiolate monolayer showed stochastic switching that was attributed to conformational changes^[29,34] and modulation of hybridization states resulting in variation of the tilt angle of the active molecules.^[27,153] However, a theoretical study showed that thermal Au–Au and Au–molecule fluctuations can produce a range of conductance values in Au/molecule/Au junctions.^[57] There is also a possibility that the conductance changes are caused by the Au–S bond breaking and re-forming.^[42] An elegant example of single-molecule conductance modulation was demonstrated to occur through changes in the proximity or charge state of a silicon surface atom adjacent to an active molecule bonded to silicon.^[23] In addition, conductance changes associated with different charge states in a single Mg porphyrin molecule have been monitored with STM at cryogenic temperatures.^[154] Conductance changes have also been induced in single molecules by photochemistry,^[95] Coulomb blockade,^[22,155] and redox changes in the molecule induced in a surrounding solution.^[50,95,156] Multilevel molecular memory devices based on monolayers and multilayers of conjugated organic species

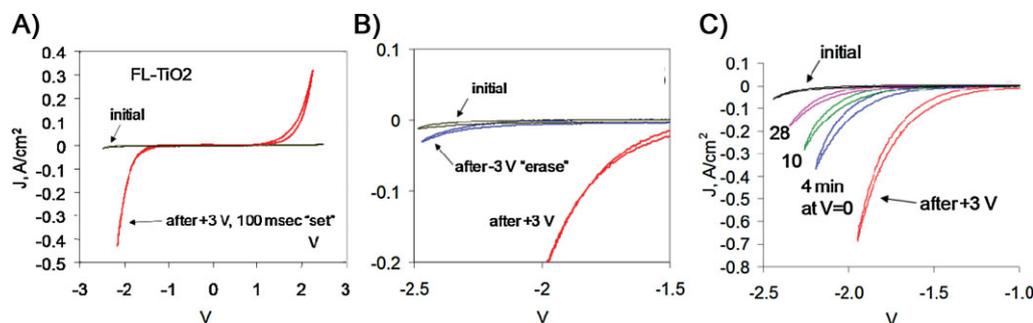


Figure 18. Carbon/fluroene (FL)/TiO₂/Au junction, which exhibits conductance switching. A) Overlay of J - V curves (1000 V s⁻¹) illustrating the initial off state can be switched to a higher conductance state using a 100 ms, +3 V pulse. B) Magnified J - V curves from (A) show both “set” and “erased” states. C) The higher conductance state of the device persists at least tens of minutes. Adapted with permission from [121]. Copyright 2007 American Institute of Physics.

between conducting contacts have been described in several manifestations,^[157–160] as have memory devices based on charge storage in redox active molecules.^[13,161–163] As noted below, redox-induced conductance changes have a strong precedent in the conducting polymer literature, although such changes are more often described as doping than as reduction or oxidation of a conjugated polymer.^[164–166]

Conductance switching in ensemble molecular junctions has been studied to a greater extent than in single molecules, due in part to possible commercial importance in the microelectronic memory arena. The Scott and Bozano^[15] review cited earlier discusses a wide range of switching phenomena in organic materials; in nearly all cases, the active layers are much thicker than those normally considered in molecular electronics. The rotaxane molecular junction noted in the introduction was the first example of conductance switching in a monolayer device, and the prospect of nanoscale memory devices drove a significant research effort in molecular electronics. The concept of the rotaxane switch was bistability based on two different conformations of a molecule.^[3,14,123,125] A device made by orienting a layer of rotaxane molecules onto n-doped Si using the L–B technique and finished by evaporation of Ti and Al metal as top contacts showed an increase in conductance after a voltage scan in one direction. This higher conductance state persisted until the junction was reset to a low conductance state by an opposite bias voltage pulse.^[167,168] The switching phenomenon was attributed to a bias-driven conformation change mediated by a solid state redox reaction. Subsequent to the initial reports, the devices were characterized by FTIR^[125] and demonstrated in ultrahigh-density memory devices.^[79,169] In addition, theory showed that the high and low conductance states of the rotaxane devices were consistent with the predictions of density functional theory.^[170]

Although the rotaxane junctions showed great promise as molecular memory devices, the mechanistic picture was convoluted by subsequent reports from other laboratories that demonstrated switching behavior for similar devices containing non-redox-active molecules,^[171] and for molecular junctions known to contain titanium oxide^[74,121,126] (titanium was used as an adhesion layer in the rotaxane devices, and partial oxidation of the Ti during evaporation is likely at the backpressures typically used in metal deposition). An example of conductance switching in a molecule/TiO₂ junction is shown in Figure 18. The molecular component in this case is fluorene, which is unlikely to be redox

active under the conditions employed.^[121] The switching mechanism in this junction was shown to be related to changes in the conductivity of the TiO_x layer (i.e., reduction of TiO₂ to a much higher conducting mixture of titanium oxides), with the molecule providing a barrier that enables efficient reduction through the generation of a high electric field, and also slows recombination such that the more conductive TiO_x state persists for several minutes. More recent reports from the Hewlett Packard Quantum Electronics group describe a memory effect in devices containing only Pt and TiO₂, which were dubbed “memristors” to emphasize that the devices have electronic properties distinct from conventional resistors and semiconductors.^[128,172] Related work on memory devices containing thicker films of TiO₂ was reviewed in 2007,^[173] with attention to various possible mechanisms for conductance switching. For both the rotaxane and TiO₂ memory devices, the bistability is enabled by redox reactions that result in two states with different conductivity. A recent extension of this principle is a polypyrrole/TiO₂ memory device in which both the polymer and oxide layers undergo redox-driven conductance changes.^[166] It should be noted that bias-induced redox reactions in molecular junctions are examples of the broader area of solid state electrochemistry, with possible involvement of mobile ions and space charge accompanying the redox events.^[121,128,173]

Although it was recognized as early as 2004^[74,127] that molecular junctions containing titanium may contain TiO₂ which can exhibit switching behavior, it should be noted that switching is a generic term that may apply to different mechanisms. The observation of conductance changes in devices containing TiO₂ does not invalidate a switching mechanism based on molecular conformation changes, as both results are possible for appropriate junctions.^[5] However, the involvement of Ti oxide as an active switching element or as a passive adhesion layer does emphasize the importance of device characterization when investigating mechanisms. Since there are many possible mechanisms based on stochastic fluctuations, bond breaking, redox reactions, conformational changes, ion motion, vacancy drift, etc., it is critical to be sure about the junction structure before considering the switching mechanism. Furthermore, in situ probes of structural dynamics provided by optical spectroscopy^[74] and IETS are invaluable for narrowing down possible mechanisms of conductance changes and bistability.

5. Where are we now?

The first decade of experimental research on molecular junctions has exhibited both rapid growth and significant scientific achievement. As described in previous sections, the single-molecule, mesoscale, and ensemble paradigms have established that molecules can indeed act as circuit elements, and structural variation can be exploited to vary their current/voltage behavior. Notable highlights include single-molecule conductors^[39,56] and transistors,^[23] low-volatility memory devices,^[8,14,121,166] demonstration of strong dependence on molecule length and structure,^[82,96] fabrication of thousands of molecular junctions in parallel,^[80] and three-terminal molecular devices^[174] in addition to more common two-terminal junctions. In the context of these significant achievements, we can consider progress toward the goals outlined in Section 2 (i.e., robust junctions, molecular signature, in situ spectroscopy, integration). As already noted, individual labs have achieved acceptable yield and reproducibility, but there is not yet an agreed-upon standard junction that can serve as a starting point for correlating junction structure with electronic properties. Once such a standard junction can be made reliably in many laboratories, it will be possible to make changes to the contacts, molecular components, geometry, etc., and assess their effect on electronic behavior. Low-yield fabrication and observations made on a subset of data chosen by the investigator are accompanied by a high risk of observational bias that could potentially become pathological science. Even in 2008, there are papers reporting nominally identical devices whose conductance varies over more than five orders of magnitude, making it very difficult to form any quantitative conclusions. The time is past being ripe for the development of a robust junction design with known structure and reproducible electronic behavior. A rather stern warning in the Scott and Bozano review made in the context of nonvolatile organic memory devices might well be applied to molecular junctions: "In our opinion, progress towards a viable new resistive memory technology will depend on careful science to clarify conclusively the relevant switching and transport mechanisms in any particular device structure... These studies need to be focused more on eliminating artifacts and irreproducible response, and less on creating new materials and poorly characterized devices that add to the confusion."^[15]

In the view of the current authors, the difficulty of achieving reproducible junction behavior despite >10 years of effort by many laboratories is a consequence largely of the choice of SAM and L-B structures as the most common experimental paradigms. As noted above, these structures must involve labile surface bonds so that they can assemble into a minimum-energy conformation. This instability makes it difficult to deposit top contacts, and it can also lead to stochastic behavior of the electronic properties. Furthermore, the prospect of integration with conventional microelectronics is much less likely when the molecular components are unstable to the temperature cycling involved in packaging. While SAM and L-B structures have provided significant new scientific information about surface phenomena, they are likely too fragile for practical fabrication of molecular electronic devices. A related but distinct issue involving reproducibility is the choice between single-molecule and ensemble junctions to investigate electronic properties of

molecules. The emphasis on device size and Moore's law has "crowded out" the equally important issue of how electrons are transported through molecules, whether they are single molecules or many molecules in parallel. Single-molecule paradigms add to the already difficult question of transport mechanisms the uncertainties of contact effects, thermal fluctuations, and molecular conformation. While single-molecule experiments can yield both fascinating and useful scientific information, it is the authors' firm opinion that practical molecular electronic devices will more likely result from robust ensemble junctions that are thermally stable and whose electronic behavior represents an average of a large number of molecules.

Moving on to the second target listed in Section 2, dealing with observation of a molecular structure–function relationship, the evidence is quite strong for the existence of a molecular signature in the case of single-molecule junctions (e.g., see Fig. 4, 5, and 6). The good correlation of theory and experiment in the repetitive break junction paradigm^[56] implies that the major factors controlling single-molecule conductance have been identified and largely understood. There are also clear cases of structural control of electronic conductance for mesoscale and ensemble junctions (e.g., see Fig. 7, 8, 9, 12, 14, 16, and 17). In some cases, the observed conductance of an ensemble junction varies by orders of magnitude when the only known structural change is the thickness or identity of the molecular layer. The greater complexity of ensemble devices has complicated theoretical correlations, but the principles revealed by single-molecule experiments serve as very useful guides for predicting the electronic properties of ensemble junctions. It is fair to say that a molecular signature has been realized in that strong effects of structure on conductance have been established in both single-molecule and ensemble junctions. However, such structure–conductance correlations have not been observed quantitatively across several laboratories or platforms, and there is no consensus on how to predict the conductance of a new molecular structure. Until we have a robust junction design that is readily duplicated by several research groups and has consistent electronic behavior, it will be very difficult to have confidence in statements about structural effects on molecular conductance. Without such a standard junction to investigate the factors that control molecular conductance, rational design of molecular electronic components is difficult to imagine.

There are relatively few examples of spectroscopy applied to molecular junctions during fabrication or in finished devices, although those examples have been informative. Notable examples include assessment of structural changes in the molecular layer accompanying metal deposition^[75,77,84,130,149,152] and in situ spectroscopy of finished^[76,152] and functional^[74,85,175] molecular junctions. While these experiments are far from simple, an analogy from chemistry illustrates their importance. Whenever a chemist synthesizes a new compound, a mass spectrum, an NMR spectrum, and often an X-ray crystal structure are obtained as a matter of routine to verify the correct structure. Attempting a long series of synthetic steps would be very risky without structural verification of intermediate steps, and the synthetic effort would likely be wasted. Without similar characterization of molecular electronic devices during fabrication and in working junctions, the end result is very likely to be a "house of cards". The authors strongly agree with

the NSF conclusion that we need "...optical spectroscopies and imaging schemes to probe molecular structure in operating devices."^[16]

To the authors' knowledge, there is only one ongoing effort to integrate molecular electronic components with modern microelectronics, involving redox charge storage based on porphyrin monolayers.^[13,161,162,176,177] On the other hand, there are many examples of organic electronics in commercial ventures to draw from, such as thin film transistors and light emitting diodes with molecular layers much thicker than those discussed here. Two observations about integration from these examples are relevant: 1) a significantly enhanced function or cost advantage must be demonstrated before the CMOS industry will consider a new technology and 2) the electronics industry will not yield readily to radical changes in the highly sophisticated and extensive fabrication infrastructure that may be required to incorporate molecular components. Although the day when molecules serve electronic functions may come fairly soon, it is likely to first involve hybrid circuits, in which the molecule provides some advantage that can be added to the massively parallel and well-developed world of CMOS microelectronics. Even when a commercially interesting electronic function is demonstrated with molecular electronic components, the task of making it compatible with existing semiconductor processing is nontrivial. The achievement of high yield of ensemble molecular junctions at the 150 mm level noted earlier is a significant step along the path from laboratory device to commercial integrations, but there is still a long way to go.^[80]

6. A Molecular Junction Road Map

Toward the long-term goal of enhancing commercial microelectronics with molecular components, we can envision a road map of steps likely to be involved in realizing this goal. Predictions are inherently speculative, of course, but the following steps are likely to be essential:

1. *Reproducibility within a given laboratory and paradigm.* Low-yield observations of interesting electronic phenomena provided much of the early stimulus for the field, but mechanistic insights and conclusions are dependent on high yield and good reproducibility.
2. *Reproducibility for a given paradigm across several laboratories.* We need a standard junction that is characterized both electronically and structurally and can be used to qualify a fabrication process or measurement technique.
3. *Consistency across experimental paradigms.* The electronic behavior of a given set of molecules should be consistent across paradigms if the factors controlling conduction are indeed understood. For example, the effect of changing a contact material or junction area should be predictable and consistent with theory. The predictive nature of this step is analogous to a "box of parts" for molecular electronics, in that molecules, contacts, junction geometry, etc., are elements that can be combined to perform complex electronic functions in the same way that resistors, capacitors, etc. can be utilized along with Ohm's law in conventional electronics.
4. *Rational design.* Once the "rules" of molecular conduction are known, predictions of behavior from structure may be extended to rational design of electronic function. Given the wide variety of molecules and their quantum mechanical nature, rational design is likely to involve a heavy theory component.
5. *Manufacturability.* For molecular electronic devices with a useful function, commercial applications will depend on manufacturability, meaning tolerance to thermal cycling during fabrication and packaging, as well as in operation. Significant research and development will be required to scale up a laboratory device for commercial operation, particularly in the areas of yield and thermal stability.
6. *Integration with commercial materials and structures,* likely involving hybrid devices with conventional semiconductor structures such as CMOS. Molecular components and processing must be compatible with existing fabrication techniques, unless the molecular devices can be useful without exploiting the massively parallel and highly developed semiconductor industry.

7. Summary and Outlook

The rapid growth of molecular electronics and research on molecular junctions has yielded new phenomena and devices with possibly vast applications in microelectronics, photonics, chemical sensing, and display technology. The initial excitement over the prospect of a wide variety of electronic properties derived from variations in molecular structure has not been diminished by subsequent research, and the growth potential of molecular circuit components remains. Many paradigms have been explored for both single-molecule and ensemble electronic junctions, and many of the factors which control junction electronic behavior have been identified. However, the strong motivation for rapid exploration of a new area has in some cases worked against the need for careful, systematic science. As a result, we have not reached a consensus on a robust and reproducible junction design, and we are a long way from the massively parallel, very high yield fabrication that is essential in the microelectronics industry. In our opinion, the essential ingredients of robust molecular junctions are covalent, thermally stable bonds between contacts and molecules, strong electronic coupling between contacts and molecular components, and sufficiently large area to permit both spectroscopic monitoring and integration with conventional microelectronics. The first decade of research on molecular junctions has demonstrated the possibilities for major advances in both science and technology, but much of the hard work remains before molecular junctions are understood and applied in commercially viable manifestations. Perhaps we could consider the current juncture to be the "end of the beginning," where new devices, phenomena, and electronic functions have been identified validating the promise of molecular devices in electronics; however at this point, we also need to embrace rigorous, systematic investigations to understand electron transport in molecular junctions and to eventually design and fabricate new and reliable devices with useful electronic functions.

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