

# Molecular Electronics

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## Abstract

Molecular electronics describes the field in which molecules are utilized as the active (switching, sensing, etc.) or passive (current rectifiers, surface passivants) elements in electronic devices. This review focuses on experimental aspects of molecular electronics that researchers have elucidated over the past decade or so and that relate to the fabrication of molecular electronic devices in which the molecular components are readily distinguished within the electronic properties of the device. Materials, fabrication methods, and methods for characterizing electrode materials, molecular monolayers, and molecule/electrode interfaces are discussed. A particular focus is on devices in which the molecules or molecular monolayer are sandwiched between two immobile electrodes. Four specific examples of such devices, in which the electron transport characteristics reflect distinctly molecular properties, are discussed.

## 1. INTRODUCTION

Molecular electronics describes the field in which molecules are utilized as the active (switching, sensing, etc.) or passive (current rectifiers, surface passivants) elements in electronic devices. In molecular electronics devices, molecules either serve as conduits of electrical current or influence the charge transport properties of the electrodes to which they are connected. Glucose sensors that are based upon the electrochemical detection of glucose via the action of the electrode-bound enzyme glucose oxidase constitute one practical example of molecular electronics (1). For that case, the sensor is designed to take advantage of a uniquely molecular property that would be challenging to replicate using solid-state components. In many other examples, the molecules themselves are designed to emulate the properties of traditional solid-state devices. Classic examples include the molecular current rectifier that was proposed in 1974 by Aviram & Ratner (2) or the molecular-based tunnel junction (resistors) that Polymeropoulos & Sagiv (3) first investigated 30 years ago.

The field of molecular electronics has significantly expanded over the past decade, and a subset of that activity is the subject of this review. This increased effort has been driven by a number of factors. First, there has been significant interest in finding electronic devices that can offer potentially viable additions or alternatives to the complementary metal-oxide-semiconductor (CMOS) technologies that comprise the heart of modern integrated electronic circuitry. For a number of reasons discussed herein, molecules offer at least an interesting alternative, if not yet a viable one. Second, semiconductor manufacturing methods and materials synthesis techniques have been adapted in ways that now allow for the nearly routine fabrication of a host of exotic and interesting devices, such as single-molecule devices (4) or carbon nanotube/molecular junctions (5, 6). Third, surface chemistries that can be harnessed to prepare very high-quality molecular films on a host of metal (7) and semiconducting (8) substrates (9) have been developed, as have the analytical techniques necessary to characterize such molecular films. This has permitted the relatively high-yield fabrication, characterization, and testing of many different types of molecular electronics devices (10). Fourth, a number of organic chemists have begun to design molecular-based switches, motors, and other mechanical machines that are specifically intended for solid-state demonstrations (11). Such unique molecules are providing a fascinating chemical motivation for the pursuit of molecular electronics devices. Finally, the integration of molecules, nanowires, and other nanoscale structures has led to a number of demonstrations of new and potentially useful applications (12, 13).

Molecular electronics is a very large field, components of which have been the subject of recent and excellent reviews, several of which are cited throughout this paper. This article does not attempt to replicate that work. Instead, I focus on the experimental and fabrication aspects of molecular electronics devices that are largely designed to exploit properties that can be tuned via control over molecular structure. In other words, I want to review what is known about designing devices in which, through a charge transport characterization of the device, one can “see” the molecule. Although I cover a few device platforms, my focus is largely on molecules that are sandwiched between two fixed electrodes, because this arrangement constitutes perhaps the most challenging platform for seeing the molecule, and I believe it highlights both the best and the worst characteristics of molecular electronics. My interest is in covering certain issues at a fundamental level. In some cases, molecular electronics devices replicate known solid-state device properties, and this is useful primarily because solid-state devices provide performance metrics against which molecular electronics devices can be measured. However, in other cases, the observed device properties are uniquely molecular in nature, and this is where the richness of molecular electronics emerges. Even within this theme, this review is not comprehensive. Theoretical aspects of molecular electronics (14) are not reviewed here.

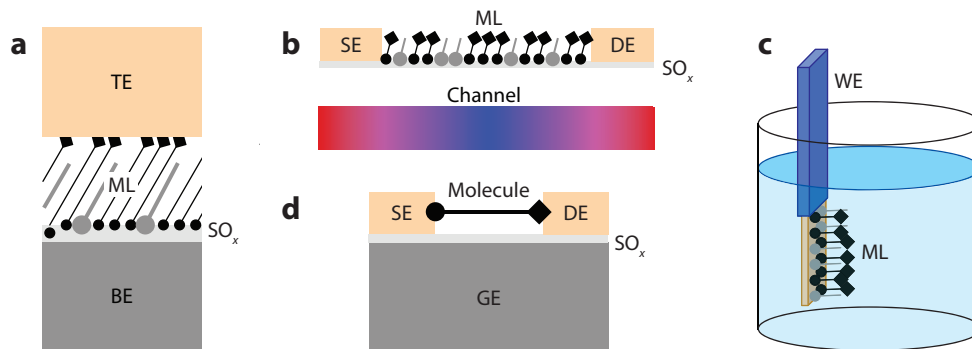
This review begins with a brief overview of some general molecular electronics device structures. I then discuss how each of the components within such constructs can influence the measured transport properties, device robustness, etc. For example, I review what has been found in terms of how the electrode choices can influence the molecular properties and, conversely, examples of how the molecular film itself can influence the electrical and chemical properties of the electrodes. I also cover much of what has been learned in terms of the molecule/electrode interface. Included in these discussions is an overview of certain fabrication approaches that have been developed specifically for molecular electronics. Such methods take into account the relatively fragile nature of molecular monolayers by avoiding thermally or chemically harsh processing steps. Finally, I discuss four specific examples of devices, ranging from tunnel junctions to switches, that have been demonstrated over the past few years to yield distinctly molecular properties. These devices provide a gauge for measuring the progress and assessing the potential of the field. I conclude with some thoughts as to where this field is headed in the near future.

## 2. OVERVIEW: MOLECULAR ELECTRONICS DEVICE CONSTRUCTS

Molecular electronics devices fall into four general categories (**Figure 1**), which I discuss below.

### 2.1. Two-Terminal Molecular Junctions

A molecular monolayer is sandwiched between two solid electrodes. This is the most common construct and is used for molecular tunnel junctions, diodes (15), and some switches. There



**Figure 1**

Common molecular electronics device architectures. (*a*) Two-terminal molecular junction, with a molecular monolayer (ML) sandwiched between a top electrode (TE) and a bottom electrode (BE). For this device, the ML can influence the conductivity between the TE and the BE. (*b*) Two-terminal channel device with the source (SE) and drain (DE) electrodes labeled. Here the molecules can influence the conductivity of the semiconducting channel region. The semiconductor is shown with a color gradient to represent potential impurity doping differences between the source and drain electrical contacts and the ML-coated channel region. (*c*) Three-terminal electrochemical devices, shown with an ML coating the surface of the working electrode (WE), which is immersed in solution. Counter and reference electrodes are not shown. This is a standard analytical device and can provide useful, quantitative information about an ML that complements what can be measured by use of the other device architectures. (*d*) Three-terminal field-effect, single-molecule (or few-molecule) device. Various electrodes, including a gate electrode (GE), are labeled. The devices in panels *a–c* utilize a molecular monolayer that is shown here, for the sake of generality, to be a multicomponent ML (gray and black sticks). The devices in panels *a*, *b*, and *d* are shown with an insulating dielectric layer (SO<sub>x</sub>), which is required for the device in panel *d* but optional for the devices in panels *a* and *b*. The various electrodes in any of the devices may or may not be of similar materials.

exist a tremendous number of variations on this theme, based upon different electrode materials, different molecules, and different methods for depositing both the molecular monolayer and the top electrode. As examples, the molecular monolayer may be physisorbed [e.g., as a Langmuir monolayer (16)] or chemisorbed [e.g., as a self-assembled monolayer (17)]. Molecular monolayers that are probed by use of scanning tunneling microscopy (18, 19) fall into this category, as do crossbar molecular electronics memories (20, 21) and crossbar logic circuits (22). The heart of this review focuses on this type of device, although I do not spend much time discussing devices in which one electrode is a scanning probe microscope tip.

## 2.2. Two-Terminal Channel Devices

In two-terminal channel devices, the molecular monolayer is assembled onto the channel region of a field-effect transistor. The molecular monolayer may exert a gating influence on the source drain conductivity (23) or may modify the mobility of the carriers in the source drain channel via passivating the surface of that channel (24). Occasionally a gate electrode is utilized with this type of device. Nanowire (25) and nanotube (26) chemical and biomolecular sensors are based upon this construct.

## 2.3. Three-Terminal Electrochemical Devices

In three-terminal electrochemical devices, the molecular monolayer is assembled onto the surface of the working electrode in an electrochemical cell (13, 27, 28). Standard electrochemical measurements are then utilized to interrogate the molecular monolayer.

## 2.4. Three-Terminal Field-Effect Devices

Here, one or a small number of molecules bridge a nanometer-scale gap that separates source and drain electrodes. The conductance of the junction may be modulated with a third gate electrode. The source and drain electrodes are typically constructed from various metals (29–31) or can also be carbon (32) nanotubes.

## 3. TWO-TERMINAL MOLECULAR JUNCTIONS

Two-terminal molecular junctions are the prototype molecular electronics device, reflecting both the phenomenology and the science within the field. They comprise the most investigated of all molecular electronics devices, and they have been plagued by a literature of seemingly contradictory results. Such contradictions have been due, in large part, to the fact that virtually every group in the field is making different device types. For example, issues such as the composition, smoothness, dimensions, and doping of the bottom electrode material can profoundly influence the device characteristics. In terms of the molecular monolayer, the choice of molecule, the packing density (33, 34) and structure of that monolayer, and the chemical nature of the molecule/electrode interfaces (35) are all important variables. Other than the molecules themselves, the most widely investigated component is the top electrode. Here, electrode composition and dimension, as well as the manner in which the electrode is deposited onto the molecular monolayer, are important. The relative weight of almost all of these dozen or so parameters is not always clear and can even vary from system to system. By contrast, for a typical solid-state device such as a field-effect transistor, the rules for achieving a robust and reproducible operation are well-established, and small, atomic-scale variations in such devices are not likely to significantly influence the device

properties. Answering even the most basic molecular electronics questions, such as, What is the conductance through a single alkane molecule?, has proven to be quite challenging (4, 36). In fact, advances in the field may often appear to be based more upon a phenomenological understanding than upon quantitative science. Thus, it is no wonder that researchers have continued to return to even the simplest of all two-terminal molecular junctions—linear alkanes sandwiched between two metal electrodes (37)—and to learn new science (38) a few decades after some of the basic rules for transport through such systems were established (39).

A good analogy for the field of molecular electronics is the case of taking a canoe across a large lake. Anyone who has done this knows that you can paddle for a long time, and yet the opposite shore still appears quite distant. However, when you look back, you realize you have also come a long way.

#### 4. BOTTOM ELECTRODE MATERIALS

By far the most common choice of bottom electrode material for two-terminal molecular junctions is Au (and occasionally Ag). This may be attributed to the ease with which self-assembled molecular monolayers (SAMs) may be formed on Au or Ag through the use of thiol or disulfide functionalities (7). Various device architectures, ranging from the nanopore structures developed by Reed, Tour, and colleagues (40) to the Hg drop electrode systems first developed by Majda's group (41), have been utilized to interrogate such SAM-based junctions. However, even for these systems, minor variations in surface roughness and other small imperfections can have dramatic consequences. For example, Weiss et al. (42) found that electrical current through SAMs prepared on as-deposited Ag surfaces was often orders of magnitude higher than that found on atomically flat (templated) Ag surfaces. In addition, devices that were prepared from as-deposited surfaces exhibited higher rates of failure.

A second electrode system that has begun to achieve significant attention is that of Si. Si provides an attractive choice for a bottom electrode for molecular electronics because (a) it is compatible with more standard solid-state devices, (b) atomically flat Si substrates (for at least some types of Si) may be readily prepared by use of standard processing or chemical methods, (c) the native oxide of Si provides for a stable and reproducible tunnel barrier, and (d) the electronic properties of the Si wafer may be broadly controlled via impurity doping. Other electrode materials, such as graphite (or graphene sheets) (43), have also been explored for molecular electronics junctions, but they are not discussed here.

The following story highlights the importance of the bottom electrode. My own group began utilizing an Si/molecule/metal junction construct almost a decade ago (44). The Si electrodes were patterned from a polySi film that was prepared in house. As is the case for metal bottom electrodes, the use of very flat, low-defect Si electrodes was critical for achieving a high yield of working devices, with uniform and reproducible performance metrics. Our particular two-terminal junctions utilized molecules that ranged from simple alkyl amphiphiles to electrochemically driven, bistable molecular mechanical switching molecules (discussed in more detail in Section 7.4) called [2]catenanes (45). Reversible, hysteretic switching responses that could be attributed as arising from electrochemical switching of the [2]catenanes were observed only when Si [and, later, carbon nanotube (5)] bottom electrodes were utilized. Those molecular-based switching responses had several characteristics. Non-bistable [2]catenanes and amphiphilic alkyl molecules did not switch. The recorded bistable switching was thermally activated, the switching amplitude was relatively low (open/closed current ratios were  $\sim 3$ – $5$ ), the switching was current driven, the switching occurred over a voltage range of  $\sim 0.25$  V, and the switches could be cycled typically a few tens of times before failure.

A metal (Al or Pt)/molecule/metal configuration was also explored for those same bistable switching molecules. However, for that construct, the measured response was completely different. A very sharp, much larger amplitude, field-driven, nonthermally activated hysteretic switching response dominated the device performance, and that switching mechanism could be cycled many times (47).

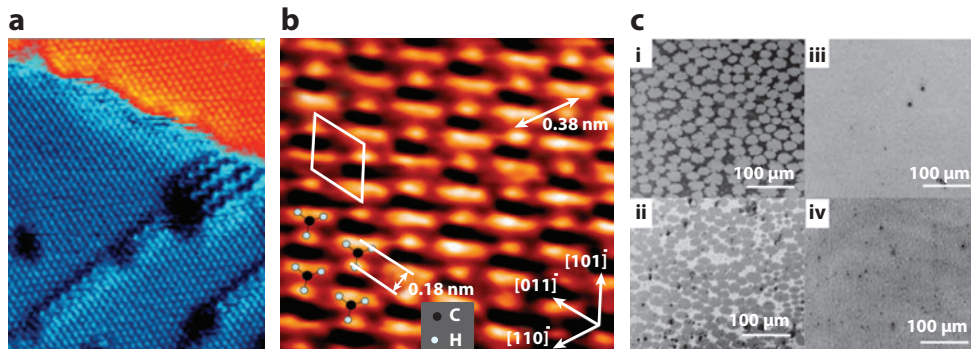
This difference between how Si/molecule/metal and metal/molecule/metal junctions performed (when the same molecules and top electrode materials were used) caused quite a bit of confusion [and controversy (46)] that took some time to resolve. This difference also highlights, again, how seemingly subtle changes in device design can lead to huge changes in device response.

Williams's group at Hewlett-Packard later showed the mechanism of the metal/molecule/metal junction switching response to be molecule independent (47) and to originate from events that occurred in localized hot spots across the junction (48). In fact, the molecular film could be replaced with an inorganic insulator film, and similar switching responses occurred. Yang and coworkers (49), using Pt/TiO<sub>2</sub>/metal junctions, recently showed that the switching mechanism involves changes to the electronic barrier at the Pt/TiO<sub>2</sub> interface owing to the drift of positively charged oxygen vacancies under an applied electric field. The result is the reversible formation of conducting channels that short-circuit the electronic barrier to current flow, thus leading to a very sharp, large-amplitude reconfigurable switch (49). The switching mechanism for the semiconductor/molecule/metal junction was later demonstrated as arising from the switching of the bistable molecular mechanical switches, as initially hypothesized (see Section 7.4).

## 5. MOLECULAR MONOLAYER FILMS IN MOLECULAR ELECTRONICS DEVICES

This section provides a brief overview of the various classes of molecular monolayers that are utilized for molecular electronics devices, with an emphasis on the three most common classes of monolayers: thiols on Au(111), alkyl groups on Si(111), and Langmuir-Blodgett (LB) monolayers on various bottom electrode materials (**Figure 2**). I then discuss the relative merits of each of these systems in turn—especially with regard to their applications to particular molecular electronics device types.

Molecular films for molecular electronics devices are most often monolayers that are covalently bonded to Au, although other metals, such as Ag (42), Ti, or Al (50), are occasionally utilized. SAMs of alkyl thiols bonded to the lowest energy surface of gold, Au(111), have provided the model system for chemisorbed monolayers on metal surfaces. Chemisorbed monolayers on semiconductor surfaces are relatively less studied, but especially for the case of Si surfaces, there is a significant literature on the subject (51, 52). Organic groups bonded directly via Si-C covalent linkages to nonoxidized Si(111) surfaces have been a model system (53), although there are only a few examples of molecular electronics devices based upon this motif (24, 54, 55). The Si(100) surface is both difficult to prepare as an atomically flat surface, and H-terminated Si(100) [H-/Si(100)] is less stable toward oxidation than is H-/Si(111) (56). However, Si(100) is by far the most technologically relevant Si surface. Nevertheless, Si(100) has received only a small amount of attention as a platform for the chemisorption of organic molecules (33, 34, 57–60). Other types of semiconductors, such as GaAs, are much less studied as molecular electronics substrates (61). Molecules chemisorbed onto a native-oxide-passivated Si surface (via Si-O-C linkages) form disordered and imperfect films relative to SAMs on Au and are typically not used for two-terminal molecular junctions or for three-terminal electrochemical cells. For two-terminal molecular junctions, a few research groups have used monolayers on oxide-passivated Si, prepared by the LB



**Figure 2**

Molecular monolayer films used in molecular electronics devices. (a) Dodecanethiol self-assembled monolayer on Au(111). This  $250 \times 250 \text{ \AA}$  scanning tunneling micrograph reveals both the level of ordering that can be achieved in such films as well as the various types of defects. The difference between the blue layer and the red layer is an atomic step on the Au(111) surface. Courtesy of P.S. Weiss. (b) Methylated Si(111) surface, as imaged by scanning tunneling microscopy at 4 K. At 77 K, the trigonal symmetry of the methyl groups is unresolved because they are freely rotating at that temperature. This surface is stable against oxidation, and methylation can significantly improve the carrier mobility of very thin (10–20-nm-thick) Si(111) on insulator films. Adapted from Reference 70. (c) Brewster angle micrographs: [2]pseudorotaxane molecular switch Langmuir monolayers on water (*i* and *iii*) and those same monolayers transferred as Langmuir-Blodgett films (*ii* and *iv*) onto a glass surface. Langmuir monolayers and Langmuir-Blodgett films can often exhibit domain structure, such as that seen in *i* and *ii*, which can influence the properties of devices made from those monolayers. One approach that may prevent the formation of such domains is the use of high-ionic-strength subphases—a method that was used here to transform the structured film (*i*) into an unstructured film (*ii*). Adapted from Reference 16.

technique (22, 62, 63). Those monolayers can be very high in quality, and the LB method provides a degree of control over monolayer structure and packing density that is not achievable with covalently bonded films. For such devices, the  $\sim 1\text{-nm}$ -thick native-oxide layer provides a hydrophilic surface and a tunnel barrier that separates the molecular monolayer and the underlying electrode. It is instructive to compare and contrast each of these types of monolayers because each has its own advantages and disadvantages for molecular electronics.

### 5.1. Covalently Attached Monolayers on Au(111)

For Au or Ag surfaces, alkyl thiols with a carbon length longer than 9 form SAMs. This implies that the monolayers have a large degree of order that arises from both the underlying structure of the Au surface [commonly Au(111)] as well as interactions between adjacent alkyl groups within the film. The best models indicate that standard, SAM-forming alkyl thiols occupy threefold hollows on Au(111), with a thiol-thiol separation distance of  $\sim 5 \text{ \AA}$ . Detailed descriptions of this surface structure can be found elsewhere (64). The van der Waals diameter of methyl groups within alkyl chains is estimated to be  $4.5\text{--}5 \text{ \AA}$ —and so a closest packed arrangement of alkyl thiols on the Au surface involves both registry with the underlying Au(111) surface and van der Waals interactions between adjacent chains. As a result of these energetics and significant developments in terms of chemical and characterization methods (65), it is possible to prepare extremely high-quality SAMs on Au surfaces that are effectively free of pinhole defects.

Single-component SAMs on Au are largely composed of alkyl thiols, and associated molecular electronics applications have been limited to two-terminal tunnel junctions. Adding additional

functions while maintaining a high coverage requires the use of two-component SAMs. The molecular species of interest is prepared with a pendant thiol group and then mixed with a diluent thiol to form the SAM. The two components are often designed so that the molecule of interest extends above the diluent thiol on the surface and so is accessible for subsequent chemistry (discussed below) or for interrogating with scanning probe measurements. In other cases, the molecule of interest is embedded within a monolayer formed from a larger molecule—a strategy designed to protect the molecules of interest from top electrode deposition (19, 40).

An interesting question surrounding the properties of molecular monolayers bonded to metal surfaces is whether (*a*) the molecules influence the work function of the metal or (*b*) whether the metal influences the highest occupied molecular orbitals of the molecules. Although situation (*a*) can be potentially useful for improving the charge injection across metal/organic semiconductor interfaces, situation (*b*) can potentially mask the electronic transport properties of the surface-bound molecules, especially in dry environments. UV photoemission spectra taken from a number of ( $\pi$ -conjugated) molecular monolayers on various metal electrodes indicate that the binding energy of the highest occupied  $\pi$ -state, as well as the work function of the modified surface, is more strongly dependent on the molecular film than on the elemental composition of the metal electrode (66). However, it is not yet clear how to harness this effect to produce energy-level alignment between metal electrodes and organic semiconductors (67).

## 5.2. Covalently Attached Monolayers on Si

The nonoxidized Si(111) surface provides a template for molecular monolayer formation (68) that is significantly more sterically restricted than in the case of Au(111). The distance between Si atop sites on an unreconstructed  $1 \times 1$  Si(111) surface is 3.8 Å. The van der Waals diameter of a methyl group is 2.3 Å, and so complete methylation of Si(111) [to form  $\text{H}_3\text{C}/\text{Si}(111)$ ] is possible (69, 70). Although the methyl group is effectively inert for subsequent chemical steps,  $\text{H}_3\text{C}/\text{Si}(111)$  is an interesting surface for electronics—primarily because of the influence of the methyl passivation on the underlying substrate.  $\text{H}_3\text{C}/\text{Si}(111)$  surfaces exhibit long-term protection against oxidation, and the  $\text{H}_3\text{C}/\text{Si}(111)$  surface is free of dangling bonds and associated surface charges. These characteristics mean that, even for very thin (10–20-nm-thick) single-crystal  $\text{H}_3\text{C}/\text{Si}(111)$  surfaces [starting from very flat silicon-on-insulator (SOI) substrates], the underlying Si epilayer exhibits near-bulk-like carrier mobilities, as measured by Hall probes (24). This is consistent with optical measurements of low carrier recombination velocities at such surfaces (53). However, for alkyl groups larger than methyl, steric interactions limit the molecular coverage of Si atop sites to significantly less than 100% (71, 72).

## 5.3. Monolayers Prepared by the Langmuir-Blodgett Method

A third method for monolayer formation that is used in molecular electronics devices is the LB method (73). The LB method requires spreading the molecular film at an air/water interface and then compressing that monolayer to a desired area/molecule prior to transferring the film to the solid substrate. The low-throughput aspect of this method precludes its use as a manufacturing technique, and its applications are limited to amphiphilic molecules. However, as a scientific tool, it has tremendous flexibility. The ability to control the area per molecule is, by and large, independent of substrate, and this approach allows tightly packed, single-component Langmuir monolayers of quite complex and highly functional molecules to be prepared. Effectively defect-free monolayers on (very smooth) lithographically patterned substrates such as poly-Si (44) or Si(100)-on insulator (21) or even single-walled carbon nanotubes (5) are possible. Bilayer and other multilayer films are



also readily prepared. LB films often exhibit a rich phase behavior as a function of changing area per molecule, temperature, or other parameters (73). This can add unwanted complications, but fortunately methods such as Brewster angle microscopy, scanning probe microscopy, and other techniques can be harnessed to investigate the structure of the monolayer film both before and after transfer from the water surface to the solid substrate (74), and parameters such as the ionic strength of the water subphase can often be tuned to minimize phase separation.

#### 5.4. Increasing the Function of Molecular Monolayers

It is often desirable to investigate a variety of different molecular structures for molecular electronics applications. These structures may impart redox or biochemical activity or some other interesting property. Although the LB method allows for the formation of such films, those films are delicate (they are only physisorbed), and the amphiphilic criterion limits the permitted molecular flexibility. For covalently bonded monolayers, the preparation of multicomponent monolayers provides a straightforward avenue toward adding increased monolayer function, but each film (and perhaps each molecular component within each film) must be separately prepared and characterized, and this can prohibit large-scale investigations of molecular structure/monolayer properties. More versatile and convenient approaches have begun to appear in the literature, with applications to monolayers covalently attached to both metal and semiconductor surfaces. An example of such an approach is to prepare a mixed monolayer in which one component provides a chemical handle for attaching the redox or biochemically active molecule. Examples include mixed azide-terminated monolayers on Au (75) or Si (76). The function of such surfaces can be expanded by reacting the azide terminus with an acetyl-containing molecule to produce a 1,2,3-triazole via click chemistry. An alternative is to employ Diels–Alder cycloadditions following the electrochemical activation of surface-bound benzoquinone—again a chemistry that has been demonstrated on both Au (77) and nonoxidized Si (78) surfaces. To date, the coverages achieved from such approaches are low, and so such monolayers have found uses in two-terminal channel devices (60) and in three-terminal electrochemical devices (77), but not in two-terminal molecular junctions (other than those interrogated by scanning probe microscopy). However, as described in the next section, researchers are developing a number of new methods that may eventually permit the deposition of top electrode materials onto less-than-perfect molecular monolayers.

### 6. TOP ELECTRODE MATERIALS AND METHODS

Molecular electronics junctions are typically not robust—especially when compared with solid-state devices. Whether the lack of robustness is an intrinsic characteristic of molecules, or whether it is related to some aspect of the devices themselves, is not well understood. Certainly organic polymer-based electronics can be very robust, and so it may be that molecular electronics devices can be made robust as well. A leading culprit with respect to device robustness is likely the top electrode and the associated processes by which it is deposited (79). The top (usually metal) electrode in two-terminal molecular junctions has historically been the most ill-understood aspect of such devices. Deposited metal can react with the monolayer to form metal carbides or the metal can penetrate through the monolayer to cause electrical shorts, or the oxides on the metal surface may provide charge traps or other chemical reaction sites that degrade device performance. Furthermore, once the electrode is deposited, the molecular monolayer and the top electrode/molecule interface are hidden from many of the same characterization methods that are utilized to interrogate the monolayer and the bottom electrode/molecular interface. In short, the top electrode has introduced a tremendous amount of phenomenology into the field. However, improved methods

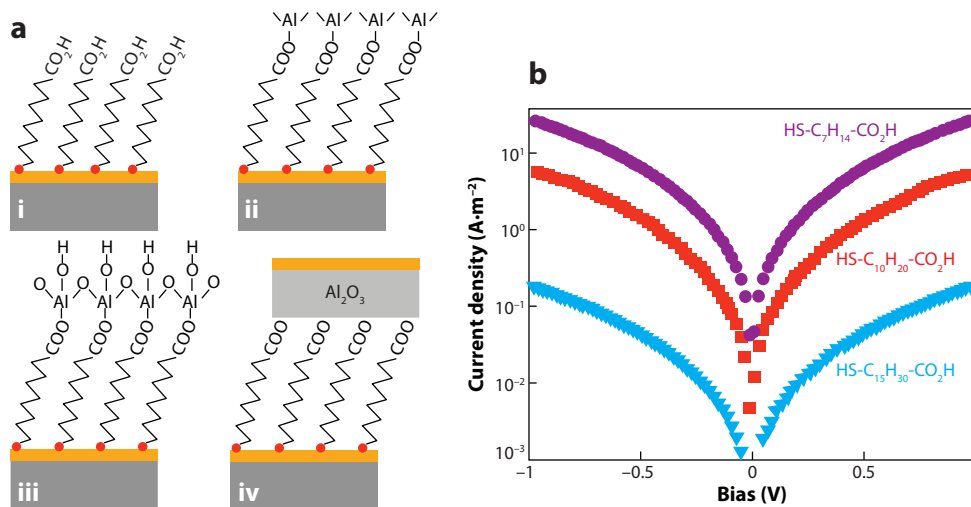
for electrode deposition, and methods for interrogating the molecular film once that electrode has been deposited (80, 81), have greatly improved over the past several years.

The molecular monolayers within molecular electronics devices often contain small defects, the consequences of which can be large. The defects can be intrinsic to the film. For example, pinholes can permit a deposited top electrode material to penetrate through the monolayer film and electrically short the device. Even if the monolayer is perfect, a large molecular tilt angle with respect to the surface normal will result in overexposure of the monolayer to the top electrode material, which can have aberrant influences on device performance. A host of other defects are also possible. The structure and packing of the molecules that compose the monolayer and the smoothness of the bottom electrode surface are also important parameters for optimization, even prior to consideration of how the top electrode is deposited.

Several solutions, most of which have focused on establishing reliable contacts, have emerged, but often at the cost of introducing fabrication methods that are not compatible with standard semiconductor processing methods. An early solution was the nanopore junctions reported by Reed, Tour, and colleagues (40). These researchers utilized a vapor-deposited Ti top electrode, and the nanopores were designed so that the monolayer area was smaller than the average area per pinhole defect. As a result, many nanopore devices did not exhibit electrical shorts. Evaporated Ti films are discussed in more detail below. More recently, a couple of research groups have developed methods that allow for an intact, top metal electrode to be deposited onto a molecular monolayer under gentle conditions; these methods have been demonstrated for large-area monolayers. The general idea is to deposit the electrode, through use of some metals deposition scheme, onto one substrate. The electrode is lifted off so that it floats on a water surface and is then transferred, in a way similar to how a Langmuir monolayer is transferred, onto the device. Vilan & Cahen (82) reported using this method to fabricate large-area two-terminal molecular electronics junctions, and Melosh's group (83) utilized a significantly more robust variant of this theme to transfer a whole top set of 10-micrometer-wide electrodes to form a crossbar circuit. In both cases, SAMs on Au were utilized as the molecular monolayer. Majda and colleagues' (41, 42) Hg drop electrode approach, mentioned above, constitutes a variant on this theme.

Another approach toward establishing top contacts to SAMs on Au has been to deposit some interfacial layer between the molecular monolayer and the top electrode. For example, Akkerman and coworkers (84) utilized a conducting polymer as an interface between a top, evaporated metal electrode and a SAM on Au. They demonstrated a high yield of relatively large (10-micrometer-diameter and larger) devices that were designed to act as alkyl thiol tunnel junctions. An extremely promising approach, reported by Preiner & Melosh (85), has been to prepare monolayers with carboxylate groups at the air/monolayer interface (**Figure 3**). Those carboxylate groups are then utilized to promote the atomic-layer deposition of an  $\text{Al}_2\text{O}_3$  dielectric. Metal electrodes are deposited on top of this dielectric. Nonshorting tunnel junctions as large as  $9 \text{ nm}^2$  were reliably fabricated and tested (**Figure 4**).

Many reports on molecular electronics devices utilize Ti top electrodes that are deposited, via sputtering or electron-beam deposition, on top of the molecular monolayer. Although methods such as X-ray photoelectron spectroscopy have been employed for several years to study this Ti/molecular interface (86, 87), a number of improved versions of traditional techniques such as photoelectron spectroscopy (88), infrared absorbance/reflectance spectroscopy (89, 90), and Raman spectroscopy (91) have allowed researchers to interrogate specific molecular spectroscopic fingerprints and how they are influenced by the deposition of a metal top electrode. There is now a significant amount of evidence that metals evaporated on top of organo-thiol SAMs on Au damage the SAM (82, 92–94) either by penetration of the evaporated metal layer into the molecular film or by direct reaction of the metal atoms with the molecules. However, this is not the complete story.



**Figure 3**

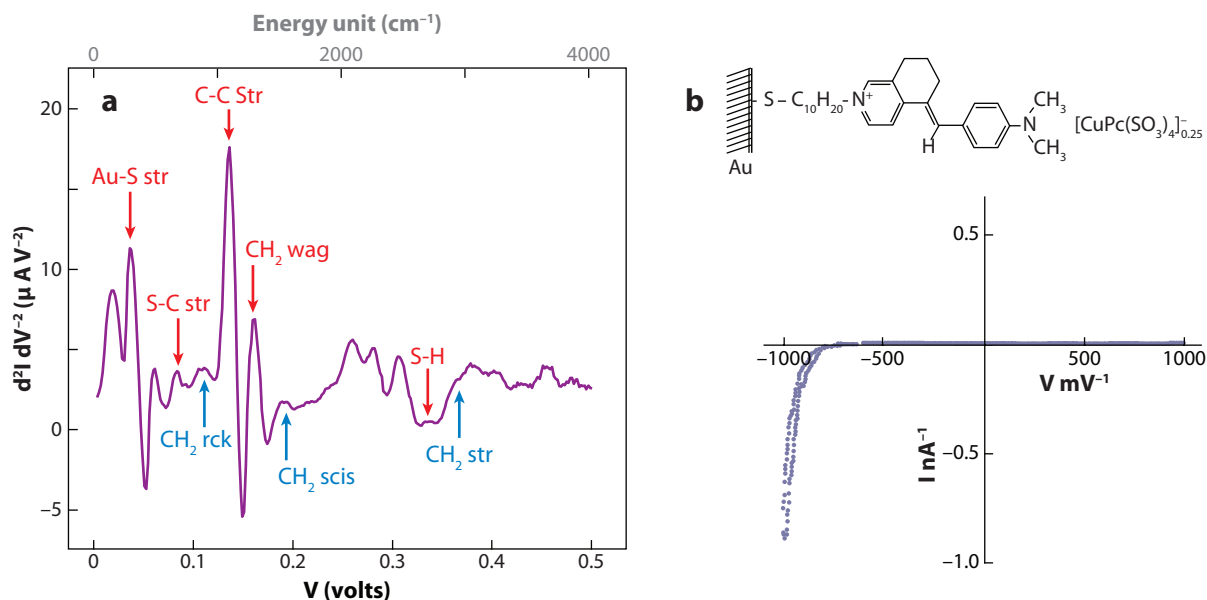
Top electrode deposition method developed by Preiner & Melosh (85). (a) Scheme for the atomic-layer deposition of an insulating and uniform  $\text{Al}_2\text{O}_3$  dielectric film, beginning with a self-assembled monolayer of a thiol-terminated alkyl carboxylate on Au (i). Trimethylaluminum is deposited on this monolayer (ii) and then reacted with water vapor (iii). The process is repeated until a dielectric film of a (controllable) thickness of 1–4 nm is grown (iv). (b) Current density versus applied bias for three large-area (0.03–0.05 mm<sup>2</sup>) films of molecular monolayers, onto which a 2-nm-thick  $\text{Al}_2\text{O}_3$  dielectric film was grown via atomic-layer deposition. These are robust tunnel junctions: The current density decreases exponentially with alkyl chain length and is temperature independent.

There is also compelling evidence that, for other types of molecular monolayers [certain LB films (90, 91) and certain SAMs (89)], the deposition of Ti electrodes leaves the monolayer relatively intact. Although there may be some subtle factors at play, such as the background pressure in the metal deposition chamber, the key parameters appear to be the packing density and molecular orientation within the monolayer, as well as the structure of the molecule at the air/molecule interface that is presented to the evaporated metal. Nevertheless, reactions of the molecule with the top metal electrode that occur some time after deposition of the electrode (for example, during device operation) may be a key factor that limits device robustness (91).

In my mind, the method of Preiner & Melosh (85) that enables the growth of an inorganic dielectric via atomic-layer deposition on presenting carboxylate groups at the molecule/air interface is the most promising (although still largely untested) approach for the production of top metal electrodes that are high-quality contacts, are compatible with many processing steps, can scale to the limits of lithographic patterning, and can potentially lead to more robust molecular electronics devices.

## 7. MOLECULAR PROPERTIES IN ELECTRONIC DEVICES

The central motivation that has driven the science of molecular electronics has been to find ways to exploit the beauty and complexity of the molecular world within solid-state settings. For example, the molecular diode hypothesized by Aviram & Ratner (2) constituted a proposal to harness the unique electronic structure of charge-transfer molecules comprising  $\sigma$ -bridged electron-donor and electron-acceptor groups (denoted a D- $\sigma$ -A arrangement). The idea was that the molecular electronics device performance metrics could be optimized in feedback with synthetic control over



**Figure 4**

Molecular signatures from the current-voltage characteristics of two-terminal (passive) molecular junctions. (a) Inelastic tunneling spectra from a C<sub>8</sub>-dithiol that bridges between two Au electrodes within a nanopore structure, collected at 4.2 K. An energy axis in  $cm^{-1}$  is provided at top, and assignments for several of the observed vibrational modes are indicated (str, stretching; rck, rocking; scis, scissoring; wag, wagging). Courtesy of Mark Reed. (b) A donor- $\pi$ -bridge-acceptor molecular rectifier, exhibiting a rectification ratio of  $>10^3$ . The bottom contact was an Au electrode, and the top contact was a metal scanning probe tip. Adapted from Reference 105.

the structure of the D- $\sigma$ -A molecule. This is similar to how materials are rationally engineered through doping or other stoichiometric control to produce highly designed solid-state diodes. For two-terminal channel devices, three-terminal electrochemical devices, or devices in which a scanning probe microscope constitutes one of the electrodes, there are many examples in the literature of devices that successfully utilize and harness distinctly molecular properties. However, for devices in which the molecules are sandwiched or bridge between two immobile electrodes, identifying device properties that are distinctly molecular, and that can be rationally altered via chemical synthetic modification of the molecular component, has been challenging. Nevertheless, over the past decade, several excellent examples have appeared, and they provide instructive lessons of progress in the field. In this section, I briefly review four of these cases: tunnel junctions exhibiting inelastic tunneling spectra, molecular rectifiers, bistable molecular mechanical switches, and single-molecule transistors exhibiting a Kondo resonance.

### 7.1. Inelastic Tunneling Through Alkane Thiol SAMs in Molecular Electronics Junctions

The simplest two-terminal molecular junction is a tunnel junction device comprising an alkyl thiol SAM formed onto a bottom Au electrode, with various top electrodes. After many years of work by a number of groups, this has become a standard device for testing two-terminal platforms. Indeed, most of the above-mentioned methods for establishing top electrode contacts to molecules were demonstrated as reproducing reliable tunnel junctions (4, 84, 85). The current through a

tunnel junction device has a number of characteristics, and only some of the most practical aspects that are related to device construction and testing are mentioned here. Detailed descriptions of various tunneling-based transport mechanisms may be found elsewhere (82, 83). For different tunnel junctions, investigated at a constant applied voltage, the current decreases exponentially with increasing thickness of the tunnel barrier. This means that as the chain length of alkyl thiols is increased, the current density decreases exponentially—dropping a factor of approximately 10 for every additional 1 Å of tunnel barrier width. In addition, a fingerprint signature of the tunneling mechanism that distinguishes it from other mechanisms, such as hopping-based conduction, is that tunneling is independent of temperature.

In most cases, tunneling current through a two-terminal molecular junction does not yield molecule-specific information, other than perhaps through the correlation of the tunneling current with the thickness of the molecular monolayer. However, as researchers have become more adept at all aspects of fabricating molecular junctions, the reproducibility and uniformity of the resultant devices have allowed for the uncovering of fine features within the differential conductance spectra ( $d^2I/dV^2$  versus  $V$ ) of such junctions. At cryogenic temperatures (generally <20 K), differential conductance plots can yield information relevant to inelastic tunneling processes, which, in turn, yield signature molecular information (95). Inelastic tunneling spectroscopy (ITS) can yield the vibrational spectra of molecules (96). Unlike for infrared or Raman spectroscopy, there are no strict selection rules for ITS, but there are selection preferences (97), and the result is a distinctly molecular signature embedded within the current-voltage transport characteristics of the devices. As described above, a number of groups have measured molecular vibrational spectra from molecular monolayers sandwiched between two electrodes. In addition, ITS spectra on single molecules using cryogenic, scanning tunneling microscopy techniques have also been reported (98). The extraction of similar spectroscopic information from two-terminal molecular junctions that contain statistical numbers of molecules is a strong testament to the control that researchers have achieved over many of key molecular electronics device fabrication issues—at least for the simplest devices.

## 7.2. Highly Rectifying Molecular Junctions

Aside from alkane thiol tunnel junctions, no molecular electronics target has received more attention than molecular rectifiers, and the pathway toward achieving true molecular rectification is an illustration of science eventually winning out over phenomenology. Almost 45 years ago, Meinhard (99) reported (probably incorrectly) on rectifying junctions in which the rectification originated from transport through adjacent layers of electron-donor and electron-acceptor molecules. Aviram & Ratner's (2) proposal was to include both donor and acceptor groups within the same (D- $\sigma$ -A) molecule and to bridge that molecule between two electrodes. Over the years, many research groups have engaged in this field (15), and there have been a host of claims of molecular rectification, many of which have been subsequently cast into doubt. These difficulties have arisen because almost any asymmetry in a molecular junction device can generate rectification. For example, asymmetry can arise from electrodes that oxidize (and thus generate Schottky barriers) (89), or it may arise from asymmetric molecular contacts across the junction (31). Thus, certain criteria, some of which are nontrivial to achieve experimentally, have emerged for demonstrating molecular rectification. First, the direction of current rectification should switch if the orientation of the molecular components within the device is reversed while the electrode orientation is held constant. Second, either the electrodes should not oxidize, or the current rectification should be robust across multiple electrode sets or experimental setups. Finally, current rectification should depend upon molecular structure, not upon device structure. For example, early reports of

molecular rectification from LB films of  $C_{16}H_{33}-Q3CNQ$ , Z-b-(*N*-hexadecyl-4-quinolinium)-a-cyano-4-styryldicyanomethanide (100) have managed to stand the test of time; multiple research groups have investigated this system, using various fabrication methods and device platforms (101, 102).

As research groups began to validate observations of molecular rectification, it became possible to more fully investigate molecular structure/device property relationships for current rectification. For example, although a few molecular rectifiers with the D- $\sigma$ -A structure have been demonstrated (103, 104), the flexible nature of the  $\sigma$ -linkage has proven to be a hindrance because the molecule may adopt a much more compact (and nonideal) structure within the junction than is implied by an electrode-D- $\sigma$ -A-electrode geometry. Thus, researchers have successfully explored alternatives that utilize much stiffer  $\pi$ -bridges (e.g., a D- $\pi$ -A molecule) instead (105).

More recently, the experimental challenge has been to design molecules that yield much stronger diode characteristics. For example, Ashwell's group (106) has demonstrated rectification ratios (calculated as the forward current/reverse current) of up to 3000 for the system of Au(s)-S- $C_{10}H_{20}-A^+-\pi-D|D^-$  structures. Here,  $A^+$  (a cationic acceptor) is 5-(4-dimethylaminobenzylidene)-5,6,7,8-tetrahydroisoquinolinium, and  $D^-$  (an anionic donor) is copper(II) phthalocyanine-3,4',4'',4'''-tetrasulfonate (106).

### 7.3. Molecular Switch Tunnel Junction Devices

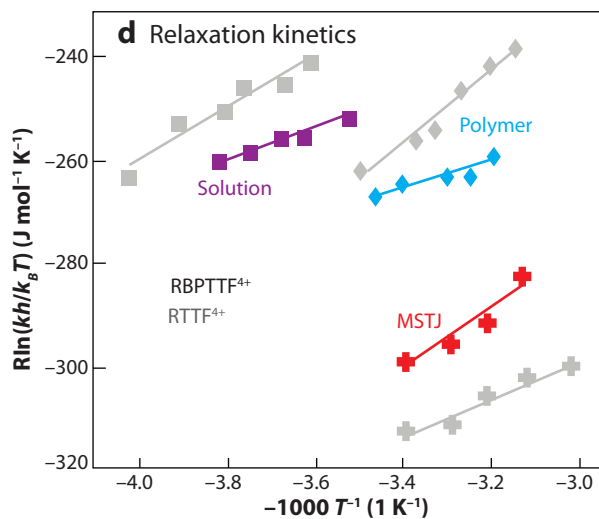
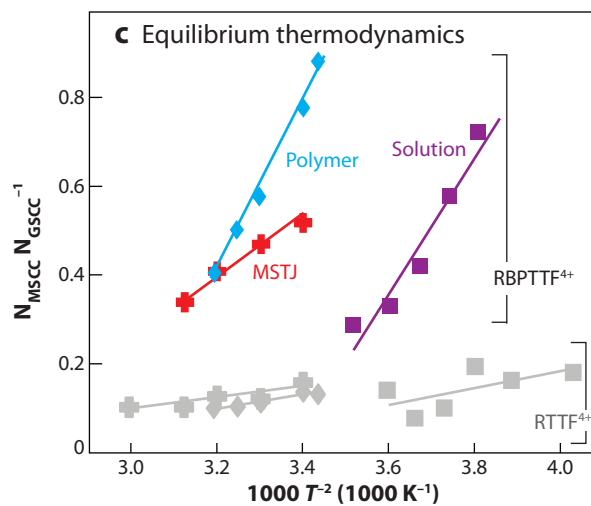
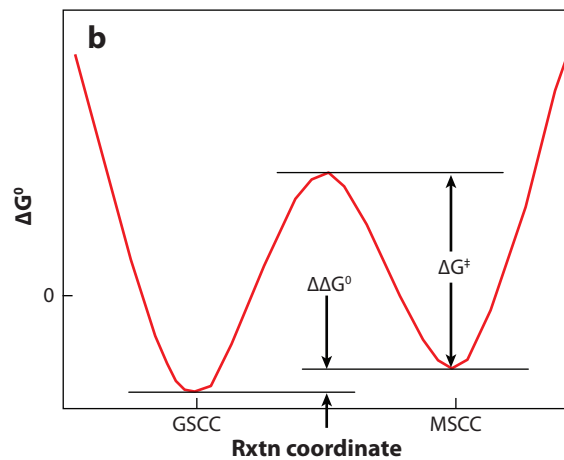
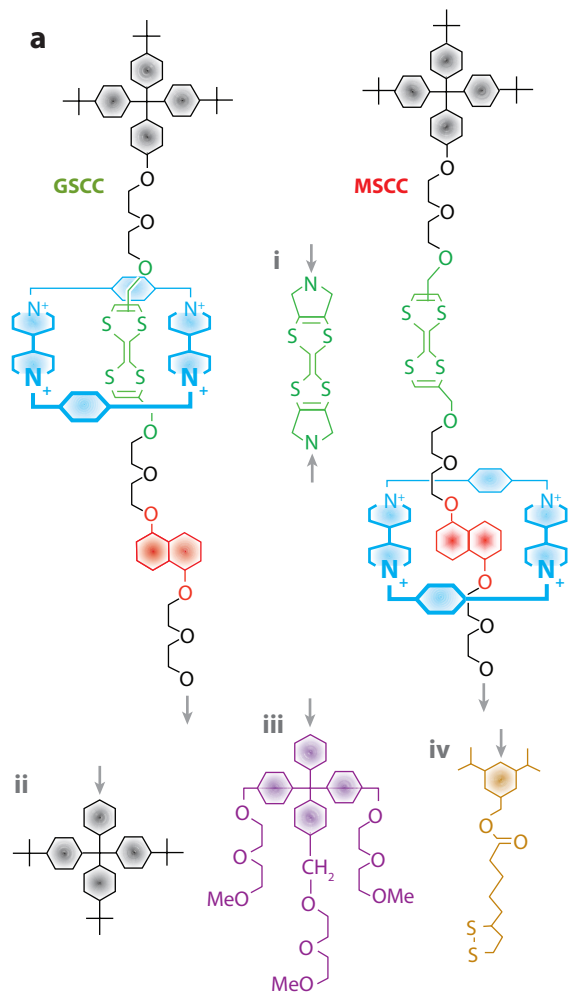
Molecular switch tunnel junction devices represent bistable, two-terminal molecular junctions in which the molecule performs the electrochemically driven, active function of a resettable switch. This contrasts with the passive role that molecules play in either tunnel junctions or molecular current rectifiers. As such, the molecular signatures within the device that can correlate device performance with molecular properties are those that reflect the bistable nature of the molecules.

The molecular switches that have been investigated within two-terminal molecular junction devices include various bistable [2]catenanes (comprising two mechanically interlocked rings) and bistable [2]rotaxanes (comprising a ring that encircles a dumbbell structure) (**Figure 5a**). The switching mechanism in both molecular architectures is similar (107, 108): A cyclobis(paraquat-*p*-phenylene) (CBPQT<sup>4+</sup>) ring component encircles one of two recognition sites, a tetrathiafulvalene

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#### Figure 5

The molecular structure and switching characteristics of bistable [2]rotaxane molecular switches, as designed for and measured in various physical environments. (a) The molecular structure of a [2]rotaxane bistable molecular switch. The ground-state coconformers (GSCC) and metastable-state coconformers (MSCC) are shown. The nature of the bistability of these switches can be modified chemically. One example is a substitution of the tetrathiafulvalene (TTF) recognition element (*green*) with the bispyrrolotetrathiafulvalene (BPTTF) group (*i*). These molecular switches can also be adapted into a variety of physical environments by varying the bottom stopper. The stoppers shown allow for investigations of the bistable [2]rotaxane switching properties (*ii*) in solution or polymer gels, (*iii*) as an amphiphile for embedding in a molecular switch tunnel junction (MSTJ), or (*iv*) for attaching as a covalently bound monolayer to an Au surface for investigation within a traditional three-terminal electrochemical cell. (b) Energy-level diagram describing the bistability of these [2]rotaxanes. The free energy of activation ( $\Delta G^\circ$ ) describes the (temperature-dependent) relaxation of the MSCC (switch closed) to the GSCC (switch open) state.  $\Delta\Delta G^\circ$  describes the temperature-dependent relative populations of the GSCC and MSCC at equilibrium. (c) The temperature-dependent MSCC:GSCC ratios for [2]rotaxanes containing either the TTF or the BPTTF recognition elements in an MSTJ, in a solid-state polymer gel, and in solution. The slopes of these lines are mostly determined by the molecular structure, not the physical environment. (d) The measured MSCC  $\rightarrow$  GSCC relaxation kinetics for TTF- and BPTTF-containing [2]rotaxanes. Here,  $\Delta G^\circ$  is strongly influenced by both physical environment and molecular structure.  $\Delta G^\circ_{298}$  increases in steps of 8–15% in moving from the solution phase to the polymer gel to the MSTJ. Similar rotaxanes, investigated on surfaces, exhibit consistent behavior, with relaxation kinetics falling in between those of polymer gels and MSTJs. Adapted from Reference 107.



group (TTF) or a dioxynaphthyl (DNP) site (although variations on these themes are possible). The structure with the CBPQT<sup>4+</sup> ring encircling the TTF group is the ground-state coconformer (GSCC). The CBPQT<sup>4+</sup> ring encircling the DNP site describes the metastable-state coconformer (MSCC). The switching process is an electrochemically driven switching between the GSCC and the MSCC. The lowest oxidation state of either molecular switch corresponds to oxidation of the TTF<sup>0</sup> to TTF<sup>+</sup>. Once the TTF<sup>+</sup> is oxidized, the CBPQT<sup>4+</sup> ring experiences Coulomb repulsion and thus quickly moves to encircle the DNP site. When the TTF<sup>+</sup> is reduced back to TTF<sup>0</sup>, the MSCC coconformer is obtained. Over some time period (up to hours) that depends upon the temperature, the detailed molecular structure of the [2]catenane or [2]rotaxane, or the physical environment, the MSCC will relax back to the GSCC (**Figure 5d**). The MSCC → GSCC relaxation time is an important parameter because, for the two-terminal molecular switch tunnel junction, it corresponds to the retention time of a memory bit (or the volatility of a switch). We initially hypothesized that, within a two-terminal molecular junction, the MSCC corresponded to the high conductance, or switch closed state, whereas the GSCC corresponded to the switch open state, results that were later confirmed by experiment (described below) and by theoretical calculations from Goddard's group (109). In addition, on the basis of how the device operated, we hypothesized that reduction of the CBPQT<sup>4+</sup> ring led to a rapid interconversion of the MSCC to the GSCC and so provided a mechanism for electronically opening a closed switch (44).

These MSCC and GSCC structures are described by different electronic structures, oxidation potentials, etc., and so the switching cycle can be followed in the solution phase by use of nuclear magnetic resonance, cyclic voltammetry, optical spectroscopy, or combinations thereof. Measuring the switching cycle within the solid-state device, however, proved more challenging and was done piecemeal.

An initial goal was to quantitatively prove that the molecular switches worked within solid-state settings. A monolayer of thiol-terminated [2]rotaxane molecular switches was assembled onto an Au surface, which served as the working electrode in a three-terminal electrochemical device (see Section 2.4) (27). Time- and temperature-dependent cyclic voltammetry studies were very revealing. First, the first oxidation state of the TTF group in the GSCC was measured to be +490 mV and in the MSCC to be +310 mV (relative to Ag/AgCl). By voltage ramping the [2]rotaxane monolayer through the switching cycle, it was thus possible to obtain the absolute and relative abundances of the GSCC and the MSCC as a function of time and temperature. This allowed for the kinetics of the MSCC → GSCC relaxation process to be quantified and also allowed for a direct assessment of energy difference between the GSCC and the MSCC. Finally, cyclic voltammetry experiments also unambiguously confirmed that reduction of the CBPQT<sup>4+</sup> ring led to a very rapid interconversion of the MSCC to the GSCC.

Following this work, similar experiments were carried out on these and related bistable [2]catenane and [2]rotaxane molecular switches entrained within three other environments (107, 108): solution phase (at reduced temperatures), very high-viscosity polymer gels (the consistency of a rubber tire), and molecular switch tunnel junction devices. These experiments are summarized in **Figure 5c** and **5d**. Other groups also began to report on bistable [2]rotaxanes and related molecules switching in solid-state settings (110). The picture that emerged is the following: As a [2]rotaxane or [2]catenane molecular mechanical switch is moved from the solution phase environment to an environment more sterically confined (such as a SAM, two-terminal junction, or polymer gel), the activation barrier for the MSCC → GSCC relaxation increases significantly, with the two-terminal molecular junction exhibiting the highest activation barrier. Changing the molecular structure can also have a strong influence on this activation barrier. The thermodynamic equilibrium between the GSCC and the MSCC structures, however, is relatively invariant



to physical environment but strongly dependent upon molecular structure. Thus, a feedback loop was established. This feedback loop connected the performance metrics of a two-terminal molecular junction to the molecular structure of the switches and to the properties of those switches as measured in solution.

#### 7.4. Kondo Resonances in Single-Molecule Transistors

Single-molecule (or few-molecule) devices represent a sort of ultimate limit for molecular electronics, and the fabrication and testing of such devices are nontrivial endeavors that usually share more in common with a low-temperature physics measurement than with most molecular electronics experiments. Unlike the other devices discussed in this section, the only way to characterize a molecule, once it is in a single-molecule transistor setting, is through electron transport measurements. Thus, obtaining any information about the molecule(s) within the device represents a distinct challenge.

The earliest single-molecule devices (not counting scanning probe-based measurements) were two-terminal, mechanical break junction devices (111), which yielded useful but limited information. For example, Kergueris and coworkers investigated break junctions comprising two Au electrodes bridged by a bisthiolterthiophene molecule (112) and observed that the transport characteristics of their devices would reproducibly switch between very different types of current-voltage responses. Although these responses could be modeled, assigning these responses to different molecular characteristics, to different numbers of molecules within the junction, or to molecule/electrode contact properties was not possible. Basically, single-molecule devices needed to be modified so that they could be utilized to perform some sort of molecular spectroscopy. This was first reported in 2000 by Park and coworkers (113), who introduced gate electrodes into single-molecule devices. Nanometer-wide gaps were established by use of electromigration to break a thin metal wire. A measurement of the tunneling current across the broken gap established the gap distance.  $C_{60}$  molecules were then introduced into the gap. The ability to tune the junction conductance using a gate electrode permitted a number of sharp and reproducible features to be observed in the conductance spectra. This allowed the researchers to conclude that much of what they observed arose from single-molecule phenomena. In addition, the researchers reported quantized, high-frequency mechanical oscillations of the  $C_{60}$  molecule against one of the Au electrode surfaces. However, no transport characteristics that could uniquely distinguish a  $C_{60}$  molecule from, for example, a  $C_{70}$  molecule could be unambiguously assigned. A big part of the challenge associated with single-molecule transistors is that, when a molecule (or nanoparticle) bridges two electrodes and contacts those electrodes via tunnel barriers, single-electron charging and electronic energy level quantization can dominate the transport characteristics. These relatively high-energy phenomena are very sensitive to small fluctuations in the local environment of the molecular bridge. Thus, specifically identifying a unique molecular feature, even with a high-resolution spectroscopic platform such as a single-molecule transistor, is difficult.

In 2002, the McEuen and Ralph group (29) and the Long and Park group (30) separately reported observing a Kondo resonance with single-molecule transistors. In general, a Kondo resonance results from a quantum exchange interaction between a localized electron spin and (delocalized) conduction electrons in metallic electrodes. In both papers, the single-electron spin was designed into the molecule via chemical synthesis, and the Kondo resonance was experimentally proven through the use of a magnetic field as an additional, tunable experimental parameter. Both papers reported that the resonance could be turned on or off by modulation of the oxidation state of a metal atom within the bridging molecule through use of the gate electrode. For the

McEuen/Ralph paper (29), the molecule comprised a Co atom complexed by two terpyridinyl linker molecules that were bonded, via thiol tethers, to the source and drain electrodes. The researchers employed different tether lengths to change the coupling strength between the Co atom and the metal electrodes. For a long ( $C_5$ -alkyl) tether, Coulomb charging but no Kondo resonance was observed. Kondo resonance was observed for the short tether.

From a molecular electronics perspective, these two papers (29, 30) together reported that (a) molecules could be reversibly oxidized and reduced within a junction, (b) molecular oxidation states of the molecules could potentially be identified via charge transport measurements, (c) unique properties could be specifically designed into a molecular junction via chemical synthesis, and (d) the coupling between the molecule and the electrode is a variable that either can permit observation of unique molecular characteristics or could mask such characteristics. Some of these conclusions are robust, and as described above, have been made in other, very different molecular electronics devices. However, the interpretation of some of the details from these papers is still being debated. For example, recent work has indicated that the Kondo effect in molecular junctions can originate from sources that were not envisioned in the original work (114).

## 8. CONCLUDING THOUGHTS AND THE FUTURE OF MOLECULAR ELECTRONICS

Molecular electronics, despite having origins that date back some 40–50 years, is still a young field. Researchers spent much of the 1990s struggling with device platforms, phenomenology, and the development and application of new analytical methods. However, over the past half-dozen years or so, a number of well-defined (and constantly improving) device constructs have emerged. These devices are now permitting researchers to begin stressing the science of molecules in their molecular electronics work, rather than investigating phenomenology. In addition, the platforms are also permitting researchers to do fairly remarkable things. In 2007 my group reported on a 160,000-bit crossbar-structure molecular electronics memory circuit (21). The entire nanowire/molecular switch crossbar circuit was smaller than a typical white blood cell, and in terms of density, the memory circuit represented a technology node of approximately 2020 (115). However, when there is a big breakthrough in the field, science reporters are always quick to ask when the development will turn into a real commercial technology. I believe that the answer to that question, at least for most of the types of devices discussed herein, is “not soon.” This is because there are several outstanding, unsolved issues, the top three of which are robustness, robustness, and robustness. If a solid-state device fails after 10 million cycles, then it is considered a failure. If a molecular electronics device works 10 times, it is considered a success. It does not really matter what novel and potentially useful function that the device performs—it must perform that function reliably. For example, the ultrahigh-density molecular electronics memory circuit referred to above had only approximately 25% of its bits working. That was likely a result of fabrication issues, not molecular robustness. However, of those 25% working bits, the bits could be cycled only a few times. That is problematic and more fundamental. Solving this issue of molecular robustness will undoubtedly lead to new science both related and unrelated to molecular electronics. However, given how rapidly the field has advanced over the past decade, I am very optimistic that the issue of molecular electronics device robustness will be resolved.

## DISCLOSURE STATEMENT

The author is not aware of any biases that might be perceived as affecting the objectivity of this review.

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## Errata

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