

Topical Review

Key research development by Prof Mark Reed in molecular electronic devices

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**Abstract**

In memory of Professor Mark Reed, who passed away on May 5, 2021, this article summarizes a series of his past groundbreaking developments in molecular electronic devices. Specifically, three key reports are summarized; measurement of the electrical conductance of molecular junctions using the mechanically controlled break junction technique and demonstration of negative differential resistance and orbital gating effect observed in molecular junctions. Also, a brief outlook on molecular electronics research field is addressed.

Keywords: molecular electronic devices, electrical properties, charge transport, self-assembled monolayer

(Some figures may appear in colour only in the online journal)

1. Introduction

Molecular electronics is a research field that explores the development of electronic devices by understanding the phenomenon of charge transport in structures composed of single molecules or molecular monolayers. This research is already a mature field of study as it has already been introduced in several review papers and books [1–4]. As the beginning, in 1974, Aviram and Ratner made a theoretical proposal that an organic molecule could be used as a rectifying device like a diode [5]. But it was not until 1997 that Reed's group succeeded in manufacturing and measuring the first electronic junction made with a single molecule by using a mechanically controlled break junction [6]. Since then, a lot of active research has been conducted worldwide, and various molecular electronic devices such as molecular wires, molecular switching, molecular transistors, and molecular memories made of single molecules or molecular thin films have

been experimentally demonstrated. In particular, Reed's group continuously pioneered key breakthroughs in this research field. For example, in 1999, Reed's group demonstrated a negative differential resistance behavior observed in molecular junctions formed in a structure called 'nanopore' [7]. And in 2009, Reed's group together with Lee's group demonstrated the molecular orbital gating effect observed in single molecular junctions formed by an electromigration technique [8]. In this article in memory of Professor Mark Reed, we summarized these pioneering studies in molecular electronics that have been carried out in his research group.

2. Pioneering research work by Reed's group in molecular electronics*2.1. Measurement of conductance of a molecular Junction*

In order to understand the charge transport of molecular devices and the fundamental physical properties of molecules, it is necessary to create electrical contact between molecules

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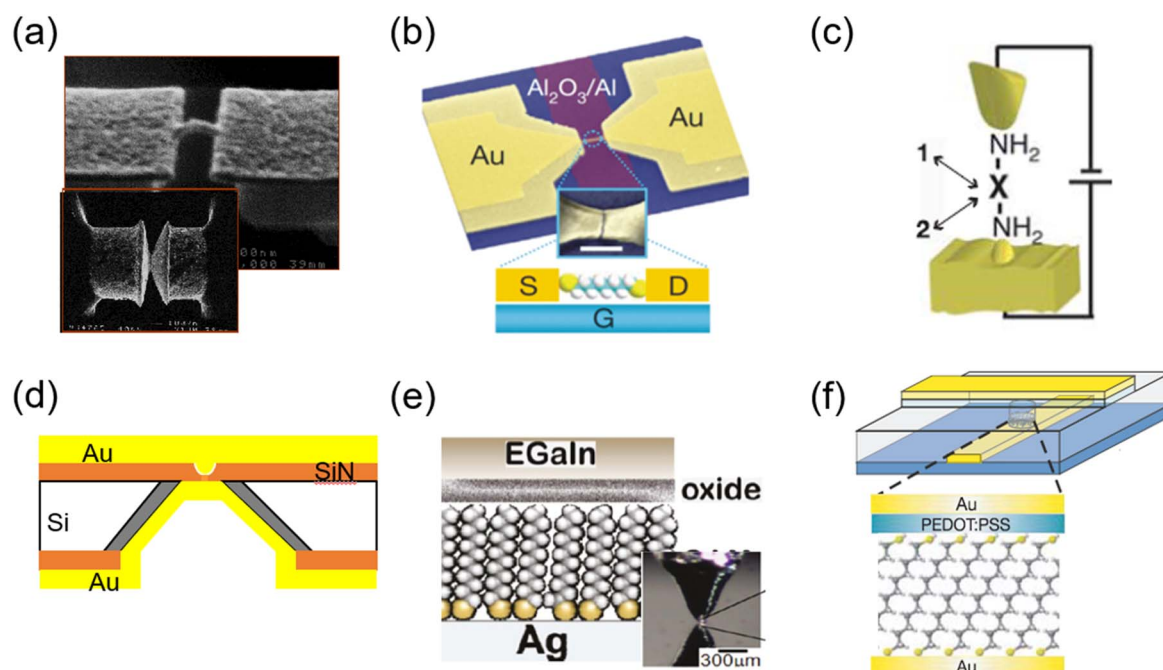


Figure 1. Characterization platforms for molecule electronics. (a)–(c) Single-molecule junction. (d)–(f) Monolayer-based molecular junctions. (a) Mechanically controllable break junction. From [6]. Reprinted with permission from AAAS. (b) Electromigration nanogap junction. Reproduced from [8], with permission from Springer Nature. (c) Scanning probe microscope-based break junction. Reproduced from [9], with permission from Springer Nature. (d) Nanopore junction. From [7]. Reprinted with permission from AAAS. (e) Eutectic Ga–In contact junction. Adapted from [10], with permission from Springer Nature. (f) Conducting polymer-interlayer junction. Reproduced from [11], with permission from Springer Nature.

and electrodes and to be able to control and measure the current flowing through the molecular junction. And, various experimental platforms have been devised for this purpose. These experimental techniques can be broadly classified into those using single molecules (figures 1(a)–(c)) and those using self-assembled monolayers (SAMs) (figures 1(d)–(f)). In addition to the number of molecules connected to the electrode, these two classes also have differences in the shape of the electrode, the electric field, and the interaction between molecules, and each experimental technique has its own characteristics and advantages and disadvantages in terms of bond formation with molecules.

Figure 1(a) shows a method of forming a nanogap by precisely breaking the middle of a very thin metal wire with a device called a mechanically controllable break junction (MCBJ) and bonding molecules between them. Through this method, Reed's group successfully measured the electrical properties of benzene-based molecules [6]. In this approach, a notched metal wire was glued onto a flexible substrate and was fractured by bending of the substrate, after which an adjustable tunneling gap could be formed (figure 2(a)). In this experiment, benzene-1,4-dithiol (benzenedithiol) was adsorbed from a 1 mM solution in tetrahydrofuran (THF) onto the two Au electrodes of the MCBJ, which were broken in solution under ambient argon (Ar) atmosphere, resulting in the formation of a SAM on the Au electrodes (figure 2(b)). The THF solvent was allowed to evaporate in the ambient Ar atmosphere before the conductance measurements. The removal of the THF led to thermal gradients that disturbed the picometer static dimensional stability of the MCBJ, requiring

the tips to be withdrawn and then returned to measure the electrical properties of the molecules adsorbed on the surfaces. As the electrodes' tips were brought together, current–voltage ($I(V)$) and conductance $G(V)$ ($=dI/dV$) measurements showed characteristic features that proved to be highly reproducible (figure 2(c)). An apparent gap of ~ 0.7 V was observed, which was interpreted as a Coulomb gap or due to the mismatch between the contact Fermi level and the lowest unoccupied molecular orbital (LUMO) of benzenedithiol. This study is regarded as the first electrical conductance measurement of a single molecular junction. Since this study, many research groups have used the MCBJ technique to study the electrical properties of molecular junctions [3].

2.2. Observation of negative differential resistance

Although the MCBJ promotes steps toward the development of molecular electronics, the MCBJ technique has some limitations because it is not comparable to lithographical fabrication. In contrast, a device structure called 'nanopore' provides a stable device structure and makes cryogenic measurements possible. In this device, as illustrated in figure 3, the number of molecules (\sim several thousand) are sandwiched between two metallic contacts. The device fabrication starts with a high-resistivity silicon wafer with low-stress Si_3N_4 film deposited on both sides by low-pressure chemical vapor deposition. By standard photolithography processing, a suspended Si_3N_4 membrane (size of $40 \mu\text{m} \times 40 \mu\text{m}$ and thickness of ~ 70 nm) is fabricated on the top side of the wafer. Subsequent electron-beam lithography

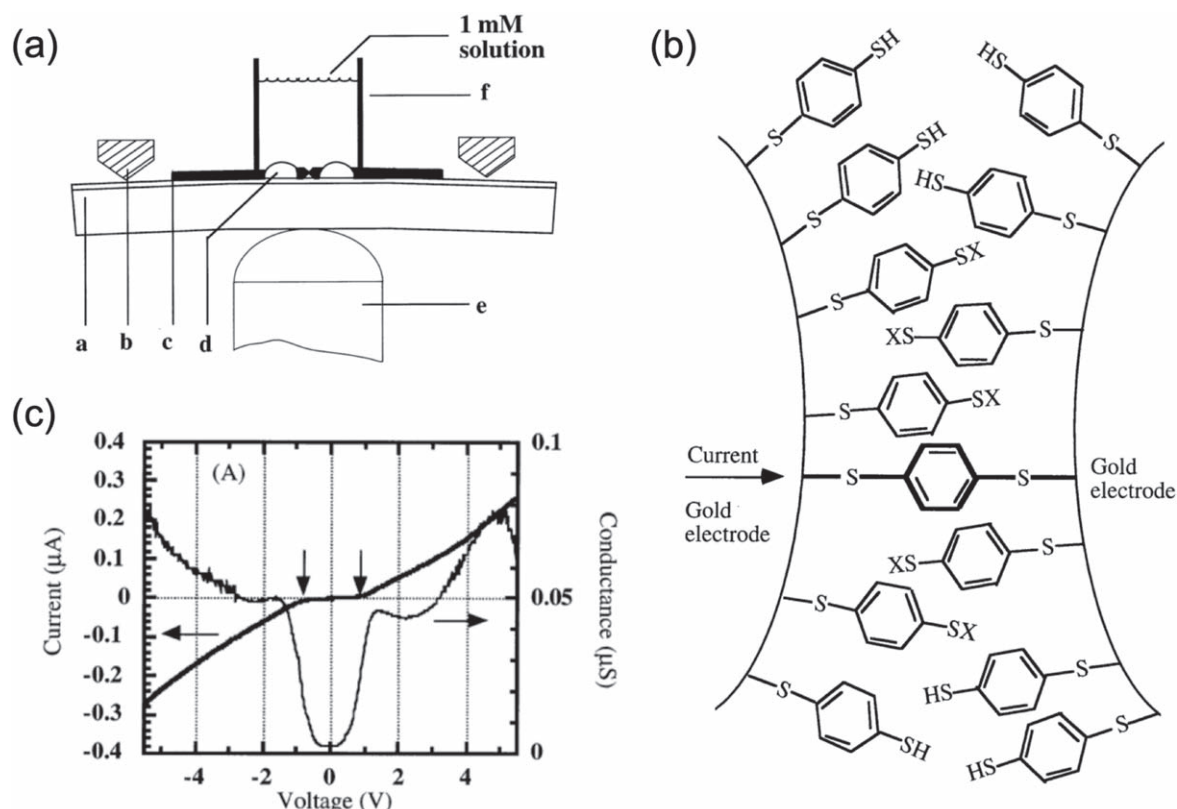


Figure 2. (a) Schematic of the measurement process in MCBJ. (b) Schematic of a benzenedithiol between Au electrodes. (c) The measured electric data. From [6]. Reprinted with permission from AAAS.

and reactive ion etching create a single pore with a diameter of tens of nanometers through the membrane. As the next step, 150 nm Au is thermally evaporated onto the topside of the wafer to fill the pore and form one of the metallic contacts. The device is then transferred into a molecular solution to deposit the SAM layer. The essential feature of the fabrication process is the use of a nanoscale junction area (typically 30 to 50 nm in diameter), which gives rise to a small number of molecules (~ 1000) and also eliminates pinhole and other defect mechanisms that hamper through-monolayer electronic transport measurements. This device structure allows good control over the device area while also creating intrinsic contact stability, and it also produces a large number of devices with acceptable yield, so that statistically significant results can be obtained.

When a SAM of 2'-amino-4-ethynylphenyl-4'-ethynylphenyl-5'-nitro-1-benzenethiolate (shown in figure 3(a)(C)) was used, a negative differential resistance (NDR) behavior was observed at 60 K (figure 3(b)). Positive bias corresponds to hole injection from the chemisorbed thiol-Au contact (bottom contact) and electron injection from the evaporated contact (top contact) (figure 3(a)(C)). The peak current density for this device was $>53 \text{ A cm}^{-2}$, the NDR was $> -380 \mu\text{ohm cm}^2$, and the peak-to-valley ratio (PVR) was 1030:1. The mechanism of such NRD observed in this molecule is generally not clear. Nevertheless, a potential candidate mechanism was proposed with a two-step reduction process that modifies charge transport through the molecule, as

illustrated in figure 3(c). As the voltage is increased, the molecule initially undergoes a one-electron reduction, thereby supplying a charge carrier for electron flow through the system (although the nitro moiety is the most electron-withdrawing group in the molecule, the charge is probably dispersed throughout the entire molecule). A further increase in voltage causes a second electron reduction with subsequent blocking of the current. The width of the $I(V)$ peak ($\sim 0.7 \text{ V}$) correlates well with the difference between the one electron and two-electron peak reduction potentials. The advantages of the nanopore platform are to provide a stable solid-state device structure and allow temperature-variable electrical characterization. For example, using this nanopore platform, Reed's group identified the mechanism of electron conduction [12] and investigated inelastic electron tunneling characteristics in alkanethiol SAMs [13].

2.3. Observation of molecular orbital gating

A single-molecule device containing a nanoscale gap can be fabricated by an electromigration method (figure 1(b)). When a high-density current flows through a thin metal wire, the electromigration effect of the metal occurs and the wire is eventually broken. It is a method of forming and bonding molecules between them. In particular, this method is very useful for forming a single-molecule-based field effect transistor (FET) structure because it is easy to insert a gate electrode.

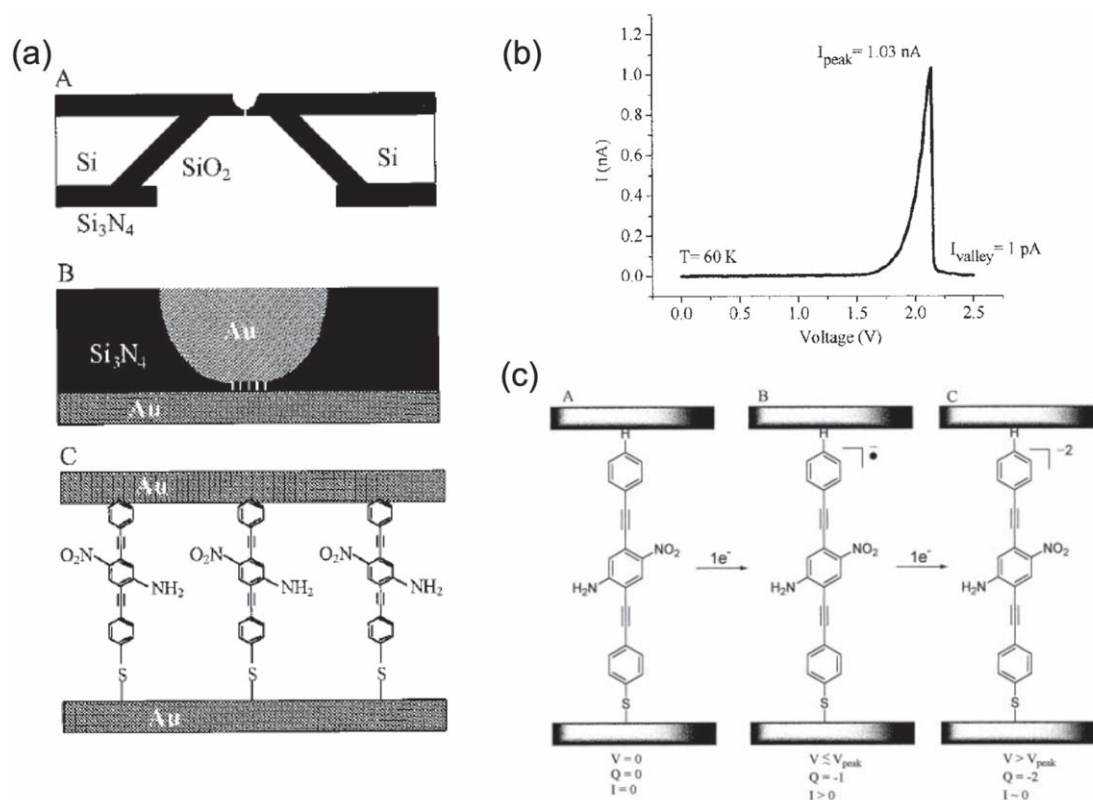


Figure 3. (a) Nanopore fabrication. (A) Cross section of a silicon wafer with a nanopore etched through a suspended silicon nitride membrane. (B) Au-SAM-Au junction in the pore area. (C) Schematic image of molecules sandwiched in the junction. (b) $I(V)$ characteristics of a Au-SAM-Au device at 60 K. The peak current density is $\sim 50 \text{ A cm}^{-2}$, the NDR is $2400 \mu\text{ohm cm}^2$, and the peak-to-valley ratio is 1030:1. (c) Proposed mechanism for the NDR effect. From [7]. Reprinted with permission from AAAS.

In molecular-scale devices, a longstanding challenge has been to create a true three-terminal device that operates in this manner (that is, by modifying orbital energy). Reed's group in collaboration with Lee's group demonstrated direct electrostatic modulation of orbitals in a molecular FET configuration made with the electromigration nanogap technique, with both effective gate control and enhanced resonant coupling of the molecular orbitals to the source and drain electrodes [8]. As illustrated in the inset of figure 4(a), individual molecules are connected to source and drain electrodes with a bottom-gate control electrode in a FET configuration. In such devices, the energies of the molecular orbitals with respect to the Fermi level of the electrodes can be directly tuned by adjusting a gate voltage, V_G . Such devices can be made by fracturing a continuous Au wire (coated with the desired molecules, in vacuum, at 4.2 K) that is placed over an oxidized Al gate electrode. This produces source and drain electrodes with a nanometre-scale gap, which are often bridged by single or very few molecules, creating molecular junctions. Using this device structure, 1,8-octanedithiol (denoted as ODT) with an alkyl backbone as a σ -saturated aliphatic molecule and 1,4-benzenedithiol (denoted as BDT) with a delocalized aromatic ring as a π -conjugated molecule were studied. In this study, the success rate for observing a characteristic that indicated a molecular junction was typically less than 10%. Specifically, a yield of 35/418 was reported for 'working devices' [8]. Figure 4(a) shows representative $I(V)$ curves for a Au-ODT-

Au junction measured at different V_G values. The tunneling current passing through the ODT junction increases as V_G becomes increasingly negative. The corresponding analysis of $\ln(I/V^2)$ versus $1/V$, the graph of which is known as a Fowler-Nordheim plot, is shown in figure 4(b). Here, two distinct transport regimes are evident; the boundary between them, which occurs at the transition voltage, V_{trans} , is indicated with an arrow and exhibits a clear gate dependence. In the low-bias region, the logarithmic dependence is characteristic of direct tunneling ($V < \Phi_B/e$, where Φ_B is the barrier height and e is the elementary charge), whereas in the high-bias region above V_{trans} , the curves yield a linear relation with a negative slope, indicative of Fowler-Nordheim tunneling or field emission ($V > \Phi_B/e$). So, V_{trans} distinguishes direct tunneling (low-bias) region and Fowler-Nordheim tunneling (high-bias) region. And, the measurement of V_{trans} allows an experimental determination of the height of the energy barrier associated with the tunneling transport in molecular junctions, given by the difference between the electrode Fermi energy, E_F , and the energy of the nearest molecular orbital (the highest occupied molecular orbital (HOMO) or the LUMO). Here, a controllable gate-voltage dependence of V_{trans} in the molecular junction was clearly observed. For Au-ODT-Au junctions, V_{trans} shifts to a lower bias as a more negative V_G is applied (figure 4(b)), indicating HOMO-mediated hole tunneling (p-type-like). Similar gate-modulated transport behavior was also observed in Au-BDT-

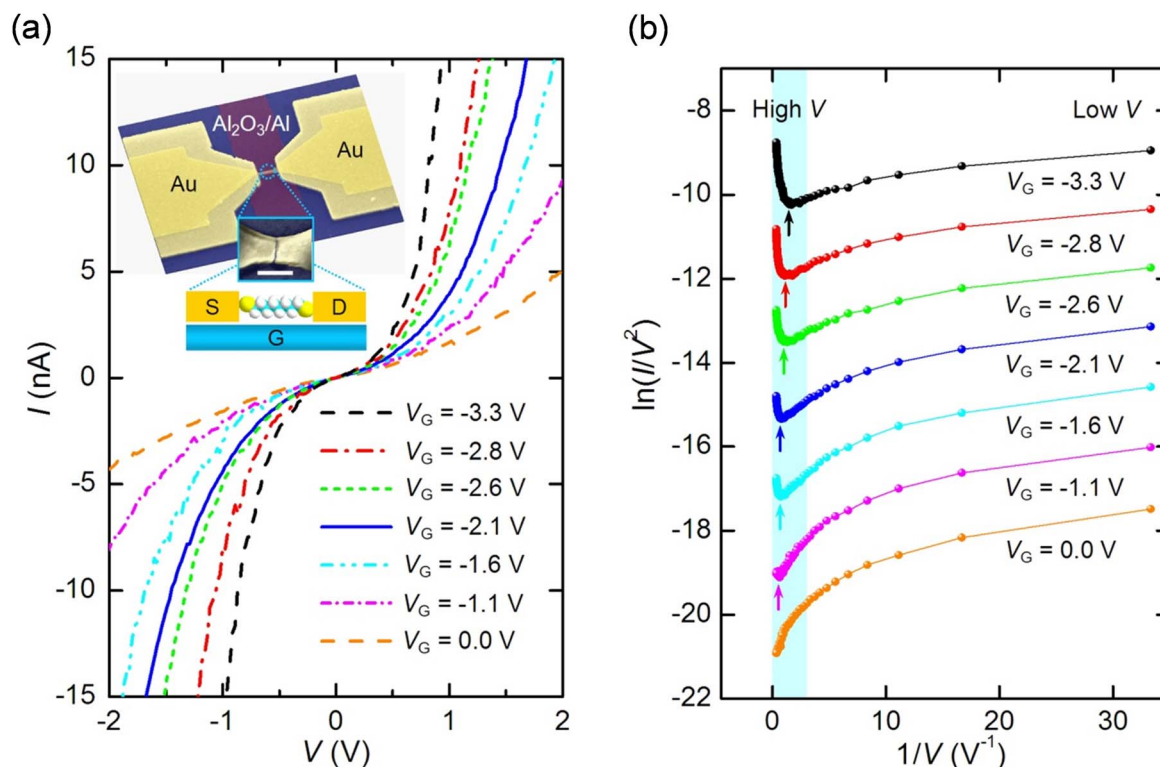


Figure 4. (a) Gate-controlled $I(V)$ curves of a Au-ODT-Au junction, measured at 4.2 K for different values of V_G . Inset shows the device structure and schematic. S: source, D: drain, G: gate, and scale bar: 100 nm. (b) Fowler-Nordheim plots corresponding to the $I(V)$ curves in (a), exhibiting the transition from direct to Fowler-Nordheim tunneling with a gate dependence. The plots are offset vertically for clarity. The arrows (corresponding to V_{trans}) indicate the boundaries between direct tunneling (low-bias) and Fowler-Nordheim tunneling (high-bias) regions. Adapted from [8], with permission from Springer Nature.

Au junctions [8]. The tunneling current flowing through the BDT junction is enhanced when a negative V_G is applied, whereas a positive V_G suppresses the current level (p-type-like). This study validated the concept of molecular-orbital-modulated carrier transport with enhancing the prospects for molecularly engineered electronic devices.

3. Conclusion and outlook

In this article, we summarized a series of pioneering research works made by Prof Mark Reed. He demonstrated the first single-molecule conductance measurements in 1997. Then, he demonstrated electronic device elements such as resonant tunneling diode and transistor using molecules in 1999 and 2009, respectively. His pioneering research has inspired many researchers in the field of molecular electronics research. Over a couple of decades, we have witnessed tremendous progresses in understanding the electrical, optical, thermal, spin, and quantum properties of molecular junctions. Although it is difficult to realize industrial molecular electronic devices in the near future, molecular electronic research is still expected to attract the attention of many researchers for academic curiosity and the possibility of miniaturization of devices.

Acknowledgments

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Data availability statement

All data that support the findings of this study are included within the article (and any supplementary files).

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