Carbon–Based Molecular Electronic Junctions

by Richard McCreery

Amolecular junction is conceptually a combination of classical electron transfer (ET) phenomena with the practical microelectronic structure known as a "two-terminal device". ET within and between molecules, such as donor-acceptor molecules and biological reaction centers, has been a very active research topic, recognized by the Nobel Prize in 1992 to Rudolph Marcus. Replacement of the donor or acceptor by a conductor leads to modified electrodes in electrochemical experiments, in which electron transport occurs from the conductor through a molecular layer to a redox component tethered to the electrode. As shown in Fig. 1, a molecular junction is a logical extension of donor-bridge-acceptor molecules and modified electrodes, in which both the "donor" and "acceptor" are conductors, usually metals.[1-7] Unusual electronic behavior in molecular junctions provided much of the early incentive for investigating molecular electronics. Since the mid-1990s, molecular junctions made from either single molecules or a collection of parallel, oriented molecules have shown rectification,[5,8] negative differential resistance,[9] conductance switching,[2,10,11] and bistable memory behavior.[12-16]

Several examples of current molecular junction designs are shown in Fig. 2. The Au/thiol self-assembled monolayers (SAMs) and Langmuir-Blodgett (LB) monolayers are at the heart of the majority of junctions studied to date, in part because such monolayers have been characterized in detail in other contexts. While carbon nanotubes are not exactly "molecules", they have been incorporated into molecular junctions and do exhibit strong structural effects on junction behavior.[17-20] A few technical and conceptual challenges are evident from the designs in Fig. 2, which must be overcome to make and understand useful electronic junctions. On the practical side, the contact materials must be flat relative to the length of the molecule, typically 1-4 nm. Pinholes in the molecular layer must either be absent, or prevented from causing short circuits. In addition, the
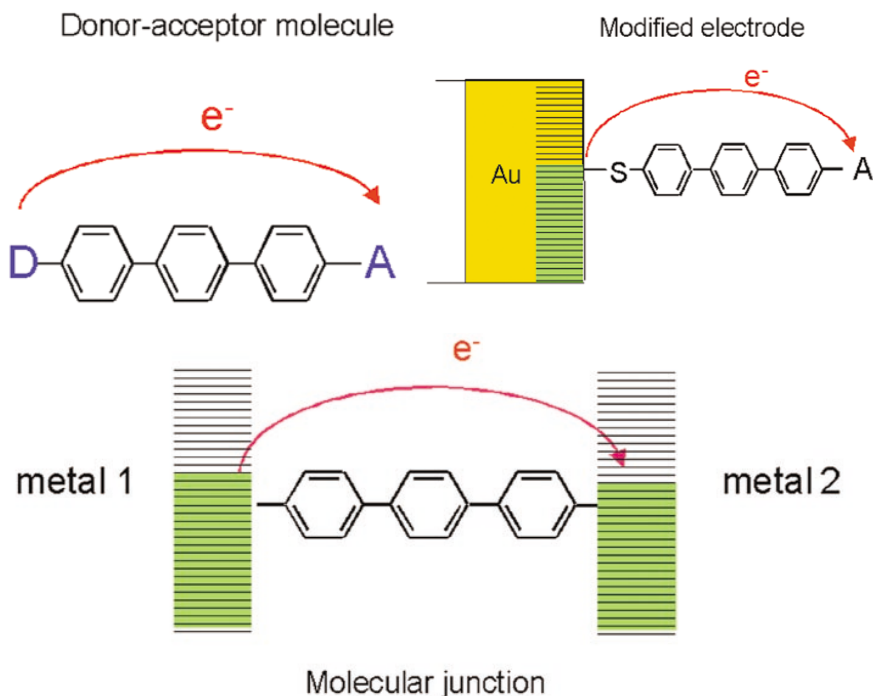

FIG. 1. ET in donor-bridge-acceptor molecules, modified electrodes, and molecular junctions. Horizontal lines in metals represent electronic states, and green shading indicates which states are occupied.
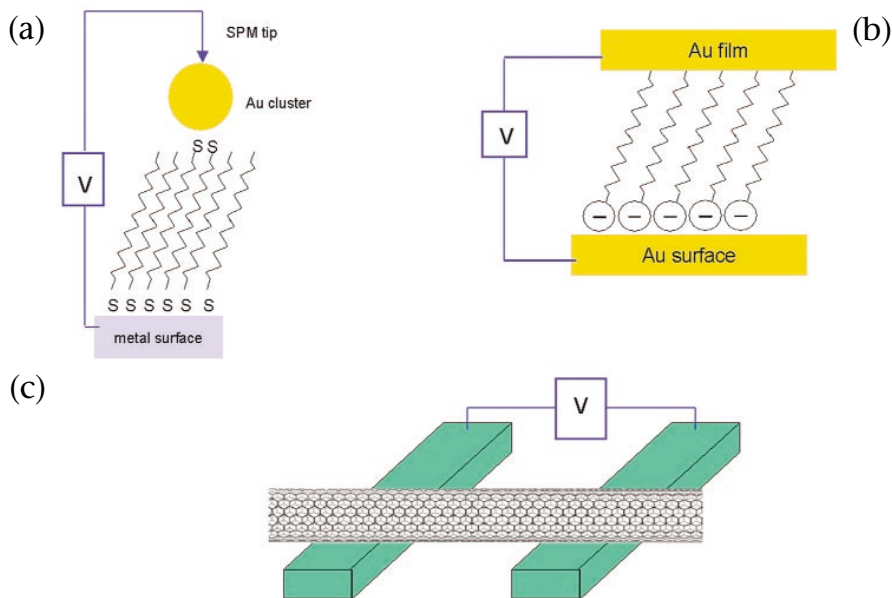

FIG. 2. Several molecular junction designs studied to date, with "V" representing an external circuit or voltage source; (a) SAM between a metal substrate and gold cluster, with top contact provided by a scanning probe microscopy tip; (b) LB monolayer between a gold substrate and a vapor deposited Au film; (c) carbon nanotube on lithographically formed metal contacts.

	Temperature (T) dependence	Voltage (V) dependence	Monolayer thickness (d) dependence
Coherent tunneling, "superexchange"	None	Linear (low V)	$\exp(-\beta d)$
Incoherent, diffusive tunneling "tight binding model"	None	Linear (low V)	$\exp(-cd)$
Thermionic (Schottky) emission	$\exp(-a/T)$	$\exp(bV^{1/2})$	$\exp(-cd^{1/2})$
"Hopping" (i.e., "Ohmic")	$\exp(-a/T)$	Linear (low V)	d^{-1}
Poole Frenkel effect ("traps")	$\exp(-a/T)$	$\exp(bV^{1/2})$	$\exp(-cd^{1/2})$
Field emission (high E-field, "Fowler Nordheim")	None	$V^2 \exp(-b/V)$	$\exp(-cd)$

a, b, and c denote constants which are independent of temperature, voltage, and thickness, respectively.
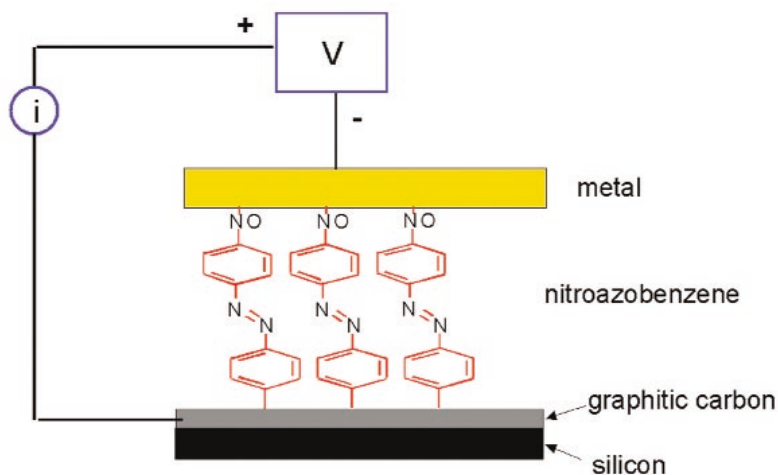

FIG. 3. Metal/molecule/carbon molecular junction with covalent bonding of both conductors to the molecular layer. Carbon is a PPF, and metal is either Hg or vapor-deposited Ti or Ag. The PPF layer is ~2 µm thick, and the silicon is not involved electronically.

top contact must be applied by a means which retains the integrity and structure of the molecular layer without penetrating to create shorts. These technical issues are nontrivial, but the conceptual hurdles are even greater. The energy barrier for electrons at the contacts between molecule and conductor (often called an "injection barrier") should not dominate electron transport, lest it negate any effects of molecular structure.[21-25] It is likely that a close-packed layer of identical molecules will not behave as a simple parallel combination of individual molecular "conductors". Lateral interactions and electrostatics may prevent linear scaling between single molecule and junction conductivities.[26,27] Possibly the largest conceptual issue is the mechanism of electron transport through the junction. Phenomena occurring both within the molecular layer and at the molecule/contact interfaces may affect conductivity, including tunneling, thermionic emission, activated conformational changes, and conjugation within molecular orbitals. The temperature and voltage dependencies of several commonly considered electron transport mechanisms are summarized in Table I.

Although the vast majority of molecular junctions studied to date are based on SAMs, LB, and nanotube structures, our approach to junction fabrication is quite different. In part, our motivation was a search for very stable junctions based on carbon-carbon covalent bonds. A schematic is shown in Fig. 3, for a nitroazobenzene monolayer between a carbon substrate and a metal top contact.[8,11,28,29] The carbon is sp^2 hybridized and disordered, and is made by pyrolysis of commercial photoresist films on a silicon substrate. The root-mean-square surface roughness is 5 Å, and patterns may be created before pyrolysis with conventional photolithography. Electronically, the pyrolyzed photoresist film (PPF) resembles glassy carbon, which is a disordered semimetal with a resistivity of ~5 mΩ-cm.[30] The molecular layer is bonded to the PPF via reduction of a diazonium ion precursor, to yield covalent, conjugated C-C bonds and dense molecular packing.[31,32] As noted earlier, application of a top contact is problematic, both because of possible damage to the monolayer and because a covalent bond is attractive for stability and stronger electronic coupling. We and others have made contact with a mercury drop, sputtered metal, or electron-beam deposited titanium.[22,33-38] For the examples described here, two methods were used, either 400 Å of Ti and 1000 Å of Au vapor deposited at a pressure of ~5 x 10^{-6} Torr, or a Hg drop lowered onto the monolayer in air.

Before describing the current/voltage response of molecular junctions, it is useful to reflect on their relationship to conventional electrochemical experi-

ments. A molecular junction is akin to a modified electrode in solution, but without the solvent or electrolyte. An electric field is present when a voltage is applied to the junction (in addition to any "built-in potential" due to the work functions of the conductors), which can approach or exceed the field in an electrochemical double layer. Unlike the electrochemical analog, there is no reference electrode, hence no redox potential scale. Both cases have an electric field, and possibly ET reactions, but it is not meaningful to compare a voltage applied to a molecular junction to a potential relative to some reference such as a hydrogen or calomel electrode.

A current voltage (i/V) curve for a biphenyl junction with a Hg top contact is shown in Fig. 4. The current increases nonlinearly with voltage until apparent dielectric breakdown at ~1.6 V. The electric field across the biphenyl monolayer at this point is very large, about 13 MV/cm. Breakdown fields for various dielectrics range from 0.2-20 MV/cm, so the sudden increase in current is likely to be due to dielectric breakdown. If this catastrophic failure is avoided, the i/V curve is independent of scan rate and repeatable indefinitely. Figure 5 shows several i/V curves for Hg junctions of four different molecules, all with the same area of 0.008 cm^2. The conductance of the junction is strongly dependent on structure, particularly the length of the monolayer molecule. An increase in the number of CH$_2$ units of an alkane chain on a phenyl ring from 1 to 2 to 4 leads to an increase in resistance (measured near V=0) by a factor of ~1000. The dependence of ET on chain length has been studied in detail in donor-acceptor ET and electrochemical kinetics, and is usually attributed to electron tunneling, possibly involving "superexchange".[39-41] Note also that stilbene yields a much higher current than C$_4$H$_9$-phenyl, even though stilbene is longer (~13.4 Å compared to ~11.2 Å). Presumably the conjugation in stilbene results in a lower tunneling barrier, or better delocalization of electron density.

To consider a wide range of molecules and conductivities, it is convenient to plot ln G (G = conductance = R^{-1}) vs. monolayer thickness. The conductance was determined at low V (±50 mV), and the thickness is taken as the distance between the carbon surface and the van der Waal radius of the terminal atom of the monolayer. A plot of ln (G) vs. thickness is shown in Fig. 6, for Hg junctions made from eight aromatic molecules. A least squares line has a slope of approximate-
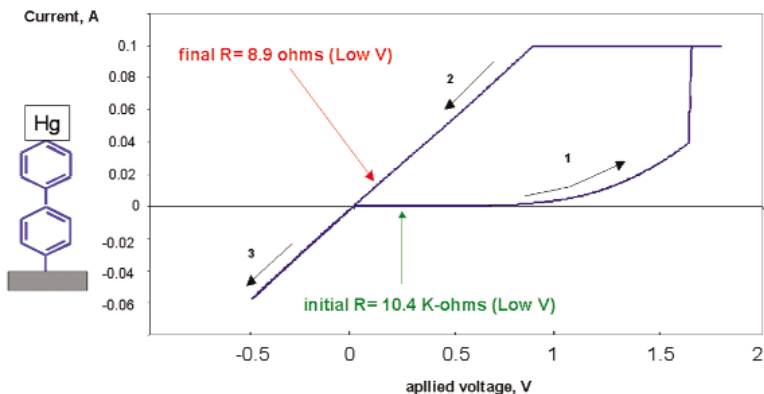

FIG. 4. i/V curve for a Hg/biphenyl/PPF molecular junction with an area of ~ 0.008 cm^2. The initial junction resistance is ~10 kΩ at low voltage, but increases nonlinearly until breakdown at ~1.6 V. See Ref. 29 for details.
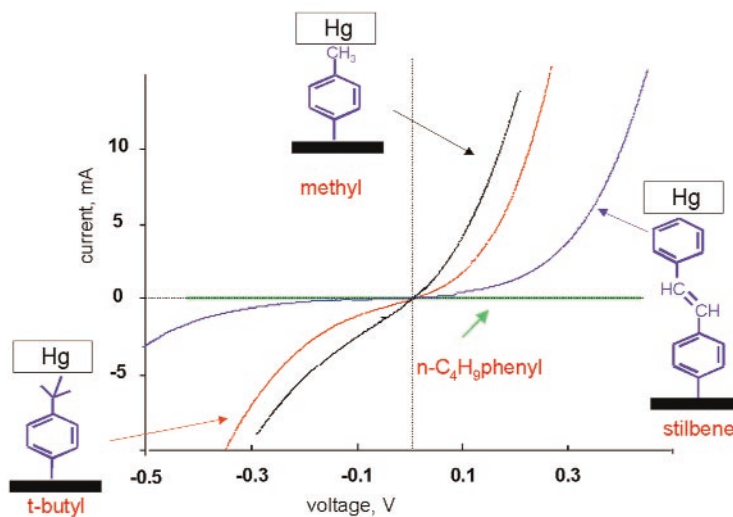

FIG. 5. i/V curves for four Hg/molecule/PPF junctions, all with areas of ~ 0.008 cm^2. The current for the n-butylphenyl junction is too small to observe on this scale, but the strong dependence of current on molecule length is apparent. See Ref. 28 for details.
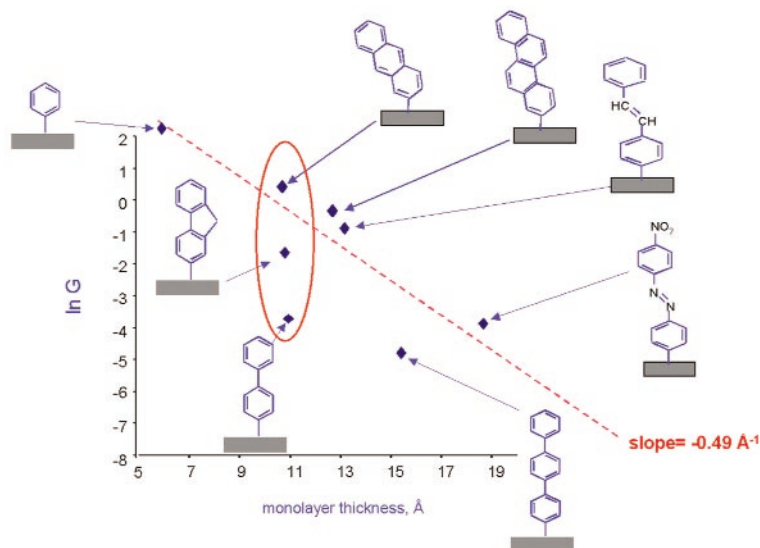

FIG. 6. Low voltage conductance of eight Hg/molecule/PPF junctions, plotted as ln G vs. monolayer thickness. G determined the slope of the i/V curve in the range V = + 50 mV. Anthracene, fluorene, and biphenyl are highlighted as molecules with nearly equal lengths, but different conductivities.
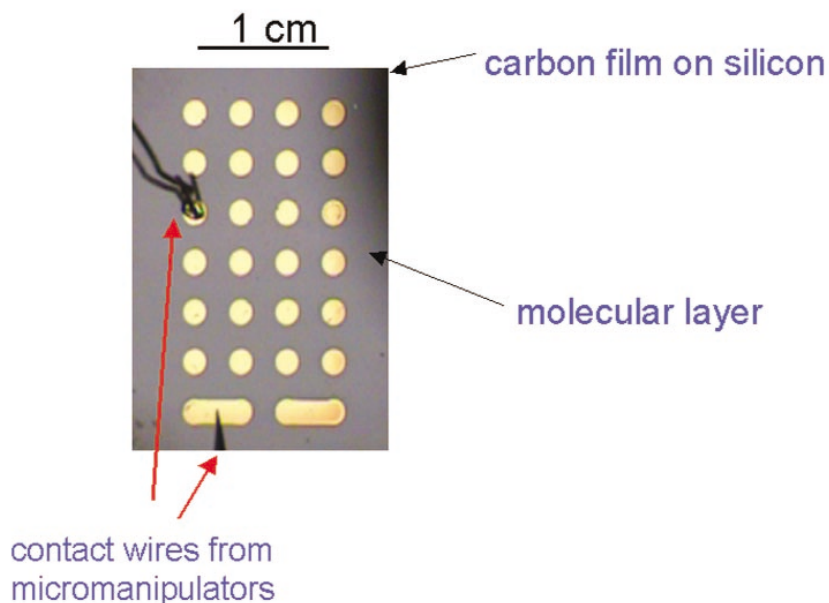
Fig. 7. Photograph of 24 Au/Ti/molecule/PPF molecular junctions made by vapor deposition of Ti and Au onto chemically modified PPF on silicon. Contacts were made with fine Pt wire positioned with micromanipulators and a video camera.
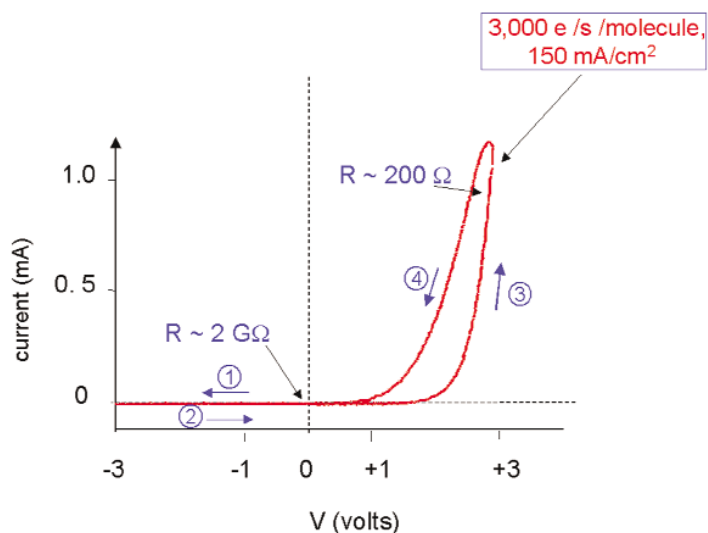

Fig. 8. i/V curve for a Au/Ti/NAB/PPF junction with a 37 Å thick molecular layer. The scan proceeded in the order and direction indicated by the arrows, at a rate of 1 V/s. See Ref. 8 for details.

have nearly identical interfaces with the PPF and Hg, except for nitroazobenzene (NAB), with its nitro group. So unless there is some unknown difference in junction structure, the wide range of observed conductivity (about three orders of magnitude) must be due to differences in structure and/or thickness.

The Hg top contact is a convenient "screening" technique, but suffers from uncertainty about contact area and cleanliness, and is not suitable for commercial application. Titanium metal deposited by electron-beam evaporation provides an alternative that is amenable to lithographic patterning. Slow deposition of Ti in a high vacuum (~10^{-6} Torr), followed by a gold layer to protect the Ti layer from oxidation has been used by several groups to make metal/molecule/metal junctions.[8,22,43] Although there is a possibility of monolayer damage due to the high reactivity of Ti atoms, Raman and Fourier transform infrared (FTIR) spectroscopies have shown that structural changes can be minor, and short circuits avoided.[8,44] Figure 7 is a photograph of 24 Au/Ti/biphenyl/PPF junctions, in which the probe leads to the instrumentation are visible. Once electrical contact is made with micromanipulators and wire probes, the i/V curves may be obtained with a conventional potentiostat or electronic test components.

The i/V curve for a PPF/nitroazobenzene/Ti/Au junction shown in Fig. 8 exhibits hysteresis and rectification, both of which may have useful electronic applications. Hysteresis is a sign of conductivity change during the positive scan that has a time scale comparable to that of the voltage scan. During the initial positive scan (indicated by the numbered arrow), the junction undergoes a transition to a more conductive state, yielding high current on the return scan (arrow 2). This conductivity change is more obvious in Fig. 9, which shows i/V curves obtained before and after a +4 V potential pulse. The junction resistance decreases by a factor of ~10^6 as a consequence of the voltage pulse, and slowly returns to the high resistance state after a few minutes. This phenomenon has been dubbed "conductance switching", and has been observed for several distinct junction designs.[2,8,45] Although the mechanism is somewhat controversial, the potential applications as molecular memory devices are important commercially. If a single molecule or

ly -0.5 Å⁻¹, but there is significant scatter away from the line that exceeds the error bars of each point. A slope of 0.5 Å⁻¹ is in the range reported for ET through phenylene and phenylethynyl oligomers in electrochemical experiments, suggesting a superexchange tunneling mechanism.[41,42] However, the deviations from the least squares line are significant, and provide important clues about how molecular structure affects conductivity. Consider biphenyl, fluorene, and anthracene, which all have a thickness close to 11 Å. Fluorene and biphenyl differ structurally only in the presence of a bridging CH_2 group which forces the aromatic rings in fluorene to be coplanar, while biphenyl has a dihedral angle of 37 Å. This difference causes a factor of 10 increase in conductivity, presumably due to greater electronic coupling between the aromatic rings in fluorene. Anthracene is also planar, but the fused rings are expected to be conjugated more extensively than those in fluorene, thus further increasing conductivity. All the molecules in Fig. 6

group of molecules can exhibit two stable conductivity states, there may be major advantages over capacitors or magnetic storage media in terms of data density, volatility, and cost.

The field of molecular electronics is definitely in its infancy, but results obtained to date are cause for significant optimism about its future. Electron transport in donor acceptor compounds, modified electrodes, and molecular junctions has been established, and sometimes occurs over long distances compared to those expected for electron tunneling. Furthermore, the demonstration of molecular rectifiers and conductance switching shows that single molecules, or collections of molecules in molecular junctions can perform electronically useful functions. It is too early to predict how the scientific story of molecular electronics will unfold, but a few technical challenges are evident from the experimental and theoretical results to date:

Can a "molecular wire" be made with a low barrier to ET over distances of 50-100 Å? Tunneling is efficient over very short distances (<15 Å) and conducting polymers show nearly metallic conduction over at least micron dimensions. For practical molecular circuits, we must learn to control ET over distances greater than those accessible by coherent tunneling, but well below those relevant to bulk materials.

How does ET in molecules depend on structure? It is becoming apparent how structural parameters such as conjugation, conformation, redox centers, and unsaturation affect ET rates through molecules. Can these observations be organized into a systematic description of the "rules" affecting ET rates?

Which electronic, chemical, or biological functions can be incorporated into molecular circuits, to collect a "box of parts" for molecular electronics? By analogy to conventional electronics, will it be possible to "wire up" molecular circuits to carry out complex functions?

Can we rationally design molecular circuits with predictable ET behavior? Once we understand some of the rules affecting ET in molecular circuits, can we prospectively design molecular assemblies with desired behavior? Such a design may require computer modeling and substantial theoretical effort, but in some ways represents the ultimate test of our understanding of molecular circuit components.

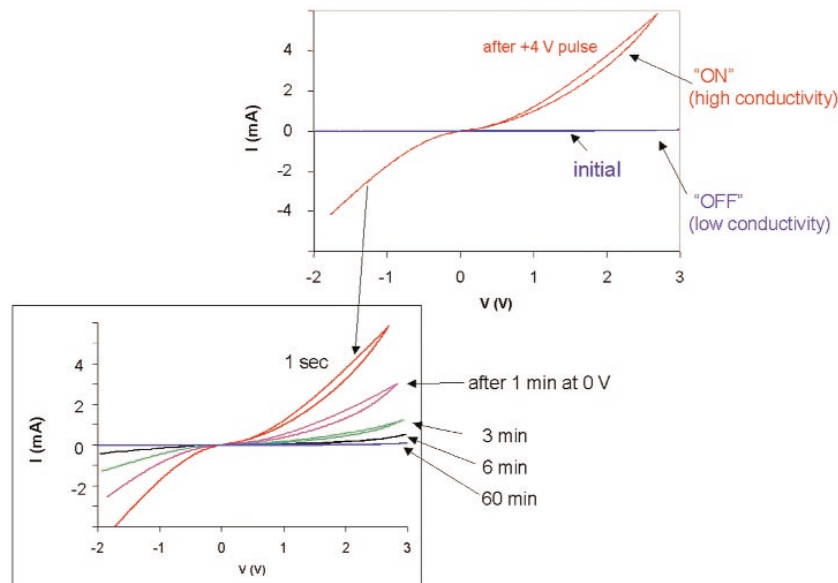Will molecular electronic devices be practical in terms of fabrication, cost, and lifetime compared to existing semi-conductor devices? The present semiconductor industry is highly refined and efficient, and silicon or metal oxide circuit components can run for years at gigahertz frequencies. To compete, molecular electronic devices must offer significant advantages in terms of cost, data density, power consumption, functionality, etc.

In summary, the carbon-based molecular junctions described here are only one entry in the already crowded and exciting field of molecular electronics. The progress to date in understanding how electrons propagate in molecules is substantial, and highlights the enormous promise of molecular electronics. Although many scientific investigations and commercial applications are in their infancy and their possibility of success is unclear, the road ahead should be interesting, indeed. ∎

FIG. 9. Rapid i/V curves (1000 V/) of a Au/Ti/NAB/PPF junction obtained before and after a +4 V potential pulse lasting 5 s. The high conductance "ON" state lasts for several minutes after the pulse, and the switching process may be repeated many times. The initial "OFF" curve is flat on the current scale shown because the rapid scan rate did not permit conductance switching. See Ref. 8 for details.

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