Single Molecule Electronics

by S. M. Lindsay

Most people date modern interest in using molecules as electronic devices to the publication of a classic paper by Aviram and Ratner.[1] Their paper outlined a scheme for a molecular rectifier and drew attention to the concept of using molecules as incredibly small electronic components. Despite thirty years of subsequent research, a central challenge remains: How can molecules be connected between wires to make useful molecular electronic devices?

One macroscopic approach, subject to failures at a microscopic level, is to lay a metal film on top of a self-assembled monolayer that sits on a metal electrode.[2] A microscopic approach uses a scanning tunneling microscope (STM) to address one or a few molecules.[3-6] In this case, the contact between the tip and the molecule is characterized only through measurement of the current itself, making independent characterization of the contact geometry difficult. Somewhat better control of the contact is obtained by using an atomic force microscope with a conducting probe.[7-9] Despite this work, many questions remain: Is just one molecule contacted? What is the atomic arrangement of the top contact? Does contamination on the probe affect the current? Reed and co-workers[10] used a breakjunction and molecules with two "sticky ends". The junction was made of a gold film that was cracked open to a remarkable degree of precision with a mechanical lever. The molecule, benzenedithiol, had opposing ends of the benzene ring functionalized with thiol groups. These thiol groups react with gold, so that careful breaking of the junction in the presence of the molecules should result in two macroscopic metal contacts bridged by one, or a few, molecules. This system is much better defined than the scanning probe experiments, but even so, the interpretation is open to question because the microscopic nature of the junction was unknown. The results of theoretical modeling underpin this concern. Currents calculated for this system with modern density-functional methods[11] are some 500 times larger than the experimental values, assuming that, in the best case, the experiment really measures the conduc-
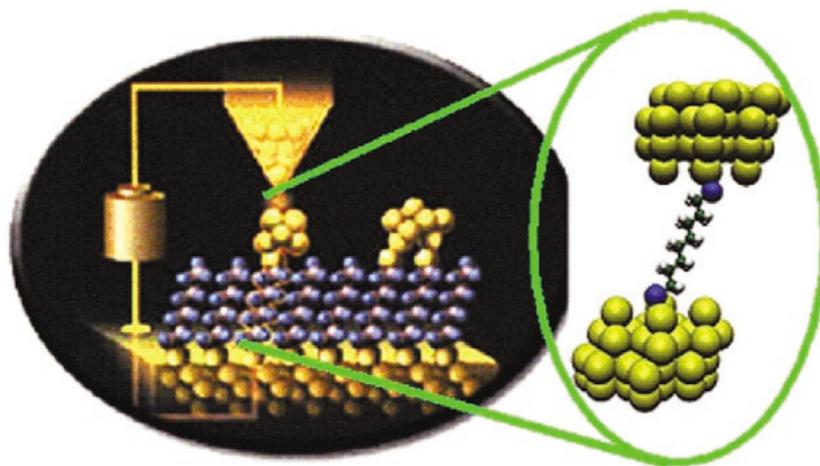

FIG. 1. The self-assembled metal-single molecule-metal junction. The molecule to be measured has a reactive thiol group at both ends and is inserted into a self-assembled alkanethiol monolayer of the same height. A gold NP is attached to the protruding thiol group at the top of the inserted molecule. A gold-coated CAFM probe is then pressed into the NP to complete the circuit. The molecule, attached to electrodes, is shown expanded on the right.

tance of a single molecule. This discrepancy is hard to understand, because modern calculations are generally reliable. Therefore, the problem lies with uncertainties about the atomic structure of the junction. Complex electronic responses can be obtained from metallic nanojunctions in the absence of molecules spanning the gap.[12]

Uncertainties about contacts plague many measurements. For example, experiments show that deoxyribonucleic acid (DNA) is an insulator,[13] semiconductor,[14] metal,[15] and superconductor![16]

Thus, we decided to tackle the problem of making well-defined contacts to a single, simple molecule in a well-defined environment, with the goal of comparing our results to first-principles calculations with no adjustable parameters. For this purpose, we chose to start with alkanedithiol molecules. The alkanes have a large highest occupied molecular orbital-lowest unoccupied molecular orbital (HOMO-LUMO) gap, with strongly localized σ orbitals. Electrochemical studies have shown that electrons are transported by tunneling with an exponential decay constant, β, of about 1 per added methylene group.[17-19] Methylene groups are simple to model theoretically and easy to handle experimentally.

To hold the dithiolated molecules in a well-defined orientation, we inserted them end-on into a preformed alkanethiol monolayer on the gold (111) surface.[20] This resulted in well-spaced dithiol molecules attached at one end to the gold substrate, with the thiol group at the other end protruding from the top of the monolayer. We began with octanedithiol inserted into an octane(mono)thiol monolayer. Even with the dithiol molecules oriented in this way, it was difficult to make contact to the top thiol group with a metal probe.[9] The problem is that a second, fixed contact, cannot be positioned precisely enough to permit good chemical bonding between the thiol and the gold solid. To get around this problem, we attached a second contact using wet chemistry. 1.5 nm diameter gold nanoparticles (NPs), suspended in solution, were incubated with the film, finding the protruding thiol groups by diffusion. Once attached, the thiol groups remained in place even after vigorous rinsing. These NPs were much better targets for the probe of a conducting atomic force microscope (CAFM), and we used a CAFM to locate the NPs and make contact to them.[21] This experiment is illustrated schematically in Fig. 1.
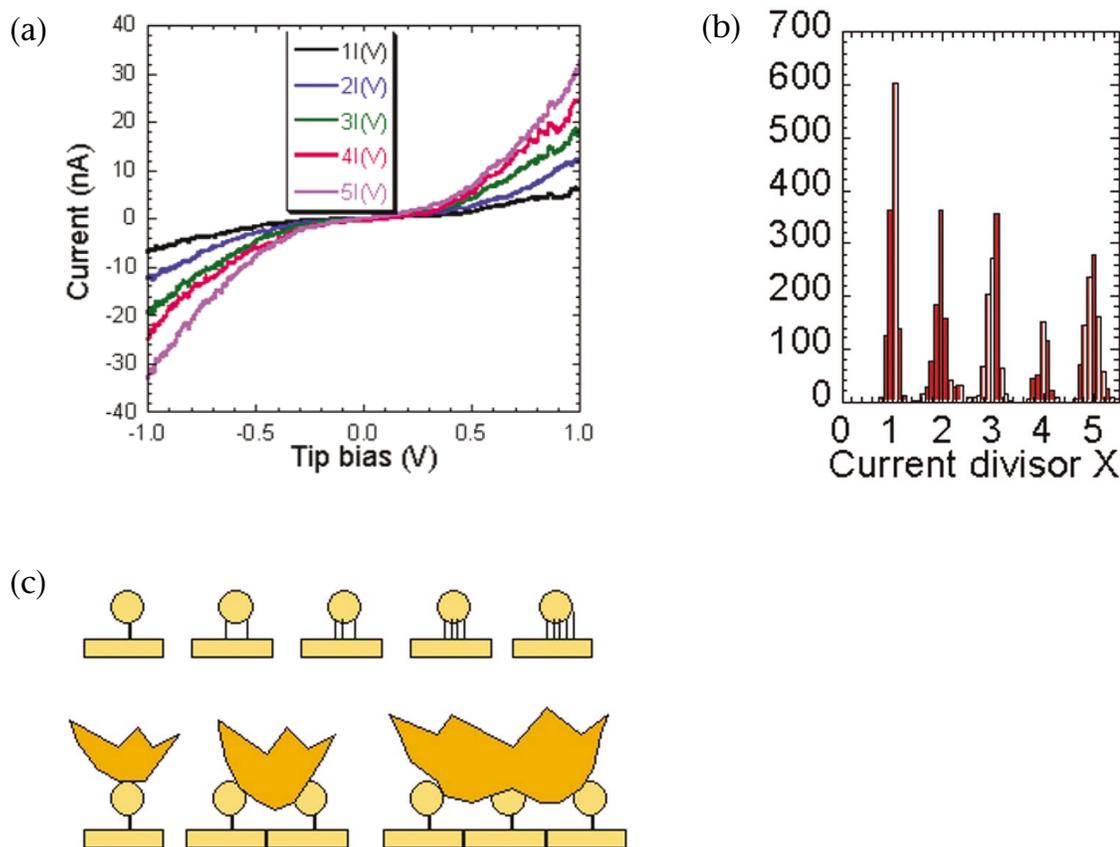
FIG. 2. (a) A family of I-V curves taken from few-molecule nanojunctions. The black curve is characteristic of the smallest currents observed, and therefore probably comes from a single molecule in the junction. The blue curve is everywhere double the current, the green curve three times, and so on. (b) Histogram of the divisor, x, used to minimize the variance between pairs of curves, showing the remarkable quantization of the I-V curves more clearly. In this experiment, over a thousand junctions contained a single molecule (x = 1). (c) Two models to account for the observed quantization: Top, one, two, three, etc., molecules connect the NP to the substrate. Bottom, a wide AFM probe contacts several different NPs.

The measured current-voltage (I-V) curves were dramatically different from previous measurements made by only pressing against an alkanethiol monolayer.[9] The currents were much larger (about a thousand times) and much more reproducible. The I-V data were tightly clustered around sets of curves that had the remarkable property of being integral multiples of a fundamental curve, as shown in Fig. 2a. Figure 2a shows a selection of typical curves; the current in the blue curve is everywhere twice that in the black curve, the current in the green curve is everywhere three times that in the black curve, and so on. There were no curves in the gaps between data. In other words, the current was quantized. A more objective analysis of the data is obtained from an automatic analysis of all the curves in a given experiment. We wrote a computer program to find the divisor that minimizes the variance between any pair of curves, dividing one of the pair with the overall larger current by this number. A

histogram of values of this scaling factor is shown in Fig. 2b. It is neatly peaked at integer values 1, 2, 3, etc. Thus, the current, at a given voltage, is really an integer multiple of a fundamental value. Two models that account for this behavior are shown in Fig. 2c. One possibility is that the AFM probe contacts several single-molecule junctions at one time, the currents adding up like the currents through resistors connected in parallel. Another possibility is that multiple molecules may span the gap between the NP and the substrate. Sorting out the correct model is complicated because AFM probes that make good electrical contacts are usually too blunt to give high-resolution topographic images. Whatever the correct interpretation, the fundamental curve is surely that owing to a single molecule in the gap.

Thus, we can identify the I-V curves from a single molecule covalently connected to two metal electrodes. Interpretation of the data is further simplified because the measured current

appears to be insensitive to even large strains, adjusted by altering the contact force of the AFM probe.[21] This is in sharp contrast to measurements made by merely pressing against a monolayer[9] where the current increases exponentially with contact force. One interpretation of this observation is that the use of a chemically bonded assembly has changed the dominant pathway from a chain-to-chain mechanism to a through-bond mechanism.[18] The through-bond mechanism is the bond-mediated transport usually assumed to be the case in theoretical models.

Tomfohr and Sankey calculated the expected I-V curves using a density-functional method[22] to obtain matrix elements for a Green's function from which the electron transmission could be calculated.[23,24] There were no adjustable parameters in these calculations. The location of the bonded sulfur is found by minimizing the system's electronic energy, and the position of the gold Fermi energy with respect to the HOMO-

LUMO gap is set by self-consistent calculation of the charge distribution at the interface. Density functional theory tends to underestimate bandgaps, but the HOMO-LUMO gap of *n*-alkanes is so large that little error results from this. The result is a predicted I-V curve that is within a factor of ten of the absolute magnitudes of the measured currents.[21] This is a big improvement (compared to factors of 500), but the remaining discrepancy is interesting.

We then measured a series of *n*-alkane molecules of various lengths, similarly connected to metal electrodes in self-assembled junctions using thiol groups at each end of the molecules. Good, reproducible data was obtained[25] but it was hard to interpret. The decay of current with increasing molecular length yielded a value for β that was too small (0.6 per methylene compared with the expected 1.0). Furthermore, β appeared to be dependent on the applied bias, in contrast to theoretical predictions and the results of electrochemical measurements.[26] The mystery was resolved by realizing that the contact between the AFM probe and the gold NP is not perfect. The NP is functionalized with triphenyl phosphate ligands, and measurements are made in a liquid (toluene) to minimize friction between the probe and the sample, and both the liquid and attached ligands may interfere with the contact to the AFM probe. Only a very small contact resistance is needed (the quantum of resistance, $h / 2e$ or 12.9 kΩ) for the NP to charge independently of the AFM probe. Because the charging energy of the NP is $e / (4\pi\varepsilon\varepsilon_0 R)$ where $\varepsilon\varepsilon_0$ is the appropriate dielectric constant), it becomes significant (on the order of volts) when the NP radius, R, is on the order of nanometers. Thus, current is suppressed at low bias, a phenomenon known as Coulomb blockading. Close inspection of a typical I-V curve shows this clearly (Fig. 3). Rather than growing exponentially, the I-V curve abruptly increases, as though a lower resistance were suddenly switched into the circuit at ±0.5 V. We used a well-established parametric model[27] of the Coulomb blockade to fit these curves. The entire data set (for octanedithiol, decanedithiol, and dodecanedithiol) was well fitted with one set of parameters for the NP capacitance (unpublished data). The same set of parameters was used successfully to fit data obtained on carotene molecules using similar NPs.[28] Thus, we believe that the residual discrepancy between theory and experiment is now resolved by taking account of the Coulomb
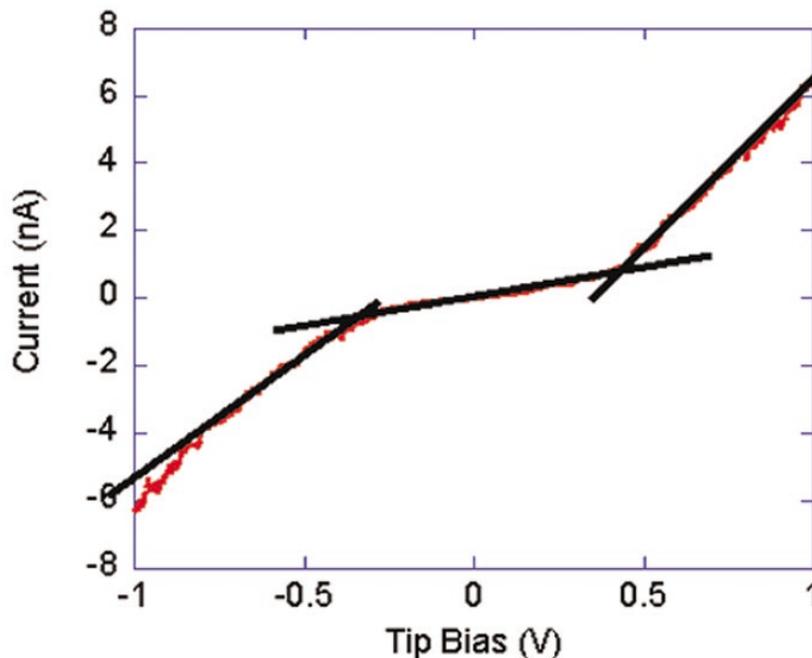

Fig. 3. *Current vs. voltage curve for a single molecule of octanedithiol connected to gold electrodes (red data points). The black lines correspond to one Ohmic regime below ±0.5 V and a second at higher bias. These data are well fitted by a Coulomb blockade model.*

blockade. With the Coulomb blockade accounted for, we find that β for the alkanes is about 1 per added methylene, and independent of the applied bias (over ±1 V). The original goal, of obtaining and understanding I-V data from a single molecule in a metal-molecule-metal junction has thus largely been achieved. Some residual small discrepancies remain and may be important, but the most important aspects of transport are understood.

The NP-contact technique has been applied to molecules of more functional interest. One example is a nitro-modified phenylene ethynylene, a molecule shown to display negative differential resistance (NDR) when assembled into nanopore devices.[29] The geometry of the molecules in the nanopore device is uncertain, and there has been debate about whether the phenomenon has anything to do with the intrinsic properties of the molecules. We used the same techniques described above to assemble single-molecule junctions containing phenylene ethynylene molecules with, and without a pendant nitro group. Molecules with the nitro group exhibited a variable Ohmic (linear I-V) background that precluded the automated statistical analysis applied to the *n*-alkane molecules. However, a clear NDR peak was observed in the curves (Fig. 4). The similar size of this peak in the vari-

ous curves suggests that single molecules are being measured. This observation of NDR in single molecules confirms the original report of NDR in the nanopore structures[29] and shows that the phenomenon is intrinsic to the molecule. NDR is absent in the molecules lacking the nitro group (green curve in Fig. 4). The nitro group is responsible for the reducibility of these molecules, so it is tempting to assume that electrochemical reactions underlie the observed NDR. Reversible reactions should give rise to a sigmoidal I-V curve,[30] but reactions that involve depletion of factors in the environment of the molecules could explain the peak (*i.e.,* NDR) observed in the curves.

Most single (or few) molecule measurements have been made using gold electrodes. But gold is a remarkably pliable metal, and many experiments have shown that thiolated molecules move easily on the gold surface. They can even dissolve into a solvent, carrying a gold atom with them! In light of this, it is not surprising that we see random fluctuations in the conductivity of single molecules tethered to a gold surface.[31] The fluctuations increase at the mildly elevated temperatures used to anneal the self-assembled monolayers, adding credence to the idea that the gold-sulfur bond is intrinsically unstable (it is more likely that the gold-sulfur bond remains
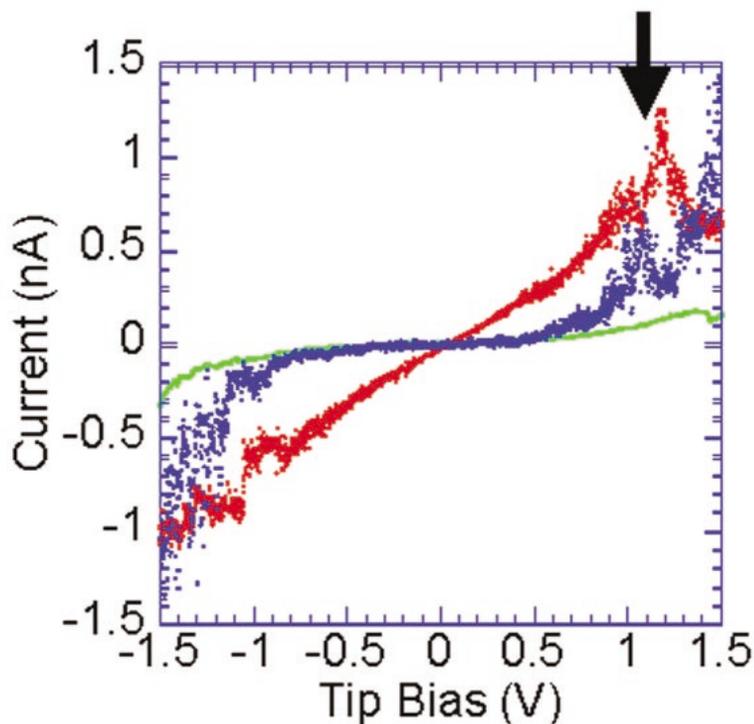
FIG. 4. Blue and red curves show extremes of the data measured for nitro-modified phenylene ethynylene molecules. The Ohmic background varies a lot, but the NDR peak (arrow) is about the same in each case. The green curve is characteristic of the molecule without a nitro group. Thus NDR is an inherent property of these molecules and requires the presence of the nitro group.

intact and the connection between the gold atom attached to the sulfur and its neighboring gold atoms fluctuates – see the references in Ramachandran *et al.*).[31] Because the fluctuation rates are similar in different molecules tethered to gold surfaces by thiol groups, this observation offers a plausible explanation of random switching fluctuations found in more complicated molecules tethered to gold surfaces.[31,32] Fluctuations of the gold in the immediate vicinity of the sulfur attachment may disconnect the molecule altogether as important electronic overlaps change with the changing position of gold atoms near the tether point of the molecule.

Recently, Xu and Tao[33] introduced a version of the breakjunction that avoids some of the difficulties of our NP technique. In their approach, a gold STM probe is pushed into a gold surface and then pulled away to form atomically thin filaments of gold between the tip and the substrate. These filaments are characterized by quantized steps in the conductance [multiples of 1/(12.9 kΩ)].[34] When the junction is submerged in a solution of dithiolated molecules (or bipyridine) a series of much smaller conductance steps is observed [multiples of 1/(mega/gigaohms)]. In alkane dithiols,

where the work described above has established a value for single-molecule conductance, these peaks in the distribution of conductance plateaus are separated by exact multiples of the known single-molecule conductance. Thus, this simple technique (no self-assembly required!) can be used as a quick assay of molecular conductance. The results raise an interesting question. The conductance steps are separated by plateaus of constant conductance (over some nanometers), so how can the conductance remain constant as the STM tip is pulled away after the gold nanowire has broken? Xu and Tao[35] used a CAFM to measure the force between the probe and surface at these conductance plateaus. Remarkably, the molecules remained stable as the nanojunction extended by gold extrusion from the surface of the substrate and the probe. Evidently, gold electrodes behave like runny cheese at room temperature, flowing out of the surfaces as the molecule remains relatively unperturbed!

The measurements described above provide a basis for testing more manufacturable technologies. No one will make computer chips from scanning probe microscope connections to molecules, but data such as those described

above will prove useful in validating other means for connecting to single molecules.

The connection of molecules to fixed electrodes remains a thorny problem. The difficulty is that, given a molecule of fixed geometry, fixed to an electrode of fixed geometry, how can a second electrode be placed in exactly the right position to form a proper chemical bond with another part of the molecule? One solution to the problem is to use only one covalent bond, sensing electronic changes by electrochemical means.[36,37] This solution may be valuable in some applications, but does not address the problem of connecting candidate electronic devices. There are many reports of electronic measurements of molecules, perhaps even single molecules, attached between pairs of fixed electrodes that form a nanometer-scale gap (see, for example, the work of Park *et al.*[38]) but these experiments require careful selection of good devices. One way to make this selection more objective is to use molecules that respond to an external stimulus, so that the gap can be tested for the presence of a molecule independently. As an example, a photo-switchable (photochromic) molecule has been shown to change conductance dramatically on illumination.[39] Interestingly, this work was carried out using an adjustable breakjunction, mitigating the problem of constraints in a fixed gap.

Will single (or few) molecule devices ever be manufacturable? The answer is probably yes. But getting there will require atomic control over the way in which nanogaps are fabricated. If devices are shrunk to the single-molecule scale, their contacts must be controlled to a similar level of precision. ∎

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