Charge Transport and Scaling in Molecular Wires

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The scaling of conductance across metal–molecule–metal junctions consisting of self-assembled monolayers of dithiol molecular wire candidates is demonstrated through current–voltage measurements carried out by two experimental techniques. We show that scanning tunneling microscopy measurements on single molecules are correlated with crossed-wire measurements of $\sim 10^3$ molecules. This implies that the conductance through a group of parallel molecules is a linear superposition of the individual molecular conductance. Our results also indicate that intermolecular charge hopping does not strongly contribute to charge transport in a self-assembled monolayer, an important factor for the design of future molecular-based devices.

1. Introduction

Although charge transport across organic molecules as a function of molecular structure has previously been investigated using a variety of experimental techniques such as nanopores,[1–4] mercury drop electrodes,[5,6] crossed wire junctions,[7,8] and scanning probe techniques,[9–14] the nature of conductance through collections of parallel molecules still remains an open question. For a macroscopic system of parallel conductors, the total conductance is equal to the individual conductance multiplied by the number of conductors. However, it is unclear that this relation holds true on a molecular scale, particularly when large numbers of molecules, coupled on both sides to metal contacts, are involved. Previous experiments have shown that for small numbers (1–5) of insulating alkanethiols, the total conductance is a superposition of the number of conductors.[12] In addition, our earlier study indicated that the linear superposition law of molecular conductance is valid for a large number of conjugated molecules.[15] In that study, which involved molecules with asymmetric contacts, the number of molecules across which the conductance was measured was essentially inferred on the basis of the underlying structure of the lattice of the self-assembled monolayer. Hence, a direct experimental demonstration of the conductance scaling involving a large number of molecules that are in symmetrical contact with metal on both sides has yet to be established.

2. Experimental Section

We have carried out current vs voltage (I–V) measurements on two different effective sample sizes. In one experiment, the I–V characteristics of self-assembled monolayers (SAMs) of the three molecules investigated (shown in Table 1) were measured with a crossed-wire tunnel junction (Figure 1a).[8] It should be noted that all of the experimental molecules are dithiols: 1,12-dodecanedithiol (C12) is a saturated molecule, and oligophenylene–ethynylenedithiol (OPE) and oligophenylene–vinylenedithiol (OPV) are conjugated systems consid-

ered molecular wire candidates. The I–V characteristics of metal–molecule–metal junctions were measured using a crossed-wire tunnel junction method, which has been previously described.[16] Briefly, a junction is formed from two 10 μm diameter gold wires, one modified with a self-assembled monolayer of the molecule to be measured. The wires are mounted in a custom-built test stage so that they are crossed and the wire spacing is controlled by the Lorentz force: dc current in one wire deflects it in a magnetic field. The deflection current is slowly increased to bring the wires gently together forming a junction at the contact point. The I–V characteristics were obtained with an Agilent 4155B parametric analyzer (Agilent, Palo Alto, CA) under computer control. All measurements were made at room temperature in a nitrogen environment.

In the other experiment, the conductance of individual dithiol molecules inserted into a tightly packed self-assembled matrix of undecanethiol (C11) (Figure 1b) was measured by scanning tunneling microscopy (STM).[9,10,12,14,17] For these experiments, SAMs of C11 alkane were deposited out of ethanol onto a Au (111) surface evaporated onto a mica substrate (SPI, West Chester, PA). The C11 monolayers were then exposed to the dithiol molecule of interest for 1 h, allowing the test molecule to insert into the alkane matrix at defect sites such as step edges and domain boundaries (Figure 1c). After insertion, the films were exposed to unfunctionalized 2 nm gold colloidal particles (SPI, West Chester, PA), used as received, for 30 min. The gold nanoparticles bind to the inserted dithiol molecules, making visualization and measurement with the STM easier (Figure 1d). Control experiments on C11 SAMs without inserted dithiol molecules show no nanoparticle attachment. STM measurements were performed under ambient conditions with a Digital Instruments Multimode STM with low current attachment using a Nanoscope IIIa controller (Veeco Metrology, Santa Barbara, CA).

3. Results and Discussion

Table 1 shows the normalized conductance for the four molecules studied. As in the crossed-wire tunnel junction method, the molecular conductance trend measured by the STM is C12 < OPE < OPV. Thus, the STM measurements of single (or a small number of) molecules reproduce the same trend

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TABLE 1: Molecular Structures, Lengths, Measured Resistance, and Relative Conductance

sample	molecular structure	length[a]	crossed wire resistance[b]	STM resistance[b]	crossed wire G_{rel}[c]	STM G_{rel}[c]
C11	AcS	1.45	-	-	-	-
C12	AcS ... SAc	1.69	1.1 ± 0.4 GΩ	5.0 ± 1.5 GΩ	1	1
OPE	SAc ... SAc	2.02	1.7 ± 0.6 MΩ	1.7 ± 0.4 GΩ	14	3
OPV	AcS ... SAc	2.07	0.5 ± 0.2 MΩ	0.6 ± 0.1 GΩ	45	9

[a] Length is the calculated length of the molecule in nm from sulfur atom to sulfur atom. [b] Resistance is measured from the slope of the line in the Ohmic region (-0.1 to $+0.1$ V). [c] G_{rel} is the conductance from the slope of the line in the Ohmic region (-0.1 to $+0.1$ V), normalized to the conductance of the C12 molecule.
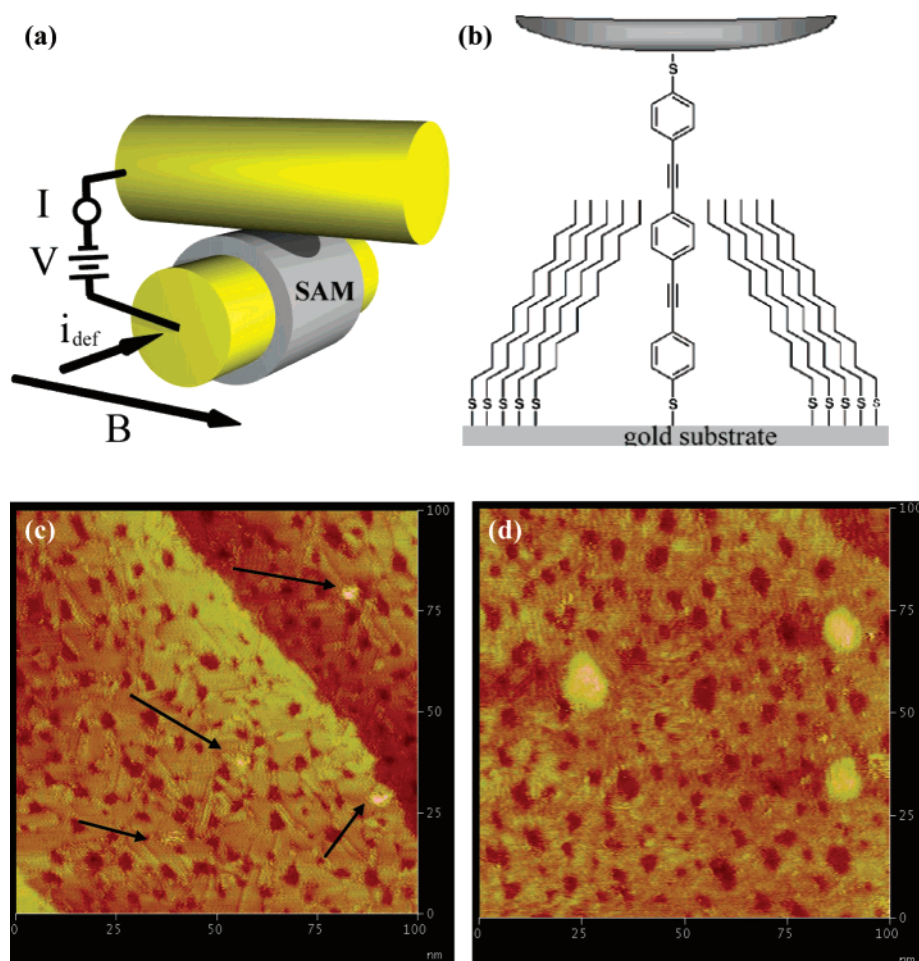

Figure 1. (a) Schematic showing the crossed-wire tunnel junction. (b) Schematic showing OPE dithiol molecule inserted into a defect in a C11 alkanethiol film with a nanoparticle attached. (c) STM image of C11 alkanethiol film with inserted OPE molecules, indicated by arrows. $I_t = 2.5$ pA, $V_{bias} = 1$ V. (d) STM image of C11 alkanethiol film with inserted OPE molecules and 2 nm gold nanoparticles bound to the OPE. $I_t = 2.5$ pA, $V_{bias} = 1$ V.

observed for larger self-assembled films.[8,14] Because the crossed-wire tunnel junction and the STM measurements of molecular conductance are done on very different size scales, a careful examination of the two types of data can lead to a better understanding of scaling in molecular systems. It is clear from simple geometric considerations that the crossed-wire tunnel junction probes orders of magnitude more molecules than the STM. We calculate by comparison to other charge transport measurements that the crossed-wire tunnel junction contains $\sim 10^3$ molecules.[2,18] In contrast, in the STM experiments, the experimental molecules are individually inserted into the C11 matrix, suggesting that the STM data are likely for only a single molecule (Figure 1c).[14] The molecules inserted into the C11 matrix appear larger than expected for a single molecule. This can be readily explained through the relative sizes of the protruding molecule vs the scanning tip. Because the molecule
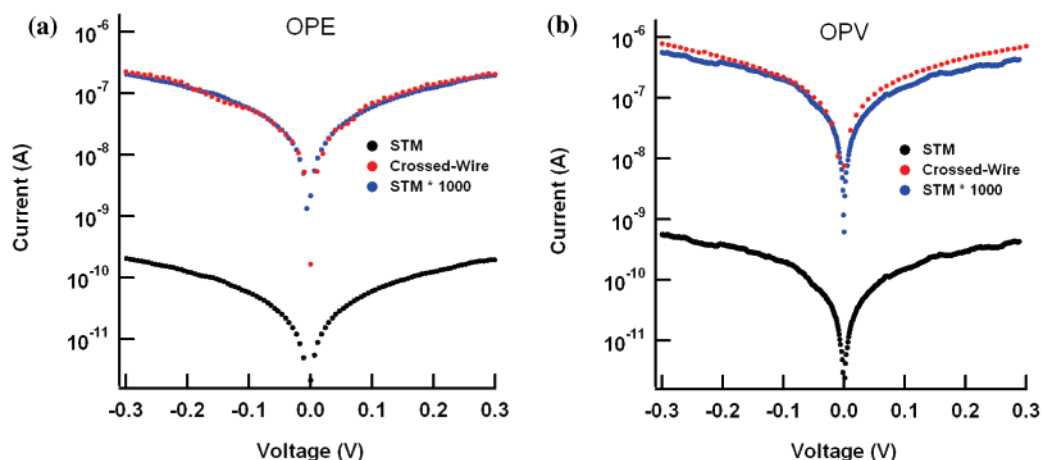
Figure 2. (a) *I*−*V* characteristics for the OPE molecule. (b) *I*−*V* characteristics for the OPV molecule. STM current shown in black, crossed-wire tunnel junction current shown in red, STM current multiplied by 10^3 shown in blue. STM current $\times$ 10^3 is a good fit for the crossed-wire data.
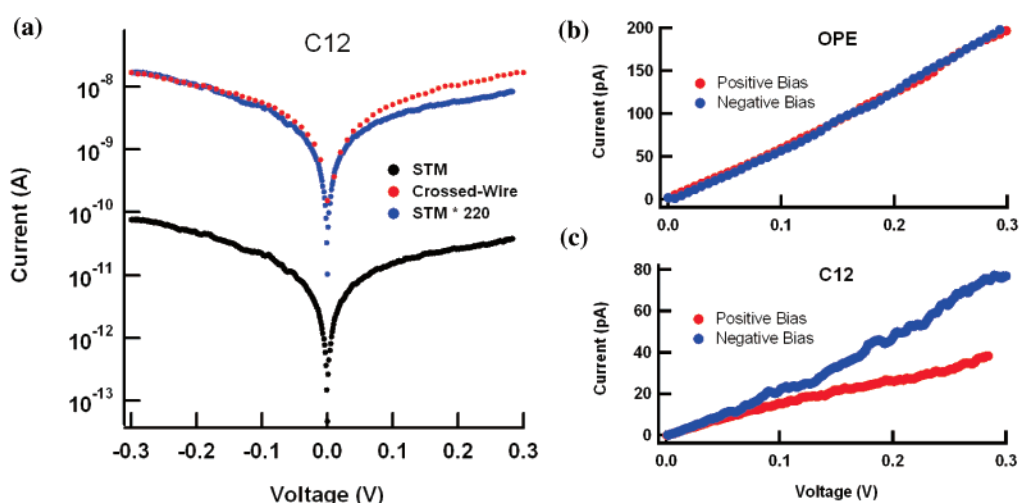

Figure 3. (a) *I*−*V* characteristics for the C12 molecule. STM current shown in black, crossed-wire tunnel junction current shown in red, STM current multiplied by 220 shown in blue. STM current $\times$ 220 is a better fit for negative bias polarity than for positive. (b) Current vs absolute value of bias voltage for OPE and (c) C12 from STM data. OPE shows symmetric current with respect to bias polarity due to symmetric contacts, whereas C12 shows asymmetric current due to additional contributions from mechanically coupled C11 molecules.

is much smaller than the tip, the STM image shows the shape of the tip rather than the shape of the molecule. If more than one molecule were inserted into the film, each molecule would contribute to the tunneling current, resulting in a convolution of images of the tip. Because we do not see this in our images (Figure 1c), we assume that most of the insertions are single, isolated molecules and not bundles of molecules. However, we cannot rule out the possibility that more than one molecule is inserted at each site.

One potential complication in comparing data between the crossed-wire tunnel junction and the STM tunnel junction is in the type of coupling of the measured molecules to the probe wire or tip. In the crossed-wire tunnel junction, the molecules are chemically attached to the two gold wires via thiolate linkages. In the STM, the molecules also are bound on both sides—to the substrate on one end, and to a gold nanoparticle on the other, via sulfur−gold bond formation. However, the junction between the STM tip and nanoparticle is less defined. It can be argued that due to an intervening vacuum gap between the tip and the sample that contributes to the measured gap resistance, the STM *I*−*V* measurement is not a direct measurement of the molecule.[19] Nevertheless, in our experiment, the STM tip is believed to be in good mechanical and electrical contact with the gold nanoparticle. Evidence for this comes from both topographic images and electronic measurements. The gold

nanoparticles used in this experiment have a diameter of 2.5 nm, as measured by TEM.[20] However, in STM images these 2.5 nm diameter nanoparticles appear to be 0.63 ± 0.09 nm above the C11 matrix (Figure 1d). Even if the gold nanoparticles were in physical contact with the gold substrate, they would still protrude 1.25 nm above the C11 film, assuming an alkyl chain tilt of 30° from the surface normal. Direct measurement of the true height of the gold nanoparticles above the C11 film could be measured through a contact technique such as atomic force microscopy; however, such measurements were not done on these samples. In either geometrical extreme, the STM tip is not retracting the full distance required to maintain a constant vacuum gap over the nanoparticles and may instead be in direct contact with the gold nanoparticles.

In addition, the excellent experimental agreement between conductance measurements in the STM and the crossed-wire tunnel suggests that the STM tip is mechanically coupled to the gold nanoparticles. A direct comparison of the *I*−*V* measurements from the STM tunnel junction with the crossed-wire tunnel junction is plotted on a log scale in Figure 2a for OPE and Figure 2b for OPV. For both of these π-conjugated molecules, the measured tunneling current in the crossed-wire tunnel junction is a factor of 10^3 larger than the tunneling current from a single molecule measured by STM. As previously described, the crossed-wire tunnel junction measures 10^3

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molecules, whereas the STM probes a single molecule. Because a direct comparison of the two measurements shows a factor of 10^3 difference in the measured current, we confirm that the overall conductance of a set of parallel conjugated molecules is indeed a linear superposition of the individual conductances, as has been suggested by previous experiments.[12,15] Also, because differences in coupling to the electrode can cause the measured conductance to change by 1−3 orders of magnitude,[7,12,21] the data imply that the STM tip is indeed in good contact with the attached gold nanoparticle.

In contrast, the *I*−*V* measurements of the C12 compound are different from the π-conjugated molecules. Figure 3a shows a direct comparison of the *I*−*V* measurements from the STM and the crossed-wire tunnel junction. Unlike for the conjugated systems, the tunneling current measured by the crossed-wire tunnel junction is only a factor of 220 larger than the tunneling current measured by STM. One explanation for the difference in behavior is in the relative measurement geometry. In the STM experiment, we have no control over the force applied to the nanoparticle. If the STM tip is in contact with the nanoparticle, this uncontrolled applied force can push the attached gold nanoparticle into mechanical contact with the surrounding C11 alkane matrix. Instead of measuring a single dithiol test molecule, the STM experiment measures a test molecule chemically coupled to the nanoparticle along with a number of additional C11 molecules from the matrix that are in mechanical contact with the gold nanoparticle. For OPE and OPV, the conductance of the conjugated molecules is at least 2 orders of magnitude larger than that of the C11 molecules. Thus, even if there were C11 molecules in contact with the nanoparticle, the contribution of any mechanically coupled C11 molecules to the overall measured conductance is insignificant for these systems. In contrast, given that the measured β for alkanethiols is 1.0 Å^{-1},[13,19,22] the difference in conductance between a C11 molecule and a C12 molecule is small enough that several C11 molecules interacting with the gold nanoparticle can contribute to the overall measured current.

Previous studies have demonstrated that gold nanoparticles have a truncated octahedral shape, resulting in hexagonal and octahedral facets.[23−25] Measurements show that a 2.4 nm gold nanoparticle has 8 hexagonal facets with an area of ~9.5 nm^2 and 6 square facets with an area of ~3.6 nm^2.[25] On the basis of these areas and the nearest neighbor distance of 0.5 nm for a SAM of C11 alkanes,[14] calculations based on a statistical average of the two facet surface areas show that it is possible to contact nominally 34 additional molecules, which can then contribute to the measured conductance. Further evidence for a contribution to the measured current from mechanically coupled molecules can be seen in Figure 3b,c. These graphs show the measured tunneling current plotted against the absolute value of the applied bias. For the OPE and OPV (not shown) molecules, the top and bottom contacts are both chemically coupled through a gold−sulfur bond and the *I*−*V* behavior is symmetric with respect to bias polarity. However, for the C12 measurement, there is a noticeable asymmetry in the measured *I*−*V* behavior. This observed asymmetry is consistent with a higher conductance for electron injection through the chemically coupled substrate at negative bias polarity and a lower conductance at positive polarity when injecting electrons through the mechanically coupled nanoparticle. Such *I*−*V* behavior has been observed previously for systems with asymmetric contacts, where one side is chemically coupled and the other is mechanically coupled.[7,16] The asymmetry observed in this measurement implies that there is a substantial contribution in conductance

from mechanically coupled C11 molecules from the matrix. Although the conductance of a mechanically coupled system is at least an order of magnitude smaller than that of a chemically coupled system,[16] the slightly shorter length and the relatively large number of C11 molecules means that mechanically coupled C11 molecules could contribute a large fraction of the overall conductance.

4. Conclusion

We have found that in π-conjugated molecular wire systems, the conductance of molecular wires connected in parallel scales linearly with the number of molecules. Geometrical considerations demonstrate that the crossed-wire tunnel junction measures 10^3 molecules, whereas the STM probes individual isolated molecules in a C11 alkane matrix. A direct comparison of *I*−*V* measurements taken in both experimental systems shows that 10^3 times more current flows in the crossed-wire tunnel junction vs the STM. This indicates that electron transport occurs through discrete individual molecules and does not involve intermolecular hopping. This is an important consideration in the design of future molecular devices. A detailed study of the temperature dependence of the conductance of OPE and OPV would be important to establish that tunneling is the primary mechanism of conduction in the case of the molecular wires. Such studies are currently in progress.

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