Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions

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Measurement of Single-Molecule Resistance by Repeated Formation of Molecular Junctions

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The conductance of a single molecule connected to two gold electrodes was determined by repeatedly forming thousands of gold-molecule-gold junctions. Conductance histograms revealed well-defined peaks at integer multiples of a fundamental conductance value, which was used to identify the conductance of a single molecule. The resistances near zero bias were 10.5 ± 0.5, 51 ± 5, 630 ± 50, and 1.3 ± 0.1 megohms for hexanedithiol, octanedithiol, decanedithiol, and 4,4′ bipyridine, respectively. The tunneling decay constant (β_N) for N-alkanedithiols was 1.0 ± 0.1 per carbon atom and was weakly dependent on the applied bias. The resistance and β_N values are consistent with first-principles calculations.

Wiring individual molecules into an electronic circuit is an exciting idea that has been pursued actively by many groups (1). Although recent advances have been impressive (2–6), a basic question that remains a subject of debate is what is the resistance of a simple molecule, such as an alkane chain, covalently attached to two electrodes? Large disparities have been found between different experiments (7–10), which reflects the difficulty of forming identical molecular junctions. Even if the resistance of a molecular junction is reproducibly measured, ensuring that the resistance is really due to a single molecule is another substantial challenge. For molecules with a metal redox center, a single-electron charging effect has been used as a signature of single-molecule measurement (5, 6). For many other molecules, a different signature is required. Cui *et al.* (11) reported a conducting atomic force microscope (AFM) method to measure the resistance of octanedithiol that has one end of the molecule anchored to a gold substrate and the other end attached to a gold nanoparticle. In that work, the molecular junction was measured hundreds of times so that statistical analysis could be performed. However, the procedure involves several elaborate assembly steps, and the measured resistance is complicated by a Coulomb blockade effect due to finite contact resistance between the AFM probe and the gold nanoparticle (12, 13).

Here we report on a simple and unambiguous measurement of single-molecule resistance, achieved by repeatedly forming thousands of molecular junctions in which molecules are directly connected to two electrodes. The resistance for N-alkanedithiol connected to gold electrodes near zero bias is approximately given by $A_{\exp}(\beta_N N)$, where $A \sim 1.3 \times h/2e^2$ (h is Planck's constant and e is the electron charge), N is the number of carbon atoms along the tunneling pathway, and β_N is the decay constant determined by the electronic coupling strength along the molecule. The resistance is in good agreement with theoretical calculations (14, 15). The decay constant, $\beta_N = 1.0 \pm 0.1$ per carbon atom, is weakly dependent on the applied bias, which is consistent with both theory (14, 16) and previous experimental evidence (17–21). We demonstrate that the method can be applied to other bifunctional molecules, such as 4,4′ bipyridine, which binds to gold electrodes via nitrogen-gold affinity.

We created individual molecular junctions by repeatedly moving a gold scanning tunneling microscope (STM) tip into and out of contact with a gold substrate in a solution containing the sample molecules (4,4′ bipyridine and N-alkanedithiols) (22). 4,4′ bipyridine, a heterocyclic molecule, has two nitrogen atoms on its two ends that can bind strongly to gold electrodes to form a molecular junction (inset, Fig. 1D) (23). During the initial stage of pulling the tip out of contact with the substrate, the conductance decreased in a stepwise fashion, with each step occurring preferentially at an integer multiple of conductance quantum $G_0 = 2e^2/h$ (Fig. 1A). A histogram constructed from ~1000 such conductance curves shows pronounced peaks at 1 G_0, 2 G_0, and 3 G_0 (Fig. 1B). This value is the well-known conductance quantization, which occurs when the size of a metallic contact is decreased to a chain of Au atoms (inset, Fig. 1A) (24, 25). When the atomic chain was broken by pulling the tip away farther, a new sequence of steps in a lower conductance regime appeared in the presence of 4,4′-bipyridine (Fig. 1C). The correspond-
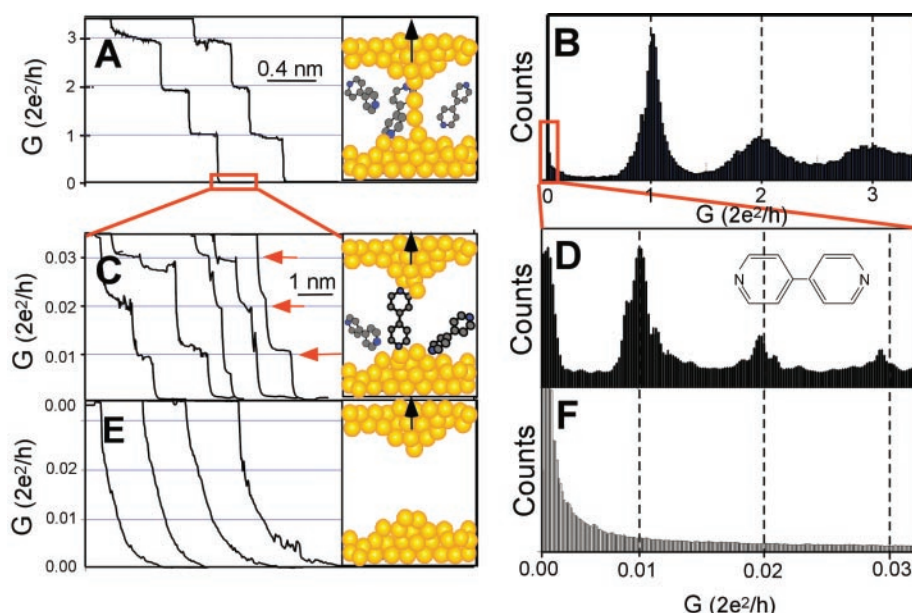

Fig. 1. (A) Conductance of a gold contact formed between a gold STM tip and a gold substrate decreases in quantum steps near multiples of G_0 (= $2e^2/h$) as the tip is pulled away from the substrate. **(B)** A corresponding conductance histogram constructed from 1000 conductance curves as shown in (A) shows well-defined peaks near 1 G_0, 2 G_0, and 3 G_0 due to conductance quantization. **(C)** When the contact shown in (A) is completely broken, corresponding to the collapse of the last quantum step, a new series of conductance steps appears if molecules such as 4,4′ bipyridine are present in the solution. These steps are due to the formation of the stable molecular junction between the tip and the substrate electrodes. **(D)** A conductance histogram obtained from 1000 measurements as shown in (C) shows peaks near 1 ×, 2 ×, and 3 × 0.01 G_0 that are ascribed to one, two, and three molecules, respectively. **(E and F)** In the absence of molecules, no such steps or peaks are observed within the same conductance range.

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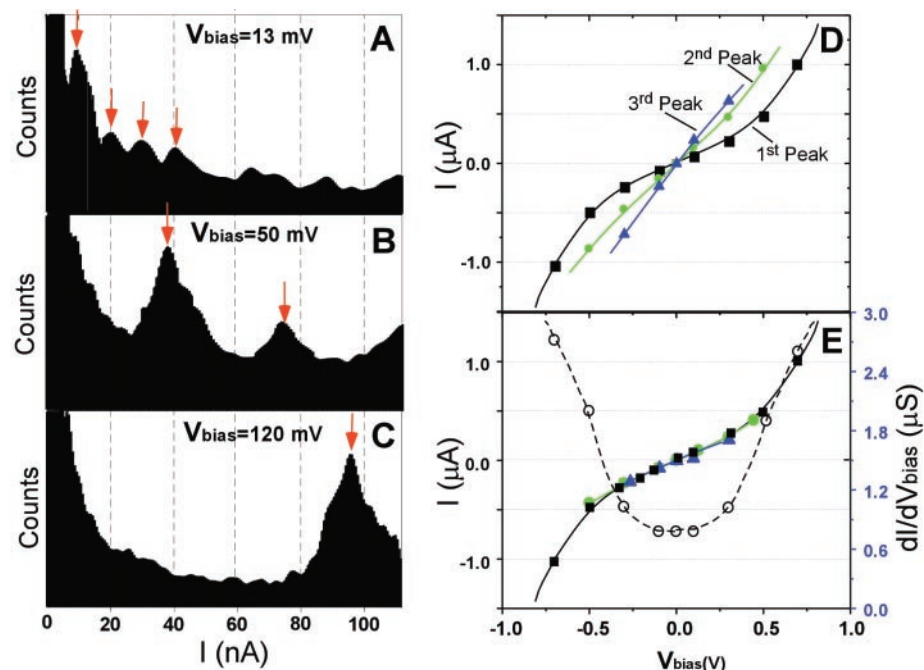*To whom correspondence should be addressed.

Fig. 2. (A to C) Current histograms of 4,4′ bipyridine constructed from 1000 measurements at different bias voltages (V_{bias}). Peak currents increase with the bias voltage and are used to obtain characteristic *I-V* curves. (D) *I-V* curves from the first three peaks. (E) When the second peak is divided by 2 and the third peak by 3, all the three curves collapse into a single curve. The dashed line shows the differential conductance (dI/dV).

ing histogram shows pronounced peaks near 0.01 G_0, 0.02 G_0, and 0.03 G_0 (Fig. 1D), which is two orders of magnitude lower than those that arose through the conductance quantization. The average width of the molecule-induced steps was determined to be 0.9 ± 0.2 nm, which is three to four times longer than that of the conductance quantization steps (*26*). We ascribe the conductance steps that appeared after the breaking of the gold contact to the formation of stable molecular junctions, and the corresponding conductance peaks at 1 ×, 2 ×, and 3 × 0.01 G_0 to one, two, and three molecules, respectively, in the junctions. This conclusion is supported by the following control experiments.

First, in the absence of molecules, no peaks below 1 G_0 are observed in the conductance histogram (Fig. 1, E and F). Second, in order to test the idea that the conductance peaks are caused by the formation of stable molecular junctions, we performed the measurement in the presence of 2,2′ bipyridine. This molecule is structurally similar to 4,4′ bipyridine, except for the positions of the two nitrogen atoms, which prevent the molecule from simultaneously binding to two electrodes (*27*). As expected, we did not observe the conductance peaks in 2,2′ bipyridine. Third, because the binding strength of 4,4′ bipyridine to a gold electrode depends on the electrode potential (*23*), we performed the experiment at different potentials with respect to a reference electrode in the solution (*28*). At negative potentials, where the molecule does not bind to the electrodes, the

conductance peaks disappear. The peaks reappear at positive potentials. Finally, the positions of the conductance peaks were different for different molecules. For instance, the conductance of *N*-alkanedithiols decreased exponentially with the length of the molecule, as we describe below.

We determined the current-voltage (*I-V*) characteristics of 4,4′-bipyridine by performing the measurement at different bias voltages. A current histogram of the molecule with bias voltage set at 13 mV is shown in Fig. 2A. The first three peaks near 10, 20, and 30 nA are pronounced. When the bias voltage was increased to 50 mV, the first two peaks shifted to ~38 and ~75 nA, respectively, and the third peak shifted out of range of the amplifier (Fig. 2B). When the bias voltage was further increased to 120 mV, the first peak shifted to ~95 nA, and the second peak also shifted out of range (Fig. 2C). In order to follow these peaks at higher bias voltages, we decreased the gain of the current amplifier. By plotting the currents of the first three peaks as functions of the bias voltage, we obtained the *I-V* curves (Fig. 2D). When the *I-V* curves of the second and third peaks were divided by 2 and 3, respectively, all three curves collapsed into a single one (Fig. 2E). The conductance near zero bias was about 0.01 G_0, corresponding to a resistance of 1.3 ± 0.1 megohms for a single 4,4′ bipyridine molecule.

We performed these measurements for hexanedithiol, octanedithiol, and decanedithiol and found peaks in the conductance
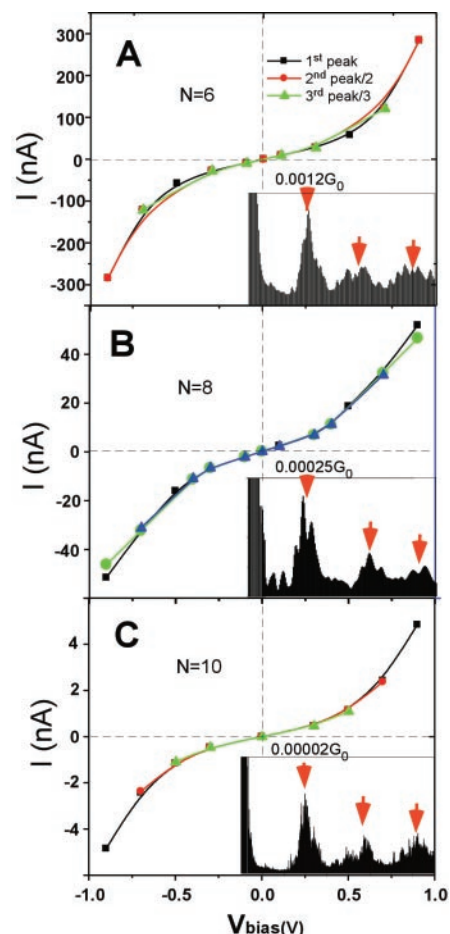

Fig. 3. *I-V* curves for hexanedithiol (A), octanedithiol (B), and decanedithiol (C). In each case, the *I-V* curves from the second and third current peaks are also plotted together with that of the first peak after dividing them by 2 and 3. The inset in the lower right corner of each panel is a conductance histogram for each molecule.

histograms, which occurred at different conductance values (insets, Fig. 3). At low bias voltages (<0.3 V), the first conductance peaks for the three alkanedithiols were located at 0.0012 G_0, 0.00025 G_0, and 0.00002 G_0, corresponding to resistances of 10.5 ± 0.5, 51 ± 5, and 630 ± 50 megohms, respectively, which is in excellent agreement with the first-principles calculations (*14*). The resistances are about an order of magnitude smaller than the values found by Cui *et al.* (*11*, *29*), reflecting the finite resistance between the AFM probe and the gold nanoparticles in their measurements (*12*). By plotting the currents of the first three peaks as functions of the bias voltage, we obtained the *I-V* characteristics of the molecules. Similar to 4,4′ bipyridine, the *I-V* curves of the second and third peaks overlap with that of the first peak when they are divided by 2 and 3, respectively (Fig. 3).

As a process dominated by electron tunneling, the resistance of a *N*-alkanedithiol is
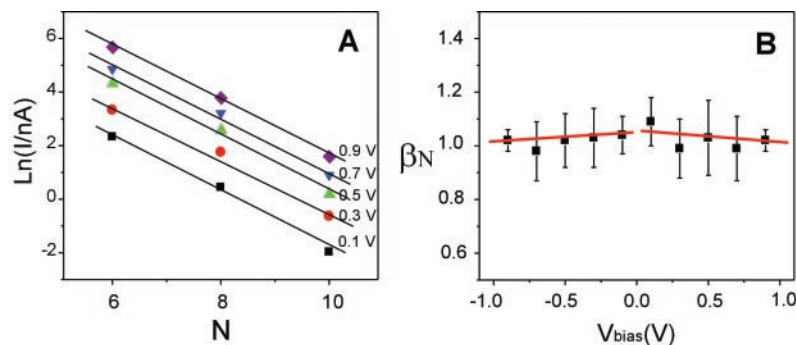
Fig. 4. (A) Natural logarithm of current versus N (the number of carbon atoms in the N-alkanedithiols) at various bias voltages. The solid lines are linear fits that yield β_N. **(B)** β_N versus V. The solid line is a fit to the simple square barrier model $\beta_N(V) = \beta_N(0) \sqrt{1 - \alpha V/\Delta E}$, where ΔE is the energy difference between the Fermi level and the closest molecular orbital, and $\alpha = 0.5$ reflects a uniform electric field. The fitting parameters are $\beta_N(0) = 1.04 \pm 0.05$ and $\Delta E = 5 \pm 2$ eV.

expected to increase exponentially with chain length, according to $R = A_{\exp}(\beta_N N)$ (Fig. 4). Our data can be described by the above simple relation, with $\beta_N = 1.0 \pm 0.05$, which agrees with the widely accepted value for electron transfer through alkanethiol monolayers in which the contacts are mercury (*17, 19, 21*) or an AFM probe (*30*) or with a redox group (*18, 20*). This observation supports the conclusion that the values obtained in our conductance experiments are identical to those produced by the electron transfer rate experiments with large–band gap molecules (*16, 31*). β_N versus V is plotted in Fig. 4B, which shows rather weak dependence of β_N on V. An interesting observation is that $A \sim 1.3 \times (h/2e^2)$, which confirms the simple theoretical relation given by Timfohr *et al.* (*15*) indicating that the conductance of a molecule is $R \sim (h/2e^2)_{\exp}(\beta_N N)$. The excellent agreement with the simple theory may reflect the large band gaps of the molecules.

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22. We used a modified STM (Pico-STM) to quickly and repeatedly form a large number of molecular junctions with a feedback control. The feedback loop was started by driving a gold STM tip into contact with the substrate at a rate of 40 nm/s. Once the contact was fully established, as the conductance between the tip and the substrate reached a preset value (4 G_0), the feedback loop activated the piezoelectric transducer to pull the STM tip out of the contact. We performed the measurements in solutions containing molecules (1 mM N-alkanedithiols in toluene and 1 mM 4,4′ bipyridine and 2,2′ bipyridine in 0.1 M $NaClO_4$ aqueous solution) in a Teflon cell. Before each experiment, the cell was cleaned by being boiled in Piranha solution (98% H_2SO_4:30% H_2O_2 = 3:1, v/v) and then thoroughly sonicated in 18-megohm water three times (using a Nanopure system fed with campus-distilled water). The substrate was a gold film evaporated on mica in an ultrahigh-vacuum chamber. The STM tip was made of 0.25-mm gold wire (99.999% purity).
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26. The average width of the molecules was about 0.9 nm for the lowest step (a single molecule) and was much shorter (~0.3 nm) for higher steps. This width is not the length to which a molecule was stretched. Instead, it measures the distance over which a particular junction can be stretched before losing stability. At least part of the width comes from the stretching of the gold atoms in the contacts and from changes in the atomic configurations of the contacts as individual molecules break away.
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28. We controlled the potential of the tip and the substrate with respect to a reference electrode (an Ag wire) in the aqueous 4,4′-bipyridine solutions by means of a Pt counter electrode and a bipotentiostat. We coated the tip with Apiezon wax in order to reduce ionic conduction and polarization currents below ~1 pA.
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32. We thank S. Lindsay, O. Sankey, A. Nitzan, D. Ferry, L. Nagahara, G. Speyer, S. Boussaad, J. Li, and X. Xiao for discussions and the U.S. Department of Energy, NSF, and the U.S. Environmental Protection Agency for support.

Synthesis of Carbenes Through Substitution Reactions at a Carbene Center

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An (amino)(phosphino)carbene can be transformed into (amino)(phosphonio) carbenes, which undergo nucleophilic intermolecular as well as intramolecular substitution reactions at the carbene center. A variety of carbenes can be synthesized starting from a single carbene precursor. The resulting gamut of electronic and steric effects possible should open the way not only to a detailed study of the mechanism, but also to the subsequent improvement of catalytic reactions that involve carbene–transition metal complexes.

Carbenes are neutral compounds that defy the octet rule, because they feature a divalent carbon atom with only six electrons in its valence shell. For a long time, they have been considered as prototypical reactive intermediates (*1, 2*). However, in the last few years, singlet carbenes have been isolated (*3–6*) and carbenes, with their available lone pair of electrons, have
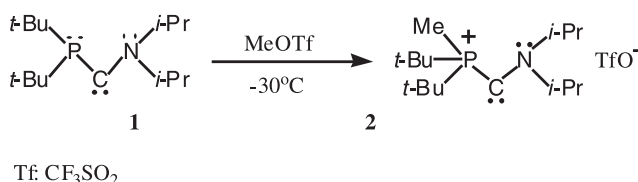

Fig. 1. Synthesis of the (amino)(phosphonio)carbene 2.