

Measurements of Single-Molecule Electromechanical Properties

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Building a device with a molecule demands a better understanding of various properties of the molecule wired to electrodes. The electrical properties of a single molecule have been investigated by many groups,¹ and it is recognized that the measured conductance depends on the bonding of the molecule to the electrodes.² However, determining if and how the molecule is bonded to the electrodes has been a challenge. While most efforts to date have focused on electronics, an electromechanical device based on a molecule is also attractive.^{1b,3} We report here on an electromechanical measurement of a molecule covalently attached to two electrodes during mechanical stretching, which allows us to determine the electromechanical properties of the molecular junction and the molecule–electrode bonding nature.

We choose well-characterized molecular systems, 1,8'-octanedithiol (C8) and 4,4' bipyridine (BPY) covalently bonded to two Au electrodes via the S–Au and N–Au bonds, for our studies. We created individual molecular junctions by repeatedly moving a Au electrode into and out of contact with a Au substrate in toluene containing 1 mM of the molecules. The moving electrode is a Au-coated Si tip mounted on an atomic force microscope (AFM), which is used to simultaneously measure the conductance and the force applied to the molecule. AFM has been used to study bond rupture forces in biopolymers attached to a surface.⁴ During the pulling process, the conductance decreased initially in discrete steps with each occurring near an integer multiple of $G_0 = 2e^2/h$, due to the formation of a quantum point contact between the Au electrodes. After the contact was broken, a new sequence of conductance steps appeared, signaling the formation of a molecular junction (Figure 1a).¹ⁱ

Figure 1b shows a simultaneously recorded conductance and force curve during the stretching of a C8 junction. While the conductance decreases in discrete steps, the corresponding force decreases like sawtooth-waves. Each discrete conductance decrease is accompanied by an abrupt decrease in the force, which is due to the breakdown of a molecule from contacting with the electrodes. Further stretching causes a linear increase in the force. When the force increases to a certain threshold, another molecule breaks. The process continues until the last molecule breaks, resulting in a series of steps in the conductance curve and sawtooth-waves in the force curve. By analyzing the last conductance step and the last force sawtooth-wave, we can obtain electromechanical properties of the molecule. However, because not all of the conductance and force curves are identical due to variations in the microscopic details of different molecular junctions, a statistical analysis is necessary. In fact, carefully examining the curves often reveals small irregular conductance variations (inset of Figure 1d) accompanied by oscillations in the simultaneously recorded force, which are likely due to a subtle rearrangement of Au atoms at the molecule–Au contacts.

By repeatedly performing the measurement described above, we have constructed both conductance and force histograms from individual curves shown in Figure 1. The conductance histogram

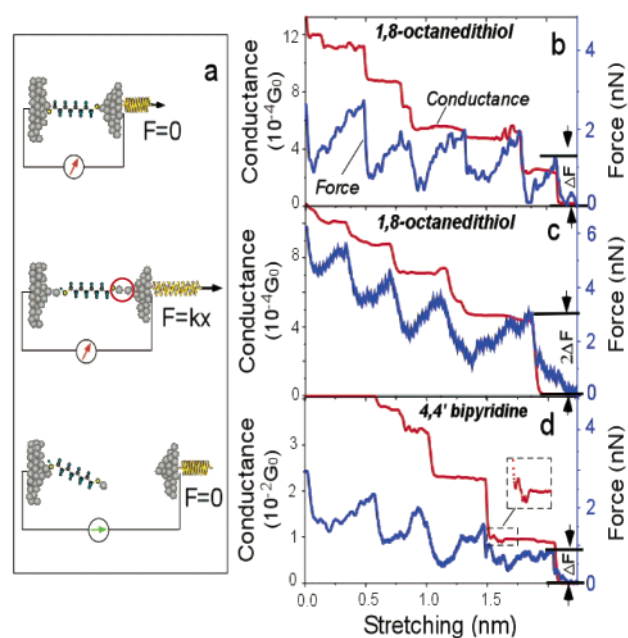


Figure 1. (a) Schematic illustration of a molecule covalently bonded to two Au electrodes under mechanical stretching, during which both the conductance and the force are measured. (b–d) Simultaneously recorded conductance and force curves of C8 (b–c) and BPY junctions (d) during stretching. (c) shows that two molecules can break simultaneously at the last stage, resulting in twice as much change in the conductance and the force. The inset in (d) shows that the force fluctuations are correlated with conductance fluctuations.

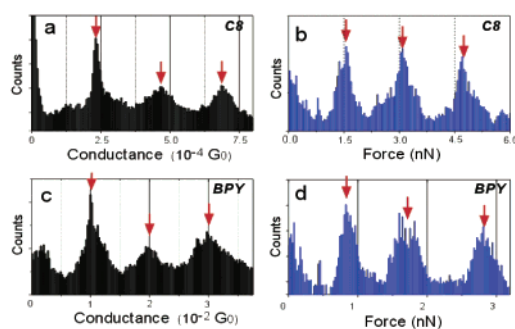


Figure 2. Conductance and force histograms for C8 and BPY constructed from over 600 curves.

for C8 shows pronounced peaks near multiples of $2.5 \times 10^{-4} G_0$ (Figure 2a). The force histogram reveals also pronounced peaks with a force quantum of 1.5 ± 0.2 nN (Figure 2b). This is the force required to break a C8 junction. In principle, the breakdown can take place at one of the three bonds, C–C, S–Au, or Au–Au. The force required to break a Au–Au has been determined to be ~ 1.5 nN,⁵ similar to the measured force here. So, unless the S–Au bond strength coincides with the Au–Au bond strength, the measured 1.5 nN indicates that the Au–Au bond is responsible

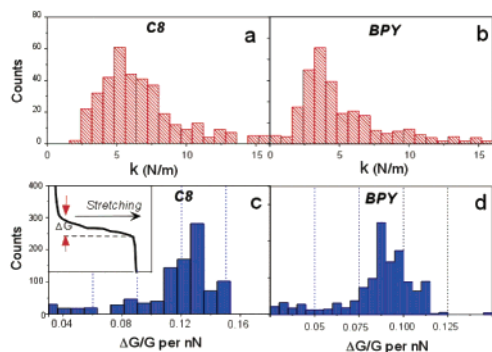


Figure 3. (a–b) Histograms and spring constants of C8 and BPY. The spring constants are determined from the slopes of force curves with stretching lengths near the average values. (c–d) Histograms of stretching-induced conductance changes. The inset in (c) is an example of the conductance change of a C8.

for the breakdown of the C8 junction. This is supported by the observation of Au atoms attached to thiol molecules stripped off a Au electrode.⁶

We have performed the measurements on BPY and observed similar discrete changes in the conductance and the force (see Figure 1d). The conductance quantum for BPY is $0.01 G_0$, much greater than the conductance of a C8 (Figure 2c). The force quantum is 0.8 ± 0.2 nN, considerably smaller than the force required to break a Au–Au bond (Figure 2d). The smaller force is expected because BPY binds to Au electrodes via N–Au affinity, which is weaker than the S–Au bond.⁷ The observation of the force quanta not only provides direct evidence that the studied molecule is indeed bonded to both Au electrodes, but also reveals the bonding nature of the molecule to the electrodes.

The distance over which a molecular junction can be stretched before breakdown can be > 1 nm (see Supporting Information). At first glance, this distance is surprisingly large because neither the molecules nor the bonds at the molecule–Au contacts are expected to stretch over such a large distance before breaking. So, the apparent large stretching distance must be due to the stretching of Au atoms at the contacts. When a Au atom is pulled out of the electrode, a nearby surface Au atom moves behind the first atom (red circle in Figure 1a). Further pulling can cause a third atom to move behind the second one and form a linear chain of Au atoms. A similar situation has been observed in the stretching of two Au electrodes from contact, where a chain of Au atoms can be elongated as long as 2 nm.⁸

From the force curves, we have determined the spring constant of a single molecular junction (Figure 3a and b). The average spring constants are ~ 7.2 and ~ 5.3 N/m for C8 and BPY, respectively. Because stretching a molecular junction inevitably involves stretching the Au–Au bonds at the contacts, the above values are effective spring constants that include the Au–Au bonds in series with the molecules plus molecule–Au bonds. Using the previously determined spring constant of Au–Au (~ 8 N/m),⁵ we found that the spring constants of Au–C8–Au and Au–BPY–Au are ~ 72 and ~ 16 N/m, respectively. These values contain the contributions from the S–Au and N–Au bonds. The spring constant of a C8 attached to two Au electrodes, estimated from the stretching frequencies of Au–S, S–C, and C–C bonds, is ~ 30 N/m, which is reasonably close to the extracted value. BPY is stiffer, so the primary contribution of the BPY junction comes from the N–Au bonds. Using the N–Au bonding energy, we found that the spring constant of N–Au is about 12 N/m, which is also consistent with the experiment.

The dependence of the conductance on the applied force before

the molecule breaks down is shown in Figure 3c,d. The average changes are $\sim 14\%$ per nN for C8 and $\sim 9\%$ per nN for BPY. We have discussed that the stretching involves a Au–Au bond at the contact. However, because a chain of Au atoms has a conductance of $\sim 1 G_0$, several orders of magnitude greater than the conductance of a molecule, the observed conductance comes from the molecule and the molecule–Au bonds. A mechanical stretching can change the molecule conductance via the molecular length (L), which is given by $G = A \exp(-\beta L)$, where the tunneling decay constant β is about 8 nm^{-1} for C8.¹¹ Using this relation, the extracted spring constant, and the break force of C8, we found $\Delta G/G \approx 17\%$ per nN, in agreement with the observed value. For BPY, if $\beta = 6 \text{ nm}^{-1}$ is used,⁹ one obtains $\Delta G/G \approx 30\%$ per nN, considerably greater than the observed value. So clearly, the above simple tunneling model provides, at most, only a partial explanation of the observation.

In summary, we have determined the conductance, the spring constant of a single molecule covalently bonded to two electrodes, and the dependence of the conductance on the applied force. The measurement allows us to determine unambiguously if and how a molecule is bonded to the probing electrodes. It shows that, like conductance, the electromechanical properties of a molecule depend on the molecule–electrode contacts. It also opens the door to the study of single-molecule electromechanical properties.

Acknowledgment. We thank C. Joachim, H.X. He, S. Boussaad, R. Vaidyanathan, and E. Forzani for discussions, and DOE (DE-FG03-01ER45943) (B.X.) and NSF (CHE-0243423) (X.X.) for financial support.

Supporting Information Available: Experimental details; distribution of stretching distances (PDF). This material is available free of charge via the Internet at <http://pubs.acs.org>.

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JA038949J