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, and it is recognized that the measured conductance depends on the bonding of the molecule to the electrodes. 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. 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-octanethiol (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. 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).

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) 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.

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 $1.5 \pm 0.2 \text{nN}$ (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 bond has been determined to be $\sim 1.5 \text{nN}$, 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.
The molecule breaks down 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 \( \sim 1 \, \text{G}_{\circ} \), 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 \( \beta \) is about 8 nm\(^{-1}\). 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, \( \Delta G / G \approx 30\% \) 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.

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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.

References


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