

Bond Fluctuation of S/Se Anchoring Observed in Single-Molecule Conductance Measurements using the Point Contact Method with Scanning Tunneling Microscopy

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Understanding and controlling the characteristics of the electric contact between a molecule and an electrode has become one of the major objectives in recent research.^{1–3} For example, stochastic switching of wired molecules exhibits interesting but puzzling phenomena, which is a hotly debated issue.^{4–6} Additionally, the effect of the different anchoring groups and their adsorption sites on the electric contact is another urgent issue to be clarified.⁷ To achieve further advances, precise measurement of the electronic properties of a specific single molecule, which is wired to metal electrodes, is extremely important.

Here, we show the results obtained using the point contact method with scanning tunneling microscopy (STM) that enables us to selectively perform a repeated analysis of a chosen target molecule.

We used α,ω -bis(acetylthio)terthiophene (3TS₂) and α,ω -bis(acetylseleno)terthiophene (3TSe₂) molecules as illustrated in Figure 1a as samples because of their high potential for application in molecular devices.^{8,9} Isolated 3TS₂ or 3TSe₂ molecules embedded in a self-assembled monolayer (SAM) of octanethiol (C₈) molecules were prepared by immersing a Au(111) substrate into a solution containing a predefined amount of 3TS₂ (or 3TSe₂) and C₈ molecules. (Free thiol and selenol groups were prepared by adding pyrrolidine molecules.) All conductance measurements were performed in ultrahigh vacuum (UHV) at room temperature. In UHV, contamination of the sample surface is prevented, and the STM tip can be cleaned and fabricated by heat treatment.

Figure 1b shows an STM image of isolated 3TS₂ molecules embedded in a C₈ SAM, where bright spots are 3TS₂ molecules.

After we located target molecules, we placed a Au STM tip above a 3TS₂ molecule and moved it toward the chosen molecule until an electric contact was achieved, where the sample bias voltage was kept at 0.5 V during the process. Since the thiol group at one end of the isolated 3TS₂ molecule is exposed to the STM tip, a chemical bond is formed between the thiol group and the Au tip (Figure 1c).

Graphs a and b of Figure 2 show plots of the I – Z curves obtained for a C₈ molecule and a 3TS₂ molecule, respectively. The exponential change in the current exhibits two different slopes; see inset in Figure 2a. This is explained by the change in the local barrier height caused by the contact of the STM tip with the C₈ molecule. In contrast, an abrupt jump in the current was observed for the 3TS₂ molecule (Figure 2b) because of the formation of a chemical bond between the Au tip and the 3TS₂ molecule, as shown in Figure 1c. The current observed for the 3TS₂ molecule was insensitive to further approach of the STM tip (~ 0.2 nm) after the formation of the electric contact, indicating that a slight change in

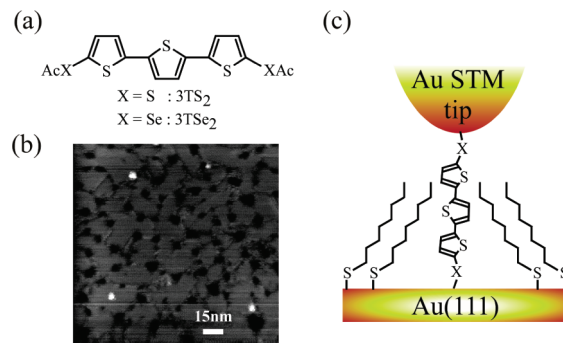


Figure 1. (a) Molecular structure. (b) An STM image of isolated single 3TS₂ molecules embedded in a C₈ SAM (sample bias +1.0 V, tunneling current 10 pA). (c) Measurement conformation by the "point contact method" using STM.

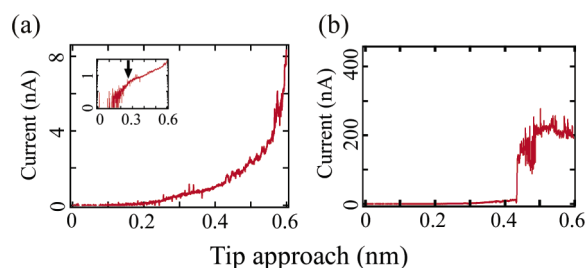


Figure 2. I – Z curves obtained for (a) C₈ and (b) 3TS₂ molecules. Inset in (a) is the logarithmic plot of the I – Z curve. Tip approach position is related to the set point (sample bias +1.0 V, tunneling current 10 pA).

the molecular conformation has little influence on the subsequent conductance measurement.¹

After a junction was formed, the bias voltage was swept repeatedly between -1 and $+1$ V, and the corresponding change in the current for each sweep was measured. The I – V curves are almost linear between -0.1 and $+0.1$ V, as shown in Figures 3 and 4, and the conductance of each measurement was determined from the gradient of each I – V curve in this voltage region.

In Figure 3a, all of the I – V curves obtained from more than 400 individual measurements are presented as a contour plot, where several measurements were performed for each molecule. Contrast of the overlapped I – V curves in the low bias voltage region clearly shows the existence of several groups of I – V curves. Since the I – V curves were observed over the different 3TS₂ molecules, the obtained result represents the characteristic response of this molecule, including the electric contact with the electrodes.

Figure 3b is a histogram consisting of all the values of conductance determined from the I – V curves in Figure 3a. In accordance with the groups in Figure 3a, the histogram consists of several subpeaks, as indicated by arrows. To examine the details,

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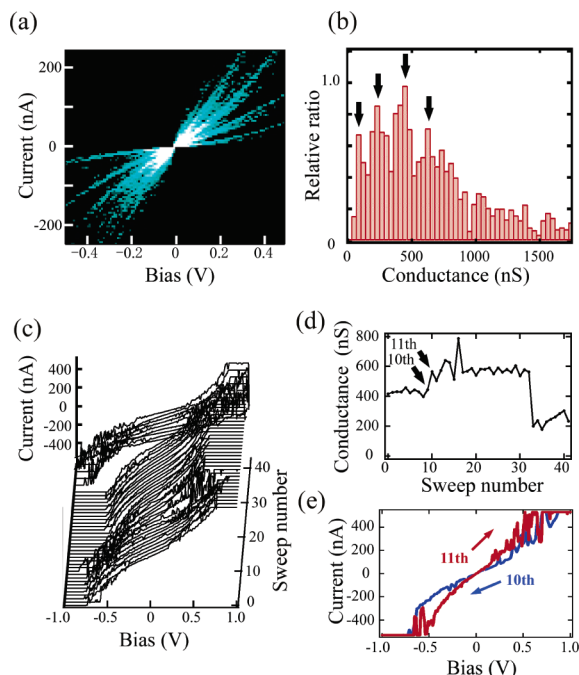


Figure 3. Results obtained for the 3TS₂ molecule. (a) All I - V curves obtained for the single 3TS₂ molecules. (b) Histogram consisting of all values of conductance obtained from all I - V curves in (a). Peaks indicated by the arrows are at 70, 220, 440, and 620 nS. (c) I - V curves sequentially obtained for 20 cycles, and (d) conductance obtained from the I - V curves. Flat area in (c) at high bias voltage region is due to saturation of the current. (e) Two sequential I - V curves corresponding to the 10th and 11th measurements in (d).

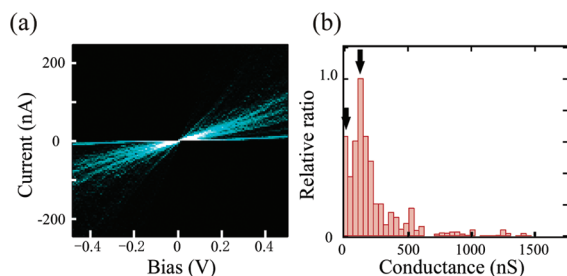


Figure 4. All I - V curves (a) and the conductance histogram (b) obtained for 3TSe₂ molecules, respectively. Peaks indicated by the arrows are at 10 and 120 nS.

I - V curves were sequentially measured for 20 cycles on the same 3TS₂ molecule (Figure 3c), and the obtained values of conductance are plotted as a function of bias voltage sweeps (Figure 3d). Figure 3c shows smooth slopes in the low bias voltage region, where stable measurement can be obtained. As seen in panels c and d of Figure 3, there are three or four groups of different conductance, the values of which correspond to the peaks in the histogram of Figure 3b.

What causes the instability of the junction? Figure 3e shows two sequential I - V curves corresponding to the 10th and 11th measurements in Figure 3d. In the high bias voltage region, there appear to be rapid changes in the current between the two envelopes of the I - V curves extrapolated from those in the low bias region. This fluctuation between the two states resulted in the observed change in the conductance. In some cases, for a high voltage region, the current measured was found to be zero, which can correspond to

the off-states in the stochastic switching process that have been observed for various molecules.^{4,5} The fluctuation occurs in both the positive and negative bias voltage regions. Since conformational change, which, for example, is induced for the azo-molecule because of the interaction between the applied electric field and the molecular dipole moment,¹⁰ does not exist for this molecule, the role of the current in the production of such phenomena as inelastic tunneling and electro-migration processes may be essential to the case.^{6,11,12}

A possible mechanism to explain the observed change in the conductance is the thiol-gold bond fluctuation among the adsorption sites, which has been discussed in recent papers.^{7,13} It is important to note that the relative relationship among the observed values of the conductance is comparable with that predicted by the theoretical analysis.⁷

A similar experiment was performed for a single 3TSe₂ molecule. Figure 4a shows all the I - V curves obtained for the single 3TSe₂ molecules. Figure 4b is a histogram of all the values of conductance obtained from the I - V curves in Figure 4a. In contrast to the case of the 3TS₂ (Figure 3b), two dominant peaks are apparent in the low conductance region for the 3TSe molecule. This difference is considered to reflect the difference in the stability of the S/Se anchoring on the Au surface.

In summary, we have shown the results of single-molecule conductance measurements that enable us to selectively perform a repeated analysis of a chosen target molecule. Bond fluctuations of the S/Se anchoring, which may explain the stochastic switching observed in previous works,^{4,5} were directly observed at the single-molecule level. As mentioned earlier, understanding and controlling the characteristics of the electric contact between a molecule and an electrode is the major challenge. The method outlined is expected to contribute to the understanding of single-molecule electronics and to the future development of molecular devices.

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