

**Supplementary information**

**Revealing the Conformational Dynamics in a Single-molecule Junction  
by Site- and Angle-Resolved Dynamic Probe Method**

Shoji Yoshida, Atsushi Taninaka, Yoshihiro Sugita, Tomoki Katayama, Osamu Takeuchi,  
and Hidemi Shigekawa

Faculty of Pure and Applied Sciences, University of Tsukuba, Tsukuba 305-8571, Japan

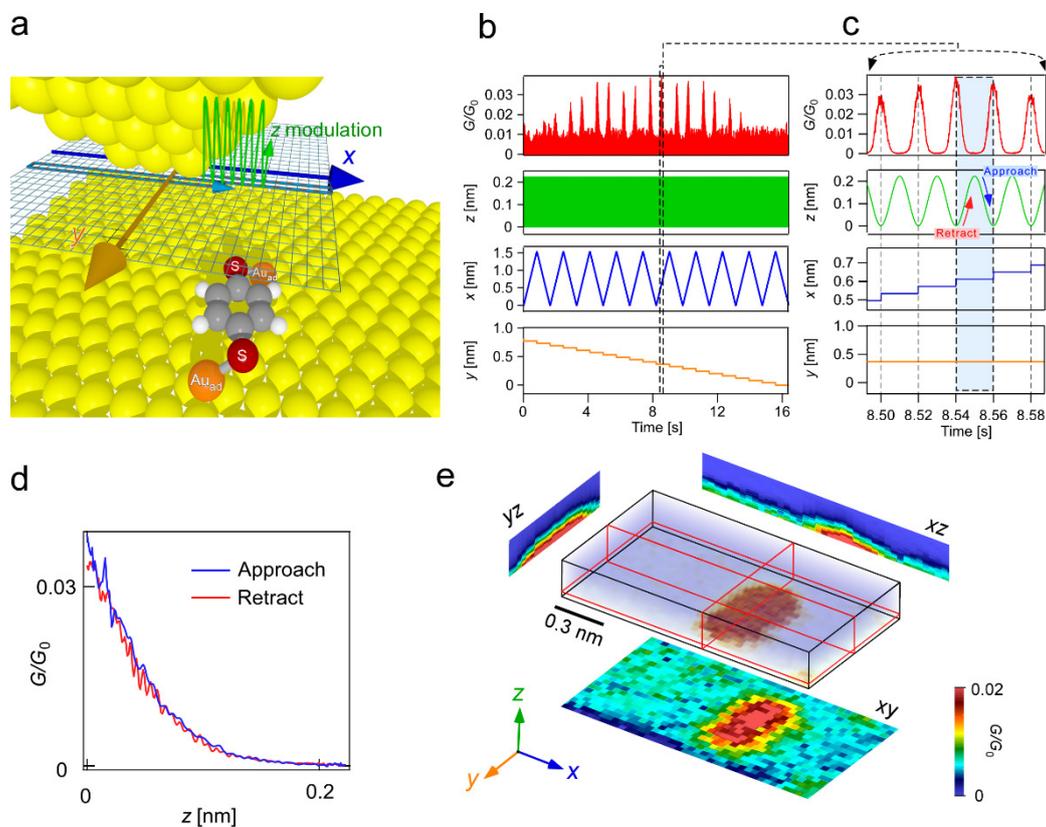


Fig. S1 **Measurement scheme and example of data for BDT/Au(111).** *a* Schematic illustration of the 3D dynamic probe. *b*, *c* Measurement scheme and an example of a signal. A high-conductance signal was obtained above the molecule. *d*  $G$ - $z$  curves showing an exponential characteristic. *e* Volume plot of the 3D dynamic probe data obtained for a BDT/Au(111) surface before forming a junction (data for STM tip retraction). The cross sections correspond to the frames indicated by the red lines in the volume plot.

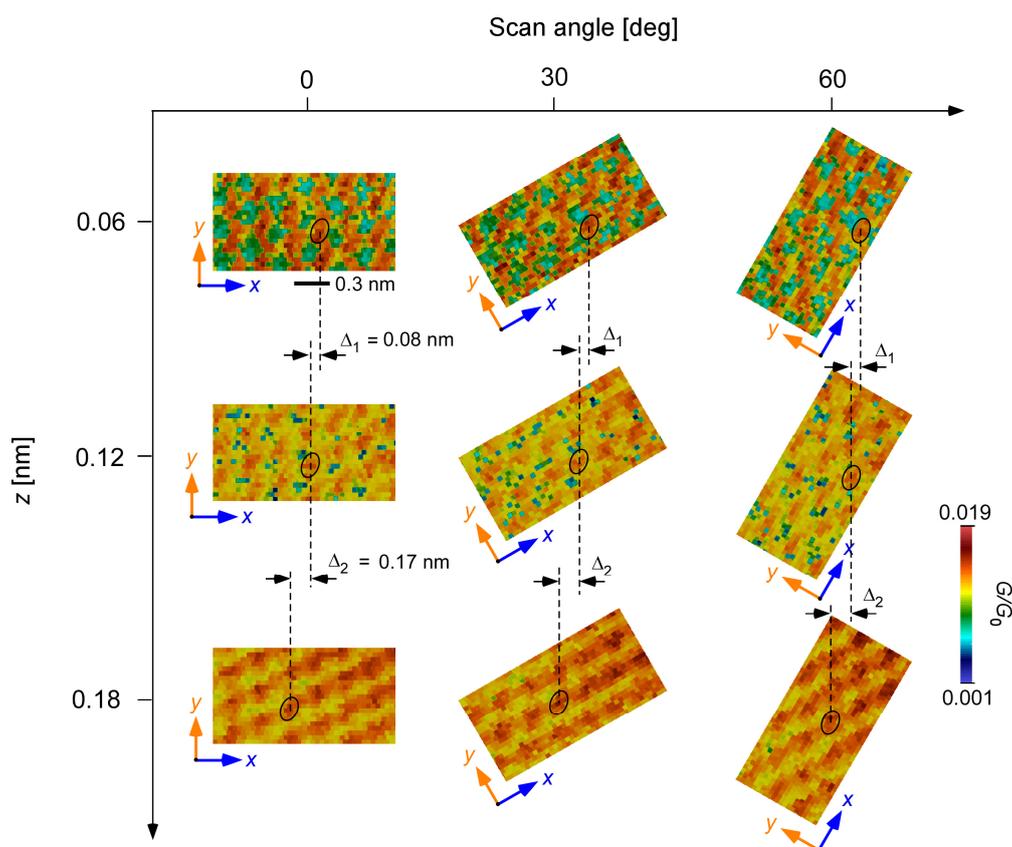


Fig. S2 **Stability of the bond structure at the STM tip apex.** The  $z$ -dependences of the Hc patterns in the  $xy$  cross sections obtained for three different scan angles ( $x$ - and  $y$ -directions) are shown with the angle of the left patterns set to  $0^\circ$ . The dotted lines indicate the  $z$ -dependent positional change. As shown by the images and  $\Delta_1$  and  $\Delta_2$ , Hc patterns were stably observed for different scan angles, indicating the stability of the bond structure at the STM tip apex. The high reproducibility of the 3D patterns in  $xy$ -planes reflecting the periodicity of the Au(111) atomic structure indicates that the substrate-side  $\text{Au}_{\text{ad}}$  atom reproducibly changed its position on the Au surface while the STM tip position was three-dimensionally controlled. In other words, if the bonds at the apex were not stably fixed, the Hc pattern would have changed during the measurement, or no stable patterns would have been obtained. In fact, several scans were necessary to obtain a clear pattern after a junction was formed. See Fig. S4 regarding the instability of the bond structure at the STM tip apex.

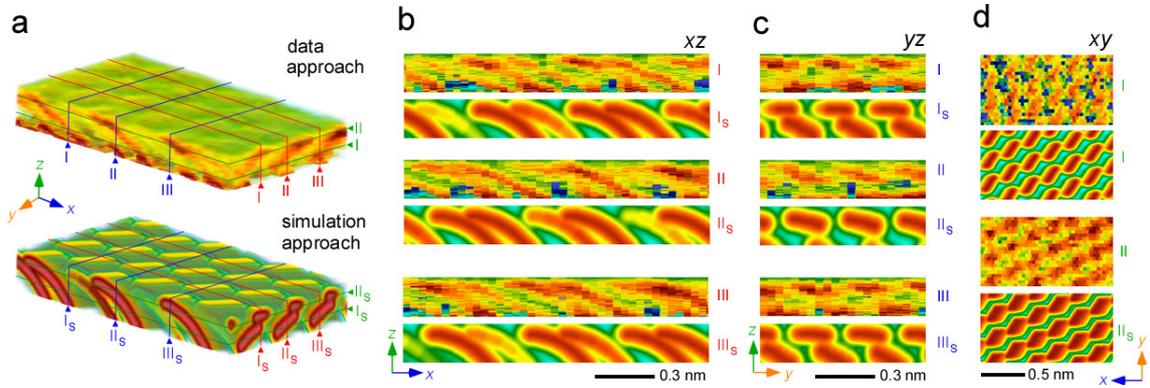


Fig. S3 **Variations in a volume plot and fitting.** *a* Volume plot shown in Fig. 1h, the color scale of which is changed to increase the contrast. When arcs were drawn on the H<sub>C</sub> patterns in the *xy*-plane with the hollow and bridge sites as centers, which were brightly imaged in experiments, the H<sub>C</sub> patterns were almost completely reproduced as shown in *b* to *d*. The cross sections indicated in red and blue and labeled I to III (experimental) and I<sub>s</sub> to III<sub>s</sub> (simulated) correspond to the frames indicated by the same letters in the volume plots shown in *d*. Three movies have been prepared to show the 3D reproducibility.  $\theta$  and  $\phi$  were obtained from the 3D fitting.

movie 1: Movie to show the *y*-dependence of *G* in the *xz* cross section.

movie 2: Movie to show the *x*-dependence of *G* in the *yz* cross section.

movie 3: Movie to show the *z*-dependence of *G* in the *xy* cross section.

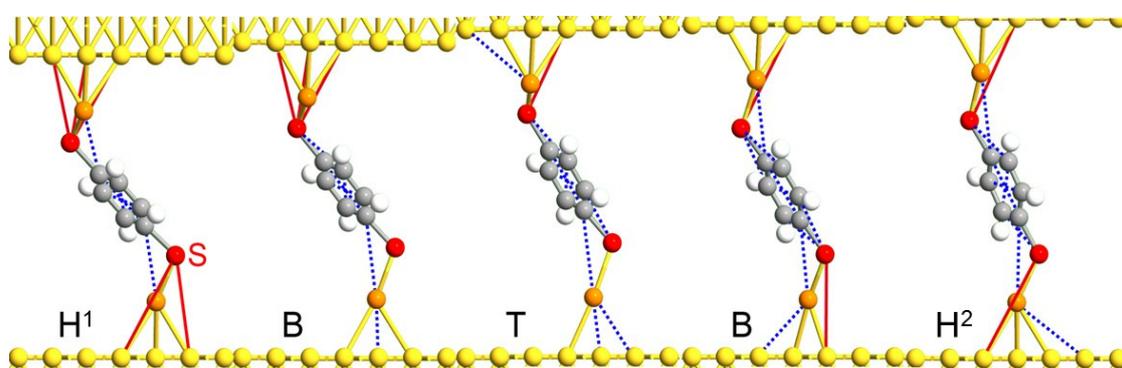
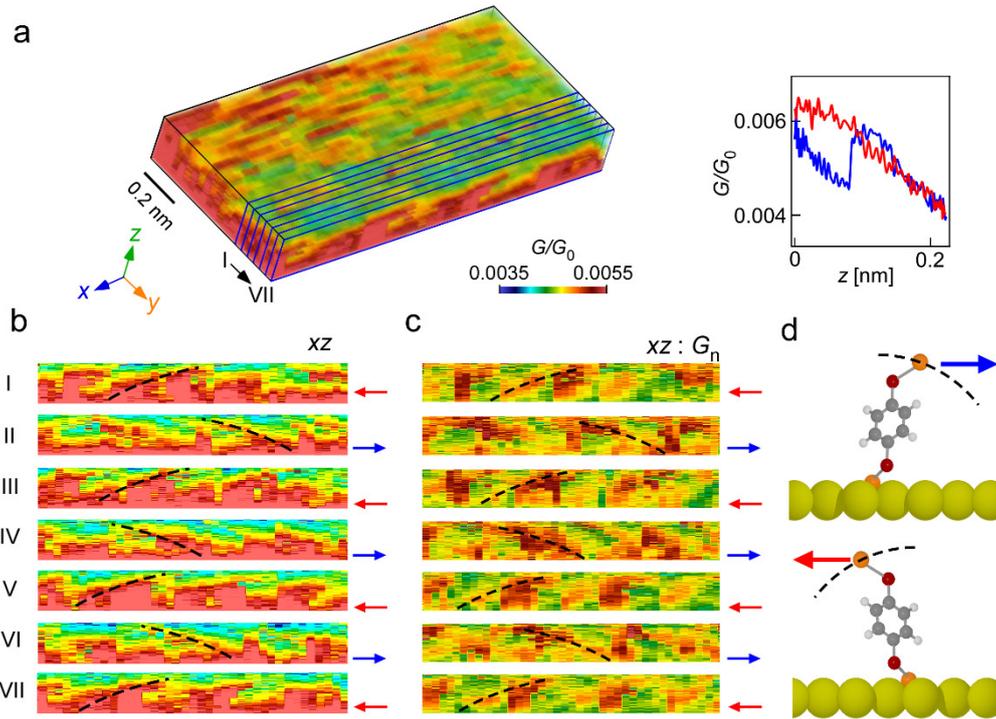


Fig. S4 **Transmission pathway (TP) between S and Au atoms.** The TP between S and Au atoms, which is formed by the overlap of S-p and Au-d orbitals, is shown by the solid red lines. Its appearance and disappearance were caused by the change in the distance between S and Au atoms corresponding to the change in the molecular structure shown in Fig. 4e. The blue dashed lines show other TPs without direct bonds. The angle of the view point here was adjusted to make it easier to see the TPs.



**Fig. S5 Examination of effect of bond structure at STM tip apex in the case of low  $G$ .** **a** Example of a volume plot and  $G$ - $d$  curves with one order lower ( $\sim 0.005$ ) values of  $G/G_0$  despite having  $G$ - $z$  curves similar to those shown in Figs. 1 and 2 ( $G/G_0 \sim 0.01$  for  $\phi$  from  $\sim 50^\circ$  to  $\sim 80^\circ$ ). For the examples shown in **b** and **c**, the direction of bright image of arc indicated by dashed lines changed alternately with the  $x$ -direction of the STM scan, as schematically shown in **d**, suggesting a weaker bond structure at the STM tip apex in this case, allowing the rotation of the molecule around the  $\text{Au}_{\text{ad}}\text{-Au}_{\text{ad}}$  axis.