Investigation of Conformational Effects in Single-Molecule Junction using Molecular Dynamics Simulation and Dynamic Probe Method

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In the previous paper, a methodology using scanning tunneling microscopy (STM) for realizing a three-dimensional (3D) dynamic probe of single-molecule conductance was reported, in which the conformational effect of 1,4-benzenedithiol molecule (BDT) on its electronic structure was analyzed in detail [1]. However, the measurements in the study were carried out with the condition in which a gold STM tip was sufficiently retracted from the Au surface where the BDT molecules were deposited, namely, the molecule in measurement was in a standing form. To consider the conformational effect further, in the present study, we carried out experiments and simulation under the condition in which the distance between a gold STM tip and the Au(111) surface was shorter, namely, the target molecule was in a lying form as shown in Fig 1(a).

In the simulation, the STM tip was replaced by another Au(111) surface and covalent bonds were assumed between the molecule and gold adatoms on the planer electrodes. The optimized structure of the metal-molecule-metal junction and its electric conductance were calculated with the density functional theory and the non-equilibrium Green's function method while the distance between the two electrodes was increased stepwise by 0.02 nm in each step.

Figures 1(b) and 1(c) respectively show a conductance curve obtained by the simulation and an experiment. According to the simulation, the conductance was rapidly reduced to half value (I to II) and then gradually decreased (II to III). Experimentally, a gradual decrease region (IV to V) was observed before its rapid change to half value (V to VI). These characteristics were explained by the conformational changes in such as the number of bonding sites and rotation of benzene ring. Details will be discussed at the colloquium.

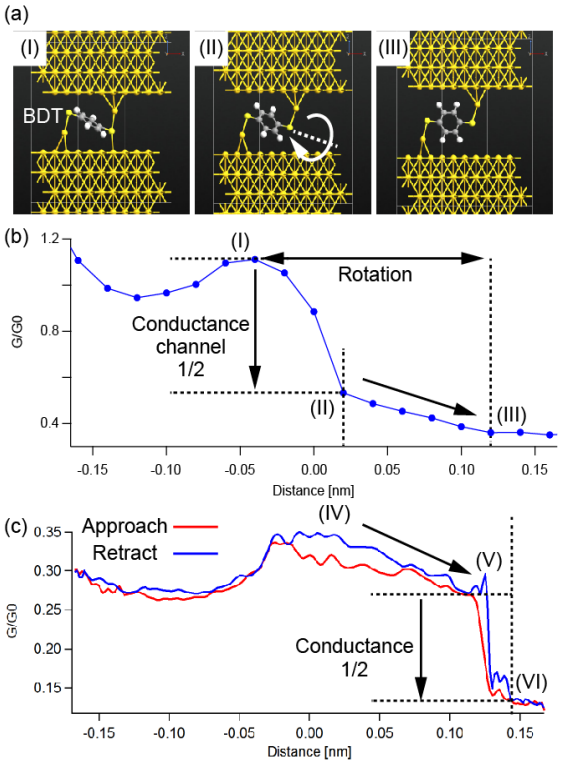

Fig. 1 Changes in the (a) molecular conformation and (b) conductance obtained by the simulation for an Au/BDT/Au junction. (c) Experimental result.

[1] S. Yoshida *et al.*, *ACS Nano* 2016, 10, 11211-11218.