Geometrical Analysis of the Single- π -Stacked Dimer using SERS and Electron Transport Measurement

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Single-molecule junctions (SMJs), where single-molecule connects to the metal electrode, have attracted fundamental interest owing to their unique electric structure. Recent techniques enabled the observation of the electron transport through single-π stacked junction, showing the quantum interference effects [1]. Though a variety of molecules have been evaluated to demonstrate the control of the electron transport of the single-π stacked junction, the experimental evidence for the insight into the structure-property relationship is insufficient. Our group has been engaged in the geometrical analysis of SMJs using the combined analysis of surface-enhanced Raman scattering (SERS) and electron transport measurements [2,3]. In this research, we tackle the geometrical analysis of the single-π-stacked dimer of 2-naphthalenethiol (2-NT), which can be regarded as the simple model system for π-stacked system.

We fabricated 2-NT SMJs using the Mechanically controllable break junction (MCBJ) method under ambient conditions [4]. The 1 mM ethanol solution of 2-NT was dropped and cast on the gold electrode. Disconnection of the gold nanocontact allows the formation of nanogap to connect the 2-NT. Figure 1 (a) is the two-dimensional (2D) conductance histogram for the disconnecting process of the gold nanocontact in the presence of 2-NT. The states originating from 2-NT were observed around 10^{-3} G_0 (G_0: $2e^2/h$). The geometry of the 2-NT junction was investigated with synchronized measurement of *I-V* curves and SERS spectra. At the conductance of 10^{-3} G_0, we obtained a strong SERS signal with vibrational peaks which is characteristic of 2-NT (Fig.1. (b)). To analyze the geometry of the 2-NT SMJs, we analyzed the correlation between conductance and the vibrational energy of the ring breathing mode (ν_{RB}) around 1065 cm^{-1}, which is the prominent marker of 2-NT. Figure 1 (c) clearly showed three distinct regions, i.e., high conductive (H) around 10^{-2} G_0 and two low conductive (L1, L2) states around $10^{-2.5}$ G_0. Following the vibrational analysis, the density-functional theory allows the identification of each state L1 state originates from π-π interaction, while H and L2 states originate from gold-π interaction through π-orbital (H) and space (L2). Because the vibrational energy of the o_{rb} mode was reduced by the metal-molecule interaction and π-π interaction, we recognized the L1 and L2 states by SERS spectra. We, therefore, distinguished the single-π-stacked dimer from other non-covalent bonding states by the SERS and electron transport measurements.

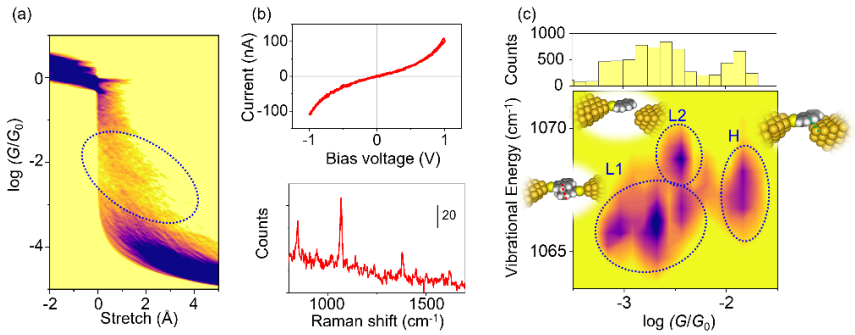

Fig.1. (a) 2D conductance stretch (b) typical *I-V* curve (top) and SERS spectrum (bottom) for 2-NT SMJs obtained at 10^{-3} G_0. (b) 2D histogram regarding vibrational energy of the ring breathing mode and conductance (G).

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