Characterization of Molecular Adsorption Site of Single Molecular Device based on Simultaneous SERS and Electrical Measurement

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Understanding of the metal-molecule interface is a key issue in organic electronics, because the interface influences the molecular orbital that participate in charge transport, and determines the electrical performance of the organic devices [1]. However, metal-molecule interface structure in atomic scale molecular devices remains poorly characterized owing to experimental challenges [2]. In this study, we report a new methodology for identification of the molecular adsorption site of the single molecular junction, by the combination analysis of Raman shift of intramolecular vibrational mode and strength of the metal-molecule electric coupling obtained by the current-voltage characteristic. The benzenedithiol (BDT) and aminobenzendithiol (ABT) single molecular junctions were fabricated using mechanically controllable break junction (MCBJ), which offered high electrode stability and fine tuning of the electrode spacing. By breaking the Au wire covered with target molecules, the molecule diffuse on the electrode surface, and bridge Au electrodes after breaking the Au wire.The combined analysis characterizes three typical molecular adsorption sites for BDT and ABT single molecule junctions and establishes the relationship between conductance and molecular adsorption sites unambiguously for the first time. The high, meduium and low conductance states observed in electrical measurements were assigned to the bridge, hollow and atop site, respectively, by comapring the experimentally and theoretically obtained vibrational and electrical properties. The conductance of BDT and ABT single molecule junction is found to vary up to two orders of magnitude depending on the adsorption site. We further observe the bias voltage induced switching of molecular adsorption site and enhancement of surface enhanced Raman scattering (SERS) signal by the simultaneous SERS and current-voltage characteristic measurements.

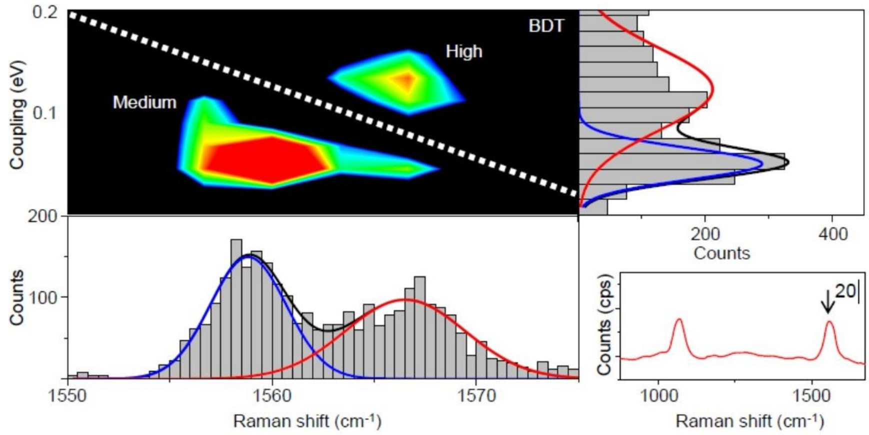

Figure: Two dimensional electronic coupling-Raman shift histogram of BDT single molecular junctions.

References:

[1] S. Fujii, M. Kiguchi, et al. ***Nat. Comm***. 8, 15984 (2017).

[2] S. Kaneko, M. Kiguchi, et al. ***J. Am. Chem. Soc.*** *138*, 1294–1300 (2016).