Large Stochastic Binary Fluctuation of Single Molecule Conductance of POM-dithiols

Nunik Nurhayati, Zhijin Chen, Yosuke Tani, Ken-ichi Yamashita, Takuji Ogawa

Graduate School of Science, Osaka University

E-mail: ogawa@chem.sci.osaka-u.ac.jp

Recently we have reported a molecular neuromorphic network device consisting of single-walled carbon nanotubes (SWNT) complexed with polyoxometalate (POM), in which we observed spontaneous spike generation and used for reservoir computing based on a modelling.[1] In order to study the detailed mechanism of the spike generation, here we studied single molecule electric properties of POMs having dithiol functional groups as the anchor for the gold electrodes.

The molecular structure of the target molecule ((tetrabutylammonium)$_3$ $PW_{11}O_{39}$[{$HS(CH_2)_3Si$}$_2$O]) is shown in the Figure (left), which has two -$(CH_2)_2SH$ groups connected to the POM core through Si atoms. The *I-V* and conductance-*V* curves were measured using mechanically-controllable-break-junction (MCBJ) method with gold as the electrodes. A typical example is shown in the Figure (right). Clearly, the conductance fluctuated stochastically between two values at any bias voltage. The two conductance differs four or five times depending on the bias voltage. When time courses of the current were measured at a fixed bias voltage, stochastic fluctuation between the two conductance were observed. However, constant frequency oscillation which were observed in the cases of SWNT-POM complex networks did not occur in the case of single molecule measurements. The result indicates that the oscillation occurs by cooperative phenomena of the POM networks.

There are several possible mechanisms of the single molecule conductance fluctuation of the present POM molecule: (1) Mechanical movement of the molecule between the electrodes. (2) Isomerization of the POM molecule by the applied bias voltage. (3) Stochastic redox reaction of the molecule and the static electronic repulsion of the electrons like Coulomb blockade.[2] (4) Stochastic redox reaction of the molecule and the difference of the conductance because of the open or closed shell electronic structure of the resultant products.

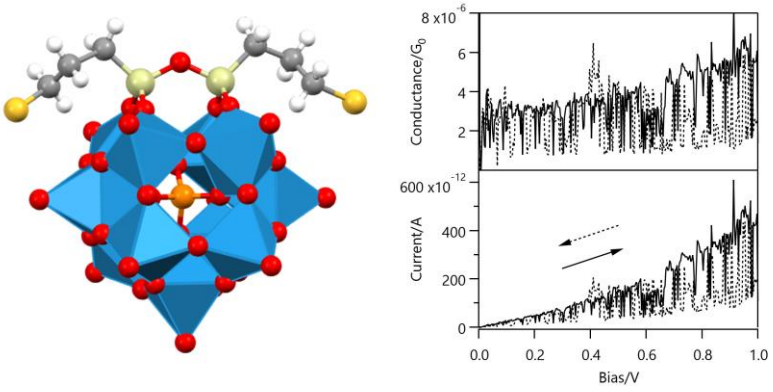

Figure. Left: Structure of $PW_{11}O_{39}$[{$HS(CH_2)_3Si$}$_2$O]. Tetrabutylammonium is removed. Right: Single molecule *I-V* and conductance-*V* curves of the molecule.

References

1. Tanaka, H., and Ogawa, T. et al., *Nat. Commun.* **9**, 2693 (2018). 2. Park, J. et al., *Nature*, **417**, 722 (2002). 3. Chen, J.; Reed, M. A. et al., *Scienc*, **286**, 1550 (1999).