Nonlinear Electric Transport in Macromolecular System

Takuya Matsumoto, Haruka Matsuo, Yoshiaki Hirano

Department of Chemistry, Graduate School of Science, Osaka University
1-1 Machikaneyama-cho, Toyonaka, Osaka 560-0043 Japan
Email: matsumoto-t@chem.sci.osaka-u.ac.jp

Abstract– Nonlinearity is a factor role in electronic circuit which realize a various functions including oscillation, amplification, frequency conversion, etc. Considering conduction through molecules, electron tunneling gives simple ohmic character. The expression of nonlinearity in molecular systems requires Coulomb repulsion and/or weakly coupled discrete energy levels in conduction paths. In search of nonlinear electric properties, we investigated electronic properties of polyoxometalate (POM), cytochorome c, and cytochrome c/DNA networks. In these nano-molecular systems, nonlinear current-voltage characteristics are observed.

1. Introduction

Molecular electronics has attracted much attention due to the potential of device miniaturization and the prospect of novel principle-based information processing. In past decade the investigations concerning single molecular conductance has been developed well by scanning probe and break junctions methods. The physics and chemistry of single molecular conductance are interesting but mostly reported current-voltage curve at low bias indicate linear characteristics reflecting tunneling conduction thorough a molecule between electrodes [1].

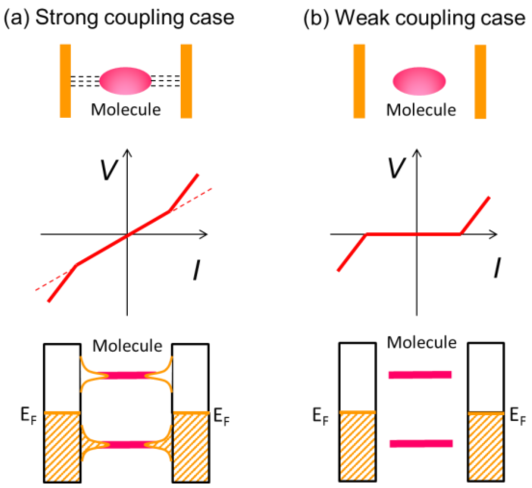

Fig.1. Schematic representation of energy diagrams and current-voltage characteristics of metal/molecule/metal junction for (a) strong coupling and (b) weak coupling cases.

In general, nonlinearity is a key factor in electronic circuits which realize a various functions including oscillation, amplification, frequency conversion, etc. Therefore the appearance of nonlinearity in molecular system is one of the most important issue in molecular electronics. Figure 1 illustrates energy diagrams of electrode/molecule/electrode junction for strong coupling and weak coupling cases. In the strong coupling junction as shown in Fig.1 (a), molecular levels are broadened at the molecule/electrode interface due to formation of chemical bonds. As a result, electron tunneling occurs at Fermi level and zero-bias conductance is observed. On the other hand, in the weak coupling junction as illustrated in Fig.1 (b), the molecules has no chemical interaction with electrodes and the electronic states at molecule/electrode interface are little or nothing. In consequence, current-voltage curve exhibits gap-like structure where conductance around zero-bias is not observed and the current arise with clear threshold.

Intensive studies have been made to increase single molecular conductivity in accordance with the strong coupling case. This direction is useful to achieve single molecular field effect transistors but not appropriate to derive functions based on nonlinearity. In this paper, we report recent investigations of nonlinear electric conduction for single molecules and nano-scale molecular networks which are weak coupling systems.

2. Single molecular conduction of {$Mo_{154/152}$}-ring

Polyoxometalates (POMs) are condensed molecules which consist of transition metal oxyanions. POMs indicate high redox potential and semiconductive properties which are useful for catalysis, electrode and other applications related with electron transfer. Recently, POMs are expected for the elemental device of molecular electronics due to their multiple redox states [3]. For this reason, we focus single molecular conductance of {$Mo_{154/152}$}-ring which is a huge ring-shaped POM [2]. This molecule has the diameter of 3.7 nm as shown in Fig. 2 and thickness of 1.4 nm and contains pentavalent and hexavalent Mo atoms indicating multi-step redox states.

Current-voltage characteristics of single molecular $Mo_{154/152}$ molecule were taken by point-contact measurement using atomic force microscopy. Conventional conductive atomic force microscopy is operated by contact mode which is inappropriate to obtain

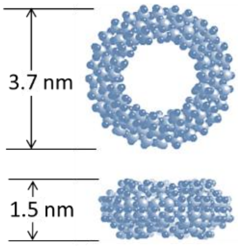

Fig.2. Molecular structure of polyoxometarate $\{Mo_{154/152}\}$-ring.

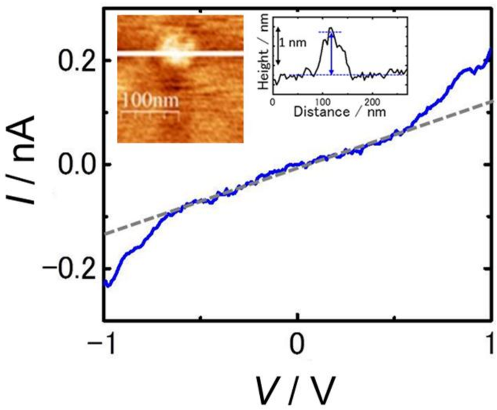

Fig.3 Current-voltage characteristics and atomic force microscopy image of single {Mo154/152}-ring molecule.

electric properties of nano-material, in particular single molecule, because the nano-structures are degraded easily by contact-mode scan. For this reason, we performed point-contact measurements during the interruption of tapping-mode feedback. We have developed this kinds of operation mode as the point-contact current imaging atomic force microscopy (PCI-AFM) and the performance of such methods has been demonstrated for many kinds of nano-materials [4,5].

Figure 3 shows current-voltage (I-V) characteristics and atomic force microscopy image (inset) of single molecule $\{Mo_{154/152}\}$-ring [6]. The observed I-V curve arises with clear threshold at ±0.5 eV and exhibits ohmic baseline for whole bias range including zero-bias. The results imply that there are no obvious interfacial electronic states and the current include the component of direct tunneling between the tip and substrate as illustrated schematically in energy diagram of Fig.4. Actually, the AFM image shows the height of $\{Mo_{154/152}\}$-ring is 1.3 nm that agrees in the molecular thickness of 1.4nm. This indicates that the $\{Mo_{154/152}\}$-rings lie down on Au(111) surface. As a result, the distance between two electrodes, namely the tip and the substrate is only 1.3 nm that is enough short to occur direct tunneling between the tip and the substrate. Such direct tunneling is unfavorable to achieve strong nonlinearity.

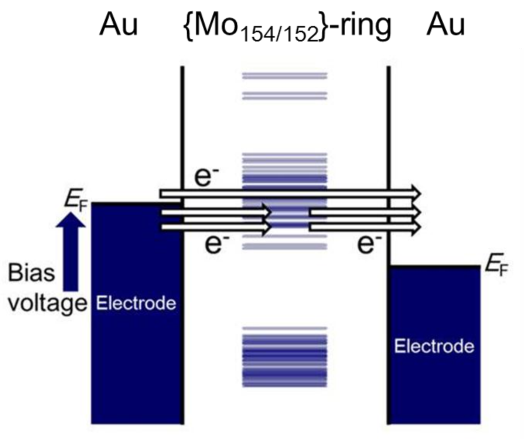

Fig.4. Energy diagram and schematic representation of tunneling conduction of Au/$\{Mo_{154/152}\}$-ring/Au junction.

Single molecular conduction of cytochrome *c*

Cytochrome *c*, electron transfer protein in biological system, is a candidate for elemental device in molecular electronics due to the suitable structure comprised of insulating and active parts. Cytochrome *c* has well-known structure including a heme, an iron redox center, that has two discrete energy levels corresponding to the oxidized (3+) and reduced (2+) states. Since this redox center is isolated from the surroundings by the insulating peptide, the structure of cytochrome c can be regarded as a double tunneling device for single electron tunneling as illustrated in Figure 5. This structure can be categorized in to weak coupling case (Figure 1b) and the I-V characteristics is expected to have strong nonlinearity by Coulomb blockade effect.

In general, proteins are degraded easily when they are adsorbed on metal surface. In order to avoid this problem, chemical modification on electrode surface is necessary at electrode/protein interface. Figure 5 shows the setup of point contact measurement based on atomic force microscopy for single cytochrome *c* molecule. Both

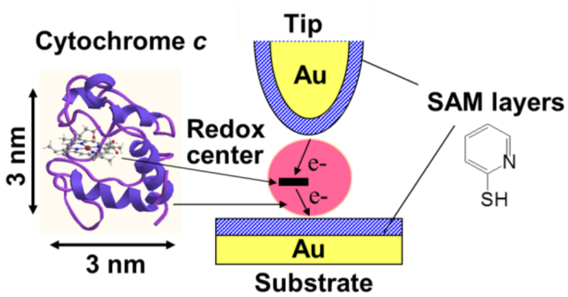

Fig.5. Molecular structure of cytochrome *c* molecule and setup of point-contact measurement with SAM modified tip and substrate using conductive atomic force microscopy.

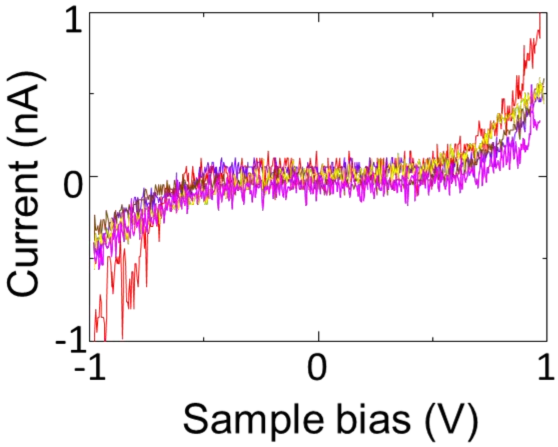

Fig.6. Current-voltage characteristics of single cytochrome *c* molecule. Four curves are superimposed.

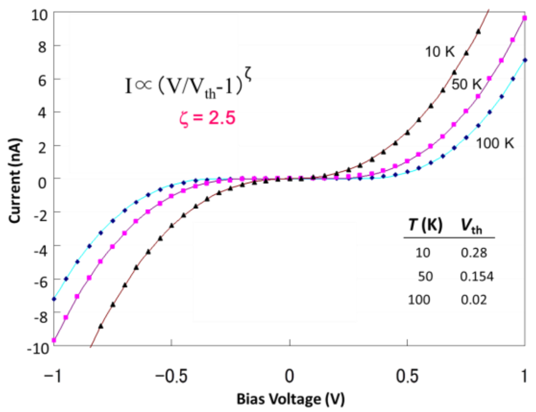

Fig.7. Current-voltage characteristics of cytochrome *c* /DNA network at 10, 50, 100 K. Plots are experimental data and solid line is curve fits calculated by Coulomb blockade network model.

Au(111) substrate and Au-coated tip surfaces are modified by self-assembled monolayer (SAM) of bis-2-pyridyl disulfide (2,2'-PySSPy). It was well established by electrochemical studies that the electron-transfer function of cytochrome c is preserved on the SAM.

Figure 6 shows I-V characteristics of single cytochrome c molecule where clear nonlinear gap-like structure is observed. The current is completely zero within the gap and arise at ±0.3 eV with clear threshold. This type of behavior can be understood by Coulomb blockade in double tunneling system.

4. Cytochrome *c*/DNA network

Single molecular conductance measurements are essential to understand electronic structure and properties of molecules and molecule/electrode interfaces. However, such measurements have been performed by scanning probe or break junction methods. This type of investigations does not connect directly to any actual devices. As mentioned above, Coulomb blockade is one of the dominant phenomena to appear strong nonlinearity. Coulomb blockade network which is an extension of single molecular Coulomb islands, has a way to fabricate actual device.

The devices were fabricated with DNA scaffold for the formation of the molecular network. The mixed solution of cytochrome *c* and DNA was deposited on the SiO_2 substrate. After drying gold (Au) nano-gap electrodes (ca. 50 nm thickness) were fabricated on the molecular network using a top-contact configuration by angled incidence deposition under vacuum [7].

Figure 7 shows temperature-dependent current-voltage characteristics of cytochrome *c* /DNA network that indicate gap-like structures consisting of zero current within the gap and rising edge with clear thresholds. The observed I-V curves are very similar to those of single cytochrome *c*. However the most remarkable feature is the reduction of gap width as increasing temperature. The threshold voltages shift ca. 0.3 eV which is far larger than the thermal energy.

Such electric properties can be described by Coulomb blockade (CB) network model. The $I-V$ characteristic is well represented by simple formula $I \propto \{(V/V_{th})-1\}^{\zeta}$, where I, V, V_{th}, and ζ are the current, bias voltage, threshold voltage, and order parameter meaning dimension of conduction paths, respectively. The obtained $\zeta = 2.5$ is in good agreement with those ($2.2 < \zeta < 2.8$) that of two-dimensional nanoparticles array. This correspondence suggests that cytochrome *c* /DNA network include a number of Coulomb islands which have threshold properties, respectively.

Since a step function of threshold device can be considered as an analog of neuron firing, artificial network of threshold device has a significance from the viewpoint of the mimic of information process of living matter including nerve circuits. Such threshold characteristics should yield stochastic resonance (SR) which enhances signal detection by superimposing noise. It has found in nonlinear response system, as typical example of sensors of living organisms and the neural network of the brain, and it is used in artificial systems for visual processing and associative functions.

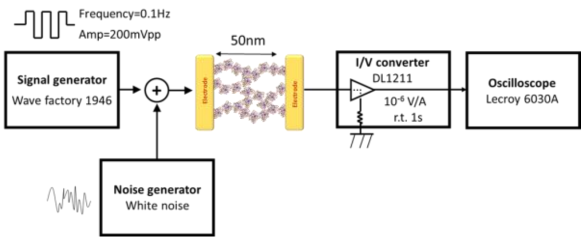

Fig.8. Setup for stochastic resonance experiment for cytochrome c/DNA network device.

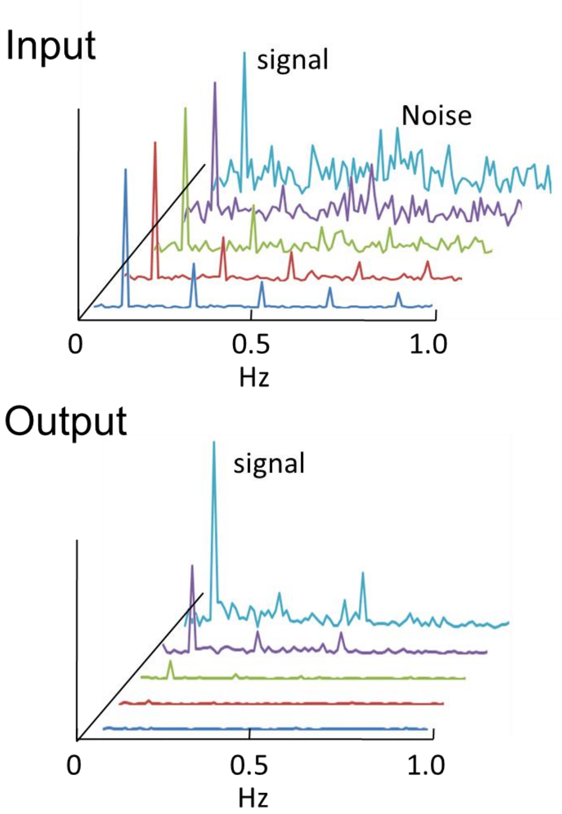

Fig.9. Fast Fourie transform power specta of input voltage and output current for cytochrome *c*/DNA network device.

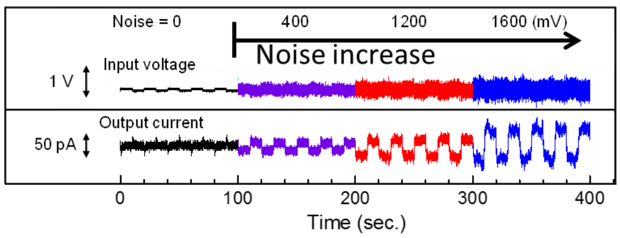

Fig.10. Oscilloscope records of input voltage and output current of cytochrome c/ DNA device.

Figure 8 represents experimental setup for observation of stochastic resonance where output signals were systematically measured by changing the amplitude of white noise against the small periodic square wave as input signal. Figure 9 shows fast Fourier transform (FFT) power spectra of input (a) and output (b) signals with various noise amplitude. No output signal is detected for the small input of periodic square wave with no noise. When the amplitude of white noise exceeds the threshold, the output signals corresponding to the input signal are clearly observed. Time-course records of input and output signals are also presented in Figure 10. As increasing noise amplitude, periodic signal synchronized to original signal appear with enhancement in output signal [8]. These results indicate that SR phenomena occur in the molecular network suggesting first step toward next-generation architecture for future molecular neural network devices in molecular electronics.

Acknowledgments

The author thank R. Tsunashima for providing $\{Mo_{154/152}\}$-ring molecule. This work was supported by Grants-in-Aid for Scientific Research in Innovative Areas (No. 20111016, No. 25110014), a Grant-in-Aid for Young Scientists (B) (No. 22760007), and Grants-in-Aid for Scientific Research (B) (No. 24360011) and Scientific Research (C) (No. 25390056) from the Ministry of Education, Culture, Sports, Science and Technology (MEXT) of Japan.

References

[1] A.Troisi and M. A. Ratner, “Molecular signatures in the transport properties of molecular wire junctions: What makes a junction “Molecular”?,” *small*, vol.2, pp.172-181, 2006.

[2] C. Busche, L. V-Nadal, J. Yan, H. N. Miras, D. L. Long, V. P. Georgiev, A. Asenov, R. H. Pedersen, N. Gadegaard, M. M. Mirza, D. J. Paul, J. M. Poblet, L. Cronin, “Design and fabrication of memory devices based on nanoscale polyoxometalate clusters,” *Nature*, vol. 515, pp.545-549, 2014.

[3] A. Müller, S. K. Das, V. P. Fedin, E. Krickemeyer, C. Beugholt, H. Bögge, M. Schmidtmann, B. Hauptfleisch, “Rapid and simple isolation of the crystalline molybdenum-blue compounds with discrete and linked nanosized ring-shaped anions: $Na_{15}[Mo^{VI}_{126}Mo^{V}_{28}O_{462}H_{14}(H_2O)_{70}]_{0.5}[Mo^{VI}_{124}Mo^{V}_{28}O_{457}H_{14}(H_2O)_{68}]_{0.5}\cdot ca.400H_2O$ and $Na_{22}[Mo^{VI}_{118}Mo^{V}_{28}O_{442}H_{14}(H_2O)_{58}]\cdot ca.250H_2O$,” *Z. Anorg. Allg. Chem.*, vol.625, 1187-1192 ,1999.

[4] Y. Otsuka, Y. Naitoh, T. Matsumoto, T. Kawai “A Nanotester: A new technique for nanoscale electrical characterization by point-contact current-imaging atomic force microscopy,” *Jpn. J. Appl. Phys.*, vol.41, pp.L742-L744, 2002.

[5] R. Tsunashima, Y. Noda, Y. Tatewaki, S. Noro, T. Akutagawa, T. Nakamura, T. Matsumoto, T. Kawai, “Electrical resistivity of molecular-assembly nanowires of amphiphilic bis-TTF macrocycle/2,3,5,6-tetrafluoro-7,7,8,8-tetracyano-p-quinodimethane charge transfer complex characterized by PCI-AFM,” *Appl. Phy. Lett.*, vol. 93, 173102-1-3, 2008.

[7] H. Matsuo, S.Sumida, D.C. Che, H. Ohoyama, I. Nakamura, R. Tsunashima, T. Matsumoto, “Conductance of single $\{Mo_{154/152}\}$-ring probed by conductive AFM,” *Hyomen-Kagaku*, 2015, in press

[8] Y. Hirano, Y. Segawa, T. Kawai, T. Matsumoto, “Stochastic resonance in a molecular redox circuit,” *J. Phys. Chem.* C, vol. 117, 140−145, 2013.