Form 3

Abstract of Thesis

Name	(Nunik Nurhayati)
Title	**Signal Dynamics from Single Molecule Junction of Organic Polyoxometalate Derivatives** (有機ポリオキソメタレート誘導体単分子架橋のシグナルダイナミクス)

Abstract of Thesis

In recent years, investigation about single organic molecule as an active electronic component for electronic device is growing up rapidly. The pioneers of single molecule device are Aviram and Ratner. In 1974 theoretically they proposed the construction of a very simple single organic molecule device that consists of donor π – insulating bridge - acceptor π system which has rectifier properties.[1] Single molecule device can reduce the size of molecular device so that it can miniaturize the device. Compared to traditional inorganic-based device, such as silicon device, organic molecule device has some advantages such as high-speed fabrication which makes it is low cost, low temperature processing on flexible substrate, and tunable properties of the molecule. As a consequent, single organic molecule device is promising for alternation to inorganic-based device.[2,3]

Polyoxometalates, which is abbreviated as POMs, are discrete metal oxide clusters consist of early transition metal ions and oxygen atoms.[4,5] POMs are very special molecules. They are capable to accept many electrons so that they are utilized in many electrochemical and electrocatalytic processes such as molecular cluster battery,[6,7] photoanode of dye-sensitized solar cells[8], and catalyst.[9,10]

Recently we have reported a molecular neuromorphic network device consisting of single-walled carbon nanotubes (SWNT) complexed with POM. Experimentally, we observed dynamic properties of SWNT-POM complex networks where that networks can generate spontaneous spikes and noises. By introducing reservoir computing through modelling, it shows that SWNT-POM complex networks can be applied to a molecular device as a neuromorphic device construction.[11] Achieving this phenomena, now our research is focusing on investigation of single molecule POM whether those kind of spikes and noises can also be generated by single molecule not only by SWNT/POM network using mechanically controllable break junction method.

There are two POM molecules were addressed in this work. (1) *POM-to-Rings* (labelled as **POM-1**) was synthesized by Okujima and Uno *et. al.*[12]. It is a double decker complex of cyclo[8]pyrrole coordinating to Keggin type POM, dodecatungstosilicate ion $(SiW_{12}O_{40})^{4-}$ (Figure 1a). In this molecule, cyclo[8]pyrrole acts as anchoring group that will tether to gold electrode. According to our recent results, transmission probability of free-base porphyrin ring interacting with the gold electrode is greater than transmission probability of thiolate and gold electrode.[13] Similar with free-base porphyrin ring, cyclo[8]pyrrole has π conjugation system so that it will work as good anchoring group attached to gold electrode.

(2) **POM-2** is the ammonium salt of $(PW_{11}O_{39})^{7-}$ that has been modified by linking thiol groups as anchoring group. Molecular structure of **POM-2** contains two -$(CH_2)_3$SH groups connected to the POM core through Si atoms (Figure 1c). This -$(CH_2)_3$SH group is as anchoring group (which is different from **POM-1**) that will attach to gold electrodes via covalent bonding Au-S. The molecule was synthesized based on the reported procedure.[4]

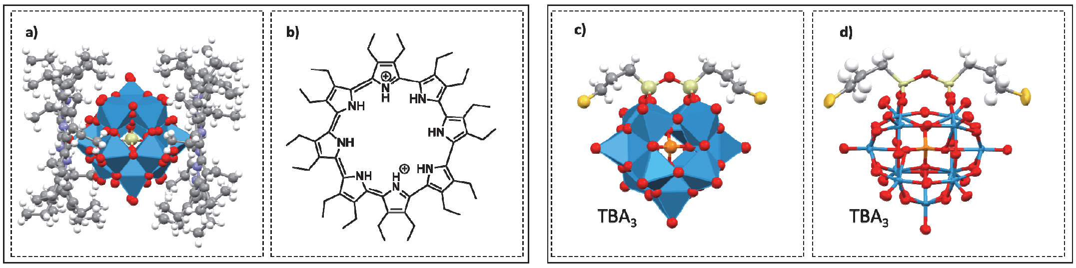


Figure 1. (a) Polyhedral shape of cyclo[8]pyrrole-$SiW_{12}O_{40}$- called as POM-to-Rings or **POM-1**. An $SiW_{12}O_{40}$ is attached to two cyclo[8]pyrroles. Yellow, red, grey, white, and purple blue balls are for Si, O, C, H, and N, respectively. Tungsten atoms are in the center of octahedron blue. (b) Chemical structure of cyclo[8]pyrrole[54]. Copyright 2016 with Elsevier's permission. Polyhedral (c) and ellipsoid (d) shape of $TBA_3PW_{11}O_{39}[\{HS(CH_2)_3Si\}2O]$, called as **POM-2**. Orange, red, grey, white, pale yellow, and yellow balls are for P, O, C, H, Si and S, respectively. Tungsten atoms are in the center of octahedron blue. Tetra-n-butyl ammonium is abbreviated as TBA.[25] Copyright 2011 with the permission from RSC.

Current versus voltage (*I-V*) curve of the **POM-1** was measured with the bias scan from $0\ V$ to $0.5\ V$ (forward) and from $0.5\ V$ to $0\ V$ (backward) at RTV condition (Figure 2). A typical *I-V* curve was shown with red and blue line for the forward and backward scan, respectively. The *I-V* curve switch stochastically between low conductance ($\sim 4.4 \times 10^{-9}\ S = 5.7 \times 10^{-5} G_0$ at $0.3\ V$) and high conductance ($\sim 8.2 \times 10^{-8}\ S = 1.\times 10^{-3}\ G_0$ at $0.3\ V$) states, to afford the high/low ratio ~ 19. 2D histogram of the *I-V* curves of 6 scans indicates the high reproducibility of the stochastic fluctuation of the single molecule conductance between the two states. It can be concluded that POM molecule can generate dynamic signals or noises. Stochastic fluctuation appears at some threshold voltage which means that redox reaction is responsible for this fluctuation.

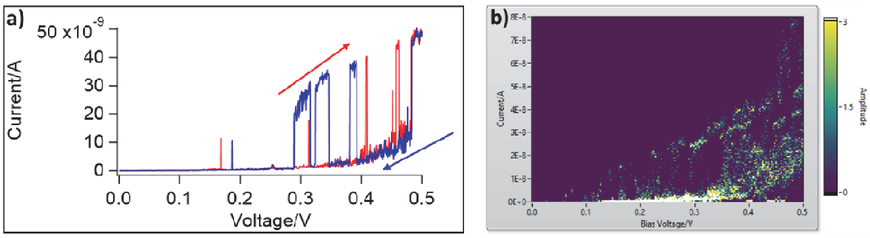


Figure 2. (a) Current versus voltage (I-V) curve of POM-to-Rings when bias voltage (red = bias forward; blue = bias backward) applied at room temperature and its 2D histogram of bias forward from 6 data (b).

Current versus voltage (*I-V*) of the **POM-2** was measured with the bias scan from $0\ V$ to $1.0\ V$ (forward) and from $1.0\ V$ to $0\ V$ (backward) at RTV condition (Figure 3). 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.

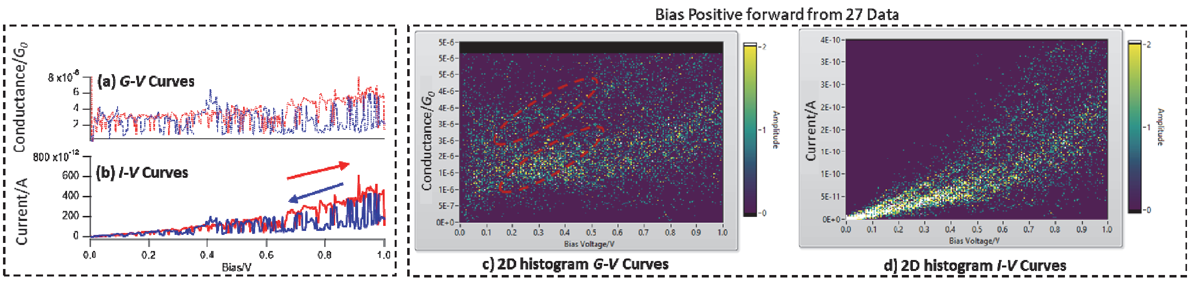
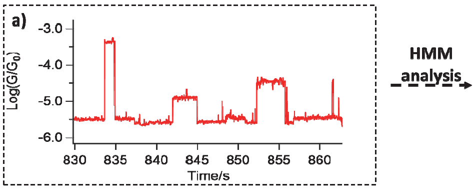
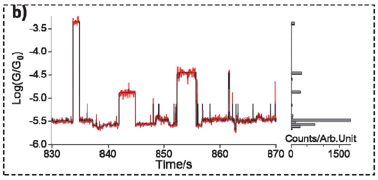


Figure 3. A typical *I-V* and *G*(conductance)-*V* curves were shown with red line for the forward scan, and with blue line for the backward scan.

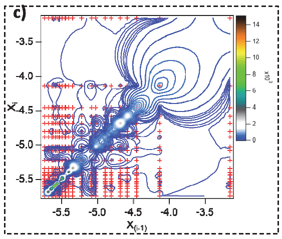
In order to clarify the mechanisms of the dynamic properties of the single molecule conductance, time courses of current were conducted to single molecule **POM-1** and **POM-2**. Hidden Markov Model (HMM) was applied to the data for conductance state. The HMM models the dynamics of an observed time series (Y) as conditionally dependent on a hidden process (X).[14]



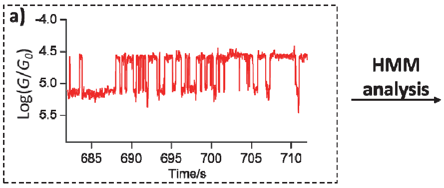
(a) Time traces of single molecule **POM-1** when 0.3 V bias voltage was applied at room temperature under vacuum condition



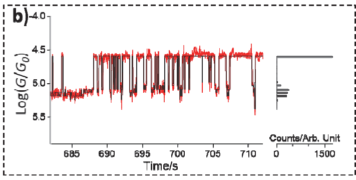
(b) Corresponding HMM fitting analysis (left) and its histogram (right) of (a)



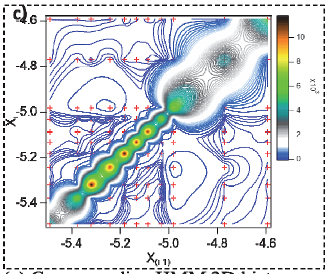
(c) Corresponding HMM 2D histogram



(a) Time traces of single molecule **POM-2** when 0.3 V bias voltage was applied at room temperature under vacuum condition



(b) Corresponding HMM fitting analysis (left) and its histogram (right) of (a)



(c) Corresponding HMM 2D histogram

Stochastic fluctuations appear in both **POM-1** and **POM-2** as a response of voltage. **POM-1** shows multistate of conductance with large high/low ratio. While in case of **POM-2**, two states of conductance appear with small high/low ration. It can be concluded that stochastic current fluctuation is depending on molecule.

However, constant frequency oscillation which were observed in the cases of SWNT-POM complex networks did not occur in the case of single molecule POM measurements. The result indicates that the oscillation occurs by cooperative phenomena of the POM networks.

*RTV = Room Temperature under Vacuum

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様式 7

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨

単一分子の静的な特性として、整流効果、メモリ効果、トランジスタ効果などが興味を持たれ、多くの研究がなされてきた。最近になり、単一分子の動的なふるまいにも興味が持たれ始めている。多数の分子の集団であると現象が平均化されて動的に見えなかった現象も、単一分子で観測するとその動的な振る舞いが明らかになり、これまで見られなかった興味深い現象が明らかになってきている。申請者の所属研究室において、ポリオキソメタレート（POM）を単層カーボンナノチューブ（SWNT）上に吸着させた系が、周期的なコンダクタンス変化や、パルス状の信号を出すことが見出されていた。この振る舞いは、動物の神経と類似しており大変興味深い。また、この動的信号のモデルを利用すると、機械学習の一種であるリザーバー計算を効率よく行うことが分かっている。

申請者は、この現象の機構や、信号の性質をより明らかにするため、２種類の POM を用いて単一分子電気特性を詳細に研究し、分子構造と単一分子物性の関連を明らかにした。２種類の POM の内、cyclo[8]pyrrole という大きなπ電子系を持つ有機分子で挟まれた POM を POM-1、アルキルチオールが伸びている POM を POM-2 と名付ける。これらの POM を機械的制御破断接合法(MCBJ 法)という手法で、単分子接合を作り、一定電圧を加えてその電流変化を観測し、次の結果を得た。

（１） いずれも、ランダムテレグラフノイズ(RTN)と呼ばれる形状の信号を示した。この信号が、完璧にランダムなのか、なんらかの規則性があるのかを明らかにするため、自己相関係数を求めたところ、比較的大きな相関係数を持っており、ランダムではないことが明らかになった。

（２） 観測された信号（y_i）が隠された状態（x_i）からノイズを含めて発生するという仮定を作り、隠れマルコフモデル（HMM）の手法で解析した。その結果、POM-2 は２～４状態から信号を出しているが、POM-1 はより多数の状態から信号を出している事。POM-2 の２状態の伝導度の違いは４倍程度であるが、POM-1 の各状態の伝導度の違いは大きい場合には 1000 倍程度異なる事が明らかとなった。

（３） 時間 t_iの伝導度を $G(t_i)$、そのひとつ前の観測値を $G(t_{i-1})$として、y 軸に $G(t_i)$を x 軸に $G(t_{i-1})$を取って、その頻度の 2 次元ヒストグラムを描くと、一つの伝導度状態 Gi から別の伝導度状態 Gj への遷移確立 Pij が逆の遷移の確率 Pji とほぼ等しいことが分かった。もし、3 状態以上の間で遷移が起こっていると Pij と Pji は大きく異なるはずであることから、複数の状態が見えていても、実際の遷移は 2 状態間でしか起こっていないことが分かった。

以上のことから、POM の分子軌道と電極金属のフェルミ準位に依存する酸化還元反応が伝導度変化の要因であり、ストカスティックな酸化還元が RTN の原因であると考えると説明できる事を示した。

これまで明らかでなかった POM の動的挙動の原因の一端を明らかにした本論文は、博士（理学）の学位論文として十分価値のあるものと認める。