

Non-Symmetric Single-Molecule Electrical Properties

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Abstract– Non-symmetric electrical properties, such as rectification, negative differential resistance, threshold gate, hysteresis effect, and integrated threshold gate, are essential to realize brain oriented electronic devices, which are believed to withstand noise and fluctuations. So far, there is no concrete design principle for single-molecule electronic devices. In the tunneling regime of the molecules, the I - V characteristics are essentially dependent on the density of states (DOS) of the system, while in the hopping mechanisms, the molecules can be charged to change their electronic properties. To understand this principle, we have synthesized a series of molecules to study the single-molecule electrical properties.

1. Introduction

1.1. The Concept of Single Molecule Devices

Many types of devices are referred to as “single-molecule devices.” In this paper, I will refer to the three types of devices shown in Figure 1 as single-molecule devices. Type A is the most scientifically correct “single-molecule device,” in which the electrical properties of the single molecules are measured using metallic break junction methods or by using carbon electrode junctions.[1-4] Using carbon nanotube electrodes, it is possible to obtain the three-terminal measurements of “integrated single-molecule devices”.[5] However, it would be very difficult to make working devices using these measurement methods. Type B and Type C devices are similar to macro-sized molecular electronic devices.

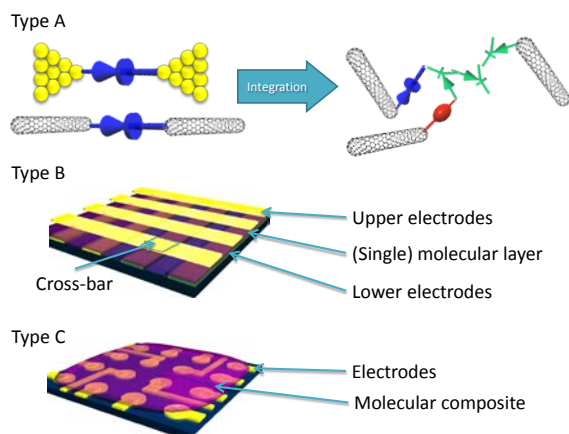


Figure 1. Three types of “single-molecule devices.”

The important difference between conventional devices and “single-molecule electronic devices” is that in the latter, the physical properties of the molecule of interest can be retained even with a single molecular size. Some physical properties are observed only in larger size than certain limitations, because they arise from collaborative phenomena between molecules or atoms. For example, the doping effect, ferromagnetic effect, ferroelectric effect, super conductivity, and negative differential resistance (NDR) of molecular materials are in most cases properties that are characterized by the collaborative phenomena of large number of molecules, however, these properties do not occur when the size of the device unit is reduced to molecular scale ($\sim 1 \text{ nm}^3$).

Another merit of using a single molecule is that some multifaceted properties can be realized in one molecule through careful design, allowing the size of one device unit to be reduced to molecular scale without losing its properties. In Type B and Type C “single-molecule devices,” the size of the device unit is defined by the size of the electrodes, which is prepared by the conventional lithographic technique. For an electrode width of $\sim 10 \text{ nm}$, the cross-bar section in Type B device contains hundreds of molecules. An important point to note is that once these devices work well with this size, the electrodes width can be reduced to $\sim 1 \text{ nm}$ while retaining single molecular properties.

This concept can be easily understood by considering the atomic switch devices developed by Aono.[6] The atomic switch devices are made from two wires spaced $\sim 1 \text{ nm}$ apart, and one of the wires is made from silver sulfide (Ag_2S), from which the atomic bridges of silver are formed. The concept of the devices is utilized for practically working memories, which are now considered to commercialize by a private company. In this case, the size of one memory unit is defined by the width of the electrodes; however, it is smaller than the circuit size fabricated using conventional transistors. In other words, by choosing appropriate materials (in this case Ag_2S) some functionality can be realized by just sandwiching them between two electrodes, which is simpler and easier than using transistors. Moreover, if the materials are “single molecules,” the size of one cross-bar can be reduced to the molecular size. Aono and Gimzewski have made use of atomic switch networks for natural computing by using Type C devices.[7] We have developed atomic switch devices functionalized by

organic molecules,[8-9] and volatile/nonvolatile dual-functional atom transistor.[10]

1.2. Utilization of noise and fluctuation

In general, nano-sized devices should withstand noises and fluctuation, as observed in single-molecule devices. However, utilization of noises and fluctuation can improve the performance of the system if it is adequately designed. For example, small signal detection using stochastic resonance is often observed in the behavior of animate beings.[11-15] Recently, Matsumoto reported usage of molecular redox for stochastic resonant devices.[16]

During the discussion with Asai and Kasai in Hokkaido University about “bridging material science with information science,” they proposed the importance of non-linearity of the unit single-molecule devices to realize information processing utilizing noise and fluctuation.

2. Non-linear behaviors in single-molecule devices

We are interested in non-linear responses, such as rectification, NDR, hysteresis, and those shown in Figure 2, to be realized in single-molecule devices. If these properties can be realized in single molecules, by combining them as shown in Figure 1, higher functionalities are possible, in which noise and fluctuation can be utilized.

However, in the tunneling regime, the current-voltages (I - V s) of single molecules are proportional to the integral of the density of states (DOS) (Figure 2, lower right), and they increase monotonically. It has long been unclear whether such complex non-linear and non-symmetric responses are possible in single-molecule devices or not.

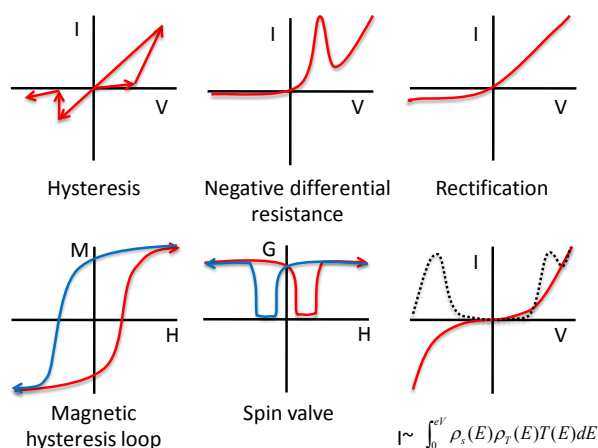


Figure 2. Non-linear behaviors to be realized in single-molecule devices and a typical response curve of single-molecule devices (lower right). V is for voltage, I for current, H for magnetic field, M for magnetization, G for conductance, ρ for density of states. Current is approximately proportional to the integral of the density of states of the molecule in the tunneling regime.

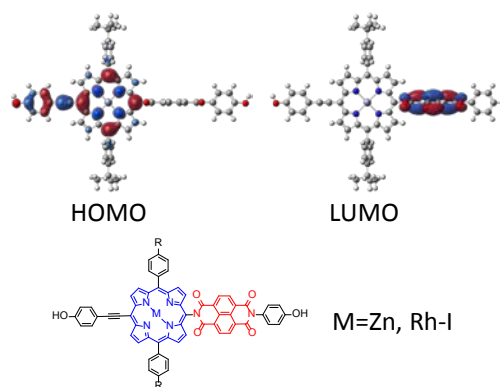


Figure 3. Structure and molecular orbitals of porphyrin-imide single-molecule diodes.

Through advancements in measurement techniques, some clarity has been achieved but not entirely.

2.1. Rectification

Rectification is a very important functionality to be realized by single-molecule devices. It was first proposed, by Aviram and Ratner in 1974, that by using donor- σ -acceptor (D- σ -A) molecules, rectification was possible.[17] Metzger succeeded in showing that the monolayer of D- σ -A molecules can show rectification.[18] Tao clearly showed that single-molecule rectification is possible by using D- π -A molecules.[19]

We have developed a new type of single-molecule diode, as shown in Figure 3, where the donor porphyrin is directly linked to the acceptor imide with perpendicular arrangement.[5] The characteristic feature of this molecule is that the donor part (D) and acceptor part (A) are not electronically connected strongly, because two π -electronic systems are separated by the perpendicular bonding. In the first proposal by Aviram and Ratner, such an isolation of D from A is achieved by insertion of σ moiety, which works as the insulating part. However, such an insulating part diminishes conductivity of the molecule. In the present molecule D and A are separated electronically without inserting the insulating part, so that high performance is expected. Another characteristic feature is that the electronic state of the molecule can be tuned by changing the central metal ion in the porphyrin moiety.

We measured the single molecule I - V characteristics of the molecule using the mechanically controllable break junction method (MCBJ)[2] and single-walled carbon nanotube electrodes with the PCI-AFM method[20-23], to show that these molecules show high rectification ratio, and the rectification ratio can be tuned by changing the central metal ion in the porphyrin core.

2.2. Negative differential resistance

NDR is another important feature to be realized by single molecules, because the response is known to be the key component of the FitzHugh-Nagumo model of neuronal excitability.[24-25] There are several reports of NDR observed in single molecules.[26-29]

As described in the earlier section, the single molecule in the tunneling regime should show a monotonic increase in the I - V characteristics, so that NDR cannot be expected with this mechanism. One possible way to show NDR is chemical reaction during scanning the potential. As shown in Figure 4, if the molecule is in “state 1” within a lower potential range and shifts to “state 2” at a certain potential, which has higher conductivity, then again returns to low conductive “state 3”, this molecule will exhibit NDR.

Phosphododecamolybdic acid (PMO_{12}) is a kind of polyoxometalate compounds, which are known to be redox active molecules.[30] We found that PMO_{12} grafted on the single-walled carbon nanotube (SWNT) shows reproducible NDR peaks, and when high voltage is applied to the device, periodic pulse generation is observed.

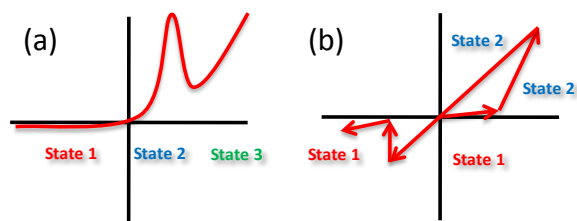


Figure 4. Possible mechanism to exhibit NDR and hysteresis in single-molecule devices.

2.3. Hysteresis and magnetic hysteresis (Single molecule magnets)

Hysteresis behavior is also expected when the molecule can perform some chemical reactions by the applied potential, as shown in Figure 4b.

Terbium porphyrin double-decker complexes (**Por₂Tb** in Figure 5) are interesting compounds, when they are protonated they do not show any magnetism; however, once a proton is removed to give the anionic or radical form, they exhibit single molecular magnetism. Therefore, a magnetic hysteresis loop is observed, as shown in Figure 2 (lower left).[31-32] The technique of electron impact apart from chemical conversion can also be used to achieve the radical form from the protonated form, as shown in Figure 5, by using scanning tunneling microscopy (STM) under high vacuum. This experiment indicates that by applying a certain potential to the molecule by using the conventional nano-gapped electrodes, we can achieve the conversion of the protonated form to the radical form. Using terbium porphyrin phthalocyanine double-decker complexes (**PorPcTb** in Figure 5), the presence and absence of proton did not affect the single-molecule magnets.[33] However, the conductance of the protonated **PorPcTb** is 16 times greater than that of **PorPcTb** in the anionic form.

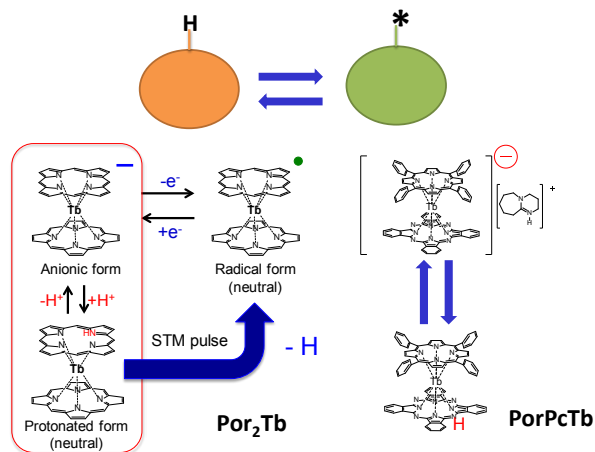


Figure 5. Switching of magnetic hysteresis and conductivity by removing and adding H atom to terbium double decker complexes.

This result indicates that it is possible to achieve conductance hysteresis by using these compounds, as shown in Figure 4b. We have proposed molecules in which reversible conversion of protonated and anionic forms can be determined by DFT calculations.[34]

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