A Grant-in-Aid for Scientific Research on Innovative Areas
The Area Number 2509 (2013-2018)

MOLECULAR ARCHITECTONICS

MolArch

Orchestration of Single Molecules for Novel Functions

News Letter No.6 April 2015

Achievement

A01 Prof. Hiroshi Nishihara

Nickelladithilene π–Nanosheet

We presented redox control and high conductivity of nickel bis(dithiolene) complex p–nanosheet, **1** (Fig. 1a) in the recent publication (T. Kambe *et al.*, *J. Am. Chem. Soc.* **136** (2014) 14357). The average oxidation number of the nanosheet is −3/4 for each complex unit in the as–prepared sample; oxidation or reduction respectively can change this to 0 or −1. Electrical conductivity measurement of the stacked **1** reveals a conductivity of 1.6 x 10^2 S cm^{-1}, which is remarkably high for a coordination polymeric material. Conductivity is also noted to modulate with the change of oxidation state (Fig. 1b). Theoretical calculation and photoelectron emission spectroscopy reveal the stacked nanosheets to have a metallic nature. This work provides a foothold for the development of the first organic–based two–dimensional topological insulator (cf. Liu, F. et al. *Nano Lett.* **13** (2013) 2842). This work is collaborated with Prof. Shuji Hasegawa (A03).

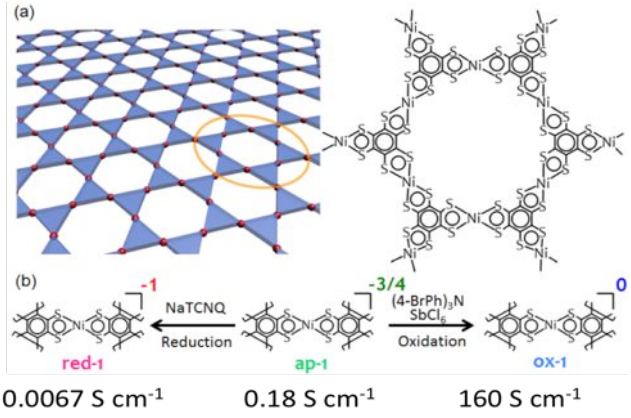


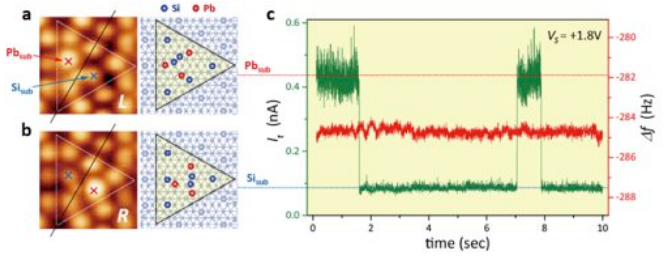
Fig. 1. Illustration of **1** (a) and its redox control with change in electrical conductivity (b).

Achievement

A03 Prof. Yoshiaki Sugimoto

Room-temperature Nano-switch

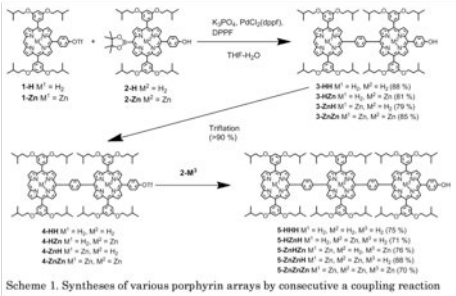
Single-atom or single-molecule manipulation for fabricating and operating an atomic-scale device is a promising technology to reach the ultimate limit of integration. Recent scanning probe microscopy studies have demonstrated a variety of atomic-scale switches involving lateral/vertical displacements, rotational motions and conformational changes. Nevertheless, the performance of most switches requires cryogenic temperatures. A room-temperature (RT) environment is essential for most practical applications, and this remains a challenging obstacle to overcome. We report an atomic-scale switch composed of a binary Pb_3Si_2 'molecule' on Si(111) surface. At RT, the switch was performed by constructing an atomically size-defined 'molecule', and was then operated using a tunneling carrier injection from a scanning probe microscopy tip. Unidirectional or bidirectional switch behavior could be regulated by selecting electrons or holes as injection carriers, demonstrating a directionally controlled switch. Our approach opens up novel nanofabrication to achieve molecular-scale integrated electronics for use at RT. (*Nat. Commun.* **6** (2015) 6231)



A01
Synthesis of Porphyrin Arrays for Single Molecule Electronics

Mr. Takashi Tamaki
(Osaka University)

Porphyrin arrays have attracted much attention in a wide range of scientific applications such as in artificial photosynthetic antenna, electronic devices, and single-molecule devices. Recently, Sedghi and coworkers have reported that zinc porphyrin arrays with more than three porphyrin subunits show hopping conduction in a single-molecule measurement. In hopping conduction, the charge carrier can stay in a part of the molecule to modify the physical properties. Consequently, nonlinear and non-symmetric single-molecule current-voltage (I-V) characteristics such as rectification, negative differential resistance, and hysteresis could be expected with these molecules. It was still difficult to synthesize elaborate porphyrin arrays with programmable order of each unit. Thus we attempted to synthesize such porphyrin arrays by a consecutive coupling reaction. Consecutive coupling can be performed by varying the reactivity of functional groups. Finally we succeeded in developing a novel synthesis method for porphyrin arrays with various central metals. With this method, we have synthesized porphyrin arrays with not only zinc but also nickel, palladium, iron and/or copper as central metals. We will measure the single molecule I-V characteristics of these various porphyrin arrays.



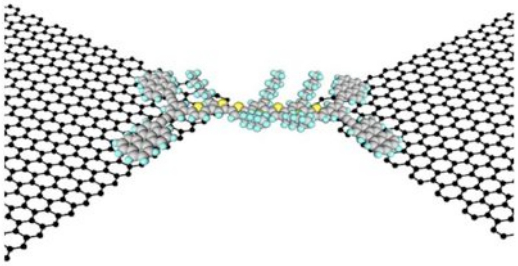
Scheme 1. Syntheses of various porphyrin arrays by consecutive a coupling reaction

A02
Development of graphene nanogap electrodes for fabrication of molecular devices

Mr. Takashi Ikuta
(Osaka University)

Development of single-molecular devices is one of the most important goals in molecular architectonics. In single-molecular devices, contact electrodes for molecules occupy a prominent position. Normally, σ-bonding is formed in metal-molecular contacts and this bonding prevents from evaluating transfer characteristics of single-molecule. Thus, the conductive materials with π-orbit have been desired to be used for electrodes. Graphene has been attracted attention as electrodes in single-molecular devices owing to its unique properties, such as high conductivity and easy modification of molecule on its surface.

In Matsumoto Lab, we have succeeded in fabrication of the graphene nanogap to measure electrical properties of single molecules. In recent work, we have collaborated with Prof. Ie (A01 group) and challenged to measure transfer characteristics of single polythiophene molecules with graphene nanogap electrodes. We have succeeded in bridging polythiophene molecules between graphene nanogaps and observing p-type semiconductor characteristics using the back gate. We will challenge to change single molecules with functionalized molecule for development of low dimensional physics, such as single electron transports.



Architects~

A03
Inelastic Electron Tunneling Spectroscopy of Au-Oligthiophene-Au

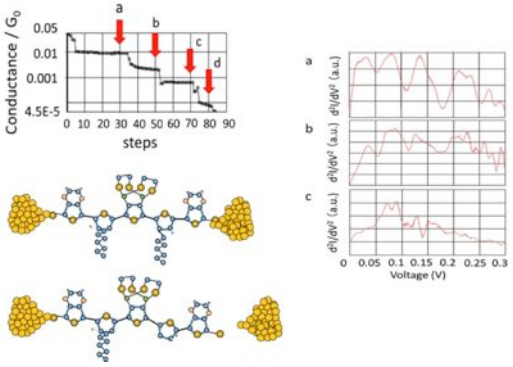
Mr. Takashi Shimomise
(Osaka University)

Inelastic Electron Tunneling Spectroscopy (IETS) can provide information on single molecular vibrations due to electron-phonon coupling and can be measured while measuring the electrical conductance. IETS is expected to provide information on the configuration of single molecular junctions and on the contribution of molecular orbitals in the transport mechanism.

The IETS signal is due to electron-phonon coupling and appears as peaks in the second derivative of the current-voltage characteristics. The IETS signal is usually measured by using a lock-in amplifier at the second harmonic 2ω of the added modulation.

So far, IETS of small and simple molecules, for example benzenedithiol and alkanedithiol, has been reported by many groups, but large molecules have not yet been measured. Large molecules have many degrees of freedom in the metal-molecule-metal configuration. It is thus important to gain a good understanding of the relationship between the molecular characteristics and the molecular configuration.

We have measured large oligothiophene molecules synthesized by Dr. Tanaka in IMS and would like to investigate the molecular configuration by using the IETS technique.



A04
Development of a high-precision wet chemical etching technique for GaAs-based nanowire formation

Mr. Ryota Kuroda
(Hokkaido University)

We are working on electronic implementation of bio-inspired functionalities, such as stochastic resonance and molecular motor, using a III-V compound semiconductor nanowire and its network. My research focuses on high-precision wet chemical etching technique for GaAs nanowire formation. We have developed a novel digital wet chemical etching system as shown in Fig. 1 in cooperation with a manufacturing company. Conventional wet chemical etching is performed by dipping the sample in etchant, which often lacks controllability of etching depth and reproducibility due to fluctuation of etching time, rinse time, and so on. Our newly developed machine injects the etchant and the rinse solution on the sample sequentially in digital manner. Injection rate, timing, and cycles are perfectly controlled by a digital computer. The amount of etching is digitally defined by the number of cycles of the sequence. Recently we successfully demonstrated the digital etching of GaAs using this system as shown in Fig. 2. We pursue further development of this etching technique to achieve further precise size control and high reproducibility.

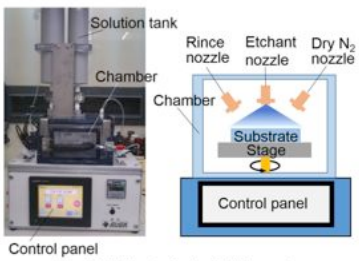


Fig. 1 Digital wet chemical etching system

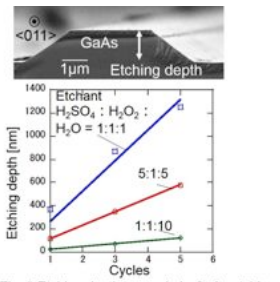


Fig. 2 Etching depth vs. cycle in GaAs etching

Report of the 2nd Workshop for Young Researchers
19-20/December/2014, IIAS, Kyoto

The 2nd Workshop for Young Researchers was held from December 19 to 20, 2014 at IIAS, Kyoto. Approximately 20 students and staff from our area were in attendance.

On the first day, we received a lecture on English technical writing by invited speaker Ron Read. He is a board member and Kansai branch manager of Kurdyla and Associates Co., Ltd. He gave us an interesting talk and some general tips about technical writing. His first advice was, "Keep your sentences short!" In the afternoon, we had a group competition. The task was to make a system with limited materials. The goal of the system was to enable a bell to ring 30 seconds after releasing a marble. We worked on this task in groups of three and after a close race, group number four won the first prize, managing to ring the bell after about 16 seconds (lower right picture with Prof. Tada (A03, field representative), Congratulations!). They received a special prize from Prof. Kasai (A04, workshop organizer). On the second day, there were two basic lectures. The first one was about information processing given by Prof. Asai (A04). He lectured about generation and propagation of pulse in the brain system, and proposed some hints for applying it to the molecular system. The final lecture, given by Dr. Ohto (A03), was about carrier transport in single molecules. He gave a talk about the interaction between a molecule and the surface of electrodes, and how this is expressed by transmission function. Thanks to these lectures, we are confident we have received a better understanding of these topics.

We all look forward to the next Workshop for Younger Researchers! (M. Yamaguchi (A03))

Next Meeting

International Workshop on Molecular Architectonics
3-6, August 2015, Shiretoko Grand Hotel "Kita Kobushi"

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