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

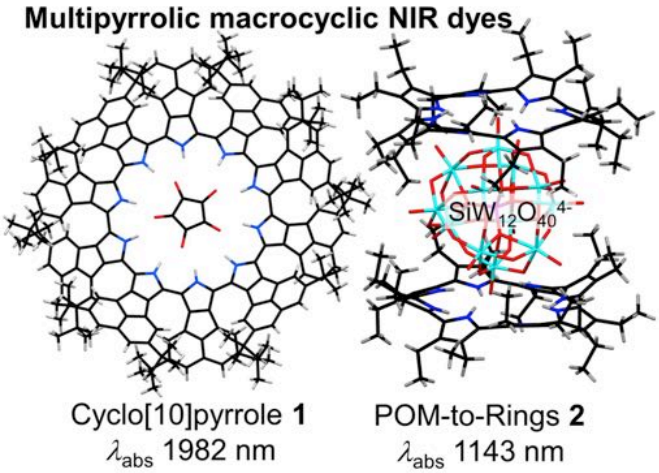
News Letter No.10 November 2016

Achievement

A01 Prof. Hidemitsu Uno

Ring-expanded porphyrins without meso-bridges

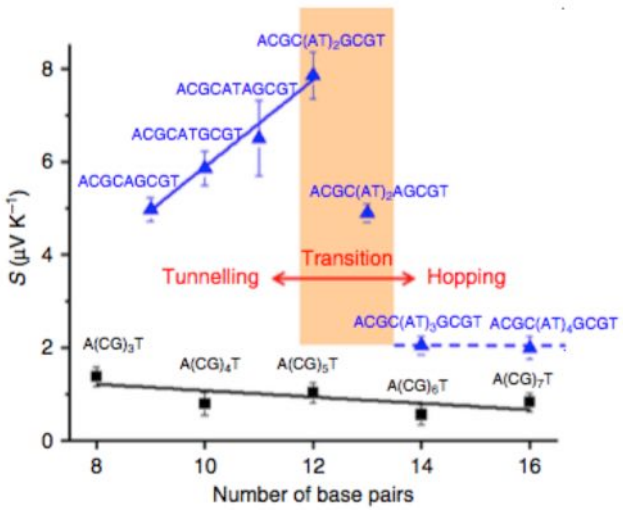
We have successfully synthesized cyclo[10]pyrrole **1** and POM-to-Rings **2**. The absorption spectrum of **1** exhibited a markedly red-shifted, intensified L band at 1982 nm. X-ray crystallographic analysis revealed the structure of **1** as the isolated largest cyclo[n]pyrrolethe and the sandwich structure of **2**, the POM anion held between two cyclo[8]pyrroles with weak hydrogen-bonding interaction with the POM to the pyrrolic NH groups. The CV of **2** showed positively shifted redox waves of cyclo[8]pyrrole and no wave of the POM anion in contrast with the double-decker complex of porphyrin directly coordinated with POM. The further investigations for the NDR measurement of POM-to-Rings **2** are under way with Ogawa group. (T. Okujima *et al.*, *JACS* **2016**, *138*, 7540; *TL* **2016**, *57*, 3160.).



A03 Prof. Yoshihiro Asai

Thermoelectric effect and its dependence on molecular length and sequence in single DNA molecules

Studying the thermoelectric effect in DNA is important for unravelling charge transport mechanisms and for developing relevant applications of DNA molecules. Here we report a study of the thermoelectric effect in single DNA molecules. By varying the molecular length and sequence, we tune the charge transport in DNA to either a hopping- or tunnelling- dominated regimes. The thermoelectric effect is small and insensitive to the molecular length in the hopping regime. In contrast, the thermoelectric effect is large and sensitive to the length in the tunnelling regime. These findings indicate that one may control the thermo- electric effect in DNA by varying its sequence and length. We describe the experimental results in terms of hopping and tunnelling charge transport models. (Y. Li *et al.*, *Nature Communication*. 2016, 7, 11294).

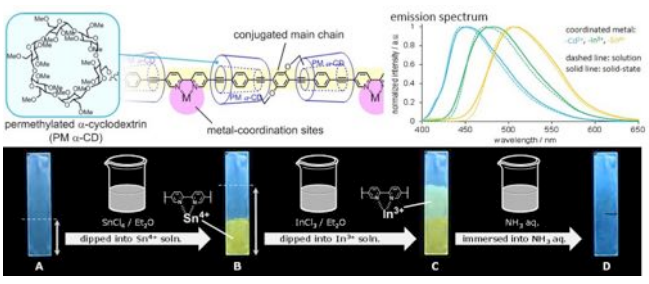


A01

Optical effect of metal-coordination to an insulated molecular wire

Mr. Takuro Hosomi
(Kyoto University)

π-conjugated polymers are promising materials for use in molecular devices due to their superior optical or electrical properties. However, their physical properties were known to be dramatically decreased in the condensed phases, due to their strong interpolymer π-π interactions. To suppress the interpolymer π-π interactions, we previously developed polyrotaxane-type insulated molecular wires (IMWs), which have macrocycles that cover π-conjugated main chains to suppress intermolecular interactions. They exhibited superior physical properties, such as high conductivity, high emission efficiency and efficient wiring to nanoelectrodes. We recently focuses on the effect of metal-coordination to the IMWs. For this purpose, a platform-type IMW which has metal-coordination sites on the backbone was synthesized (figure). This structure allows metal ions to access the coordination sites, simultaneously preventing interactions between the wires by insulation. Metal coordination to the polymer caused various change of their emission color, enabling easy and reversible tuning of the luminescent color. The tuned results and efficient emission were maintained even in the solid-state due to their three-dimensional insulation structures, which demonstrated superior molecular properties of the material.



A02

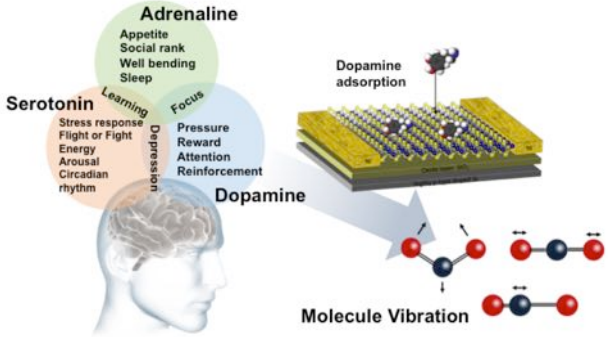
Novel molecule sensor by using atomic layered material technology

Mr. Nguyen Tat Trung
(Tohoku University)

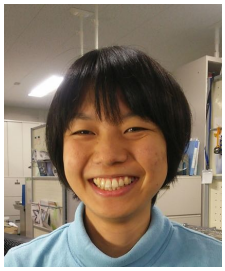
Molecule detection in a variety of environments is indispensable technology for understand the life phenomena and development of science society. Electronic device is one of application resolve the matter of previous molecule detection technique such as chemical reaction, fluorescence marker and radiation marker. In recent year, as the material of electronic device, atomic layered material is paid attention.

Atomic layered material like MoS2, WSe2 has two-dimensional structure. The biggest advantage of two-dimensional structure is that it itself is ultrathin film less than 1 nm. In other words, the surface states much effect on solid states, for the surface area is very big against its volumes.

In this study, we try to read out the peculiar information of molecule from electronic device adsorbed bio-molecules by only using current. To realize brain mapping by development of novel high accuracy molecule sensor is our priority.



Architects~



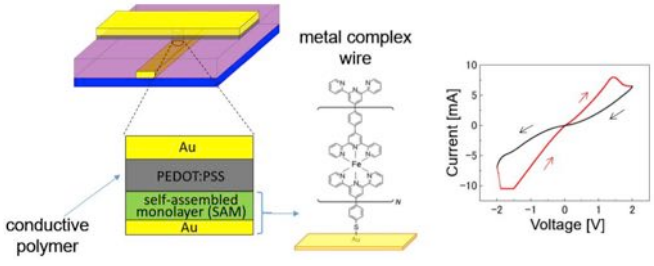
A03

Resistive Switching Effects in Large-Area Molecular Junctions with Metal Complex Molecular Wires

Ms. Mariko Yamaguchi
(Osaka University)

Electrical switching from a low- to a high-conductance state is one of the basic elements for application of data storage, logic operations or electric circuits to signal processing. It has been reported that the electrical properties of molecular junctions using redox-active molecules show resistive switching. For practical applications of such kind of junctions, a two-terminal crossbar structure is considered to be suitable.

We made large-area molecular junctions[1] with metal complex molecular wires synthesized in a stepwise manner on the Au bottom electrode[2]. First, a 40 nm thick Au electrode was prepared. Bis(terpyridine)iron complex wires were then coordinated in the holes of 10 μm in diameter. Finally, conductive poly(3,4-ethylene-dioxythio-phene)-poly(styrenesulfonate) (PEDOT: PSS, 100 nm) was spin-coated in order to avoid the penetration of metal atoms during the deposition of the top Au electrode (100 nm). Devices showed hysteretic current-voltage characteristics as shown in the figure. Moreover, nonvolatile resistive switching performances were observed with applying pulse voltage. By impedance measurement, it is suggested that these resistive switching effects mainly occur at the molecular wire/conductive polymer interface.



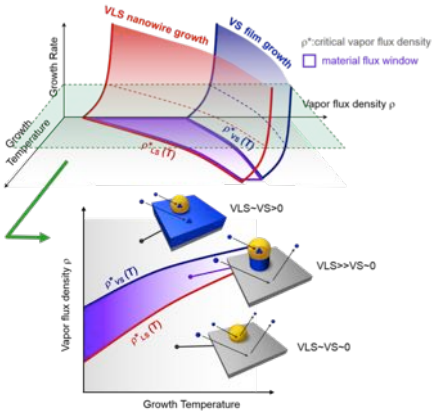
[1] H.B. Akkerman *et al.*, *Nature* **441**, 69 (2006).
[2] Y. Nishimori *et al.*, *Chem. Asian. J.* **4**, 1361 (2009).

A04

Rational Concept for Reducing Growth Temperature in Vapor-Liquid-Solid Process of Metal Oxide Nanowires

Mr. Zetao Zhu
(Kyushu University)

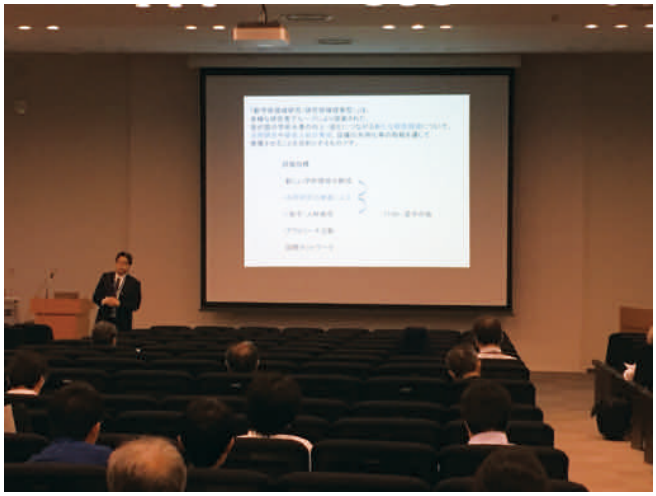
Vapor-liquid-solid (VLS) growth process of single crystalline metal oxide nanowires has proved the excellent ability to tailor the nanostructures. However, the VLS process of metal oxides in general requires relatively high growth temperatures, which essentially limits the application range. Here we propose a rational concept to reduce the growth temperature in VLS growth process of various metal oxide nanowires. Molecular dynamics simulations theoretically predict that it is possible to reduce the growth temperature in VLS process of metal oxide nanowires by precisely controlling the vapor flux. This concept is based on the temperature dependent material flux window that the appropriate vapor flux for VLS process of nanowire growth decreases with decreasing the growth temperature. Experimentally, we found the applicability of this concept for reducing the growth temperature of VLS processes for various metal oxides including MgO, SnO2 and ZnO. In addition, we show the successful applications of this concept to VLS nanowire growths of metal oxides onto tin-doped indium oxide (ITO) glass and polyimide substrates, which require relatively low growth temperatures.



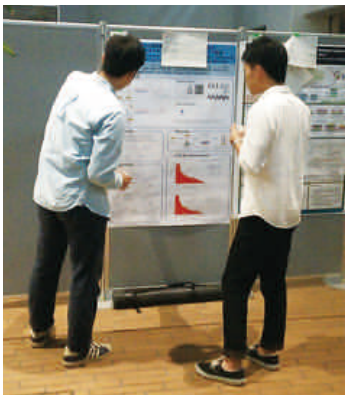
7th Area Meeting
19 October, 2016
Chikushi Hall, Fukuoka

The 7th Area Meeting of Molecular Architectonics was held on October 19, 2016 at Chikushi Hall, Kyushu University, Fukuoka. There were more than 50 attendees including all the group leaders, group members, students and collaborators.

In this meeting, all presentators reported their collaborations. 53 intra-area and 105 inter-area collaborations have been promoted since the start of our project. It is important to have suggestions from the members of our area, particularly to early stage collaborations. Finally we are grateful that Prof. Fukuyama and Prof. Matsushige, the academic evaluators, and Prof. Tanaka, the academic investigator, also attended the meeting and provided invaluable advice.



5th Workshop for Young Researchers
19 October, 2016
Chikushi Campus, Fukuoka



The 5th Workshop for Young Researchers, attended by approximately 30 students from our area, was held on the same day as the Area Meeting.

We had a very long poster session, from 5 p.m. to 10 p.m., with sandwiches and snacks. Every attendee voted for the best poster at the end of the poster session. The best poster award winners are listed below:

Mr. Yoichi Sasaki (Kyushu Univ.)
Mr. Takashi Tamaki (Osaka Univ.)
Ms. Chie Nakamura (Kyushu Univ.)
Mr. Zetao Zhu (Kyushu Univ.)

We also discussed the plan for the next workshop for young researchers.

Edited by "Molecular Architectonics" Chief Office
1-3 Machikaneyama, Toyonaka, Osaka 560-8531
Mail: office@molarch.jp

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