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.5 November 2014

Now at Work

A04 Prof. Kasai's group

Implementation of information processing function on single-molecule-integrated networks and improvement of its reliability

We are working on bio-inspired electron nanodevices and systems, especially focusing on coexisting with fluctuation. Amoeba-*inspired* computer, called as "electronic amoeba", is one of such systems. Amoeba-*based* computing is well known as an Ig Nobel Prize research by Prof. T. Nakagaki. Our electronic amoeba implements a sophisticated algorithm to solve optimization problems, obtained from the amoeba's behaviors by Prof. M. Aono, Tokyo Inst. of Tech. Of course, the electronic amoeba can find solutions extremely faster than the actual amoeba! An interesting feature of our system is that fluctuation emerges an ability of spontaneous solution searching. Very recently Mr. Wakamiya successfully demonstrated it using a real electronic circuit by intentionally introducing random bit signals. This result suggests that the electronic amoeba made of a single molecule network efficiently search the solutions owing to its dynamics with temporal fluctuation intrinsically involved in the system.

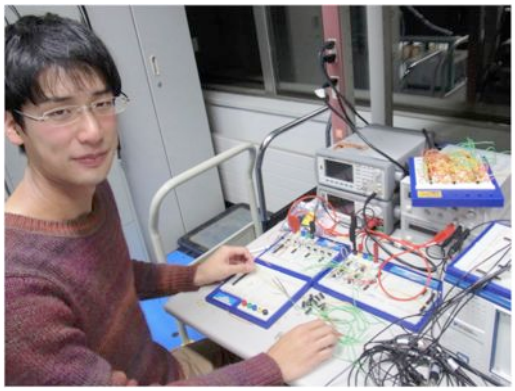


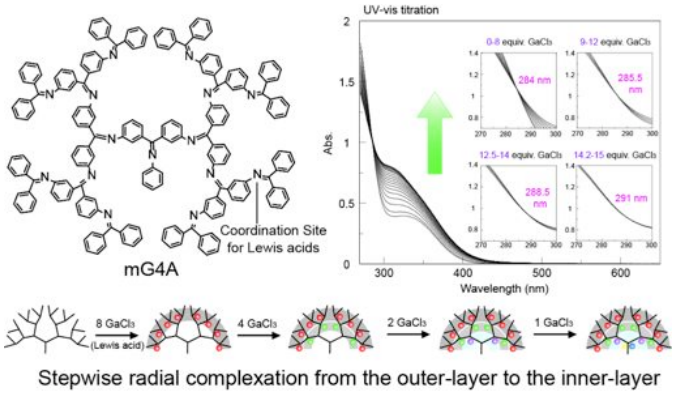
Photo : Mr. Wakamiya constructing electronic amoeba.

Achievement

A01 Dr. Ken Albrecht

Stepwise radical complexation based on designed potential gradient

Para-substituted phenylazomethine dendrimer (pDPA) coordinates to Lewis acids in a stepwise radial fashion from the inner-layer to the outer-layer (*Nature*, 2002, *415*, 509). We presented a new type phenylazomethine dendrimer (*meta*-substituted phenylazomethine dendrimer, mDPA) that has inverted coordination sequence, i.e., the stepwise radial coordination from the outer-layer to the inner-layer. The inversion of the potential gradient could be explained by the substituent effect of the repeating unit. The pDPA has a resonant donation effect to the inner-layer and the mDPA has inductive withdrawal to the outer-layer. This sequential coordination is reflecting the electron density gradient of the dendrimer. Therefore, the discovery of the simple mechanism is useful as a novel method to design and control the intramolecular potential structure that should be applicable to design a single molecular diode (*Chem. Commun.*, 2014, *50*, 12177).



Stepwise radial complexation from the outer-layer to the inner-layer

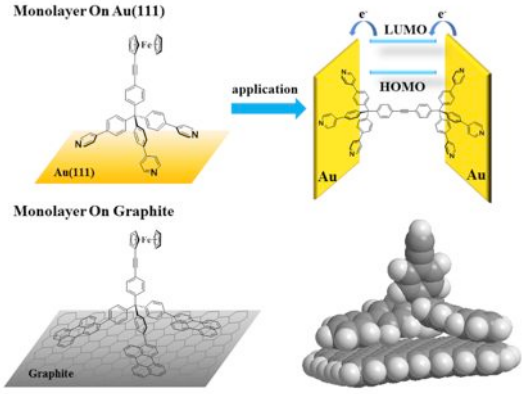
A01

Development of tripodal anchor compounds for having π-channel adsorption on gold or graphite electrodes

Ms. Aya Tashiro
(Osaka University)

Development of functional organic electronic devices is one of the most active research fields in nanoscience. Especially, single-molecular electronics have been attracted in terms of ultimate miniaturization. They have a number of potential advantages for constructing functional devices. Given that the advantages of molecular electronics relies on a variety of molecules and their fine-tuned properties, organic synthetic chemistry should play a key role in designing and synthesizing functional electric materials.

In Aso Lab, new advanced functional compounds for organic electronics and molecular electronics have been developed. Among them, I focus on development of tripodal anchor compounds toward π-channel adsorption on gold or graphite electrodes. In 5th Molecular Architectonics Symposium, I will report tripodal anchor compounds having π-channel adsorption on graphite electrode. When the fused aromatic rings were used as anchor units, van der Waals interaction between the anchor compounds and the graphite electrode plays an important role in the adsorption. In the near future, I will figure out the potential of the hetero rings as anchor units.



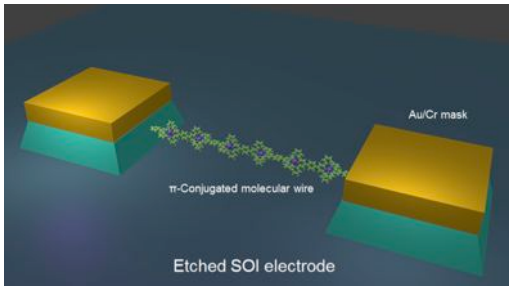
A02

Connection of silicon nanoelectrodes with π-conjugated molecular wires

Mr. Tetsuhiro Kobayashi
(The University of Tokyo)

π-Conjugated molecular wires have high electron transport ability and are expected to be wiring materials for integrated molecular devices. Therefore, it is very important to immobilize π-conjugated molecular wires onto substrates in an effective method. Among numerous kinds of substrates, silicon is valuable because of the application to semiconductor devices. We have developed Pd-catalyzed arylation on hydrogen-terminated silicon surface with various kinds of aryl iodides. The advantages of this method are the generation of a uniform monolayer without overreaction and direct connection between phenylene ring and silicon surface. Efficient electron transfer can be expected through π-conjugated system.

In order to realize the final target of molecular architectonics, we have started a new project for the connection of two silicon nanoelectrodes using π-conjugated molecular wire. Silicon nanoelectrodes (length: > 70 nm) were prepared by anisotropic etching of SOI (Silicon-on-Insulator) electrodes after Au/Cr masking. We have succeeded in modifying silicon nano-electrodes with π-conjugated molecules in the presence of palladium catalyst. We are planning to fabricate π-conjugated linkages between two nanoelectrodes and to measure their electric properties.



A03
Electrical conduction measurements of fine samples by four-tip STM

Mr. Naoya Fukui
(The University of Tokyo)

Measurement of electrical conductivity of small samples is highly required for understanding the intrinsic nature of materials. The four-tip STM is one of the most suitable techniques for it because the measurement of sub-micron-size samples by the four-terminal method is available with versatile arrangement of the probes. Here we show two examples. The first one is the measurement of wires etched from an ultrathin film of a topological material Bi_2Se_3 by Focused Ion Beam [1]. We changed the length and width of the wire and found that the resistance was consistent with one-dimensional conduction, indicating that all the current passed through the wire without leakage. The other example is the measurement of Nickel-dithiolene (NiDT) micro-flakes [2]. The NiDT sheet is expected to be a two-dimensional topological insulator. The electrical property of NiDT can be tuned by changing the degree of oxidation. The measured conductivity was much higher than that previously measured with a pellet of the material.

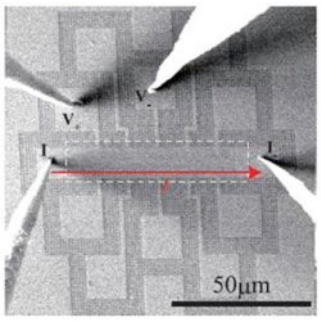


Fig. 1 Measurement of Bi_2Se_3 wire [1].

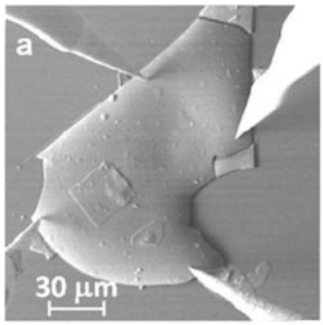


Fig. 2 Measurement of a Ni-dithiolene flake [2].

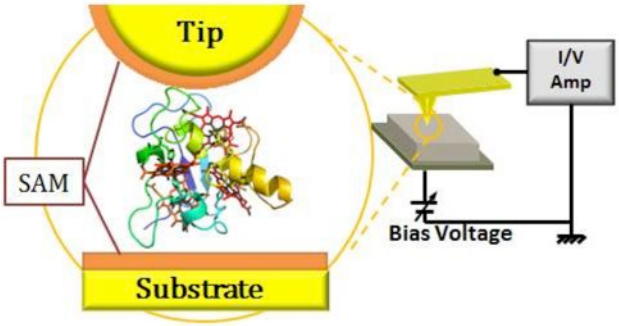
[1] N. Fukui et al., e-J. Surf. Sci. Nanotech. 12, 423-430 (2014).
[2] T. Kambe et al., J. Am. Chem. Soc. 136, 14357-14360 (2014).

A04
Non-linear I-V characteristics of a single molecule probed by conductive-AFM

Ms. Saki Sumida
(Osaka University)

Control of single electron tunneling is an important challenge in the field of nanoelectronics because of the low energies and small circuit involved. We expect that molecules containing multiple redox sites show an effect in the current-voltage (*I-V*) characteristics such as hysteresis, polytomous response and are applicable to single molecular devices having novel functions.

In a recent study, we paid attention to a material containing the multiple redox sites: cytochrome c3 (Cyt c3). Cyt c3 is an electron transfer protein and has four hemes per molecule. As the proteins structures are optimized the electron transfer, we expect that the molecular devices consisting of proteins imitate biological systems. We used conductive atomic force microscopy (C-AFM) to measure the *I-V* characteristics of a Cyt c3 single molecule with self-assembled monolayer (SAM) modified electrodes. We found that the *I-V* curves of Cyt c3 have non-linear characteristics. Such a non-linearity in molecular electric conduction is a fundamental portion for the neuron firing and directional signal propagation in brain-inspired molecular electronics.



Report of the 4th Area Meeting
24-26/November/2014, Toyonaka, Osaka

The fourth area meeting of Molecular Architectonics was held from November 24 to 26, 2014 at Σ-hall, Toyonaka, Osaka. There were about 60 members and students from our area.

Firstly, four group leaders summarized the achievements made by their group members. Many collaborating works and plans emerging from our area were reported on. Following this, researchers reported their progresses, plans and their candidate projects for future collaborations. In particular, the members of the A04 group actively talked about the possible applications of molecular devices for brain-like information processing. Prof. Tetsuya Asai (A04) pointed out that the generation and propagation of the pulse with molecules as well as the plasticity of the system are very important for the brain-inspired molecular devices. The candidate molecules for these functions proposed from A04 members were respectively: the molecular thyristor, molecular ratchet and nanowire reversible switch for the pulse generator, propagator and plastic material. We received valuable hints for the next synthesis and measurements.

Prof. Matsushige (an evaluator) and Prof. Katagiri (an academic investigator) encouraged us leading up to the middle evaluation at the next year. We discussed the collaboration between A01~03 and A04 which is an important point for the evaluation throughout the meeting.

Next Meeting

5th Area Meeting
April 2015, Chiba

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