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

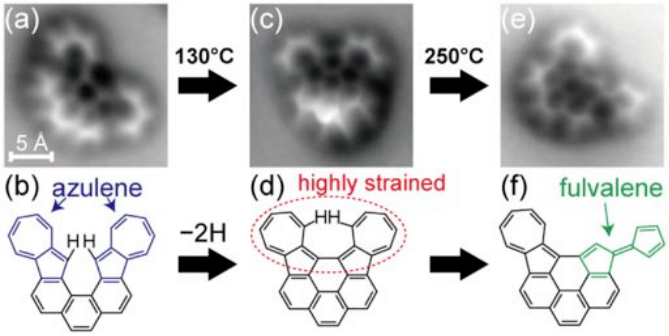
News Letter No.12 March 2018

Achievement

A03 Dr. Akitoshi Shiotari

Structural strain in a hydrocarbon on a surface produces an unprecedented molecule

Controlling the structural deformation of organic molecules can drive unique reactions that cannot be induced only by thermal, optical, or electrochemical procedures. However, in conventional organic synthesis, it is difficult to control skeletal rearrangement in polycyclic aromatic hydrocarbons (PAHs). We recently demonstrated a characteristic rearrangement of an azulene-derivative PAH on a metal surface driven by the intramolecular structural strain (A. Shiotari, T. Nakae, *et al.*, *Nat. Commun.* 2017, 8, 16089). Noncontact atomic force microscopy visualized the carbon skeletons of reactants, intermediates, and products of the on-surface reaction. An azulene group in the PAH was converted into a fulvaleno group, so as to eliminate the structural strain localized in the azuleno moieties on the surface. Such strain-induced reactions of PAHs would be a useful approach to designing and fabricating unprecedented, functional nanocarbon materials.

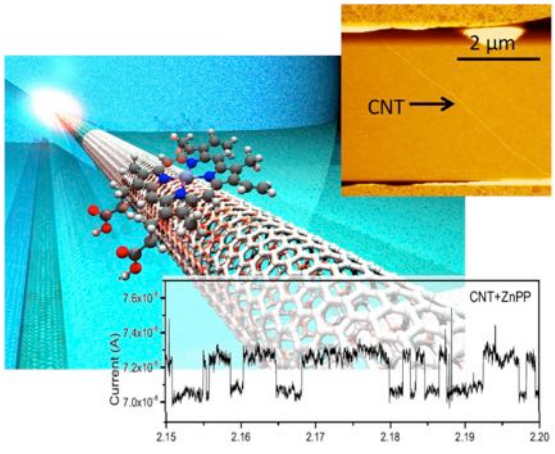


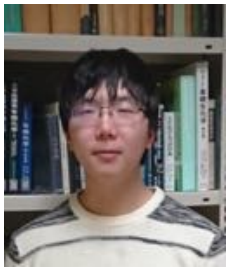
A04 Dr. Megumi Akai

Signature analysis of single molecules using their noise signals

We explored the ability of single molecules to affect the noise generated by carbon nanotube-based nanoscale electronic devices. The devices were exposed to different large molecules, causing some to bind to the carbon nanotube surface. It was found that different molecules gave unique noise signals related to the properties of the molecules. The strength of the interaction between the carbon nanotubes and molecules was able to be predicted from the obtained noise signals.

The noise signal is generated by single molecules because the adsorbed molecule generated a trap state in the carbon nanotube, which changed its conductance. The ability to characterize single molecules using highly sensitive nanoelectronics is an exciting prospect in the field of sensors, particularly for neuro- and biosensor applications. Improved knowledge of the molecular-level origin of noise should lead to the development of electronics that use noise to improve their performance rather than degrade it.





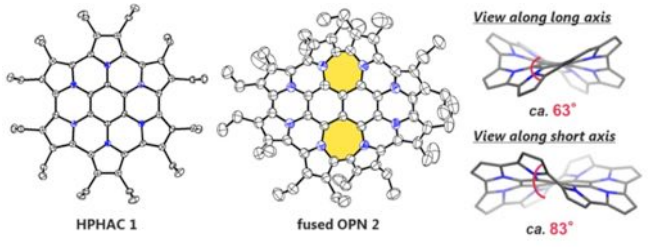
A01

Synthesis of π-Expanded Azacoronene Derivatives toward Post-Nanocarbon

Mr. Kosuke Oki
(Ehime University)

Doped large polycyclic aromatic hydrocarbons (PAHs) with heteroatoms is one of the key exploration areas in current nanographene research. Nonplanar PAHs also have much attention because of their unique structure and physical properties. However, the figuration of curved π-systems with internal heteroatoms has been still challenging.

Recently, we successfully synthesized fused-OPN 2 as a nitrogen-doped curved nanocarbon in only two steps from commercially available octafluoronaphthalene via nucleophilic substitution and oxidative cyclodehydrogenation. The molecular structure of 2 was confirmed by single-crystal X-ray diffraction. In contrast to the planar structure of hexapyrrolohexaazacoronene (HPHAC 1), negatively curved structure owing to formation of heptagons was detected. The electrochemical properties of 1 and 2 were studied by cyclic voltammetry (CV) and exhibited up to three and four reversible oxidation peaks, respectively. The UV-vis-NIR spectra of 2 changed dramatically with isosbestic points when the oxidant was added incrementally to the solutions. This result supports the sequential oxidation of the π-systems from a neutral to a radical cation, dication, and then to a radical trication. The further investigations for the dynamic behavior of 2 are under way.

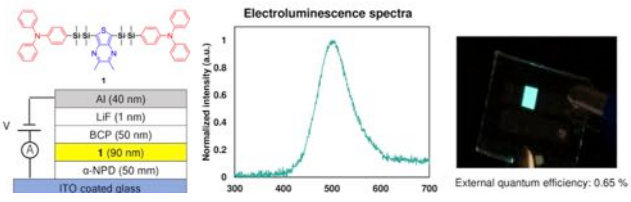


A02

Synthesis and Applicaiton of disilane-bridged donor-acceptor molecules which have triarylamine moieties

Mr. Tsukasa Usuki
(University of Tokyo)

Recently, donor-acceptor molecules consisting of electron-donating (D) and electron-accepting (A) moieties have received attention because of their potential for photonic and electronic materials. They showed remarkable light-emitting properties, however, in the solid state, π-conjugated molecules often exhibit weak emission by aggregation-caused quenching (ACQ) due to π–π stacking. Previously, we synthesized disilane-bridged DA molecules which displayed strong solid state emission. Disilane units decrease π-π interactions and suppress ACQ.
In this work, we focused on the application of this type molecules to organic light-emitting diodes (OLEDs). Firstly, we applied DA molecules reported previously. However, electroluminescence was not observed because of their large HOMO-LUMO gap and extremely low electric conductivity. Next, we synthesized new disilane-bridged DA molecules possessing triarylamine groups as donor moieties. Triarylamine groups are well-known as strong electron-donating and hole-transporting properties. By introducing triarylamine groups, reducing HOMO-LUMO gap and improving carrier mobility were expected. The device was fabricated by vacuum deposition and the construction is shown in figure. Consequently, the device exhibited blue-green electroluminescence. This is the first report of electroluminescence from disilane-bridged DA molecules in undoped devices.



Architects~

A03

Single-molecule spintronics

Mr. Keigo Minode (Osaka University)

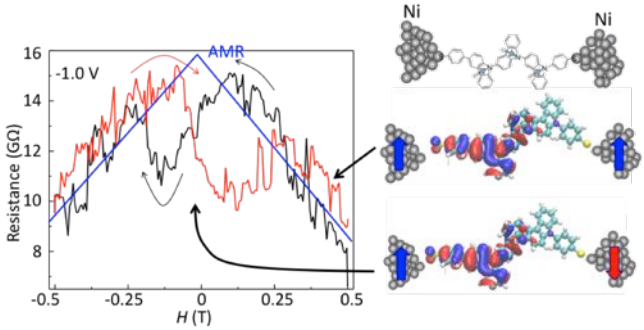
I am engaged in research about magnetic field dependence of resistance, *i.e.*, magnetoresistance (MR) of single-molecule junctions with ferromagnetic electrodes.

MR is an important phenomenon for magnetic sensors and is used in a reading head of hard disk drives.

Single-molecule spintronics is paid attention to exhibit higher MR ratio due to spin-dependent electronic states caused by electronic coupling between ferromagnetic electrodes and the molecule.

Interpretation of experimental MR was difficult because of the huge Anisotropic MR originate from ferromagnetic nano-junctions.

To detect MR originated from single-molecule junctions, I focused on modulation of junction symmetry because theoretical study predicted that MR ratio will change according to symmetry of junction. I measured Ni/carbazole 3-mer/Ni single-molecule junctions. Previous study showed that symmetry of molecular orbital of carbazole 3-mer is deformed by applying voltage between electrodes. Therefore, voltage dependence of MR would contain information on characteristics originated to molecule. I have constructed measurement system and obtained results.

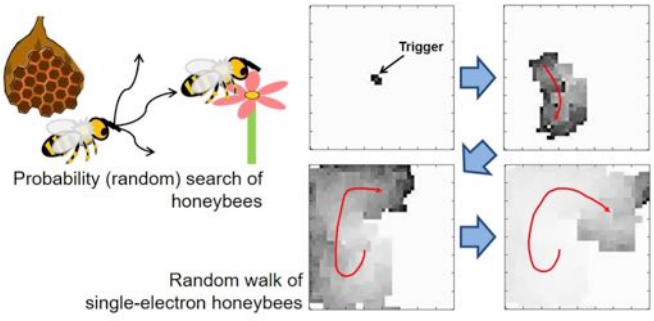


A04

Design of unique information-processing coarse-grained devices mimicking foraging behavior of honeybee swarm

Mr. Toshihiko Tanabe (Yokohama National University)

What is the most appropriate information processing way for coarse-grained devices including single-molecule devices and single-electron devices? We think it has not been established yet. As one approach to find the suitable way, we focus on a natural phenomenon, specifically, the behaviors of honeybee swarm. Recently, a "nature-inspired" or "biomimetic" technology has been attracting attention for developing innovative functional systems applying emerging nanoscale devices. In particular, the foraging behavior of honeybees is focused on as architecture for an electronic circuit. It is known that the honeybees show two foraging behaviors, namely, a probability search and a "waggle dance" (sharing information). By combining these behaviors, it can be considered that the foraging behavior is a unique information-processing act. For constructing a new system, we are now designing, simulating, and evaluating our coarse-grained circuit mimicking the behavior. We are here focusing on a single-electron circuit as one of coarse-grained devices and designing a honeybee-inspired system for it. The results of the simulation indicated that our honeybee-inspired single-electron circuit can perform functional information processing.



8th Workshop for Young Researchers
2 - 3 December 2017
TKP Matsuyama Conference Center, Matsuyama, Ehime

On the first day, we received two lectures. The first lecture was given by invited speakers Mr. Sato and Mr. Nagayoshi (Renesas Electronics Corporation) on the topic of 'Business Trends of Semiconductors and Expectations for Chemical Engineers'. We learned about recent trends in the semiconductor industry. The second lecture was given by invited speakers Dr. Akai (A04) and Dr. Yamada (A03) on the topic of 'How to Make your Paper Attractive'. They gave us an interesting talk and useful advice. In the second lecture workshop, we discussed how to write a good title and summarize experimental results for our paper. This lecture was helpful in learning how to make a paper and write a thesis in English. We give our thanks to all the speakers for their excellent lectures.

(A01 Kohta Muramatsu)

On the second day of the workshop, a group discussion was held in English on the topic of "The Current Status and Future of Molecular Architectonics". 20 young researchers, including international members, were separated into four groups. For the first hour, they summarized the current issues based on their firsthand experience in experimenting, and actively discussed possible solutions. Then in the second hour, a representative from each group explained their discussion results. Wide points of view, from single molecule function and device structure, to system integration, were deliberated and many inspiring ideas were proposed. This workshop was a great opportunity for young scientists to practice oral English and share thoughts from different fields.

(A04 Xiang Yin)

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