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

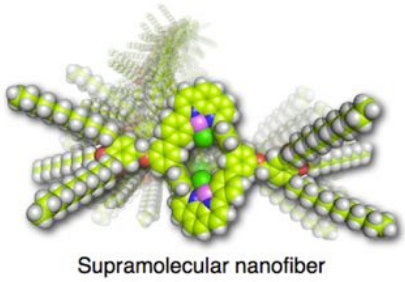
News Letter No.9 May 2016

Achievement

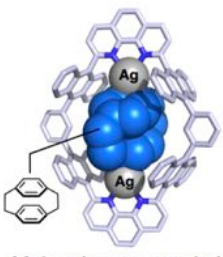
A01 Associate Prof. Shohei Tashiro

Molecular encapsulation within a disilver nano-ring

We have demonstrated the construction of supramolecular nanofibers through non-covalent stacking of organic nano-rings or metal-included nano-rings (*Chem. Asian J.* **2013**, *8*, 1368) to develop new building blocks for molecular architectonics. As one of the next steps of this research, we presented the chemical modification of this nano-ring by encapsulation of several functional molecules in the cavity (*J. Am. Chem. Soc.* **2014**, *136*, 17946). For instance, a disilver-included nano-ring strongly bound with one molecule of [2.2]paracyclophane through multipoint Ag–π interactions in the cavity as revealed by a single-crystal X-ray diffraction analysis. In a similar way, a typical redox-active organometallic molecule, ferrocene, was encapsulated in the disilver nano-ring, and the redox potential of the bound ferrocene was significantly shifted owing to the electrostatic repulsion between Ag^{I} ions and oxidized ferrocene. This achievement would enable us to modulate the electrical or ionic conductivities, structural diversity, and coordination dynamics of our supramolecular nanofibers through molecular encapsulation.



Supramolecular nanofiber

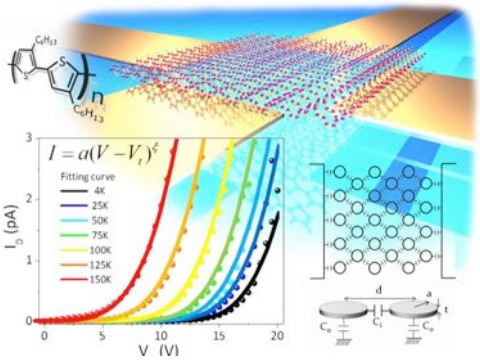


Molecular encapsulation

A04 Dr. Megumi Akai-Kasaya

Coulomb-blockade transport in two-dimensional conductive polymer monolayer

We succeeded in showing experimental evidence to prove Coulomb blockade (CB) taking place on two-dimensional organic conducting polymer films. Electronic transport was investigated in poly(3-hexyl-thiophene-2,5-diyl) monolayers. The current flowing in the molecular membrane showed the temperature-dependent threshold voltage in the low temperature range of 150K-4K and increased in power law of the current-voltage beyond the threshold. This is a typical feature of CB. We theoretically verified the onset of two-dimensional CB in the organic thin film through the calculation of the delocalization of electric charge in the molecular film and the verification of a distribution model of conductive segment in the two-dimensional film. These results will possibly overturn conventional understanding of conduction mechanism of organic conductors and help one to understand and design properties of organic and molecular devices. This research was reported in Physical Review Letters on November 4, 2015.

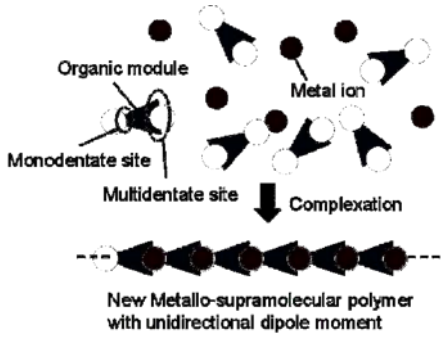


A01

Development of metallo-supramolecular polymer having rectification properties and the device application

Dr. Masayoshi Higuchi
(NIMS)

Metallo-supramolecular polymers are a new type of polymer, which are prepared by complexation of metal ions with ditopic organic ligands. Unique electronic and optical properties are expected in the polymers due to the electronic interaction between the metal ions and the ligands. We have revealed excellent electrochromic properties in Fe(II)-, Co(II)-, Ru(II)-, and Cu(II)-based metallo-supramolecular polymers, which are synthesized by the 1:1 complexation of the metal ions with bis(terpyridine)s or bis(phenanthroline)s. Electrochromism means electrochemical color change in materials. For example, the Fe(II)-based polymers have blue color based on the metal-to-ligand charge transfer (MLCT) absorption around 580 nm. When Fe(II) is electrochemically oxidized to Fe(III) in the polymer film, the color changes from blue to colorless. This result suggests the ON/OFF switching of the MLCT absorption can be controlled by the electrochemical redox of Fe(II). In the project of "Molecular Architectonics" we aim to achieve tunable rectification in metallo-supramolecular polymer film by designing the polymer with controlled unidirectional dipoles.



A02

Fabrication of atomic layer/molecular assembly heterostructures and their electronic properties

Dr. Ryo Kitaura
(Nagoya University)

The recent advancement in researches on atomic layers has led to isolation of various one-atom-thick layered materials: graphene, transition metal dichalcogenides (TMD) and hexagonal boron nitride (hBN). One of the most important characteristics of atomic layers is that they can be assembled to form new type of heterostructures with new functionalities. In fact, atomic layer heterostacks and heterojunctions have recently been a focus of research, providing wide variety of artificial 2-dimensional structures.[1]

In this area, I am going to work on fabrication of heterostructures composed of an atomic layer, hBN, and molecular assemblies. hBN in the heterostructures works as an ultrathin diffusion barrier, which can lead to stabilization of molecular assemblies under external stimuli. In this work, electronic properties of this heterostructures, in particular, electric double layer transistor characteristics will be investigated. In addition, application of various atomic layers, including hBN, graphene and TMD, to substrates and electrodes for investigation of transport properties of various molecular wires will also be addressed.

[1] A. Geim and I. V. Grigorieva, Nature 499, 419 (2013).

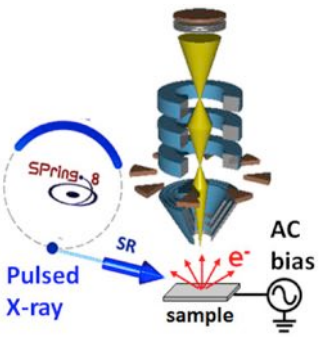
Leaders~

A03

Exploitation of spatio-temporarily resolved operando x-ray spectroscopy

Dr. Hirokazu Fukidome (RIEC)

Active-layer performance (e.g., a carrier mobility of a FET channel) is enhanced through the use of novel materials, such as graphene. Ironically, parasitic contribution such as contact resistance becomes remarkable as the active-layer performance is enhanced. This makes it difficult to directly relate material properties with device functionality. This issue can be resolved by microscopically observing the electronic states of devices such as GFETs; thus, I have developed operando x-ray spectromicroscopy, i.e., x-ray spectroscopy under a direct-current (DC) bias application with high resolution. This technology bridges the gap between the material properties and the device functionality. However, operando spectromicroscopy under DC bias application is insufficient for the research and development of high-frequency devices. Therefore, I will exploit spatio-temporally resolved x-ray microscopy with high temporal (<10 ps) and high spatial (<10 nm) resolution, by modifying the DC operando spectromicroscopy instrument used in my previous work. The realization of spatio-temporally resolved operando x-ray spectroscopy is directly related to the dynamics of the physical quantities (i.e., the carrier dynamics) of high-frequency devices such as graphene HEMTs.

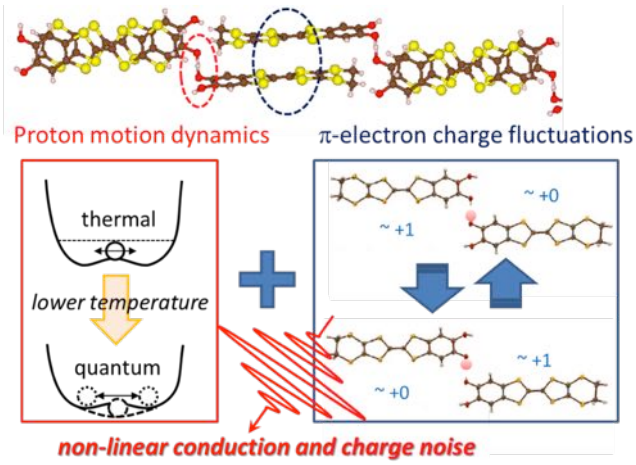


A04

Charge fluctuation spectroscopy on strongly correlated π-electron system coupled with cooperative proton dynamics in κ-H₃(Cat-EDT-TTF)₂

Dr. Takahiko Sasaki (Tohoku University)

Molecular materials have characteristic soft structural properties in comparison to the inorganic materials. One of the most interesting such lattice degrees of freedom in molecular materials is motional dynamics of intra- and/or inter-molecule proton. Recently, novel cooperative couplings between charge and proton dynamics have been found in an molecular conductor κ-H3(Cat-EDT-TTF)2. A proton bridges two Cat-EDT-TTF segments, and p-electrons make two-dimensional conductive network. In this study, we focus on the critical slowing down of the proton motion toward a freezing of the thermal proton dynamics or a quantum tunneling at lower temperatures. The charge dynamics coupled with such proton dynamics induces slow charge fluctuations, detected as transport noise simultaneously with nonlinear transport. We try to understand the noise properties mainly $1/f$ noise and possible stochastic resonance injecting external signals.



6th Area Meeting
13-14 May, 2016 Osaka University Hall, Osaka

The 6th Area Meeting of Molecular Architectonics was held from May 13 to 14, 2016 at the Osaka University Hall, Osaka. There were more than 50 attendees including all the group leaders, group members and the collaborators.

From April, the four groups leaders introduced in this newsletter have been newly joined our group. To accelerate collaborations among the groups through active discussion, every group leader gave a 5 minutes presentation with 10 minutes discussion time. Furthermore, we clarified what is required to realize the bio-inspired device introduced in the panel discussion held by the A04 group.

In the panel discussion, a recently developed molecular device that outputs pulse-like signals was introduced. Following this, we discussed the role of such a function inside brain-inspired devices and how to design such a molecule and how to connect it to electrodes. Some models to explain the pulse-like output have been proposed, which will be examined by detailed experiments performed by A02 and A03 groups.

The evaluators (Prof. Murai, Prof. Fukuyama, and Prof. Matsushige) and the academic investigator, Prof. Katagiri also attended the meeting and encouraged us to make further progress in the final two years.

Next Meeting

Molecular Architectonics Meeting
20-21, October 2016, Kyushu

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