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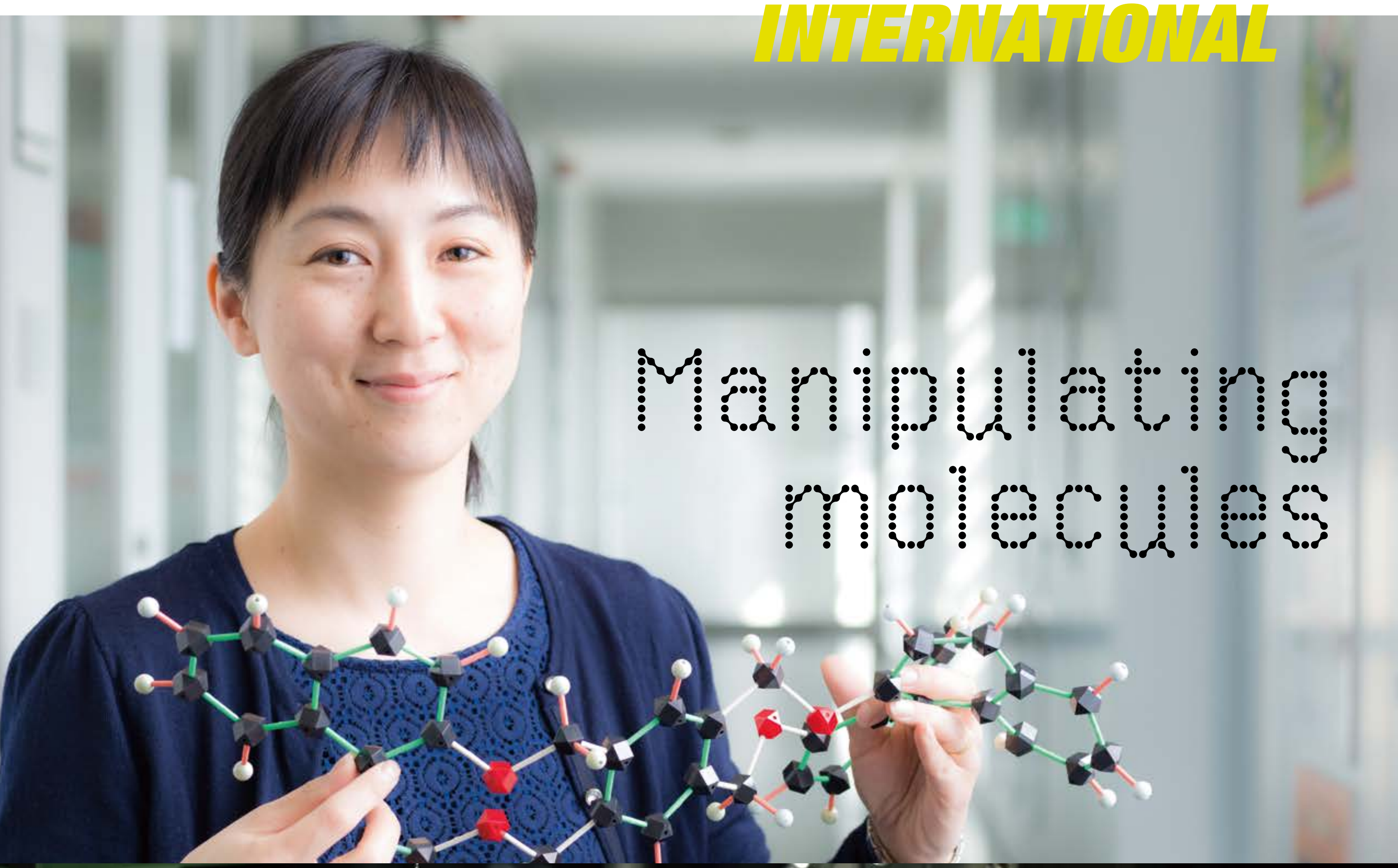


Manipulating molecules

Manipulating molecules

It had seemed a distant dream for scientists to freely design molecules and create custom-made materials with novel and useful functions.

However, many years of painstaking molecular manipulation research is finally bearing fruit due to advances in nanotechnology. It is now possible to manipulate individual molecules and atoms. Using this newly developed precision control and their creativity, scientists are developing devices based on novel principles which will enable them to create molecules with desirable capabilities.

The future of the development of materials through molecular manipulation is beyond our imagination, but this innovative technology is certain to continue to evolve.

Designing molecules:

Christian Joachim × Katsuhiko Ariga

designing the future

–Molecular machines, nanocars and future developments–

NIMS NOW INTERVIEW

K.Ariga and **C.Joachim**

Principal Investigator at MANA

Director of Research at Pico-Lab CEMES-CNRS

Christian Joachim × Katsuhiko Ariga

Designing molecules: designing the future

–Molecular machines, nanocars and future developments–

The field of nanotechnology is expanding at an exponential rate. NIMS Now recently sat down with two scientists who are at the forefront of this field – Katsuhiko Ariga, Principal Investigator at the International Center for Materials Nanoarchitectonics (WPI-MANA) and an expert in supramolecular chemistry; and Christian Joachim, Director of Research at Pico-Lab CEMES-CNRS in France, and also Principal Investigator at WPI-MANA and a leader in nanotechnology and single molecule machines – to discuss their work, as well as the upcoming Nano-Car Race, which is sparking interest worldwide.

—Tell us about your research field.

Ariga: With supramolecular chemistry, we associate individual molecules to make new ones that exhibit novel functions not seen in their component molecules. These can have some functional units that can for example self-assemble to make new materials. We use spectroscopy and expect motion; the nanotech people specify a particular molecule, then analyze the motion.

Joachim: With atomic scale nanotech, you can start with a single atom and build up step by step. We want to know, when assembling atoms one after the other, whether chemically or atom by atom, at what level you find a machinery function? A big question in physics is how many atoms do you need to make a computer – do you need thousands and thousands, or do you need just two? This is for the calculator core, that is – not to enter data or be able to dispatch the results on a screen, just the machinery for computation. This is what we are investigating and the same question holds for a motor and mechanical power at the atomic scale.

Ariga: This is a very promising field. Supramolecular chemistry won the Nobel Prize in 1987 and last year, for work making molecular machines by synthesizing entangled molecules, which exhibit machine-like motion in solution. This field has very huge potential.

— What are the applications of molecular machines?

Ariga: This research is applicable to

self-assembly, drug delivery, and interaction with biological systems, because biology – our body, our cell membranes – is basically just about assembly of molecules. For example, I am now doing research using molecular machines embedded on dynamic interfaces, just hand-like motion control, which allows catch and release of individual molecules – for example of a target drug. Other applications could include sensing, molecular electronics, materials sequestration and photovoltaic materials.

Joachim: On-surface synthesis, for example – we will soon be able to use single molecule machinery to clean the surface after each on-surface synthesis step, just by exploring the surface with molecular robots at the atomic scale, select the good molecules that are products of the on-surface chemical reaction and clean the other reaction intermediates. This is a new field that did not exist 10 years ago.

Ariga: NIMS is the best place in the world to do this research. We have a very high skill level – we have organic chemists, as well as people who can observe and analyze nanoimages and such things. Usually chemists just synthesize molecules, and don't work with these other people. But here we can. This is extremely useful for research.

—We've heard about the Nano-Car Race that you're organizing. What is a nano car, and how do you drive it?

Joachim: In the beginning it was just a little joke. But because of all the interest, we started to take it seriously.

A molecule-car is a molecule with a chassis, wheels, legs or paddles and an intramolecular motor principle. Wheels can have a diameter of about 1nm. To drive such a car, you place the tip of a Scanning Tunneling Microscope over this molecule-vehicle, and just pass a little tunneling current through it. You pulse a bit the bias voltage at the good position on the molecule (the chassis, a wheel) and the molecule-car goes this way, pulse there it goes that way, so you can redirect the molecule-car on the surface. If you know its chemistry, where the energy goes after this local excitation, you can improve the design to go faster, farther, etc. So like any competition, this nano car exploration is pushing the research.

There will be six teams, from NIMS, University of Toulouse, University of Basel, Ohio University, Rice University with Graz University and Technische Universitat Dresden. All six teams will gather at my lab in Toulouse with their drivers and chemists, and drive their cars around a 100 nm track on an ultra-clean gold surface. To drive well along this atomic scale track, you have to understand how a little bit of electrical current passing though a molecule-vehicle is able to activate its intramolecular motor – this is real research.

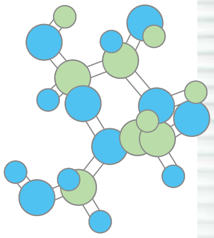
—NIMS is participating in the Nano-Car Race representing Japan. Is NIMS especially strong in this field?

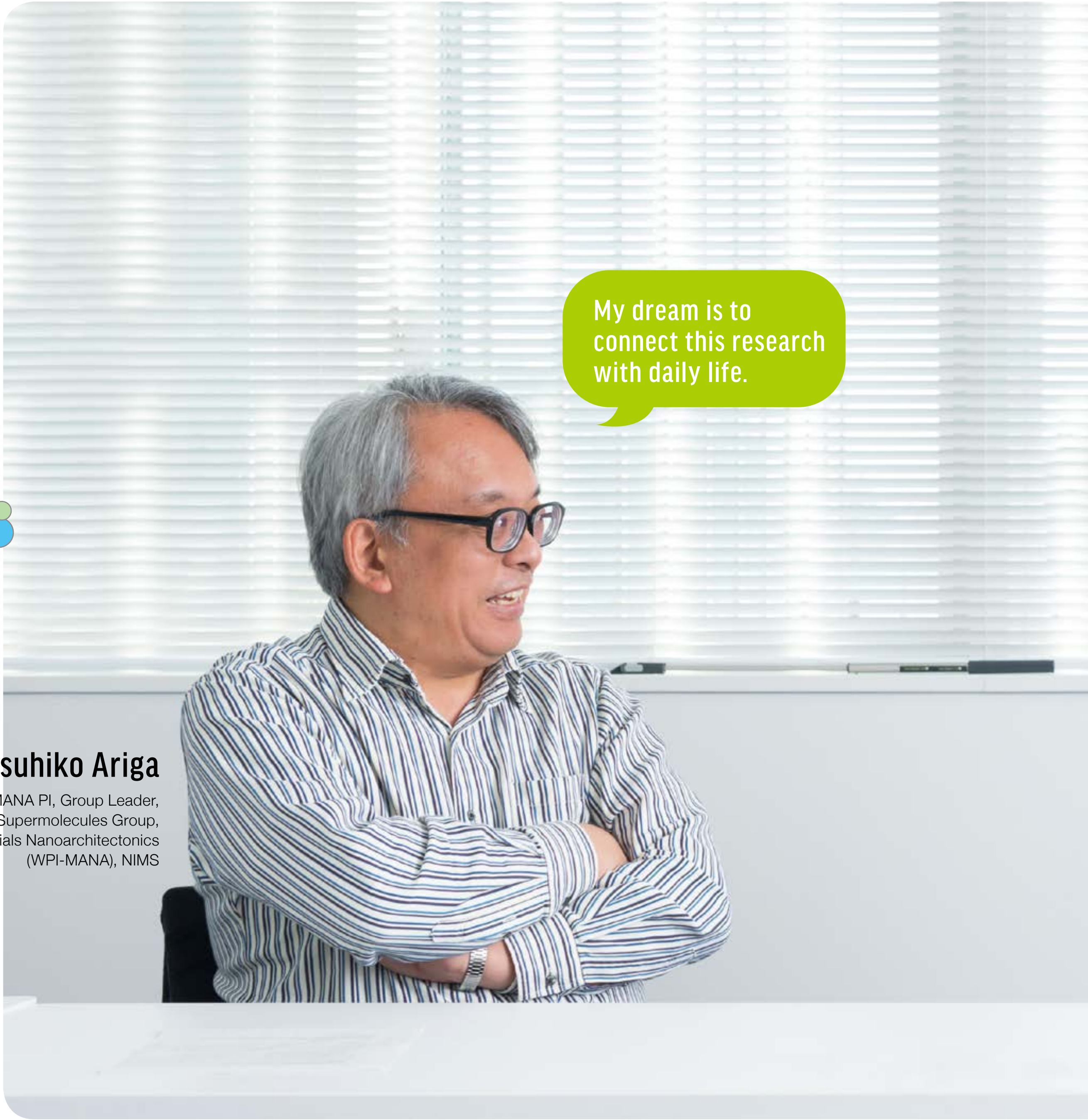
Ariga: We are doing research making synthetic molecular machines, as well as in self-assembly. Most people in this field are just making molecules and discussing them. But at NIMS we can directly see and manipulate them, which gives us an edge in the Nanocar Race. For example, one of my colleagues is working on molecular pliers, which operate in a hand-like motion, to open and close. She can calculate the energy needed to motivate them.

Joachim: At NIMS, you have the researchers that can do calculations and theory for molecular machines, and also to reproduce the surface experiments on the computer, which is very useful in designing a molecular machine for driving on a surface. So here, you have people to perform design and calculation together with organic synthesis and surface science researchers with very high performance scanning tunneling microscopes – this is unique, and special.

—What is the future of this field?

Joachim: There will be a big jump, because now we have STM with four tips, which is fantastic, because we can manipulate atoms in more ways and push further surface planar atom tech. We can drive, measure and give orders to a single molecule, not only with one tip, but with many with picometer precision. So we will be able to accommodate molecules one by one and create atomic circuits. This is new tech, and NIMS is part of it. Right now there is also the merging of two very different fields for exploring atomic scale calculators – quantum computing and molecular electronics (using molecular building blocks to fabricate electronic circuits) – to observe the quantum behavior inside a single molecule and manipulate it at atomic scale. This is real-





Katsuhiko Ariga
MANA PI, Group Leader,
Supermolecules Group,
International Center for Materials Nanoarchitectonics
(WPI-MANA), NIMS

ity already; people are exploring such a marriage in Europe and the U.S. It will be an incredible jump for the miniaturization of computing machines — it will allow a huge boost in speed, as well as reducing drastically the power needs.

Ariga: My dream is to connect this research with daily life. You could deconstruct garbage atom by atom to recycle it. For that you would need machines that could pick up molecules of water, carbon, metals, etc. Or for example on a Mars mission, you have to recycle everything, as well as extract materials from the surrounding environment, and this research could enable that.

Joachim: Also, the coupling of our science with artificial intelligence will hugely accelerate development.

Ariga: Absolutely. For example, for sensing, we have to make a very precise structure to catch specific molecules. We have to do everything at present – we have to set all the parameters, and tell the system exactly what to look for. With AI, this requirement disappears – we can just input a rough idea and the AI can optimize and use "ambiguous catching" even if a particular molecule is not the best match. This is also applicable to nanotech.

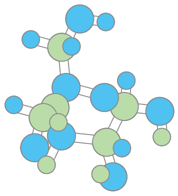
(interview by Robert Cameron)

It will be an incredible jump for the miniaturization of computing machines.

Christian Joachim

Director of Research at Pico-Lab CEMES-CNRS (France)

MANA PI,
International Center for Materials Nanoarchitectonics (WPI-MANA), NIMS



Research Highlights

Takashi Uchihashi

Group Leader,
Surface Quantum Phase Materials Group,
Nano-System Field,
WPI-MANA

World’s first development of molecular motors capable of switching rotational directions

Nanomachines (molecular machines) entered the spotlight when the 2016 Nobel Prize in Chemistry was awarded to researchers in the field. Molecular motors are one kind of nanomachine. Until recently, all molecular motors that had been developed were capable of rotating only in one direction. However, using supramolecules, a research team led by Takashi Uchihashi succeeded in developing the first ever molecular motors whose rotational directions can be controlled freely.

Molecular motors indispensable to biological processes in living organisms

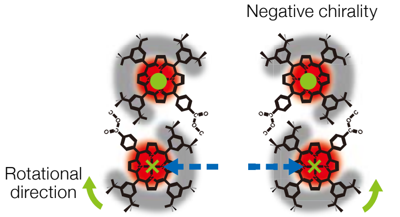
The 2016 Nobel Prize in Chemistry was awarded to three scientists who demonstrated the potential of nanomachines. Molecular motors and “nanocars” equipped with four molecular motors serving as wheels, developed by Professor Bernard Feringa of the University of Groningen, the Netherlands, using organic molecules, were particularly attracted a lot of attentions. Uchihashi said, “Professor Feringa inspired me to pursue research and development in molecular motors although I have been working in the field of surface science.”

A molecular motor is a tiny motor composed of molecules. Living organisms are actually equipped with numerous molecular motors in their bodies. For example, ATP synthases produces substance which play vital roles in biological processes by rotating itself. If we can develop molecular motor like this, we can apply it to the nanomachines. But molecular motors developed in the past offered a limited degree of freedom as they were capable of rotating only in one direction and because rotational direction could not be switched freely. Uchihashi’s research group resolved these issues for the first time in the world in 2015.

Conventional molecular motors can rotate only in one direction because the organic molecules of which they are composed have a structure which prevents them from moving in more than one direction. To switch the rotational direction of these molecular motors, their structures need to be changed. However, the atoms in these organic molecules are firmly bound via covalent bonds, and thus lack flexibility. This property have prevented conventional molecular motors from changing rotational directions.

In contrast, the molecular motor developed by Uchihashi’s group consists of a pair of organic molecules called porphyrins which are linked together via a weak hydrogen bond, forming an S-shaped structure (Fig. 1). A complex of molecules held together by weak bonds, such as hydrogen bonds, is called a supramolecule, and is very structurally flexible. This flexibility is the key factor allowing supramolecules to change rotational directions. Jonathan Hill and other NIMS researchers synthesized organic molecules (i.e., porphyrins) for use in forming supramolecules.

Figure 1.
Schematic diagrams of artificial molecular motors composed of supramolecules



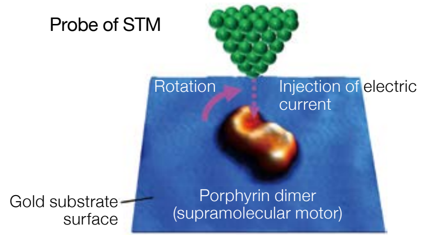
An artificial molecular motor is composed of a pair of porphyrins. Uchihashi’s group first attached a “leg” to three of the four substituents a porphyrin has, thereby lifting the molecule from the surface and making it stand. The group then attached a “hand” to the remaining substituent, so that a pair of porphyrins form a hydrogen bond in a manner analogous to holding hands. A porphyrin holds a platinum ion at its center by way of coordinate bonds. Blue dotted arrows indicate locations at which electric current is injected, and green circles indicate the sites of rotation axes.

Overcoming challenges using flexible supramolecules

Uchihashi and his colleagues first placed a molecular motor consisting of a pair of porphyrins on a metal substrate, injected electric current into the motor using a scanning tunneling microscope (STM), and observed the motor rotating in one direction (Fig. 2).

They then applied a negative voltage while injecting electric current into the motor. This caused a structural rearrangement of the supramolecule, changing its chirality. Chirality here refers to a geometric property of a molecule; a chiral molecule cannot be superimposed on its mirror image. When electric current was injected into the chirality-changed molecular motor with an inverted S-shape, its rotational direction was reversed (Fig. 3).

Figure 2.
Artificial molecular motor in action



Another fortunate discovery was made during this endeavor. Molecular motors are normally operated on a gold substrate with protruding individual gold atoms scattered across its surface. A protruding gold atom forms a weak bond with the platinum ion in a porphyrin, causing the motor to rotate around the gold atom, which serves as a central axis. “We found this phenomenon by chance, but it was a convenient discovery for us because without a central axis, molecular motors will move randomly, making them less practical.”

This series of discoveries led Uchihashi’s group to develop molecular motors whose rotational directions can be controlled freely by manipulating voltage and electric current.

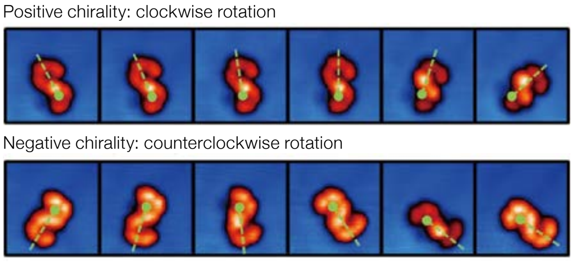
Uchihashi’s group initially planned to develop molecular motors driven by electron spin in collaboration with Professor Teruo Ono at Kyoto University, an authority in spintronics. However, electron spin did not generate sufficient force to rotate molecular motors. Consequently, the group pursued a different direction and came up with the molecular motor in its current form.

“Our next step is to create nanomachines by assembling molecular motors and other molecular parts. In addition, we want to pursue the possibility of integrating spintronics, our original research direction, with nanomachines.”

(by Kumi Yamada)

Figure 3.
Rotation of molecular motors

When electric current is injected into the artificial molecular motor, it rotates clockwise around the platinum ion. If a negative voltage is applied while injecting electric current, rearrangement of the molecules in the supramolecule occurs, changing the chirality and enabling it to rotate counterclockwise.



Molecule Car Race!

Nanocar race held in April 2017

The first ever international nanocar race was held in Toulouse, France on April 28 and 29, 2017. Six teams representing six countries participated in this event. A team of researchers from the International Center for Materials Nanoarchitectonics (WPI-MANA) at NIMS represented Japan. The race took place on a gold substrate under STM equipped with four probes set up at the French National Center for Scientific Research. The race consisted of each team placing the nanocar it had developed (or synthesized) on the substrate and driving it forward using electrical stimuli supplied by the STM probes. The first car to complete a 100-nanometer-long course would be the winner. USA-Austria team was a co-winner of the race, along with Swiss team. Team Japan was regrettably forced to withdraw from the race, due to a malfunction in its STM-controlling PC.

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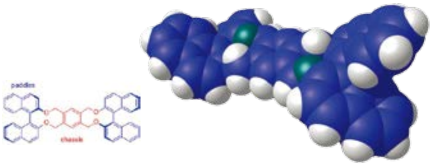
Team JAPAN

About NIMS-MANA team

Seven NIMS-MANA researchers represented Team Japan. The team’s nanocar consisted of a pair of linked soft organic binaphthyl molecules. The concept was that the nanocar would vibrate up and down in response to electrical stimuli, thereby generating the necessary force for forward motion.



In preparation for the race, we deposited molecules to form the nanocars on the substrate, identified molecules suitable for the race out of randomly chosen molecules, and determined the route to take. The molecules were fragile and the metal substrate surface had grooves and defects. During this race, I experienced many scientific challenges, including molecular design and techniques for observing and moving nanocars.

Yasuhiro Shirai
(nanocar designer)
Senior Researcher,
Interfacial Energy Conversion Group,
Center for Green Research on Energy and Environmental Materials

Due to a malfunction in its STM-controlling PC, Team Japan was regrettably forced to withdraw from the race with an official record of having moved one nanometer. However, the main purpose of this nanocar race was to support and promote R&D related to scientific methods concerning the design, synthesis and manipulation of molecules, rather than to compete on the basis of the speed of the nanocars. In that sense, I think this international competition was very meaningful.

Waka Nakanishi
(team leader and nanocar designer)
Senior Researcher,
Supermolecules Group,
Nanomaterials Field,
WPI-MANA

Katsuhiko Ariga
Group Leader,
Supermolecules Group,
Nano-Materials Field,
WPI-MANA

Lok Kumar Shrestha
Senior Researcher,
Supermolecules Group,
Nano-Materials Field,
WPI-MANA

Kazunori Sugiyasu
Principal Researcher,
Molecular Design and Function Group,
Organic Molecules and Polymers Field,
Research Center for Functional Materials

Controlling self-assembly of supramolecules

Supramolecules have been attracting attention as a new material for the molecular systems with specific functions, such as nanomachines. However, the structures and sizes of supramolecules are not easily controllable as they form spontaneously through self-assembly processes. A research group led by Katsuhiko Ariga and Lok Kumar Shrestha, Leader and Senior Researcher, respectively, of the Supermolecules Group, and Kazunori Sugiyasu of the Molecular Design and Function Group, has been addressing these issues by studying methods of forming supramolecules with desired structures or functions.

Exploring the mystery of life's origins using artificial supramolecules

A supramolecule refers to an association of molecules held together by weak attraction, such as hydrogen bonds and van der Waals forces. It is so named because it possesses "beyond molecular" physical properties and functions which are not exhibited by the individual molecules which compose it.

In fact, the human body contains countless supramolecules. Some examples are the double-helix structure of DNA, enzymes and cell membranes. Living organisms produce these highly functional supramolecules through self-assembly processes.

Ariga has been studying supramolecules for many years.

"Until now, the mainstream approach in nanotechnology was top-down in the sense that tiny structures were created from larger materials by removing unnecessary portions," he said. "However, the limitations of this approach have become apparent. I expect that demand will increase for a bottom-up approach whereby tiny structures are created in a manner analogous to the molecular self-assembly occurring in biological systems. Since the latter approach involves spontaneous processes, it has energy conservation potential."

Ariga's real interest in studying supramolecules relates to biological processes rather than the technology itself. His study objectives are twofold.

"The first objective is to investigate how biological systems began on ancient Earth by way of self-assembly. The second objective is to actually create something similar to biological systems."

Senior researcher Shrestha, who is affiliated with the Supermolecules Group which Ariga leads, published a study on the "differentiation" of supramolecules in August 2016. Differentiation in biology refers to a process by which a fertilized egg develops through repeated cell divisions into cells with specialized functions, such as heart and lung cells.

Shrestha discovered that supramolecules composed of fullerene derivatives differentiate. A fullerene derivative consists of a carbon molecule—fullerene—with a functional group attached to it. More specifically, when a spherical supramolecule composed of multiple fullerene derivatives is left in a solvent, a supramolecular tube composed of fullerene derivatives self-assembles onto the spherical supramolecule (Fig. 1). This phenomenon was referred to as supramolecular differentiation, because the product resembled a newly born tadpole with its tail emerging from the egg membrane.

Ariga finds differentiation to be a very intriguing phenomenon because the same material can differentiate into completely different structures. “Diverse life forms were generated by molecular assembly followed by the differentiation of these assemblies into various forms. Shrestha’s study results might lead to the understanding of a mechanism involved in the origin of life,” Ariga said hopefully. Shrestha also said, with excitement, “I will continue to research this subject with the goal of finding methods of controlling the formation of more complex structures by means of self-assembly.”

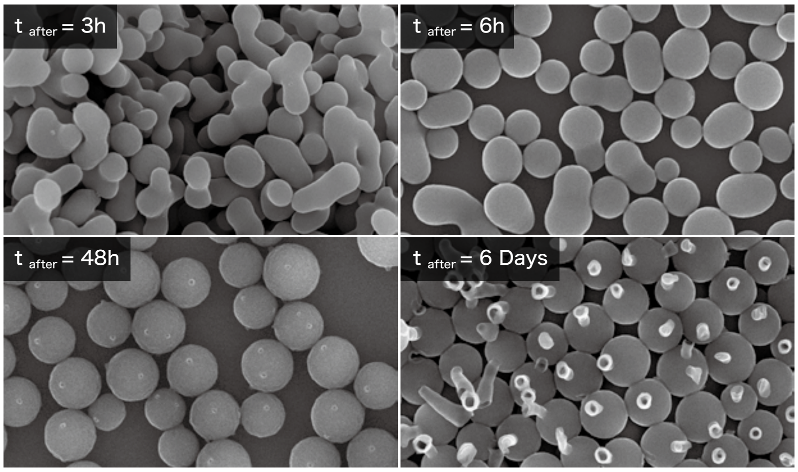


Figure 1. Specific method for forming supramolecules. First, two types of solvents—one in which fullerene derivatives dissolve easily and one in which they do not—are placed in a container. These solvents separate into layers. In the bottom layer, which consists of the solvent with well-dissolved fullerene derivatives, the solvent molecules surround the fullerene derivatives, except at the interface between the solvent layers, where the solvent molecules disassociate from the fullerene derivatives. Consequently, fullerene derivatives aggregate in the vicinity of the interface and form spherical supramolecules. When the supramolecules grow to a certain size, their mass causes them to sink to the bottom of the container. If they are left there, supramolecular tubes eventually grow on the spherical supramolecules. It was confirmed that the length and amount of tubular growth can be controlled by adjusting the length of time that the spherical supramolecules are left in the solvent and the type of solvent used.

Structure and size of supramolecules successfully controlled

On the other hand, methods of selectively creating supramolecules with different dimensionalities, such as fibers and sheets, from the same types of molecules have been studied. This selective creation had been thought to be difficult to control until recently, but Kazunori Sugiyasu of the Research Center for Functional Materials overcame this issue.

Sugiyasu began researching porphyrin molecules around 2008. To fabricate supramolecular fibers, he placed monomeric porphyrins in a solvent, heated the solution until they dissolved, and left them to cool.

“I was able to obtain supramolecular fibers as expected, but it took several days. I found during this process that porphyrins first formed particulate aggregates which then slowly transformed into supramolecular fibers.”

Sugiyasu investigated the transformation mechanism in detail, and added short segments of supramolecular fibers as “seeds” to a solvent containing supramolecular particles, which led to the formation of supramolecular fibers. In 2014, he found that the length of the fibers could be controlled by varying the ratio between the amount of supramolecular particles and the amount of seed material added.

Also, Sugiyasu and colleagues synthesized porphyrins with changing the number of carbons in their side chains and analyzed the properties of each supramolecules. When side chains contained fewer than five carbons, supramolecular particles transformed into supramolecular fibers as before. However, when the side chains contained six or more carbons, they discovered that supramolecular particles transformed into two types of supramolecules: fiber and sheet forms. They succeeded in controlling the transformations pathway to achieve the desired outcome (Fig. 2). In 2017, the team further succeeded in controlling the area of supramolecular sheets based on the results of a study he conducted in 2014.

“Molecular self-assembly occurs spontaneously such that the free energy of the system becomes minimun,” Sugiyasu said. “Therefore, it had been thought that the resulting supramolecular structures are always the identical. However, these studies revealed that porphyrins with longer side chains could transform into both fiber- and sheet-form structures by way of self-assembly. We also found that by applying different conditions, these structures can be created selectively and their sizes can be controlled. The same phenomenon is likely to occur with other molecules.”

Sugiyasu hopes that his recent research results will serve as a foothold for the development of methods of freely controlling molecular self-assembly processes, and lead to the creation of novel materials that autonomously function like biomolecular systems in response to environmental or situational changes.

(by Kumi Yamada)

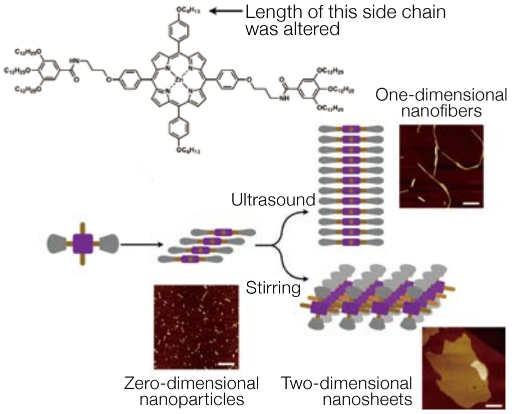


Figure 2. Sugiyasu and colleagues discovered that supramolecular particles transform into supramolecular fibers if they are subjected to ultrasound, and into supramolecular sheets if they are gently stirred. In addition, Sugiyasu succeeded in controlling the area of supramolecular sheets based on the results of his previous study in 2014. He broke supramolecular sheets into smaller fragments and added them as “seeds” to a solution containing supramolecular particles. He confirmed that the supramolecular particles transformed into supramolecular sheets, and that the area of the sheet structures can be controlled by varying the ratio between the amount of supramolecular particles and the amount of seed material added.

Research Highlights

Yuji Okawa
Chief Researcher,
Nanoionic Devices Group,
Nano-System Field,
WPI-MANA

Developing single organic molecular devices using chemical domino effect and soldering

“Single organic molecular devices offer a promising alternative to silicon-based devices, which are approaching their theoretical and technical miniaturization limits,” says Yuji Okawa. While the development of single organic molecular devices is making slow progress, Okawa has developed a groundbreaking wiring technology using chain polymerization of molecules. The new technology is drawing attention as a major step toward the realization of the devices.

Many organic molecules possess electronically or optically useful functions. The concept of single organic molecular devices involves the use of those molecules as diodes, switches and transistors. They are promising materials for use in the development of compact, high-performance and energy-efficient information processors. However, Okawa was cautious. “It has been more than 40 years since the idea of single molecular devices was first proposed,” he said. “Devices have not yet been realized despite active research efforts. The slow advancement is attributed to difficulty in attaching electric wires to single molecules, which is a critical aspect of the technology.”

It is difficult to reduce the diameter of a metal wire to the size of a molecule. Instead of using metal wires, creating electrically conductive molecular wires has been regarded as a promising method. “To implement this, I came up with a strategy of creating conductive polymer wires and connecting them to single molecules directly on a substrate.”

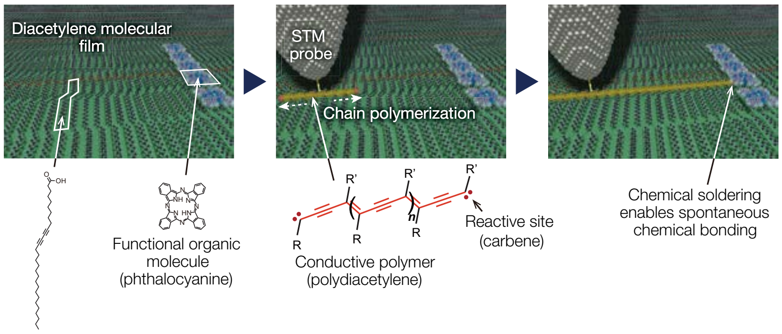
Okawa chose diacetylene compound molecules as a wiring material. To create the polymer wire, a film composed of orderly aligned diacetylene compound molecules was first created on a graphite substrate onto which single organic molecules were placed. A scanning tunneling microscope probe was then positioned in close proximity to the molecular film and used to apply a pulse voltage to it. The pulse voltage excited a molecule directly beneath the probe, causing it to form a bond with an adjacent molecule. This intermolecular bonding spreads outward from the probe in a kind of “domino effect.” This reaction is called chain polymerization and leads to the formation of a single wire composed of conductive polydiacetylene (Fig.).

“When the chain polymerization reaches the single organic molecules, chemical reactions occur there, forming an automatic connection between the conductive polymers and single organic molecules. I have named this technique ‘chemical soldering.’ I have been using phthalocyanine as my choice of single organic molecules. A system composed of phthalocyanine connected to two polydiacetylene wires serves as a resonant tunneling diode and is anticipated to make ultra-high-speed communication possible. However, no one has actually confirmed this. I am currently conducting experiments to verify its functionality. This will require the measurement of electric current passing through single organic molecular devices on an insulating substrate. Okawa has already succeeded in creating polydiacetylene wires on an insulating, hexagonal boron nitride substrate. Once the functionality of a singular organic molecular device is demonstrated, the next step will be the development of device integration techniques.

“There is still a long way to go, but I really hope to put single organic molecular devices into practice.”

(by Shino Suzuki, PhotonCreate)

Figure. Conceptual diagrams of molecular wiring using chain polymerization.



Research Highlights

Shigeki Kawai

Principal Researcher,
Nano Functionality Integration Group,
Nano-System Field,
WPI-MANA

Identifying molecular structures and properties using an ultra-high-resolution AFM

In order to create novel function with molecules, it is vital to observe molecular structures and evaluate their properties at atomic scale. For these purposes, ultra-high-resolution scanning probe microscopes (SPMs) recently became an important tool. Shigeki Kawai worked in Switzerland for approximately one decade, where innovative research and development activities have been conducted since its invention. He became a leading expert in scanning probe microscopy in Japan, and is currently engaged in the creation and evaluation of molecules using SPMs.

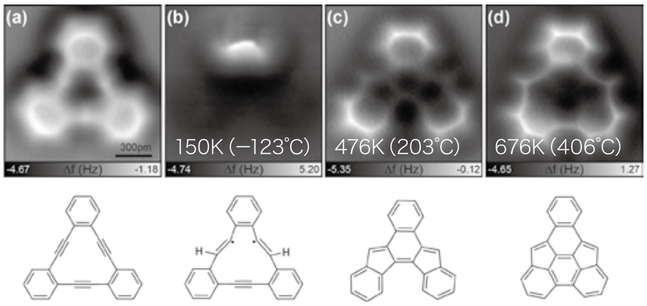
A scanning probe microscope (SPM) is an instrument, allowing us to observe structures and electronic states of molecules as its fine-tipped probe traces and scans surfaces with high-resolution. Two types of SPMs exist which scan specimens differently: scanning tunneling microscopes (STMs), which use a tunneling current, and atomic force microscopes (AFMs), which use interatomic forces. “After graduating from university, I worked for a company to develop and sell analytical instruments for materials, where I encountered and became very interested in SPMs. I later engaged in development of SPMs at the University of Tokyo Graduate School, and then studied nano-physics and materials at University of Basel in Switzerland,” Kawai looks back.

In 2013, Kawai engaged in developing an ultra-high-resolution AFM enabling direct observation of molecular structures. Using the AFM, he is currently evaluating single molecules and chemical synthesis involving these molecules as well as the electrical and mechanical properties of products in-situ synthesized on surface. This is one of the most advanced fields in surface science. “Recent hot topics in surface chemistry include a bottom-up synthesis to create functional membranes by depositing small carbon compounds on a metal surface. In connection with this, I have succeeded in doping boron atoms in ribbon-like nanographene in such a way that the boron atoms were evenly distributed with a high density. Furthermore, I investigated the mechanism of superlubricity with such a ribbon-like graphene.”

In more recent research, Kawai synthesized novel compounds by depositing triangular dehydrobenzo annulene (tDBA) on a metal surface, and discovered that the structures were changed successively in response to the annealing temperatures (Fig.). The study revealed the reaction process by clearly identifying structural changes of intermediates and final products involved in the reaction.

Kawai further investigated why the structural changes occurred in connection with temperature using theoretical calculations. “The results indicate that it is possible to create desirable compounds using chemical reactions if the temperature in the reaction is precisely controlled. This synthesis technique may lead the production of novel drugs or luminescent materials. Besides this, I hope to further improve the AFM to visualize not only intramolecular bonds but also their states. If this can be achieved, the AFM will be indispensable for creating new materials and functions using molecules in a bottom-up manner analogous to building structures using Lego bricks®.”
(by Kumi Yamada)

Figure. High-resolution AFM images capturing structural changes in tDBA in response to heating.



(a) Intact structure as deposited on a silver surface. A triangular structure composed of three benzenes linked by three acetylene moieties is visible. (b) As deposited but on a highly reactive copper surface. The symmetry of the triangle distorted. (c) and (d) The structure of the molecule transformed successively by annealing at a higher temperature.

Research Highlights

Tomonobu Nakayama

Developing revolutionary data storage by manipulating chemical reactions between C_{60} molecules at a single molecular scale

"Generally speaking, the total storage capacity realized by current technology is insufficient to record the whole amount of information we want to record," says Tomonobu Nakayama. To resolve this issue, Nakayama has been developing a new technology to store information based on novel principles. The research results could potentially lead to the development of high-capacity, compact recording devices.

Hard disks coated with thin magnetic films are currently the mainstream recording media. However, the information storage density of magnetic disks has almost reached its full capacity. "Accordingly, we were inspired to develop a new recording technology based on a totally different principle from that of conventional magnetic disks."

Nakayama focused on C_{60} molecules with the concept of using atoms and molecules to store information, thereby dramatically increasing storage density. A problem with this idea is that many atoms and molecules are not stationary preserved at designated positions at room temperature and do not function properly as recording media.

After much trial and error, Nakayama discovered a method of freely manipulating polymerization, a process by which monomers link to form a oligomer, and a process by which a oligomer is broken down into monomers, at a single molecular scale. With this method, information can be recorded in molecules by setting unbound and bound states to correspond to "0" and "1," respectively.

More specifically, an ultra-thin film is first fabricated by stacking three or so layers of C_{60} molecules on a conductive substrate. A scanning tunneling microscope (STM) probe is then positioned so that the probe is one nanometer or less from the film. A negative voltage is then applied to the film on the substrate side. This process causes a single C_{60} molecule directly beneath the probe to undergo a chemical reaction with another C_{60} molecule below it, forming a dimer, for example. When a positive voltage is applied at the same probe position, the dimer breaks down into monomers (Fig.). "We are the first to succeed in controlling both polymerization and depolymerization reactions at a single molecular scale," explains Nakayama. These chemical reactions are repeatable and therefore can be applied to the devices which would allow information to be repeatedly recorded and deleted. Also, it works only by the alternative application of positive and negative voltages.

A square inch of ultra-thin C_{60} film can record 190 terabits of information; more than 1,000 times the capacity of current magnetic disks. Operating speed is also an important factor. "We developed the world's first multiple-probe scanning probe microscope (MPSPM) which equips two to four independently-driven SPM probes. By expanding this multiple-probe technology, we expect to develop high-speed recording devices."

Other issues must be addressed toward practical application. The device currently operates only in a vacuum environment. It is also critical that it be possible to produce the device using general-use, mass-producible equipment, rather than specialized equipment like STM probes. "I think we can overcome these issues," Nakayama says confidently. "We plan to move our R&D efforts forward with the vision that ultra-thin C_{60} films will serve as a major recording technology for personal computers within 10 to 20 years."

(by Shino Suzuki, PhotonCreate)

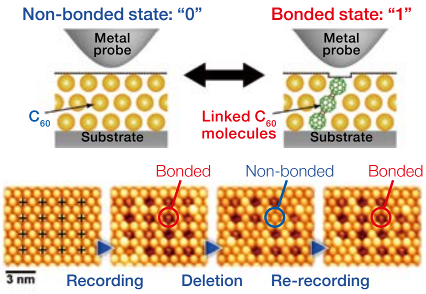
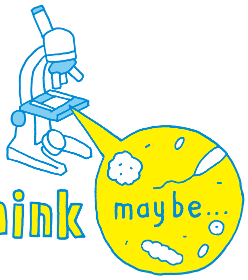


Figure. Method of controlling bonding between C_{60} molecules (top) and STM images (bottom).

Science is even more amazing than you think



Protein 3000 Project

Text by Akio Etori

Illustration by Joe Okada (vision track)

Proteins are indispensable life-sustaining molecules (nanomaterials) that play diverse roles in all living organisms, including humans.

Humans possess tens of thousands of different proteins, each playing a different role.

Protein functions are determined by their structures, which range from simple to complex. Relatively simple structures include a primary structure composed of a linear sequence of amino acids, and a secondary, ribbon-like helical structure resulting from the folding of the primary structure. Very complex protein structures include three-dimensional tertiary and quaternary structures. Proteins are capable of modifying their three dimensional structures and thereby their functions in response to their environments. In addition, if critical proteins undergo deformation, they no longer function properly, and may cause illness. For this reason, most medicines are designed to act on specific proteins.

Japan launched a five-year initiative commonly known as the “Protein 3000 Project” (known formally as the National Project on Protein Structural and Functional Analyses) in 2002 for the purposes of analyzing protein structures and functions, making academic contributions and creating novel drugs. The project was conducted based on the internationally agreed estimate that the number of protein families in existence is about 10,000. Japan decided to identify 30% of them, or 3,000 families. This ambitious goal was set partly because Japan wanted to regain its reputation in this field after making only a 10% contribution to the Human Genome Project, which was near completion at that time.

The Protein 3000 Project had two parts: a program for comprehensively analyzing protein structures at the family level and a program for analyzing individual proteins. RIKEN was responsible for the first program, and eight university-led core institutes conducted the second program. Despite various criticisms of the project, it certainly made major accomplishments.

Ten years have already passed since the completion of the project. Scientists in the United States also conducted a similar project, called the Protein Structure Initiative (PSI), from 2000 to 2015. They analyzed tens of thousands of different proteins and made many discoveries. However, their studies of protein structures at the family level found no new structures that could be added to those identified in the Protein 3000 Project.

These results suggest that only several thousand protein families vital to life forms on Earth exist. Various combinations of proteins in these families form structures and functions critical to all life forms.

The Protein 3000 Project did not reveal all family-level protein structures, but it did identify more than half. I think this is a significant accomplishment in the history of biological science.

In addition, the range of techniques used for protein structural analysis, including magnetic resonance imaging (MRI), was as expansive as the techniques used in physics and chemistry. The development of these protein analysis techniques can be viewed as a landmark effort in the history of biological science.

Project leader Dr. Shigeyuki Yokoyama once said that these accomplishments may have raised the status of biology to the level as high as that of physics and chemistry in terms of technical advances.

Akio Etori: Born in 1934. Science journalist. After graduating from College of Arts and Sciences, the University of Tokyo, he produced mainly science programs as a television producer and director at Nihon Educational Television (current TV Asahi) and TV Tokyo, after which he became the editor in chief of the science magazine Nikkei Science. Successively he held posts including director of Nikkei Science Inc., executive director of Mita Press Inc., visiting professor of the Research Center for Advanced Science and Technology, the University of Tokyo, and director of the Japan Science Foundation.

NIMS NEWS

1 NIMS and Four Chemical Companies to Develop a Framework for Promoting Open Innovation

NIMS, Mitsubishi Chemical Corporation, Sumitomo Chemical Company, Ltd., Asahi Kasei Corporation, and Mitsui Chemicals, Inc. signed a memorandum of understanding on the operation of the Materials Open Platform (MOP) on June 19, 2017. The MOP initiative is expected to promote open innovation in the chemical industry.

Chemical companies often share similar mid- to long-term issues that are difficult for them to address alone. The goal of the MOP is to respond to these common issues by developing fundamental technologies leading to innovation by facilitating large-scale collaboration across the chemical industry in Japan. The MOP will also support the global competitiveness of Japanese chemical companies by promoting the pursuit of bilateral collaboration to leverage research accomplishments produced by MOP initiatives for their specific needs. NIMS and the four chemical companies aim to further enhance the performance of polymer materials in FY2017 under the MOP framework.

2 NIMS and Three Steel Companies to Develop a Framework for Open Innovation

NIMS, Nippon Steel & Sumitomo Metal Corporation, JFE Steel Corporation, and Kobe Steel, Ltd. signed a memorandum of understanding on the operation of the Materials Open Platform (MOP) on June 30, 2017. The MOP initiative is expected to promote NIMS-led open innovation in the steel industry.

Dramatic changes in the industrial environment driven by the development of AI, big data and IoT are making it difficult for individual manufacturers to engage in basic research leading to transformational innovations in materials. The goal of the MOP is to respond to mid- to long-term issues common to steel companies by developing fundamental technologies leading to innovation through large-scale collaboration across the steel industry in Japan. The MOP will also support the global competitiveness of Japanese steel businesses by promoting the pursuit of bilateral collaboration to leverage research accomplishments produced by MOP initiatives for their specific needs. In addition, the MOP will work to reduce environmental impact, make society safer, and promote infrastructure-related exports.

Hello From NIMS

Hello! My name is Wipakorn Jevasuwan, and I am from Thailand. I am working as a researcher in the Nanostructured Semiconducting Materials group at MANA, NIMS. I have been living in Tsukuba, science city, since 2010. It has been almost 7 years until now to gather my wonderful experiences here. Excellent working environment, warm hospitality of people, and many beautiful sightseeing spots made me fell in love with Japan, and I enjoy my life everyday. Thanks to many strong research networks and plenty instruments of NIMS, I have many favorable opportunities to attend the lectures, discussions, and directly learn from world-class scientists from all around the world. Moreover, the unique colorful natures in every seasons accompanied with beautiful high-tech buildings and ancient sites around me fulfill my energy and warm up my heart for whole time. These are much more than what I have imagined about Japan before I came here. I would like to recommend everyone to visit Japan for at least once in a lifetime. It's so amazing!

Enjoying wintertime in Nagano prefecture.

Attending the lecture of Prof. Hiroshi Amano, 2014 Nobel laureate in Physics.

JEVASUWAN Wipakorn (Thai)
Three years (From March 2014 to present)
Researcher,
Nanostructured Semiconducting Materials Group,
WPI-MANA

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R70
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