RCMS NEWS 19
2018
NAGOYA UNIVERSITY
RESEARCH CENTER FOR MATERIALS SCIENCE
Reports and Communications of RCMS Activities
June 2018
Issue #19

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※ This newsletter is also available in PDF format from the RCMS homepage (ihttp://www.rcms.nagoya-u.ac.jp/).

Integrated Research Consortium on Chemical Sciences 2017

In 2017, IRCCS, Integrated Research Consortium on Chemical Sciences, a pioneering synthesis of a new scientific base and nurturing the next generation of researchers (Hokkaido University Institute for Catalysis, Nagoya University Research Center for Materials Science, Kyoto University International Research Center for Elements Science Institute for Chemical Research, Kyushu University Institute for Materials Chemistry and Engineering) held the symposium below.

The 1st Young Researchers Forum

(Inuyama city, Aichi, July 28–29, 2017)

Asst. Prof. Naka, organizer, Nagoya University

Prof. Awaga, Observer

Round-table discussion

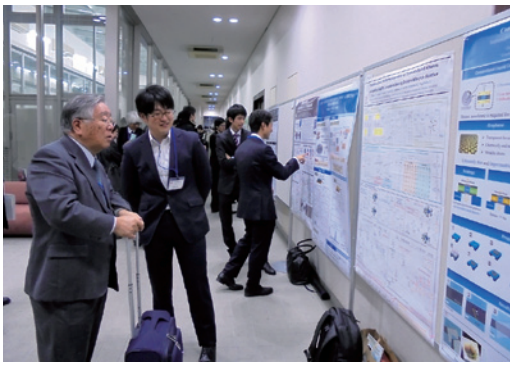
Breakfast

Group photo

Inuyama castle

The 3rd Symposium

(Kyoto University, October 30–31, 2017)



Poster session

Asst. Prof. Omachi, Nagoya

Group photo

The 1st International Symposium

(Kyushu University, January 24–26, 2018)

Director of IRCCS, Prof. Tatsumi

Chair, Prof. Yamaguchi

Asst. Prof. Ogi, Nagoya

Poster

Core-to-Core Program

The 21st Joint Symposium

As part of the Core-to-Core Program "Strategic Research Networks (Type A)" operated by the Japan Society for the Promotion of Science (JSPS), the program "Elements Function for Transformative Catalysis and Materials" is promoted by the Research Center fo Materials Science and the Department of Chemistry, Graduate School of Science at Nagoya University, with Professor Shigehiro Yamaguchi serving as Project Coordinator. In this program, joint research and dispatch of researchers is actively performed with the participating institutions at the University of Munster (Germany), the Technical University of Berlin (Germany), Queen's University (Canada), and Kyoto University (Japan).

The Core-to-Core Program has enabled the deployment of master's students, and outstanding young researchers expected to perform globally in the future can now be refined through participation in international joint research performed overseas at an early stage.

The 2017 academic year featured the 21st Joint Symposium when counting from the Japanese-German Graduate Externship program. The symposium was held at University of Muenster.

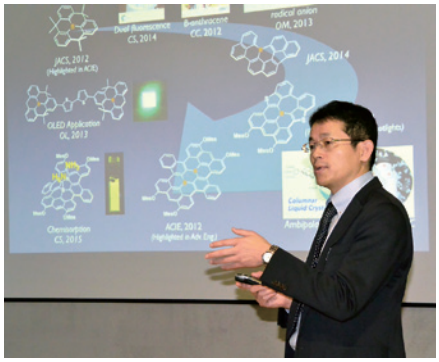
The 21st Joint Seminar

February 2 (Fri.), 2018; held at University of Münster, Germany

Participants from Japan: 8 professors, 6 students

Prof. Studer, Muenster

Chair, Muenster student



Prof. Yamaguchi, Nagoya

Prof. Crudden, Queen's

Research Topic

(Inorganic Synthesis)

Synthesis of a Supramolecular Cage Inspired by Induced-Fit-Type Molecular Recognition of Enzymes

Enzymes are the proteins that catalyze various biological reactions in living systems. It is well known that enzymes achieve highly efficient and substrate-specific catalytic reactions by utilizing their sophisticated molecular recognition abilities. There are two main models proposed to explain their molecular recognition abilities, namely "lock and key" and "induced-fit" models. In the "lock and key" model, the shape of the active site of the enzyme is considered to be perfectly complementary to the shape of the substrate, whereas in the "induced-fit" model, bindings of a substrate induce the change in the shape of the active site so that it become suitable for the molecular recognition. It is apparent that induced-fit model requires the structural flexibility as well as the huge protein structure as prerequisites.

Inspired by the induced-fit-type molecular recognition of enzymes, we recently developed a novel supramolecular cage, which is capable of recognizing various substrates strongly by changing its own structure to be suitable for the molecular recognition. In general, it is difficult to design a molecular cage having both of the abilities to change its own structure flexibly and to bind strongly to a substrate. In the case when the structure of the molecular cage is rigid enough as in the case with the "lock and key" model, the molecular cage can recognize its complementary substrate strongly. However, the more the structure of the cage becomes flexible, the cage-substrate complex becomes thermodynamically less stable because its structure is easy to be distorted.

To overcome this difficulty, we utilized the "rotaxane", a well-known supramolecular structure, in which a ring molecule is threaded by a thread molecule. The structure of the supramoelcular cage **1** is shown in **Fig. 1**. **1** is a multiply interlocked molecular assembly in which a phthalocyanine bearing four peripheral crown ethers are quadruply interlocked with a porphyrin dimer bridged quadruply with flexible alkylammonium chains. As a result, **1** has two nanospaces in between a phthalocyanine unit and the edge porphyrins. Furthermore, the phthalocynine unit can slide along the alkylammonium sidechains of the porphyrin dimer like a slide-door because they are connected each other via rotaxane structure. Actually, we confirmed that **1** could encapsulate a molecule whose size is larger than that of the accesses to the inner nanospaces of **1**. It was also found that **1** showed unique molecular recognition processes. During the recognition of **2** (**Fig. 2(a)**), two **2** was found to bind one by one in each nanospace of **1**. This implies that the affinity of the first binding is much larger than the second binding. We suppose that this molecular recognition might be due to that **1** could undergo the slide door-type structural transformation as described in **Fig. 2(b)**.

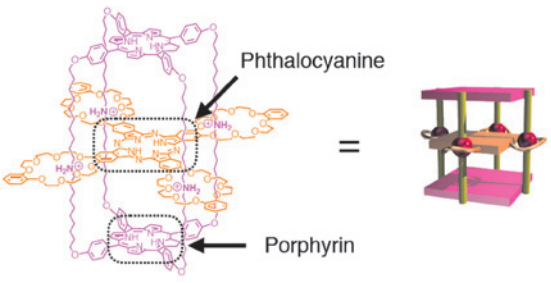


Fig. 1. Structure of a supramolecular cage **1**.

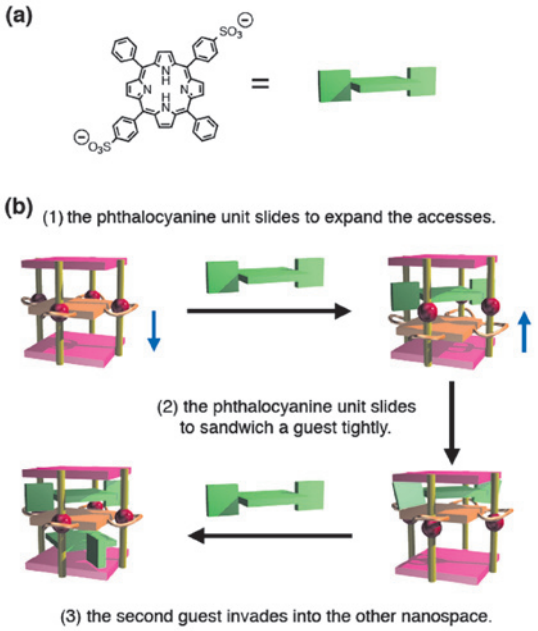


Fig. 2. (a) Structure of a guest molecule **2** and (b) a schematic representation of the encapsulation process of **2** by **1**.

Reference

[1] Y. Yamada, R. Itoh, S. Ogino, T. Kato, K. Tanaka, *Angew. Chem. Int. Ed.*, **2017**, 56, 14124-14129.

(Yasuyuki Yamada)

Research Topic
(Molecular Catalysis)
Conversion of Water for Organic Synthesis

The title statement may sound strange, especially to experts in organic chemistry, because water is a popular "enemy" in organic synthesis. In standard organic synthesis, chemists usually remove water from their flasks completely, in order to avoid any type of undesirable side-reactions caused by water. However, Nature often produces numerous kinds of organic products by using water as a starting material. For example, cells in your body rapidly produce organic materials by using water and enzymes under aqueous conditions for keeping your life sustainable; plants produce carbohydrates and dioxygen from water and carbon dioxide through photosynthesis. Inspired by the above-mentioned splendid activities in Nature, we set our research focus to develop new methods for organic synthesis using water as a starting material.

Catalytic Hydration of Organic Compounds

Catalytic hydration of organic compounds is a fundamental reaction both in the academic chemistry and industrial chemical production. We have recently disclosed that a fluorinated cobalt(III) porphyrin complex effectively promotes the hydroalkoxylation of terminal alkynes to give acetals (Figure 1).[1] Because the acetals are very easily hydrolyzed to ketones, this transformation can be regarded as the formal hydration of alkynes to ketones. The current method was found to be more efficient than our previous method for the hydration of terminal alkynes.[2]

Organic Synthesis with Light Energy

Chemical synthesis using sunlight energy is a dream of the whole human beings. Photochemical transformation of biomass-derived or renewable substances using water as a hydrogen source is an important challenge for promoting green and sustainable chemistry. Aiming at establishing a new scientific basis for such artificial photosynthesis, we have recently developed the photocatalytic dehydrogenation of primary alcohols to aldehydes (Figure 2).[3] Noteworthy in this transformation is the unusual selectivity for C–O bond cleavage over C=C double bond reduction under the photo-redox-conditions.

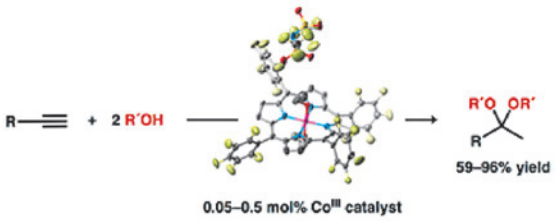


Figure 1. Cobalt-catalyzed hydroalkoxylation of alkynes

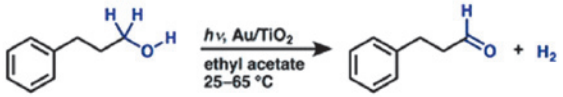


Figure 2. Photocatalytic dehydrogenation of alcohols

References

[1] R. Ushimaru, T. Nishimura, T. Iwatsuki, H. Naka, A Fluorinated Cobalt(III) Porphyrin Complex for Hydroalkoxylation of Alkynes. *Chem. Pharm. Bull.* **65**, 1000–1003 (2017).

[2] T. Tachinami, T. Nishimura, R. Ushimaru, R. Noyori, H. Naka, Hydration of Terminal Alkynes Catalyzed by Water-Soluble Cobalt Porphyrin Complexes. *J. Am. Chem. Soc.* **135**, 50–53 (2013).

[3] M. Shibata, R. Nagata, S. Saito, H. Naka, Dehydrogenation of Primary Aliphatic Alcohols by Au/TiO_2 Photocatalysts. *Chem. Lett.* **46**, 580–582 (2017).

(Hiroshi Naka)

Integrative Graduate Education and Research Program in Green Natural Sciences (IGER)

Integrative Graduate Education and Research (IGER) Program in Green Natural Sciences was launched in 2011, and built on three pillars: (I) practicing cutting-edge fundamental natural science research, (II) completion of sufficient coursework to enable that research, and (III) graduate school literacy education (English training, studying abroad, skill seminars, etc.). Based on these, the program aims to nurture the "scientific ability and social skills to view situations from a broad perspective," "developmental ability to extract practical results from fundamental research," and "active international citizenship on a global scale," along with fostering "corporate researchers cultivated as seeds in industry," "academic researchers raised in the scholarly domain," and "environmental coordinators and mentors active throughout global society" that will carry the environmental fields of the next generation.

In FY2017, the program provided opportunity for 60 students to participate in international conferences held at outside Japan, and also provided opportunity of mid-term (2–3 months) overseas research exchange for 14 students. Furthermore, the program hosted various international symposium / workshop where lots of students could have opportunities to discuss with foreign researchers.

Eleven students participated in the Leadership Program at North Carolina (NC), US. All students not only attended lectures regarding Leadership, Entrepreneurship and Technology Transfer but also visited many laboratories in universities at NC to build networks with PIs, postdocs and graduate students. In addition, all of them had opportunities to do presentations on their research to these researchers and have discussions. Furthermore, they visited some companies to learn some ideas of working in industry as a researcher and business environment in the USA from entrepreneurs and researchers.

Group photo in International Conference

Farewell Party in the NC Program

Collaboration Research in University of Glasgow

Visiting Professor 2017

Prof. Michael P. Shaver

Professor,
The University of Edinburgh

Period of Stay:
December 5, 2017 – January 26, 2018
Research Theme:
Synthesis of Functional Polymers

Prof. Michael P. Shaver from the University of Edinburgh, the United Kingdom, stayed as a vising professor in RCMS for two months since Dec. 5th, 2017, working on synthesis of functional polymers. He is a rising star in the field of organic polymer chemistry, and is the youngest professor in Department of Chemistry, UoE. During his stay, we collaborated on application of finely-designed organic polymers with specific structures to organic electronics.

In Nagoya University, he attended to the group meetings of the Saito and Awaga groups, and visited many laboratories in Department of Chemistry, School of Science, giving valuable advices to students and young researchers. He was full of curiosity and had an interest in everything. He gave an IGER-RCMS seminar, "New Monomers in Ring-opening and Radical Polymerisations for Sustainable and Functional Polymers" on Dec. 8th. He also visited several laboratories in Department of Applied Chemistry, School of Engineering, and gave a seminar there. His contribution to Nagoya University was very significant in both research and education. He will be a key person for future collaboration between NU and UoE.

Prof. Shaver, born in Canada, is a great beer lover, and has a deep knowledge on craft beer in the world. He loves a Nagoya craft beer, which is not well known among us. He visited a craft beer bar in Nagoya almost every weekend, and made many friends there. When he tried the NU beer in a banquet, we received his strong admiration for its flavor.

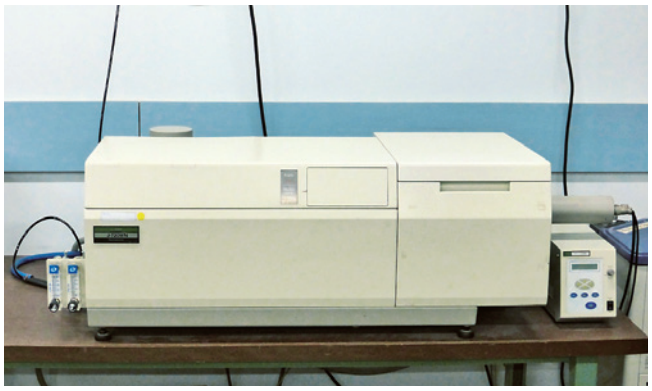
With a lot of good memories in Japan, he returned to the UK on Jan. 27th, 2018.

Report on the Chemical Instrumentation Facility

The Chemical Instrumentation Facility is a facility shared by the whole university that contains instrumental analysis equipment including a nuclear magnetic resonance (NMR) spectrometer, mass spectrometer, and spectroscopic analysis equipment for analyzing molecular structures. In the Chemical Instrumentation Facility, services are provided to users including teaching faculty, researchers, and students through maintenance of these measurement instruments, lectures on measurement methods, consultations for specific measurements, and entrusted measurement. In 2017, Prof. Susumu Saito took the position of president of our facility. We conducted the management and operation under his direction in order to improve our services. During the 2017 fiscal year, as shown in "CIF Utilization Status", 74 research groups from the university registered to use the facility, and the number of teaching faculty, students, and researchers who registered to use the facility during the year was 746.

NMR Room

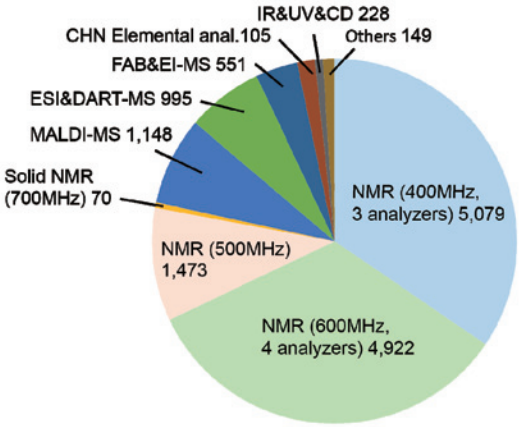
DART-MS (JMS-T100TD, JEOL)



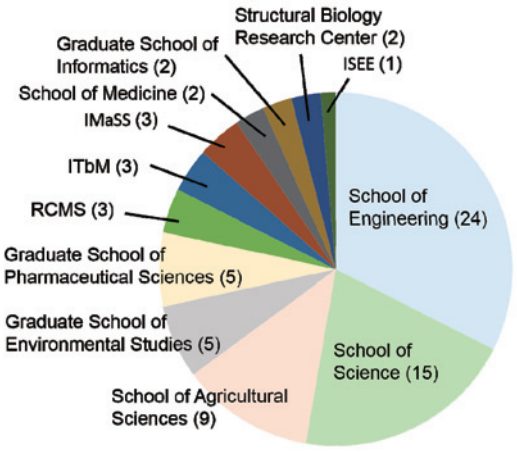
Circular Dichroism spectrometer (J-720, JASCO)

[CIF Utilization Status]

Utilization Status for the Academic Year 2017
(April 2017 – February 2018)

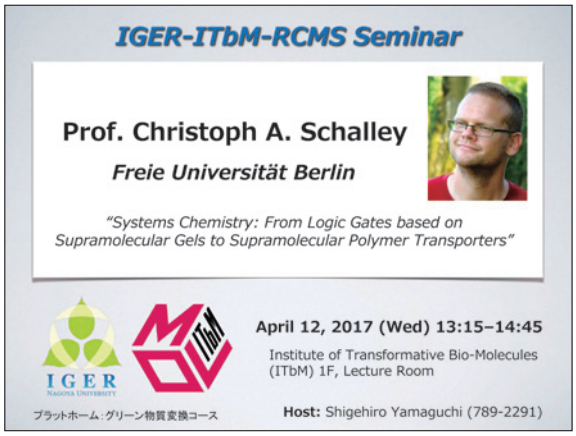


Number of Uses/Measurements by Instrument



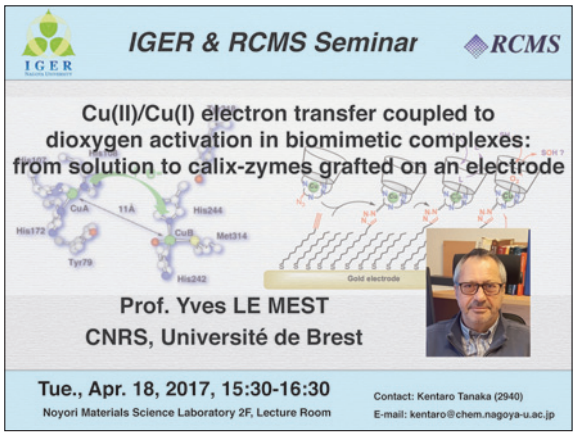
Utilization Status by Department
(Total: 74 Groups, 746 People)

RCMS Seminars

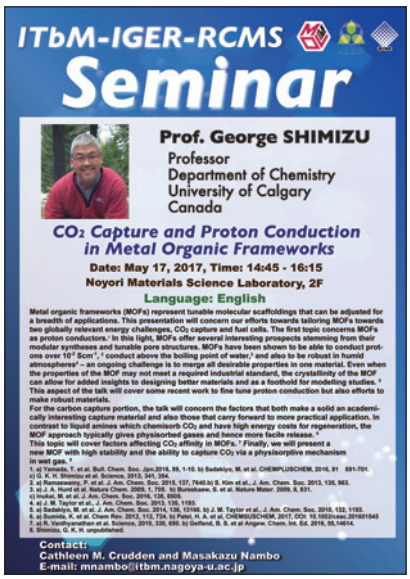


April 12, 2017 Prof. Christoph A. Schalley
(Freie Universität Berlin)
"Systems Chemistry: From Logic Gates based on Supramolecular Gels to Supramolecular Polymer Transporters"

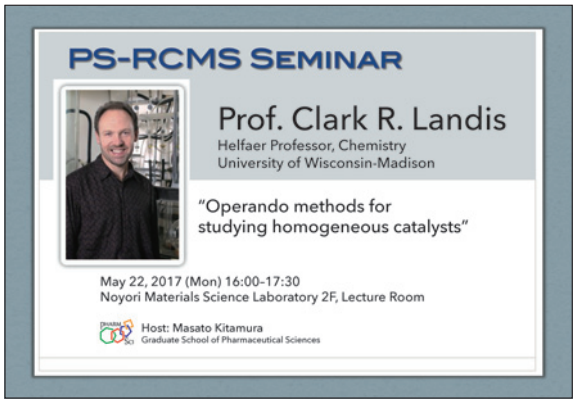
April 12, 2017 Prof. Patrick G. Harran
(D.J. & J.M. Cram Chair in Organic Chemistry, UCLA, USA)
"Tactics and Strategy in Complex Molecule Synthesis"



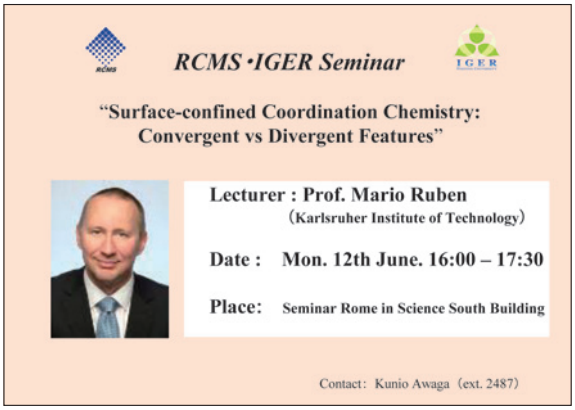
April 18, 2017 Prof. Yves LE MEST
(CNRS, Université de Brest)
"Cu(II)/Cu(I) electron transfer coupled to dioxygen activation in biomimetic complexes: from solution to calix-zymes grafted on an electrode"



May 17, 2017 Prof. George SHIMIZU
(Department of Chemistry, University of Calgary, Canada)
"CO_2 Capture and Proton Conduction in Metal Organic Frameworks"

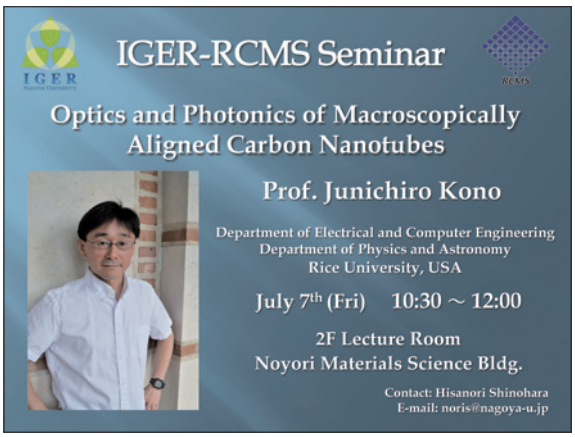


May 22, 2017 Prof. Clark R. Landis
(Helfaer Professor, Chemistry University of Wisconsin-Madison)
"Operando methods for studying homogeneous catalysts"



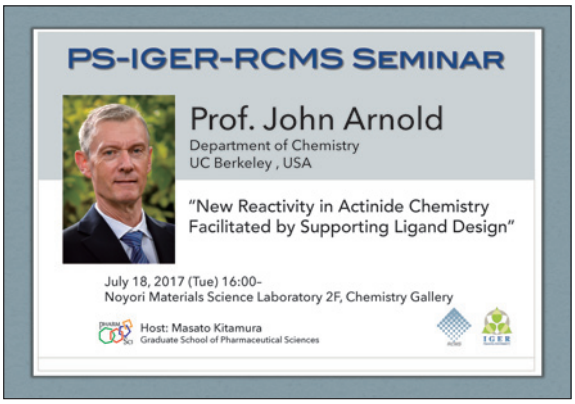
June 12, 2017 Prof. Mario Ruben
(Karlsruher Institute of Technology)
"Surface-confined Coordination Chemistry: Convergent vs Divergent Features"

June 28, 2017 Prof. Atsuhiro Osuka
(Graduate School of Science, Kyoto University)

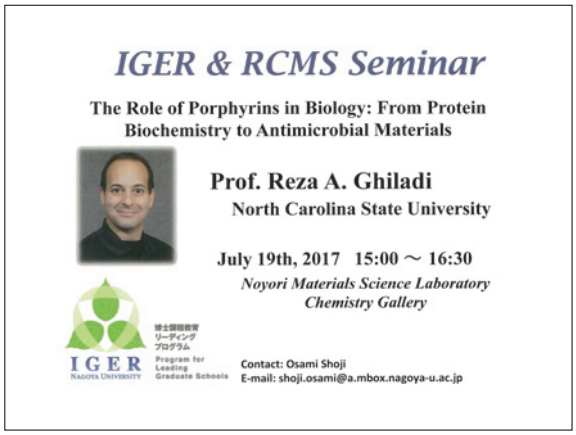


July 7, 2017 Prof. Junichiro Kono
(Department of Electrical and Computer Engineering, Department of Physics and Astronomy, Rice University, USA)
"Optics and Photonics of Macroscopically Aligned Carbon Nanotubes"

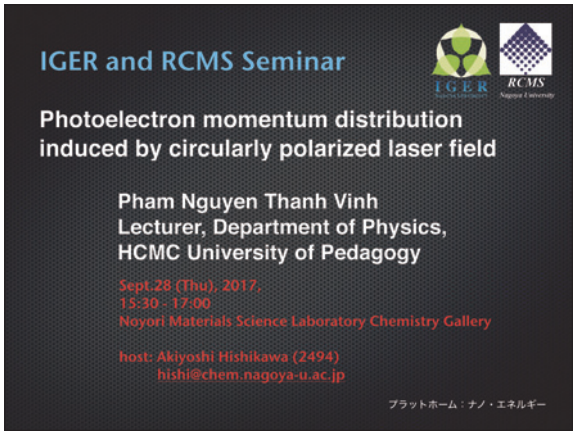
July 11, 2017 Prof. Yuh-Lin Wang
(IAMS, Distinguished Research Fellow, Taiwan)
"Surface-Enhanced Raman Scattering (SERS) for Rapid Antibiotic Susceptibility Test of Bacteria from Sepsis Patients"



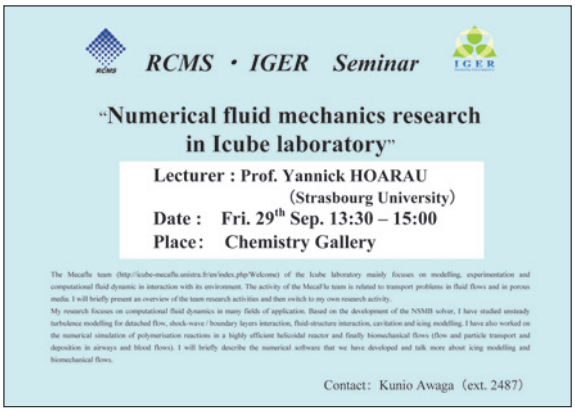
July 18, 2017 Prof. John Arnold
(Department of Chemistry, UC Berkeley, USA)
"New Reactivity in Actinide Chemistry Facilitated by Supporting Ligand Design"



July 19, 2017 Prof. Reza A. Ghiladi
(North Carolina State University)
"The Role of Porphyrins in Biology: From Protein Biochemistry to Antimicrobial Materials"

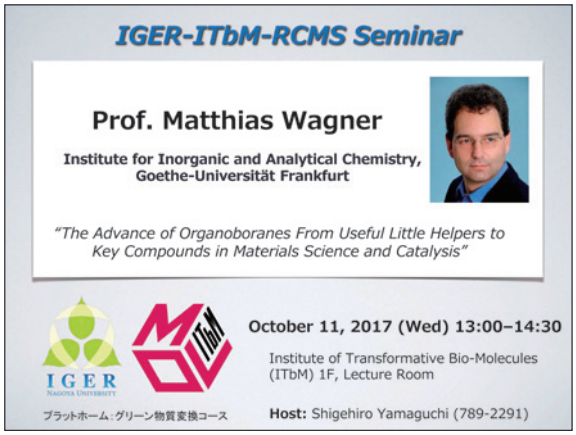


September 28, 2017 Pham Nguyen Thanh Vinh
(Lecturer, Department of Physics, HCMC University of Pedagogy)
"Photoelectron momentum distribution induced by circularly polarized laser field"

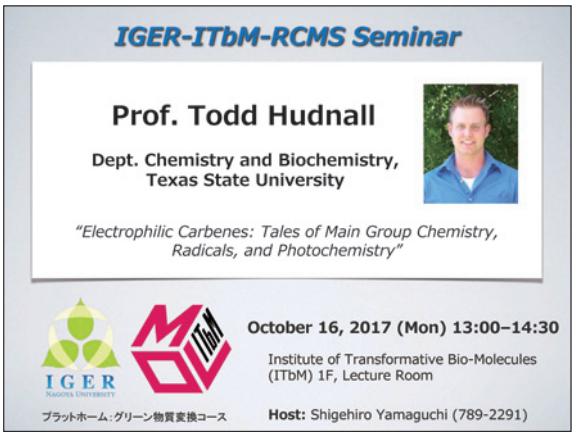


September 29, 2017 Prof. Yannick HOARAU
(Strasbourg University)
"Numerical fluid mechanics research in Icube laboratory"

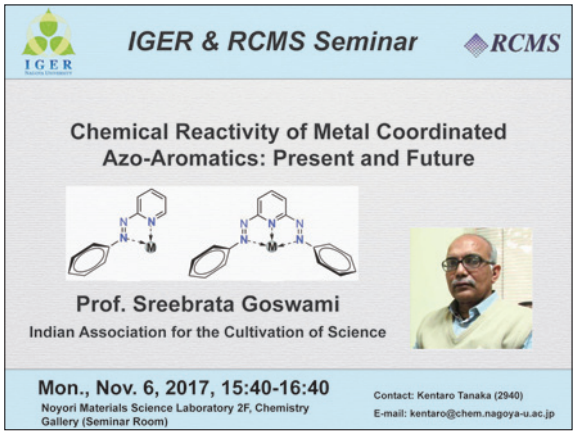
October 2, 2017 Prof. Jihong Yu
(Jilin University)
"Construction and Application of Zeolitic Nanoporous Materials"



October 11, 2017 Prof. Matthias Wagner
(Institute for Inorganic and Analytical Chemistry, Goethe-Universität Frankfurt)
"The Advance of Organoboranes From Useful Little Helpers to Key Compounds in Materials Science and Catalysis"

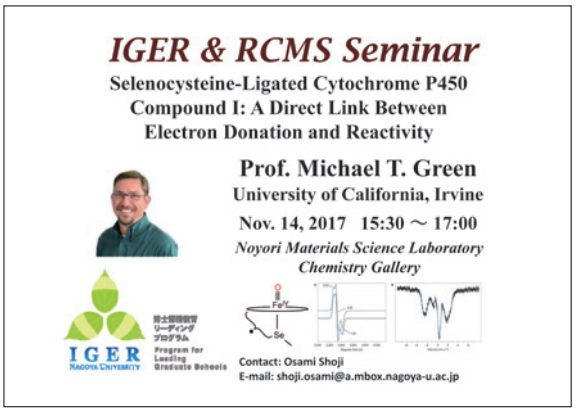


October 16, 2017 Prof. Todd Hudnall
(Dept. Chemistry and Biochemistry, Texas State University)
"Electrophilic Carbenes: Tales of Main Group Chemistry, Radicals, and Photochemistry"

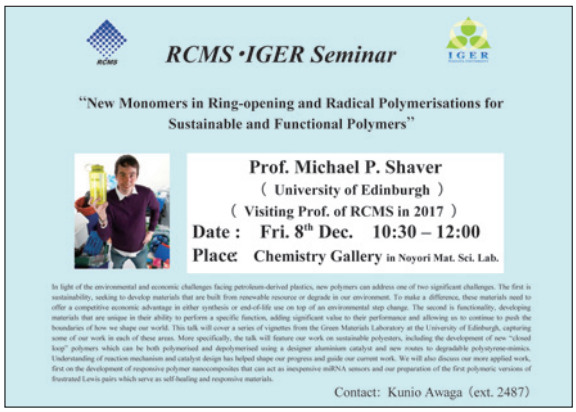


November 6, 2017 Prof. Sreebrata Goswami
(Indian Association for the Cultivation of Science)
"Chemical Reactivity of Metal Coordinated Azo-Aromatics: Present and Future"

November 9, 2017 Associate Prof. Jiro Itatani
(Laser and Syncrotron Research Center (LASOR)
The Institute for Solid State Physics (ISSP), the University of Tokyo)



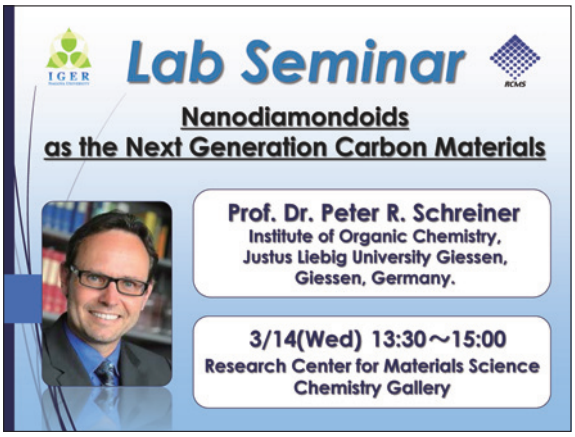
November 14, 2017 Prof. Michael T. Green
(University of California, Irvine)
"Selenocysteine-Ligated Cytochrome P450 Compound I : A Direct Link Between Electron Donation and Reactivity"



December 8, 2017 Prof. Michael P. Shaver
(University of Edinburgh)
"New Monomers in Ring-opening and Radical Polymerisations for Sustainable and Functional Polymers"

February 7, 2018　Prof. Hiroshi Kitagawa
(Graduate School of Science, Kyoto University)

March 14, 2018　Prof. Dr. Peter R. Schreiner
(Institute of Organic Chemistry, Justus Liebig University Giessen, Giessen, Germany)
"Nanodiamondoids as the Next Generation Carbon Materials"



March 15, 2018　Dr. John C. Gordon
(Scientist 5, AAAS Fellow, Los Alamos National Laboratory, USA)
"Some New Insights into the Efficient Outer Sphere Hydrogenation of Carbonyl Containing Substrates"

Chemistry Gallery

The Chemistry Gallery (2nd Floor of the Noyori Materials Science Laboratory) welcomed many visitors again in the 2017 academic year.

13,089 people visited the gallery as of March 31, 2018 (according to an automatic counter for entry/exit to the gallery).

A particularly large number of visitors were welcomed during the following periods when Nagoya University was open to the public.

Number of visitors during Open Campus : 816 (August 8 to 10)

Number of visitors on Homecoming Day : 510 (October 21)

At the Chemistry Gallery, guest can experience Dr. Noyori's sincere commitment, philosophy and passion that earned him the Nobel Prize, the gratest honor for a scientist. There is also a message to the next generation from Dr. Noyori. Symbolical words from Dr. Noyori's research handing down the profound mystery of Chemistry and the attitude of a genuine scientist of future chemists.

Awards 2017

Asst. Prof. Shinji Tanaka (The second from the right)
Incentive Award in Synthetic Organic Chemistry, Japan
February 15, 2018

拓く 研究人 182

名古屋大学物質科学国際研究センター教授 唯 美津木 氏 (38歳)

触媒の可視化技術 研究

名古屋大学物質科学国際研究センターの唯美津木教授は、燃料電池などに用いる固体触媒の合成・構造解析できるX線コンピューター断層撮影装置技術を研究している。高活性、高耐久性の触媒を合成するには、燃料電池の発電中に何が起きているのかを調べる必要性を感じ、触媒の可視化技術（XAFS）法と顕微鏡を組み合わせ、触媒の分布や化学状態の可視化を実現した。

触媒は、燃料電池のオンオフのくり返しなどで劣化する。3次元的に構造解析できるX線コンピューター断層撮影装置（CT）と、特定元素の化学状態を得られるX線吸収微細構造（XAFS）法とを組み合わせ、触媒の劣化過程を観察する技術を研究している。高活性、高耐久性の触媒を合成するには、燃料電池の発電中に何が起きているのかを調べる必要性を感じ、触媒の可視化技術（XAFS）法と顕微鏡を組み合わせ、触媒の分布や化学状態の可視化を実現した。

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Prof. Mizuki Tada

Prof. Mizuki Tada
"The Kao Prize for Science 2016"
The Kao Foundation for Arts and Sciences
June 16, 2017

S. Ozawa, H. Matsui, M. Tada, et al. PCCP Poster Prize NENCS-RSC
October 28, 2017

Y. Tan, H. Matsui, M. Tada et al. Energy & Environmental Science
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