RCMS NEWS
20
2019
NAGOYA UNIVERSITY
RESEARCH CENTER FOR MATERIALS SCIENCE
Reports and Communications of RCMS Activities
June 2019
Issue #20

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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 2018

In 2018, 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 2nd Young Researchers Forum

Chitose city, Hokkaido, June 15-16, 2018

Group photo

********** **The 2nd International Symposium**

"New Future by Chemical Synthesis and Energy Materials"
Kyoto University, January 25-26, 2019

Director, Prof. Tatsumi

Prof. Yasuhiro Tachibana

The 4th Symposium

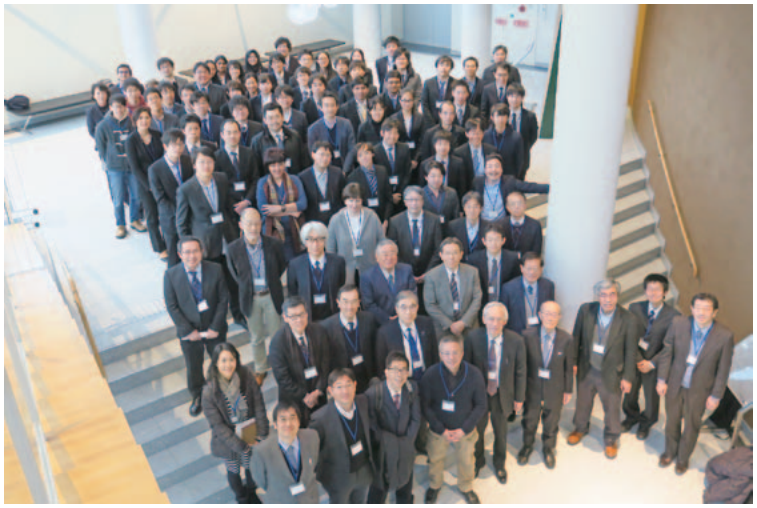
Kyushu University, October 29-30, 2018

Prof. Tomooka

Prof. Yanai

Group photo

Prof. Durrant



Group photo

Core-to-Core Program

"Elements Function for Transformative Catalysis and Materials"

2014 - 2018

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 for 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 2018 academic year was the last year of this program. The final joint Symposium featured with GTR; Graduate Program of Transformative Chem-Bio Research at Nagoya University.

Prof. Nakamura

Prof. Crudden

Prof. Glorius

Prof. Yamaguchi

Prof. Saito

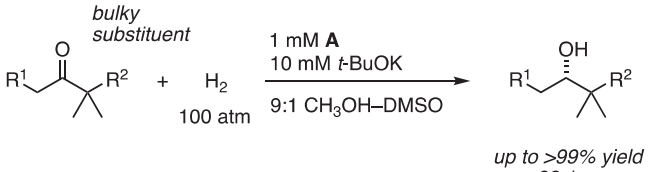
Group photo

Research Topic

(Molecular Catalysis)

Mechanistic Study of Asymmetric Hydrogenation of Sterically Demanding Ketones using PNN–Ru complex

A ruthenium complex having a linear tridentate $sp^3P/sp^3NH/sp^2N$ ligand PN(H)N ((*R*)-2′-(diphenylphosphino)-*N*-(pyridin-2-ylmethyl)[1,1′-binaphthalen]-2-amine) efficiently hydrogenates both nonchelatable and chelatable sterically-demanding ketones under the presence of a catalytic amount of CH_3OK with high enantioselectivity in CH_3OH–DMSO solvent (Figure 1)[1,2].



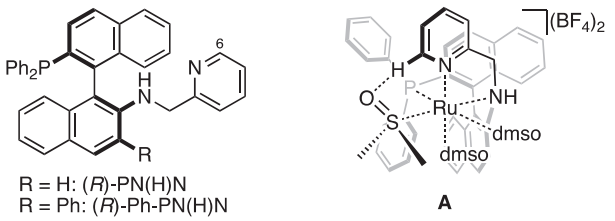
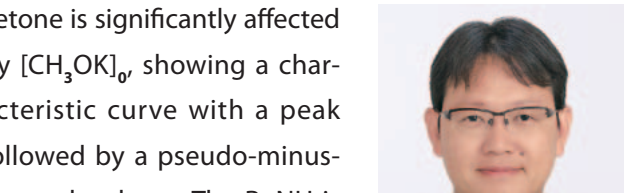


Figure. 1. Caatalytic asymmetric hydrogenation of sterically demanding ketones using PNN-Ru compiex.

The complex exclusively forms *fac*-[Ru(PN(H)N)-$(dmso)_3$]$(BF_4)_2$ (**A**) over the mer isomer with the help of the three strongly π-accepting DMSO ligands. The three different ligating atoms exert a divergent effect on the trans-DMSO—Ru bond strengths. This enables the stereoselective generation of *fac*-RuH(CH_3O)(PN(H)N)- (dmso) (**RuNH**). The reaction proceeds at the H—sp^3N—Ru—H bifunctional reaction site of *fac*-RuH_2(PN(H)N)(dmso), and high enantioselectivity is attained in a chiral 3D cavity constructed by the sp^3N trans DMSO, the conformation of which is fixed by a PyC(6)H—O=S hydrogen bond. We determined the structures of RuNH, the K amide RuNK, Ru dihydride, and Ru amido species by detailed NMR analysis using ^{15}N-labeled PN(H)N and C(3)-Ph-substituted PN(H)N.[3]

The reaction rate of hydrogenation of simple ketone is significantly affected by $[CH_3OK]_0$, showing a characteristic curve with a peak followed by a pseudo-minus-first-order decay. The RuNH is easily deprotonated by CH_3OK to generate RuNK, which is less reactive but has the same enantioselectivity. Increased contribution of the slow RuNK cycle decreases the rate at higher $[CH_3OK]_0$. The RuNH- and RuNK-involved dual catalytic cycle is supported by curve-fitting analyses and K^+ trapping experiments (Figure 2)[3]. In hydrogenation of β-keto ester as functionalized ketone, only the RuNH cycle operates because the substrate is preferentially deprotonated over RuNH.



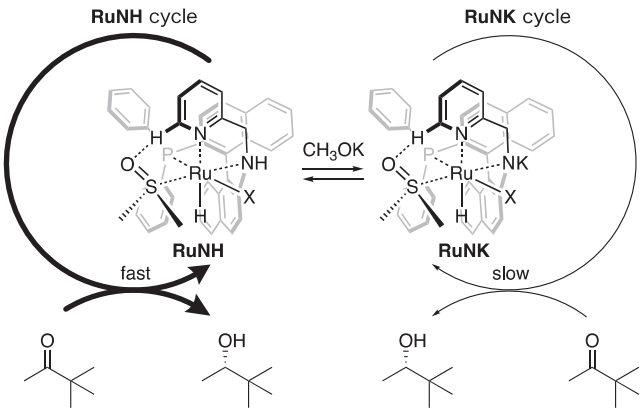


Figure. 2. Dual catalytic cycle.

References

[1] T. Yamamura, H. Nakatsuka, S. Tanaka, M. Kitamura, *Angew. Chem. Int. Ed.* **2013**, *52*, 9313–9315.

[2] T. Yamamura, S. Nakane, Y. Nomura, S. Tanaka, M. Kitamura, *Tetrahedron* **2016**, *55*, 3781–3789.

[3] S. Nakane, T. Yamamura, S. K. Manna, S. Tanaka, M. Kitamura, *ACS Catal.* **2018**, *8*, 11059–11075.

(Assistant professor, Shinji TANAKA)

Research Topic

(Functional Materials)

Accurate wave function theories for large, real-life molecules

Molecular properties such as electronic energy, dipole moment and electron density are solely determined by knowing quantum mechanical behavior of the electrons in the molecule itself. To this end, the only thing we have to do is just to solve the Schrödinger equation for this "many-electron system" in the electric field created by the spatially-clamped nucleus. However, as predicted by Dirac in 1920s [1], the many-electron Schrödinger equation is so complicated that, even with the power of modern supercomputers, the exact and analytical solutions have never been possible to obtain. Due to this Dirac's nightmare, quantum chemists have put tremendous efforts to develop accurate approximation schemes for calculating molecular electronic structures in a reasonable computational time. Amongst them, the density-functional theory (DFT) has become a widely-accepted tool not only by computational chemists but also by experimental chemists. In order to model the electronic structure of molecules with quantitative accuracy, inclusion of the correlation effect plays a central role. My primary interest consists in development and application of efficient and accurate electronic structure theories for large, real-life molecules.

In the Max-Planck-Institute, under the supervision of Prof. Dr. Frank Neese, we developed an accurate and near-linear scaling wave function theory named domain-based local pair-natural orbital coupled- cluster (DLPNO-CC) theory [2]. The CC theory has been one of the most accurate electronic structure theories. However, due to the steep computational scaling with respect to the molecular size, the applicability has been limited only to approximately 10 atoms. In DLPNO-CC scheme, which belongs to the local correlation theories, short-range nature of dynamic electron correlation is exploited to achieve reduced-scaling computational costs. As can be seen from Figure 1, CPU times spent for solving the DLPNO-CC equation are approximately 40 % of that for DFT calculation accelerated resolution-of-the-identity algorithm (RI-DFT). The DLPNO-CC methods have been extended to open-shell molecules and shown applicable to real-life molecules composed of several hundred atoms independent of its spin-state. Moreover, we have developed a linear-response theory in the DLPNO-CC framework and succeeded to enable accurate computation on various magnetic and electronic properties [3]. We used the DLPNO-CC methods to calculate the conduction properties of carbon nanotubes and succeeded to obtain good agreement with the experimental values [4].

Currently, as a member of division of functional materials, I am working on development and application of accurate and efficient electronic structure theory for large, highly-correlated systems such as realistic active-site model of metalloenzymes. Combination of ab initio density matrix renormalization group (DMRG) theory as a static correlation solver and the local correlation scheme for the remaining dynamic correlation plays a key role.

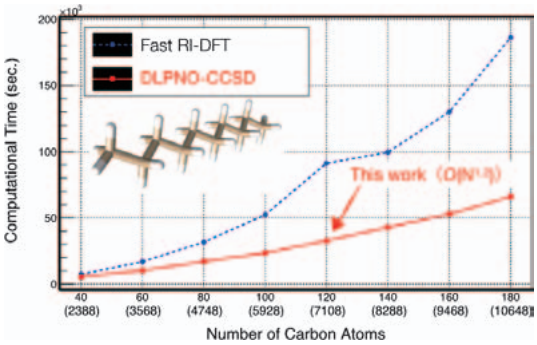


Figure 1. Computational timings of DLPNO-CCSD in comparison to that of DFT accelerated by resolution-of-the-identity algorithm.

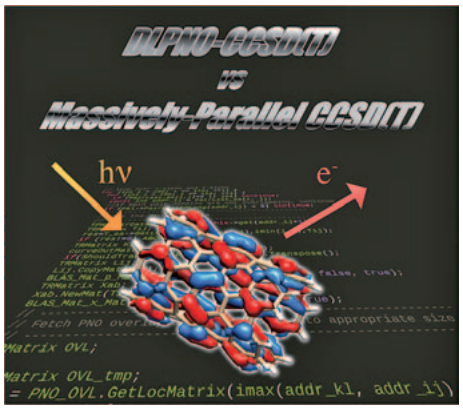


Figure 2. Benchmarking DLPNO-CCSD against conventional CCSD and various DFT functionals.

References

[1] P. A. M. Dirac, *Proc. Royal Soc. A* **123**, 714 (1929).

[2] M. Saitow, U. Becker, C. Riplinger, E. F. Valeev, F. Neese, *J. Chem. Phys.* **146**, 164105 (2017).

[3] M. Saitow, F. Neese, *J. Chem. Phys.* **149**, 034104 (2018).

[4] M. Saitow, A. K. Dutta, F. Neese, *Bull. Chem. Soc. Jpn.* **92**, 170 (2018).

(Assistant professor, Masaaki Saiow)

Visiting Professor 2018

Assoc. Prof. Franklin (Feng) Tao

Associate Professor
University of Kansas, U.S.A.

Period of Stay: June 5, 2018 – July 24, 2018
Research Theme:
"Operando characterization of heterogeneous catalysts"

Since June 4th, 2018, Prof. Franklin (Feng) Tao, an associate professor of Kansas University, USA, visited RCMS for the collaborative work on operando characterization of heterogeneous catalysts for 2 months. Prof. Tao is one of the top young scientists in the fields of heterogeneous catalysis and surface science. He discussed on recent progresses on operando characterization techniques using hard X-rays at synchrotron facilities and started new collaborative works on operando XAFS imaging and hard X-ray ambient pressure XPS (HAXPES) analysis of heterogeneous bimetallic catalysts.

During his stay at RCMS, he joined group seminars at the laboratory of inorganic chemistry and discussed with young researchers and graduate students. He also visited various laboratories at department of chemistry and department of chemical engineering at Nagoya university and discussed with various researchers in the departments. On 2nd July, he had an IGER-RCMS seminar "Road to Smallest Bimetallic Catalysts" on the design, characterization, and remarkable catalysis of single-atom catalysts and contributed education and research at Nagoya university.

At Pacifichem congress in 2020, we are organizing a symposium on in-situ and operando studies of spectroscopy, microscopy, and catalysis for chemical and energy transformations together and have continuous collaborations.

Professor 2018

Prof. Kaoru Yamanouchi

Professor,
Graduate School of Science, Univ. of Tokyo

Prof. Kaoru Yamanouchi graduated from Department of Chemistry, School of Science, The University of Tokyo in 1981, and received Doctor's Degree from the same department in 1986. In 1985, he was appointed as Research Associate at Department of Pure and Applied Sciences, College of Arts and Sciences, The University of Tokyo, and was promoted to Associate Professor in 1990. Since 1997, he has been Professor of Chemistry at Department of Chemistry, School of Science, The University of Tokyo. For more than 20 years, Professor Yamanouchi has been investigating atoms and molecules interacting with intense laser fields for exploring frontiers in ultrafast intense laser science.

Visiting Professor 2018

Prof. Lahcène Ouahab

Professor
Chemical Institute of Rennes, CNRS

Period of Stay:
January 8, 2019 – February 27, 2019

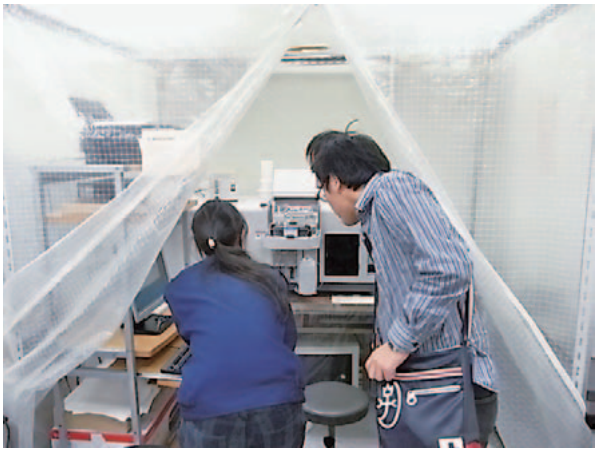
Research Theme:
Research on Molecular Magnetism

Prof. Lahcène Ouahab from the Chemical Institute of Rennes, France, stayed as a vising professor in RCMS for two months since the beginning of January, 2019, working on the research of molecular magnets. He has been working in this field for many years and is well known as the organizer of the International Conference on Coordination Chemistry (ICCC) at Brest, France, in 2016, During his stay, we collaborated on synthesis of novel molecular magnets and their application to organic electronics and spintronics.

In Nagoya University, he attended to the group meetings of the Awaga group, and visited many chemistry laboratories in the Schools of Science and Engineering, 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, "Lanthanides Complexes containing TTFs Ligands : Single Molecule Magnet behaviour and Luminescence" on Feb. 15th, in which we had good discussion. With a lot of good memories in Japan, he returned to France on Feb. 27th, 2019.

Report on the Chemical Instrumentation Facility

The Chemical Instrumentation Facility (CIF) 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 CIF, 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. At the end of fiscal 2018, Two Mass spectrometers of ESI-Q-TOF-MS (compact, Bruker) and MALDI-TOF/TOF-MS (ultrafleXtream, Bruker) were introduced to CIF with the cooperation of Graduate Program of Transformative Chem-Bio Research (Program Coordinator: Prof. Shigehiro Yamaguchi). These new MSS enabled to conduct higher sensitive and accurate MS measurement. During the 2018 fiscal year, as shown in "CIF Utilization Status", 68 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 757.



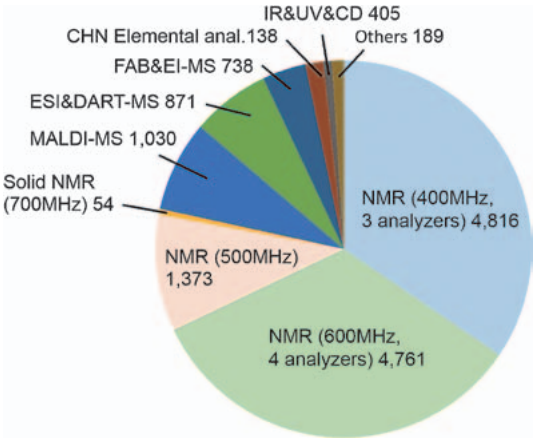
Training session of atomic absorption spectrometer (Z-5710, HITACHI)

ESI-Q-TOF-MS (compact, Bruker)

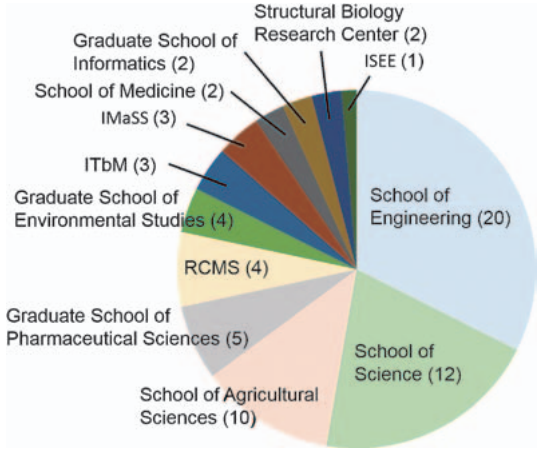
MALDI-TOF/TOF-MS (ultrafleXtream, Bruker)

[CIF Utilization Status]

Utilization Status for the Academic Year 2018
(April 2018 – March 2019)



Number of Uses/Measurements by Instrument



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

Chemistry Gallery

The Chemistry Gallery (2nd Floor of the Noyori Materials Science Laboratory) welcomed many visitors again in the 2018 academic year.

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 : 808 (August 8 to 10)
Number of visitors on Homecoming Day : 720 (October 20)

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.

Prof. Noyori visited Chemistry Gallery to say hello to visitors.

Retirement Address
Professor Yoshihito Watanabe

Professor Yoshihito Watanabe, who retired on March 2019, gave his final lecture at the Lecture Hall in the Noyori Materials Science Laboratory at 16:30 on Tuesday, March 12, 2019. In addition to faculty members of Department of Chemistry, Graduate School of Science and Research Center for Materials Science, a large number of participants inside and outside the university gathered at the venue and listened intently to Professor Watanabe's final lecture.

In the lecture entitled "40 years with metalloproteins" Professor Watanabe talked about his research life and achievements so that participants from various backgrounds could understand them, going back to his studies as an undergraduate student. It was impressive that Professor Watanabe, who has spent time of multiple universities and research environments including both inside and outside of Japan, introduced various chapters that shaped his research philosophy. At the end of the lecture, a flower bouquet was presented by a student from his laboratory, and the final lecture was concluded with a big applause.

Since April 2019, he has been managing the university and carrying out research activities as a senior presidential advisor of Nagoya University and a director of Integrated Research Consortium on Chemical Sciences (IRCCS). We appreciate his efforts in research and education.

Farewell Party

March 12, 2019, Chemistry Lounge, Noyori Materials Science Laboratory

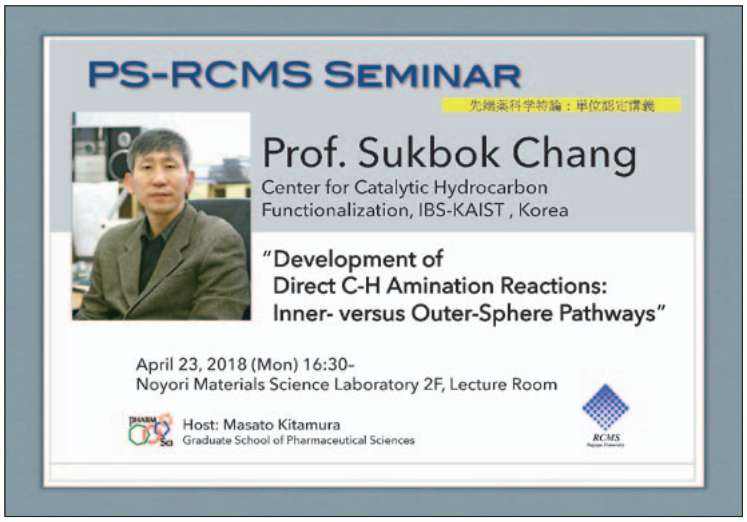
Prof. Yoshihito Watanabe
Assistant Prof. Fumiaki Tomoike
Mrs. Masako Kitamura (Chemistry Department Office)

From left to right; Mrs. Kitamura, Asst. Prof. Tomoike, Prof. Watanabe

Abe group

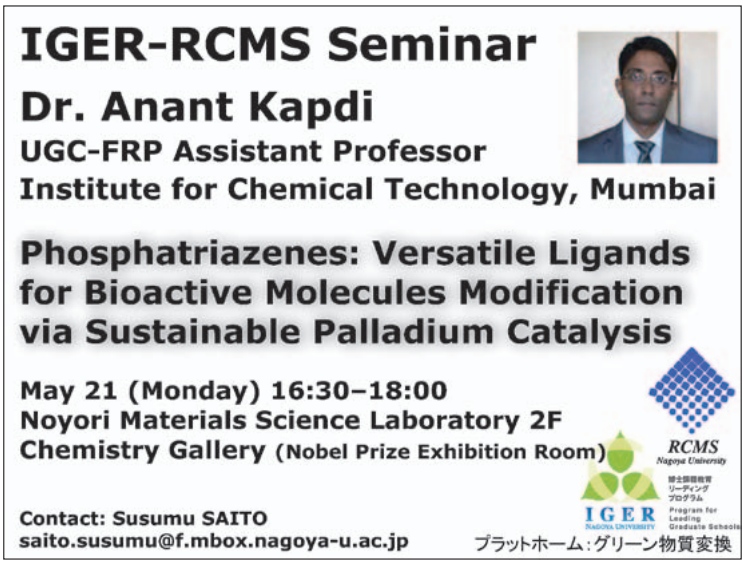
Watanabe group

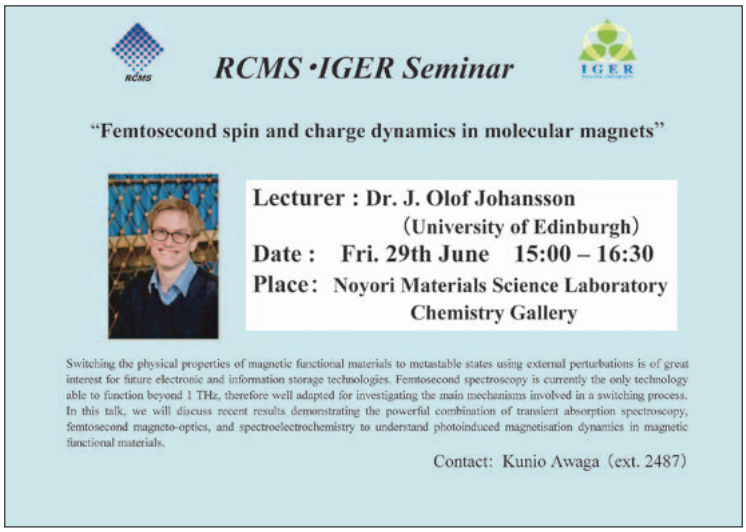
RCMS Seminars



April 23, 2018 Prof. Sukbok Chang (Center for Catalytic Hydrocarbon Functionalization, IBS-KAIST, Korea) "Development of Direct C-H Amination Reactions: Inner-versus Outer-Sphere Pathways"

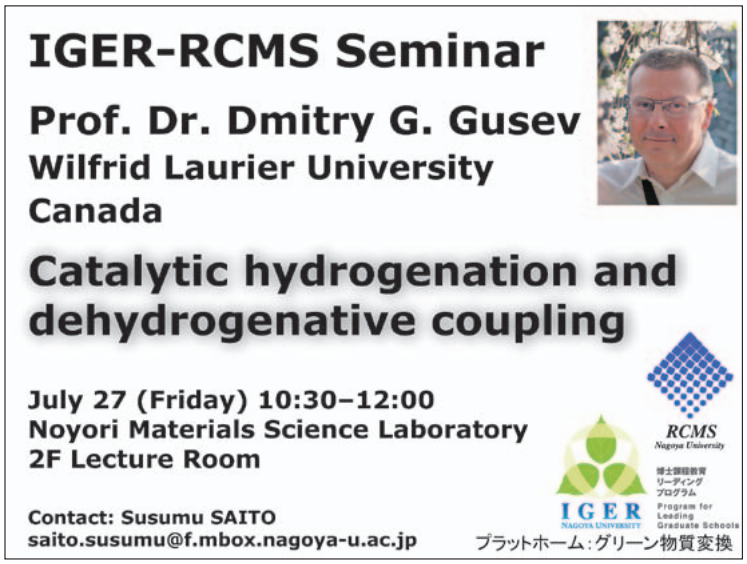
May 21, 2018 Dr. Anant Kapdi (UGC-FRP Assistant Professor, Institute for Chemical Technology, Mumbai, India) "Phosphatriazenes: Versatile Ligands for Bioactive Molecules Modification via Sustainable Palladium Catalysis"





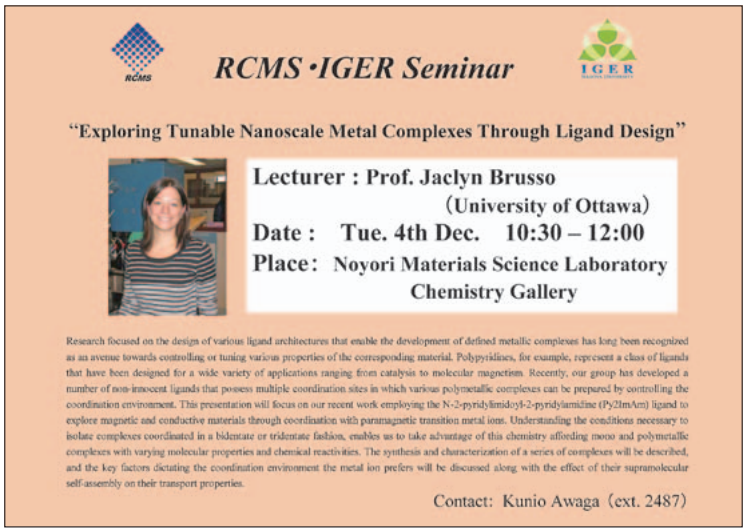
June 29, 2018 Dr. J. Olof Johansson
(University of Edinburgh)
"Femtosecond spin and charge dynamics in molecular magnets"

July 2, 2018 Assoc. Prof. Franklin (Feng) TAO
(Dept. Chem., Univ. Kansas)
" Road to Smallest Bimetallic Catalysts"



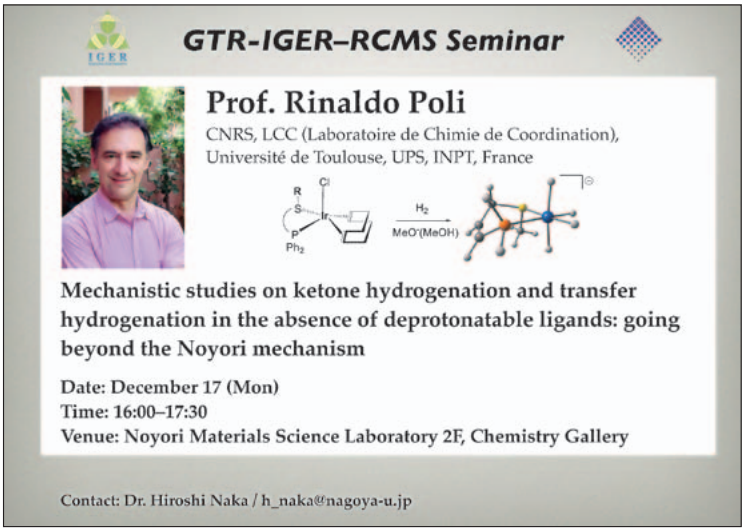
July 27, 2018 Prof. Dr. Dmitry G. Gusev (Wilfrid Laurier University, Canada)
"Catalytic hydrogenation and dehydrogenative coupling"

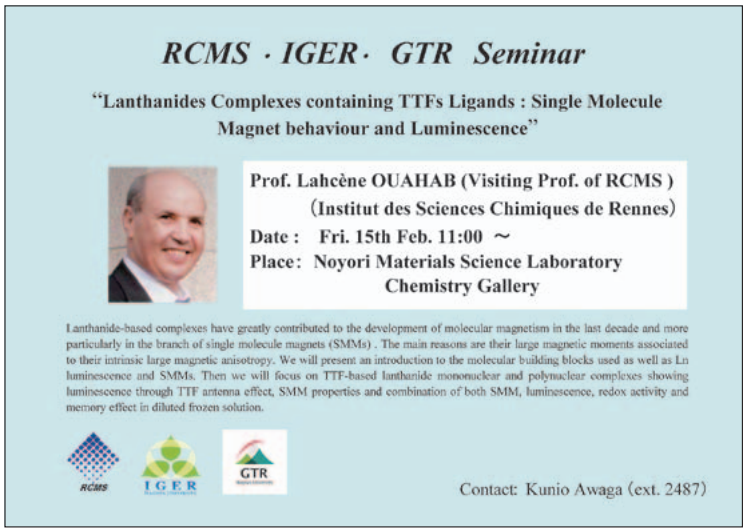
December 3, 2018 Prof. Lionel Cheruzel (San José State University)
"Hybrid P450 Enzymes Featuring Ru(II)-diimine Complexes"



December 4, 2018 Prof. Jaclyn Brusso (University of Ottawa)
"Exploring Tunable Nanoscale Metal Complexes Through Ligand Design"

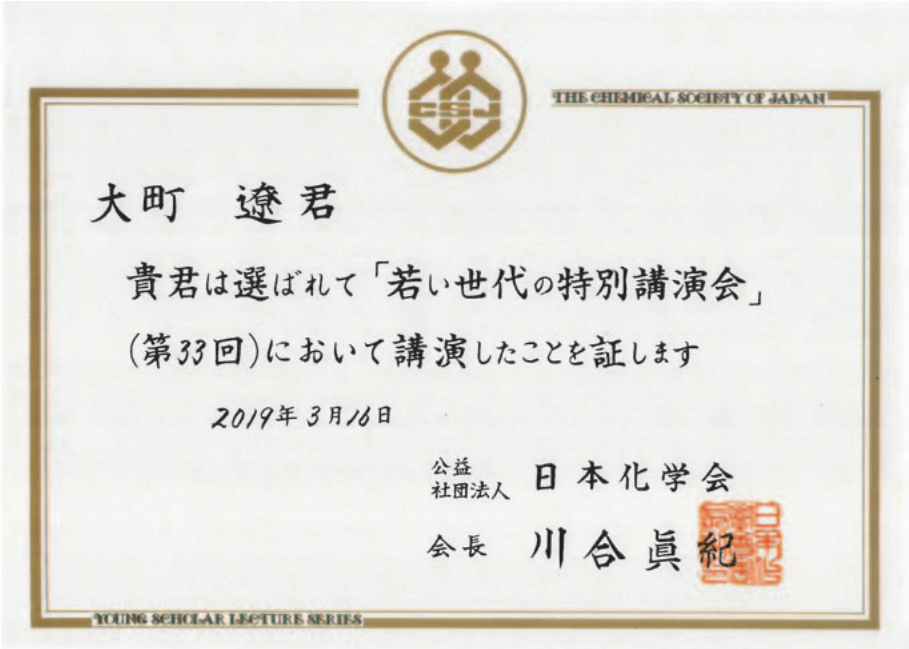
December 17, 2018 Prof. Rinaldo Poli (Université de Toulouse, UPS, INPT, France)
"Mechanistic studies on ketone hydrogenation and transfer hydrogenation in the absence of deprotonatable ligands:going beyond the Noyori mechanism"





February 15, 2019 Prof. Lahcène OUAHAB (Institut des Sciences Chimiques de Rennes) "Lanthanides Complexes containing TTFs Ligands : Single Molecule magnet behaviour and Luminescence"

Awards 2018


THE CHEMICAL SOCIETY OF JAPAN

大町　遼君

貴君は選ばれて「若い世代の特別講演会」
(第33回)において講演したことを証します

2019年3月16日

公益
社団法人　日本化学会

会長　川合眞紀

YOUNG SCHOLAR LECTURE SERIES

Assistant Prof. Haruka Omachi

Alexander von Humboldt Foundation Research Award
Prof. Shigehiro Yamaguchi, Director of RCMS, in the middle
(March 29th, 2019 in Bamberg, Germany)

Staff List

Director	Professor	Shigehiro Yamaguchi	(2291)	yamaguchi@mbox.chem.nagoya-u.ac.jp
Special Advisor	University Professor	Ryoji Noyori		
Organic Synthesis	Professor	Shigehiro Yamaguchi	(2291)	yamaguchi@mbox.chem.nagoya-u.ac.jp
	Assistant Professor	Soichiro Ogi	(5750)	ogi.soichiro@chem.nagoya-u.ac.jp
	Assistant Professor	Akiko Yagi	(5873)	yagi.akiko@d.mbox.nagoya-u.ac.jp
Inorganic Synthesis	Professor	Mizuki Tada	(6200)	mtada@chem.nagoya-u.ac.jp
	Associate Professor	Hideo Takagi	(5473)	htakagi@chem.nagoya-u.ac.jp
	Associate Professor	Yasuyuki Yamada	(2471)	yy@chem.nagoya-u.ac.jp
	Designated Professor	Kazuyuki Tatsumi	(2474)	i45100a@nucc.cc.nagoya-u.ac.jp
Functional Materials	Professor	Akiyoshi Hishikawa	(2494)	hishi@chem.nagoya-u.ac.jp
	Assistant Professor	Zhang Zhongyue	(5106)	zhangzhongyue@i.mbox.nagoya-u.ac.jp
	Assistant Professor	Haruka Omachi	(3660)	omachi.haruka@a.mbox.nagoya-u.ac.jp
	Assistant Professor	Masaaki Saitow	(2851)	masa.saitow@chem.nagoya-u.ac.jp
Biomaterials Research	Professor	Yoshihito Watanabe	(3049)	p47297a@nucc.cc.nagoya-u.ac.jp
	Assistant Professor	Fumiaki Tomoike	(2950)	tomoike@chem.nagoya-u.ac.jp
Molecular Catalysis	University Professor	Ryoji Noyori	(2956)	noyori@chem3.chem.nagoya-u.ac.jp
	Assistant Professor	Hiroshi Naka	(5411)	h_naka@nagoya-u.jp
	Assistant Professor	Shinji Tanaka	(2960)	tanaka@os.rcms.nagoya-u.ac.jp
Collaborative Studies	Guest Professor	Kaoru Yamanouchi (Professor, The University of Tokyo)		
	Guest Professor	Lahcène Ouahab (Professor, Chemical Institute of Rennes, CNRS)		
	Guest Associate Professor	Feng Tao (Associate Professor, University of Kansas)		
Chemical Instrumentation Facility	Manager / Professor	Susumu Saito	(5945)	saito.susumu@f.mbox.nagoya-u.ac.jp
	Technical official	Yutaka Maeda	(3069)	maeda@cic.nagoya-u.ac.jp
	Technical official	Kin-ichi Oyama	(3069)	oyama@cic.nagoya-u.ac.jp
International Advisory Board		Michael Grunze (Professor Emeritus, Heidelberg University)		
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		Henri Boris Kagan (Professor Emeritus, Paris-Sud 11 University)		
		Atsuko Tsuji (Designated Professor, Nagoya University)		
Cooperating Faculty	Professor	Hisanori Shinohara (Graduate School of Science)	(2482)	noris@nagoya-u.jp
	Professor	Kenichiro Itami (Institute of Transformative Bio-Molecules)	(6098)	itami.kenichiro@a.mbox.nagoya-u.ac.jp
	Professor	Masato Kitamura (Graduate School of Pharmaceutical Sciences)	(2957)	kitamura@os.rcms.nagoya-u.ac.jp
	Distinguished Invited University Professor	Sumio Iijima	(6460)	iijimas@nagoya-u.jp
RCMS Office	Administrative Staff	Yuko Kihara	(5907)	kihara@os.rcms.nagoya-u.ac.jp
	Administrative Staff	Sonoe Tankiku	(5908)	tankiku@os.rcms.nagoya-u.ac.jp