Department of Chemistry
Graduate School of Science
Nagoya University
http://www.chem.nagoya-u.ac.jp/

Graduate Studies in Chemistry

2010/2011

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Introduction

Introduction

The 21st century has been referred to as the era of the environment, nanotechnology, biology, and information. With its origins in the natural sciences, chemistry was concerned primarily with the study of the structure, properties, and reactions of materials. These discoveries led to the creation of new materials, and this in turn has become increasingly important for solving various problems of this century. The laboratories in the Department of Chemistry, Division of Material Science, Graduate School of Science, at Nagoya University are conducting research programs based on a traditional academic approach to the study of chemistry such as organic chemistry, biochemistry, inorganic chemistry, and physical chemistry.

The research outputs of the laboratories in the Department of Chemistry include the development of asymmetric synthesis, research of carbon nanotubes and similar work that has been well received worldwide. Consequently, we have cultivated researchers and educators who are active internationally through the establishment of collaborative efforts in all of the scientific fields, including engineering, agriculture, pharmacology, and medicine. As you well know, the first Nobel Prize in chemistry in this century was conferred upon Professor Noyori who has led the field of organic chemical reactions for a long time. This represents the high and international level of research conducted in our laboratories. Furthermore, our department has been selected to be part of the Global COE Program in Chemistry that started in 2007. This is yet another telling indicator of how high the quality of our research is. You will find details of these and other aspects of our Department in the pages that follow.

This pamphlet has been compiled for prospective students who want to conduct research and study in the laboratories of the Department of Chemistry at Nagoya University. If you are interested in joining one of our laboratories, please contact the Chief of Department, the Chemistry Department Office, or the laboratories directly for more information, all of which is also available on the internet (http://www.chem.nagoya-u.ac.jp/). Telephone numbers and e-mail addresses for each laboratory are listed at the end of this pamphlet.

2010
Kentaro Tanaka
Chair of Department of Chemistry
Division of Material Science, Graduate School of Science, Nagoya University

The Principle of Education in the Department of Chemistry

By talking with nature at the level of atoms and molecules, we understand nature. The origin of chemistry comes from the joy making new materials based on knowledge. Natural materials have diverse structures and qualities with many useful physical and physiological activation properties, which human beings have had the wisdom to exploit since ancient times. The principal focus of traditional chemistry is elucidating of the structure of various materials, clarifying their reactions, and synthesizing useful substances that exist in nature. Modern chemistry has advanced this scope further by creating chemical compounds that have new structures and physical properties, studying their properties, clarifying the structures and the reaction mechanisms of organic molecules, and synthesizing physiologically active substances. Thus, modern chemistry has come to assume the role of being the key science in the study of materials in the broad academic fields of both materials and life sciences. Along with developing new materials to create a prosperous and civilized society, it is also expected that chemistry will play an active role in solving environmental problems such as global warming and destruction of the ozone layer, and, thus, that it might have to be applied to ensure the very existence of human beings.

The Department of Chemistry intends to cultivate talented people capable of doing the following: 1) Becoming internationally respected researchers who will lead and be at the forefront of research in chemistry at both public and private research institutes, and who plan to create new research fields, 2) educators of chemistry who will be capable of transferring both chemical knowledge and associated technology to the many educational institutes of higher learning and that have the creativity to exploit future opportunities, and 3) advanced professionals who are well versed and highly specialized in their fields at the forefront chemical technology. We have internationally active researchers as faculty members in each of the fundamental fields of chemistry (organic chemistry, biochemistry, inorganic chemistry, and physical chemistry), and we foster the most radical environment within which to conduct research and education.

History of the Department of Chemistry

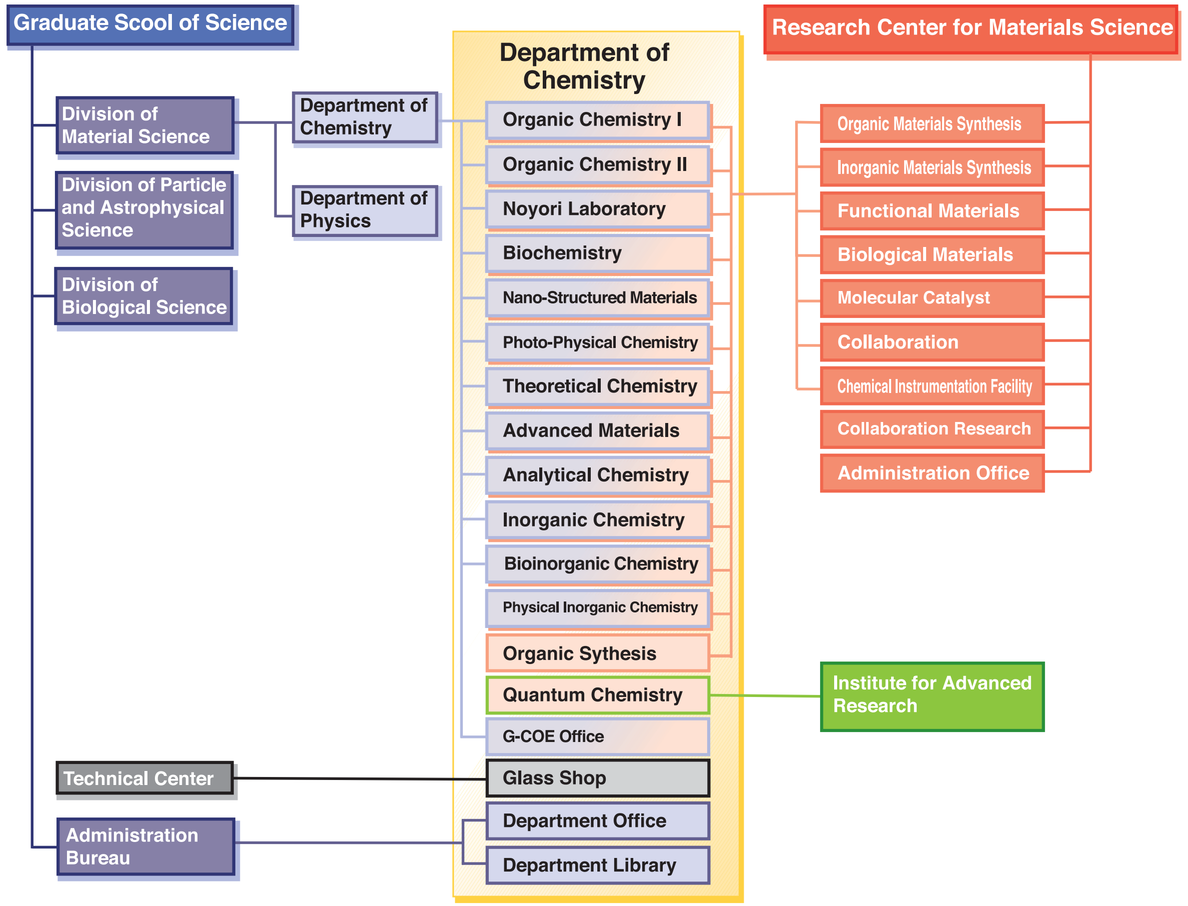
The history of Department of Chemistry, Division of Material Science, Graduate School of Science can be traced back to the foundation of Nagoya Imperial University in 1939, and the establishment of the Department of Chemistry, School of Science, to 1942. After shifting from the old to the new education system, new courses were successively established to correspond with the diverse needs of chemistry. The number of teaching staff was increased, and facilities for research and education were improved. In the interim, the department was able to send many graduates off to industry, the public service, and academic circles.

More recent improvements and diversification of the graduate school came into being in 1996 with the faculty activities in School of Science transferred to the Graduate School of Science, which had been established as a new department. At that time, all of the laboratories from the Department of Chemistry, the solid-state physics and biophysics laboratories of the Department of Physics were amalgamated into the Division of Material Science that would concern itself the creation of new materials and potential application of those materials. The faculty members of the Chemistry Department now belonged to the Graduate School of Science and took charge of research and the education of graduate students in the Division of Material Science, as well as the education of undergraduate students.

These activities all happened against the background of the establishment of the Center of Excellence (COE) Program in 1995. The outstanding results of the COE program were acknowledged, and the Research Center for Material Science was established in 1998. Moreover, in 2000 the Division of Material Sciences was identified as being the first Education COE to implement a system of praising graduate students publicly for unrecognized efforts, resulting in outstanding research achievements. In 2002 we were selected to be part of the 21st Century COE Establishment Program, and have consequently been able to prepare various forms of support for our graduate doctoral students. Moreover, these high activities have been succeeded by the Global COE program which has just launched in 2007. These four COEs have brought laboratories in the Department of Chemistry dramatically improved conditions for conducting research and education, and have made it possible for us to offer the best environment for research and education at home and abroad.

Organization of the Department of Chemistry

There are 11 laboratories in the Department of Chemistry, including: Organic Chemistry I, Organic Chemistry II, Biochemistry, Nano-Structured Materials, Solid State Chemistry, Theoretical Chemistry, Advanced Materials, Analytical Chemistry, Inorganic Chemistry, Bioinorganic Chemistry, and the Noyori Laboratory. The members of the Research Center for Materials Science belong to any one of these 11 laboratories, or to the Organic Synthesis Group and Physical Inorganic Chemistry Subgroup, and they serve as the core of the research activities at Department of Chemistry (see figure below). Each laboratory in the Department of Chemistry has an intimate relationship with the Research Center for Materials Science for both research and education. In addition, there are Chemistry Department Office, Chemistry Department Library, and the Glass Shop at the Technical Center that all support the laboratories and groups.



Construction of Laboratories

Organic Chemistry I	
Professor	ITAMI, Kenichiro
Assistant Professor	YAMAGUCHI, Junichiro
Assistant Professor	SEGAWA, Yasutomo
Organic Chemistry II	
Professor	YAMAGUCHI, Shigehiro
Assistant Professor	FUKAZAWA, Aiko
Assistant Professor	SAITO, Shohei
Biochemistry	
Professor	ENDO, Toshiya
Associate Professor	YOSHIHISA, Tohru
Associate Professor	NISHIKAWA, Shuh-ichi
Noyori Laboratory	
Professor	NOYORI, Ryoji
Associate Professor	SAITO, Susumu
Assistant Professor	NAKA, Hiroshi
Assistant Professor	TANAKA, Shinji
Nano-Structured Materials	
Professor	SHINOHARA, Hisanori
Associate Professor	KITAURA, Ryo
Assistant Professor	TOMIYAMA, Tetsuo
Assistant Professor	MIYATA, Yasumitsu
Photo-Physical Chemistry	
Professor	HISHIKAWA, Akiyoshi
Associate Professor	OUCHI, Yukio
Theoretical Chemistry	
Assistant Professor	MATSUMOTO, Masakazu
Advanced Materials	
Professor	AWAGA, Kunio
Associate Professor	MATSUSHITA, Michio M.
Assistant Professor	YOSHIKAWA, Hirofumi
Analytical Chemistry	
Professor	TANAKA, Kentaro
Assistant Professor	YAMADA, Yasuyuki
Assistant Professor	KAWANO, Shin-ichiro
Inorganic Chemistry	
Professor	TATSUMI, Kazuyuki
Associate Professor	OHKI, Yasuhiro
Assistant Professor	MATSUMOTO, Tsuyoshi
Bioinorganic Chemistry	
Professor	WATANABE, Yoshihito
Associate Professor	NAKAJIMA, Hiroshi
Assistant Professor	SHOJI, Osami
Assistant Professor	FUKUSHIMA, Takashi
Organic Synthesis	
Professor	KITAMURA, Masato
Quantum Chemistry	
Associate Professor	IRLE, Stephan
Physical Inorganic Chemistry	
Associate Professor	TAKAGI, Hideo D.
G-COE Office	
Associate Professor	FISCHER, Berthold
Associate Professor	KATO, Kiyonori
Glass Shop	
Head Technical Staff	NODA, Toshiaki
Technical Staff	NATSUME, Hideko
Technical Staff	OKAMOTO, Hisakazu

Entrance Examination for the Graduate Course

The Division of Material Science is a new major that is supported by the laboratories of the Departments of Chemistry and Physics. While respecting the traditions of chemistry and physics, we maintain interchanges in this division with some programs. These programs include having special talks to discuss excellent or interesting masters' theses, etc.

There are two routes to enroll for the master's course in the Department of Chemistry. One is to take the entrance exam held for senior and graduated students in August or September. Another way is to enter through the educational system in which students are allowed to skip grades if they qualify in their third year of undergraduate school (a total of 10 students have taken advantage of this system since 1992 when it started.) In the latter case, prospective applicants need to apply to be recognized as an "excellent student" in December and are provisionally accepted until such time as they successfully complete the entrance exam in February.

The Division of Material Science encourages, and has a preference for, graduate students who have studied at different universities and that have majors in various fields. We are wide open to prospective students from our own department as well students who have different majors or are from other universities. The administration of entrance examinations for the graduate school is only done to assess the general academic ability of potential applicants. We also permit applicants from other universities to skip grades in cases of excellent academic ability. Furthermore, we examine a variety of subjects so as to better appraise applications from applicants with different majors.

If you are from another university and are thinking of taking the examination, we would strongly recommend that you contact the professor of the laboratory you hope to join and also that you try to consult with him/her in person whenever possible. A summary of research interests for each laboratory can be found in this pamphlet, and if you like to have more information about laboratories, past examples of entrance examination questions (except for foreign languages), and instructions regarding the entrance examination for our graduate school from our homepage (http://www.chem.nagoya-u.ac.jp/). Please see phone numbers and e-mail addresses listed at the end of the pamphlet (page 37) to make contact with relevant laboratories.

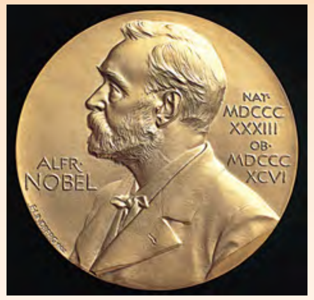
Professor Noyori Wins the Nobel Prize in Chemistry 2001

In October 2001, the Royal Swedish Academy announced that Professor Ryoji Noyori and Dr. William S. Knowles (a former researcher at Monsanto Company, U.S.A.) would be awarded the Nobel Prize for Chemistry for their work on chirally catalyzed hydrogenation reactions and Professor K. Barry Sharpless (The Scripps Research Institute, U.S.A.) for his work on chirally catalyzed oxidation reactions. Their research made the artificial production of ‘Enantiomer’ possible; a subject that had comprised a very important topic of study in the 20th century. Prof. Noyori et al. had realized their dreams.

Enantiomers make a pair of molecules that are mirror images of each other (left-right hand relationship) but are not identical. These molecules frequently have totally opposing characteristics depending on whether the molecule is of the right or left hand form. While one hand has the potential for being an excellent medicine, the other hand can be a dangerous poison. Traditional organic synthesis results in the production of a racemate, a 1:1 mixture of such right hand (good) and left hand (bad) substances. However, natural enzymes can make molecules of only one of the two forms. Consequently, preferential production of the right or left forms using non-enzymatic methods is a major issue for chemistry.

Professor Noyori suggested that a novel type of ‘organometallic molecular catalysis’, one that does not rely on natural enzymes, is representative of the universal process of ‘asymmetric multiplication.’ His innovative research facilitated the synthesis of artificially created right and left hand forms using chiral catalysts and has tremendous potential in the production of medicines, aromatic chemicals, and materials in harmony with the global environment.

Professor Noyori exploited many kinds of asymmetric catalyses, especially the asymmetric hydrogenation of olefins and ketones by chiral homogeneous catalysts. These catalysts consist of a transition metal and BINAP (or its derivatives), a chiral diphosphine ligand(s) originally devised by him and his coworkers. In particular, by inventing a catalyst comprising BINAP and ruthenium (Ru), he markedly expanded the scope of asymmetric hydrogenation to extremely practicable levels. Furthermore, significant progress was made in the ‘asymmetric amplification’ phenomena observed during the addition of organozinc compounds to aldehydes in the presence of catalytic chiral amino alcohol. Thereafter, he elucidated the reaction mechanism underlying such catalytic processes and applied them to the creation of many useful substances. In fact, using his own methods, Professor Noyori made numerous successive innovations in the synthesis of physiologically active substances such as terpenes, alkaloids, amino acids, vitamins and nucleic-acid-related substances. His contribution of these fundamental principles and techniques also led to the industrial production of more complex compounds including prostaglandins, carbapenem antibiotics, and quinolone-type anti-bacterial agents. In addition, Professor Noyori’s research has resulted in the large-scale production of the aromatic substance (–)-menthol at unprecedented levels since 1983, having a marked impact on the industrial world. His creative efforts have expanded to the hydrogenation of carbon dioxide in its super-critical state, as well as environmentally benign oxidation reactions by a tungsten complex in aqueous hydrogen peroxide. All of these impressive contributions keep fueling a worldwide campaign to promote the development of chemical technology for environmentally compliant engineering in the 21st century.



Global COE Program

"Establishment of COE for Elucidation and Design of Materials and Molecular Functions"

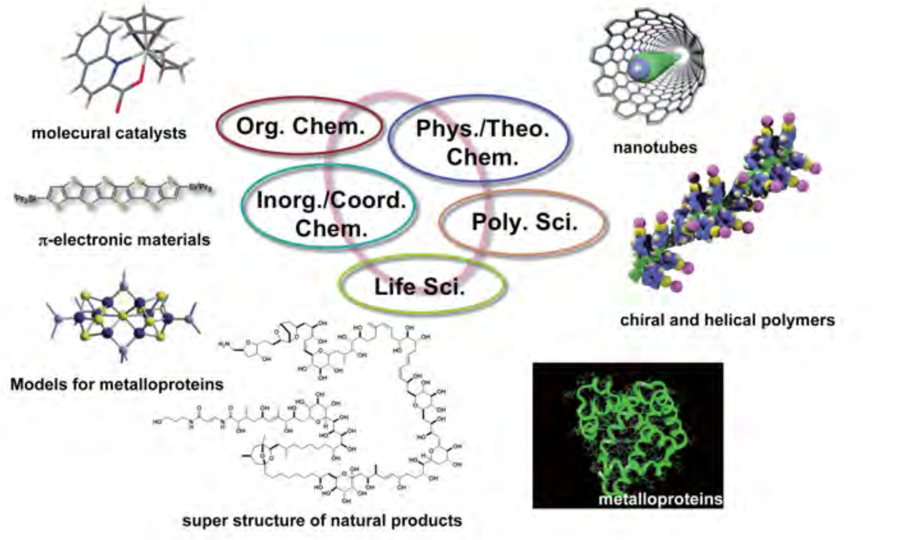
Chemistry expands and creates research areas in collaboration with physics and life science, continually producing functional materials which support the development of modern society. Today, at the beginning of the 21st century, this trend is growing stronger. However, new developments should be consistent with harmonization of the global environment and social ethics. It is an urgent issue to foster the growth of individuals who can lead such developments in chemistry. With this situation in mind, world-leading researchers gathered from the chemistry group* and the applied chemistry group** of Nagoya University to establish a global education and research center in fundamental chemistry with a focus on molecular materials. During the period of this Global COE program, we aim to develop young global research leaders responsible for the future of materials science through comprehensive and world-class education and research for creating new trends in the development of molecular functions in materials science.

***Chemistry group:** Department of Chemistry, Graduate School of Science; Research Center for Materials Science. ****Applied Chemistry group:** Department of Applied Chemistry, Graduate School of Engineering.

Research Projects – Creation of new trends in molecular functional materials science:

The main target of this COE is the creation of new functional materials in conjunction with acquiring a deep understanding of biological functions. To this end, four research teams have been organized to pursue the following sub-themes as we develop advanced research activities that include collaboration amongst the teams:

1) "*Highly Efficient Chemical Synthesis*" which underlies the creation of materials as the basis of materials science and life science, reduces environmental load, and provides the means for efficient syntheses of organic/inorganic and organometallic compounds to produce valuable new materials.
2) "*Use of Polymer Science for Development of Molecules with Novel Properties and Functions*" through first-order structure control and hierarchical self-organization by rational design of various molecules ranging from functional molecules to biomolecules, polymers and organic-inorganic composite higher-order systems.
3) "*Development of Molecules with New Functions Through Nano-chemistry*" on the nano-scale such as fullerenes, nanocarbons, thin films, and supramolecular materials.
4) "*Chemical Aspects of Life Science*" for gaining an understanding of the complexity of biological phenomena by elucidating the mechanisms of action of bioactive natural products, protein transport processes, and enzyme-catalyzed reactions.



Human resource development and education – Producing global leaders in molecular functional materials science:

Research leaders of the next generation must acquire advanced expertise and wide-ranging basic knowledge in related areas. These individuals should also have a high standard social conscience as well as the ability to apply their expertise to unexplored fields and inter-disciplinary areas. Thus, we foster the development of global leaders in molecular functional materials science through education and research while instilling values such as morality, independence and respect for other cultures. In order to provide a high level of expertise and wide vision, we introduced an integrated and systematic program for graduate school education across the School of Science and the School of Engineering. As a complement to the graduate school lectures, we hold various seminars to foster development of broad academic knowledge. Specifically, in addition to traditional seminars in each area, we will organize cross-disciplinary seminars attended by coordinators to cultivate basic knowledge in related areas. Furthermore, we provide seminars on "Science in Society" and career path education seminars.

Establishing a hub in the international research network:

In order to develop comprehensive materials science, we continuously promote global and inter-disciplinary collaborations, establish an information network, and increase academic exchange by holding international conferences and inviting researchers. We will thus establish a center serving as a hub for the scientific network to facilitate collaborations and sharing of information in a safe research environment in conformity with global standards.

***Hosting international researchers and supporting overseas appointments of domestic researchers* -** We invite distinguished overseas researchers on a short- or mid-term basis. We also send doctoral students to overseas research institutes on a mid- or long-term basis to expand their research vision and to cultivate their research frontier spirit.

***International conferences* -** We hold international conferences and workshops to exchange latest research information and to promote academic exchange.

***Recruiting foreign faculty and postdoctoral fellows* -** We recruit foreign faculty and postdoctoral fellows by international promotion of research fellow and faculty positions.

***Collaborating with overseas graduate schools* -** Through the "Japanese-German Graduate Externship" program with the University of Münster (Germany), we have implemented the mid- and long-term mutual exchange of doctoral students and young faculty members. We are also engaged in personnel exchange and joint research with the University of Minnesota (US). We will expand this global academic exchange and collaboration as part of the COE program to the Tata Institute (India), NIST (US), and the University of Groningen (Netherlands).

***Foreign visiting professors* -** We actively pursue joint research with long-term visiting researchers (6–12 months) using the 3 positions of foreign visiting professors at the Research Center for Materials Science.

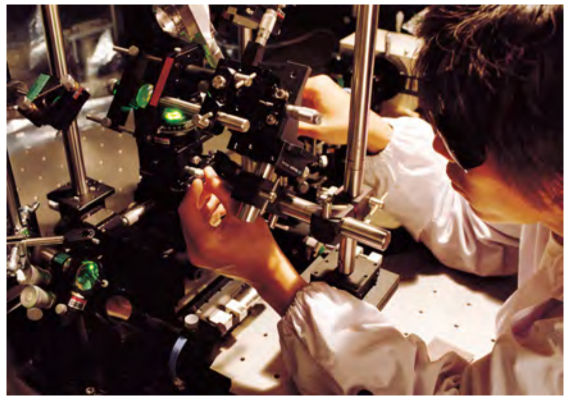
University Life of Graduate Students and Their Academic Program

Master course students belong to one of 14 laboratories and groups and do their research under the guidance of a professor for their degree along with taking lectures. There are various classes for graduate students; some are advanced studies in chemistry and others are interdisciplinary studies, which is one of guiding principles of the Graduate School of Science. Students are required to earn both credits, and also required to get credits of colloquium through seminars at individual laboratories. It takes approximately 2 years to complete a master's thesis after entering graduate school and the master's degree is awarded. There is an award for an "Outstanding masters thesis", a system to publicly acknowledge the efforts of hardworking students so that graduate students will get more motivated to do their research.

After getting a master's degree, some students stay to go on to the doctoral course and do more advanced research to get a doctor's degree, while others get a job in the private sector. In the 3 years from 2007 through 2009, 38 out of 117 graduate students with a master's degree went on to the doctoral course, 68 were employed by private enterprise, and 11 went into other lines of work. There are some students who received a master's degree at other universities and entered the doctoral course of Department of Chemistry. In either case, it takes approximately 3 years to complete a doctoral thesis. The degree of Doctor of Science will be awarded if they pass the examination for becoming a professional researcher. There are circumstances in which particularly talented students can receive their doctoral degree in less than 3 years. After getting the degree, some become researchers at universities and research institutes, while others are employed by private enterprise or become postdoctoral researchers, and so on.

For financial support to attend school, you can apply for a scholarship from the organizations such as the Japan Student Services Organization. For the 3 years from 2007 through 2009, 70 out of the 126 graduate students reading for a master's course that applied for the scholarship, 81 students (including those who where awarded bursaries while in the middle of their degree) received financial assistance. All of the 18 doctoral applicants were awarded the loan. In addition, there is the Research Fellowship for Young Scientists from the Japan Society for the Promotion of Science directed at supporting talented doctoral students. If selected, you will receive a salary (¥200,000 per month in 2009) and a research fund (¥1,500,000 or less per year) from the onset of the doctoral course at the earliest. From 2007 through 2009, 14 students were awarded the assistance for 3 years.

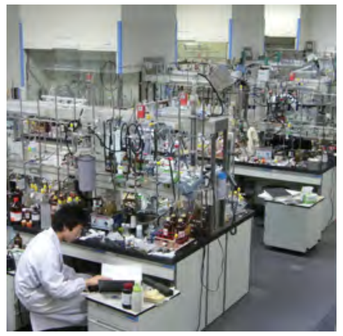
In recent years, graduate students have come to participate actively in the education and research in the Department of Chemistry as teaching assistants (TA) or research assistants (RA). Being a TA means that you give assistance in classes and chemical experiments, and about 60 students in the master's degree course are adopted every year. Conversely, RAs take part in on going research projects in each laboratory and takes care of necessary equipment and gives assistance in promoting effective research activities. Approximately five doctoral students are awarded these positions every year. This means that graduate students have great training opportunities and to become leaders in education and research along with getting paid for working as TAs or RAs.



Research Center for Materials Science

Research Center for Materials Science: RCMS was established in April 1998 and was the first core research center in Japan to comprehensively and internationally promote fundamental research for the creation of "materials" that have the potential to improve human society in the future. Aimed at finding solutions to important problems faced by contemporary society, such as global environment, energy, food, and health. We aim to produce materials that can be used to create a new scientific concepts and for building a rich society.

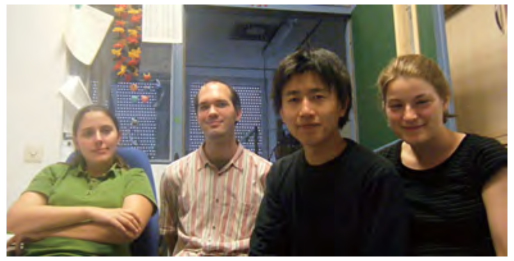
Molecules and their assemblies consist of a finite number of different atoms. New materials with various properties can be obtained by controlling the composition, bonding, and spatial arrangements of the atoms. The core activity of research dedicated to the creation of materials at RCMS is to investigate the properties of a large variety of molecules accurately and closely, to then design and synthesize materials with new proprties as necessary. To realize these aims, it is important to elucidate the mechanisms of the chemical phenomena that affect the target molecules and assemblies at the molecular level and to find efficient methods for the conversion of these materials. Advanced material science is expected to accelerate development of the field of chemistry. In turn, chemistry learns from, and is compatible with, nature through the search for physiologically active natural substances and investigation of chemical reactions of life phenomena, such as metal enzyme functions.

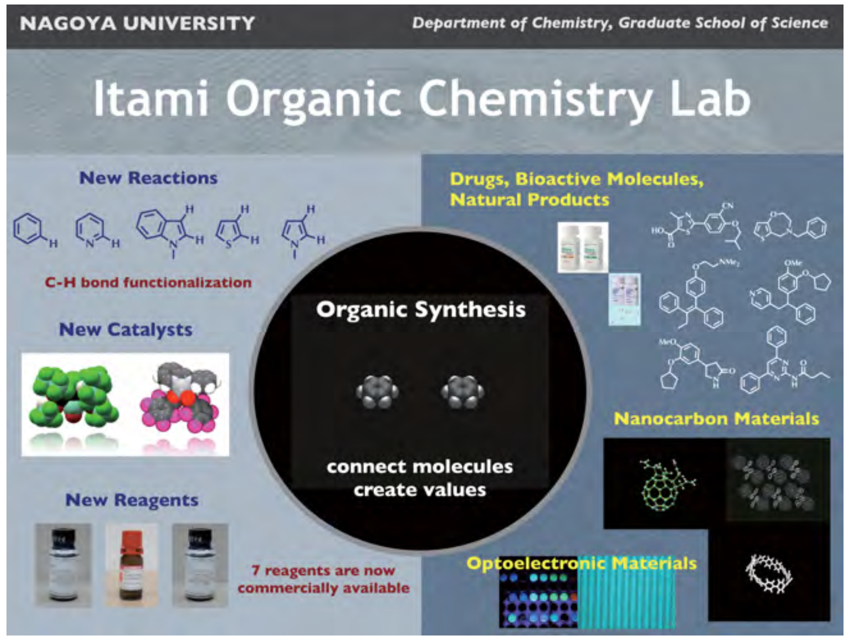


From this background, it is apparent that all of the members of RCMS perform research in organic and inorganic materials synthesis, functional and biomaterials research, and molecular catalysts. The research achievements will be integrated into new basic science for the creation of novel functional materials that surpass those currently in existence. Furthermore, these activities will be essential for the development of many new kinds of basic science and new technologies, and will be a key component of the international contributions Japan will be able to make as a nation of science and technology. Research in RCMS is being observed with keen interest from both within and outside the country, and the research achievements are publicized internationally.

RCMS was combined with Chemical Instrument Center in April 2004 to become a more integrated research organization. The amalgamation of RCMS and Chemical Instrument Center, the latter of which was founded in 1980 as an intra-university shared facility, meant that the former gained access to advanced measuring instruments and sophisticated measuring techniques. The research activities which had been performed in Chemical Instrument Center are continued in Chemical Instrumentation Facility.

The research structure of RCMS is organized flexibly to give the organic chemists, inorganic chemists, physical chemists, and bioorganic chemists a core research base from which they can undertake fundamental research of international importance concerning the creation of the materials. We actively promote the development of new interdisciplinary fields and are not limited by the boundaries set by the traditional academic fields. By way of support for research activities we have 15 full-time faculty members, 1 university professor, 1 domestic visiting professor, 3 visiting professors from overseas, 2 technical assistants, 6 research associates (doctoral researchers), 2 administrative assistants, and 2 assistants for research support. RCMS is run in close association with the laboratories of the Department of Chemistry in both research and education. This means that full-time teaching staff can cooperate with other units at the Graduate School of Science to give students education and research guidance, and to make efforts to cultivate young researchers who will be capable of carrying the future on their shoulders in the international arena.





Overview of Our Research

有機化学研究室

Laboratory of Organic Chemistry I

The main emphasis of our research is on the development of new synthetic methods, strategies, and concepts to solve challenging synthetic problems to realize ideal chemical synthesis, and for generating as-yet unexplored molecules of significant interest. Our parallel objective is to coordinate a broad multidisciplinary effort designed to generate/discover new functional molecules useful in the development and understanding of pure chemistry, materials science, and life science. The followings are representative projects.

1. Ideal Chemical Synthesis through C-H Bond Transformation

The selective transformation of ubiquitous but inert C-H bonds not only represents an important and long-standing goal in chemistry, but also has far-reaching practical implications. Minimizing waste and unwanted steps during synthesis is critical for the future of organic chemistry. We have developed a number of metal-based catalysts enabling the direct transformation of C-H bonds (arene-sp^2 C-H, alkene-sp^2 C-H, alkane-sp^3 C-H). We believe that such a direct transformation technology not only contributes to the realization of "greener" chemistry, but also unlocks opportunities for markedly different strategies in chemical synthesis.

2. Programmed Chemical Synthesis through Bond-Selective Transformation

Chemical synthesis has not yet reached a level where the programmed construction of every imaginable molecule is possible. Rather than making a specific isomer of a specific class of molecule, we try to advance our synthesis to a level all possible isomers of important general types of molecules can be made at will. Our approach toward this end is to establish bond-forming reactions with complete bond selectivity, enabling a programmed chemical synthesis. We have developed several unique synthetic strategies, including a platform strategy for programmed and diversity-oriented synthesis of multisubstituted olefins and aromatics.

Professor **ITAMI, Kenichiro**
Assistant Professor **YAMAGUCHI, Junichiro**
Assistant Professor **SEGAWA, Yasutomo**

http://synth.chem.nagoya-u.ac.jp/

Drs. Y. Segawa (left) and J.Yamaguchi

3. Synthesis of Biologically Active Molecules and Natural Products

The synthesis of biologically active molecules (drugs or drug-like molecules) and natural products is also an important subject in the group. Tamoxifen (anti-breast-cancer drug), rolipram (phosphodiesterase-4 inhibitor), CDP840 (potential drug for asthma), LUF5735 (adenosine A1 receptor antagonist), and Febuxostat (drug for gout and hyperuricemia) are representative examples of molecules that have been prepared in our group. The total synthesis of complex natural products based on C-H bond functionalization is also ongoing in our lab.

4. Synthesis and Properties of Optoelectronic Materials

The application of our methodologies to the synthesis of novel optoelectronic materials is an ongoing endeavor in the group. These molecules include tri- and tetraarylethene-based conjugated molecules, arylenevinylene-based dendrimers, and heteroarene-core starburst pi-systems. We not only constructed chemical libraries of extended pi-systems, but also succeeded in discovering a number of interesting materials (full-color fluorescent materials, fluorescent nanoparticles, and solvatofluorochromic materials) as well as interesting photophysical phenomena.

5. Synthesis and Properties of Nano-Carbon Materials

Chemical synthesis of as-yet unexplored nano-carbon materials has been a hot topic in the group. For example, we established a strategy for the synthesis of cycloparaphenylenes, a shortest sidewall segment of armchair carbon nanotubes, in a selective and modular fashion. Our current focus is to achieve bottom-up synthesis of structurally uniform carbon nanotubes using cycloparaphenylenes as a building block or as a seed. We have also developed several new catalytic methods to functionalize fullerenes, enabling the synthesis of new fullerene-based materials.

◆ Current Articles ◆

1) M. Nambo, A. Wakamiya, S. Yamaguchi, and K. Itami, "*Regioselective Unsymmetrical Tetraallylation of C60 through Palladium Catalysis*," *J. Am. Chem. Soc.*, **131**, 15112-15113 (2009).

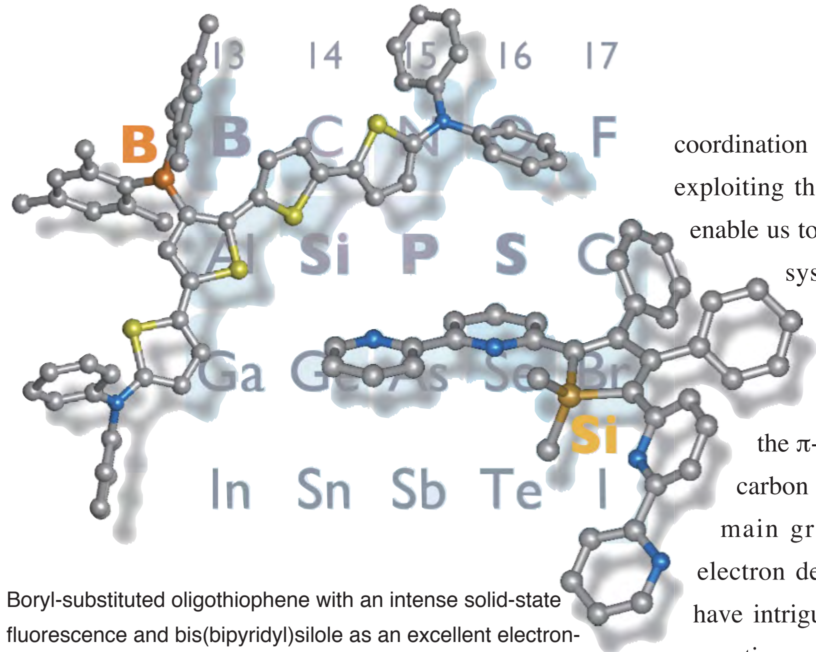
2) S. Yanagisawa, K. Ueda, H. Sekizawa, and K. Itami, "*Programmed Synthesis of Tetraarylthiophenes through Sequential C-H Arylation*," *J. Am. Chem. Soc.*, **131**, 14622-14623 (2009).

3) H. Takaba, H. Omachi, Y. Yamamoto, J. Bouffard, and K. Itami, "*Selective Synthesis of [12]Cycloparaphenylene*," *Angew. Chem. Int. Ed.*, **48**, 6112-6116 (2009).

4) B. Join, T. Yamamoto, and K. Itami, "*Iridium Catalysis for C-H Bond Arylation of Heteroarenes with Iodoarenes*," *Angew. Chem. Int. Ed.*, **48**, 3644-3647 (2009).

5) J. Canivet, J. Yamaguchi, I. Ban, and K. Itami, "*Nickel-Catalyzed Biaryl Coupling of Heteroarenes and Aryl Halides/Triflates*," *Org. Lett.*, **11**, 1733-1736 (2009).

6) M. Ohta, M. P. Quick, J. Yamaguchi, B. Wünsch, and K. Itami, "*Fe-Catalyzed Oxidative Coupling of Heteroarenes and Methylamines*," *Chem. Asian J.*, **4**, 1416-1419 (2009).



Boryl-substituted oligothiophene with an intense solid-state fluorescence and bis(bipyridyl)silole as an excellent electron-transporting material

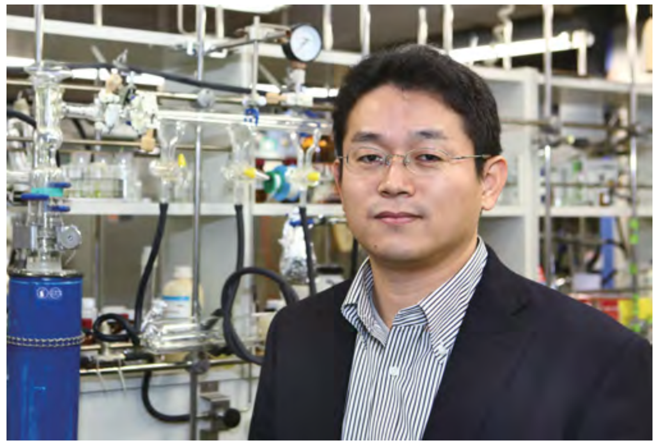
反応有機化学研究室
Laboratory of Organic Chemistry II

Professor **YAMAGUCHI, Shigehiro**
Assistant Professor **FUKAZAWA, Aiko**
Assistant Professor **SAITO, Shohei**
http://orgreact.chem.nagoya-u.ac.jp/en/Home.html

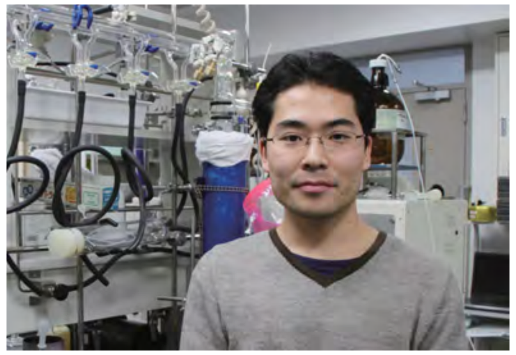
The progress in the materials science, exemplified by organic electronics and optoelectronics, primarily depends on the development of new materials. The creation of conceptually new and excellent molecular systems would lead to certain breakthroughs in these fields. From this point of view, our research is directed at the design and synthesis of new organic materials, particularly on the basis of the main group chemistry. Thus, among a number of elements, we focus our attention on the main group elements from group 13 to group 16, such as boron, silicon, phosphorus, and sulfur. These elements have diversity in many aspects, such as the number of electrons included, electronegativity, and coordination numbers. The molecular designs exploiting these characteristic features would enable us to create new fascinating molecular systems which cannot be achieved by the ordinary organic chemistry.

Our major target molecules are the π-electron systems consisting of the carbon π-conjugated framework and the main group elements. Because of π-electron delocalization, π-electron systems have intriguing photophysical and electronic properties and serve as the key materials in the organic electronics and optoelectronics. The embedding of the main group elements into the π-conjugated frameworks would provide opportunities to modify their inherent properties and add new functions. Our molecular designs rely on three features of the main group elements, that is, "unique orbital interaction," "diversity in coordination number," and "unique structural characteristics." On the basis of these "element-organic" approaches, we aim at the creation of new fundamental molecular materials for the applications in these fields.

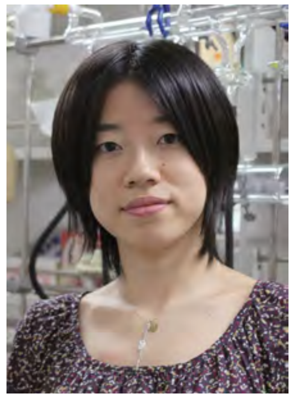
One representative accomplishment from our research is the silole chemistry. We have already synthesized a variety of silole-containing oligomeric and polymeric materials based on the newly developed silole cyclization reaction. All of the synthesized silole derivatives show interesting photophysical and electronic properties due to a unique orbital interaction between the silicon moiety and the π-conjugated moiety (σ^*-π^* conjugation). Among them, most worthy of note is 2,5-bis(bipyridyl)-substituted silole that shows extremely high performance as an electron-transporting material and has already been put into the commercial use in the organic electroluminescent (EL) display for cellular phones.



Our current efforts have been mainly devoted on two research subjects. One is the chemistry of ladder π-electron systems containing main group elements. The silicon-bridged ladder oligo(*p*-phenylenevinylene)s and sulfur- and selenium-containing heteroacenes are representative examples which we have recently synthesized. These compounds are promising materials for organic EL devices and organic thin film transistors, respectively. The other research subject is the exploration of new functional organoboron materials. On the basis of the characteristic nature of the boron atom, we are going to synthesize several types of attractive boron compounds, including borole-based π-electron materials, organic semiconductors with intramolecular B-N coordination, and borazine-based π-conjugated molecular bundles.



Dr. S. SAITO



Dr. A. Fukazawa

In our research, we also place the emphasis on the development of new efficient synthetic methodology. Exploiting the characteristic reactivity of the main group elements and transition metals, we have already developed several types of new reactions, such as the intramolecular reductive cyclizations of acetylenic compounds that produce new π-conjugated skeletons. Our ultimate goal is the creation of newly designed functional molecular systems based on the newly developed own synthetic methodology. We hope that this synthetic chemistry will open a new field in materials science.

◆ Current Articles ◆

1) A. Fukazawa, Y. Ichihashi, Y. Kosaka, and S. Yamaguchi, "*Benzo[b]phosphole-Containing π-Electron Systems: Synthesis Based on an Intramolecular trans-Halophosphanylation and Some Insights into Their Properties*," *Chem. Asian J.*, **4**, 1729-1740 (2009).

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3) C.-H. Zhao, E. Sakuda, A. Wakamiya, and S. Yamaguchi, "*Highly Emissive Diborylphenylene-Containing Bis (phenylethynyl) benzenes: Structure-Photophysical Property Correlations and Fluoride Ion Sensing*," *Chem. Eur. J.*, **15**, 10603-10612 (2009).

4) A. Iida, and S. Yamaguchi, "*Intense Solid-State Blue Emission with a Small Stokes' Shift: π-Stacking Protection of Diphenylanthracene Skeleton*," *Chem. Commun.*, 3002-3004 (2009).

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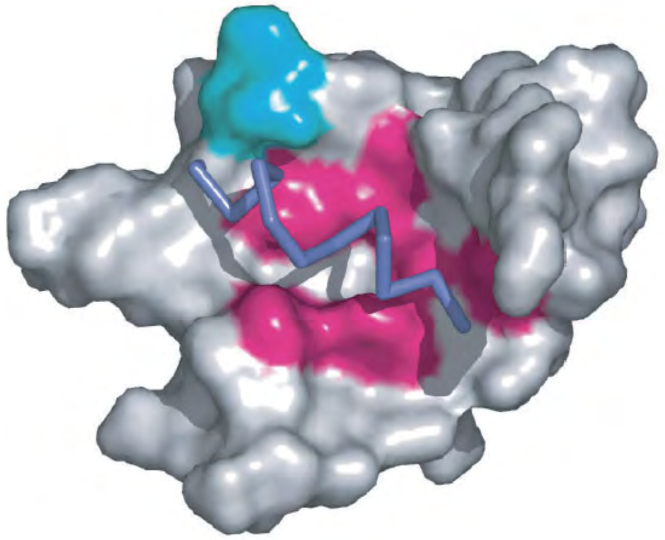

A redox translocator, Tim40 in yeast mitochondria; Identification and X-ray structural determination have been made in our laboratory.

生物化学研究室
Laboratory of Biochemistry

Professor **ENDO, Toshiya**
Associate Professor **YOSHIHISA, Tohru**
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Proteins are major key players in the living systems. They are independent entities that start with spontaneous folding, acquire native functional structures, and end by random degradation --- this classical view of proteins may not be true. Rather, accumulated evidence suggests that the life of proteins depends on other players and that many proteins cannot become functional by themselves. The cell therefore provides elaborate systems to monitor, assist, and control the behaviors of proteins and to make them function properly.

Many newly synthesized proteins have to reach their specific sites of functions, i.e. such organelles as mitochondria, chloroplasts, the ER, and the nucleus, before they fold and/or assemble into functional structures. Since the organellar interior is separated from the cytosol, the sites of protein synthesis, by the permeability barrier of organellar membrane(s), proteins have to move across the membranes with the aid of so-called translocator systems in the membranes. The translocator is a protein assembly that accepts a specific set of proteins by checking the destination ticket or targeting signal of the protein, opens the gate of the path for crossing the barrier of the membrane, and directs the protein to the other side of the membrane. It is known that the targeting signals are encoded within proteins themselves, but what do they look like and how does the translocator read them out? The NMR structure of the targeting signal in a complex with its cognate receptor subunit of the translocator revealed in our lab opened up the way to understanding of the mechanism of targeting signal recognition.

Lipid bilayers of the membranes surrounding organelles do not allow passage of such large molecules as proteins. Then questions may arise: how can the organellar proteins go through the lipid bilayer efficiently, and what mediates this translocation? Another important issue is what drives the vectorial movement of proteins. Is that a mechanistic molecular motor or Maxwell's demon utilizing the Brownian movement? Proteins often have to move across more than one membrane to reach their final destinations. In such cases, multiple translocators in distinct membranes need to cooperate to mediate efficient translocation, but how do they cooperate?

Once delivered to appropriate destinations, can proteins live their peaceful lives? Life of proteins is not so simple and some proteins may fail to attain their native structures. Even after achieving native structures, some proteins may drop out of the protein community due to stresses placed on cells including high temperature. In such cases, various types of molecular chaperones are called to repair the aberrant proteins. Besides, our lab recently found that cells have a novel system to utilize glycosylation for protein quality control. If efforts to renature proteins fail, the aberrant proteins are subjected to disposal by degradation systems. The questions of how one can discriminate normal and aberrant proteins and what makes the final judgment to determine the fate of proteins is one of the central issues in molecular cell biology.

It also remains vague if functions of molecular chaperones and translocators have profound biological significance at the level of multicellular organisms as well. We have thus extended our analyses to the protein quality control in a model plant, *Arabidopsis*. tRNAs have been believed to be exported from the nucleus to the cytoplasm only once in their life. However, recent results from our lab indicate that some tRNAs could shuttle between the nucleus and cytoplasm multiple times to even after maturation. Then, what is the biological significance of such a complex detour of tRNA molecules in cells?

Drs. S. Nishikawa (left) and T. Yoshihisa

When we look at entire organellar structures, their shapes, numbers and positions change significantly and frequently in response to intra- and extra-cellular conditions. Some organelles can divide and fuse each other. However, it still remains obscure what mediates such morphological alteration of organelles and what are the underlying mechanisms. We have recently found a new chaperone that mediates nuclear membrane fusion, and are trying to reveal the mechanism of the chaperone-mediated membrane fusion.

Our lab is making every endeavor to address the questions listed up above by using various techniques that cover biochemistry, molecular biology, cell biology, structural biology, and genetics etc. We are also developing a new methodology to deal with these issues in the life of proteins and organelle biogenesis.

◆ Current Articles ◆

1) D. Maruyama, T. Endo, and S. Nishikawa, "*Bip-mediated polar nuclei fusion is essential for the regulation of endosperm nuclei proliferation in Arabidopsis thaliana*," *Proc. Natl. Acad. Sci. USA.*, **107**, 1684-1689 (2010).

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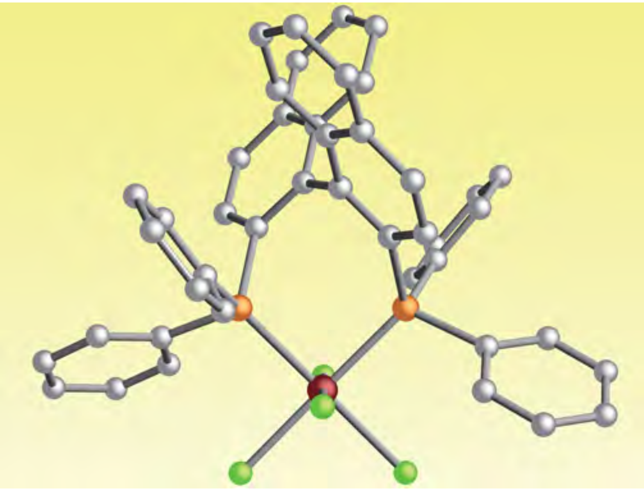

The crystal structure of asymmetric catalyst

特別研究室

Noyori Laboratory

Chemistry is not merely a science of making observations in order to better understand Nature. It is creative and productive. We chemists are proud of our ability to create high values from almost nothing on the basis of accumulated scientific knowledge. Our field of study has greatly enhanced the quality of life worldwide by providing an impressive range of useful man-made substances and materials. Despite the extraordinary masterworks of total synthesis in the last century, the development of practical and efficient synthetic methodologies is still in its infancy. The need for efficient and practical synthesis remains one of the greatest intellectual challenges with which chemists are faced in the 21st Century. The achievement of this goal will require the highest level of scientific creativity, insight and understanding.

Our research group has consistently focused on molecular catalysis and, consequently, contributed in many ways to the progress of modern chemistry.

Professor Noyori is well known for his initiation, development and establishment of asymmetric catalysis using chiral metal complexes. In particular, chemistry based on BINAP ligand has been practiced in research laboratories worldwide as well as on an industrial scale. Other major accomplishments in this area include the development of practical asymmetric hydrogenation of olefins and ketones; the demonstration of the general utility of dynamic kinetic resolution in asymmetric catalysis; the discovery of highly enantioselective addition of dialkylzincs to aldehydes catalyzed by chiral amino alcohols, and the elucidation of the molecular mechanism of the chirality amplification phenomenon. These methods have found application in syntheses of numerous important products including menthol, carbapenem antibiotics, and prostaglandins. More recent achievements extended to the DNA synthesis using organometallic methodologies, the catalytic hydrogenation of carbon dioxide in its supercritical state, the environmentally benign oxidation methods using a tungsten catalyst in an aqueous hydrogen peroxide solution, and the contribution to the brain science research via the synthesis of prostaglandins by the three-component coupling.

The current research programs of our laboratory are directed toward (1) invention of efficient synthetic methods, strategies, and concepts to solve challenging synthetic problems, (2) cost-effective and/or programmable synthesis of various classes of important compounds, (3) creation of significant properties or functions (catalysts and materials) utilizing synergistic effects of intra-and inter-molecular recognition, (4) synthesis of previously unexplored molecules that are architecturally interesting, (5) discovery of new functional molecules (or molecular assemblies) useful in the development and understanding of materials science and life science.

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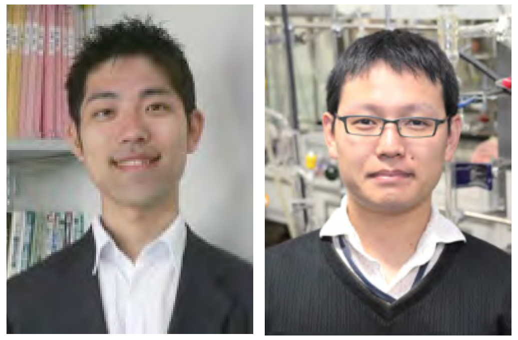

Drs. H. Naka (left) and S. Tanaka

Dr. S. Saito

◆ Current Articles ◆

1) C. A. Sandoval, F. Bie, A. Matsuoka, Y. Yamaguchi, H. Naka, Y. Li, K. Kato, N. Utsumi, K. Tsutsumi, T. Ohkuma, K. Murata, and R. Noyori, *"Chiral η^6-Arene/N-Tosylethylenediamine-Ruthenium(II) Complexes: Solution Behavior and Catalytic Activity for Asymmetric Hydrogenation," Chem. Asian J., in press* (2010).
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9) H. Naka, D. Koseki, and Y. Kondo, "*Catalytic Deprotonative Functionalization of Propargyl Silyl Ethers with Imines*," *Adv. Synth. Catal.*, **350**, 1901-1906 (2008).
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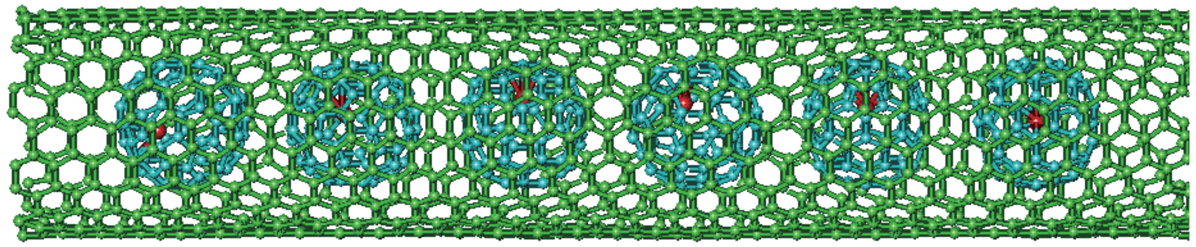

A model structure of metal containing fullerenes inserted in a single-wall carobon nanotube

物理化学研究室
Laboratory of Nano-Structured Materials

Since today's device engineering is facing technical and economic difficulty in further miniaturizing electronic devices with the current fabrication technologies, the need for alternative device-channels is particularly imminent. Fullerenes and carbon nanotubes have been considered as one of the most promising nano-materials in today's nanoscience and nanotechnology since Kraetschmer and Huffman's first report on the macroscopic synthesis of C_{60} in 1990. In fact, fullerenes and carbon nanotubes have been successfully used for nanometer-sized devices such as diodes, transistors, and random memory cells during the past several years.

During the past decade, we have been trying to elucidate structures and electronic properties of the so-called nano-carbon materials, such as fullerenes, endohedral metallofullerenes, carbon nanotubes and nanotube-peapods. We have paid particular attentions to (1) synthesis, characterization and applications of endohedral metallofullerenes; (2) selective and high-yield synthesis of carbon nanotubes, and (3) synthesis, characterization and device applications of nanotube-peapods. The followings are some details on these research projects.

Synthesis, characterization and applications of endohedral metallofullerenes:

The structures of endohedral metallofullerenes have been studied by using ^{13}C NMR, UHV-STM/STS (scanning tunneling microscopy/spectroscopy) and synchrotron X-ray diffraction. For example, we have synthesized and characterized for the first time "metal-carbide" metallofullerenes such as $(Sc_2C_2)@C_{84}$ and $(Y_2C_2)@C_{82}$ and found that a C_2 cluster is encapsulated in $Sc_2@C_{84}$ and $Y_2@C_{82}$, respectively. This is the first example that C_2 radical is trapped in a molecule. Furthermore, our recent UHV-STM/STS studies show that metallofullerenes do not rotate at temperatures below 50 K on $Si(100)2\times 1$ hydrogen-terminated clean surfaces.

Selective and high-yield synthesis of carbon nanotubes:

Single-, double- and multi-wall carbon nanotubes have been synthesized selectively in high-yield by using the methods developed in our laboratory such as zeolite-CCVD (catalyst-supported chemical vapor deposition), HFCVD (hot-filament assisted CVD) and HTPAD (high-temperature pulsed arc-discharge) methods. In particular, double-wall carbon nanotubes (DWNTs), which is the thinnest multi-wall carbon nanotubes, have been synthesized in high-yield. Since DWNTs are the key carbon nanotubes materials in the application of field-emission display and tips for scanning probe microscopy, the synthesis of high-quality DWNTs is particularly needed. To apply the DWNTs synthesized in our laboratory in these rapidly growing area, we have been collaborating with various industrial companies in Japan and abroad.

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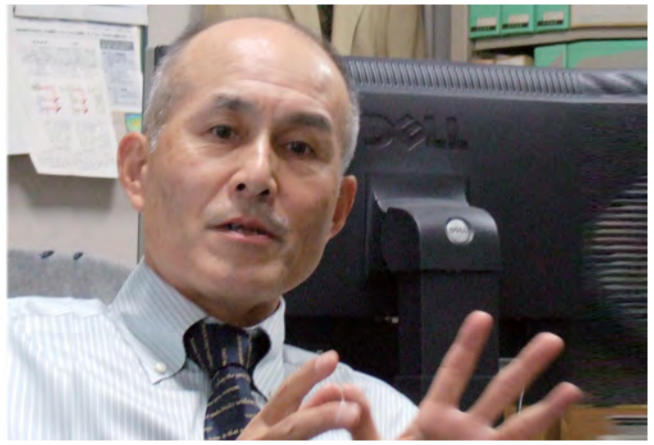
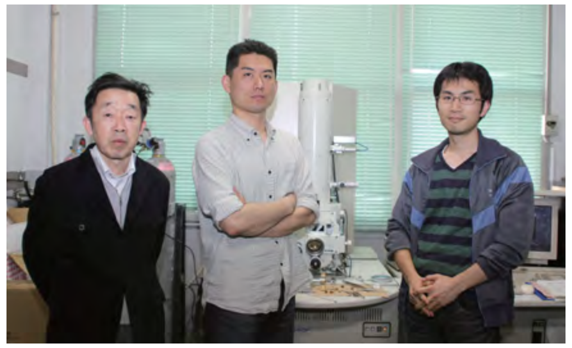
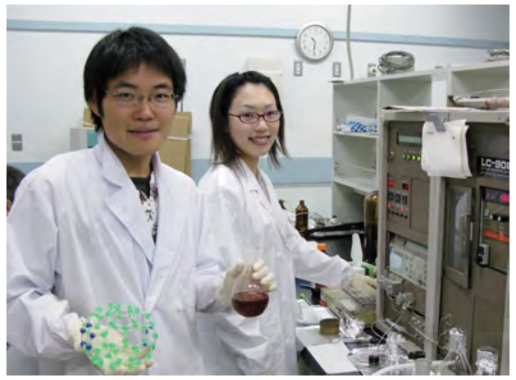




Drs. T.Tomiyama (left) R. Kitaura.(center) and Y.Miyata

Synthesis, characterization and device applications of nanotube-peapods:

Carbon nanotubes encapsulating fullerenes, metallofullerenes and other novel molecules (the so-called "peapods") have been synthesized in high-yield. Such peapods materials have been found to possess not only unique structural properties but more importantly novel electronic transport properties as revealed by HRTEM-EELS (high-resolution transmission electron microscopy/electron energy loss spectroscopy), STM/STS and FET (field effect transistors) measurements. We have found that peapods encaging metallo-fullerenes exhibit the band-gap modulation due to the electron transfer from metallofullerenes to carbon nanotubes. Such peapods have been applied to FET with novel device properties.



◆ Current Articles ◆

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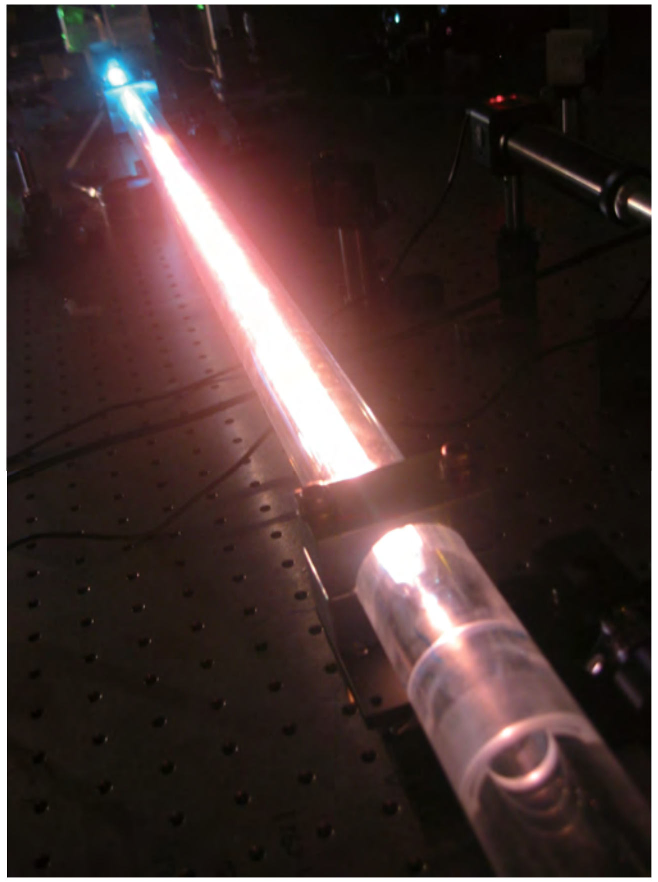
5) L. G. Moura, L. M. Malard, M. A. Carneiro, P. Venezuela, R. B. Capaz, D. Nishide, Y. Achiba, H. Shinohara, and M. A. Pimenta, "*Charge Transfer and Screening Effects in Polyynes Encapsupated inside Single-Wall Carbon Nanotubes*," *Phys. Rev. B,* **80**, 161401-1-4 (2009).



Generation of few-cycle intense laser pulses with a hollow fiber.

光物理化学研究室
Laboratory of Photo-Physical Chemistry

Professor **HISHIKAWA, Akiyoshi**
Associate Professor **OUCHI, Yukio**
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Understanding of light-matter interaction is central in modern chemistry. Spectroscopy utilizing the responses of matter upon the changes in the "wavelength" of light, for example, serves as a versatile tool to probe the state of the matter in various phases, thus contributing the rapid development of material science in the last decades. The advent of laser having a high spatio-temporal coherence has opened a new research field, which additionally uses the "intensity" of light as a new parameter. Recent studies revealed that molecules exposed to an intense laser fields comparable with the intramolecular electric fields show a variety of exotic features, such as the formation of "light-dressed states" and the generation of "attosecond" (10^{-18} s) light pulses.

We are exploring a new research field of chemistry by utilizing the full functions of light. Our laboratory aims (i) to seek and clarify new phenomena in gas, condensed, and solid phases as well as on interfaces by new state-of-art spectroscopic techniques, and (ii) to find new chemical reaction pathways and their control by using strong laser pulses as the reaction fields.

(i) Visualization of ultrafast molecular dynamics by femto- and atto-second pulses

Real-time probing of molecular dynamics is of fundamental importance in understanding of chemical reaction processes and in their control. We are developping novel approaches to visualize ultrafast dynamics of polyatomic molecules with unprecedented time resolution. Time-resolved Coulomb explosion imaging is one such approach, which allows us to discuss how the molecular structure changes during the reaction in real time. When irradiated by intense laser pulses (~10^{15} W/cm^2), molecules usually undergo ultrafast fission process called "Coulomb explosion" after multiple ionization. As may be imagined from the anaology of fireworks in the night sky, the momenta of the resultant fragment ions reflect sensitivly the molecular geometry just before the Coulomb explosion. This has been successfully applied to the ultrafast acetylene-vinylidene isomerization in $C_2D_2^{2+}$, $DCCD^{2+} \leftrightarrow D_2CC^{2+}$.

Another approach being persued in our laboratory utilizes the laser high-order harmonics, which have unique features not avaiable with other sources: i) a high photon energy up to several keV, ii) an extremely short pulse duration in the "attosecond" regime, iii) a high-quality spatiotemporal coherence, and iv) simple and precise synchronization with other laser light sources. Researches using free electron laser (FEL) in extreme ultraviolet are also in progress.

(ii) Chemical reaction control with strong laser reaction fields

Strong preturbation from the intense laser fields changes the landscape of the potential energy surfaces as the interaction is comparable with the Coulombic fields within a molecule. This may be compared with the function of an enzyme in a biosynthetic process, which modifies the potential of the reactants by an electrostatic interation. Flexibility in laser waveform design offers a unique opportunity to seek new reaction pathways and their control. A simple reaction control of polyatomic molecules has been demonstrated in our laboratory by changing the orientation to the direction of laser polazation, which shows that the reaction can be controled by steering electrons in the molecular frame. Basic understanding of the molecular dynamics in intense laser fields is important in further developments.

Dr. Y. Ouchi

(iii) Structural studies of surfaces and interfaces including their dynamics.

Second order nonlinear spectroscopies such as optical second harmonic generation (SHG) and sum-frequency generation (SFG) are powerful tools to study surfaces and interfaces. They are non-destructive and surface- or interface-sensitive up to a submonolayer thickness, and do not require any vacuum condition. With these and other synchrotron based surface analytical techniques, we are investigating the molecular arrangements of organic functional molecules, polymer films, and the surface layer of ionic liquids.

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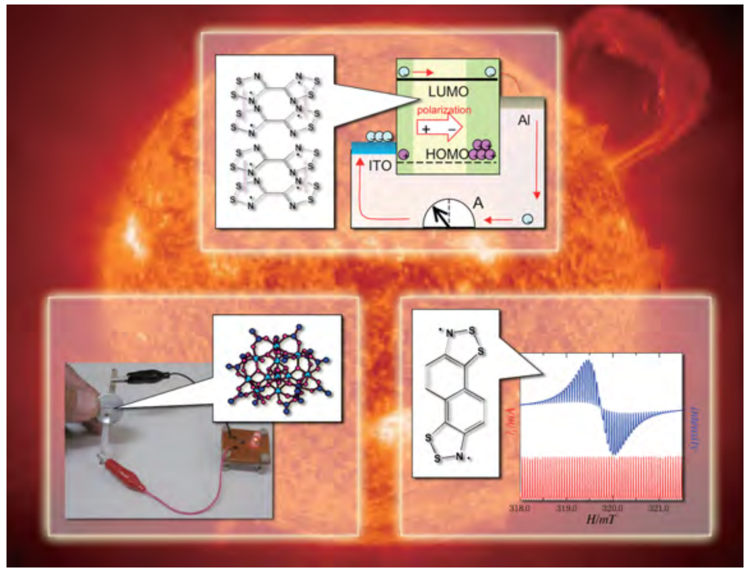
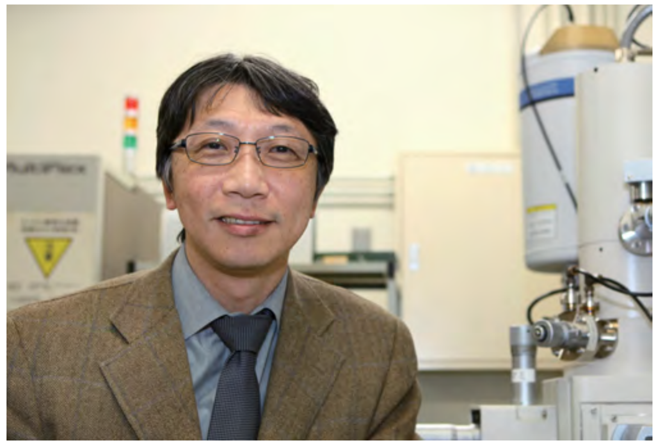


Studies on Molecular Spin Functions

分子機能化学研究室
Laboratory of Advanced Materials

Professor **AWAGA, Kunio**
Associate Professor **MATSUSHITA, Michio M.**
Assistant Professor **YOSHIKAWA, Hirofumi**
http://www.chem.nagoya-u.ac.jp/awagak/



Our modern life is made wealthy by a lot of new materials. It is easy to recognize that we are indebted to chemistry as a major discipline in material sciences. While the needed materials of the times may change year by year, the demand to chemistry for producing new materials would continue. The mission of the laboratory of advanced materials is to research various electronic functions of molecule-base and nano-scale materials. These materials are advantageous in manifestations of controllable properties and quantum phenomena.

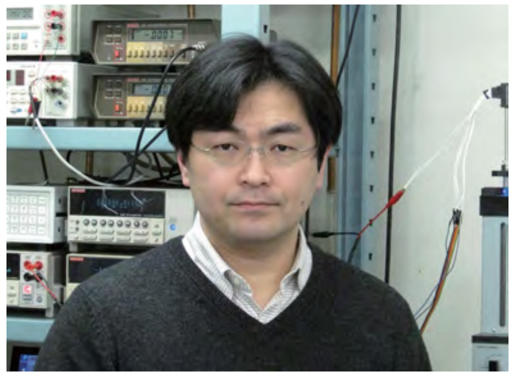
Science and technology of organic/molecular electronic devices have been developed in recent years. This field was founded by researches of molecular semiconductors, metals and superconductors.

Study of molecule-based magnetic materials has also been improved in the last three decades. While such materials had been considered to be far from magnetic substances, discoveries of organic ferromagnets, photomagnets, single-molecule magnets, etc. continued recently. After these fundamental discoveries, organic electronic devises, such as organic light emitting diode, organic solar cell, and organic transistor, have attracted much attention. While the studies on organic conductors, super conductors, and magnets mainly focus on static intermolecular interactions in single crystals, development of organic devises require the integration of several fundamental properties linking with electron and/or energy transfer in molecular thin films fabricated on electrode surfaces. Organic thin films on electrode surface is also interested from the viewpoint of solid state electrochemistry, which is applicable for rechargeable batteries. Nowadays, energy and ecology become serious global issues and organic electronics is expected to be a key technology to achieve the sustainable society. Since the major part of energy resources in the world derive from the solar energy, we are attempting to solve above problems refering the energy conversion systems in nature.

1) Organic Radical Electronics.

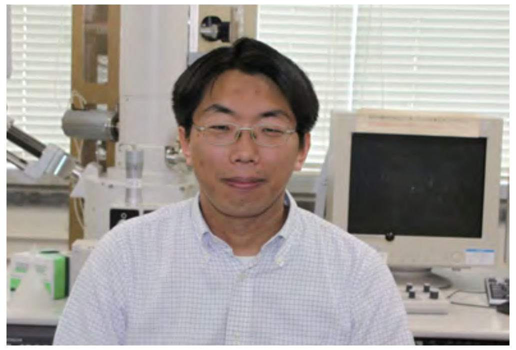
An organic radical has unpaired electron and it can be a conduction electron in the solid state. However, usual organic radical crystal shows an insulating property due to the electron-electron repulsion and/or electron-lattice interaction in the solid state. Inversely, if some trick to remove the cause of the insulating property is introduced in the organic radical crystal, conductivity will be recovered drastically. This is our fundamental strategy on organic radical electronics. We are performing molecular design, chemical syntheses, structural analyses, and physical measurements on these materials, aiming for organic transistors and solar cells driven by completely new principles. We are also developing novel analytical method to reveal the individual property of newly synthesized materials.

2) Molecular Cluster Batteries



Dr. M. M. Matsushita

Recently, much attention has been focused on the creation of new energy systems, such as high-performance rechargeable batteries, as a solution to the global energy and environmental crises. To achieve both high capacity and rapid charging/discharging, we have fabricated rechargeable molecular cluster batteries, in which Mn12 clusters [$Mn_{12}O_{12}(CH_3COO)_{16}(H_2O)_4$] were utilized as a cathode active material. They are well known as single molecule magnets and undergo multi-step redox reactions. The first Mn12 battery exhibited a rechargeable battery performance with a capacity of ca. 90 Ah/kg, while the first discharging capacity was an extremely high value of ca. 250 Ah/kg, which is higher than that of a usual lithium ion battery (180 Ah/kg). To improve these battery performances, we carry out material research on metal complex clusters for cathode active materials. We also develop the methodology of in-situ physical measurements during charging/discharging to determine the valence change in Mn ions and structural change in the cluster.



Dr. H. Yoshikawa

◆ Current Articles ◆

1) H. Fujimoto, M. M. Matsushita, and K. Awaga, "*Electrochemical Field-Effect Transistors of Octathio[8]Circulene Robust Thin Films with Ionic Liquids*," *Chem. Phys. Lett*., **483**, 81-83 (2009).

2) H. Yoshikawa, S. Hamanaka, Y. Miyoshi, K. Kondo, S. Shigematsu, N. Akutagawa, M. Sato, T. Yokoyama, and K. Awaga, "*Rechargeable Batteries Driven by Redox Reactions of Mn12 Clusters with Structural Changes: XAFS Analyses of the Charging/Discharging Processes in Molecular Cluster Batteries*," *Inorg. Chem*., **48**, 9057-9059 (2009).

3) A. Iwasaki, L. Hu, R. Suizu, H. Yoshikawa, and K. Awaga, "*Interactive Radical Dimers in Photoconductive Organic Thin Films*," *Angew. Chem. Int. Ed*., **48**, 4022-4024 (2009).

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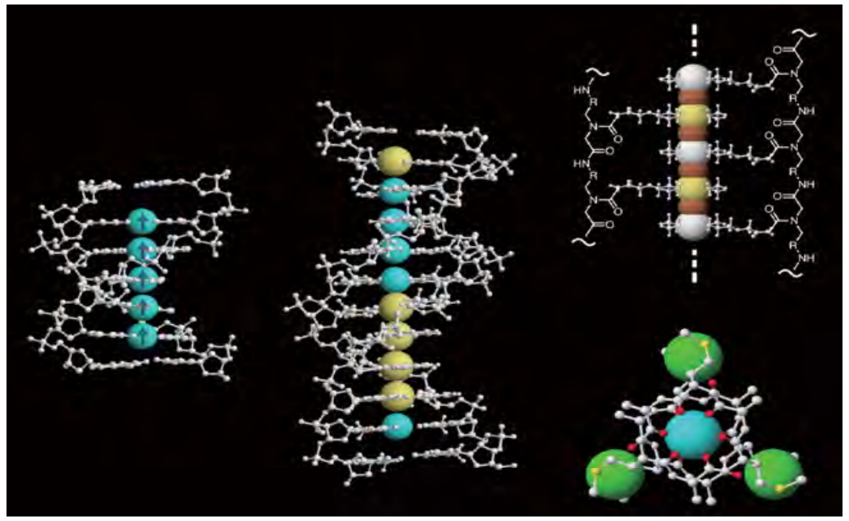

Precise Array of Metal Complexes on Bio-Inspired Templates

分析化学研究室
Laboratory of Analytical Chemistry

The ultimate goal of molecular architecture is to arrange atoms and/or molecules precisely in space and to make it operate efficiently, which is ingredient essential for expansion of nanoscience and nanotechnology. Our laboratory is concerned with developing new types of molecular level architectures to control and influence function and properties by basic ideas and concepts across the traditional branches of the molecular, biomolecular and materials sciences: (1) Bio-inspired supramolecular chemistry (synthesis and functionalization of artificial DNAs and peptides toward nanomaterials and physiological control); (2) Self-assembled molecular architecture involving organic, inorganic and biomolecular components; (3) Interactive control between nanoscale (molelcular) properties and meso- or macroscopic phenomena of materials.

Programming of organic linkage of molecular functions is nothing more or less than to control of the molecular interactions and reactions in three-dimensional space. Biological system generates biopolymers such as DNA, protein, and polysaccharide without any dispersion in "number", "composition", "sequence", and "direction" of the building blocks such as nucleosides, amino acids, and sugars. These molecules organize with highly "selective" and "specific" spatial arrangement. Hence, the structural motifs of biopolymers, which have been optimized by evolution over several billion years, have great potential as functional templates for programmable self-assembly to generate well-defined molecular architectures. More over, because of their easy solid-phase synthesis protocols, oligonucleotides and peptides became of interest as well-defined molecular scaffolds on the multi-nanometer scale. Hence, besides the role in biology, biopolymers have also become of interest in other areas such as nanoscience, nanotechnology, and materials science. From the point of view, we have developed an artificial metallo-DNA, in which hydrogen-bonded base pairing was replaced by metal-mediated one, thereby creating a novel base-pairing motif in duplex DNA. The artificial DNA with metal ligands instead of canonical nucleobases forms double helical structure through metal-mediated base pairing in the presence of appropriate metal ions. Actually, metal ions could be arrayed in the center of the duplex site-selectively along with the programmed sequences of the ligand-type nucleotides. The metal complexes have been quantitatively incorporated into the middle of a DNA duplex, resulting in the formation of a ferromagnetic chain by the line-up of assembled metal complexes stacked within the DNA right-handed helix through thermodynamically stable self-assembly. The strategy for programmable metal arrays can be further extended to quantitative and site-selective array of heterogeneous metal ions. Peptides and other biopolymers are also promising molecules to be functional templates for molecular assembly and could expand design of architectures. We have recently reported discrete one dimensional metal wire formation via duplexation of artificial peptides. This allows one to strongly increase the complexity and diversity of potential molecular arrays under precise control of the sequence and the distance between the individual molecular units. Precise assembly of molecular units is becoming increasingly important as a key strategy to develop functional materials, molecular devices and catalysis. We are continuously creating basic concepts of higher hierarchy control of molecular assembly and functions by innovating strategies to create materials used in other field such as surface sciences, electronic engineering, biosciences, and so on.

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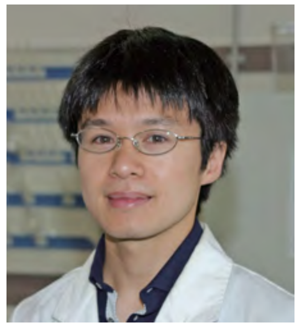
Dr. Y. Yamada



Dr. S. Kawano

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1) Y. Takezawa, W. Maeda, K. Tanaka, and M. Shionoya, "*Discrete Self-Assembly of Iron(III) Ions inside Triple-Stranded Artificial DNA*," *Angew. Chem. Int. Ed.*, **48**, 1081-1084 (2009).

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4) K. Tanaka, T. Tanaka, T. Hasegawa, and M. Shionoya, "*A Closed-packed, Highly-insulating Organic Thin Monolayer on Si(111)*," *Chem. Lett.*, **37**, 440-441 (2008).

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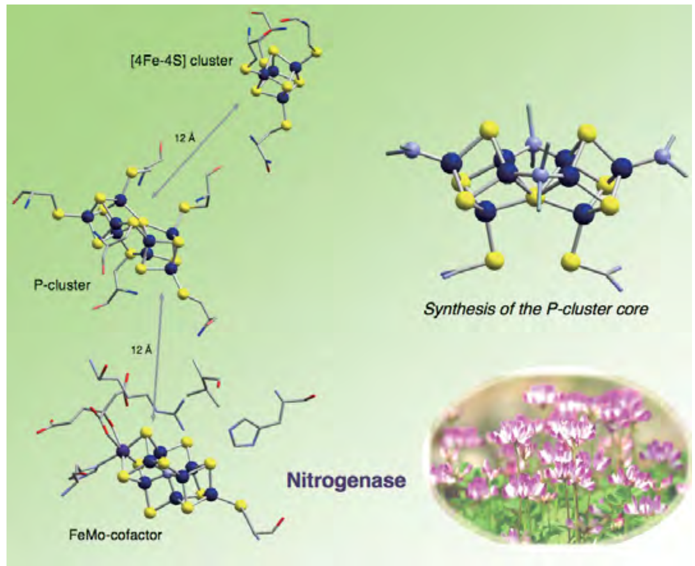
7) K. Tanaka, G. Clever, Y. Takezawa, Y. Yamada, C. Kaul, M. Shionoya, and T. Carell, "*Programmable Self-Asembly of Metal Ions Inside Artificial DNA Duplexes*," *Nature Nanotech.*, **1**, 190-194 (2006).



無機化学研究室
Laboratory of Inorganic Chemistry

Professor **TATSUMI, Kazuyuki**
Associate Professor **OHKI, Yasuhiro**
Assistant Professor **MATSUMOTO, Tsuyoshi**
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Transition metal chemistry and modern inorganic chemistry are rapidly growing and appealing areas of research. Systems of importance include:metalloproteins that play important roles for life, transition metal catalysts that are indispensable to organic syntheses and to environmental benignity, high-temperature superconductors such as copper oxides and niobium chalcogenides, and non-linear optical and magnetic/electronic materials of practical use. These are highly organized inorganic substances with transition metals.

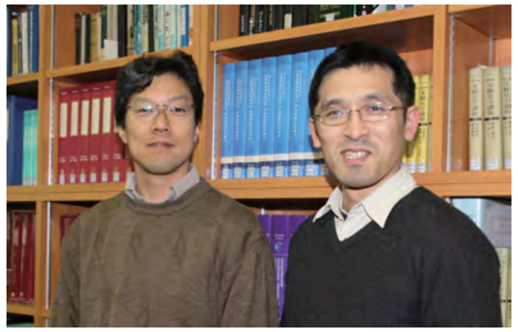
Our research group has been engaged in such emerging areas of inorganic chemistry. Specific interests include structures and reactions that are unique to the active sites of various metallo-enzymes, the development of new, catalytically active organometallic compounds, and the synthesis of inorganic supramolecules relevant to nano-sciences. The research subjects are broad in scope, yet rigorous in approach, encompassing bioinorganic chemistry, organometallic chemistry, materials chemistry, and the interface with other disciplines. We are aiming at a comprehensive and fundamental understanding of the role transision metals play in various inorganic systems, in order to design more efficient syntheses of the target compounds.

In the area of bioinorganic chemistry, our research is focused on metalloenzymes consisting of transition metal clusters with sulfur-donor ligands and/or cystein; nitorogenase, CO dehydrogenase, acetyl-CoA synthase, hydrogenase, molybdoenzyme, and iron-sulfur proteins. We are actively seeking to reproduce the fascinating structures and reactivity of their active sites in vitro. Recently we have successfully synthesized an [8Fe-7S] iron-sulfur cluster, which reproduces the core geometry of P-cluster in nitrogenases. The isolation of this is a breakthrough in synthetic inorganic chemistry, indeed the geometry of the cluster is so unusual among the known naturally occurring iron-sulfur clusters that the structure has been thought to exist only in certain protein environments. We have also achieved synthesis of Mo/Fe/S clusters, the structures of which not yet reproducing exactry, but, are close to the FeMo-co core of nitrogenase.

The second major area of our research is organometallic chemistry. We have been particularly interested in developing coordinatively unsaturated and/or chemically flexible complexes which show high reactivity toward organic/inorganic substrates. Bulky thiolate ligands are often utilized as supporting ligands. A tipical recent example is a novel molybdenum(II) compound with a metal center π-sandwiched by two arylthiolato ligands which features a highly labile aryl-Mo bond. Another specific example is an electron-deficient ruthenium(II) complex with the bulky 2,6-dimesitylphenyl thiolate ligand. The compound serves as precursor to coordinatively unsaturated species in dual capacity; lability of the ipso-carbon and reversible dissociation/association of the thiolate ligand. We have also synthesized a series of S-bridged dinuclear W-Ru complexes that are capable of heterolytic activation of molecular hydrogen under mild conditions, mimicking the function of hydrogenase.

The third major area of research concerns the construction of gigantic nano-scale transition metal sulfide clusters and polymers. We have developed a new synthetic strategy to preformed molybdenum/iron/sulfide cubes, leading to an unprecedented cyclic tricubane and higher clusters. Also synthesized are heterometallic sulfide clusters and polymers showing characteristic non-linear optical properties. Furthermore, use of thiolate/thioether hybrid ligands was found to give large-size iron and nickel clusters and 1-dimensional polymers. An interesting feature of the polymers is their solubility in toluene by virtue of coordination of thioether-type sulfur atoms, and that the polymeric structure is regenerated upon recrystallization.

Modern inorganic chemistry is a realm of unlimited possibility. Our research laboratory deals with nearly all the elements in the periodic table. We endeavor to discover something new, something important, and something to fulfil our intellectual curiosity in chemistry. A group of able and dedicated students, postdocs and young researchers from various countries are responsoble for the excellent research atmosphere of our laboratory, with an international flavor.



Drs. T. Matsumoto (left) and Y. Ohki

◆ Current Articles ◆

1) Y. Ohki, M. Imada, A. Murata, Y. Sunada, S. Ohta, M. Honda, T. Sasamori, N. Tokitoh, M. Katada, and K. Tatsumi, "*Synthesis, Structures, and Electronic Properties of [8Fe-7S] Cluster Complexes Modeling the Nitrogenase P-Cluster*," *J. Am. Chem. Soc.*, **131**, 13168-13178 (2009).

2) T. Hakoyama, K. Niimi, H. Watanabe, R. Tabata, J. Matsubara, S. Sato, Y. Nakamura, S. Tabata, L. Jichun, T. Matsumoto, K. Tatsumi, M. Nomura, S. Tajima, M. Ishizuka, K. Yano, H. Imaizumi-Anraku, M. Kawaguchi, H. Kouchi, and N. Suganuma, "*Host Plant Genome Overcomes the Lack of a Bacterial Gene for Symbiotic Nitrogen Fixation*," *Nature*, **462**, 514-518 (2009).

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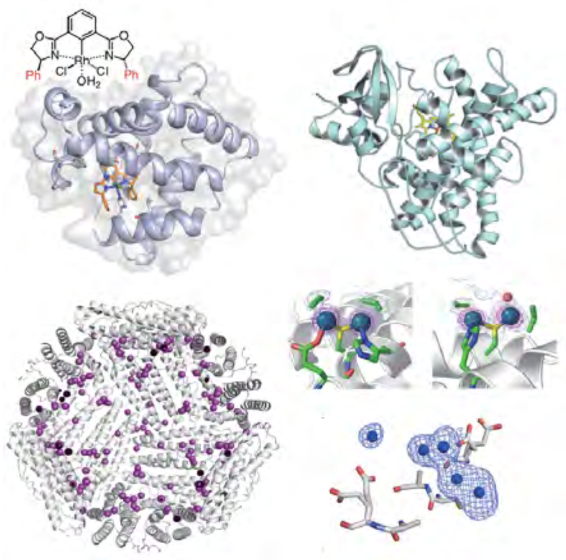

Some structures of metalloenzymes designed by our group

生物無機化学研究室
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Associate Professor **NAKAJIMA,Hiroshi**
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Assistant Professor **FUKUSHIMA, Takashi**
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We have been engaged the design and construction of metallo-enzymes on the basis of molecular mechanisms of metal catalyzed reactions. Followings are the current major projects in the group.

Introduction of peroxygenase and catalase activities in myoglobin (Mb):

To understand the function-structure relationship of hemoproteins and enzymes, we have been working hard to introduce activities of P450, peroxidase, and catalase into myoglobin by designing its heme vicinity. Basic idea of our approach is that we could be able to construct myoglobin-based P-450, peroxidase, and catalase if we really understand the enzymatic reaction mechanisms of the target heme enzymes. Finally, we have successfully prepared a series of myoglobin mutants exhibiting the targeted enzymatic activities. For example, some mutants are able to catalyze sulfoxidation and epoxidation with high enantiomeric selectivity (up to 97%). More importantly, we have characterized the active intermediates responsible for the oxidations.

P450 BSβ:

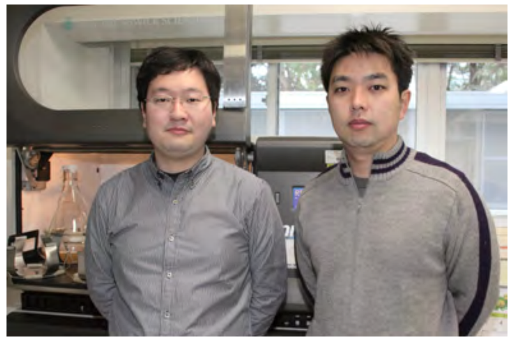
P450BSβ from Bacillus subtilis utilizes hydrogen peroxide for the hydroxylation of fatty acids. The crystal structure of P450BSβ reveals the electrostatic interaction of the guanidium group of Arg-242 located nearby the heme with the terminal carboxyl group of fatty acid. In nature, P450BSβ does not oxidize foreign compounds such as styrene and ethyl benzene due to the lack of the carboxylic acid in the substrate. However, we have recently demonstrated that P450BSβ is able to oxidize a wide variety of foreign compounds such as styrene, and ethylbenzene in the presence of a simple substrate trick, i.e., decoy molecules having a carboxylate group with a series of short alkyl-chain are misrecognised as substrates and P450BSβ starts to catalyze oxidation of non-natural substrates.

Construction of organometalo-enzymes:

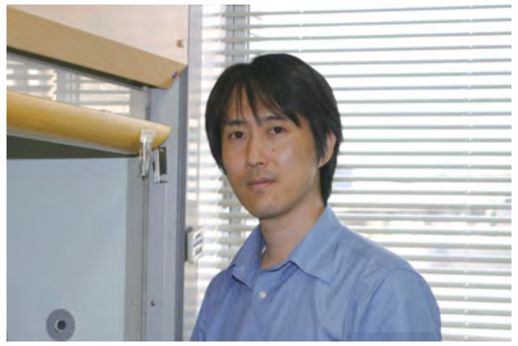
Ferritin (Fr) is an iron storage protein having a spherical structure. Instead of iron ions, we have introduced Pd ions in the apo-ferritin cage and reduced them to prepare a zero-valent palladium cluster and examined its catalytic reduction activity. The palladium clusters catalyzes size-selective olefin hydrogenation because substrates must penetrate into the ferritin cavity through the size restricted channels. The crystal structure of Pd•apo-Fr has been refined to 1.65Å resolution. We have further found that Pd(allyl)•apo-Fr composites catalyze the Suzuki-Miyaura coupling in an aqueous solution.

Functional analysis of a transcriptional regulator for nitrogenase

The conversion of atmospheric nitrogen into a usable form to plants and microorganisms is a part of fundamental processes in the nitrogen circuit on earth. Scientific studies on the nitrogen fixation is classified into two parts in general. Our focus is on the regulation mechanism of the nitrogenases in free-living diazotroph, Azotobacter vinelandii. Spending more than 5 years, we have succeeded in production and purification of VnfA. Spectroscopic and biochemical characterization of the recombinant VnfA in vitro and in vivo show that VnfA function requires iron-sulfur (Fe-S) clusters as a prosthetic group. This is the first example as nitrogenase regulators involving bears a Fe-S cluster. Besides the interesting prosthetic group, we have revealed that VnfA bears unique properties as a nitrogenase transcriptional regulator. Our present concern is in the overall sensing process of the environmental factor; the reaction of the Fe-S cluster with reactive oxygen species and molecular mechanism of how VnfA transduce sensing information into change in the transcription level of nitrogenase genes. Physiological significance of the Fe-S cluster in VnfA also retains to be solved.



Drs. T. Fukushima (left) and O. Shoji



Dr. H. Nakajima

◆ **Current Articles** ◆

1) H. Nakajima, N. Takatani, K. Yoshimitsu1, M. Itoh, S. Aono, Y. Takahashi, and Y. Watanabe, “*The Role of the Fe-S Cluster in the Ssensory Domain of Nitrogenase Transcriptional Activator VnfA from Azotobacter vinelandii*,” *FEBS J*., **277**, 817–832 (2010).

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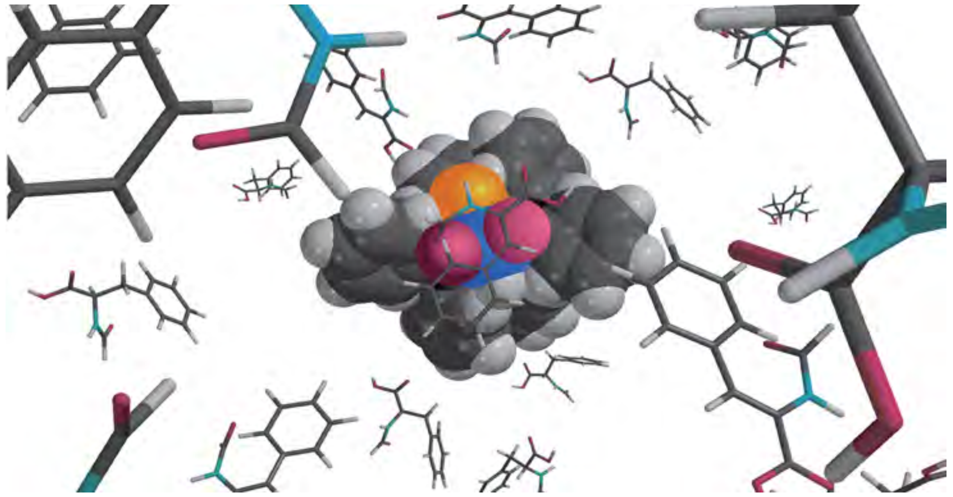

Image of catalysis for the production of amino acids.

有機合成化学グループ

Organic Synthesis Group

Invention or creation of useful materials having valuable properties and functions is indispensable for human being in order to survive in future, sustaining highly civilized societies. Organic chemistry constitutes a basis of such techniques. Technology to supply necessary amounts of any necessary materials at any time is totally required. Starting materials must be converted to target materials, whatever the amount may be, in an environmentally friendly, safe, resource-saving as well as energy-saving method, and also with low E-factor (ratio of the amount of by-products to that of target material) and with high atomic efficiency. It must be prohibited to supply materials to our society by means of any compromising method even in case where it gives us great economical advantages or it is still technologically pre-matured. This is the reason why we are expected to modify the methods from stoichiometric ones to catalytic ones in all the organic conversion. Environmentally friendly and potential usefulness of catalytic methods is excellent, though actual efficiency must be evaluated taking all the other factors into consideration. All the members of this laboratory are engaged in germinal discovery of catalyst and its development, and also in catalytic synthesis of useful organic compounds. And they try to understand quantitatively the mechanism of catalytic reactions on the basis of our profound information on the dependence of general applicability of substrates and catalytic efficiency upon reaction conditions. They also make use of intellectual database together with the methodology which have been accumulated in the field of chemistry, and cooperate with researchers of theoretical chemistry. Effective catalytic reaction is a kind of treasury containing lots of basic scientific information. Clarification of reaction mechanism is academically important, and at the same time it sometimes gives rise to a drastic breakthrough of a new methodology of material production. We are going to develop various catalysts according to the leading guidelines which have been constituted on the basis of information we obtained from a series of our studies concerning mechanism of catalytic reaction, such as bi-functional catalysts of donor-acceptor type, metastable coordination molecule, improvement of electronic and stereo-chemical supplementation in the transition state of reaction, unstabilization of complex of reaction products and catalyst, stabilization of reaction product by self-association, etc. By clarifying the reaction mechanism, we are going to make a useful database for investigation of new reactions of new generation, which will be made use of to synthesize organic compounds with valuable performances.

We are going to advance level of our study step by step in a spiral manner, repeating a cycle of development of catalyst, its application, and then clarification of reaction mechanism.

Professor **KITAMURA, Masato**

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◆ Current Articles ◆

1) M. Kitamura, Y. Takenaka, T. Okuno, R. Holl, and B. Wünsch, "*A New, Efficient and Direct Preparation of TlTp and Related Complexes with TlBH*$_4$," *Eur. J. Inorg. Chem.*, 1188–1192 (2008).
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3) K. Tsuda, K. Miyata, T. Okuno, M. Yoshimura, S. Tanaka, and M. Kitamura, "*Solvent-free One-pot Synthesis of Thallium Complexes of Tp* $[BH(Pz)_3]^-$ *(Pz = pyrazolate) and Its Derivatives*," *Tetrahedron Lett.*, **49**, 2990–2993 (2008).
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5) S. Tanaka, H. Saburi, T. Hirakawa, T. Seki, and M. Kitamura, "*Dehydrative Allylation of Alcohols and Deallylation of Allyl Ethers Catalyzed by* $[CpRu(CH_3CN)_3]PF_6$ *and 2-Pyridinecarboxylic Acid Derivatives. Effect of π-Accepting Ability and COOH Acidity of Ligand on Reactivity*," *Chem. Lett.*, **38**, 188–189 (2009).
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7) M. Tsukamoto and M. Kitamura, "*Reduction by Homogeneous Catalysis or Biocatalysis. In Science of Synthesis, Houben-Weyl Methods of Molecular Transformations*," H. Hiemstra, Ed., Thieme, Stuttgart, Vol. 48: Alkanes, Chapter 48.1.3.6.2 (2009).
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9) S. Tanaka, T. Seki, and M. Kitamura, "*Asymmetric Dehydrative Cyclization of ω-Hydroxy Allyl Alcohols Catalyzed by Ruthenium Complexes*," *Angew. Chem. Int. Ed.*, **48**, 8948–8951 (2009).
10) Y. Ishibashi and M. Kitamura, "*Solid-phase Synthesis of Protected α-Amino Phosphonic Acid Oligomers*," *Chem. Commun.*, 6985–6987 (2009).

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理論化学研究室
Laboratory of Theoretical Chemistry

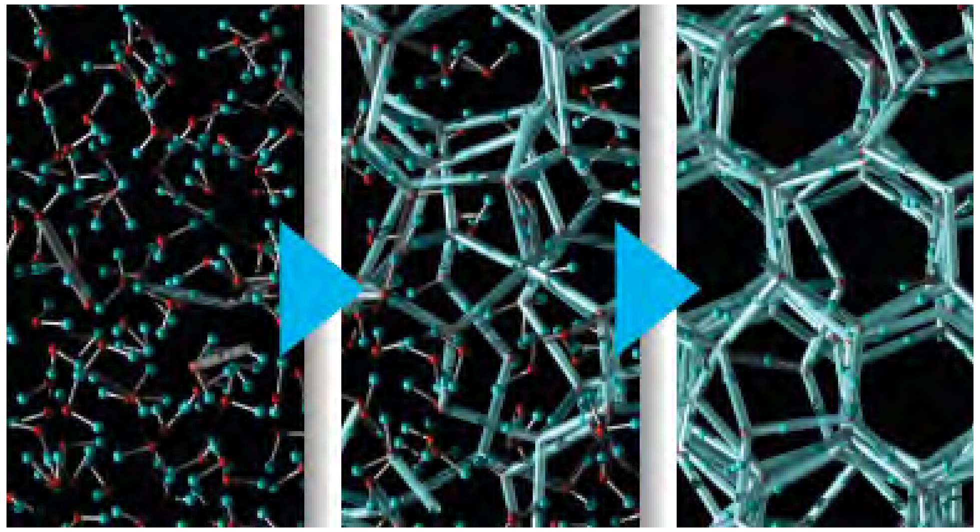
When you watch the earth from space, you will find that its surface is covered with ocean, ice fields at the pole, and clouds, i.e. the three phases of water. Water works as the blood for the ecological system by stabilizing the surface temperature of the earth, dissolving nutritions, and transporting materials.

Water has many anomalous properties, but we are too familiar with water to be aware of its anomalies: water expands when it cools, ice floats on the water, water has very high boiling point for small molecular size, there are more than 10 different ice crystal structures, etc. Life emerged and evolved in such an aqueous environment by fully utilizing its anomalies. Most of these anomalies originate not in the property of single water molecule but in the geometry and topology of the 3-dimensionally interconnected hydrogen bond network of water.

Our missions are to explore and explain these anomalies and functionality of water in terms of molecular dynamics and mechanics. We have been exploring the dynamics and structure of the hydrogen bond network of water and aqueous solutions by computer simulations and finding hidden order and rules behind the complicated transient network.

Our subjects of research are wide-ranging: freezing dynamics of liquid water, proton transfer reactions in water, ice, and aqueous solutions, melting dynamics of ice, crystallization of methane hydrate, cavitation in water, polyamorphism in supercooled liquid water, reactivity of supercritical water, hydration of biomolecules, chemical reactions in aqueous solutions, etc.

Network-forming feature of water plays the crucial role in all of these properties. Knowledges on the hydrogen bond network of water are applicable to other network-forming materials such as silicon, silica, certain kind of polymer, etc. It is also an our subject to find the anomalies of these network-forming materials and give a unified explanation.



Snapshots of crystallization process of water.

◆ Current Articles ◆

1) M. Matsumoto, “*Why does Water Expand when it Cools?*,” *Phys. Rev. Lett.*, **103**, 017801 (2009).
2) M. Matsumoto, A. Baba, and I. Ohmine, “*Network Motif of Water*,” *AIP Conference Proceedings*, **982,** (1): 219-222 (2008).
3) M. Matsumoto, A. Baba, and I. Ohmine, “*Topological Building Blocks of Hydrogen Bond Network in Water*,” *The Journal of Chemical Physics*, **127,** (13): 134504 (2007).
4) M. Matsumoto, “*Relevance of Hydrogen Bond Definitions in Liquid Water*,” *The Journal of Chemical Physics*, **126,** (5): 054503 (2007).
5) M. Matsumoto, S. Saito, and I. Ohmine, “*Molecular Dynamics Simulation of the Ice Nucleation and Growth Process Leading to Water Freezing*,” *Nature*, **416,** (6879): 409-413 (2002).

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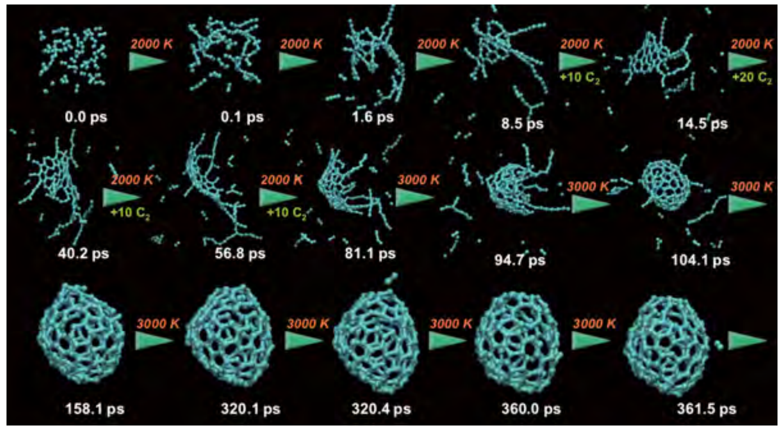
量子化学グループ
Quantum Chemistry Group

Our group is applying quantum chemical methods in nanomaterials design by devising practical strategies aimed at overcoming the problem of dimensional complexity associated with large molecular systems. Focus of our efforts in "applied quantum chemical materials design" is the theoretical exploration of formation mechanisms, dynamics, reactions, spectroscopic properties, and functionality of nanocarbon (fullerenes, nanopeapods, nanographenes, large-scale π-conjugated organic polymers) and nanobio (DNA and metalated DNA (M-DNA) computing, nanobiosensors, transition-metal free organic catalyst) materials. In particular we employ computationally economical methods such as density functional tight binding (DFTB), resolution-of-identity (RI) DFT, RI-MP2, and ONIOM, emphasizing the integrated molecular orbital-molecular orbital (IMOMO) approach, and facilitate ONIOM during molecular dynamics (ONIOM/MD) simulations. The IMOMO version of ONIOM has been widely used in the computational chemistry



QM/MD simulation following the "shrinking hot giant" road of dynamic fullerene self-assembly

community, and it can be expected that ONIOM/MD will be of even greater use as quantum chemical molecular dynamics (QM/MD) simulations have become increasingly popular in recent times.

More specifically, our research aims to

1) formulate a feasible methodology to employ quantum chemical molecular structure methodology in high-dimensional, rugged PESs systems, combining DFTB- and ONIOM(DFT:DFTB)-based QM/MD simulations followed by transition path sampling and high-level quantum chemical energy calculations and evaluate the quality of such simulations,

2) understand the *principles* of nanocarbon and nanobio structure self-assembly,

3) reliably compute experimentally accessible properties (IR, Raman, UV spectra) for novel compounds and elucidate the relationship between structure and intended functionality.

The term "nanobio materials design" is loosely used here and encompasses both concepts of "interface between the natural and the man-made" as well as "synthetic biology for nanotechnology". The common factor shared by high-temperature carbon chemistry and low-temperature biochemistry is (besides their large molecular size domains) the occurance of PESs rough on the scale of thermal energies k_bT introduced by the breaking and formation of C-C covalent bonds in case of the former, and hydrogen-bond fluctuation in case of the latter chemistries. For high-level reaction energetics as needed for instance in the study of catalysis reaction energy pathways we are using an extrapolation method similar to Curtiss' G4 method for both ground and electronically excited states.

◆ Current Articles ◆

1) Y. Ohta, A. J. Page, Y. Okamoto, S. Irle, and K. Morokuma, "*Quantum Chemical Molecular Dynamics Simulation of Single-Walled Carbon Nanotube Cap Nucleation on an Iron Particle,*" *ACS Nano,* **3**, 3413-20 (2009).

2) E. Malolepsza, Y.-P. Lee, H. A. Witek, S. Irle, C.-F. Lin, and H.-M. Hsieh, "*Comparison of Geometric, Electronic, and Vibrational Properties for all Pentagon/Hexagon-Bearing Isomers of Fullerenes C38, C40, and C42,*" *Int. J. Quant. Chem.*, **109**, 1999 (2009).

3) S. C. Xu, D. G. Musaev, S. Irle, and M. C. Lin, "*Quantum Chemical Prediction of Reaction Pathways and Rate Constants for Dissociative Adsorption of CO and CO2 on Defective Graphite (0001) Surfaces,*" *J. Phys. Chem. C,* **113**, 18772-18777 (2009).

4) A. Ito, Y. Wang, S. Irle, K. Morokuma, and H. Nakamura, "*Molecular dynamics simulation of hydrogen atom sputtering on the surface of graphite with defect and edge,*" *J. Nucl. Mater.*, **390**, 183-187 (2009).

5) S. Irle, G. Zheng, Z. Wang, and K. Morokuma, "*The C60 Formation Puzzle Solved: QM/MD Simulations Reveal the Shrinking Hot Giant Road of the Dynamic Fullerene Self-Assembly Mechanism,*" *feature paper in J. Phys. Chem. B,* **110**, 14531-14545 (2006).

Associate Professor **TAKAGI, Hideo D.**

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物理無機化学サブグループ

Physical Inorganic Chemistry Sub-Group

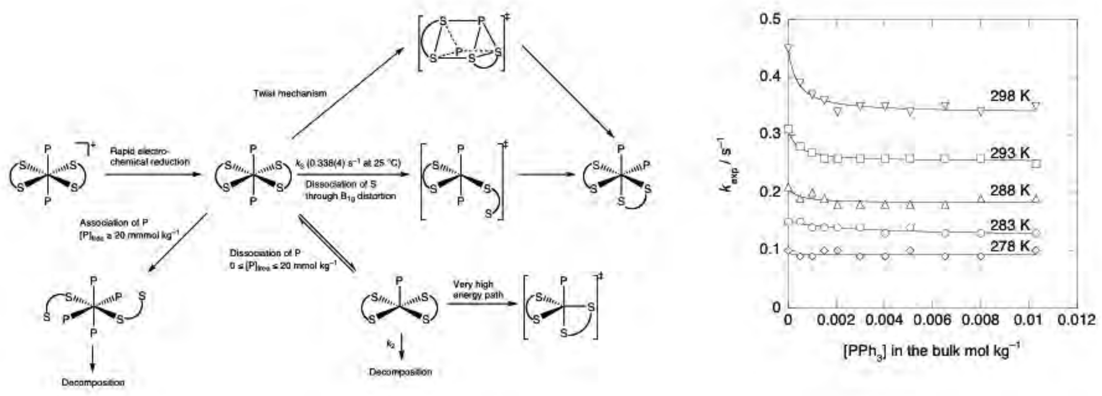
Research projects of this laboratory are related not only to the creation of new materials but to the highly intellectual activity of human beings, the pursuit of principles that govern the Chemical/Natural phenomena. For this purpose, Physical Inorganic Chemistry Laboratory at Nagoya University provides excellent education program with the emphasis on physical theory and classical experimental techniques necessary to implement precise chemical analyses such as equilibrium and kinetic measurements in solution.

It should be noted that a strong background of Physical Inorganic Chemistry, especially symmetry considerations for chemical processes on the basis of Group theory and Spectroscopy enables us to analyze not only the geometries of chemical species including the reaction intermediates but also reaction pathways of metal complexes with different coordination geometries. The followings are only a few of the achievements born out of the research projects conducted in this Laboratory.

(1) Factors that control biologically-important Gated electron transfer processes has been revealed: our intensive research of the reactions involving simple copper (II)/(I)-polypyridine complexes revealed that the Gating phenomenon is observed when (1) the direct (concerted) ET between the ground state species is non-adiabatic, and (2) a low energy CT band is provided by the " uneven" structural change, and (3) the change in the coordination geometry around the Cu(II) complexes is governed by the Symmetry Rules and the Principle of the Least Motion. Such findings are important not only to understand the efficiency of biological ET reactions but also to design efficient artificial catalysts.

(2) Further understanding of *Trans Influence* and *Trans Effect* has been put forward: kinetic studies of the thermal *trans* to *cis* isomerization reactions of various cobalt(III)/(II) and Ru(III)/Ru(II) complexes with ligands containing phosphorous/sulfur donor atoms revealed that the reactions proceed through the intramolecular twist mechanism accompanied by the ligand dissociation of a B_{1g} mode. It was also found that the kinetic *trans effect* is governed by the combination of π-acidity of P-ligand and the electron sponge effect of the spectator ligand.

(3) Very slow solvent reorganization in Ionic Liquids can be utilized for the separation of complicated reaction steps: *cis* to *trans* isomerization of azobenzene derivatives proceeds via a polrarized intermedeiate, which was significantly retarded by the very slow reorganization process of the cationic and anionic components of ionic liquids. Such a slow reorganization of cationic and anionic components can be used to separate a reaction step involving polarized intermediate by using ionic liquids as reaction media.



Mechanism of the EC Reaction involving Ru(III)/(II)-dtc complexes

◆ Current Articles ◆

1) Akira Hashimoto, Hiroshi Yamaguchi, Takayoshi Suzuki, Kazuo Kashiwabara, Masaaki Kojima, and Hideo D. Takagi, "*Preparation, Crystal Structures, and Spectroscopic and Redox Properties of Nickel(II) Complexes Containing Phosphine-(A mine or Quinoline)-Type Hybrid Ligands and a Nickel(I) Complex Bearing 8-(Diphenylphosphino)quinoline*," *European Journal of Inorganic Chemistry, in press*.

2) Kaori Aoki, Toshimitsu Goshima, Yohei Kozuka, Yukiko Kawamori, Noboru Ono, Yoshio Hisaeda, Hideo D. Takagi, and Masahiko Inamo, "*Electron transfer reaction of porphyrin and porphycene complexes of Cu(II) and Zn(II) in acetonitrile*," *Dalton Trans*., 119-125 (2009).

3) Chiaki Miyamato, Kazunori Suzuki, Satochi Iwatsuki, Masahiko Inamo, Hideo D. Takagi, and Koji Ishihara, "*Kinetic Evidence for high reactivity of 3-nitrophenylboric acid compare to its conhugate boronate ino in reactions with ethylene and propylene glycols*," *Inorg. Chem*., **47**, 1417-1419 (2008).

4) Satoshi Iwatsuki, Shihoko Nakajima, Masahiko Inamo, Hideo D. Takagi, and Koji Ishihara, "*Which Is Reactive in Alkaline Solution, Boronate Ion or Boronic Acid ? - Kinetic Evidence for Reactive Trigonal Boronic Acid in Alkaline Solution -*," *Inorg. Chem*., **46**, 354-356 (2007).

5) Sumitaka Itoh, Kyoko Noda, Ryouhei Yamane, Nobuyuki Kishikawa, and Hideo D. Takagi, "*First Investigation at Elevated Pressures to Confirm Exact Nature of the Gated Electron Transfer Systems: Volume Profiles of the Gated Reduction Reaction and Non-Gated Reverse Oxidation Reaction Involving* $[Cu(dmp)_2(solvent)]^{2+}/[Cu(dmp)_2]^{+}$ *Couple (dmp = 2,9-dimethyl-1,10-phenanthroline)*," *Inorg. Chem*., **46**, 1419-1425 (2007).

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FISCHER, Berthold
Associate Professor/ Manager
KATO, Kiyonori

G-COEオフィス
Global COE Office

Drs.
K. Kiyonori (left)
and B. Fischer

To establish a vibrant global environment for education and research and foster young researchers who can independently play an active role in international research, we promote our graduate school to high caliber international graduate students, offer lectures to provide English literacy education to our Japanese students, and collaborate with overseas graduate schools. The Global COE Office supports these programs and projects, and takes care of international graduate students.

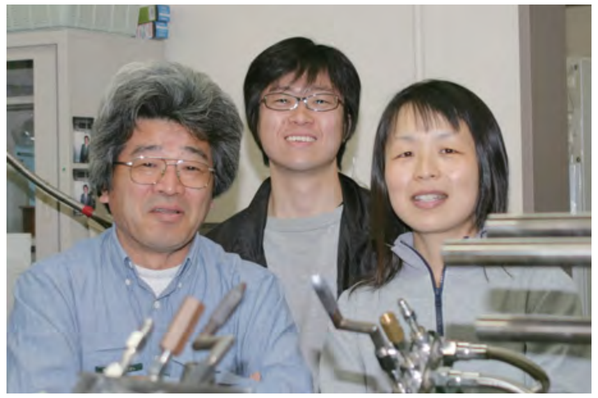
ガラス工作室
Glass Shop

Head Techical Staff **NODA, Toshiaki**
Techical Staff **NATSUME, Hideko**
Techical Staff **OKAMOTO, Hisakazu**
http/c60.chem.nagoya-u.ac.jp/~glass/index.html

Glass Shop belongs to the Technical Center of Nagoya University and is fully equipped for support conditions indispensable to education and research.

In recent years, more requests for large equipment and precision instruments have come to the Shop. There have also been many for making vacuum devices, cryogenic apparatuses, and solvent distillation apparatuses. To design and make this equipment effectively, it is important to understand the kind of research that is being conducted within the department and to appreciate experimental design, particularly in response to conditions of low temperature and vacuum. Meeting these demands, such as designing glass bellows, or how to get glass and metal to fit into each other, etc. has required highly advanced technical skills and broad knowledge of necessary skills. We are fortunate in that we have this expertise available to us. To meet these requests, a large caliber glass lathe, a large electric furnace, precision grinders (an outside grinder, an inside grinder, and a diamond surface polishing machine) have been acquired. The equipment and technical skills are of the highest caliber in glass shops nationwide.

By way of example, a solvent distillation apparatus capable of producing samples of high purity (patent publication 2000-126401) was developed in our glass shop. The design incorporates special glass flanges designed by the staff, and the water content of anhydrous solvents was reduced by 1/20 when compared to another solvent distillation apparatus.



(from left)T. Noda, H. Okamoto, H. Natsume

The evacuation apparatus usable also for introducing inert gas (patent publication 2000-130124) is used in experiments that require the use of substances that are unstable in air, and is indispensable for deaeration of chemical samples and the introduction of inert gas. The apparatus makes it easy to deareate and introduce inert gas with a cock designed for both vacuum and pressure work, and was developed by the staff.

Moreover, in conjunction with the Nano-Structured Materials Laboratory, the Shop developed a "method and apparatus for manufacturing fullerene and carbon nanotubes" that has been submitted for a patent (patent application number 2002-372004).

As previously mentioned, the Shop makes a variety of highly specialized glass equipment that is indispensable to the many fields of chemistry. The Shop also offers technical guidance in response to the demands from laboratories.

The Shop received the award for technical achievement from the Chemical Society of Japan and a prize from the Japan Society for Analytical Chemistry for its considerable achievements.

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Ngagoya University
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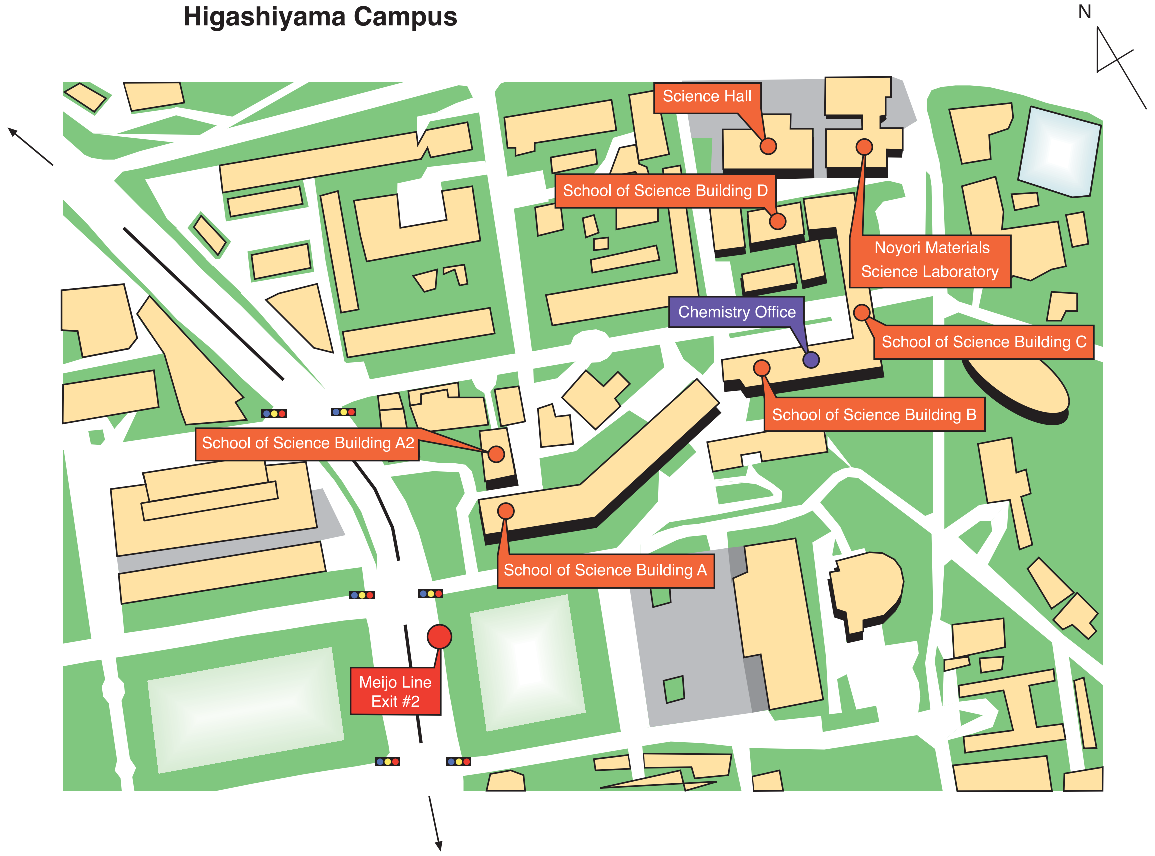

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