Institute for Molecular Science

annual review

2020

Published by
Institute for Molecular Science
National Institutes of Natural Sciences
Myodaiji, Okazaki 444-8585, Japan
Phone: +81-564-55-7418 (Secretary Room)
Fax: +81-564-54-2254 (Secretary Room)
URL: https://www.ims.ac.jp/en/

Editorial Committee 2020

Institute for Molecular Science (IMS) is one of the world's core research facilities for molecular science and is also a center for inter-university joint research in Japan. It sets an extremely wide range of research goals, from understanding the behavior of individual molecules to that of collective molecular systems. These molecular systems have close relation to scientific understanding of biology, engineering and space sciences. Currently, IMS is engaged in six (four plus two) areas of research: Theoretical and computational molecular science, Photo-molecular science, Materials molecular science, and Life and coordination-complex molecular science. Research Center of Integrative Molecular Systems (CIMoS) has started from April 2013 to develop the highly functional molecular systems such as molecular rhythms, sensing and response, and even self-repair. Starting from April 2017, Center for Mesoscopic Sciences (CMS) is launched to develop innovative methodology of studying mesoscopic molecular systems, covering from theoretical methods to leading-edge measurement methods. Division of Advanced Molecular Science is launched to promote outstanding research example of Molecular Science from April 2018. From April 2019, Division of Research Innovation and Collaboration is launched to strengthen the tie between the social activities. In addition to these research divisions, IMS has three research facilities; UVSOR Synchrotron Facility, Instrument Center facilitated with various molecular detectors, and Equipment Development Center. IMS also operates the Research Center for Computational Science, jointly with National Institute for Physiological Sciences and National Institute for Basic Biology in the same campus. From April 2018, Exploratory Research Center on Life and Living Systems (ExCELLS) is launched directly under the National Institutes of Natural Sciences to advance the activity of Okazaki Institute for Integrative Bioscience (OIIB).

Annual Review 2020 is a summary of research activities performed in IMS during September 2019–August 2020. Individual research groups at IMS are making steady progress in basic research on molecular structures, reactions and functions demonstrating "novel molecular capabilities," as reported in this Review. In addition to these individual activities, IMS conducts the six special programs in the institute basis: (i) Emerging innovation in computational science of energy from post-K computer (ended in March 2020); (ii) Development of cold-atom based quantum simulators and their applications to quantum computing within the framework of Japan's flagship program on quantum sciences and technologies "Q-LEAP" by MEXT (2018–2028); (iii) Nano science project, called Nanotechnology Platform; (iv) Inter-University Network for Common Utilization of Research Equipments; (v) Project on trans-hierarchical studies of materials and biological systems with molecular observations, as a joint program of NINS; (vi) IMS runs several international collaboration programs and also owns an internship program for young scientists: Institute for Molecular Science International Internship Program (IMS-IIP). IMS-IIP provides the opportunity of internship for young researchers (e.g., master's and doctoral students, postdoctoral researchers and young faculty members of MOU partners) from overseas to stay in IMS laboratories.

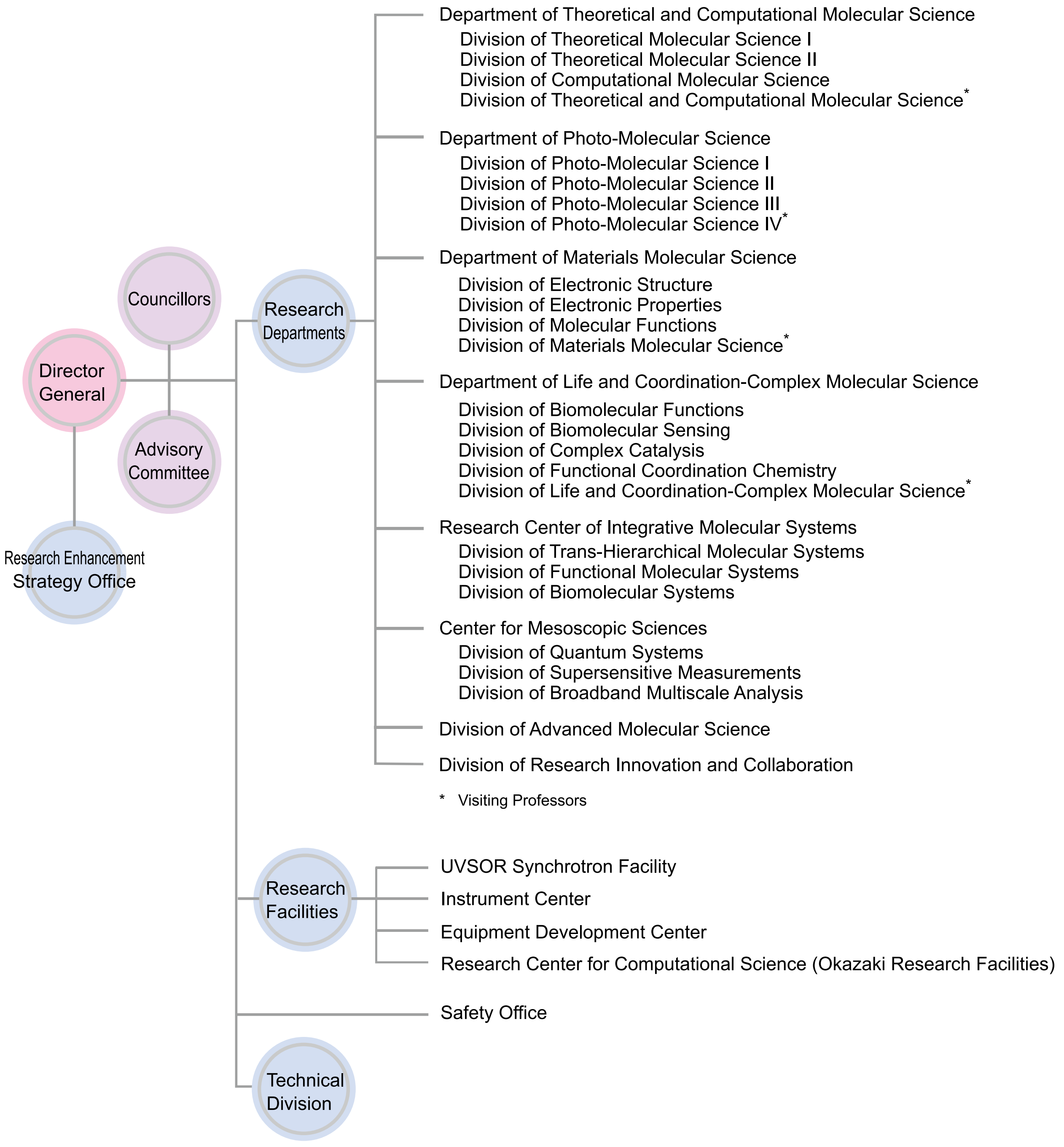
IMS will continue to contribute to lead the Molecular Science together with many young promising and well-established senior scientists. This institute has been most benefited with your constant support and we do expect your further support and advice for creating this new era of molecular science.

September, 2020

Maki Kawai

KAWAI, Maki
Director General, Institute for Molecular Science

ORGANIZATION



- Councillors
- Director General
- Advisory Committee
- Research Enhancement Strategy Office
- Research Departments
  - Department of Theoretical and Computational Molecular Science
    - Division of Theoretical Molecular Science I
    - Division of Theoretical Molecular Science II
    - Division of Computational Molecular Science
    - Division of Theoretical and Computational Molecular Science*
  - Department of Photo-Molecular Science
    - Division of Photo-Molecular Science I
    - Division of Photo-Molecular Science II
    - Division of Photo-Molecular Science III
    - Division of Photo-Molecular Science IV*
  - Department of Materials Molecular Science
    - Division of Electronic Structure
    - Division of Electronic Properties
    - Division of Molecular Functions
    - Division of Materials Molecular Science*
  - Department of Life and Coordination-Complex Molecular Science
    - Division of Biomolecular Functions
    - Division of Biomolecular Sensing
    - Division of Complex Catalysis
    - Division of Functional Coordination Chemistry
    - Division of Life and Coordination-Complex Molecular Science*
  - Research Center of Integrative Molecular Systems
    - Division of Trans-Hierarchical Molecular Systems
    - Division of Functional Molecular Systems
    - Division of Biomolecular Systems
  - Center for Mesoscopic Sciences
    - Division of Quantum Systems
    - Division of Supersensitive Measurements
    - Division of Broadband Multiscale Analysis
  - Division of Advanced Molecular Science
  - Division of Research Innovation and Collaboration

* Visiting Professors

- Research Facilities
  - UVSOR Synchrotron Facility
  - Instrument Center
  - Equipment Development Center
  - Research Center for Computational Science (Okazaki Research Facilities)
- Safety Office
- Technical Division

COUNCIL

KAWAI, Maki	**Director General**

Senior Scientific Advisors

NAKAJIMA, Atsushi	Professor, Keio University
PETEK, Hrvoje	Professor, University of Pittsburgh

Councillors

KIKUCHI, Noboru	President, Toyota Central R&D Labs., Inc.
TAKIGAWA, Masashi	Professor, The University of Tokyo
OSAKABE, Nobuyuki	General Manager, Hitachi, Ltd.
MATSUMOTO, Yoshiyasu	Fellow, Toyota Physical and Chemical Research Institute
TANG, Ching Wan*	Chair Professor, The Hong Kong University of Science and Technology
MICHL, Josef*	Professor, University of Colorado Boulder

The Council is the advisory board for the Director General.
* Two of the councillors are selected among distinguished foreign scientists.

Distinguished Consultants

NAKAMURA, Hiroki	Professor Emeritus, Institute for Molecular Science, The Graduate University for Advanced Studies
OHMINE, Iwao	Professor Emeritus, Institute for Molecular Science, The Graduate University for Advanced Studies

Advisory Committee

AKIYOSHI, Kazunari	Professor, Kyoto University
FUJII, Masaaki	Professor, Tokyo Institute of Technology
FUKUI, Kenichi	Professor, Osaka University
HAGA, Masaaki	Professor Emeritus, Chuo University
KANODA, Kazushi	Professor, The University of Tokyo
MURAKOSHI, Kei	Professor, Hokkaido University (Vice chair)
NAKAI, Hiromi	Professor, Waseda University
SHINOKUBO, Hiroshi	Professor, Nagoya University
SODEOKA, Mikiko	Chief Scienntist, RIKEN
TANIMURA, Yoshitaka	Professor, Kyoto University
AKIYAMA, Shuji	Professor, Institute for Molecular Science (Chair)
EHARA, Masahiro	Professor, Institute for Molecular Science
IINO, Ryota	Professor, Institute for Molecular Science
ISHIZAKI, Akihito	Professor, Institute for Molecular Science
KATO, Koichi	Professor, Institute for Molecular Science
KERA, Satoshi	Professor, Institute for Molecular Science
OKAMOTO, Hiromi	Professor, Institute for Molecular Science
SAITO, Shinji	Professor, Institute for Molecular Science
UOZUMI, Yasuhiro	Professor, Institute for Molecular Science
YAMAMOTO, Hiroshi	Professor, Institute for Molecular Science
YOKOYAMA, Toshihiko	Professor, Institute for Molecular Science

Administration Bureau

TAKEDA, Kazuhiko	Director, Okazaki Administration Office
	Director, General Affairs Department
KUBOTA, Manabu	Director, Financial Affairs Department
	Head, Procurement Division
KUWABARA, Hiroaki	Head, General Affairs Division
HIROOKA, Nobuyuki	Head, International Relations and Research Cooperation Division
SASABE, Shin	Head, Financial Affairs Division
MORI, Akira	Head, Facilities Division

Professor Emeritus

HIROTA, Eizi	Professor Emeritus, The Graduate University for Advanced Studies
KIMURA, Katsumi	Professor Emeritus, Japan Advanced Institute of Science and Technology
YOSHIHARA, Keitaro	Professor Emeritus, The Graduate University for Advanced Studies
IWAMURA, Hiizu	Professor Emeritus, The University of Tokyo
SAITO, Shuji	Professor Emeritus, The Graduate University for Advanced Studies
IWATA, Suehiro	Professor Emeritus, The Graduate University for Advanced Studies
KITAGAWA, Teizo	Professor Emeritus, The Graduate University for Advanced Studies and Visiting Researcher, The University of Hyogo
KOBAYASHI, Hayao	Professor Emeritus, The Graduate University for Advanced Studies
NAKAMURA, Hiroki	Professor Emeritus, The Graduate University for Advanced Studies
NISHI, Nobuyuki	Professor Emeritus, The Graduate University for Advanced Studies
YAKUSHI, Kyuya	Professor Emeritus, The Graduate University for Advanced Studies
URISU, Tsuneo	President, NANORUS Co., Ltd.
NAGASE, Shigeru	FIFC Research Fellow, Fukui Institute for Fundamental Chemistry, Kyoto University
HIRATA, Fumio	Fellow, Toyota Physical and Chemical Research Institute
TANAKA, Koji	Specially Appointed Professor, Institute for Integrated Cell-Material Sciences, Kyoto University
KUWAJIMA, Kunihiro	Professor Emeritus, The Graduate University for Advanced Studies and The University of Tokyo
OHMINE, Iwao	Professor Emeritus, The Graduate University for Advanced Studies
KOSUGI, Nobuhiro	Director, Institute of Materials Structure Science, High Energy Accelerator Research Organization
WATANABE, Yoshihito	Director, Integrated Research Consortium on Chemical Sciences
OKAZAKI, Susumu	Specially Appointed Professor, The University of Tokyo

GROUP LEADERS

Theoretical and Computational Molecular Science

SAITO, Shinji
Professor
p. 10

MINAMITANI, Emi
Associate Professor
p. 12

ISHIZAKI, Akihito
Professor
p. 14

EHARA, Masahiro
Professor
p. 16

OKUMURA, Hisashi
Associate Professor
p. 18

FUJITA, Takatoshi
Research Associate
Professor
p. 20

OKAZAKI, Kei-ichi
Research Associate
Professor
p. 22

Photo-Molecular Science

OHMORI, Kenji
Professor
p. 28

KERA, Satoshi
Professor
p. 30

KATOH, Masahiro
Project Professor
p. 32

TAIRA, Yoshitaka
Associate Professor
p. 34

TANAKA, Kiyohisa
Associate Professor
p. 36

Materials Molecular Science

YOKOYAMA, Toshihiko
Professor
p. 44

SUGIMOTO, Toshiki
Associate Professor
p. 46

HIRAMOTO, Masahiro
Professor
p. 48

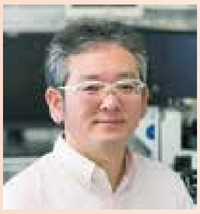
NISHIMURA, Katsuyuki
Associate Professor
p. 50

KOBAYASHI, Genki
Associate Professor
p. 52

Life and Coordination-Complex Molecular Science

AONO, Shigetoshi
Professor
p. 58

KATO, Koichi
Professor
p. 60



IINO, Ryota
Professor
p. 62

KURIHARA, Kensuke
Research Associate Professor
p. 64

UOZUMI, Yasuhiro
Professor
p. 66

MOMIYAMA, Norie
Associate Professor
p. 68

KUSAMOTO, Tetsuro
Associate Professor
p. 70

SEGAWA, Yasutomo
Associate Professor
p. 72

Research Center of Integrative Molecular Systems

AKIYAMA, Shuji
Professor
p. 76

KOGA, Nobuyasu
Associate Professor
p. 78

KURAMOCHI, Hikaru
Associate Professor
p. 80

YAMAMOTO, Hiroshi
Professor
p. 82

Center for Mesoscopic Sciences

OKAMOTO, Hiromi
Professor
p. 86

Division of Advanced Molecular Science

FUJITA, Makoto
Distinguished Professor
p. 90

KIMURA, Shin-ichi
Professor
(Cross Appointment)
p. 92

TAKAYA, Hikaru
Associate Professor
(Cross Appointment)
p. 94

Division of Research Innovation and Collaboration

TAIRA, Takunori
Project Professor
p. 98

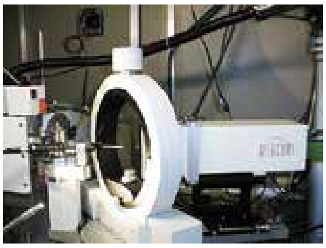
RESEARCH FACILITIES

UVSOR Synchrotron Facility p. 102

KERA, Satoshi
Director

Instrument Center p. 104

YOKOYAMA, Toshihiko
Director



Equipment Development Center p. 106

YAMAMOTO, Hiroshi
Director

Research Center for Computational Science p. 107

EHARA, Masahiro
Director

PERSONNEL CHANGES

Moving In

Nov. 1, 2019	Dr. SHITADE, Atsuo joined IMS as an Assist. Prof. in the Department of Theoretical and Computational Molecular Science
Dec. 1, 2019	Dr. TAKAYA, Hikaru joined IMS as an Assoc. Prof. (Cross Appointment) in the Division of Advanced Molecular Science
Dec. 16, 2019	Dr. MATSUOKA, Ryota joined IMS as an Assist. Prof. in the Department of Life and Coordination-Complex Molecular Science
Jan. 1, 2020	Dr. OKUMURA, Shintaro joined IMS as an Assist. Prof. in the Department of Life and Coordination-Complex Molecular Science
Mar. 1, 2020	Dr. OHTSUKA, Naoya joined IMS as an assist. prof. in the Department of Life and Coordination-Complex Molecular Science
Apr. 1, 2020	Dr. SEGAWA, Yasutomo joined IMS as an Assoc. Prof. in the Department of Life and Coordination-Complex Molecular Science
Apr. 1, 2020	Dr. KURAMOCHI, Hikaru joined IMS as an Assoc. Prof. in Research Center of Integrative Molecular Systems
Apr. 1, 2020	Dr. TAIRA, Yoshitaka joined IMS as an Assoc. Prof. in the UVSOR Synchrotron Facility
Apr. 1, 2020	Dr. KIMURA, Shin-ichi joined IMS as a Prof. (Cross Appointment) in the Division of Advanced Molecular Science
May 1, 2020	Dr. OTOMO, Akihiro joined IMS as an Assist. Prof. in the Department of Life and Coordination-Complex Molecular Science
Jun. 1, 2020	Dr. MINATO, Taketoshi joined IMS as a Senior Researcher in Instrument Center

Moving Out

Nov. 30, 2019	Assist. Prof. ANDO, Jun (Department of Life and Coordination-Complex Molecular Science) moved out as a tenured Research Scientist of RIKEN
Dec. 31, 2019	Assist. Prof. IIDA, Kenji (Department of Theoretical and Computational Molecular Science) moved out as an Assoc. Prof. of Hokkaido University
Dec. 31, 2019	Assist. Prof. NAKAMURA, Akihiko (Department of Life and Coordination-Complex Molecular Science) moved out as an Assoc. Prof. of Shizuoka University (Tenure track Position)
Mar. 31, 2020	Assist. Prof. SUDA, Masayuki (Research Center of Integrative Molecular Systems) moved out as an Assoc. Prof. of Kyoto University
Mar. 31, 2020	Assist. Prof. KURAHASHI, Takuya (Department of Life and Coordination-Complex Molecular Science) moved out as a Prof. of University of Nagasaki
Mar. 31, 2020	Res. Assoc. Prof. KURIHARA, Kensuke (Department of Life and Coordination-Complex Molecular Science) moved out
May 15, 2020	Assist. Prof. NOMURA, Yutaka (Center for Mesoscopic Sciences) moved out to Furukawa Electric Co., Ltd.
May 31, 2020	Assist. Prof. TSUKAMOTO, Hisao (Department of Life and Coordination-Complex Molecular Science) moved out as an Assoc. Prof. of Kobe University
Aug. 31, 2020	Assist. Prof. NGUYEN, Thanh Phuc (Department of Theoretical and Computational Molecular Science) moved out as a Junior Associate Professor of Kyoto University

Graduate Programs

IMS is one of the leading national research institutes in natural science. For graduate education, IMS has two departments in Graduate School of Physical Sciences, SOKENDAI (The Graduate University for Advanced Studies): Department of Structural Molecular Science and Department of Functional Molecular Science. One year is divided into two terms, the first semester (April-to-September) and the second semester (October-to-March).

The graduate education at IMS focuses on the molecular sciences. Each graduate student can study molecular science under guidance of the IMS faculty members in the following areas: Photomolecular science, materials molecular science, biomolecular and coordination molecular science, and theoretical and computational molecular science.

In the 1st and 2nd years of the 5-year doctoral course, the programs emphasize the scientific education related to the expertises of IMS laboratories. By providing such opportunities, the program seeks to help students develop extensive knowledge on physical sciences and high degree of professional quality as well as to help them prepare for the education in their 3rd to 5th years of the 5-year doctoral course.

Young scientists and graduate students from abroad are also encouraged to visit IMS through several opportunities such as the IMS Open Campus and Lecture in June, Summer Training Program in August, and Asian Winter School in addition to IMS International Internship Program as shown below.

International Collaboration and Exchange Programs

Many foreign researchers and students stay for 1–12 months in IMS to collaborate with us in the field of molecular science, or stay for 1–2 weeks to use various kinds of research equipments in our research facilities such as the UVSOR Synchrotron Facility, Instrument Center, and Equipment Development Center. IMS has own budget to carry out these international exchange and collaboration programs, and covers part of research expenses and travel expenses for visitors from abroad. They can use our guest houses, Mishima Lodge and Myodaiji Lodge.

Exchange/Collaboration program		Duration of Stay	Eligibility
IMS visiting faculty program	Long-term	3–12 months	Professors, Associate Professors and other corresponding positions
	Short-term*	1–3 months	
IMS International Internship Program (IMS-IIP)	Long-term	>6 months	Ph.D. students and PostDoc.
	Short-term*	1–6 months	
IMS facility user program		1–2 weeks	Professors, Researchers, and Ph.D. students

* We preferentially invite researchers and students from MOU partnership institutions

International Symposia

We organize several kinds of international symposia based on screening of submitted proposals. In addition, we have international collaborative symposia with MOU partners at IMS or at MOU partner's country as listed in Collaboration Programs.

Program		Purpose
International Symposia and Workshop	Okazaki Conference	An international conference with distinguished foreign researchers by focusing on an emerging field as a fundamental issue in the field of molecular science and related research area
	Mini-International Workshop	A small international workshop on a specific field
	Asia/Oceania IMS Workshop	Workshop with Asian and Oceanian researchers and students
IMS Workshop	IMS Workshop (General)	Workshop on timely topics in molecular science, organized as a collaborative effort between outside and IMS researchers
	IMS Workshop in cooperation with a specified research community	
	IMS Workshop in cooperation with graduate students	Workshop and other related activities planned by graduate students

RESEARCH ACTIVITIES

Theoretical and Computational Molecular Science

The goal of the Department is to predict and elucidate static and dynamic properties, reactions, and functions in condensed phase including biomolecular and heterogeneous catalytic systems by developing novel theories and computational methods based on quantum mechanics, statistical mechanics, and solid state physics.

The Department collaborates with Research Center for Computational Science on researches.

Theoretical Studies of Reactions, Functions, and Fluctuations in Many-Body Molecular Systems

Department of Theoretical and Computational Molecular Science Division of Theoretical Molecular Science I

SAITO, Shinji
Professor
[shinji@ims.ac.jp]

Education

1988	B.S. Keio University
1990	M.E. Kyoto University
1995	Ph.D. The Graduate University for Advanced Studies

Professional Employment

1990	Technical staff, Institute for Molecular Science
1994	Research Associate, Nagoya University
1998	Associate Professor, Nagoya University
2005	Professor, Institute for Molecular Science
2006	Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
MORI, Toshifumi
KODA, Shin-ichi
JSPS Post-Doctoral Fellow
MATSUMURA, Yoshihiro
Post-Doctoral Fellow
MAURYA, Manish
Graduazte Student
KALATHINGAL, Mahroof
ZHU, Zhe
Secretary
CHIBA, Fumika

Keywords Reactions, Functions, Fluctuations

Many-body molecular systems, such as (supercooled) liquids and biomolecules, exhibit complex fluctuations. Furthermore, in these systems, various physical properties and biological functions are created and chemical reactions proceed under the fluctuations. We aim to elucidate the properties, functions, and reactions by investigating fluctuations and dynamics of the many-body molecular systems.

We investigate fluctuations and dynamics of liquids by developing computational methods for multi-dimensional nonlinear spectroscopy that can reveal detailed dynamical infomation not available from conventional linear spectroscopy. Consequently, we revealed the molecular origins of ultrafast energy relaxation and time evolution of inhomogeneous fluctuations in liquid water. In supercooled liquids, rare and non-uniform structural changes, called dynamic heterogeneity, are induced by fluctuations. We elucidated the relationship between the lifetime of the dynamic heterogeneity and the fragility using the three-time correlation function of density fluctuations.

We study the molecular origin of anomalous properties of liquid water. We revealed that the anomalies of liquid water are related to the structural and dynamical instabilities hidden in the experimentally inaccessible region and the physical reason of the low glass transition temperature of liquid water. We currently investigate how rare but persistent structural relaxation of liquid water proceeds towards the glass transition temperature.

Complex conformational fluctuations and changes can be observed in biomolecular systems. Such conformational dynamics are considered to be essential for biological functions. We examine the relationship between fluctuation and biomolecular function found in the robust circadian rhythm of the clock protein KaiC and the efficient excitation energy transfer in photosynthetic systems. We investigate dynamic effects of enzymatic reactions, and find the importance of prearranged states for the rare but persistent enzymatic reactions. Furthermore, we examine dynamic disorder in conformational changes of proteins at the molecular level.

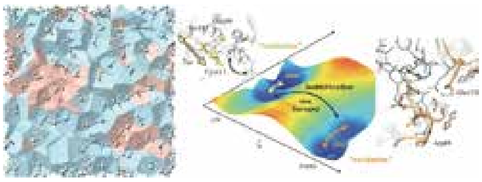


Figure 1. Snapshot of two-state model in supercooled water consisting of high- and low-density liquids (left) and schematic of 2D free energy surface for enzymatic reaction (right).

Selected Publications

- T. Yagasaki and S. Saito, *Annu. Rev. Phys. Chem.* **64**, 55–75 (2013). T. L. C. Jansen, S. Saito, J. Jeon and M. Cho, *J. Chem. Phys.* **150**, 100901 (17 pages) (2019), C. R. Baiz *et al.*, *Chem. Rev.* **120**, 7152–7218 (2020).
- K. Kim and S. Saito, *J. Chem. Phys. (Special Topic on Glass Transition)* **138**, 12A506 (12 pages) (2013).
- S. Saito, B. Bagchi and I. Ohmine, *J. Chem. Phys.* **149**, 124504 (8 pages) (2018), S. Saito and B. Bagchi, *J. Chem. Phys.* **150**, 054502 (14 pages) (2019).
- T. Mori and S. Saito, *J. Phys. Chem. Lett.* **10**, 474–480 (2019).
- S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B* **123**, 9762–9772 (2019).

1. Dissecting the Dynamics during Enzyme Catalysis: A Case Study of Pin1 Peptidyl-Prolyl Isomerase[1)]

Free energy surfaces have played a central role in studying protein conformational changes and enzymatic reactions over decades. Yet, free energy barriers and kinetics are highly dependent on the coordinates chosen to define the surface, and furthermore, the dynamics during the reactions are often overlooked. Our recent study on the Pin1-catalyzed isomerization reaction has indicated that the isomerization transition events remarkably deviate from the free energy path, highlighting the need to understand the reaction dynamics in more detail. To this end, here we investigate the reaction coordinates that describe the transition states of the free energy and transition pathways by minimizing the cross-entropy function. We show that the isomerization transition events can be expressed by the concerted changes in the improper torsion angle ζ and nearby backbone torsional angles of the ligand, whereas the transition state of the free energy surface involves changes in a broad range of coordinates including multiple protein–ligand interactions. The current result supports the previous finding that the isomerization transitions occur quickly from the conformational excited states, which is in sharp contrast to the slow and collective changes suggested from the free energy path. Our results further indicate that the coordinates derived from the transition trajectories are not sufficient for finding the transition states on the free energy surfaces due to the lack of information from conformational excited states.

2. An Alternative Interpretation of the Slow KaiB-KaiC Binding of the Cyanobacterial Clock Proteins[2)]

The biological clock of cyanobacteria is composed of three proteins, KaiA, KaiB, and KaiC. The KaiB–KaiC binding brings the slowness into the system, which is essential for the long period of the circadian rhythm. However, there is no consensus as to the origin of the slowness due to the pre-binding conformational transition of either KaiB or KaiC. In this study, we propose a simple KaiB–KaiC binding scheme in a hexameric form with an attractive interaction between adjacent bound KaiB monomers, which is independent of KaiB's conformational change. We then show that the present scheme can explain several important experimental results on the binding, including that used as evidence for the slow conformational transition of KaiB. The present result thus indicates that the slowness arises from KaiC rather than KaiB.

3. Site-Dependent Fluctuations Optimize Electronic Energy Transfer in the Fenna-Matthews-Olson Protein[3)]

Light absorbed by light-harvesting antennae is transferred to the reaction center (RC). The excitation energy transfer (EET) to the RC is known to proceed with nearly perfect quantum yield. However, understanding of EET is still limited at the molecular level. Here, we examine the dynamics in the Fenna–Matthews–Olson (FMO) protein by developing an efficient molecular dynamics simulation that can properly describe the electronic properties of bacteriochlorophylls. We find that the FMO protein consists of sites with heterogeneous fluctuations extending from fast to slow modulation. We also find that efficient EETs are facilitated by site-dependent fluctuations that enhance the resonance condition between neighboring sites with large site energy differences and circumvent exciton trapping on the pathway to the RC. Knowledge of site-dependent fluctuations is an important component of understanding optimization of EET in photosynthetic systems.

4. Molecular Mechanism of Acceleration and Retardation of Collective Orientation Relaxation of Water Molecules in Aqueous Solutions[4)]

The collective orientation relaxation (COR) of water molecules in aqueous solutions is faster or slower with the increase in concentration of the solutions than that in pure water; for example, acceleration (deceleration) of the COR is observed in a solution of sodium chloride (tetramethylammonium chloride) with increasing concentration. However, the molecular mechanism of the solution and concentration dependence of the relaxation time of the COR has not yet been clarified. We theoretically investigate the concentration dependence of the COR of water molecules in solutions of tetramethylammonium chloride (TMACl), guanidinium chloride (GdmCl), and sodium chloride (NaCl). Based on the Mori-Zwanzig equation, we identify two opposing factors that determine the COR of water molecules in any aqueous solution: The correlation of dipole moments and the single-molecule orientation relaxation. We reveal the molecular mechanism of the concentration dependence of the relaxation time of the COR in the TMACl, GdmCl, and NaCl solutions in terms of these two factors.

References

1) T. Mori and S. Saito, *J. Chem. Theory Comput.* **16**, 3396–3407 (2020).
2) S.-i. Koda and S. Saito, *Sci. Rep.* **10**, 10439 (7 pages) (2020).
3) S. Saito, M. Higashi and G. R. Fleming, *J. Phys. Chem. B* **123**, 9762–9772 (2019).
4) N. Moritsugu, T. Nara, S.-i. Koda, K. Tominaga and S. Saito, to be submitted.

Theoretical Studies on Novel Physical Properties Arising from Many-Body Interaction

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science I

MINAMITANI, Emi
Associate Professor
[eminamitani@ims.ac.jp]

Education
2005 B.S. Osaka University
2010 Ph.D. Osaka University

Professional Employment
2010 Postdoctoral Fellow, Osaka University
2011 Special Postdoctral Researcher, RIKEN
2013 Assistant Professor, The University of Tokyoy
2015 Lecturer, Cornell University
2019 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards
2008 L'Oréal–UNESCO Japan National Fellowships for Women in Science
2011 Best Poster Award in ISSS-6 Internal Symposium on Surface Science
2017 Young Scientist Award of the Physical Society of Japan
2019 The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology
The Young Scientists' Prize

Member
Assistant Professor
SHITADE, Atsuo
Research Fellow
HINODE, Kenji
OKUGAWA, Shinichi
Secretary
AKABA, Atsuko

Keywords Quantum Many-Body Interaction, Density Functional Theory, Quantum Field Theory

Quantum many-body interaction is a source of novel physical properties in the condensed matters. In our group, we develop theoretical methods by combining quantum field theory and density functional theory, and carry out collaborative research with experimental groups. As specific targets, we focus on magnetism in nanostructure and energy dissipation.

For magnetism in nanostructure, we are interested in the Kondo effect and spin–orbit interaction. The Kondo effect arises from the interaction between the localized spin and conduction electrons, which forms a characteristic many-body state so called the Kondo singlet state. The spin–orbit interaction originating from relativistic effect constrains the direction of magnetic moment to specific direction. We investigate the possibility of novel physical phenomena induced by these interactions in the nanostructure and molecules on surfaces.

For energy dissipation, we focus on the effect of electron–phonon interaction. The electron–phonon interaction is one of the most fundamental interactions in the condensed matter physics, and the quantitative evaluation in realistic materials is highly demanding. We adopt the ab-initio calculation to analyze the signal of electron–phonon coupling in surface spectroscopy and thermal properties in various kind of solids.

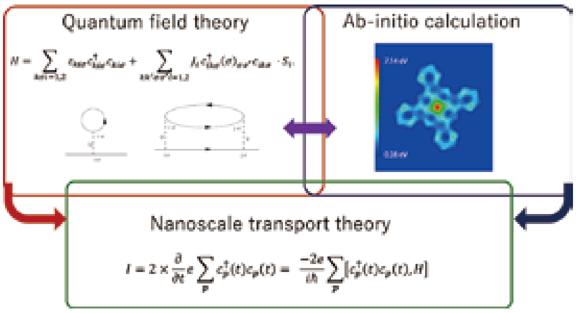


Figure 1. Schematic image of the theoretical method developed in our group.

Selected Publications

- E. Minamitani, N. Tsukahara, D. Matsunaka, Y. Kim, N. Takagi and M. Kawai, "Symmetry-Driven Novel Kondo Effect in a Molecule," *Phys. Rev. Lett.* **109**, 086602 (2012).
- E. Minamitani, R. Arafune, N. Tsukahara, Y. Ohda, S. Watanabe, M. Kawai, H. Ueba and N. Takagi, "Surface Phonon Excitation on Clean Metal Surfaces in Scanning Tunneling Microscopy," *Phys. Rev. B* **93**, 085411 (2016).
- E. Minamitani, N. Takagi and S. Watanabe, "Model Hamiltonian Approach to the Magnetic Anisotropy of Iron Phthalocyanine at Solid Surfaces," *Phys. Rev. B* **94**, 205402 (2016).
- R. Hiraoka, E. Minamitani, R. Arafune, N. Tsukahara, S. Watanabe, M. Kawai and N. Takagi, "Single-Molecule Quantum Dot as a Kondo Simulator," *Nat. Commun.* **8**, 16012 (2017).
- E. Minamitani, R. Arafune, T. Frederiksen, T. Suzuki, S. M. F. Shahed, T. Kobayashi, N. Endo, H. Fukidome, S. Watanabe and T. Komeda, "Atomic-Scale Characterization of the Interfacial Phonon in Graphene/SiC," *Phys. Rev. B* **96**, 155431 (2017).
- E. Minamitani, M. Ogura and S. Watanabe, "Simulating Lattice Thermal Conductivity in Semiconducting Materials Using High-Dimensional Neural Network Potential," *Appl. Phys. Express* **12**, 095001 (2019).

1. Superconductivity in Chemically Doped 2D Materials

Layered materials have been investigated for a long time owing to their tunable features, which enable various applications. Amongst them, superconductivity has recently attracted considerable attention. Although several types of 2D superconductors have been experimentally and/or theoretically investigated, most of them are metallic/semimetallic materials, such as metal atomic layers on semiconductor surfaces, layered materials such as FeSe and $NbSe_2$, and electron-doped graphene. The other class of 2D superconductors is doped 2D semiconductors or insulators.

We focused on hexagonal boron nitride (h-BN) as a candidate for a 2D superconductor. Bulk h-BN has a wide bandgap of approximately 6 eV, and it exists in the monolayer form. Although the application of h-BN as an inert and atomically flat insulating layer to realize novel 2D-material-based electronics has been widely investigated, its possibility as a superconductor has been untapped until recently. In our previous study, we reported that a Li-intercalated h-BN bilayer became a phonon-induced superconductor with a T_c of up to 25 K, thereby indicating that both the phonon properties and electron–phonon coupling (EPC) in doped h-BN are appropriate for realizing superconductivity.[1)] However, the fabrication of a superconducting Li-intercalated h-BN bilayer is experimentally challenging, as the stacking order of the h-BN sheets must differ from that of the original bulk structure to attain a high T_c. To seek a promising candidate for an h-BN-based superconductor with a more experimentally feasible structure than the bilayer structure, we investigated the properties of doped monolayer h-BN by using ab-initio calculation of electron–phonon interaction.

Consequently, we reveal that Sr- and Ba-doped monolayer h-BN and Ca-doped monolayer h-BN with 3.5% tensile strain are energetically stable and become superconductors.[2)] The estimated T_{cs} from McMillan–Allen–Dynes formula are approximately 5.83, 1.53, and 10.7 K, respectively. Interestingly, the T_{cs} for the Ca-, Sr-, and Ba doped graphene are lower than 0.5K.

To clarify the difference between h-BN and graphene, we analysed the electronic band structure depicted in Figure 2. The projection of the DOS from the adsorbate s-orbital onto the electronic-band structures indicated the presence of adsorbate bands that crossed the Fermi level in all systems. These bands correspond to the interlayer state reported in previous studies. In doped graphene systems, the interlayer state is crucial for determining T_c. However, the similarity in the interlayer state between doped graphene and h-BN indicates that the T_c in these systems is governed by other factors. Other than the interlayer states, several bands that originated from h-BN and graphene orbitals crossed the Fermi level.

These band structures around the Fermi level resulted in Fermi surfaces of different shapes and positions, as depicted in Figure 3. In both the h-BN and graphene cases, the Fermi surface around the K point originates from the interlayer state, and those around the Γ point correspond to the band from the h-BN or graphene states. The shape of the Fermi surfaces from the interlayer states resembled each another in both the doped h-BN and graphene cases, except for the size of the pocket. However, the shapes of the inner Fermi surfaces around the Γ point between the doped h-BN and graphene cases differed significantly. In the doped h-BN case, the inner Fermi surface exhibited a snowflake-like shape, but it was hexagram-like in the doped graphene case. The projection of the k-resolved EPC (λ_k) shows that the electron–phonon interaction in the inner Fermi surface is crucial for determining T_c. Compared with doped graphene, the doped h-BNs exhibited greater λ_k in general in the Brillouin zone. The most prominent enhancement in λ_k was observed around the Γ point.

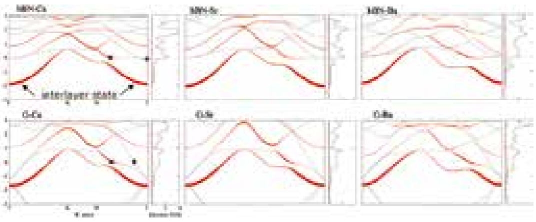


Figure 2. Electronic band dispersions and DOS for doped h-BN and graphene.

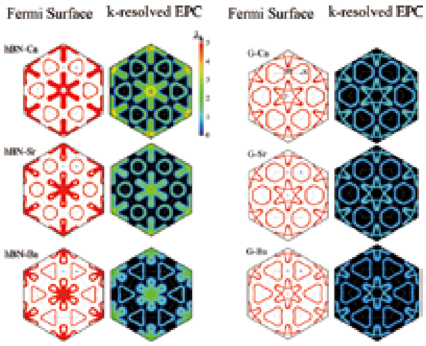


Figure 3. Fermi surfaces and k-resolved EPC projected on Fermi surface in doped h-BN and graphene.

The enhancement in λ_k around the Γ point in the Ca-doped h-BN is attributed to the spatial distribution of the wavefunction of the electronic states induced by the lower symmetry compared to the graphene case. These results indicate that instead of tuning the interlayer state, reducing the symmetry and introducing strong adsorbate–substrate interactions are alternative strategies to increase the T_c of doped 2D semiconductors/insulators.

Other Ongoing Projects:

- Geometric Spin–Orbit Coupling and Chirality-Induced Spin Selectivity

- Ab-Initio Calculation of Heat Generation in Semiconductors

References

1) N. H. Shimada, E. Minamitani and S. Watanabe, *Appl. Phys. Express* **10**, 9 (2017).

2) N. H. Shimada, E. Minamitani and S. Watanabe, *J. Phys.: Condens. Matter* **32**, 435002 (2020).

Theoretical Studies of Chemical Dynamics in Condensed and Biomolecular Systems

Department of Theoretical and Computational Molecular Science
Division of Theoretical Molecular Science II

ISHIZAKI, Akihito
Professor
[ishizaki@ims.ac.jp]

Education

2008	D.S. Kyoto University

Professional Employment

2006	JPSP Research Fellow, Kyoto University
2008	JPSP Postdoctoral Fellow for Research Abroad, University of California, Berkeley
2010	Postdoctoral Fellow, Lawrence Berkeley National Laboratory
2012	Research Associate Professor, Institute for Molecular Science
2013	Fellow 2012–2013, Wissenschaftskolleg zu Berlin
2016	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Visiting professor, Nagoya University

Awards

2015	10th Condensed-Matter Science Prize, Japan
2016	10th Young Scientist Award of the Physical Society of Japan
2016	18th Sir Martin Wood Prize
2017	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2020	JSPS Prize
2020	Japan Academy Medal

Member

Assistant Professor
NGUYEN, Thanh Phuc

Post-Doctoral Fellow
FUJIHASHI, Yuta

Secretary
AKABA, Atsuko

Keywords Quantum Dissipative Systems in Complex Molecular Systems, Quantum Optics, Light-Matter Interaction

Quantum dynamic phenomena are ubiquitous in molecular processes, and yet remain a challenge for experimental and theoretical investigations. On the experimental side, it has become possible to explore molecules on a time scale down to a few femtoseconds. This progress in ultrafast spectroscopy has opened up real-time observation of dynamic processes in complex chemical and biological systems and has provided a strong impetus to theoretical studies of condensed phase quantum dynamics.

Essentially, any quantum systems can never be regarded as "isolated systems." Quantum systems are always in contact with "the outside world," and hence their quantum natures are sometimes sustained and sometimes destroyed. In condensed phase molecular systems, especially, quantum systems are affected by the huge amount of dynamic degrees of freedom such as solvent molecules, amino acid residues in proteins, and so forth. Balance between robustness and fragility of the quantum natures may dramatically alter behaviors of chemical dynamics and spectroscopic signals. Therefore, theoretical tools to adequately describe (1) dynamical behaviors of quantum systems affected by the huge amount of dynamic degrees of freedom and (2) the interaction with radiation fields should be developed.

For this purpose, our research group has been tackling the following subjects:

(1) Developments of condensed phase quantum dynamic theories
(2) Quantum theories to describe dynamical and transport processes in materials and biological systems
(3) Theoretical investigations on measurement and control with the use of atomic-molecular-optical (AMO) physics approaches.

In recent years, specifically, special attention is devoted to the subject (3). We have been examining whether ideas and concepts in the field of quantum science and technology would provide novel control knobs that supplement classical parameters in conventional spectroscopic tools such as frequencies and time delays.

Selected Publications

- A. Ishizaki and G. R. Fleming, "Quantum Coherence in Photosynthetic Light Harvesting," *Annu. Rev. Condens. Matter Phys.* **3**, 333–361 (2012). [Invited review article]
- G. D. Scholes *et al.*, "Using Coherence to Enhance Function in Chemical and Biophysical Systems," *Nature* **543**, 647–656 (2017).
- T. P. Nguyen and A. Ishizaki, "Control of Excitation Energy Transfer in Condensed Phase Molecular Systems by Floquet Engineering," *J. Phys. Chem. Lett.* **9**, 1243 (2018).
- A. Kato and A. Ishizaki, "Non-Markovian Quantum-Classical Ratchet for Ultrafast Long-Range Electron–Hole Separation in Condensed Phases," *Phys. Rev. Lett.* **121**, 647 (2018).
- Y. Fujihashi, R. Shimizu and A. Ishizaki, "Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules," *Phys. Rev. Res.* **2**, 023256 (2020).
- A. Ishizaki, "Probing Excited-State Dynamics with Quantum Entangled Photons: Correspondence to Coherent Multidimensional Spectroscopy," *J. Chem. Phys.* **153**, 051102 (2020). [Editor's Pick]

1. Precise Determination of Excitation Energies Based on Exciton-Polariton Measurements

The precise determination of the excitation energies in condensed-phase molecular systems is important for understanding system-environment interactions as well as for the prerequisite input data of theoretical models used to study the dynamics of the system. The excitation energies are usually determined by fitting of the measured optical spectra that contain broad and unresolved peaks as a result of the thermally random dynamics of the environment. Herein, we proposed a method for precise energy determination by strongly coupling the molecular system to an optical cavity and measuring the energy of the resulting polariton. The effect of thermal fluctuations induced by the environment on the polariton was also investigated, from which a power scaling law relating the polariton's linewidth to the number of molecules was obtained.1)

2. Controlling the Nonadiabatic Electron Transfer Reaction Rate through Molecular Vibration Polaritons

Recent experiments showed that the chemical reaction rate is modified by strongly coupling a nuclear vibration mode to the single mode of an optical cavity. Herein we investigated how the rate of an electron-transfer reaction depends on the molecule-cavity coupling. We found two main factors that determine the modification of the reaction rate: The relative shifts of the energy levels induced by the coupling and the mixing of the ground and excited states of molecular vibration in the ground state of the hybrid molecule-plus-cavity system through which the Franck-Condon factor between the initial and final states of the transition is altered. The effect of the mixing of molecular vibrational states on the reaction rate is, however, suppressed in a system containing a large number of molecules due to the collective nature of the resulting polariton, and thus should be observed in a system containing a small number of molecules. In contrast, the effect of the relative shifts of the energy levels should be essentially independent of the number of molecules coupled to the cavity.3)

3. Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules

Light incident upon molecules triggers fundamental processes in diverse systems present in nature. However, under natural conditions such as sunlight illumination, it is impossible to assign known times for photon arrival due to continuous pumping, and therefore the photoinduced processes cannot be easily investigated. In this work, we demonstrated theoretically that the characteristics of sunlight photons, such as photon number statistics and spectral distribution, can be emulated through a quantum entangled photon pair generated with parametric down-conversion (PDC). We showed that the average photon number of sunlight in a specific frequency spectrum, *e.g.*, the visible light, could be reconstructed by adjusting the PDC crystal length and pump frequency, and thereby the molecular dynamics induced by the pseudo-sunlight could be investigated. The entanglement time, which is the hallmark of quantum entangled photons, can serve as a control knob to resolve the photon arrival times, enabling investigations on real-time dynamics triggered by pseudo-sunlight photons.4)

4. Probing Excited-State Dynamics with Quantum Entangled Photons

Quantum light is a key resource for promoting quantum technology. One such class of technology aims to improve the precision of optical measurements using engineered quantum states of light. In this study, we investigate transmission measurement of frequency-entangled broadband photon pairs generated via parametric down-conversion with a monochromatic laser. It is observed that state-to-state dynamics in the system under study are temporally resolved by adjusting the path difference between the entangled twin beams when the entanglement time is sufficiently short. The non-classical photon correlation enables time-resolved spectroscopy with monochromatic pumping. It is further demonstrated that the signal corresponds to the spectral information along anti-diagonal lines of, for example, two-dimensional Fourier-transformed photon echo spectra. This correspondence inspires us to anticipate that more elaborately engineered photon states would broaden the availability of quantum light spectroscopy.5)

5. Prerequisites for Relevant Spectral Density and Convergence of Reduced Density Matrices at Low Temperatures

Hierarchical equations of motion approach with the Drude–Lorentz spectral density has been widely employed in investigating quantum dissipative phenomena. However, it is often computationally costly for low-temperature systems because a number of Matsubara frequencies are involved. In this work, we examined a prerequisite required for spectral density, and demonstrated that relevant spectral density significantly reduced the number of Matsubara terms to obtain convergent results for low temperatures.2)

References

1) T. P. Nguyen and A. Ishizaki, *Phys. Rev. Res.* **1**, 033019 (2019).
2) T. P. Nguyen, Q. T. Pham and A. Ishizaki, *Sci. Rep.* **10**, 7318 (2020).
3) Y. Fujihashi, R. Shimizu and A. Ishizaki, *Phys. Rev. Res.* **2**, 023256 (2020).
4) A. Ishizaki, *J. Chem. Phys.* **153**, 051102 (2020). [Editor's Pick]
5) A. Ishizaki, *J. Phys. Soc. Jpn.* **89**, 015001 (2020).

Awards

ISHIZAKI, Akihito; 16th JSPS Prize (2020).
ISHIZAKI, Akihito; 16th Japan Academy Medal (2020).

Theoretical Studies of Functional Molecular Systems and Heterogeneous Catalysts

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

EHARA, Masahiro
Professor
[ehara@ims.ac.jp]

Education

1988	B.E. Kyoto University
1990	M.E. Kyoto University
1993	Ph.D. Kyoto University

Professional Employment

1993	Postdoctral Fellow, Institute for Fundamental Chemistry
1994	JSPS Postdoctoral Fellow
1994	Visiting Researcher, Heidelberg University (–1995)
1995	Assistant Professor, Kyoto University
2002	Associate Professor, Kyoto University
2006	Theoretical Research Division Supervisor, Kyoto University (–2008)
2008	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2012	Professor, Elements Strategy Initiative for Catalysts and Batteries (ESICB), Kyoto University (additional post)

Awards

2009	APATCC Pople Medal
2009	QSCP Prize CMOA

Member
Post-Doctoral Fellow
ZHAO, Pei
VIGNESH, K. R.
Visiting Scientist
ZHAO, Xiang
PRIYAKUMAR, Deva U
BOBUATONG, Karan
Graduate Student
KANAZAWA, Yuki
SHIRAOGAWA, Takafumi
Secretary
KAWAGUCHI, Ritsuko
SUGIMOTO, Yukari

Keywords Quantum Chemistry, Photophysical Chemistry, Heterogeneous Catalysis

We develop the accurate electronic structure theories and investigate the photochemistry and catalysis theoretically. Currently, our focuses are following research subjects.

(1) Coupled cluster theory for excited states of large system

We develop the coupled cluster theories and their efficient computational algorithm aiming at large-scale calculations of molecular excited states. We also develop the basic theories and methodologies that are useful for fundamental chemistry and applied chemistry; for example, PCM SAC-CI method for effectively describing the solvent effects on excited states, CAP/SAC-CI method for locating metastable resonance states, general-R method for multiple excited states, and active-space method for efficiently describing complex electronic states.

(2) Heterogeneous catalysis

Metal nanoclusters supported by metal oxides or polymers achieve highly efficient catalytic reactions. We study the catalytic activity of these complex systems by means of quantum chemical calculations and informatics theories. We have elucidated the importance of the perimeter sites at heterojunction of Ag nanocluster supported by alumina surface in terms of H_2 activation, the mechanism of methanol oxidation on Au:PVP and the unique coupling reactions on Au/Pd:PVP. We proceed these works in the project of Elements Strategy Initiative for Catalysts and Batteries (ESICB).

(3) Photophysical chemistry

Our accurate electronic structure theories are applied to wide varieties of theoretical studies and sometimes in cooperation with experiments on the photophysical properties and excited-state dynamics of nano-bio systems like photo-electronic devices, photofunctional molecules, and biosensors. Target molecules include nanocarbons like fullerenes, near-IR absorbing phthalocyanine congeners, dye-sensitized solar cells, organometallic compounds for artificial photosynthesis, biological chemosensors, and bio-imaging probes.

(4) Theoretical spectroscopy

New quantum states, single-site and two-site double-core hole states, have been observed owing to the recent development of free electron laser and coincidence spectroscopy. We have proposed new chemical concept regarding the physical properties or relaxation processes of these quantum states in cooperation with experiments. We also perform accurate theoretical analysis for the state-of-the-art molecular spectroscopy; for example, the electronic transitions in the FUV region by ATR-FUV spectroscopy and the excited-state relaxation processes by pump–probe spectroscopy.

Selected Publications

- R. Cammi, R. Fukuda, M. Ehara and H. Nakatsuji, "SAC-CI Method in the Polarizable Continuum Model-Theory for Solvent Effect on Electronic Excitation of Molecules in Solution," *J. Chem. Phys.* **133**, 024104 (24 pages) (2010).
- N. Berrah, M. Tashiro, M. Ehara *et al.*, "Double Core-Hole Spectroscopy for Chemical Analysis with an Intense X-Ray Femtosecond Laser," *Proc. Natl. Acad. Sci. U.S.A.* **108**, 16912–16915 (2011).
- M. Ehara and T. Sommerfeld, "CAP/SAC-CI Method for Calculating Resonance States of Metastable Anions," *Chem. Phys. Lett.* **537**, 107–112 (2012).
- P. Hirunsit, K. Shimizu, R. Fukuda, S. Namuangruk, Y. Morikawa and M. Ehara, "Cooperative H_2 Activation at Ag Cluster/θ-Al_2O_3 Dual Perimeter Sites: A DFT Study," *J. Phys. Chem. C* **118**, 7996–8006 (2014).

1. Theoretical Design of Photofunctional Molecular Aggregates for Optical Properties: An Inverse Design Approach[1)]

Properties of molecular aggregates are defined by their composition and structure. It is becoming possible to control these elements via advances in experimental techniques, and therefore the design guidelines are demanded for developing efficient optical materials. Here we propose a theoretical design approach for photofunctional molecular aggregates using an inverse design framework, the linear combination of atomic potentials (LCAP). The Frenkel exciton model coupled with the LCAP is introduced for designing systems with desired optical properties by gradient-guided optimization searches in terms of constituent molecules in chemical space of molecular aggregates. We have applied this approach to design one-dimensional molecular aggregates having locally maximized absorption and/or circular dichroism (CD) intensities as an example. By exploring a small fraction of the vast chemical space of 10^{26} possible systems varying in composition and structure, we successfully obtained the optimal aggregates. The optimal structure–photofunction relationships were investigated from the designed systems. The present method is useful to design photofunctional molecular aggregates and accelerate optical material discoveries.

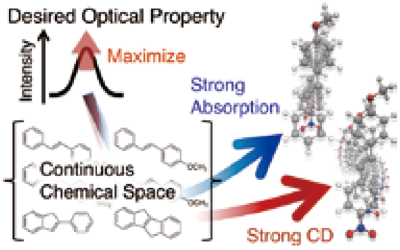


Figure 1. Schematic representation of the inverse design of photofunctional molecular aggregates with desired optical properties.

2. Importance of the Pd and Surrounding Site in Hydrosilylation of Internal Alkynes by Pd-Au Alloy Catalyst[2)]

Hydrosilylation is one of the key reactions in the formation of carbon−silicon bonds, where the addition of Si−H bonds occurs across the unsaturated bond in organic compounds. The Pd−Au alloy catalyst has been developed for the hydrosilylation of internal alkynes as well as α, β-unsaturated ketones under mild conditions. Herein, density functional theory calculations were utilized to study the mechanism of the hydrosilylation reaction of internal alkynes on the Pd−Au catalyst. The calculated energy profiles show that the reaction follows the Chalk−Harrod mechanism. The Pd site acts as the adsorption site and the reactive center as observed in experiments. The surrounding Pd−Au bridge and Au sites are also relevant for the bond activation and accepting the substrates or intermediates during the reaction, which is characteristic in the Pd−Au alloy catalysts and not available in the homogeneous catalyst. The present picture of the relevance of the Pd atomic site and its surrounding Pd−Au bridge or Au sites will be useful for developing the alloy catalysts for the related catalytic reactions.

Figure 2. Hydrosilylation on the Pd-Au Alloy Catalyst.

3. Theoretical Study on ^{31}P NMR Chemical Shifts of P-Modified CHA Zeolites[3)]

The modification of zeolites with phosphorus is a widely adopted method to tune the acidity and consequently the catalytic properties in terms of activity, shape selectivity, and hydrothermal stability. The ^{31}P MAS NMR spectra of phosphorus-modified chabazite (P-CHA) zeolites have been observed during the hydrothermal treatment to probe the structural changes of phosphorus species in zeolites. Theoretical calculations on the ^{31}P and ^{27}Al NMR chemical shifts have been systematically performed to disclose the possible phosphorus species of intra- and extra-framework and the structural changes during the hydrothermal treatment. The present theoretical results provide useful information regarding the ^{31}P NMR chemical shifts in P-CHA, which will significantly improve the ^{31}P NMR assignments in future experiments.

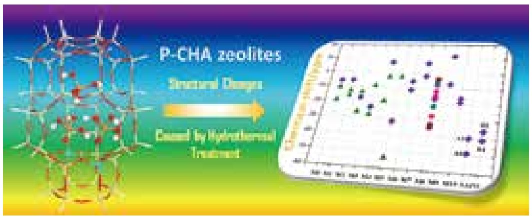


Figure 3. ^{31}P NMR chemical shifts of P-CHA zeolites.

References

1) T. Shiraogawa and M. Ehara, *J. Phys. Chem. C* **124**, 13329–13337 (2020). (Supplemental Cover)
2) T. Sadhukhan, A. Junkaew, P. Zhao, H. Miura, T. Shishido and M. Ehara, *Organometallics* **39**, 528–537 (2020). (Supplemental Cover)
3) P. Zhao, B. Boekfa, T. Nishitoba, N. Tsunoji, T. Sano, T. Yokoi, M. Ogura and M. Ehara, *Microporous Mesoporous Mater.* **294**, 109908 (2020).

Award

SHIRAOGAWA, Takafumi; Poster Award, The 13th Annual Meeting of Japan Society for Molecular Science (2019).

Development of New Simulation Algorithms and its Application to Protein Aggregates

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

OKUMURA, Hisashi
Associate Professor
[hokumura@ims.ac.jp]

Education
1998 B.S. Keio University
2002 Ph.D. Keio University

Professional Employment
2002 Postdoctoral Fellow, The University of Tokyo
2002 Research Associate, Institute for Molecular Science
2004 Research Associate, The Graduate University for Advanced Studies
2006 Research Lecturer, Nagoya University
2008 Research Assistant, Rutgers University
2009 Assistant Research Professor, Rutgers University
2009 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2018 Associate Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Award
2014 Academic Award of the Molecular Simulation Society of Japan

Member
Assistant Professor
ITOH, Satoru G.
Post-Doctoral Fellow
TANIMOTO, Shoichi
Graduate Student
YAMAUCHI, Masataka
MIYAZAWA, Kazuhisa
FUKUHARA, Daiki
Secretary
KAWAGUCHI, Ritsuko

Keywords Molecular Dynamics Simulation, Protein, Amyloid

Biomolecules such as proteins and peptides have complicated free-energy landscape with many local minima. The conventional canonical-ensemble molecular dynamics (MD) simulations tend to get trapped in a few of the local-minimum states. To overcome these difficulties, we have proposed new generalized-ensemble algorithms, such as replica-permutation method. We apply these methods to proteins and peptides and try to predict the native structures of proteins as in Figure 1.

We are also interested in protein aggregates such as spherical substances called oligomers and acicular substances called amyloid fibrils (Figure 2). These protein aggregates cause more than 30 kinds of diseases. For example, Alzheimer’s disease is thought to be caused by aggregated amyloid-β (Aβ) peptides. To overcome these diseases, it is essential to understand the aggregate genesis and disruption of Aβ peptides. We perform such MD simulations of oligomers and amyloid fibrils.

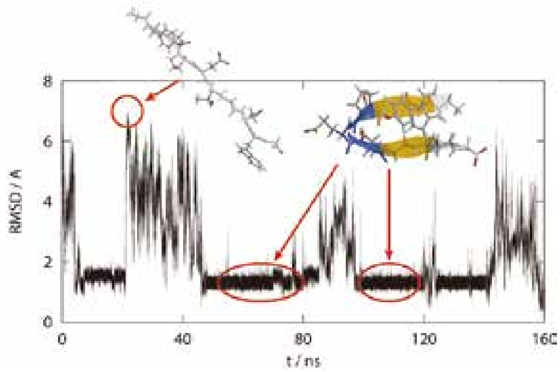


Figure 1. Time series of protein folding simulation.

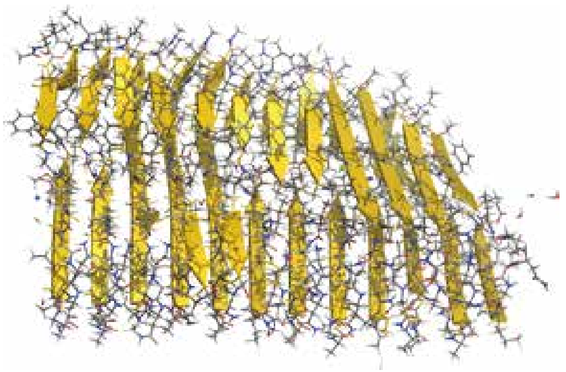


Figure 2. Snapshot of an Aβ amyloid fibril.

Selected Publications

- H. Okumura and S. G. Itoh, “Amyloid Fibril Disruption by Ultrasonic Cavitation: Nonequilibrium Molecular Dynamics Simulations,” *J. Am. Chem. Soc.* **136**, 10549–10552 (2014).
- H. Okumura and S. G. Itoh, “Structural and Fluctuational Difference between Two Ends of Aβ Amyloid Fibril: MD Simulation Predicts Only One End Has Open Conformations,” *Sci. Rep.* **6**, 38422 (9 pages) (2016).
- S. G. Itoh and H. Okumura, “Replica-Permutation Method with the Suwa-Todo Algorithm beyond the Replica-Exchange Method,” *J. Chem. Theory Comput.* **9**, 570–581 (2013).
- S. G. Itoh and H. Okumura, “Oligomer Formation of Amyloid-β(29-42) from Its Monomers Using the Hamiltonian Replica-Permutation Molecular Dynamics Simulation,” *J. Phys. Chem. B* **120**, 6555–6561 (2016).

1. Molecular Dynamics Simulations of Amyloid-β(16-22) Peptide Aggregation at Air–Water Interfaces

The formation of Aβ oligomers is accelerated at hydrophilic–hydrophobic interfaces, such as the cell membrane surface and air–water interface. To understand the effects of the interface on oligomerization at the atomic level, we performed MD simulations of aggregation of Aβ(16–22) peptides at air–water interfaces.[1] First, 100 randomly distributed Aβ(16–22) peptides (Figure 3(a)) moved to the interface (Figure 3(b)). The high concentration of peptides then accelerated their aggregation and formation of antiparallel β-sheets. Two layers of oligomers were observed near the interface. In the first layer from the interface, the oligomer with less β-bridges exposed the hydrophobic residues to the air. The second layer consisted of oligomers with more β-bridges that protruded into water. They are more soluble in water because the hydrophobic residues are covered by N- and C-terminal hydrophilic residues that are aligned well along the oligomer edge. These results indicate that amyloid protofibril formation mainly occurs in the second layer.

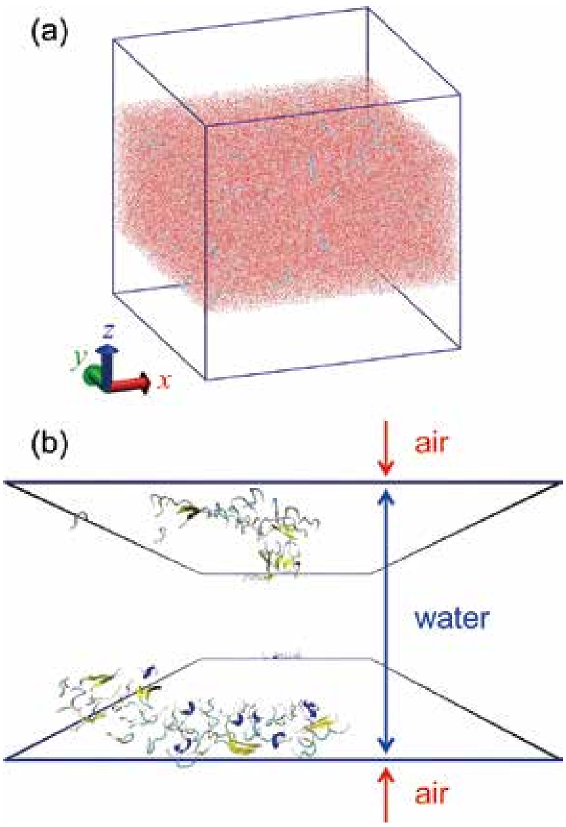


Figure 3. (a) Initial conformation of 100 Aβ(16–22) peptides (blue) and water molecules (red) with air–water interfaces. (b) Side view of the final conformation of Aβ(16–22) peptides. The water molecules are not shown here. The blue frames indicate the air–water interfaces.

2. Development of Replica Sub-Permutation Method for Efficient Molecular Dynamics Simulations

We proposed an improvement of the replica-exchange and replica-permutation methods, which we call the replica sub-permutation method (RSPM).[2] Instead of considering all permutations, this method uses a new algorithm referred to as sub-permutation to perform parameter transition, as in Figure 4. The RSPM succeeds in reducing the number of combinations between replicas and parameters without the loss of sampling efficiency. For comparison, we applied the replica sub-permutation, replica-permutation, and replica-exchange methods to a β-hairpin mini protein, chignolin, in explicit water. We calculated the transition ratio and number of tunneling events in the parameter space, the number of folding–unfolding events, the autocorrelation function, and the autocorrelation time as measures of sampling efficiency. The results indicate that among the three methods, the proposed RSPM is the most efficient in both parameter and conformational spaces.

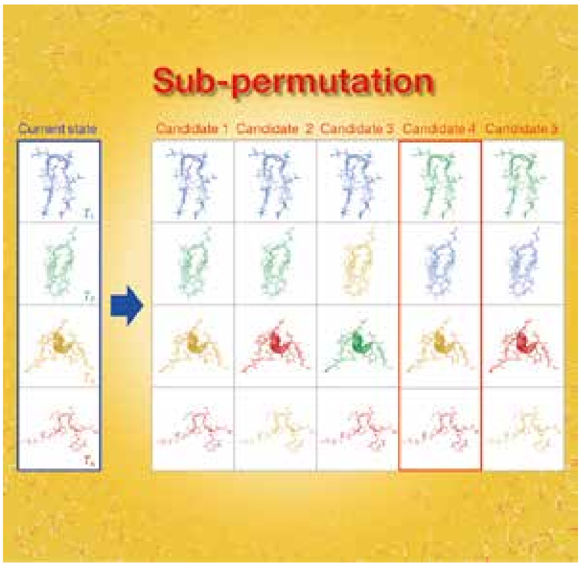


Figure 4. This image shows sub-permutation candidates for a four-replica system. The replica sub-permutation method succeeds in improving sampling efficiency both in parameter and conformational spaces.

References

1) H. Okumura and S. G. Itoh, *J. Chem. Phys.* **151**, 095101 (12 pages) (2020).

2) M. Yamauchi and H. Okumura, *J. Comput. Chem.* **40**, 2694–2711 (2019).

Theoretical Studies on Molecular Aggregates

Department of Theoretical and Computational Molecular Science
Division of Theoretical and Computational Molecular Science

FUJITA, Takatoshi
Research Associate Professor
[tfujita@ims.ac.jp]

Education

2006	B.H.D. Kobe University
2008	M.S. Kobe University
2011	Ph.D. Kobe University

Professional Employment

2010	JSPS Research Fellow (DC2)
2011	JSPS Postdoctoral Fellow (PD)
2012	Postdoctral Fellow, Harvard University
2015	Postdoctral Fellow, Kyoto University
2016	Research Associate Professor, Institute for Molecular Science

Member
Secretary
CHIBA, Fumika

Keywords Exciton, Energy and Charge Transfer, Organic Semiconductors

Organic molecules can assemble into an ordered structure by non-covalent interactions, forming various types of aggregates. Molecular aggregates can exhibit remarkable optical and electronic properties that are not observed in isolated molecules. We study optoelectronic properties and quantum dynamics of molecular aggregates. More specifically, we focus on energy and charge transfer dynamics, energy conversions, and structure-property relationship. Our research also include the developments of theoretical and computational methods.

It is still challenging to simulate quantum dynamics of energy or charge transfer in condensed systems. An exciton or electron wave functions can be delocalized over many molecules by intermolecular electronic couplings. By contrast, the wave functions can be localized because of the static disorder and interactions with nuclear degree of freedom. Therefore, successful theoretical descriptions require the inclusions of electronic couplings, static disorder, and electron-phonon or electron-vibration interaction. We develop a method to simulate quantum dynamics in condensed phase by combining molecular dynamics simulations, electronic structure theories, and quantum dynamics methods, as shown in Figure 1. Electronic states of an aggregate are obtained from a large-scale electronic structure calculation, and the model Hamiltonian for an exciton or a charge carrier is derived. The model Hamiltonian is used for simulating energy or charge dynamics by a quantum dynamics method, which incorporates finite-temperature effects and electron-vibration interactions. The combined computational approach allows for bottom-up descriptions of energy or charge transfer dynamics in realistic molecular aggregates.

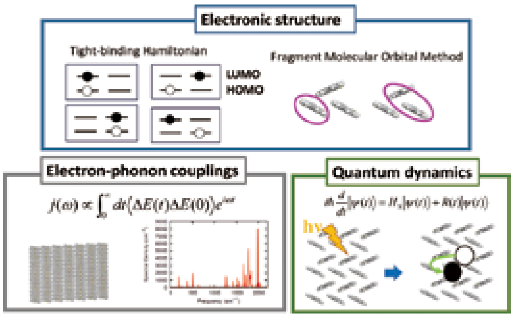


Figure 1. A combine approach to quantum dynamics in molecular aggregates.

We currently investigate electronic states and quantum dynamics at organic interfaces. We also develop the many-body perturbation theory to predict electronic levels at higher accuracy.

Selected Publications

- T. Fujita, S. Atahan-Evrenk, N. P. D. Sawaya and A. Aspuru-Guzik, "Coherent Dynamics of Mixed Frenkel and Charge Transfer Excitons in Dinaphtho[2,3-*b*:2'3'-*f*]thieno[3,2-*b*]-thiophene Thin Films: The Importance of Hole Delocalization," *J. Phys. Chem. Lett.* **7**, 1374–1380 (2016).
- T. Fujita and Y. Mochizuki, "Development of the Fragment Molecular Orbital Method for Calculating Nonlocal Excitations in Large Molecular Systems," *J. Phys. Chem. A* **122**, 3886–3898 (2018).

1. Development of FMO-Based Exciton Model within GW/BSE[1]

Organic optoelectronic devices based on π-conjugated molecules or polymers have attracted considerable attention due to their attractive features. Predicting the electronically excited states is essential for understanding the optoelectronic processes governing the device operation and for rationally designing novel materials. However, accurate calculations of electronic states of organic materials which contain a lot of organic molecules or polymers are still challenging task. Successful theoretical descriptions require an accurate quantum mechanical method. In addition, the effects of polarizable environment must be appropriately taken into account.

In this study, we present the large-scale GW/Bethe-Salpeter equation (BSE) method that enables the computations of delocalized excited states in large molecular assemblies. The many-body Green's function method within the GW approximation can offer practical schemes to calculate electronic states within reasonable accuracy. However, the applications of GW and GW/BSE to large systems were difficult because of their considerable computational times. Here, we develop large-scale GW/BSE method for large systems based on the fragment molecular orbital methods. We have proposed the fragmentation approximations of total polarization functions and ΔCOHSEX approximation that neglects the dynamical polarization of surrounding fragments. We have confirmed that the FMO-GW/BSE method enables accurate calculations of localized electronic states in large systems. Furthermore, the FMO-GW/BSE method was combined with the exciton model to calculate delocalized excited states in molecular aggregates. In the exciton model, the excited-state Hamiltonian for an entire system is calculated in the diabatic basis and then diagonalized to approximate the adiabatic excited states. The FMO-based exciton model utilizes the fragment configuration state functions (CSFs) for intrafragment excited states and for interfragment charge-transfer states, and the excited-state Hamiltonian at the GW/BSE level is calculated in the basis of fragment CSFs. We have shown that the results of unfragmented calculations can be reasonably reproduced; thus, the present FMO-GW/BSE method can offer efficient and practical schemes for investigating realistic molecular aggregates.

2. Revisiting the Electronic Structure of PEN/C_{60} Bilayer Heterojunctions[2]

Molecular orientations and interfacial morphologies have critical effects on the electronic states of donor/acceptor interfaces and thus on the performance of organic photovoltaic devices. Here, we investigate the charge-transfer (CT) states in pentacene(PEN)/C_{60} interfaces as model systems and highlight the polarization and delocalization effects. The effects of polarization and delocalization on the interfacial CT states are schematically represented in Figure 2. In a gas phase (Figure 2 (a)), the energy of the CT state is given by the highest-occupied molecular orbital (HOMO) energy of a donor molecule, the lowest-unoccupied molecular orbital (LUMO) energy of an acceptor molecule, and the Coulomb interaction between the electron and the hole. The solid-state polarization effects reduce the energy gap between the donor HOMO and the acceptor LUMO (Figure 2 (b)) and weakens the e–h interaction. In a solid phase, the electron or hole wave function can be delocalized over multiple acceptor or donor molecules, and delocalized CT states can be formed (Figure 2 (c)). This charge delocalization can further shift the energy gap and possibly weaken the e–h interaction.

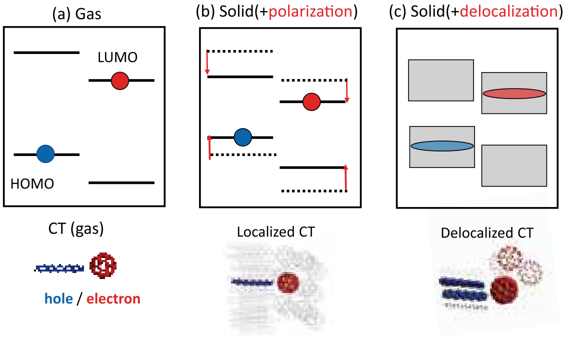


Figure 2. Schematics of solid-state effects on the interfacial charge-transfer states.

In this study, we explore the energy levels and CT states at the organic donor/acceptor interfaces on the basis of the fragment-based GW/BSE approach. The face-on and edge-on orientations of pentacene/C_{60} bilayer heterojunctions have employed as model systems. The FMO-GW/BSE calculations were performed for the local interface structures in the face-on and edge-on bilayer heterojunctions, which contain approximately 2,000 atoms. Calculated energy levels and CT state absorption spectra are in reasonable agreements with those obtained from experimental measurements. We found that the dependence of the energy levels on interfacial morphology is predominantly determined by the electrostatic contribution of polarization energy, while the effects of induction contribution in the edge-on interface are similar to those in the face-on. Moreover, the delocalized CT states contribute to the main absorption peak in the edge-on interface, while the face-on interface features relatively localized CT states in the main absorption peak. The impact of the interfacial morphologies on the polarization and charge delocalization effects is analyzed in detail.

References

1) T. Fujita and Y. Noguchi, in preparation.
2) T. Fujita, Y. Noguchi and T. Hoshi, *Materials* **13**, 2728 (2020).

Functional Dynamics of Biomolecular Machines Revealed by Theoretical Methods

Department of Theoretical and Computational Molecular Science
Division of Theoretical and Computational Molecular Science

OKAZAKI, Kei-ichi
Research Associate Professor
[keokazaki@ims.ac.jp]

Education

2004	B.S. Kyoto University
2006	M.S. Kobe University
2009	Ph.D. Kobe University

Professional Employment

2007	JSPS Research Fellow (DC2), Kobe University
2009	JSPS Postdoctoral Fellow (PD), Waseda University
2010	Part-time Lecturer, Waseda University
2012	JSPS Postdoctoral Fellow for Research Abroad, National Institutes of Health, U.S.A.
2014	Postdoctoral Fellow, Max Planck Institute of Biophysics, Germany
2016	Research Associate Professor, Institute for Molecular Science

Award

2014	Early Career Award in Biophysics, Biophysical Society of Japan

Member
Post-Doctoral Fellow
MAHMOOD, Md Iqbal
JAUNET-LAHARY, Titouan
Secretary
CHIBA, Fumika

Keywords Theoretical Biophysics, Molecular Motors, Transporter

Functional dynamics plays an important role when biomolecular machines fulfill their functions. Motor proteins move on the rail or rotate relative to the stator unidirectionally by using chemical energy. Transporter proteins transport their substrates across the membrane by changing their conformation between the inward-open and outward-open states. We aim to clarify molecular mechanism of these precise, yet dynamic nano-machines developed by nature.

Functional dynamics of biomolecular machines involve wide spectrum of intricate motions and reactions. In order to understand such dynamics, we need a multiscale approach to cover full range of these motions and reactions. Conventional atomistic molecular dynamics (MD) simulations alone cannot cover millisecond-long (or even longer) functional dynamics, especially for a large system like typical biomolecular machines. Thus, we use techniques like importance sampling, coarse-graining, and statistical/kinetic modeling to tackle this problem.

We have been working on biomolecular motors such as ATP synthase and chitinase. ATP synthase is a rotary motor that produces most of ATP required in the cell. It is composed of two rotary motors: F_o and F_1. F_o motor is embedded in the membrane driven by proton gradient, while F_1 motor is driven by ATP hydrolysis reaction. We studied how rotation of F_1 is caused by elementary steps such as product release from the catalytic site. Chitinase is a new type of molecular motor that uses hydrolysis energy of single chitin chain, a polysaccharide, for its unidirectional motion. The sliding motion of chitin chain into the catalytic site of chitinase was studied by atomistic simulations. We also developed a novel framework to estimate chemical-state-dependent free energy profile and diffusion coefficient from single-molecule trajectories.

Transporters are membrane proteins that transport their substrates across the membrane. We have studied Na^+/H^+ antiporter that exchanges sodium ions and protons inside and outside the cell. The ion-transport cycle was simulated in atomic detail with the transition path sampling technique. The simulations predicted the mutation that can speed up the ion transport, which was confirmed by experiments. Another membrane-associated protein, F-BAR protein Pacsin1 that remodels the membrane, is our interest too. The curvature induction and sensing of Pacsin1 on the membrane was studied by multiscale MD simulations using both all-atom and coarse-grained models.

Selected Publications

- K. Okazaki and G. Hummer, "Phosphate Release Coupled to Rotary Motion of F_1-ATPase," *Proc. Natl. Acad. Sci. U.S.A.* **110**, 16468–16473 (2013).
- K. Okazaki and G. Hummer, "Elasticity, Friction, and Pathway of γ-Subunit Rotation in F_oF_1-ATP Synthase," *Proc. Natl. Acad. Sci. U.S.A.* **112**, 10720–10725 (2015).
- K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, "Mechanism of the Electroneutral Sodium/Proton Antiporter PaNhaP from Transition-Path Shooting," *Nat. Commun.* **10**, 1742 (2019).
- M. I. Mahmood, H. Noguchi and K. Okazaki "Curvature Induction and Sensing of the F-BAR Protein Pacsin1 on Lipid Membranes via Molecular Dynamics Simulations," *Sci. Rep.* **9**, 14557 (2019).

1. Mechanism of Unidirectional Motions of Chitinase

Processive cellulase and chitinase recently have been cast new light as a different type of biomolecular motors that use hydrolysis energy of polysaccharides for their unidirectional movements. We used single-molecule trajectories to estimate an underlying diffusion model with chemical-state-dependent free energy profile.1) To consider nonequilibrium trajectories driven by the chemical energy consumed by biomolecular motors, we developed a novel framework based on a hidden Markov model, wherein switching among multiple energy profiles occurs reflecting the chemical state changes in motors. The chemical-state-dependent free energy profile underlying the burnt-bridge Brownian ratchet mechanism of processive chitinase was determined.1)

2. Mechanism of Na^+/H^+ Antiporter and Engineering of a Faster Transporter

Na^+/H^+ antiporters control pH and Na^+ concentration in the cell by exchanging sodium ions and protons across lipid membranes. They belong to the cation/proton antiporter (CPA) superfamily, and prevail in all domains of life. The archaeal Na^+/H^+ antiporters PaNhaP from *Pyrococcus abyssi* and MjNhaP1 from *Methanocaldococcus jannaschii* as well as human NHE1, which is linked to a wide spectrum of diseases from heart failure to autism and has no structure solved yet, are electroneutral antiporters of the CPA1 family, exchanging one proton against one sodium ion. As a model system in mechanistic studies of electroneutral Na^+/H^+ exchange, we studied the transport mechanism of PaNhaP.2)

Na^+/H^+ antiporters use the gradient of either sodium ion or proton to drive the uphill transport of the other ion (Figure 1A). The conformational transition of the transporter makes the ion-binding site accessible from either side of the membrane in the alternating manner. For PaNhaP, the inward-open conformation was obtained by X-ray crystallography, while the outward-open conformation is not known experimentally. We modelled the outward-open conformation by MDFF flexible fitting to the low-resolution outward-open structure of the homologous MjNhaP1 from cryo-EM, followed by the long equilibrium MD simulations. It was shown that the transporter domain moves ~3.5 Å in the direction normal to the membrane to take the outward-open state (Figure 1B).

The inward-open and outward-open conformations described above only provides the end points of the ion-transport. The transition dynamics between the two states is central to the transport mechanism, revealing at once rate-limiting steps, substrate pathways, and the opening and closing of the gate preventing ion leakage. However, with ion exchange occurring on a timescale of seconds at ambient conditions, regular MD simulations are far too slow to resolve transitions. Instead, we can resort to importance sampling of transition dynamics. To sample unbiased transition paths between the inward- and outward-open states, we used techniques from the transition path sampling.

In analysis of the transition paths, we found hydrophobic gates above and below the ion-binding site, which open and close in response to the domain motions (Figure 1C). From the reaction coordinate analysis, it was shown that open-close motion of the outside gate (Ile163-Tyr255) is a rate-limiting step of the alternating-access conformational change. Based on this result, we weakened the outside gate by mutating the residues to both alanine. It was expected that this mutation lowers the barrier and makes the ion transport faster. It was confirmed by experiments that the ion-transport speed of the mutant is indeed twice faster than the wild-type transporter.

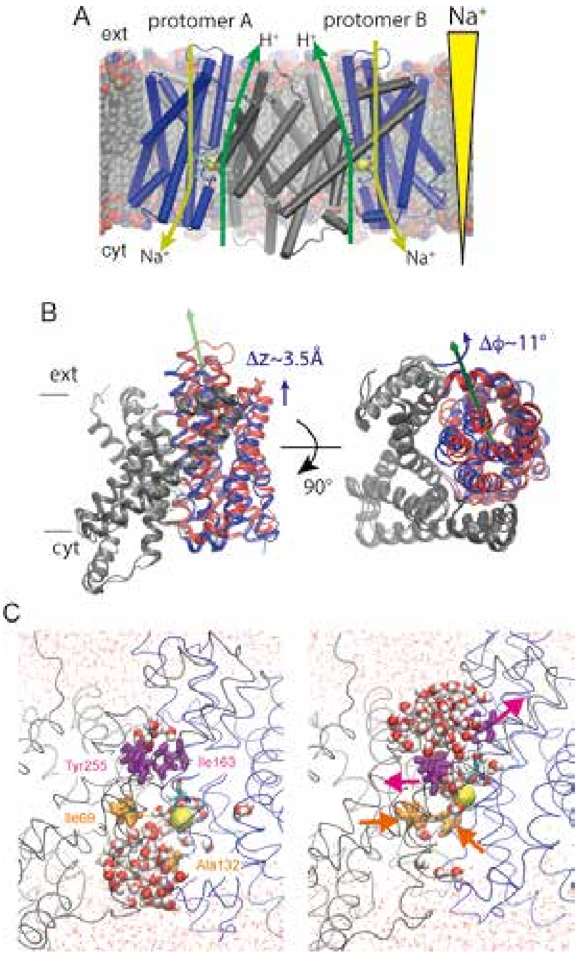


Figure 1. (A) PaNhaP dimer structure. (B) Comparison of the transporter domain between the inward-open (blue) and outward-open (red) states. (C) The outside (purple) and inside (orange) gates found in the transition paths.

References

1) K. Okazaki, A. Nakamura and R. Iino *J. Phys. Chem. B* **124**, 6475–6487 (2020).

2) K. Okazaki, D. Wöhlert, J. Warnau, H. Jung, Ö. Yildiz, W. Kühlbrandt and G. Hummer, *Nat. Commun.* **10**, 1742 (2019).

Theory and Computation of Reactions and Properties in Solutions and Liquids

Department of Theoretical and Computational Molecular Science
Division of Computational Molecular Science

ISHIDA, Tateki
Assistant Professor

We are interested in the projects on ionic liquids (ILs). ILs' projects are focused on the unique dissolution process of cellulose polysaccharides, and the investigation of statical and dynamical properties on ionic liquids including temperature effects.

1. Investigations of Dissolution and Decomposition Mechanisms of a Cellulose Fiber in Ionic Liquids[1] with Molecular Dynamics Simulation

We studied dissolution and decomposition mechanisms of cellulose ($I_β$) polymers in ILs. In order to investigate motion of cellulose fibers and intermolecular interactions between cellulose molecules and cationic and anionic species in ILs, we carried out molecular dynamics simulation. We employed the 1-ethyl-3-methylimidazolium acetate IL solvent for target system. It was found out that the intermolecular interaction energy between cellulose polymers in the IL are reduced, comparing with that in water. Also, our results suggest that the enhancement of the flexibility of rigid cellulose chains triggered by the breakage of intrachain H-bonds due to anions starts decomposition processes accompanied by dissolution processes due to the intercalation of cations, synergistically, and, then, both dissolution and decomposition processes are executed simultaneously.

2. Researches on Statical and Dynamical Properties of Ionic Liquids: Molecular Origin of Low-k Peak of ILs and Dynamical Heterogeneity

We have investigated the molecular level origin of low-k peak (< 0.5 Ang.$^{-1}$) in the structure factor in ILs. In particular, we found out that the structure factor of heterocyclic ring parts in cations largely contribute to low-k peak in ILs. Also, we are going to carry out the study of dynamical properties of ILs, dynamical heterogeneity in ILs at room temperature with molecular dynamics simulation procedure.

Reference

1) T. Ishida, *J. Phys. Chem. B* **124**, 3090–3102 (2020).

Visiting Professors

Visiting Professor
MORI, Hirotoshi *(from Chuo University)*

Electronic Structure Informatics for Designing Functional Liquid Materials

Mixed liquids exhibit various chemical functions depending on their composition and mixing ratio. Contrary to its fundamental scientific importance, however, the chemistry of mixing is an area where molecular level knowledge is not still enough. With the backgrounds, we have been challenging the predictive chemistry of functional liquid materials by developing a novel *ab initio* molecular simulation method with conventional computational cost (Effective fragment potential molecular dynamics; EFP-MD) and a data science approach. In fiscal 2020, we worked on the prediction of Henry's constant values related to the absorption of various industrial exhaust gases for non-aqueous mixed solutions (mixed ionic liquids, ionic liquids/organic solvent mixtures) which supports environmental chemical engineers shortly. We will proceed with our research aiming at the construction of statistical thermodynamic theory for real systems that predict mixed thermodynamics.

Visiting Professor
YANASE, Youichi *(from Kyoto University)*

Theoretical Study of Exotic Quantum Phases

We are working on theoretical studies of exotic quantum phases such as unconventional superconductivity, parity-violating antiferromagnet, quantum liquid crystal, and topological state of matter. In particular, my recent interest focuses on quantum phases lacking global or local space inversion symmetry. For instance, we classified such quantum phases in terms of multipole moment with the use of group theory, and explored emergent electromagnetic responses, such as magnetopiezoelectric effect and chiral photocurrent. Furthermore, a rigorous and gauge-invariant formulation of multipole moment was given by the thermodynamic definition, which is directly related to the magnetoelectric effect. Superconductivity induced by multipole fluctuations was clarified. To develop the functionality of superconductors, we showed a giant superconducting Edelstein effect in topological superconductors. By considering a light-matter interaction, we proposed laser-induced topological superconductivity in TMD.

Visiting Associate Professor
HIGASHI, Masahiro *(from Kyoto University)*

Theoretical Study on the Excited-State Reactions in Condensed Phases

We are theoretically investigating chemical reactions and physical properties in condensed phases such as solutions and proteins. In particular, we are focusing on the excited-state reaction dynamics in condensed phases. Theoretical studies on the excited-state reaction dynamics of large systems is still one of most challenging tasks due to the high computational cost of electronic structure calculations for excited states and adequate statistical samplings required for molecular dynamics simulations. To overcome this difficulty, we have been developing several efficient methods combining electronic structure calculations and molecular dynamics simulations. Recently, we analyzed the excitation energy transfer in a light-harvesting complex by using our developed methods. The calculated excitation energies of pigments and their fluctuations are in quantitative agreement with the experimental ones. It is found that the fluctuations of pigments are largely affected by the individual protein environments and that the efficient excitation energy transfer is achieved by the site-dependent fluctuations.

RESEARCH ACTIVITIES

Photo-Molecular Science

We study the interaction of atoms and molecules with optical fields with its possible applications to active control of atomic and molecular functionality and reactivity. We also develop novel light sources to promote those studies. Two research facilities, the Center for Mesoscopic Sciences and the UVSOR Synchrotron Facility, closely collaborates with the Department.

The core topics of the Department include attosecond coherent control of gas- and condensed-phase atoms and molecules, high-resolution optical microscopy applied to nanomaterials, synchrotron-based spectroscopy of core-excited molecules and solid-state materials, vacuum-UV photochemistry, and the development of novel laser- and synchrotron-radiation sources.

Exploring Quantum-Classical Boundary

Department of Photo-Molecular Science
Division of Photo-Molecular Science II

OHMORI, Kenji
Professor
[ohmori@ims.ac.jp]

Education

1987 B. E. The University of Tokyo
1992 Ph.D. The University of Tokyo

Professional Employment

1992 Research Associate, Tohoku University
2001 Associate Professor, Tohoku University
2003 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2004 Visiting Professor, Tohoku University (–2005)
2007 Visiting Professor, Tokyo Institute of Technology (–2008)
2009 Visiting Professor, The University of Tokyo (–2011)
2012 Visiting Professor, University of Heidelberg
2014 Visiting Professor, University of Strasbourg (–2016)

Awards

1998 Award by Research Foundation for Opto-Science and Technology
2007 JSPS Prize
2007 Japan Academy Medal
2009 Fellow of the American Physical Society
2012 Humboldt Research Award
2017 Hiroshi Takuma Memorial Prize of Matsuo Foundation
2018 Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology of Japan

Member

Assistant Professor
SUGAWA, Seiji
DE LÉSÉLEUC, Sylvain
IMS Research Assistant Professor
TOMITA, Takafumi
Post-Doctoral Fellow
ZHANG, Yichi
BHARTI, Vineet
KUNIMI, Masaya
Graduate Student
MIZOGUCHI, Michiteru
CHEW, Yee Lai
TIRUMALASETTY PANDURANGA, Mahesh
Secretary
KAWAMOTO, Minako

Keywords Quantum-Classical Boundary, Quantum Simulation, Quantum Computing

It is observed in a double-slit experiment by Tonomura and coworkers that single electrons recorded as dots on a detector screen build up to show an interference pattern, which is delocalized over the screen.1) This observation indicates that a delocalized wave function of an isolated electron interacts with the screen, which is composed of many nuclei and electrons interacting with each other, and becomes localized in space. This change, referred to as "collapse" in quantum theory, is often accepted as a discontinuous change, but a basic question arises: When and how the delocalized wave function becomes localized? Our objective is uncovering this mystery by observing the spatiotemporal evolution of a wave function delocalized over many particles interacting with each other. Having this objective in mind, we have developed coherent control with precisions on the picometer spatial and attosecond temporal scales. Now we apply this ultrafast and ultrahigh-precision coherent control to delocalized wave functions of macroscopic many-particle systems such as an array of ultracold rubidium (Rb) Rydberg atoms, as depicted schematically in Figure 1, envisaging the quantum-classical boundary connected smoothly.

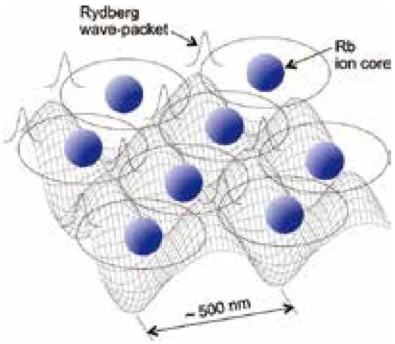


Figure 1. Metal-like quantum gas. A schematic of the many-body system of ultracold Rydberg atoms, where electronic wave functions spatially overlap between neighboring atoms.2,7)

Selected Publications

- H. Katsuki *et al.*, "Visualizing Picometric Quantum Ripples of Ultrafast Wave-Packet Interference," *Science* **311**, 1589–1592 (2006).
- H. Katsuki *et al.*, "Actively Tailored Spatiotemporal Images of Quantum Interference on the Picometer and Femtosecond Scales," *Phys. Rev. Lett.* **102**, 103602 (2009).
- K. Hosaka *et al.*, "Ultrafast Fourier Transform with a Femtosecond-Laser-Driven Molecule," *Phys. Rev. Lett.* **104**, 180501 (2010).
- H. Goto *et al.*, "Strong-Laser-Induced Quantum Interference," *Nat. Phys.* **7**, 383–385 (2011).
- H. Katsuki *et al.*, "All-Optical Control and Visualization of Ultrafast Two-Dimensional Atomic Motions in a Single Crystal of Bismuth," *Nat. Commun.* **4**, 2801 (2013).
- N. Takei *et al.*, "Direct Observation of Ultrafast Many-Body Electron Dynamics in an Ultracold Rydberg Gas," *Nat. Commun.* **7**, 13449 (2016).
- C. Liu *et al.*, "Attosecond Control of Restoration of Electronic Structure Symmetry," *Phys. Rev. Lett.* **121**, 173201 (2018).
- M. Mizoguchi *et al.*, "Ultrafast Creation of Overlapping Rydberg Electrons in an Atomic BEC and Mott-Insulator Lattice," *Phys. Rev. Lett.* **124**, 253201 (2020).

1. Development of an “Ultrafast Quantum Simulator” by Optical Control with Precisions on the Attosecond Temporal and Submicron Spatial Scales3–9)

Quantum many-body problems are at the heart of a variety of physical functionalities including superconductivity and magnetism in solid materials. It is extremely hard, however, to solve such quantum many-body problems. In solving the Hubbard model with 1000 particles, for example, the diagonalization would take 10 to the power of 573 years even with the world’s fastest supercomputers. In this project, we develop a novel quantum simulator that can simulate quantum many-body dynamics for more than 1000 particles within one nanosecond, combining our two unique experimental resources: “coherent control with attosecond precision”8) and “a strongly-correlated ultracold Rydberg gas.”9)

We have completed a standard hardware of this ultrafast quantum simulator composed of an array of ultracold Rb atoms trapped in an optical lattice and excited to Rydberg levels with a coherent picosecond (ps) laser pulse, as schematically illustrated in Figure 2.3,4,6,7) The broad bandwidth of the ps laser pulse has allowed us to excite the atoms in the neighboring lattice sites to Rydberg levels simultaneously for the first time. With this standard hardware, we have succeeded in creating an exotic electronic state with spatially overlapping wave-functions as shown schematically in Figure 2.7) The degree of spatial overlap is actively tuned with ~50 nanometer precision. This exotic metal-like quantum gas under exquisite control opens up a completely new regime of many-body physics for simulating ultrafast many-body electron dynamics dominated by Coulomb interactions.7)

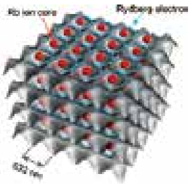


Figure 2. Schematic of the standard hardware of the ultrafast quantum simulator.3,4,7)

We have also completed a readout interface of our ultrafast quantum simulator, which is the time domain Ramsey interferometry of ultracold Rydberg atoms with attosecond precision, whose contrast is almost 100% as shown in Figure 3.5) The phase and visibility of this Ramsey interferogram are highly sensitive to the nature and strength of many-body interactions among the Rydberg atoms.

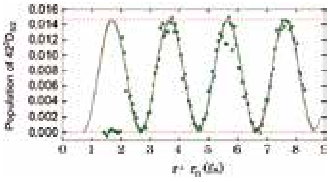


Figure 3. Time domain Ramsey interferometry of ultracold ^{87}Rb atoms with attosecond precision to be used as a readout interface of the ultrafast quantum simulator. Population of the $42^2D_{5/2}$ Rydberg state is plotted as a function of the delay τ between two laser pulses, where τ_0 ~ 50 ps. Adopted from Ref. 5).

2. Application of an “Ultrafast Quantum Simulator” to Quantum Computing3)

We are developing a cold-atom based quantum annealer with the hardware of the ultrafast quantum simulator.10) The cold-atom annealer has advantages against the one with the superconducting qubits. Those advantages include scalability and efficiency. All to all connections among physical bits necessary for quantum annealing could also be easier with cold atoms than superconducting qubits.

So far we have developed arbitrary two dimensional optical trap arrays for cold atoms, which are necessary for quantum annealing,10) in tight collaborations with Hamamatsu Photonics K.K.3) Their examples are shown in Figure 4, the world’s smallest arbitrary trap arrays whose nearest neighbor distance is only ~1 micron, which used to be typically ~4 micron in previous works.11)

We have recently succeeded in loading a single atom into each trap of those arbitrary arrays, and reassembling those atoms with an optical tweezer. Accordingly we can prepare an array of atoms we desire, as exemplified in Figure 5.

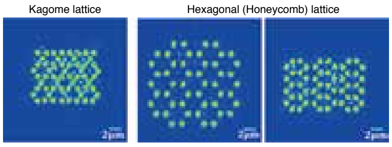


Figure 4. Examples of the world’s smallest arbitrary arrays of optical traps.3)

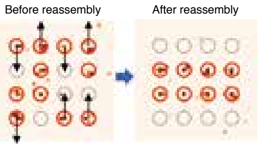


Figure 5. Assembly of an arbitrary array of single Rb atoms.

3. Engineering Quantum Wave-Packet Dispersion with a Strong Nonresonant Femtosecond Laser Pulse12)

A non-dispersing wave packet has been attracting much interest from various scientific and technological viewpoints. However, most quantum systems are accompanied by anharmonicity, so that retardation of quantum wave-packet dispersion is limited to very few examples only under specific conditions and targets. Here we demonstrate a conceptually new and universal method to retard or advance the dispersion of a quantum wave packet through “programmable time shift” induced by a strong non-resonant femtosecond laser pulse. A numerical simulation has verified that a train of such retardation pulses stops wave-packet dispersion.

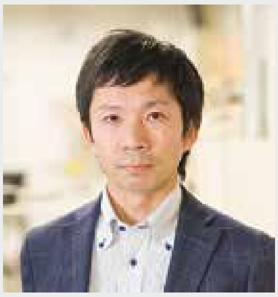
Our ultrafast quantum simulator operates with atomic Rydberg levels,3–9) whose level structure is anharmonic, so that its wave packet is dispersed and broadened quickly. The new control method for wave-packet dispersion developed here would serve as an enabling technology for our ultrafast quantum simulator to enhance its functionality for quantum simulation and computing.

References

1) K. Tonomura *et. al.*, *Am. J. Phys.* **57**, 117 (1989).
2) K. Ohmori, *Found. Phys.* **44**, 813–818 (2014).
3) US Patent (3rd Nov. 2020) “Quantum Simulator and Quantum Simulation Method,” H. Sakai (Hamamatsu Photonics K.K.), K. Ohmori (IMS) *et al.*, and one more patent publication.
4) White Paper 2018 on Manufacturing Industries published by Ministry of Economy Trade and Industry, JAPAN.
5) C. Liu *et al.*, *Phys. Rev. Lett.* **121**, 173201 (2018).
6) Highlighted in “Quantum-Technology Innovation Strategy” by the Cabinet Office of Japan, January 2020.
7) M. Mizoguchi *et al.*, *Phys. Rev. Lett.* **124**, 253201 (2020).
8) H. Katsuki *et al.*, *Acc. Chem. Res.* **51**, 1174–1184 (2018).
9) N. Takei *et al.*, *Nat. Commun.* **7**, 13449 (2016).
10) A. W. Glaetzle *et al.*, *Nat. Commun.* **8**, 15813 (2017).
11) D. Barredo *et al.*, *Science* **354**, 1021 (2016).
12) H. Katsuki *et al.*, *arXiv:*1910.08241 (2019).

Electronic Property of Functional Organic Materials

Department of Photo-Molecular Science
Division of Photo-Molecular Science III



KERA, Satoshi
Professor
[kera@ims.ac.jp]

Education

1996	B.E. Chiba University
1998	M.E. Chiba University
2001	Ph.D. Chiba University

Professional Employment

1998	JSPS Research Fellow
2001	Research Associate, Chiba University
2003	Research Associate, Institute for Molecular Science
2003	Postdoctoral Fellow, Wuerzburg University
2004	Assistant Professor, Chiba University
2007	Associate Professor, Chiba University
2009	Visiting Associate Professor, Institute for Molecular Science
2013	Adjunct Lecturer, The Open University of Japan
2013	Visiting Associate Professor, Soochow University
2014	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies Visiting Professor, Chiba University
2019	Visiting Professor, Kyoto University, Hiroshima University
2020	Visiting Professor, Tohoku University

Member
IMS Fellow
HASEGAWA, Yuri
Post-Doctoral Fellow
YAMADA, Kazuto
Visiting Scientist
YANG, Jinpeng
MADUWANTHA, Kaveendra*
Graduate Student
NAKAMURA, Takuto†
Secretary
HAGIWARA, Hisayo

Keywords Photoelectron Spectroscopy, Molecular Assemble, Electronic State

Functional organic materials (FOM) have recently attracted considerable attention both for fundamental research and device applications because of peculiar properties not found in inorganics and small molecules. However, the mechanisms and the origin of various device characteristics are still under debate. Scientific discussions have been redundant because of long-standing beliefs that the electronic structure of FOM would be conserved as in an isolated molecule even for solid phases due to the weak van der Waals interaction. To reveal characteristics of FOM, it is essential to investigate precisely the electronic structure at various interfaces, including organic–organic and organic–inorganic (metal/semiconductor) contacts. Recently we realized that the weak electronic interaction manifests itself as small intensity modulations of fine structures in photoelectron spectra, depending on the adsorption and aggregation conditions on the surface. Thanks to recent instrumentation improvements, we can assess hidden fine features in the electronic states, *e.g.* electron–phonon coupling, quasi-particle states, very small densities of gap states, narrow band dispersion, and dynamic electronic polarization. To elucidate what really impacts on the electronic states of the FOM in their assembly as well as at the interface upon weak interaction, an evaluation of the wave-function spread of the electronic states is very important because the interface states are described as a delocalized molecular orbital state depending on the strength of weak electronic coupling (hybridization). Observing modifications of electron wave functions upon weak electronic coupling as well as strong electron–phonon coupling is a central issue on our agenda.

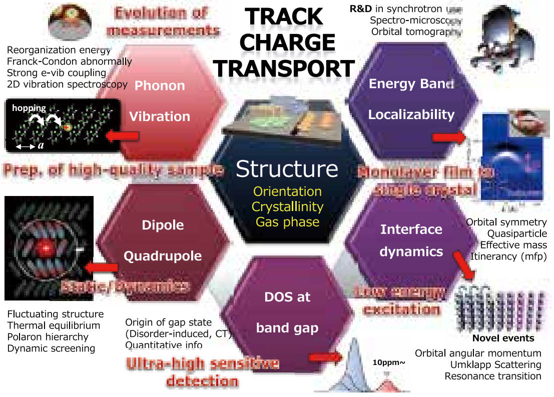


Figure 1. Overview of our agenda. A rich assortment of surface and interface structures of FOM to provide complicated spectral features of ultraviolet photoelectron spectroscopy.

Selected Publications

- Y. Nakayama, S. Kera and N. Ueno, *J. Mater. Chem. C* **8**, 9090–9132 (2020). [review]
- S. Kera, T. Hosokai and S. Duhm, *J. Phys. Soc. Jpn.* **87**, 061008 (7 pages) (2018). [review]
- J.-P. Yang, F. Bussolotti, S. Kera and N. Ueno, *J. Phys. D: Appl. Phys.* **50**, 423002 (45 pages) (2017). [review]
- S. Kera and N. Ueno, *J. Electron Spectrosc. Relat. Phenom.* **204**, 2–11 (2015). [review]

1. The Role of Initial and Final States in Molecular Spectroscopies: A Case Study of DBP[1,2]

Interpreting experimental spectra of organic semiconductor films is challenging, and understanding the relationship between experimental data obtained by different spectroscopic techniques, UPS, IPES, 2PPE and optical absorption requires a careful consideration of the initial and final states for each process. We present a coherent framework that is capable of treating on equal footing most spectroscopies. We develop a simple model for the expected energy level positions by the spectroscopies and relate them to the energies of molecular states. Molecular charging energies in photoionization processes, as well as adsorption energies and the screening of molecular charges due to environmental polarization, are taken into account as the main causes for shifts of the measured spectroscopic features. We explain the relationship between these quantities, as well as with the transport gap, the optical gap and the exciton binding energy.[1)]

Our considerations serve as a model for weakly interacting systems where wave function hybridizations between adjacent molecules are negligible as demonstrated for DBP films on graphite.[2)]

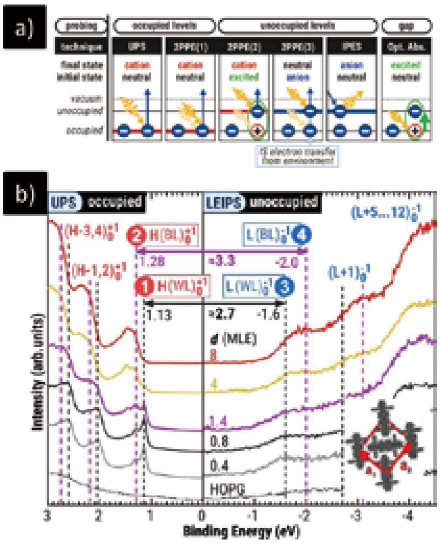


Figure 2. a) Scheme of the typical spectroscopic processes in UPS, 2PPE, IPES, and optical absorption in relation to the initial and final states. b) Thickness dependences of XeI-UPS and IPES (LEIPS) of DBP films on graphite. The energy positions of bilayer (BL) are shifted from wetting layer (WL) of monolayer. The figure is after ref 1,2).

2. Impacts of Electrostatic Interactions on the Energy Levels of Organic Semiconductor Blends[3)]

Halogenation of conjugated molecules represents a powerful approach to tune the electronic structure of molecular thin films through inductive effects and long-range intermolecular electrostatic interactions. We provide a comprehensive experimental and theoretical analysis of the prototypical blend formed by pentacene (PEN) and perfluoropentacene (PFP) to relate structure with electronic properties. We find a mixed-stack structural motif in standing and lying orientations depending on the substrate nature. In the standing orientation, the ionization potential lies in between the values of the pure components, in line with the established picture of averaged molecular quadrupole moments. For the lying orientation, however, we experimentally observe an ionization potential lower than both pristine values, which seems at odds with this simple rationale. Electrostatic simulations based on the knowledge of the atomistic structure of the films capture the complex experimental scenario for both orientations. In particular, the ultralow ionization potential of films formed by lying molecules is identified as a signature of the monolayer structure, where quadrupolar interactions are responsible for a difference of *ca.* 0.4 eV in the highest occupied molecular orbital energy as compared to thicker films with the same molecular orientation.

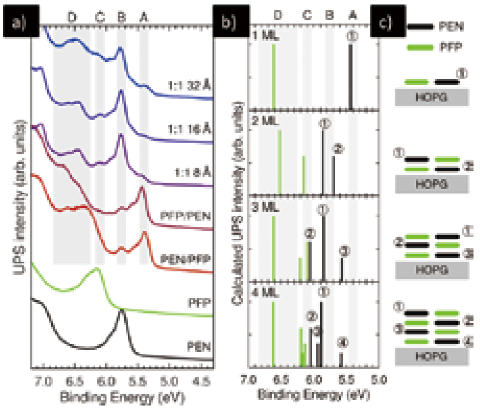


Figure 3. (a) UPS of blends PEN/PFP films of lying orientation on graphite. The spectra of PEN and PFP monolayers are shown as reference. b) Calculated energy levels of PEN:PFP layers; black and green bars correspond to the IPs of PEN and PFP, respectively. The calculated intensity (bar height) depends on the depth z of the ionized layer from the surface in Figure 3c). The figure is after ref 3).

3. Other Activities in UVSOR

We have conducted beamline R&D and user supports in collaboration with other universities. Experiments using photoelectron momentum microscope is started at BL6U.[4)]

References

1) T. Kirchhuebel, O. L. A. Monti, T. Munakata, S. Kera, R. Forker and T. Fritz., *Phys. Chem. Chem. Phys.* **21**, 12730–12747 (2019).
2) T. Kirchhuebel, S. Kera *et al.*, *J. Phys. Chem. C* **124**, 19622–19638 (2020).
3) G. D'Avinol, S. Kera *et al.*, *Chem. Mater.* **32**, 1261–1271 (2020).
4) F. Matsui *et al.*, *Jpn. J. Appl. Phys.* **59**, 067001 (2020).

---

* IMS-IIPA Program

† IMS with Osaka University (Cadet Program)

Light Source Developments by Using Relativistic Electron Beams

UVSOR Synchrotron Facility
Division of Advanced Accelerator Research

KATOH, Masahiro
Project Professor
[mkatoh@ims.ac.jp]

Education

1982 B.S. Tohoku University
1997 Ph.D. Tohoku University

Professional Employment

1986 Reseach Associate, National Laboratory for High Energy Physics
2000 Associate Professor, Institute for Molecular Science
2004 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies
2019 Professor, Hiroshima University
Project Professor, Institute for Molecular Science

Member

Assistant Professor
FUJIMOTO, Masaki
Post-Doctoral Fellow
SALEHI, Elham
Graduate Student
KIMURA, Shinnosuke*
KOSUGI, Naoki*
NAKAO, Kaito*
HORI, Haruki*

Keywords Accelerator, Beam Physics, Astrobiology

UVSOR is a synchrotron light source providing low energy synchrotron light ranging from terahertz wave to soft X-rays. Although it was constructed about 30 years ago, its performance is still in the world top level among low energy synchrotron light sources. This is the result of the continuous effort on improving the machine. Our research group has been developing and introducing new accelerator technologies toward producing bright and stable synchrotron light, such as low emittance electron beam optics, novel insertion devices or state-of-the-art beam injection technique. We have been developing novel light sources, such as free electron laser, coherent synchrotron radiation, optical vortices and laser Compton gamma-rays. We have been investigating beam physics which would be the basis of the future developments of the facility.

Figure 1. UVSOR-III Electron Storage Ring and Synchrotron Radiation Beamlines.

Selected Publications

- S. Bielawski, C. Evain, T. Hara, M. Hosaka, M. Katoh, S. Kimura, A. Mochihashi, M. Shimada, C. Szwaj, T. Takahashi and Y. Takashima, “Tunable Narrowband Terahertz Emission from Mastered Laser–Eelectron Beam Interaction,” *Nat. Phys.* **4**, 390–393 (2008).
- M. Shimada, M. Katoh, M. Adachi, T. Tanikawa, S. Kimura, M. Hosaka, N. Yamamoto, Y. Takashima and T. Takahashi, “Transverse-Longitudinal Coupling Effect in Laser Bunch Slicing,” *Phys. Rev. Lett.* **103**, 144802 (2009).
- M. Katoh, M. Fujimoto, H. Kawaguchi, K. Tsuchiya, K. Ohmi, T. Kaneyasu, Y. Taira, M. Hosaka, A. Mochihashi and Y. Takashima, “Angular Momentum of Twisted Radiation from an Electron in Spiral Motion,” *Phys. Rev. Lett.* **118**, 094801 (2017).
- Y. Taira, T. Hayakawa and M. Katoh, “Gamma-Ray Vortices from Nonlinear Inverse Thomson Scattering of Circularly Polarized Light,” *Sci. Rep.* **7**, 5018 (2017).
- S. Matsuba, K. Kawase, A. Miyamoto, S. Sasaki, M. Fujimoto, T. Konomi, N. Yamamoto, M. Hosaka and M. Katoh, “Generation of Vector Beam with Tandem Helical Undulators,” *Appl. Phys. Lett.* **113**, 021106 (2018).
- Y. Hikosaka, T. Kaneyasu, M. Fujimoto, H. Iwayama and M. Katoh, “Coherent Control in the Extreme Ultraviolet and Attosecond Regime by Synchrotron Radiation,” *Nat. Commun.* **10**, 4988 (2019).
- T. Kaneyasu, Y. Hikosaka, M. Fujimoto, H. Iwayama and M. Katoh, “Controlling the Orbital Alignment in Atoms Using Cross-Circularly Polarized Extreme Ultraviolet Wave Packets,” *Phys. Rev. Lett.* **123**, 233401 (2019).

1. Light Source Technology Developments Based on Laser and Synchrotron

We have been developing light source technologies at the UVSOR-III electron storage ring using a dedicated experimental station BL1U, which was constructed under the support of Quantum Beam Technology Program of JST/MEXT aiming to develope novel light sources and exploring their applications. The BL1U is equipped with two undulators which constitute an optical klystron, a laser system which is synchronized with the accelerator beam and a dedicated beamline consisting of mirrors and a monochromator whose arrangement can be flexibly changed according to the types of the experiments.

In these years, we are focusing on generation of spatially structured light, such as optical vortex beams and optical vector beams from undulators, in collaboration with Hiroshima Univ. and Nagoya Univ. We have succeeded in producing such novel photon beams and are exploring their applications. More recently, we have started exploring the possibility utilizing the temporal structure of undulator radiation, in collaboration with Saga Light Source and Toyama Univ. So far, we have been demonstrated the coherent controls of atoms by using radiation from two undulators arranged in tandem. It has been widely believed that such experiments were possible only with precisely controlled laser beam. Our results may open a new research field on the application of synchrotron radiation.

We have been developing a laser Compton scattering gamma-ray source at BL1U, which is capable of producing monochromatic and energy-tunable gamma-rays. Now we are exploring their applications such as isotope imaging based on nuclear fluorescence resonance in collaboration with Kyoto Univ., AIST and QST, photon-induced positron annihilation lifetime spectroscopy in collaboration with Yamagata Univ. and AIST and an experimental verification on Delbruck scattering in collaboration with QST, AIST and Kyoto Univ. Theoretically we have proven that vortex photons carrying orbital angular momentum can be produced by non-linear Compton scattering of circularly polarized photons. We are planning its experimental demonstration at BL1U in collaboration with AIST.

Figure 2. Twin Polarization-variable Undulators/Optical Klystron at UVSOR-III.

2. Accelerator Technology Developments for Electron Synchrotrons

We carried out several upgrade plans on UVSOR electron synchrotron since 2000. We designed a special beam optics intended to higher brightness. We designed necessary accelerator components, reconstructed the accelerator and commissioned it. We have designed six undulators and have successfully commissioned them. Moreover, we have been continuously introducing new technologies such as the top-up operation in which the electron beam intensity is kept quasi-constant at a high beam current, 300 mA, and the novel beam injection scheme with a pulsed sextupole magnet. As the result of all these efforts, now, the machine is one the brightest synchrotron light sources among the low energy machines below 1GeV in the world.

Currently, the storage ring is stably operated for many of the users, however, the requirements from the users for the stability is getting higher and higher. We are improving cooling water system and developing various feedback systems. As a near-term upgrade plan, we are considering replacing some of the undulators to fit the changes of the users' requirements on the wavelength. For a long-term plan, we continue the design studies on the new low emittance optics of the present synchrotron and on new accelerator systems such as a linear accelerator based free electron laser or a diffraction limited storage ring light source.

We are collaborating with Nagoya University Synchrotron Radiation Research Center (NUSR) for the accelerator technology developments. Accelerator magnets based on permanent magnets are being developed, which would contribute to the power consumption saving in the future plan. Various high brightness electron sources are being developed and tested. New beam diagnostic technologies toward beam stabilization are being developed. Several PhD students from the University are involved in these studies.

We are also collaborating with Accelerator Research Laboratory at KEK for the compact Energy Recovery Linac (cERL) project, which is a novel electron accelerator toward a diffraction-limited synchrotron light source and a free electron laser.

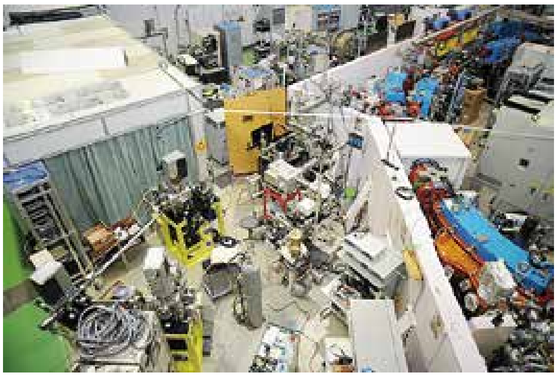


Figure 3. UVSOR BL1U experimental station for source development studies.

---

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Development and Utilization of Novel Quantum Beam Sources Using a High Energy Electron Beam

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

TAIRA, Yoshitaka
Associate Professor
[yostaira@ims.ac.jp]

Education

2007	B.S. Nagoya University
2009	M.S. Nagoya University
2012	Ph.D. Nagoya University

Professional Employment

2011	JSPS Research Fellow
2012	Research Scientist, National Institute of Advanced Industrial Science and Technology (AIST)
2018	Senior Research Scientist, National Institute of Advanced Industrial Science and Technology (AIST)
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2010	Student Presentation Award, The 23rd Annual Meeting of the Japanese Society for Synchrotron Radiation Research
2010	Young Researcher Best Presentation Award, The 53rd Annual Meeting of the Japanese Society of Radiation Chemistry
2011	Nagoya University Outstanding Graduate Student Award
2012	Oral Presentation Award, The 9th Annual Meeting of Particle Accelerator Society of Japan
2012	Young Researcher Best Poster Award, 12th International Symposium on Radiation Physics
2013	Young Scientist Award of the Physical Society of Japan
2015	Young Researcher Best Presentation Award, Beam Physics Workshop 2015

Member
Post-Doctoral Fellow
SALEHI, Elham

Keywords Electron Beams, Synchrotron Radiation, Gamma-Rays

Our group develop new electromagnetic wave sources using a high energy electron beam. In the UVSOR-III electron storage ring at the Institute for Molecular Science, a 750-MeV electron beam can be generated. Electromagnetic waves in a wide frequency range from ultraviolet waves to gamma-rays are emitted by interacting the electron beam with magnetic fileds and lasers.

Laser Thomson (Compton) scattering is a method to generate a high energy gamma-ray by the interaction between a high energy electron and a laser. We have developed ultra-short pulsed gamma-rays with the pulse width of sub-ps to ps range by using 90-degree laser Thomson scattering (Figure 1). We applied this ultra-short pulsed gamma-rays to gamma induced positron annihilation lifetime spectroscopy (GiPALS). A positron is an excellent probe of lattice defects in solids and of free volumes in polymers at the sub-nm to nm scale. GiPALS enables defect analysis of a thick material in a few cm because positrons are generated throughout a bulk material via pair production. Our group is conducting research on improving the properties of the material by using GiPALS.

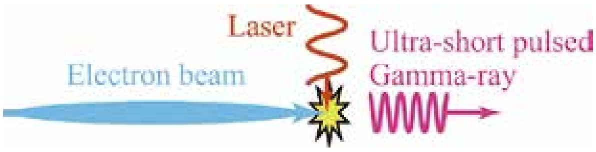


Figure 1. Schematic illustration of 90-degree laser Thomson scattering.

Selected Publications

- Y. Taira, M. Adachi, H. Zen, T. Tanikawa, N. Yamamoto, M. Hosaka, Y. Takashima, K. Soda and M. Katoh, "Generation of Energy-Tunable and Ultra-Short-Pulse Gamma Ray via Inverse Compton Scattering in an Electron Storage Ring," *Nucl. Instrum. Methods Phys. Res., Sect. A* **652**, 696 (2011).
- Y. Taira, H. Toyokawa, R. Kuroda, N. Yamamoto, M. Adachi, S. Tanaka and M. Katoh, "Photon-Induced Positron Annihilation Lifetime Spectroscopy Using Ultrashort Laser-Compton-Scattered Gamma-Ray Pulses," *Rev. Sci. Instrum.* **84**, 053305 (2013).
- Y. Taira, T. Hayakawa and M. Katoh, "Gamma-Ray Vortices from Nonlinear Inverse Thomson Scattering of Circularly Polarized Light," *Sci. Rep.* **7**, 5018 (2017).
- Y. Taira and M. Katoh, "Gamma-Ray Vortices Emitted from Nonlinear Inverse Thomson Scattering of a Two-Wavelength Laser Beam," *Phys. Rev. A* **98**, 052130 (2018).
- Y. Taira and M. Katoh, "Generation of Optical Vortices by Nonlinear Inverse Thomson Scattering at Arbitrary Angle Interactions," *Astrophys. J.* **860**, 45 (2018).

1. Gamma-Induced Positron Annihilation Lifetime Spectroscopy (GiPALS)

Positron lifetime spectrum is calculated by measuring the time difference between a reference signal and a detector output for the annihilation gamma-rays, which is emitted when a positron annihilates with an electron inside material. A reference signal is the output of a photodiode located near the injection position of a laser. A BaF_2 scintillator and a photomultiplier tube is utilized to detect the annihilation gamma-rays. Two detectors are arranged at 180 degrees because two annihilation gamma-rays are generated at 180-degree direction. The annihilation gamma-rays are generated to whole solid angle. Therefore array detectors are effective to increase the count rate of the annihilation gamma-rays and to reduce the measurement time. We have developed the array detector using 10 detectors with a help of Equipment Development Center (Figure 2).

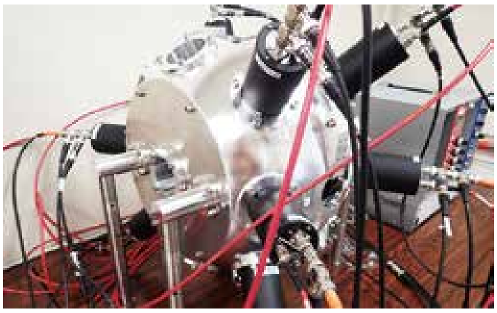


Figure 2. Positron lifetime measurement system using 10 detectors.

Users can currently utilize GiPALS at BL1U in UVSOR-III. A result of defect analysis for a GAGG scintillator was published in 2020.[1)]

We plan to change the laser injection position to increase the ultra-short pulsed gamma-ray intensity in the next fiscal year. In the current laser injection position, the opposite side of the laser injection window is the vacuum duct. Thus, the laser hits the vacuum duct and generates gas. This gas induces the background gamma-rays, which is generated by the interaction with an electron beam. As a result, the laser cannot be tightly focused and therefore the intensity of the gamma-ray is weak. The laser can be focused down to few tens of micrometers at the new laser injection position. We estimate that the intensity of the gamma-rays will be increased more than 20 times.

On the other hand, we are planning to develop other measurement technique for the annihilation gamma-rays, such as a three-dimensional distribution imaging technique for defects, spin polarized positrons generated from circularly polarized gamma-rays, and age-momentum correlation (AMOC).

2. Short Wavelength Optical Vortices

An optical vortex is an electromagnetic wave with a helical phase structure. When an optical vortex beam is viewed in a plane transverse to the direction of propagation, an annular intensity profile is observed due to the phase singularity at the center axis. An important consequence of the optical vortex is that it carries orbital angular momentum (OAM) due to the helical phase structure.

While fundamental and applied research on optical vortices using visible wavelength lasers is widely studied, much less has been done in ultraviolet, X-rays, and gamma-rays energy ranges. We have proposed for the first time a method to generate a gamma-ray vortex using nonlinear inverse Thomson scattering of a high energy electron and an intense circularly polarized laser.[2)] In our method, the circularly polarized laser is important because the helical phase structure arises from the transverse helical motion of the electron inside the circularly polarized laser field. When peak power of a laser achieves terawatt class, high harmonic gamma-rays are generated. Only gamma-rays more than the first harmonic carry OAM. High harmonic gamma-rays show the annular intensity distribution due to this characteristic.

There are few facilities in the world, where can carry out the experiment for the nonlinear inverse Thomson scattering using an intense circularly polarized laser in terawatt class. We carried out the experiment at Kansai Photon Science Institute in Japan, where a 150 MeV microtron and a petawatt laser are available. Although we were not able to achieve the measurement of an annular intensity distribution of high harmonic gamma-rays, we plan to continue the experiment this year.

On the other hand, optical vortices in the ultraviolet wavelength range can be generated using a helical undulator. Similar with a nonlinear inverse Thomson scattering, an electron obeys a helical trajectory inside an undulator. Therefore, high harmonic radiation emitted from a helical undulator forms the helical phase structure.

Generation of an optical vortex from a helical undulator has been demonstrated at UVSOR-III. Recently, we newly revealed that undulator radiation with the phase structure can be generated from an elliptically polarized undulator. We derived the analytic expressions for the emitted electric fields were fully derived and the radiation's phase structure was found to change according to polarization. Average phase gradients of the undulator's radiation were measured using a double slit interferometer. The measured phase gradients of the first through third harmonics were compared with the calculated results. The results were submitted to the journal.

References

1) K. Fujimori, M. Kitaura, Y. Taira, M. Fujimoto, H. Zen, S. Watanabe, K. Kamada, Y. Okano, M. Katoh, M. Hosaka, J. Yamazaki, T. Hirade, Y. Kobayashi and A. Ohnishi, *Appl. Phys. Express* **13**, 085505 (4 pages) (2020).

2) Y. Taira, T. Hayakawa and M. Katoh, *Sci. Rep.* **7**, 5018 (9 pages) (2017).

Angle-Resolved Photoemission Study on Strongly Correlated Electron Materials

UVSOR Synchrotron Facility
Division of Advanced Solid State Physics

TANAKA, Kiyohisa
Associate Professor
[k-tanaka@ims.ac.jp]

Education
2000 B.S. The University of Tokyo
2005 Ph.D. The University of Tokyo

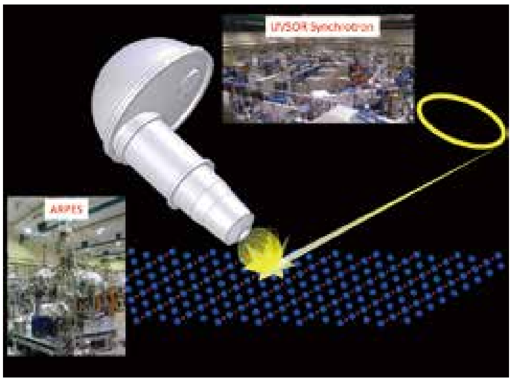
Professional Employment
2005 Postdoctoral Fellow, Stanford University and Lawrence Berkeley National Laboratory
2008 Assistant Professor, Osaka University
2013 Associate Professor, Osaka University
2014 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
IDETA, Shin-ichiro
Graduate Student
HOSOYA Tomoki*
FURUTA Kanji*

Keywords Strongly Correlated Electron System, Synchrotron Light, Photoemission

Strongly correlated electron materials has attracted more attentions in the last few decades because of their unusual and fascinating properties such as high-T_c superconductivity, giant magnetoresistance, heavy fermion and so on. Those unique properties can offer a route toward the next-generation devices. We investigate the mechanism of the physical properties as well as the electronic structure of those materials by using angle-resolved photoemission spectroscopy (ARPES). ARPES is a powerful experimental technique, directly measuring the energy (E) and momentum (k) relation, namely the band structure of solids. In the last quarter of a century, the energy resolution and angular resolution of ARPES have improved almost three order of magnitude better, which makes us possible to address the fine structure of the electronic structure near the Fermi level: Superconducting gap, kink structure and so on. The main target materials of our group is high-T_c superconductors, such as cuprates and iron pnictides and use UVSOR-III as a strong light source.

Our group is also developing high-efficiency spin-resolved ARPES system. Spintronics is a rapidly emerging field of science and technology that will most likely have a significant impact on the future of all aspects of electronics as we continue to move into the 21st century. Understanding magnetism of surfaces, interfaces, and nanostructures is greatly important for realizing the spintronics which aims to control and use the function of spin as well as the charge of electrons. Spin-resolved ARPES is one of the most powerful experimental techniques to investigate the magnetic properties of such materials.



Selected Publications

- K. Tanaka, W. S. Lee, D. H. Lu, A. Fujimori, T. Fujii, Risdiana, I. Terasaki, D. J. Scalapino, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Distinct Fermi-Momentum-Dependent Energy Gaps in Deeply Underdoped Bi2212," *Science* **314**, 1910–1913 (2006).
- W. S. Lee, I. M. Vishik, K. Tanaka, D. H. Lu, T. Sasagawa, N. Nagaosa, T. P. Devereaux, Z. Hussain and Z.-X. Shen, "Abrupt Onset of a Second Energy Gap at the Superconducting Transition of Underdoped Bi2212," *Nature* **450**, 81–84 (2007).
- K. Tanaka, N. Hieu, G. Vincini, T. Masui, S. Miyasaka, S. Tajima and T. Sasagawa, "Quantitative Comparison between Electronic Raman Scattering and Angle-Resolved Photoemission Spectra in $Bi_2Sr_2CaCu_2O_{8+\delta}$ Superconductors: Doping Dependence of Nodal and Antinodal Superconducting Gaps," *J. Phys. Soc. Jpn.* **88**, 044710 (2019).
- S. Ideta, N. Murai, M. Nakajima, R. Kajimto and K. Tanaka, "Experimental Investigation of the Suppressed Superconducting Gap and Double-Resonance Mode in $Ba_{1-x}K_xFe_2As_2$," *Phys. Rev. B* **100**, 235135 (7 pages) (2019).

1. Quantitative Comparison between ARPES and ERS on Multilayer Cuprates Superconductor[1)]

It has been well known that one of the most efficient ways to increase the critical temperature (T_c) of high-T_c cuprate superconductors (HTSCs) is to increase the number of neighboring CuO_2 planes (n). T_c of the optimally doped region ($T_{c:max}$) generally increases from single layer ($n = 1$), double layer ($n = 2$), to triple layer ($n = 3$) and then decreases for $n >$ 4. In order to explain the n dependence of T_c, several mechanisms have been proposed. However, it has been unclear which parameter governs the n dependence of $T_{c:max}$ because of the lack of detailed knowledge about the electronic structure of the multilayer cuprates. In this study, we have performed angle-resolved photoemission spectroscopy (ARPES) and electronic Raman scattering (ERS) to clarify the electronic structure of optimally doped triple-layer $Bi_2Sr_2Ca_2Cu_3O_{10+\delta}$ (Bi2223) which has the highest $T_{c:max}$ (~110 K) among Bi-based HTSCs.

Since the superconducting gap in the cuprates has a d-wave symmetry, we need k-selective experimental probes. Although ARPES and ERS are the most powerful k-selective probes, the gap sizes estimated from these two techniques are not always identical. To clarify the origin of the discrepancy, we have examined a direct comparison of ARPES and ERS through the Kubo formula analysis. In a previous study on the double layer Bi2212, we proved that this method is valid and advantageous.[2)]

In ERS study on optimally doped Bi2223, we found that B_{1g} spectra, which is sensitive to the antinodal region in the k-space, showed double peaks as shown in Figure 1a (blue curve). This is the first observation of multiple peaks in B_{1g} spectra in HTSCs. On the other hand, ARPES study on Bi2223 reveals two Fermi surfaces (FSs), which can be attributed the FS closer to the Γ point to that of the outer CuO_2 plane (OP) and the other to that of the inner CuO_2 plane (IP), assuming that the doping level is higher in the OP than in the IP. From those observations, we think that the double peak in ERS is originated from two different bands which form different FSs observed by ARPES.

To confirm our interpretation of the double peak, we calculated the Raman spectra from the ARPES, using the Kubo formula. For triple layer compounds, by separating the IP and OP bands of ARPES, we can calculate their separate contribution to the Raman spectra, and verify if the two B_{1g} Raman peaks truly originate from the two separate bands. The ARPES intensities for the IP and OP bands were separated by a Gaussian fit of the energy distribution curves using three Gaussian peaks, one for the IP and OP band each and one for the high energy incoherent intensity that originates from the strong correlations effects in the antinodal part of the k-space.

The calculated B_{1g} and B_{2g} Raman spectra for the optimally doped Bi2223 are compared with the experimental ones in Figure 1. One can find that the calculated spectra from the ARPES data successfully reproduce the experimental Raman spectra. The striking result is that, in the B_{1g} configuration, the IP and OP bands exhibit peaks at different energies that are close to the experimental B_{1g} peak energies. Here the OP peak position is slightly underestimated, which may be due to the fact that a small portion of the antinodal part of the momentum space is missing in our input ARRPES data. By summing the separate contribution of IP and OP, we obtain a thick orange line. A rather good correspondence of the calculated and experimental IP and OP peaks provides strong proof that the double B_{1g} Raman peak truly originates from the two separate bands of Bi2223 and, therefore, that it is a signature of the double superconducting gap of this material.

This results clarify systematic doping dependence of superconducting gaps of IP and OP in ERS, which reveals that the both the pair-breaking energy and the gap ratio are larger in triple layer cuprates than in single and double layer cuprates (not shown).

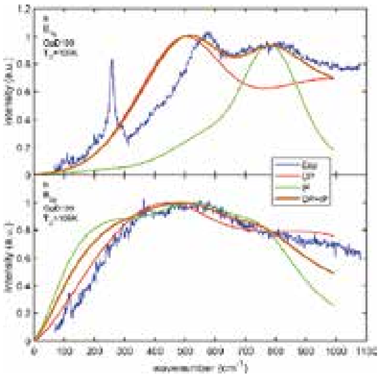


Figure 1. Comparison of the Raman spectra calculated from the ARPES (orange cruve) and the experimentally observed Raman spectra (blue curve) for B_{1g} (a) and B_{2g} (b) polarizations. The red and green curves are obtained from the ARPES data for the OP and IP, respectively. In the total curve IP+OP (thick orange), the contributions both from IP and OP are taken into account

2. Development of Low Temperature 6-Axis Manipulator for High-Resolution ARPES

We have developed low temperature 6-axis manipulator for high energy resolution ARPES measurements and achieved one of the lowest temperature 6-axis manipulators in the synchrotron radiation facilities in the world. To achieve lower temperature, we have started computational thermal simulation.

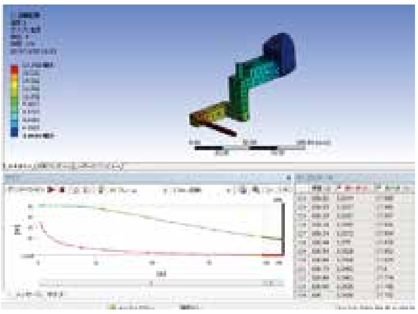


Figure 2. Modeling and simulation of thermal analysis for 6-axis manipulator.

References

1) G. Vincini *et al.*, *Supercond. Sci. Technol.* **32**, 113001 (2019).
2) K. Tanaka *et al.*, *J. Phys. Soc. Jpn.* **88**, 044710 (2019).

---

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Photoelectron Momentum Microscope at IMS

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

MATSUI, Fumihiko
Senior Researcher

The demand for photoelectron micro-spectroscopy and spectro-microscopy to characterize the electronic properties of microstructures is growing rapidly. Photoelectron spectroscopy resolved in three-dimensional momentum space with a microscopic field of view is realized by combining a so-called Momentum Microscope (MM) with a soft X-ray synchrotron radiation source. We built a new MM station at BL6U,(1) an undulator-based soft X-ray beamline. This station opens the door to direct observation of the Fermi surface of μm-sized crystals, which was difficult with conventional ARPES-type hemispherical analyzers.

1. Momentum Microscope

As shown in Figure 1, the system consists of a photoemission electron microscope (PEEM) lens, a hemispherical deflection analyzer as an imaging-type energy filter, and a 2D detector with a CMOS camera. The details of the specification evaluation result are described elsewhere.(1) In brief, the energy resolution of the analyzer was estimated to be 20 meV at pass energy of 20 eV. The spatial resolution in the microscopy mode was evaluated to be about 50 nm. The momentum resolution of 0.012 Å^{-1} has been achieved. The position of sample stage facing to the analyzer is precisely controlled by a hexapod. Samples can be cooled down to 8 K and heated up to 400 K.

Since a high voltage is applied between the sample and the PEEM lens, it is essential that the sample be flat. We have developed a technique to cleanly cleave sub-mm-sized crystals in the ultra-high vacuum condition. Figure 2 shows a valence band measurement with a wide **k** acceptance of 6 Å^{-1} in diameter.

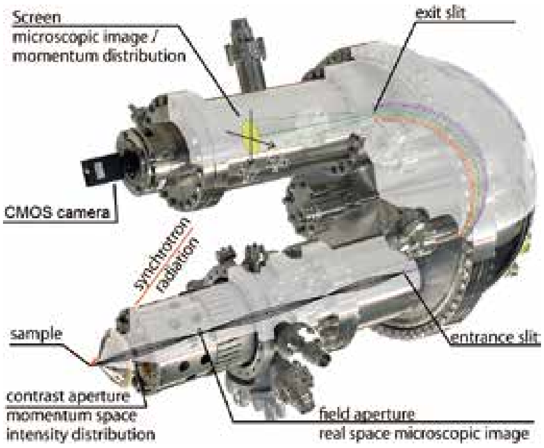


Figure 1. Schematic drawing of the momentum microscope.(1)

2. Original Electron Analyzers

Furthermore, we are aiming at highly efficient and comprehensive measurement of spin distribution as the final goal. *Omnidirectional photoelectron acceptance lens* (OPAL)(2) together with *Projector for electron spectroscopy with collimator analyzer* (PESCATORA)(3) enables photoelectron holography measurement of the full hemisphere. Moreover, we invented *Right angle deflection imaging analyzer* (RADIAN)(4) for spin vector analysis with ***k***/***r***-space resolution. We are expanding the MM system based on our original device developments.

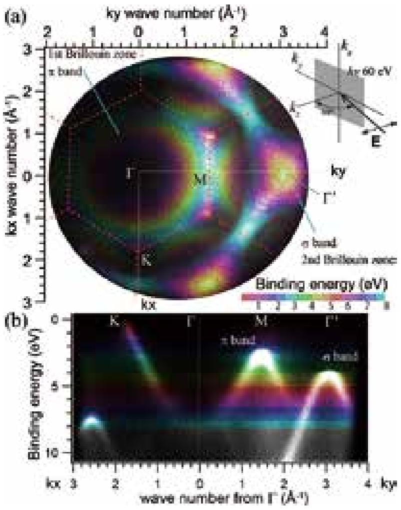


Figure 2. (a) Photoelectron angular distribution and (b) band dispersion of the cleaved graphite crystal surface.

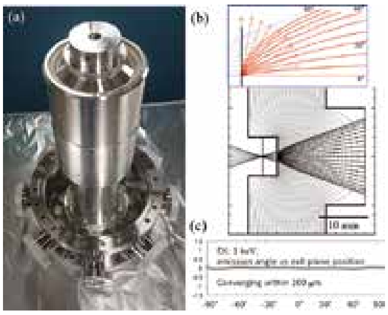


Figure 3. (a) Photograph of the omnidirectional photoelectron acceptance lens (OPAL). (b) 1-keV electron trajectory at the sample surface. (c) Performance of electrons emitted in full hemisphere.(2)

References

1) F. Matsui *et al.*, *Jpn. J. Appl. Phys.* **59**, 067001 (2020).
2) H. Matsuda and F. Matsui, *Jpn. J. Appl. Phys.* **59**, 046503 (2020).
3) F. Matsui and H. Matsuda, US Patent 10614992 (2020.04.07).
4) H. Matsuda and F. Matsui, Patent submitted (2020.07.09)

Local Structural Analyses of Liquids by Soft X-Ray Absorption Spectroscopy

Department of Photo-Molecular Science
Division of Photo-Molecular Science III

NAGASAKA, Masanari
Assistant Professor

Soft X-ray absorption spectroscopy (XAS) is an element specific method to reveal local structures of liquids with the K-edges of light elements (C, N, and O). We have investigated local structures of several liquids by using a liquid flow cell for XAS in transmission mode.[1] In this year, we have developed two techniques for applying XAS to the low energy region below 200 eV including K-edges of Li and B and L-edges of Si, P, S, and Cl, as described below.

1. Development of Soft X-Ray Transmission Argon Gas Window

XAS in the low energy region is difficult since transmitted soft X-rays mostly consist of high order X-rays due to the low transmission of first order X-rays. We have proposed the soft X-ray transmission argon gas window that removes high order X-rays by the absorption of Ar L-edges (240 eV).[2]

2. Development of Photoelectron Based Soft X-Ray Detector

We have developed a photoelectron based soft X-ray (PBSX) detector that removes high order X-rays.[3] In this detector, the Au 4f photoelectrons emitted by first order X-rays are separated from those by the high order X-rays using a difference in kinetic energy of photoelectrons.

References

1) M. Nagasaka, H. Yuzawa and N. Kosugi, *Anal. Sci.* **36**, 95–105 (2020). (Review)
2) M. Nagasaka, *J. Synchrotron Rad.* **27**, 959–962 (2020).
3) M. Nagasaka and H. Iwayama, *Rev. Sci. Instrum.* **91**, 083103 (7 pages) (2020).

Award

NAGASAKA, Masanari; YUZAWA, Hayato; KOSUGI, Nobuhiro; Analytical Sciences Hot Article Award (2020).

Development of a Surface-Sensitive Detection Method for Scanning Transmission X-Ray Microscopy

UVSOR Synchrotron Facility
Division of Beam Physics and Diagnostics Research

OHIGASHI, Takuji
Assistant Professor

A scanning transmission X-ray microscope (STXM) obtains 2-dimensional X-ray absorption of a sample to obtain chemical status. Generally, the STXM gives us integrated (bulk) information of the sample along a path of the X-ray. Alternative approach of the STXM is to detect secondary electron from the sample by using a channeltron. The detection of the secondary electron enables us to obtain information of near surface of the sample because of escape depth of the secondary electrons around a few nm. Additionally, this technique overcomes a main difficulty of the STXM by measuring a thick sample which cannot be penetrated by the X-rays.

A channeltron is used as a detector for the secondary electron and is placed upstream of the sample. This optical system can obtain an X-ray transmission image and a secondary electron image simultaneously. As a test sample, a thin section of blended polymer on a copper grid was measured. The energy of the X-ray was 400 eV and the dwell was 500 ms per pixel. In Figure 1(b), an empty space indicated by a dotted circle also shows higher signals of the secondary electron than those from the blended polymer. This problem is under discussion.

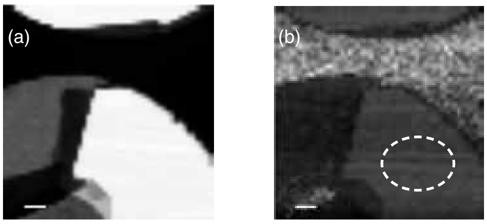


Figure 1. (a) An X-ray transmission image and (b) a secondary electron image of a thin section of blended polymer on a copper grid. Scale bars are 5 µm.

Resonant Soft X-Ray Scattering Measurements for Liquid-Crystal Materials

UVSOR Synchrotron Facility
Division of Advanced Photochemistry

IWAYAMA, Hiroshi
Assistant Professor

We study soft matters such as liquid-crystal materials with soft x-ray, whose energy region covers K-edge energies of carbon, nitrogen and oxygen. Soft matters exhibit their intriguing properties due to mesoscopic physical structures by self-organizations. To understand properties of soft matters, we need to investigate their structure in the mesoscopic scale.

1. Development of Resonant Soft X-Ray Scattering Measurements

Resonant soft x-ray scattering measurements can probe mesoscopic structures and periodic spatial variations of the orientation of molecules with both elemental and chemical environment sensitivity and have orders of magnitude scattering intensity enhancement over conventional small angle (non-resonant) x-ray scattering, which is sensitive only to the electron density modulations.

In this year, we developed an equipment for resonant soft x-ray scattering measurements. Since soft x-rays are strongly absorbed by air, all soft x-ray paths should be in high vacuum. In addition, a thickness of sample must be less than 1 micrometer to obtain transmitted scattered lights.

We were successful in developing the equipment and now confirmed vacuum test and sample holder test. Our equipment can probe structures in the range from 62 Å to 170 Å. A first sample will be liquid-crystal materials which show a twisted structure. The experiments will be performed at BL3U of UVSOR in September 2020.

Visiting Professors

Visiting Professor
FUKUI, Ken-ichi *(from Osaka University)*

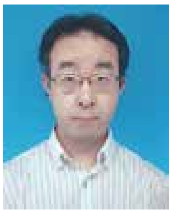
Ionic Liquid/Organic Semiconductor Interfaces for Efficient Carrier Transport

Local analyses of electrolyte/organic semiconductor electrode interfaces at controlled electrode potentials are of fundamental importance to understanding the origin and properties of the electric double layer (EDL) at the interfaces, which is necessary for their application to EDL-organic field effect transistors (OFETs). Ionic liquids (ILs) gated EDL-OFETs can be operated with ultralow voltage (~0.1 V), however, ILs sometimes cause operational instability due to their unusual interface structuring. By using an IL (EMIM-FSA) and ruburene crystal, IL-derived bias stress was observed, which increased operational voltage of the EDL-OFET by 33% in 2 h. Electrochemical FM-AFM and molecular dynamics (MD) simulation revealed that the formation of structured IL layer on the surface of hole-injected rubrene; anions in the IL monolayer probably trapped hole carriers by orienting their polar parts. Application of higher magnitude of OFF-state gate voltage immediately reset the IL-derived bias stress by separating the anion–hole pairs, but the same shift occurred in the same time scale by the local structural change of the interface.

Visiting Professor
SHIMADA, Kenya *(from Hiroshima University)*

High-Resolution Angle-Resolved Photoemission Study of Correlated Materials

In order to understand the physical properties of solids, we are studying the electronic structures by means of high-resolution angle-resolved photoemission spectroscopy (ARPES) using synchrotron radiation. We have also developed an ARPES system using an ultraviolet laser (hν = 6.36 eV) to pursuit ultimate spatial, energy, and angular resolutions (<10μm, <1meV, <0.05°). By combining synchrotron radiation and laser ARPES measurements as well as extensive density functional theory (DFT) calculations, we could elucidate the termination dependent electronic structures of an antiferromagnetic topological insulator $MnBi_4Te_7$. The topological surface state is gapped for quintuple-layer (QL) termination but gapless for the septuple-layer (SL) termination. The spin texture is expected to be different for both terminations. While the DFT calculations reasonably reproduce the s-p electron bands, it is still challenging to predict magnetic 3d electronic bands. In the case of oxygen adsorbed Fe(100) surface states, we found significant deviations from the DFT results due to momentum- and orbital-dependent electron correlation effects.



Visiting Associate Professor
KATSUKI, Hiroyuki *(from Nara Institute of Science and Technology)*

Coherent Control in Condensed Systems

My research is focused on the ultrafast dynamics and coherent control in the condensed systems, especially in strongly coupled systems. We have recently demonstrated the ultrafast visible-pump THz-probe measurement of the carrier dynamics in a thin film of $CH_3NH_3PbBr_3$. As the pump photon energy changes around the bandgap, we can observe the drastic change of the THz transmission intensity. The results are analyzed based on the efficiency of the Auger-like process which is only observable for free carriers, and it is shown that the thermal excitation of the excitons to generate free carriers in the conduction band is not efficient in this material.

We are interested in a vibrational strong-coupling system in which a mid infrared photon is mixed with molecular vibrational quanta and forms a polaritonic quasi-particle. This phenomenon accompanies the local deformation of the potential surface, which can modulate the wave packet motion on the potential. Our final goal is the control of the wave packet motion and the photochemical reaction based on the modulation of the potential surface.

RESEARCH ACTIVITIES
Materials Molecular Science

Extensive developments of new functional molecules and their assemblies are being conducted in three Divisions of Electronic Structures, Electronic Properties, and Molecular Functions, and one division for visiting professors and associate professors, in an attempt to discover new phenomena and useful functions. The physical (electric, optical, thermal and magnetic) properties on new functional materials, the chemical properties like enzymes, catalysis and photochemistry, the exploitation of new spectroscopic methods for materials molecular science, and technological applications like batteries, photocatalysts, fuel cells, solar cells and field effect transistors are investigated in this department.

Exploitation of Novel Spectroscopic Methods for Material and Surface Science

Department of Materials Molecular Science
Division of Electronic Structure

YOKOYAMA, Toshihiko
Professor
[yokoyama@ims.ac.jp]

Education

1983	B.S. The University of Tokyo
1985	M.S. The University of Tokyo
1990	Ph.D. The University of Tokyo

Professional Employment

1987	Research Associate, Hiroshima University
1993	Research Associate, The University of Tokyo
1994	Lecturer, The University of Tokyo
1996	Associate Professor, The University of Tokyo
2002	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Member
Assistant Professor
KOITAYA, Takanori
YAMAMOTO, Kohei
Post-Doctoral Fellow
NAKAMURA, Takahiro
CHAVEANGHONG, Suwilai
Graduate Student
KITOU, Shunsuke*
Secretary
ISHIKAWA, Azusa

Keywords X-Ray Absorption Spectroscopy, Surface & Thin Film Magnetism, Ambient Pressure Hard X-Ray Photoelectron Spectroscopy

For the developments of novel functional materials, it is quite important to exploit simultaneously new analytical methods based on advanced technology. Novel materials and devices often require spatial and/or time resolved analysis to optimize their qualities. In our group, we have been exploiting spectroscopic methods for material and surface science using mainly synchrotron radiation (SR) and partly lasers.

The first subject in our group is the spectroscopic analysis systems of magnetic thin films. In 2006, we successfully invented a novel magnetic nanoscope using ultraviolet magnetic circular dichroism (UV MCD) photoelectron emission microscopy (PEEM), which allows us to perform real-time and ultrafast magnetic imaging to investigate magnetic dynamics. We have also constructed *in situ* x-ray magnetic circular dichroism (XMCD) system using an ultrahigh vacuum superconducting magnet and a liq. He cryostat, which is installed at Beamline 4B of the IMS SR facility UVSOR-III. The XMCD measurement system contains ultrahigh vacuum sample preparations chamber, with which one can clean substrates (substrate single crystals *etc.*), deposit materials (metallic and molecular magnets *etc.*) and characterize the samples using low energy electron diffraction, reflection high energy electron diffraction and Auger electron spectroscopy. The apparatus is extensively open for public usage and many domestic and foreign researchers visit us every year.

The second subject is the exploitation of ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) for polymer electrolyte fuel cells (PEFC) under working conditions. Although usually photoelectron spectroscopic measurement is done under ultrahigh vacuum, recent material science requires ambient pressure measurements under working conditions. In 2017, we succeeded in real ambient pressure (10^5 Pa) HAXPES measurements for the first time using Beamline 36XU of SPring-8. This work was supported by the NEDO Fuel Cell project.

The third subject is the pico- and femtosecond pump-and-probe time resolved measurements using x-ray. Time-resolved x-ray absorption fine structure spectroscopy of photocatalysts WO_3 and $BiVO_4$ was performed and we have investigated those local geometric and electronic structures. Time-resolved measurement can be also applied to investigate the dynamics of magnetic materials with XMCD and other magneto-optical effects. We captured XMCD spectra of the photoinduced transient state. The real space image of magnetic domains can be retrieved from the diffraction patterns. We succeeded in capturing diffraction from magnetic domains and now considering the possibility of its application for time- and space-resolved imaging.

Recently, new assistant professors Drs. Koitaya and Yamamoto joined our group. We will further perform surface physics and chemistry researches for materials science including methodological exploitation using synchrotron radiation and lasers.

Selected Publications

- T. Nakagawa *et al.*, *Phys. Rev. Lett.* **96**, 237402 (2006).
- T. Yokoyama and K. Eguchi, *Phys. Rev. Lett.* **107**, 065901 (2011).
- M. Dabrowski *et al.*, *Phys. Rev. Lett.* **113**, 067203 (2014).
- Y. Uemura *et al.*, *Angew. Chem., Int. Ed.* **55**, 1364 (2015).
- Y. Takagi *et al.*, *Appl. Phys. Express* **10**, 076603 (2017).
- Y. Uemura *et al.*, *Chem. Commun.* **53**, 7314 (2017).
- Y. Takagi *et al.*, *Acc. Chem. Res.* **51**, 719 (2018).
- L. Yu *et al.*, *J. Phys. Chem. C* **123**, 603 (2019).

1. Quick *Operando* Ambient Pressure Hard X-Ray Photoelectron Spectroscopy for Reaction Kinetic Measurements of Polymer Electrolyte Fuel Cells[1)]

Polymer electrolyte fuel cells (PEFCs) are currently one of the most promising electrochemical energy conversion and storage technology. To achieve more highly efficient PEFC with longer life time, a continuous supply of more powerful materials and a further detailed understanding of the electrochemical properties of PEFC are essentially important. We have been investigating the degradation and poisoning mechanisms of PEFC using near ambient pressure *operando* HAXPES of PEFC under working conditions. To study catalytic reaction mechanisms, it is generally quite important to investigate reaction kinetics with time-resolved experimental techniques.

In this work, we have designed and constructed a quick *operando* ambient pressure hard x-ray photoelectron spectroscopy (HAXPES) measurement system for the investigations of reaction kinetics in electrochemical cells under working conditions. The HAXPES measurements can be performed at typical pressures of 1×10^4 Pa (maximum 1×10^5 Pa) with the typical time resolution of ~200 ms. To accumulate time-resolved spectra with sufficient signal-to-noise ratios, repeated cycles of the chemical reactions are conducted based on the repeated-cycle time-tagged method, requiring the identity of each event and the time trigger. As demonstrative experiments, we have successfully observed time-resolved operando Pt $3d_{5/2}$ and S 1s HAXPES from the Pt/C cathode catalyst of PEFCs. In the Pt $3d_{5/2}$ HAXPES, we have evaluated the reaction kinetics of the Pt oxidation/reduction processes at the cathode upon abrupt change of the cathode–anode bias voltage between 0.4 and 1.2 V. In the S 1s HAXPES for measurements of S species poisoning fuel cells, we have studied the contaminated anionic S adsorption and desorption kinetics on the Pt nanoparticles at the cathode. The results are comparatively discussed with previous findings.

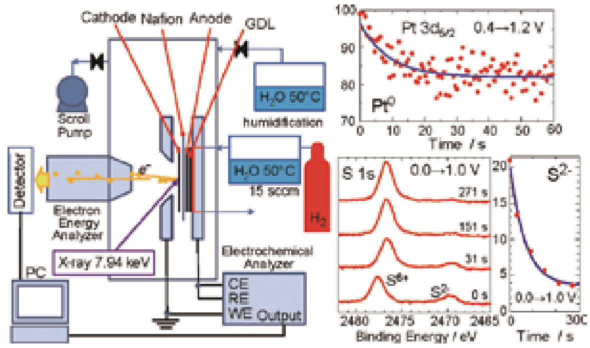


Figure 1. (left) Schematic view of the quick *operando* HAXPES measurement system installed at hard x-ray undulator station BL36XU of SPring-8. (right) Examples of time dependence of the HAXPES results. The upper panel depicts the Pt oxidation process upon an abrupt step of the bias voltage. The lower panel gives the Pt-adsorbed S desorption process upon a similar bias voltage variation.

2. Photoinduced Anisotropic Distortion as the Electron Trapping Site of WO_3 Studied by Ultrafast W L_1-Edge X-Ray Absorption Spectroscopy with Full Potential Multiple Scattering Calculations[2)]

Understanding excited states of photocatalysts is significant to improve their activity for water splitting reaction. X-ray absorption fine structure (XAFS) spectroscopy using X-ray free electron lasers (XFEL) is a powerful method to address dynamic changes in electronic states and structures of photocatalysts in the excited state in ultrafast short time scales. The ultrafast atomic-scale local structural change in photoexcited WO_3 was observed by W L_1 edge XAFS spectroscopy using an XFEL. An anisotropic local distortion around the W atom could reproduce well the spectral features at a delay time of 100 ps after photoexcitation based on full potential multiple scattering calculations. The distortion involved the movement of W to shrink the shortest W–O bonds and elongate the longest one. The movement of the W atom could be explained by the filling of the d_{xy} and d_{zx} orbitals, which were originally located at the bottom of the conduction band with photoexcited electrons.

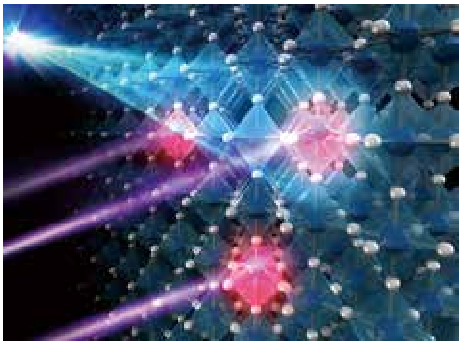


Figure 2. Schematic view of the ultrafast dynamics of WO_3 after ultraviolet laser excitation studied by the x-ray free electron laser.

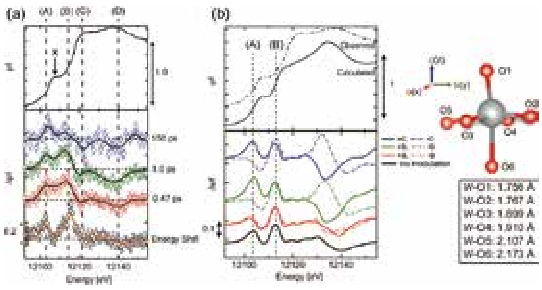


Figure 3. Experimental and calculated time-dependent W L_1-edge XAFS spectra of WO_3. Significant more distortion of the local structure around W in the photoexcited state is elucidated.

Reference

1) T. Nakamura *et al.*, *J. Phys. Chem. C* **124**, 17520–17527 (2020).
2) A. Koide *et al.*, *Phys. Chem. Chem. Phys.* **22**, 2615–2621 (2020).

---

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Exiotic Structures, Physicochemical Properties and Quantum Dynamics of Interfacial Water

Department of Materials Molecular Science
Division of Electronic Structure

SUGIMOTO, Toshiki
Associate Professor
[toshiki-sugimoto@ims.ac.jp]

Education
2007 B.S. Kyoto University
2011 Ph.D. The University of Tokyo

Professional Employment
2012 Assistant Professor, Kyoto University
2016 JST-PRESTO Researcher
2018 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies
2020 JST-PRESTO Researcher

Awards
2014 Young Scientist Award, 33rd Annual Meeting of the SSSJ
2014 39th Vacuum Science Paper Award
2018 PCCP Prize 2018
2018 CSJ Presentation Award 2018
2018 Encouragement Award, The Spectroscopic Society of Japan
2018 Morino Foundation for Molecular Science
2019 12th Young Scientist Awards of the Japan Society for Molecular Science
2019 14th Young Scientist Award of the Physical Society of Japan

Member
Assistant Professor
SAKURAI, Atsunori
Post-Doctoral Fellow
SAITO, Hikaru
TSURUOKA, Kazuyuki
Graduate Student
SATO, Hiromasa
LIN, Zhongqiu
Technical Fellow
MATSUO, Goh
Secretary
YOKOTA, Mitsuyo
SHIMURA, Maki

Keywords Water Molecules, Nonlinear Optical Spectroscopy, Surface & Interface Science

Interfacial water is ubiquitous in nature and plays crucial roles in a variety of disciplines, including physics, chemistry and biology. In such a symmetry-breaking system, not only adsorption geometry but also anisotropic molecular orientation (H-up/H-down configuration) is a key structural parameter that determines unique physicochemical properties of interfacial water systems. Nevertheless, orientation of water molecules, *i.e.* configuration of hydrogens, in the interfacial hydrogen-bond network is extremely hard to investigate with traditional experimental techniques such as electron diffraction, grazing X-ray scattering and even scanning prove microscopy, because hydrogen has only a single electron and responds extremely weakly to the probes of these techniques. Therefore, the determination of molecular orientation of interfacial water has been an experimental challenge.

We have used recently developed heterodyne-detected sum-frequency generation spectroscopy for unveiling molecular orientation of interfacial water system. The remarkable feature of this technique is that $\mathrm{Im}\chi^{(2)}$ SFG spectra ($\chi^{(2)}$: The second-order nonlinear susceptibility) obtained by the heterodyne detection exhibit positive or negative sign for net orientation of OH with hydrogen pointing away (H-up) or toward substrate (H-down), respectively. Thus, the heterodyne-detected $\mathrm{Im}\chi^{(2)}$ SFG has a great advantage to direct observation of water orientation that cannot be investigated through other traditional experimental methods. With this sophisticated molecular spectroscopy technique, we have conducted a series of pioneering research on unique structures and physicochemical properties of hydrogen bonds of interfacial water molecules.

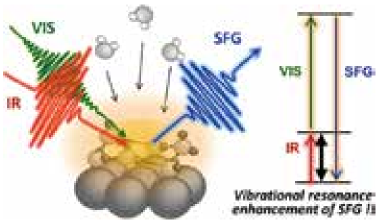


Figure 1. Infrared-visible sum-frequency-generation (SFG) spectroscopy of water molecules on solid surface.

Selected Publications

- T. Sugimoto *et al.*, "Emergent High-T_c Ferroelectric Ordering of Strongly Correlated and Frustrated Protons in Heteroepitaxial Ice Film," *Nat. Phys.* **12**, 1063–1068 (2016).
- O. Yuji *et al.*, "Unveiling Subsurface Hydrogen-Bond Structure of Hexagonal Water Ice," *Phys. Rev. B* **96**, 115405 (14 pages) (2017).
- K. Shirai *et al.*, "Water-Assisted Hole Trapping at Highly Curved Surface of Nano-TiO_2 Photocatalyst," *J. Am. Chem. Soc.* **140**, 1415–1422 (2018).
- T. Sugimoto *et al.*, "Topologically Disordered Mesophase at Topmost Surface of Crystalline Ice Between 120 and 200 K," *Phys. Rev. B* **99**, 121402(R) (2019).
- F. Kato *et al.*, "Direct Experimental Evidence for Markedly Enhanced Surface Proton Activity Inherent to Water Ice," *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).
- T. Sugimoto *et al.*, "Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces," *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).

1. Direct Evidence for Markedly Enhanced Surface Proton Activity of Crystalline Ice[1)]

Hydrated protons on the ice surfaces critically influence physical and chemical properties of ices. They are generated solely by the thermal ionization of water molecules ($H_2O \leftrightarrows H^+ + OH^-$) in pure water molecular systems. Therefore, the proton activity inherent to water ice is determined by the amount and mobility of hydrated protons derived from the autoionization. Considerable discussions have been made, yet not been settled, on whether the activity of hydrated protons is substantially enhanced at the surface of water ice.

Very recently, we succeeded in directly and quantitatively demonstrating for the first time that the proton activity is significantly enhanced at the surfaces of low-temperature ice. On the basis of simultaneous experimental observation of the H/D isotopic exchange of water molecules at the surface and in the interior of double-layer crystalline-ice films composed of H_2O and D_2O (Figure 2), we reported three major discoveries of the unique enhancement of surface proton activity: (1) proton activity proved by the H/D exchange at the topmost surface is at least three orders of magnitude higher than in the interior even below 160 K; (2) the enhanced proton activity is dominated by autoionization process of water molecules rather than proton transfer process at ice surface; (3) as a consequence of surface promoted autoionization, the concentration of surface hydrated protons is more than six orders of magnitude higher than that in the bulk.

We also found that the cooperative structural fluctuations[2–4)] allowed in the undercoordinated surface molecules but inhibited in the fully coordinated interior molecules facilitate the autoionization and dominate the proton activity at the ice surface. Because the lower limit of temperature of the earth's atmosphere is ~120 K around the mesopause, the surface of crystalline ice on earth is unlikely to be solidly ordered but would inevitably be highly fluctuated. In nature, such dynamic features facilitate the autoionization of water molecules and thus enhance the proton activity at the surface of crystalline ice.

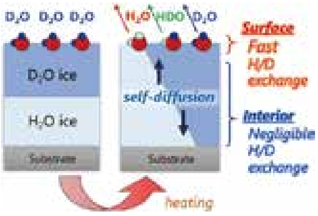


Figure 2. Simultaneous observation of the H/D isotopic exchange of water molecules at the surface and in the interior of double-layer ice films composed of H_2O and D_2O.

2. Thickness Dependent Homogeneous Crystallization of Ultrathin Amorphous Ice[5)]

The crystallization mechanism and kinetics are fundamentally important for thermal stability of amorphous materials. The crystallization of amorphous materials is generally triggered by spontaneous creation of crystalline nuclei. Two processes are distinguishable in terms of the place where crystallized nuclei are formed: *Heterogeneous nucleation* at the surface of material or the interface with the other material, and *homogeneous nucleation* in the bulk. In general, the surface and interface of amorphous thin films serve as nucleation sites. Therefore, it has been traditionally believed that crystallization of amorphous ice thin films also proceeds via the heterogeneous nucleation.

We have focused on the ultrathin films of amorphous ice grow on Pt(111) substrate and systematically investigated the crystallization process by varying the thickness of the films from a few nm to several tens of nm. Simultaneously monitoring the crystallization processes at the surface and in the interior of ice films, we found that the crystallization proceeds via homogeneous nucleation irrespective of the film thickness. This discovery overturned the conventional idea that the crystallization of amorphous ice thin films is initiated by heterogeneous nucleation. Furthermore, we found that the crystallization kinetics and temperature of amorphous ice thin films are highly modulated depending on the thickness of the film (Figure 3), although crystallization itself proceeds via the homogeneous nucleation mechanism. The structural analysis of hydrogen bonds based on vibrational spectroscopy revealed that the strength of hydrogen bonds in the thermodynamically most relaxed amorphous ice films (the state just before crystallization) changes significantly with the film thickness, which shows an evidence of a peculiar size effect.

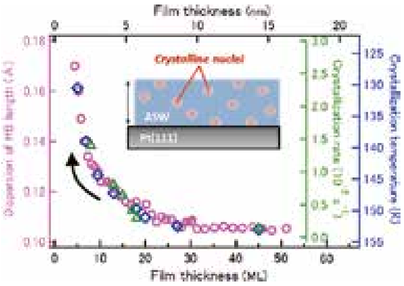


Figure 3. Thickness dependence of the distribution of O–H···O hydrogen bond length (○), crystallization rate (△) and temperature (◇) of the amorphous ice thin films on Pt(111).

References

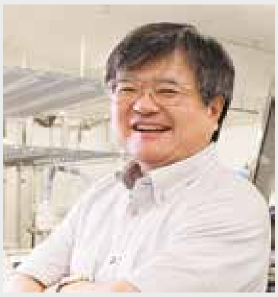
1) F. Kato, T. Sugimoto and Y. Matsumoto, *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).
2) T. Sugimoto, Y. Otsuki, T. Ishisyama, A. Morita, K. Watanabe and Y. Matsumoto, *Phys. Rev. B* **99**, 121402(R) (2019).
3) Y. Otsuki, K. Watanabe, T. Sugimoto and Y. Matsumoto, *Phys. Chem. Chem. Phys.* **21**, 20442–20453 (2019).
4) T. Sugimoto and Y. Matsumoto, *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).
5) K. Harada, T. Sugimoto, F. Kato, K. Watanabe and Y. Matsumoto, *Phys. Chem. Chem. Phys.* **22**, 1963–1973 (2020).

Awards

SUGIMOTO, Toshiki; 12th Young Scientist Awards of the Japan Society for Molecular Science (2019).
SUGIMOTO, Toshiki; 14th Young Scientist Award of the Physical Society of Japan (2019).

Organic Solar Cells

Department of Materials Molecular Science
Division of Molecular Functions



HIRAMOTO, Masahiro
Professor
[hiramoto@ims.ac.jp]

Education
1984 B.E. Osaka University
1986 Ph.D (Engineering) Osaka University

Professional Employment
1984 Technical Associate, Institute for Molecular Science
1988 Research Associate, Osaka University
1997 Associate Professor, Osaka University
2008 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Awards
2017 Fellow Award of Japan Society of Applied Physics
2006 Paper award, Molecular Electronics & Bioelectronics division, Japan Society of Applied Physics
2006 Research and Education Award, Osaka University
2004 Editor Award, Japanese Journal of Applied Physics

Member
Assistant Professor
IZAWA, Seiichiro
Research Fellow
YABARA, Yusuke
Graduate Student
LEE, Jihyun
PALASSERY ITHIKKAL, Jaseela
Secretary
SUGIHARA, Hidemi
NAKAMURA, Yuka

Keywords Organic Semiconductors, ppm-Doping, Lateral Junction

Organic solar cells have been intensively studied due to many advantages like flexible, printable, light, low-cost, fashionable, etc. Last year, we proposed a novel concept of the structure of organic solar cell, namely, a lateral multilayered junction (Figure 1). An essential point is that the photo-generated holes and electrons are laterally transported and extracted to the respective electrodes. We also investigated the reduction of open-circuit voltage loss in organic solar cells by using high-mobility organic semiconductors (Figure 2). On the other hand, we have been focused on the research on the ppm-level doping effects in organic semiconductor films and organic single crystals for organic solar cells. So far, we have reported complete *pn*-control, doping sensitization, ppm-level doping effects using an extremely low-speed deposition technique reaching 10^{-9} nm s^{-1}, in organic single crystals measured by the Hall effect, which shows a doping efficiency of 24%, and enhancement of open-circuit voltage of organic solar cells by doping. These results can be regarded as a foundation for the construction of high efficient organic solar cells.

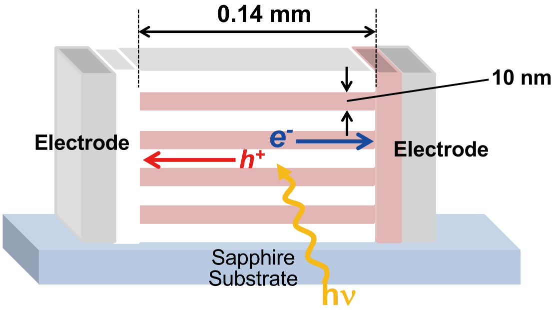


Figure 1. Lateral multilayered junction which can replace the blended junction.

Selected Publications

- M. Hiramoto, M. Kikuchi and S. Izawa, "Parts-per-Million-Level Doping Effects in Organic Semiconductor Films and Organic Single Crystals," *Adv. Mater.* **30**, 1801236 (15 pages) (2018). [Invited Progress Report]
- M. Kikuchi, M. Hirota, T. Kunawong, Y. Shinmura, M. Abe, Y.Sadamitsu, A. M. Moh, S. Izawa, M. Izaki, H. Naito and M. Hiramoto, "Lateral Alternating Donor/Acceptor Multilayered Junction for Organic Solar Cells," *ACS Appl. Energy Mater.* **2**, 2087–2093 (2019).
- S. Izawa, N. Shintaku, M. Kikuchi and M. Hiramoto, "Importance of Interfacial Crystallinity to Reduce Open-Circuit Voltage Loss in Organic Solar Cells," *Appl. Phys Lett.* **115**, 153301 (2019).

1. Reduction of Open-Circuit Voltage Loss in Organic Solar Cells[1)]

Reducing the energy loss in output voltage is critically important for further enhancing the efficiency of organic solar cells. In this work, we showed that the organic solar cells with high mobility and highly crystalline donor and acceptor materials can reduce an open-circuit voltage (V_{oc}) loss.

Two-layer cells consisting of C8-BTBT and C_n-PTCDI (Figure 2(a)), which acts as the donor and acceptor were fabricated. V_{oc} increases in the order of C3 < C6 < C8 of C_n-PTCDI (Figure 2(a)) and reached to thermodynamic (Shockley–Queisser) limit (Figure 2(b), red dots). Simultaneously, electron mobility increases by the suppression of molecular vibration of π-stacking due to the increase of crystallinity by fastener effect by increasing the chain length (C3 < C6 < C8). V_{oc} increase can be reasonably explained by the suppression of non-radiative (vibrational) recombination from CT (charge transfer) exciton (D^+/A^-) to ground state (D/A) (Figure 2(c)).

By using the high mobility (band conductive) organic semiconductors, high efficient organic solar cells would be realized by reducing V_{oc} loss.

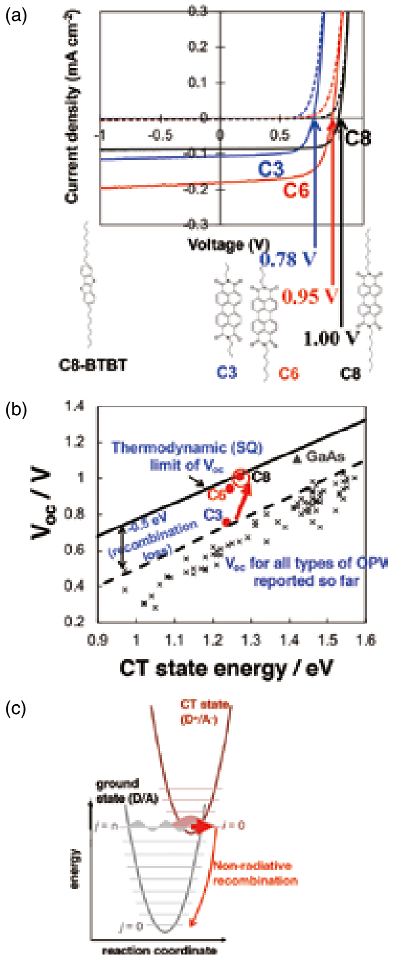


Figure 2. (a) J–V characteristics of C8-BTBT/C_n-PTCDI cells. (b) V_{oc} vs. CT state energy. (c) Non-radiative recombination from CT state to ground state.

2. Ultra-Thick Blended Layer up to 10 μm in Organic Solar Cells[2)]

Blended layer thickness of organic solar cells made with small molecules has limitation up to the order of a few hundred nm which is still not enough to absorb whole solar light. In this work, we succeeded to operate the organic solar cells having 10-μm-thick photoactive blended layer, consisting of zinc phthalocyanine (ZnPc), and fullerene (C_{60}).

A method of co-evaporant induced crystallization[3)] was used for the deposition of ZnPc:C_{60} codeposited films. Co-evaporant molecule (polydimethylsiloxane; PDMS) acts as a liquid in the vacuum, which induces the crystallization and phase separation of the codeposited film. The cross-sectional image of co-deposited films with a co-evaporant show the columnar structures of ZnPc and C_{60} which offer the vertical transport routes for holes and electrons (Figure 3, inset).

With co-evaporant, short-circuit photocurrent (J_{sc}) and fill factor (FF) showed almost constant value up to the surprising blended layer thickness of 10 μm (Figure 3, blue diamonds). However, without co-evaporant, they steeply decreased within several hundred nm (Figure 3, green crosses). Photocurrent density of 20 $mAcm^{-2}$ and the conversion efficiency (PCE) of 4.3% were observed. Whole solar light absorption by ultra-thick blended layer fabricated by co-evaporant will open the way to realize the high efficient small-molecular type organic solar cells.

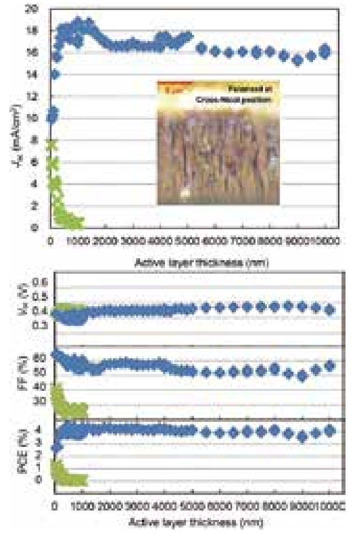


Figure 3. Dependence of cell performance on blended layer thickness. Inset: Phase separated columnar structure made by co-evaporant induced crystallization.

References

1) S. Izawa, N. Shintaku, M. Kikuchi and M. Hiramoto, *Appl. Phys. Lett.* **115**, 153301 (2019).

2) M. Katayama, T. Kaji, S. Nakao and M. Hiramoto, *Front. Energy Res., Section Solar Energy* **8:4**, 1–12 (2019).

3) T. Kaji, M. Zhang, S. Nakao, K. Iketaki, K. Yokoyama, C. W. Tang and M. Hiramoto, *Adv. Mater.* **23**, 3320–3325 (2011).

Solid-State NMR for Molecular Science

Department of Materials Molecular Science
Division of Molecular Functions

NISHIMURA, Katsuyuki
Associate Professor
[nishimur@ims.ac.jp]

Education
1994 B.S. Himeji Institute of Technology (University of Hyogo)
1999 Ph.D. Himeji Institute of Technology (University of Hyogo)

Professional Employment
1999 Postdoctoral Fellow, National High Magnetic Field Laboratory, Florida State University
2001 Assistant Professor, Yokohama National University
2006 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Award
2002 The Young Scientist Poster Award, The Nuclear Magnetic Resonance Society of Japan

Member
Secretary
YOKOTA, Mitsuyo

Keywords Solid State NMR, Biomolecules, Developments

In order to elucidate functions of molecules, characterization of the molecule is the first step. There is a variety of important molecules, which are insoluble in any solvents and functional at amorphous state. Solid-state NMR enables us to obtain a variety of information at atomic resolution without damage to molecules and significant restrictions. Thus, solid-state NMR is one of the essential tools for the characterizations of those molecules.

We have been working on methodology and hardware developments of solid-state NMR and their application to structural biology and materials science. We study characterization of membrane proteins and peptides, organic materials, natural products and synthetic polymers. Characterization of those molecules based on solid-state NMR is underway through collaborations with several research groups.

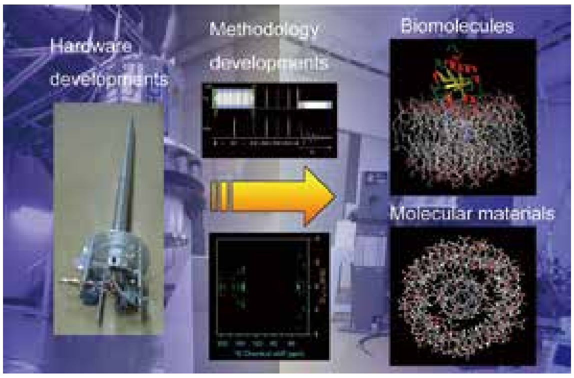


Figure 1. Outline of our studies.

Selected Publications

- N. Uekama, T. Aoki, T. Maruoka, S. Kurisu, A. Hatakeyama, S. Yamaguchi, M. Okada, H. Yagisawa, K. Nishimura and S. Tuzi, "Influence of Membrane Curvature on the Structure of the Membrane-Associated Pleckstrin Homology Domain of Phospholipase C-δ1," *Biochim. Biophys. Acta, Biomembr.* **1788**, 2575–2583 (2009).
- T. Iijima and K. Nishimura, "^{2}H Quadrupolar Carr-Purcell-Meiboom-Gill NMR for Paramagnetic Solids," *Chem. Phys. Lett.* **514**, 181–186 (2011).
- K. Yazawa, F. Suzuki, Y. Nishiyama, T. Ohata, A. Aoki, K. Nishimura, H. Kaji and T. Asakura, "Determination of Accurate ^{1}H Positions of Alanine Tripeptide with Anti-Parallel and Parallel β-Sheet Structures by High Resolution ^{1}H Solid State NMR and GIPAW Chemical Shift Calculation," *Chem. Commun.* **48**, 11199–11201 (2012).
- M. Tanio and K. Nishimura, "Intramolecular Allosteric Interaction in the Phospholipase C-δ1 Pleckstrin Homology Domain," *Biochim. Biophys. Acta, Proteins Proteomics* **1834**, 1034–1043 (2013).
- M. Yagi-Utsumi, K. Kato and K. Nishimura, "Membrane-Induced Dichotomous Conformation of Amyloid β with the Disordered N-Terminal Segment Followed by the Stable C-Terminal β Structure," *PLoS One* **11**, 0146405 (10 pages) (2016).
- N. Ousaka, F. Mamiya, Y. Iwata, K. Nishimura and E. Yashima, "'Helix-in-Helix' Superstructure Formation through Encapsulation of Fullerene-Bound Helical Peptides within a Helical Poly(methyl methacrylate) Cavity," *Angew. Chem., Int. Ed.* **56**, 791–795 (2017).

1. Development of Solid-State NMR Probe

We have built a variety of solid-state NMR probes such as static and MAS ^{1}H-X double resonance probes for 400 MHz NMR, and a variable temperature ^{1}H-X double resonance MAS probe for 920 MHz ultra-high field NMR so far. Most of these probe buildings were achieved through major modifications of commercial probes. During the past few years, we have been working on building an original solid-state NMR probe which is fully compatible with commercial instruments currently used.

We have built original narrow bore solid-state NMR ^{1}H-X ("X" indicates variable resonant frequency) double resonance magic angle spinning (MAS) probe for 2.5 mm outer diameter (O.D.) sample tube used for 400 MHz (9.4 T) NMR spectrometer. The developed probe was built with originally designed parts except for spinning and spinning rate detection modules which were purchased from NMR company. The capacitive matching network design composed of commercially available non-magnetic variable capacitors was used. Balun type electric circuit was incorporated into ^{1}H channel, in which reduces to half the effective voltage of tuning capacitor and also minimize antenna effect of rf coil and rf inhomogeneity, especially at high field. Low frequency X channel was enabled to change largely its tunable frequency range to observe various nuclei by exchanging additional non-magnetic capacitors from bottom of the probe. The used network design may be compatible at higher fields by changing the parts related to resonant frequency.

Currently, the designs of individual parts are further updated and parts positions in the probe are further optimized to improve performance of the probe and access to the parts for the maintenance of the probe. ^{1}H-^{13}C-^{15}N triple resonance MAS probe was re-designed based on improved ^{1}H-X double resonance probe and is under building. We would like to replace two NMR modules purchased from NMR company to original ones. Therefore, we are currently attempting to design original spinning module for 4 mm sample tube in which a little bit easier than that for 2.5 mm sample tube. Probe developments enable to reduce cost for acquiring probes and open up possibilities to design new experiments which are tightly related to specifically designed hardware. In near future, we would like to incorporate special functions into our original probes.

2. Structural Characterization of Amyloid β Protein Oligomer Promoted on Lipid Bilayers Using Solid-State NMR

Amyloid β (Aβ) protein is disordered in solutions under diluted conditions, however it conforms insoluble amyloid fibrils, which are found in senile plaque as a hallmark of Alzheimer's disease. Although molecular structures of amyloid fibrils have been determined, its molecular process for fibrillation in vivo has not been clarified yet. However, accumulated evidences suggest that the fibrillation process may be promoted on neuronal cell membrane. Especially, it has been reported that Aβ specifically interacts with ganglioside GM1 which is one of the key lipids in lipid raft. Therefore, GM1 embedded into lipid bilayers composed of neutral lipid DMPC may be regarded as the most simplified model neuronal cell membrane. In order to clarify the role of GM1 in the fibrillation process, first, we have successfully determined the oligomeric structure of Aβ (1-40) induced on DMPC bilayers based on solid-state NMR.1) We have been collaborated with Prof. Kato group in IMS for those Aβ studies.

In the current study, Aβ (1-40) oligomer induced on lipid bilayers consisting of GM1 and DMPC have been attempted to characterize using solid-state NMR. All of essential solid-state NMR experiments such as ^{13}C-homonuclear- and, ^{13}C-^{15}N heteronuclear correlation experiments for signal assignments and dipolar coupling based ^{13}C-homonuclear correlation experiments to obtain distance information were completed.

As reported in last report, analysis of secondary structure of Aβ based on the chemical shifts of assigned signals revealed that disordered N-terminus followed by two β-sheet structures from middle region to C-terminus, in which differ from the one induced on DMPC bilayers.

During a year, the signal assignments were reconfirmed and dipolar coupling based ^{13}C-homonuclear correlation experiments were performed for the sample of [U-^{13}C,^{15}N] Aβ diluted with natural abundant Aβ at various mixing times to differentiate intra- and intermolecular correlations. Then intra- and intermolecular distance information was extracted through the analyses of those NMR data. By considering the result of paramagnetic relaxation enhancements (PRE) experiments as reported last year, promising intermolecular packing model was successfully obtained from the NMR data.

Currently, precise molecular structure of Aβ together with intermolecular packing configuration is under investigations based on NMR data with combination of computational science through collaboration with Prof. Okumura group in IMS.

3. Structural Characterizations of Molecular Materials Using Solid-State NMR

We have also been working on collaboration works with two other research groups, Prof. Yoshito Tobe in Osaka university and Prof. Nobuyuki Nishi in Aichi university of education for the characterizations of newly designed molecular materials based on solid-state NMR. Those projects are underway.

Reference

1) M. Yagi-Utsumi, K. Kato and K. Nishimura, *PLoS One* **11**, 0146405 (10 pages) (2016).

Study on Ion Conductive Materials for Novel Energy Storage/Conversion Devices

Department of Materials Molecular Science
Division of Molecular Functions

KOBAYASHI, Genki
Associate Professor
[gkobayashi@ims.ac.jp]

Education

2006	B.E. Kanazawa University
2008	M.E. Tokyo Institute of Technology
2010	D.S. Tokyo Institute of Technology

Professional Employment

2010	Postdoctoral Fellow, Tokyo Institute of Technology
2011	Assistant Professor, Kanagawa University
2012	JST-PRESTO Researcher (Additional post)
2013	Research Associate Professor, Institute for Molecular Science
2018	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2010	ACerS Spriggs Phase Equilibria Award, American Ceramics Society
2011	Tejima Doctoral Dissertation Award, Tokyo Institute of Technology
2018	The 39th Honda Memorial Young Researcher Award, The Honda Memorial Fundation
2018	The 7th Ishida Award, Nagoya University
2019	Tagawa Solid State Chemistry Awards, Division of Solid State Chemistry, The Electrochemical Society of Japan
2019	Morino Foundation for Molecular Science

Member

Assistant Professor
TAKEIRI, Fumitaka

Graduate Student
NAWAZ, Haq
OKAMOTO, Kei
UCHIMURA, Tasuku
AYU, Nur Ika Puji*

Technical Fellow
IMAI, Yumiko
KUBOTA, Akiko

Secretary
SUZUKI, Ai

Keywords Solid State Ionics, H^- Conductor, Battery

Chemical energy conversion/storage using electrochemical devices such as fuel cells and batteries will become increasingly important for future sustainable societies. As ion transport in solids is key for determining the performance of these devices, an improved understanding of the characteristics of existing electrode and electrolyte materials is required. For example, crystal structure, thermal stability, and reaction mechanisms are important to enhancing battery performance. Furthermore, the development of novel ion conduction phenomena through the synthesis of a new class of substances will be expected to lead to the creation of novel battery systems. In this context, I have concentrated my research efforts into two main areas: (i) Studies into the reaction mechanisms of cathodic materials for lithium secondary batteries; and (ii) The synthesis of new materials exhibiting hydride ion (H^-) conductivity and the development of a novel battery system utilizing both the H^- conduction phenomenon and the H^-/H_2 redox reaction.

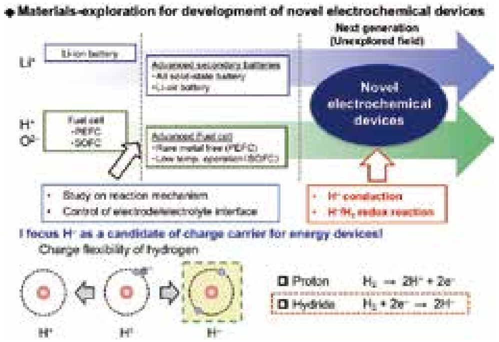


Figure 1. The concept of our research toward the realization of new energy storage/conversion devices.

Selected Publications

- G. Kobayashi, Y. Hinuma, S. Matsuoka, A. Watanabe, M. Iqbal, M. Hirayama, M. Yonemura, T. Kamiyama, I. Tanaka and R. Kanno, *Science* **351**, 1314–1317 (2016).
- G. Kobayashi, Y. Irii, F. Matsumoto, A. Ito, Y. Ohsawa, S. Yamamoto, Y. Chui, J.-Y. Son and Y. Sato, *J. Power Sources* **303**, 250–256 (2016).
- A. Watanabe, G. Kobayashi, N. Matsui, M. Yonemura, A. Kubota, K. Suzuki, M. Hirayama and R. Kanno, *Electrochemistry* **85(2)**, 88–92 (2017).
- Y. Iwasaki, N. Matsui, K. Suzuki, Y. Hinuma, M. Yonemura, G. Kobayashi, M. Hirayama, I. Tanaka and R. Kanno, *J. Mater. Chem. A* **6**, 23457–23463 (2018).
- F. Takeiri, A. Watanabe, A. Kuwabara, H. Nawaz, N. Ayu, M. Yonemura, R. Kanno and G. Kobayashi, *Inorg. Chem.* **58**, 4431–4436 (2019).
- N. Matsui, G. Kobayashi, K. Suzuki, A. Watanabe, A. Kubota, Y. Iwasaki, M. Yonemura, M. Hirayama and R. Kanno, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
- H. Nawaz, F. Takeiri, A. Kuwabara and M. Yonemura and G. Kobayashi, *Chem. Commun.* **56**, 10373–10376 (2020).

1. Study on H^- Conductive Oxyhydrides[1–5]

Ionic charge carriers include a variety of species, such as Li^+, H^+, Ag^+, Cu^+, F^-, and O^{2-}, and their conductors have found applications in energy devices such as fuel cells and batteries. A hydride ion (H^-,) is an attractive charge carrier because it exhibits promising features for fast ionic conduction; namely, monovalence, suitable ionic size similar to that of F^- and O^{2-}, and high polarizability. Furthermore, its strong reducing properties with a standard redox potential of H^-/H_2 (−2.3 V) which is close to that of Mg/Mg^{2+} (−2.4 V) may be applied in energy storage/conversion devices with high energy densities. In 2016, we synthesized a series of K_2NiF_4-type oxyhydrides, $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$, which are equipped with anion sublattices that exhibit flexibility in the storage of H^-, O^{2-}, and vacancies (Figure 2 upper) and demonstrated pure H^- conduction properties in the oxyhydrides. The Li-based oxyhydrides acted as solid electrolytes and the all-solid-state $Ti/La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}/TiH_2$ cell showed a redox reaction based on hydrogen storage/desorption on the electrodes, which is a first battery reaction using H^- conduction phenomena.

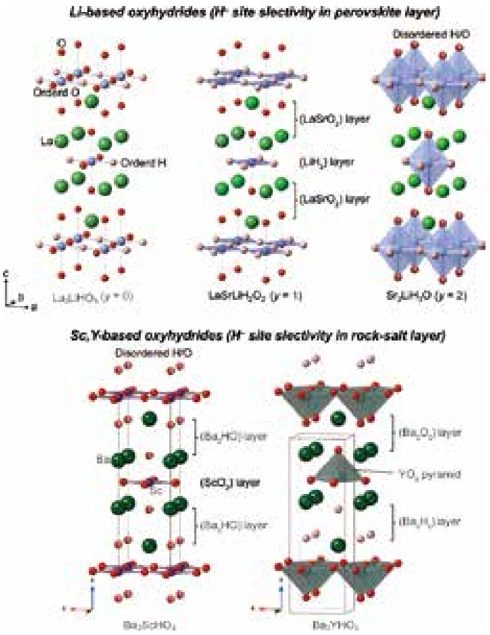


Figure 2. Crystal structures of H^- conductive oxyhydrides $La_{2-x-y}Sr_{x+y}LiH_{1-x+y}O_{3-y}$ ($x = 0$, $y = 0, 1, 2$) and Ba_2MHO_3 (M = Sc, Y).

More recently, we synthesized novel H^- conductive oxyhydrides, Ba_2MHO_3 (M = Sc, Y), with the K_2NiF_4-type structure and confirmed its unique site selectivity for H^-. In accordance with the electrostatic valence rule, it was found that the hydride ions in Ba_2MHO_3 selectively occupied the rock-salt layer, in contrast to those of the observed isostructural Li-based oxyhydrides that preferentially occupy the perovskite layer (Figure 2). The cation size at the octahedral center influences the anion arrangement within the rock salt layer, and in the Y-oxyhydride, the complete ordering of H/O led to the formation of the $[Ba_2H_2]$ layers. These results indicate that anion ordering in oxyhydrides could be tuned by appropriate element substitutions, which is a new insight for designing H^- conducting materials.

2. High-Performance of Li-Rich Layered Cathode Materials through A_2O_3-Surface Modification[6]

Controlling the cathode/electrolyte interface by surface modification of cathode materials with metal oxides or phosphate is being explored as a possible strategy for improving the electrochemical performance of such materials. We synthesized Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ and investiated the crystal structure, the chemical bonding state from bulk to surface, and the influence of the surface modification on the electrochemical performance by X-ray diffraction, hard X-ray photoelectron spectroscopy (HAXPES), and galvanostatic charge/discharge reaction. It revealed that the surface-modification layer was composed of Li-Al oxides and Al oxides and that a $LiM_{1-x}Al_xO_2$ (M = transition metals) interlayer was formed between the modification layer and the $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particles (Figure 3). The cycling performance of the Li-rich layered oxide was enhanced by the surface modification with Al_2O_3. A discharge capacity of more than 310 mA h^{-1} and excellent cycling stability at 50 °C were achieved by the combination of the gradual Li-insetion/de-insertion process (stepwise precycling treatment) and the surface-modification.

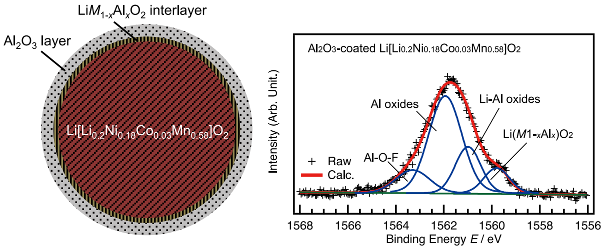


Figure 3. Schematic illustration and Al 1*s* HAXPES spectra of the 2 wt% Al_2O_3-coated $Li[Li_{0.2}Ni_{0.18}Co_{0.03}Mn_{0.58}]O_2$ particle.

References

1) H. Nawaz, G. Kobayashi* *et al.*, *Chem. Commun.* **56**, 10373–10376 (2020).
2) F. Takeiri, G. Kobayashi* *et al.*, *Inorg. Chem.* **58**, 4431–4436 (2019).
3) N. Matsui, G. Kobayashi* *et al.*, *J. Am. Ceram. Soc.* **102**, 3228–3235 (2019).
4) A. Watanabe, G. Kobayashi* *et al.*, *Electrochemistry* **85**, 88–92 (2017).
5) G. Kobayashi*, R. Kanno* *et al.*, *Science* **351**, 1314–1317 (2016).
6) G. Kobayashi* *et al.*, *J. Power Sources* **303**, 250–256 (2016).

Award

KOBAYASHI, Genki; Morino Foundation for Molecular Science (2019).

* carrying out graduate research on Cooperative Education Program of IMS with High Energy Accelerator Research Organization

Clarification of the Energy Conversion Mechanism at the Surface and Interface by Scanning Probe Microscopy

Instrument Center

MINATO, Taketoshi
Senior Researcher

Surface and interface are the places for energy conversion processes in physics, chemistry, and biology. The detailed mechanism of such energy conversion processes is yet to be clarified. The reaction at the interface between the electrode and electrolyte of rechargeable batteries are a typical system of the energy conversion. At the interface in lithium ion battery, which is most widely used rechargeable battery,[1] the energy transfer is proceeded by the insertion and extraction of the carrier ions at the interface during the charge and discharge reactions. Also, at the interface, the carrier ions, counter ions, solvents, additives, and crystal structures of the electrode surface forms characteristic structures that induce different properties from the material bulk. Traditionally, the reaction mechanism at the interface has been discussed based on electrochemical measurements. However, the nature of the interface is still unclear due to the difficulty of the analysis of the buried interface.

Figure 1. The scanning probe microscope system for the analysis of electrochemical reactions installed in the instrument center of Institute for Molecular Science.

Scanning probe microscopy (SPM) is an excellent technique to analyze the geometric, mechanical, electric, and electronic properties at the surfaces and interfaces. Thus, it has been employed for the analysis of the energy conversion processes. SPM can directly access to the buried interfaces such as the interface between electrode and electrolyte and has abilities to provide important information to clarify the reaction mechanism. In 2020, two specially designed SPMs have been launched at the instrument center of the Institution for Molecular Science. One is designed for the analysis of the geometric, mechanical, electric, and electronic properties at the surface and interface under photo excitation or magnetic field with high resolution. The another is solely designed for the analysis under electrochemical reactions (Figure 1). Using the two SPM systems, both the physical properties and the reaction mechanism of the energy conversion processes at the surface and interface could be clarified.

Figure 2. A Faraday current mapping on SiN/Pt obtained by scanning electrochemical microscopy in 5 mM hexamine $RuCl_3$ and 0.1 M KNO_3 aqueous solution. Cantilever: Pt; counter electrode: Pt, reference electrode: Ag, sample potential: −0.1 V (vs reference), image size: 25 µm × 6 µm.

In electrochemical devices, the local distribution of the reactions at the interface between the electrode and electrolyte strongly influences the device performances. The direct observation of the local distribution at the interface provides important information that aids the understanding of the reaction mechanism of the system. Using the SPM system with the specially designed cantilever having Pt tip, the local distribution of the electrochemical reactions was visualized. Figure 2 shows an example of the mapping of the electrochemical reaction on SiN/Pt in hexamine $RuCl_3$ electrolyte. The bright area shows the area with higher Faraday current than the dark area. The higher Faraday current is caused by the redox reactions of Ru ions in the electrolyte. From the simultaneous observation of the mechanical properties of the electrode surface using the SPM, the bright and dark areas are assigned to the regions of Pt and SiN, respectively. The results reveal the high reactivity of the Pt in the reaction. Employing this technique in the present and innovative battery systems,[1–3] the local distribution of the reactions in the batteries can be visualized. This will avail more vital information for the design of new energy devices.

References

1) T. Minato and T. Abe, *Prog. Surf. Sci.* **92**, 240–280 (2017).
2) T. Minato, H. Konishi, A. Celik Kucuk, T. Abe and Z. Ogumi, *Ceramics Japan* **54**, 637 (2019).
3) H. Konishi, R. Takekawa, T. Minato, Z. Ogumi and T. Abe, *Chem. Phys. Lett.* **755**, 137785 (2020).

Visiting Professors

Visiting Professor

KISHINE, Jun-ichiro *(from The Open University of Japan)*

Theoretical Studies on Chiral Material Science

We focus on chirality-induced phenomena in solids. (1) Magnetic response of a highly nonlinear soliton lattice in a monoaxial chiral helimagnet: We presented a theory of nonlinear magnetic response of a chiral soliton lattice state in a monoaxial chiral helimagnet under an oscillating magnetic field. (2) Tensile deformations of the magnetic chiral soliton lattice probed by Lorentz transmission electron microscopy: We considered the case of a chiral soliton lattice subjected to uniaxial elastic strain. We found that the strain induced anisotropies give rise to three distinct non-trivial spin textures, depending on the nature of the strain, and we show how these states may be identified by their signatures in Lorentz transmission electron microscopy (TEM). (3) Chirality-Induced Spin-Polarized State of a Chiral Crystal: Chirality-induced spin transport phenomena are investigated at room temperature without magnetic fields in a monoaxial chiral dichalcogenide $CrNb_3S_6$. We found that spin polarization occurs in these chiral bulk crystals under a charge current flowing along the principal *c* axis.

Visiting Associate Professor

FURUKAWA, Ko *(from Niigata University)*

Advanced ESR Study of Molecule-Based Functional Materials

To develop the high-efficiency molecule-based device, it's vital to clarify the mechanism of the functional molecules/materials. We investigate the mechanism of the solid-state functional materials in terms of advanced electron spin resonance (ESR) spectroscopy such as high-field/high-frequency ESR, time-resolved ESR, pulsed-ESR and so on. Recently, our themes are following three (I) spin dynamics study of molecule-based materials with the complex function combined to photoconductivity and photo-induced magnetic properties, (II) operand ESR study of the alternative catalyst for oxygen reduction reaction (ORR) in fuel cell, and (III) The ESR study aimed to investigate the paddy soil environments and to identify the rice cultivar from the trace metal in the rice bran.

Visiting Associate Professor

OSHIMA, Yugo *(from RIKEN)*

Microscopic Studies of the Bilayer-Type Molecular Ferromagnet (Et-4BrT)[Ni(dmit)$_2$]$_2$ by ESR

Recently, a novel type of ferromagnet has been developed by Kusamoto Group and Yamamoto Group in IMS. The novel molecular ferromagnet (Et-4BrT)[Ni(dmit)$_2$]$_2$, where dmit is 1,3-dithiol-2-thiole-4,5-dithiolate and Et-4BrT is ethyl-4-bromothiazolium, takes a bilayer structure, and becomes ferromagnetic below 1 K. We are considering that this ferromagnet is the first realization of the Nagaoka-Penn ferromagnetism, where the ferromagnetism is achieved by the light hole-doping of the insulating Ni(dmit)$_2$ layer owing to the internal dipole moment of the monovalent cation Et-4BrT. In collaboration with Kusamoto Group and Yamamoto Group, we have investigated the microscopic electronic state of (Et-4BrT)[Ni(dmit)$_2$]$_2$ by high-frequency ESR. We have found that ESR lineshape largely changes below 30 K, which is probably due to the effect of doping from the cation site. We are now developing an ESR sample holder for field-effect transistors (FETs), so that we can control precisely the electrical doping of (Et-4BrT)[Ni(dmit)$_2$]$_2$ by means of FET structure, and investigate its change of magnetic properties by ESR spectroscopy.

RESEARCH ACTIVITIES

Life and Coordination-Complex Molecular Science

Department of Life and Coordination-Complex Molecular Science is composed of two divisions of biomolecular science, two divisions of coordination-complex molecular science, and one adjunct division. Biomolecular science divisions cover the studies on functions, dynamic structures, and mechanisms for various biomolecules such as sensor proteins, membrane proteins, biological-clock proteins, metalloproteins, glycoconjugates, molecular chaperone, and motor proteins. Coordination-complex divisions aim to develop molecular catalysts and functional metal complexes for transformation of organic molecules, water oxidation and reduction, and molecular materials with photonic-electronic-magnetic functions. Interdisciplinary alliances in this department aim to create new basic concepts for the molecular and energy conversion through the fundamental science conducted at each divisions.

Bioinorganic Chemistry of Metalloproteins Responsible for Metal Homeostasis and Signal Sensing

Department of Life and Coordination-Complex Molecular Science Division of Biomolecular Functions

AONO, Shigetoshi
Professor
[aono@ims.ac.jp]

Education

1982	B.S. Tokyo Institute of Technology
1987	Ph.D. Tokyo Institute of Technology

Professional Employment

1988	Postdoctoral Fellow, Georgia University
1989	Assistant Professor, Tokyo Institute of Technology
1994	Associate Professor, Japan Advanced Institute of Science and Technology
2002	Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience (–2018) Professor, The Graduate University for Advanced Studies
2018	Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Member

Assistant Professor
MURAKI, Norifumi

IMS Research Assistant Professor
TAKEDA, Kouta

Post-Doctoral Fellow
NAM, Dayeon

Technical Fellow
MURAKI, Megumi

Secretary
NAKANE, Kaori

Keywords Bioinorganic Chemistry, Metalloproteins, Sensor Protein

Transition metal ions and metalloproteins play crucial roles in meeting the energy demands of the cell by playing roles in intermediary metabolism and in signal transduction processes. Although they are essential for biological function, metal ion bioavailability must be maintained within a certain range in cells due to the inherent toxicity of all metals above a threshold. This threshold varies for individual metal ions. Homeostasis of metal ions requires a balance between the processes of uptake, utilization, storage, and efflux and is achieved by the coordinated activities of a variety of proteins including extracytoplasmic metal carriers, ion channels/pumps/transporters, metal-regulated transcription and translation proteins, and enzymes involved in the biogenesis of metal-containing cofactors/metalloproteins. In order to understand the processes underlying this complex metal homeostasis network, the study of the molecular processes that determine the protein-metal ion recognition, as well as how this event is transduced into a functional output, is required. My research interests are focused on the elucidation of the structure and function relationships of metalloproteins responsible for the regulation of biological homeostasis.

I am also working on gas sensor proteins. Gas molecules such as O_2, NO, CO and ethylene are present in the environment and are endogenously (enzymatically) produced to act as signaling molecules in biological systems. Sensing these gas molecules is the first step in their acting as signaling molecules. Sensor proteins are usually required. Input signals generated by gas sensing have to transduce to output signals that regulate biological functions. This is achieved by biological signal-transduction systems. Recognition of the cognate gas molecules is a general mechanism of functional regulation for gas sensor proteins. This induces conformational changes in proteins that controls their activities for following signal transductions. Interaction between gas molecules and sensor proteins is essential for recognition of gas molecules. Metal-containing prosthetic groups are widely used. In my research group, our research focuses on transition metal-based gas-sensor proteins and the signaling systems working with them.

Selected Publications

- N. Muraki, C. Kitatsuji, Y. Okamoto, T. Uchida, K. Ishimori and S. Aono, "Structural Basis for Heme Transfer Reaction in Heme Uptake Machinery from Corynebacteria," *Chem. Commun.* **55**, 13864–13867 (2019).
- N. Muraki, K. Ishii, S. Uchiyama, S. G. Itoh, H. Okumura and S. Aono, "Structural Characterization of HypX Responsible for CO Biosynthesis in the Maturation of NiFe-Hydrogenase," *Commun. Biol.* **2**, 385 (12 pages) (2019).
- A. Pavlou, H. Yoshimura, S. Aono and E. Pinakoulaki, "Protein Dynamics of the Sensor Protein HemAT as Probed by Time-Resolved Step-Scan FTIR Spectroscopy," *Biophys. J.* **114**, 584–591 (2018).
- A. Pavlou, A. Loullis, H. Yoshimura, S. Aono and E. Pinakoulaki, "Probing the Role of the Heme Distal and Proximal Environment in Ligand Dynamics in the Signal Transducer Protein HemAT by Time-Resolved Step-Scan FTIR and Resonance Raman Spectroscopy," *Biochemistry* **56**, 5309–5317 (2017).
- N. Muraki, C. Kitatsuji, M. Ogura, T. Uchida, K. Ishimori and S. Aono, "Structural Characterization of Heme Environmental Mutants of CgHmuT that Shuttles Heme Molecules to Heme Transporters," *Int. J. Mol. Sci.* **17**, 829 (2016).
- N. Muraki and S. Aono, "Structural Basis for Heme Recognition by HmuT Responsible for Heme Transport to the Heme Transporter in *Corynebacterium glutamicum*," *Chem. Lett.* **45**, 24–26 (2015).

1. Molecular Mechanisms for Biosynthesis and Maturation of Hydrogen Sensing Regulatory Hydrogenase

Regulatory hydrogenase (RH) that acts as a H_2 sensor consists of two subunits, a large subunit containing the Ni-Fe dinuclear complex and a small subunit containing iron-sulfur clusters. Though the Ni-Fe dinuclear complex in the large subunit is assumed to be the active site for H_2 sensing by RH, the molecular mechanisms of biosynthesis and maturation of the Ni-Fe dinuclear complex are not clear yet.

CO and CN^- ligands are coordinated to the Fe in the Ni-Fe dinuclear complexe in RH. These CO and CN^- are biosynthesized and assembled into the metal clusters, for which several accessory and chaperone proteins are required, as shown in Figure1. In 2019, we have determined the crystal structure of HypX, which catalyzes CO biosynthesis for the ligand of the Ni-Fe complex in RH, to find that HypX adopt coenyzme A (CoA) as a cofactor for CO biosynthesis using formyl-tetrahydrofolate as a substrate to form formyl-CoA, and that formyl-CoA is the reaction intermediate to form CO.

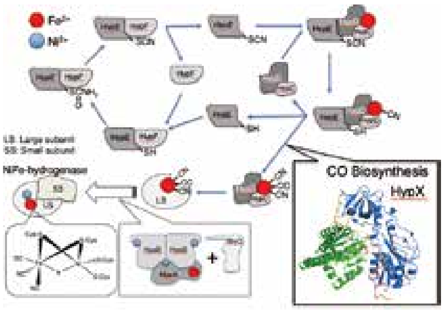


Figure 1. Reaction scheme of the biosynthesis and maturation of the Ni-Fe dinuclear complex for the active site in RH.

CO produced by HypX is used as a ligand of the iron in the $NiFe(CN)_2(CO)$ center of NiFe hydrogenases. The $Fe(CN)_2(CO)$ unit of the NiFe dinuclear center is assembled in the HypC/HypD complex as a scaffold. The binding site of the $Fe(CN)_2(CO)$ unit is proposed to be located at the bottom of a tunnel ca. 20 Å deep inside from the protein surface in the HypC/HypD complex, to which Fe is initially bound and then CN^- and CO ligands bind to the Fe. If CO produced by HypX is diffused into solvent, it will be inefficient for the assembly of the $Fe(CN)_2(CO)$ unit in the HypC/HypD. It may be a solution to utilize CO produced by HypX effectively is that HypX and HypC/HypD form a complex. The SEC analyses reveal the formation of HypC/HypD and HypC/HypD/HypX complexes as described below.

HypC (10.4 kDa in monomer) and HypD (45.0 kDa in monomer) are eluted from a Superdex75 column with an apparent mass of 21.6 kDa and 35.5 kDa, respectively, indicating that HypC and HypD exist as a homo-dimer and monomer in solution, respectively. The mixture of HypC and HypD is eluted with an apparent mass of 76.4 kDa. Though this result indicates the formation of the complex between HypC and HypD (probably $(HypC)_2HypD$ complex), its quaternary structure is not clear at present. The mixture of HypC, HypD, and HypX was eluted from a Superdex200 column with an apparent mass of 119.7 kDa, suggesting the formation of the 1:1:1 complex of HypC, HypD, and HypX. The structural characterization of this complex is now in progress.

2. Structural Basis for Heme Transfer Reaction in Heme Uptake Machinery from Corynebacteria

Corynebacteria including *Corynebacterium diphtheriae* and *Corynebacterium glutamicum*, which are classified as a high GC content Gram-positive bacteria (Actinomycetes), adopt a different heme uptake machinery (Hta/Hmu system). It consists of the membrane-bound heme binding/transport proteins (HtaA and HtaB) and the ABC-type heme transporter system (HmuTUV). HtaA and HtaB consist of two and one CR (Conserved Region) domains, respectively, which are responsible for heme binding/transport. In this study, we have determined the crystal structures of HtaA and HtaB from *C. glutamicum* to understand the structural basis of the heme-uptake in Corynebacteria.

Though these interactions and the overall structure are conserved among HtaA and HtaB, the orientation of heme is different from one another. Good fitting of the model into the electron density of heme was obtained with the single orientation of heme for HtaA. On the other hand, assuming a 1:1 mixture of two orientations of heme was needed to obtain good fitting for the electron density of heme in HtaB. Thus, heme is accommodated with a mixture of two different orientations in HtaB unlike HtaA. The difference of the heme orientation suggests that heme transfer reaction between HtaA and HtaB proceeds through the HtaA/HtaB complex formation.

We also determined the crystal structure of the apo-form of H434A-HtaA at a resolution of 2.0 Å. Though the holo-form of H434A-HtaA is a monomer, the apo-form of this variant was dimer. The N-terminal region (Ser364-Gly391) including the β1 strand and the α1 helix in each protomer are separated from the core region and each β1 strand is swapped between two protomers to form a domain-swapped dimer (Figure 2).

Figure 2. The structure of the apo-form of H343A-HtaA. The chains A and B are shown in orange and light green, respectively. A dotted line in the chain B is a disordered region including the α2 helix.

The structure of the domain-swapped dimer of apo-HtaA would be a model of a reaction intermediate for the heme transfer. In the domain-swapped dimer, the chain A would be a model of the holo-HtaA because it is superimposable to the structure of the holo-HtaA. The chain B in the domain-swapped dimer would be a model of the apo-HtaB in the holo-HtaA/apo-HtaB complex.

Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions

KATO, Koichi
Professor
[kkatonmr@ims.ac.jp]

Director, ExCELLS

Education

1986	B.S. The University of Tokyo
1991	Ph.D. The University of Tokyo

Professional Employment

1991	Assistant Professor, The University of Tokyo
1997	Lecturer, The University of Tokyo
2000	Professor, Nagoya City University
2008	Professor, Institute for Molecular Science Professor, Okazaki Institute for Integrative Bioscience (–2018) Professor, The Graduate University for Advanced Studies
2006	Visiting Professor, Ochanomizu University
2013	Project Leader, JSPS Grant in Aid for Scientific Research on Innovative Areas “Dynamical Ordering of Biomolecular Systems for Creation of Integrated Functions”
2018	Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Awards

2000	The Pharmaceutical Society of Japan Award for Young Scientists
2011	The Pharmaceutical Society of Japan Award for Divisional Scientific Promotions
2011	The 48th Baelz Prize

Member
Assistant Professor
YAGI-UTSUMI, Maho
YANAKA, Saeko
Post-Doctoral Fellow
SUZUKI, Tatsuya
Visiting Scientist
GOH, Ean Wai*
WILASRI, Thunchanok*
Graduate Student
HIRANYAKORN, Methanee
SEKIGUCHI, Taichiro
YUNOKI, Yasuhiro†
YOGO, Rina†
SAITO, Taiki†
KOFUJI, Kana†
UMEZAWA, Fumiko†
SASAKI, Yudai †
YAMADA, Rino†
Technical Fellow
ISONO, Yukiko
Secretary
TANAKA, Kei
FUKUTOMI, Yukie

Keywords Biomolecule Organization, NMR

Living systems are characterized as dynamic processes of assembly and disassembly of various biomolecules that are self-organized, interacting with the external environment. The omics-based approaches developed in recent decades have provided comprehensive information regarding biomolecules as parts of living organisms. However, fundamental questions still remain unsolved as to how these biomolecules are ordered autonomously to form flexible and robust systems (Figure 1). Biomolecules with complicated, flexible structures are self-organized through weak interactions giving rise to supramolecular complexes that adopt their own dynamic, asymmetric architectures. These processes are coupled with expression of integrated functions in the biomolecular systems.

Toward an integrative understanding of the principles behind the biomolecular ordering processes, we conduct multidisciplinary approaches based on detailed analyses of dynamic structures and interactions of biomolecules at atomic level, in conjunction with the methodologies of molecular and cellular biology along with synthetic and computational technique.

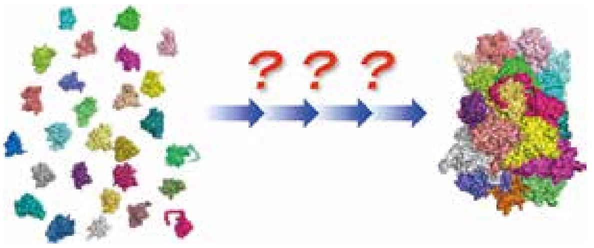


Figure 1. Formation of supramolecular machinery through dynamic assembly and disassembly of biomolecules.

Selected Publications

- S. Yanaka, R. Yogo and K. Kato, “Biophysical Characterization of Dynamic Structures of Immunoglobulin G,” *Biophys. Rev.* **12**, 637–645 (2020).
- T. Satoh and K. Kato, “Structural Aspects of ER Glycoprotein Quality-Control System Mediated by Glucose Tagging,” in *Glycobiophysics*, Y. Yamaguchi and K. Kato, Eds., Springer Nature; Singapore, pp. 149–169 (2018).
- K. Kato, H. Yagi and T. Yamaguchi, “NMR Characterization of the Dynamic Conformations of Oligosaccharides,” in *Modern Magnetic Resonance, 2nd Edition*, G. A. Webb, Ed., Springer International Publishing, pp. 737–754 (2018).
- T. Yamaguchi and K. Kato, “Molecular Dynamics of Gangliosides,” in *Gangliosides*, S. Sonnino and A. Prinetti, Eds., Methods in Molecular Biology, Humana Press; New York, **vol. 1804**, pp. 411–417 (2018).
- K. Kato and T. Satoh, “Structural Insights on the Dynamics of Proteasome Formation,” *Biophys. Rev.* **10**, 597–604 (2018).
- K. Kato, S. Yanaka and H. Yagi, “Technical Basis for Nuclear Magnetic Resonance Approach for Glycoproteins,” in *Experimental Approaches of NMR Spectroscopy*, The Nuclear Magnetic Resonance Society of Japan, Ed., Springer Nature; Singapore, pp. 415–438 (2018).

1. Conformational Dynamics of Post-Translational Protein Modifiers

A majority of proteins encoded in genomes of limited size are post-translationally diversified by covalent modifications such as glycosylation and ubiquitination. The modifiers, *i.e.*, glycans and ubiquitin (Ub) chains, carry distinct biological information in forms of “glycocode” and “Ub code,” respectively, which are read out by specific interacting proteins. Because these modifiers possess considerable degrees of motional freedom, we develop methodologies for characterizing their conformational dynamics in solution by NMR spectroscopy.

Our NMR analyses enabled the quantification of populations of individual conformers of Lys48-linked Ub chains, which serve as tags for proteasomal degradation. The data indicate that the most distal Ub unit in the Ub chains is the most apt to expose its interaction surface with the Ub-recognizing proteins. We also demonstrate that a mutational modification of the distal end of the Ub chain can remotely affect the solvent exposure of the interaction surfaces of the other Ub units, suggesting that Ub chains could be unique design frameworks for the creation of allosterically controllable multidomain proteins.1)

We also developed an approach to improve the protein-binding affinity of an oligosaccharide by remodeling its conformational space in the precomplexed state. In this approach, based on NMR-validated molecular dynamics simulations, we created an oligosaccharide analogue with an increased population of on-pathway metastable conformers that were originally very minor but exclusively accessible to the target protein without steric hindrance (Figure 2).2)

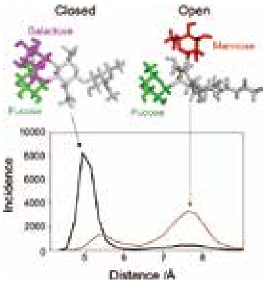


Figure 2. Remodeling of the oligosaccharide conformational space in the prebound state to improve lectin-binding affinity.

2. Integrative Biophysical Approaches to Exploring Protein Assembly Dynamics

The integrative biophysical approaches we have been developing in collaboration with several research groups in ExCELLS and our external research network could be successfully applied to a variety of biomolecular assembling systems, yielding fruitful results in the past year, as summarized below (Figure 3).

We revealed that the two functionally unannotated archaeal proteins, PbaA and PF0014, are co-assembled into a unique ancient Greek tholos-like architecture, offering a novel framework for designing functional protein cages.3) We successfully visualized the dynamic process by which the antibodies bound to antigens in membranes spontaneously assemble to form a hexameric ring structure, thereby recruiting complement component C1q on the membrane, which is the initial step of complement-mediated cell lysis.4) Assembly of amyloid β (Aβ) under microgravity conditions were explored using the International Space Station, showing that the Aβ fibrillization process significantly slowed down in the microgravity environment, giving rise to distinct morphologies of Aβ.5)

Furthermore, we demonstrated that the cargo receptor complex responsible for the intracellular transportation of blood coagulation factors V and VIII recognizes 10-amino acid sequence built into these glycoproteins as a “passport” in the secretory pathway.6) The secretion levels of recombinant glycoproteins were significantly increased simply by tagging it with the passport sequence. Our findings offer a potentially useful tool for improving the production yields of recombinant glycoproteins of biopharmaceutical interest.

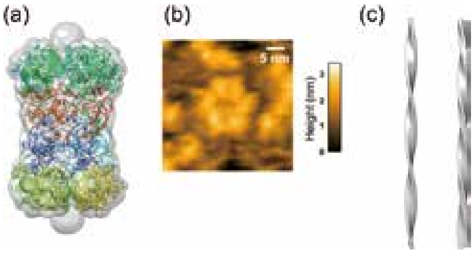


Figure 3. Integrative biophysical approaches to exploring protein assembly dynamics. The simulated model structure of the PbaA/PF0014 complex superimposed onto the cryo-EM map (a), high-speed AFM image of IgG hexamers formed on membrane (b), distinct morphologies of Aβ fibrils formed under microgravity conditions (c).

References

1) M. Hiranyakorn *et al. Int. J. Mol. Sci.* **21**, 5351 (2020).
2) T. Suzuki *et al. Biochemistry* **59**, 3180–3185 (2020).
3) M. Yagi-Utsumi *et al. Sci. Rep.* **10**, 1540 (2020).
4) S. Yanaka *et al. Int. J. Mol. Sci.* **21**, 147 (2020).
5) M. Yagi-Utsumi *et al. NPJ Micorgravity* **6**, 17 (2020).
6) H. Yagi *et al. Nat. Commun.* **11**, 1368 (2020).

Awards

SAITO, Taiki; Young Scientist Award, The Japanese Biochemical Society Chubu Branch (2019).
UMEZAWA, Fumiko; Young Scientist Award, the 3rd Glycolleague (2019).
YUNOKI, Yasuhiro; poster prize, the 26th Annual Meeting of the Japanese Society for Chronobiology (2019).

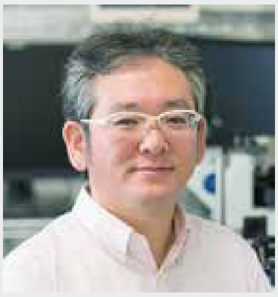
---

* IMS-IIPA Program

† carrying out graduate research on Cooperative Education Program of IMS with Nagoya City University

Operation and Design Principles of Biological Molecular Machines

Department of Life and Coordination-Complex Molecular Science
Division of Biomolecular Functions



IINO, Ryota
Professor
[iino@ims.ac.jp]

Education
1995 B.E. Kyoto University
1997 M.E. Kyoto University
2003 Ph.D. Nagoya University

Professional Employment
2000 Research Associate, Japan Science and Technology Cooperation
2002 Research Associate, Japan Science and Technology Agency
2005 Specially-Appointed Assistant Professor, Osaka University
2006 Assistant Professor, Osaka University
2011 Lecturer, The University of Tokyo
2013 Associate Professor, The University of Tokyo
2014 Professor, Institute for Molecular Science
Professor, Okazaki Institute for Integrative Bioscience (–2018)
Professor, The Graduate University for Advanced Studies

Award
2012 Emerging Investigator. Lab on a Chip., The Royal Society of Chemistry, U.K.

Member
Assistant Professor
  NAKAMURA, Akihiko
  ANDO, Jun
  OTOMO, Akihiro
Post-Doctoral Fellow
  TAKEDA, Kimitoshi
  KIM, Ju-Young
Visiting Scientist
  NOJIMA, Tatsuya
  HONSA, Monique*
  YANG, Ling*
Graduate Student
  VISOOTSAT, Akasit
  IIDA, Tatsuya
Technical Fellow
  YAMAMOTO, Mayuko
  OKUNI, Yasuko
  KON, Yayoi
Secretary
  NAKANE, Kaori

Keywords Molecular Motors, Single-Molecule Analysis, Protein Engineering

Activity of life is supported by various molecular machines made of proteins. Protein molecular machines are tiny, but show very high performance, and are superior to man-made machines in many aspects. One of the representatives of protein molecular machines is linear and rotary molecular motors (Figure 1). Molecular motors generate mechanical forces and torques that drive their unidirectional motions from the energy of chemical reaction or the electrochemical potential across the cell membrane.

We unveil operation principles of molecular motors with advanced single-molecule functional analysis. With the help of site-saturation mutagenesis and robot-based automation, we also engineer non-natural molecular motors to understand their design principles.

Figure 1. Protein molecular machines. (Left) A linear molecular motor chitinase A. (Center and Right) Rotary molecular motors F$_1$-ATPase and V$_1$-ATPase, respectively.

Selected Publications

- J. Ando, A. Nakamura, M. Yamamoto, C. Song, K. Murata and R. Iino, "Multicolor High-Speed Tracking of Single Biomolecules with Silver, Gold, Silver-Gold Alloy Nanoparticles," *ACS Photonics* **6**, 2870–2883 (2019).
- T. Iida, Y. Minagawa, H. Ueno, F. Kawai, T. Murata and R. Iino, "Single-Molecule Analysis Reveals Rotational Substeps and Chemo-Mechanical Coupling Scheme of *Enterococcus hirae* V$_1$-ATPase," *J. Biol. Chem.* **294**, 17017–17030 (2019).
- J. Ando, A. Nakamura, A. Visootsat, M. Yamamoto, C. Song, K. Murata and R. Iino, "Single-Nanoparticle Tracking with Angstrom Localization Precision and Microsecond Time Resolution," *Biophys. J.* **115**, 2413–2427 (2018).
- A. Nakamura, K. Okazaki, T. Furuta, M. Sakurai and R. Iino, "Processive Chitinase is Brownian Monorail Operated by Fast Catalysis after Peeling Rail from Crystalline Chitin," *Nat. Commun.* **9**, 3814 (2018).
- A. Nakamura, T. Tasaki, Y. Okuni, C. Song, K. Murata, T. Kozai, M. Hara, H. Sugimoto, K. Suzuki, T. Watanabe, T. Uchihashi, H. Noji and R. Iino, "Rate Constants, Processivity, and Productive Binding Ratio of Chitinase A Revealed by Single-Molecule Analysis," *Phys. Chem. Chem. Phys.* **20**, 3010–3018 (2018).
- T. Uchihashi, Y. H. Watanabe, Y. Nakazaki, Y. Yamasaki, T. Watanabe, T. Maruno, S. Uchiyama, S. Song, K. Murata, R. Iino and T. Ando, "Dynamic Structural States of ClpB Involved in Its Disaggregation Function," *Nat. Commun.* **9**, 2147 (2018).

1. Small Stepping Motion of Processive Dynein Revealed by Load-Free High-Speed Single-Particle Tracking[1)]

Cytoplasmic dynein is a dimeric motor protein which processively moves along microtubule. Its motor domain (head) hydrolyzes ATP and induces conformational changes of linker, stalk, and microtubule binding domain (MTBD) to trigger stepping motion. Here we applied scattering imaging of gold nanoparticle (AuNP) to visualize load-free stepping motion of processive dynein (Figure 2). We observed artificially-dimerized chimeric dynein, which has the head, linker, and stalk from Dictyostelium discoideum cytoplasmic dynein and the MTBD from human axonemal dynein, whose structure has been well-studied by cryo-electron microscopy. One head of a dimer was labeled with 30 nm AuNP, and stepping motions were observed with 100 µs time resolution and sub-nanometer localization precision at physiologically-relevant 1 mM ATP. We found 8 nm forward and backward steps and 5 nm side steps, consistent with on- and off-axes pitches of binding cleft between αβ-tubulin dimers on the microtubule. Probability of the forward step was 1.8 times higher than that of the backward step, and similar to those of the side steps. One-head bound states were not clearly observed, and the steps were limited by a single rate constant. Our results indicate dynein mainly moves with biased small stepping motion in which only backward steps are slightly suppressed.

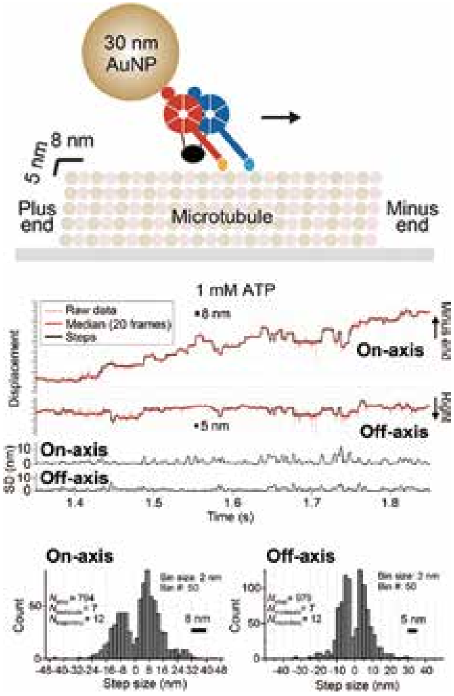


Figure 2. (Top) Schematic of single-molecule imaging of dynein motion. (Middile) Typical trajectory of motion. (Bottom) Distribution of step size in on- and off-axis.

2. Single-Molecule Imaging Analysis Reveals the Mechanism of a High-Catalytic-Activity Mutant of Chitinase A from *Serratia marcescens*[2)]

Chitin degradation is important for biomass conversion and has potential applications for agriculture, biotechnology, and the pharmaceutical industry. Chitinase A from the Gram-negative bacterium *Serratia marcescens* (*Sm*ChiA, Figure 3) is a processive enzyme that hydrolyzes crystalline chitin as it moves linearly along the substrate surface. In a previous study, the catalytic activity of *Sm*ChiA against crystalline chitin was found to increase after the tryptophan substitution of two phenylalanine residues (F232W and F396W), located at the entrance and exit of the substrate binding cleft of the catalytic domain, respectively. However, the mechanism underlying this high catalytic activity remains elusive. In this study, single-molecule fluorescence imaging and high-speed atomic force microscopy were applied to understand the mechanism of this high-catalytic-activity mutant. A reaction scheme including processive catalysis was used to reproduce the properties of *Sm*ChiA WT and F232W/F396W, in which all of the kinetic parameters were experimentally determined. High activity of F232W/F396W mutant was caused by a high processivity and a low dissociation rate constant after productive binding. The turnover numbers for both WT and F232W/F396W, determined by the biochemical analysis, were well-replicated using the kinetic parameters obtained from single-molecule imaging analysis, indicating the validity of the reaction scheme. Furthermore, alignment of amino acid sequences of 258 *Sm*ChiA-like proteins revealed that tryptophan, not phenylalanine, is the predominant amino acid at the corresponding positions (Phe-232 and Phe-396 for *Sm*ChiA). Our study will be helpful for understanding the kinetic mechanisms and further improvement of crystalline chitin hydrolytic activity of *Sm*ChiA mutants.

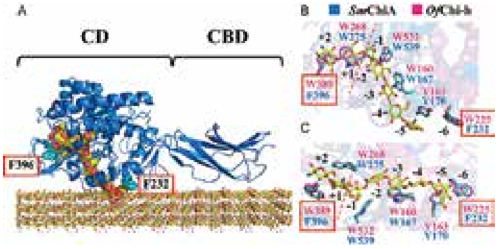


Figure 3. (A) Structural model of *Sm*ChiA bound to crystalline chitin. (B and C) Side and bottom views of aromatic amino acid residues (cyan and pink) and bound chitin (yellow) in the catalytic cleft of *Sm*ChiA and OfChi-h.

References

1) J. Ando *et al.*, *Sci. Rep.* **10**, 1080 (2020).
2) A, Visootsat *et al.*, *J. Biol. Chem.* **295**, 1915–1925 (2020).

Awards

NAKAMURA, Akihiko; Early Career Award in Biophysics, 2019 Annual Meeting of the Biophysical Society of Japan (2019).
IIDA, Tatsuya; Student Presentation Award, 2019 Annual Meeting of the Biophysical Society of Japan (2019).

* IMS International Internship Program

A Supramolecular Chemical Approach to the Construction of Artificial Cells

Department of Life and Coordination-Complex Molecular Science Division of Biomolecular Functions

KURIHARA, Kensuke
Research Associate Professor
(–March, 2020)
[kkurihara@ims.ac.jp]

Education
2005 B.S. The University of Tokyo
2010 Ph.D. The University of Tokyo

Professional Employment
2010 Technical Assistant, The University of Tokyo
2013 Postdoctoral Fellow, Research & Education Platform for Dynamics Living States, The University of Tokyo
2014 Research Associate Professor, Institute for Molecular Science
Research Associate Professor, Okazaki Institute for Integrative Bioscience (OKAZAKI ORION Project) (–2018)
2018 Research Associate Professor, Exploratory Research Center on Life and Living Systems
2020 Project Researcher, Japan Agency for Marine-Earth Science and Technology (JAMSTEC)

Award
2018 Kurita Outstanding Research Award

Member
Post-Doctoral Fellow
MATSUO, Muneyuki
Visiting Scientist
HIRATA, Yuiko
Secretary
FUKUTOMI, Yukiyo

Keywords Artificial Cell, Origin of Life, Droplet

The cell is the smallest unit of life, and the first simple cells evolved from simple molecular assemblies on prebiotic earth. To understand this transition from non-living to living structures, we use a supramolecular chemical approach. As shown in Figure 1, the key elements of a cell are a compartment, information, and a catalyst (*i.e.*, metabolism). We have attempted to construct a chemically based artificial cell endowed with these three elements.

In our laboratory, we constructed two types of artificial cells by using giant vesicles (GVs) as the compartment. The first, developed in collaboration with the Sugawara group (Kanagawa Univ.), is an artificial cell that can proliferate from generation to generation. We have improved this model by constructing a recursive vesicular artificial cell system with proliferation cycles. After self-reproduction, these second-generation GVs contain no PCR reagents by consuming and therefore cannot reproduce for a second time. However, the reagents can be replenished by using the vesicular transport system and changing the pH of the dispersion, resulting in the fusion of the GVs with conveyer GVs bearing the PCR reagents. After the PCR reagents are replenished, the GV can self-reproduce again. This system could lead to an evolvable artificial cellular system. The second type of artificial cell contains a catalyst-producing system. The GV system can generate catalysts and membrane molecules by transforming their respective precursors. The catalysts that are produced facilitate the proliferation of the GVs.

We are now tackling the creation of artificial cells that mimic cellular dynamics, such as cytoskeleton formation within the cell.

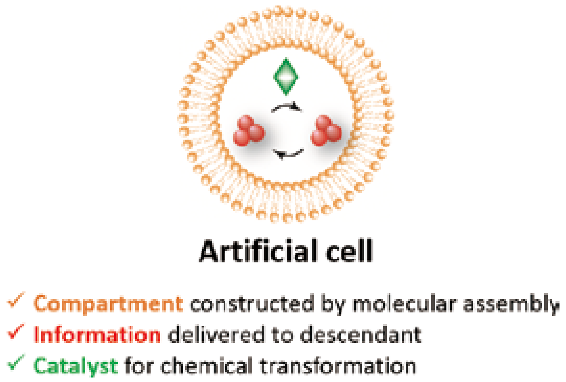


Figure 1. Artificial cell model. Materials containing heritable information are enclosed within a compartment. The reactions in the two replicating systems (compartment and information) are accelerated by appropriate catalysts The reactions in the two replicating systems are accelerated by appropriate catalysts.

Selected Publications

- Y. Natsume, E. Noguchi and K. Kurihara, “Spontaneous Localization of Particles in Giant Vesicles Owing to Depletion Force,” *J. Phys. Soc. Jpn.* **88**, 033001 (2019).
- M. Matsuo *et al.*, “Environment-Sensitive Intelligent Self-Reproducing Artificial Cell with a Modification-Active Lipo-Deoxyribozyme,” *Micromachines* **11**, 606 (2020). doi:10.3390/mi11060606

1. Construction of a LLPS-Droplet Based Model Protocell

In the prebiotic era, cooperative interaction between self-producing molecular aggregates and peptide polymers led to the emergence of primitive cells. Although the advanced membrane provides a field for catalytic reaction, it remains a mystery how cooperation between polymers and molecular aggregates occurred even in membraneless organisms like coacervate droplets. Since a coacervate droplet as a model of early life was created by Oparin about 100 years ago, interesting primitive cell models using coacervate droplets have been created. However, construction of the self-reproduction of coacervate droplets and the spontaneous formation of peptides, which are the constituents of the coacervate droplets has not been realized in the same environment. In the present study, we designed and synthesized a molecule that has both a peptide and a droplet formation site to enable the formation of the coacervate droplets. We attempted to construct a liquid–liquid phase-separated droplet that self-reproduces by constructing a reaction system in which a peptide is produced by spontaneous polymerization of an amino acid derivative in water.

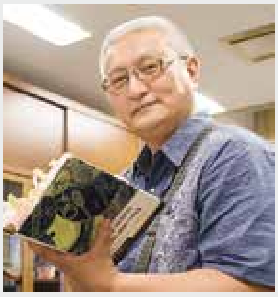
We synthesized an amino acid derivative (monomer) with two cysteine reactive sites at the N-terminus and a thioester at the C-terminus that spontaneously polymerizes in water to form a peptide. In order to prevent undesirable oxidation, a monomer precursor was obtained by crosslinking monomers with disulfide. After the addition of a reducing agent (dithiothreitol, DTT) to the monomer precursor solution, we observed the formation of droplets. We then added more precursor and DTT and examined the changes in particle size. The mean particle size increased and decreased rapidly immediately after the addition, confirming the self-reproducibility of the formed droplets. When the precursor and DTT were continuously added every 20 hours, the particle size of the droplets fluctuated recursively, indicating autocatalytic self-reproduction of the formed liquid–liquid phase-separated droplets. A detailed analysis of the particle size distribution measurements based on dynamic light scattering revealed that the growth of the droplets can be classified into two stages: The initial autocatalytic droplet formation and the fusion of the droplets. This autocatalytic droplet formation in this system is considered to be due to a physical mechanism: When a molecular assembly is created as the dehydration condensation proceeds and it forms a hydrophobic field, the assembly functions as a site for promoting dehydration condensation, thereby allowing the autocatalytic dehydration condensation to proceed. The behavior of the interface formed by this chemical reaction replicates the autocatalytic self-reproduction that might have occurred in droplets formed by liquid–liquid phase separation on the primitive, prebiotic earth.

Furthermore, we conceived that this liquid–liquid phase separation droplet would be useful as a place to integrate biomolecules representing other origin-of-life hypotheses (*e.g.*, RNA world, lipid world, *etc.*). Therefore, we attempted to investigate whether this droplet would incorporate those biomolecules. We added 20 mer RNA fragments, DNA fragments, and phospholipids to the droplets. By fluorescence microscopy observation and Raman microspectroscopy, it was found that the droplet was consisted of the hydrophobic center region and the hydrophilic peripheral region. The highly hydrophobic lipids were concentrated in the central region of the droplets and highly hydrophilic nucleic acids concentrated in the peripheral region. This hydrophilic and hydrophobic property was clear compared to the empty droplets. We suspect that the water contained in the hydrophilic region may have been replaced by nucleic acids.

In the future, we aim to construct the Droplet World Hypothesis by inducing the emergence of the primordial cell membrane via an internal chemical reaction or by functionally expressing biologically active molecular species, such as ribozymes, inside the droplet.

Development of Heterogeneous Catalysis toward Ideal Chemical Processes

Department of Life and Coordination-Complex Molecular Science
Division of Complex Catalysis



UOZUMI, Yasuhiro
Professor
[uo@ims.ac.jp]

Education

1984	B.S. Hokkaido University
1990	Ph.D. Hokkaido University

Professional Employment

1988	JSPS Research Fellow
1988	Research Associate, Hokkaido University
1990	Assistant Professor, Hokkaido University
1994	Research Associate, Columbia University
1995	Lecturer, Kyoto University
1997	Professor, Nagoya City University
2000	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies
2007	Research team leader, RIKEN
2014	Distinguished Professor, Three George University
2003	Research Project Leader, JST CREST Project (–2008)
2008	Research Project Leader, NEDO Project (–2012)
2011	Deputy Research Project Leader, JST CREST (–2016)
2014	Research Project Leader, JST ACCEL Project (–2019)

Awards

1991	Eisai Award, Synthetic Organic Chemistry
1998	The Pharmaceutical Society of Japan Award for Young Scientist
2007	The Chemical Society of Japan (CSJ) Award for Creative Work
2007	MEXT Ministerial Award for Green Sustainable Chemistry
2010	Inoue Prize for Science
2014	The Commendation for Science and Technology by the Minister of MEXT (Research Category)

Member

Visiting Professor
MASE, Toshiaki

Assistant Professor
OKUMURA, Shintaro

Post-Doctoral Fellow
PUTRA, Anggi Eka
SUGIYAMA, Yuya
SHEN, Guanshuo

Visiting Scientist
ZHANG, Kaili
KOJIMA, Keisuke

Graduate Student
ICHII, Shun
NIIMI, Ryoko
MIZUNO, Shota

Technical Fellow
TORII, Kaoru
TAZAWA, Aya

Secretary
SASAKI, Tokiyo
TANIWAKE, Mayuko

Keywords Transition Metal Catalysis, Green Chemistry, Organic Synthesis

Our research interests lie in the development of transition metal-catalyzed reaction systems toward ideal (highly efficient, selective, green, safe, simple, etc.) organic transformations. In particular, we have recently been developing the heterogeneous aquacatalytic systems, continuous flow catalytic systems, and super active catalysts working at ppm-ppb loading levels. Thus, for example, a variety of palladium catalysts were designed and prepared promoting carbon–carbon bond forming reactions at ppm-ppb loading levels (Figure 1).

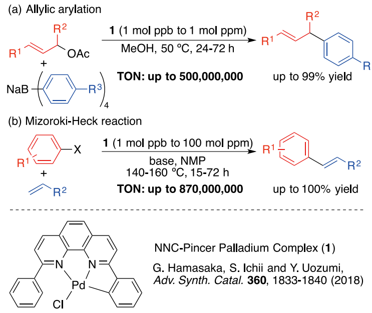


Figure 1. Typical Examples of Pd-Catalyzed Carbon–Carbon Bond Forming Reactions with ppm-ppb Loading Levels of an NNC-Pincer Pd Comples.

Selected Publications

- R. David and Y. Uozumi, "Recent Advances in Palladium-Catalyzed Cross-Coupling Reactions at ppm-ppb Molecular Catalyst Loadings (review)," *Adv. Synth. Catal.* **360**, 602–625 (2018).
- T. Osako, K. Torii, S. Hirata and Y. Uozumi, "Chemoselective Continuous-Flow Hydrogenation of Aldehydes Catalyzed by Platinum Nanoparticles Dispersed in an Amphiphilic Resin," *ACS Catal.* **7**, 7371–7377 (2017).
- Y. M. A. Yamada, S. M. Sarkar and Y. Uozumi, "Self-Assembled Poly(imidazole-palladium): Highly Active, Reusable Catalyst at Parts per Million to Parts per Billion Levels," *J. Am. Chem. Soc.* **134**, 3190–3198 (2012).
- G. Hamasaka, T. Muto and Y. Uozumi, "Molecular-Architecture-Based Administration of Catalysis in Water: Self-Assembly of an Amphiphilic Palladium Pincer Complex," *Angew. Chem., Int. Ed.* **50**, 4876–4878 (2011).
- Y. Uozumi, Y. Matsuura, T. Arakawa and Y. M. A. Yamada, "Asymmetric Suzuki-Miyaura Coupling in Water with a Chiral Pallasium Catalyst Supported on Amphiphilic Resin," *Angew. Chem., Int. Ed.* **48**, 2708–2710 (2009).
- Y. M. A. Yamada, T. Arakawa, H. Hocke and Y. Uozumi, "A Nanoplatinum Catalyst for Aerobic Oxidation of Alcohols in Water," *Angew. Chem., Int. Ed.* **46**, 704–706 (2007).
- Y. Uozumi, Y. M. A. Yamada, T. Beppu, N. Fukuyama, M. Ueno and T. Kitamori, "Instantaneous Carbon–Carbon Bond Formation Using a Microchannel Reactor with a Catalytic Membrane," *J. Am. Chem. Soc.* **128**, 15994–15995 (2006).

1. Arylation of Terminal Alkynes by Aryl Iodides Catalyzed by a Parts-per-Million Loading of Palladium Acetate[1)]

Arylation of terminal alkynes (16 varieties) by aryl iodides (28 varieties) was achieved with a mol ppm loading level of palladium catalyst, where a variety of functional groups including heteroarenes were tolerated. Thus, the arylations were carried out in the presence of palladium acetate at ppm loadings and potassium carbonate in ethanol at 80 °C to give the corresponding internal alkynes in good to excellent yields. Synthesis of 2-phenyl-3-(phenylalkynyl)benzofuran was achieved by iterative use of the alkyne arylation under mol ppm catalytic conditions. Reaction-rate analysis, transmission electron microscopic (TEM) examination of the reaction mixture, and mercury-amalgamation test were performed to gain insight into the active species of the highly active ppm catalytic species. TEM examination of the reaction mixture revealed that palladium nanoparticles were generated in situ under the reaction conditions, and their cluster size was variable during the catalytic reaction. A variation in size of palladium particles suggested that the composition-decomposition process of Pd aggregates should take place in situ via monomeric palladium(0) species and/or fine palladium(0) clusters, which might be real catalytic species in this reaction.

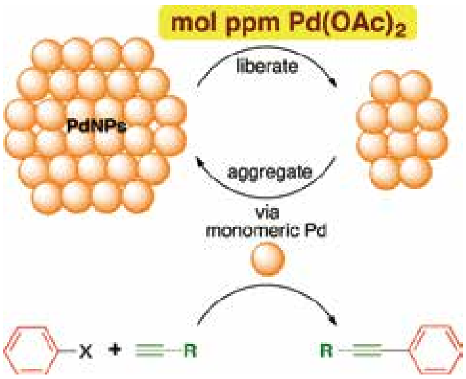


Figure 2. Arylation of Terminal Alkynes with a mol ppm Loading Level of a Palladium Catalyst.

2. Second-Generation *meta*-Phenolsulfonic Acid–Formaldehyde Resin as a Catalyst for Continuous-Flow Esterification[2)]

A second-generation *m*-phenolsulfonic acid–formaldehyde resin (PAFR II) catalyst was prepared by condensation polymerization of sodium *m*-phenolsulfonate and paraformaldehyde in an aqueous H_2SO_4 solution. This reusable, robust acid resin catalyst was improved in both catalytic activity and stability, maintaining the characteristics of the previous generation catalyst (*p*-phenolsulfonic acid–formaldehyde resin). PAFR II was applied in the batchwise and continuous-flow direct esterification without water removal and provided higher product yields in continuous-flow esterification than any other commercial ion-exchanged acid catalyst tested.

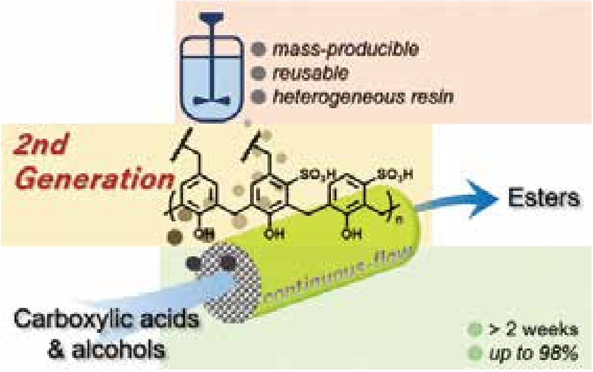


Figure 3. Continuous-Flow Esterification of Carboxylic Acid with Alcohols Using PAFR II Catalyst.

3. The Hiyama Cross-Coupling Reaction at Parts Per Million Levels of Pd: In Situ Formation of Highly Active Spirosilicates in Glycol Solvents[3)]

A palladium NNC-pincer complex at a 5 molppm loading efficiently catalyzed the Hiyama coupling reaction of aryl bromides with aryl(trialkoxy)silanes in propylene glycol to give the corresponding biaryls in excellent yields. This method was applied to the syntheses of adapalene and a biaryl-type liquid-crystalline compound, as well as to the derivatization of dextromethorphan and norfloxacin. ESI-MS and NMR analyses of the reaction mixture suggested the formation of pentacoordinate spirosilicate intermediates in situ. Preliminary theoretical studies revealed that the glycol-derived silicate intermediates formed in situ are quite reactive silicon reagents in the transmetalation step.

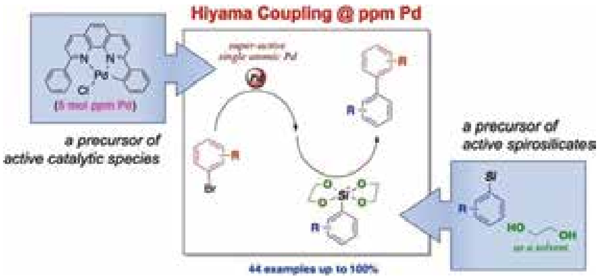


Figure 4. Hiyama Cross-Coupling Catalyzed by ppm Palladium NNC-Pincer Complex in Glycol Solvents.

References

1) G. Hamasaka, D. Roy, A. Tazawa and Y. Uozum, *ACS Catal.* **9**, 11640–11646 (2019).

2) H. Hu, H. Ota, H. Baek, K. Shinohara, T. Mase, Y. Uozumi and Y. M. A. Yamada, *Org. Lett.* **22**, 160–163 (2020).

3) S. Ichii, G. Hamasaka and Y. Uozumi, *Chem. –Asian J.* **14**, 3850–3854 (2019).

Design and Synthesis of Chiral Organic Molecules for Asymmetric Synthesis

Department of Life and Coordination-Complex Molecular Science
Division of Complex Catalysis

MOMIYAMA, Norie
Associate Professor
[momiyama@ims.ac.jp]

Education
2000 B.S. Nagoya University
2005 Ph.D. The University of Chicago

Professional Employment
2005 Postdoctoral Fellow, Harvard University
2006 Assistant Professor, Tohoku University
2014 Associate Professor, Institute for Molecular Science
Associate Professor, The Graduate University for Advanced Studies

Awards
2003 The Elizabeth R. Norton Prize for Excellence in Research in Chemistry, University of Chicago
2004 Abbott Laboratories Graduate Fellowship
2005 Damon Runyon Cancer Research Foundation Post Doctoral Research Fellowship
2008 Thieme Chemistry Journals Award
2014 The 17th Morita Science Research Award
Central Glass Co., Ltd. Award in Organic Chemistry, Japan

Member
Assistant Professor
OHTSUKA, Naoya
Post-Doctoral Fellow
FUJINAMI, Takeshi
Graduate Student
HORI, Tatsuaki
OISHI, Shunya
OTA, Hino
KATO, Masayuki
KOTANI, Shunsuke
Secretary
USHIDA, Hinano

Keywords Synthetic Chemistry, Molecular Catalyst, Non-Covalent Interaction

The field of molecular catalysis has been an attractive area of research to realize efficient and new transformations in the synthesis of functional molecules. The design of ligands and chiral molecular catalysts has been recognized as one of the most valuable strategies; therefore, a great deal of effort has been dedicated to the developments. In general, "metal" has been frequently used as the activation center, and conformationally rigid catalyst framework has been preferably components for the catalyst design. To develop new type of molecular catalysis, we have focused on the use of hydrogen and halogen atom as activation unit, and have utilized non-covalent interactions as organizing forces of catalyst framework in the molecular design of catalyst, which had not received much attention until recently. We hope that our approach will open the new frontier in chiral organic molecules from chiral molecular chemistry to chiral molecular science.

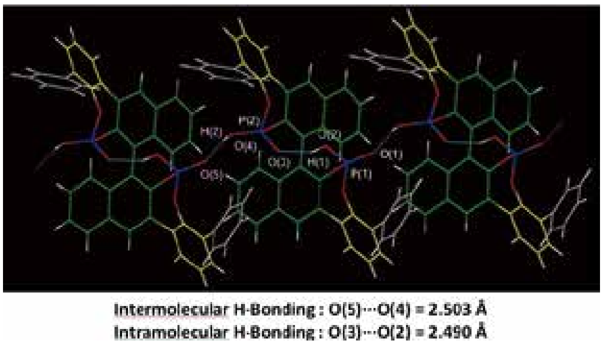


Figure 1. Hydrogen bonding network in chiral bis-phosphoric acid catalyst derived from (*R*)-3,3'-di(2-hydroxy-3 -arylphenyl)binaphthol. Hydrogen bond acts as activation unit for the substrate in asymmetric reaction space and controls atropisomeric behavior in naphthyl–phenyl axis.

Selected Publications

- T. P. Yoon and E. N. Jacobsen, *Science* **299**, 1691–1693 (2003).
- N. Momiyama and H. Yamamoto, "Brønsted Acid Catalysis of Achiral Enamine for Regio- and Enantioselective Nitroso Aldol Synthesis," *J. Am. Chem. Soc.* **127**, 1080–1081 (2005).
- N. Momiyama, H. Tabuse and M. Terada, "Chiral Phosphoric Acid-Governed Anti-Diastereoselective and Enantioselective Hetero-Diels–Alder Reaction of Glyoxylate," *J. Am. Chem. Soc.* **131**, 12882–12883 (2009).
- N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, "Design of Chiral Bis-Phosphoric Acid Catalyst Derived from (*R*)-3,3'-Di(2-hydroxy-3-arylphenyl)binaphthol: Catalytic Enantioselective Diels–Alder Reaction of α,β-Unsaturated Aldehydes with Amidodienes," *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
- N. Momiyama, H. Tabuse, H. Noda, M. Yamanaka, T. Fujinami, K. Yamanishi, A. Izumiseki, K. Funayama, F. Egawa, S. Okada, H. Adachi and M. Terada, "Molecular Design of a Chiral Brønsted Acid with Two Different Acidic Sites: Regio-, Diastereo-, and Enantioselective Hetero-Diels–Alder Reaction of Azopyridinecarboxylate with Amidodienes Catalyzed by Chiral Carboxylic Acid–Monophosphoric Acid," *J. Am. Chem. Soc.* **138**, 11353–11359 (2016).

1. Brønsted Acid Catalyzed Asymmetric Rearrangement: Asymmetric Synthesis of Linear Homoallylic Amines

Allylation of imines with allylic metal reagents has been one of the most valuable tools to synthesize enantioenriched homoallylic amines. Due to the inherent nature of allylic metal reagent, however, regioselectivity has been a long-standing subject in this area. To develop the synthetic reaction for enantioenriched linear homoallylic amines, we discovered chirality transferred formal 1,3-rearrangement of ene-aldimines in the presence of Brønsted acid, and developed it as synthetic method for variety of enantioenriched linear homoallylic amines.1) Furthermore, we studied details of reaction mechanism and succeeded catalytic asymmetric version of this rearrangement.2) To the best our knowledge, our discovery is the first example of asymmetric formal [1,3]-rearrangement and the new entry of the synthetic methodology for the linear enantioenriched homoallylic amines.

2. Design of Chiral Brønsted Acid Catalyst

Chiral Brønsted acid catalysis has been recognized as one of the useful tools in asymmetric synthesis. We have contributed to this area by focusing on the use of perfluoroaryls and C_1-symmetric design.

Perfluorinated aryls have emerged as an exquisite class of motifs in the design of molecular catalysts, and their electronic and steric alterations lead to notable changes in the chemical yields and the stereoselectivities. However, unfortunately, the distinctive potential of perfluorinated aryls has not been fully exploited as design tools in the development of chiral Brønsted acid catalysts. We developed the perfluoaryls-incorporated chiral mono-phosphoric acids as chiral Brønsted acid catalysts that can deriver high yields and stereoselectivities in the reactions of imines with unactivated alkenes. We have described the first example of a diastereo- and enantioselective [4+2] cycloaddition reaction of *N*-benzoyl imines, as well as the enantioselective three-component imino–ene reaction using aldehydes and $FmocNH_2$.3)

We have developed (*R*)-3,3'-di(2-hydroxy- 3-arylphenyl) binaphthol derived chiral bis-phosphoric acid which efficiently catalyzed enantioselective Diels–Alder reaction of acroleins with amidodienes.4,5) We demonstrated that two phosphoric acid groups with individually different acidities can play distinct roles in catalyst behavior through hydrogen bonding interactions. Hence, we were interested to explore whether a combination of *different acidic functional groups*, in particular an aryl phosphinic acid-phosphoric acid, would function as an efficient Brønsted acid catalyst. We developed a Brønsted acid with two different acidic sites, aryl phosphinic acid-phosphoric acid, and its catalytic performance was assessed in the hetero-Diels–Alder reaction of aldehyde hydrates with Danishefsky's diene, achieving high reaction efficiency.6) Furthermore, molecular design of a chiral Brønsted acid with two different acidic sites, chiral carboxylic acid–cyclic mono-phosphoric acid, was identified as a new and effective concept in asymmetric hetero-Diels–Alder reaction of 2-azopyridinoester with amidodienes.7)

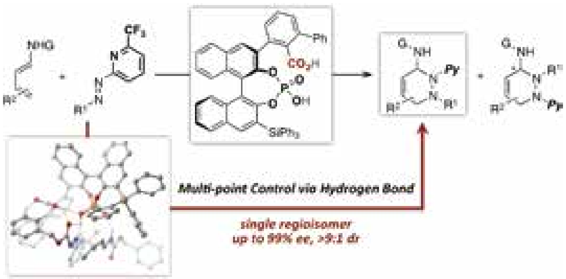


Figure 2. Chiral carboxylic acid–phosphoric acid-catalyzed azo-hetero-Diels–Alder reaction.

3. Design of Catalysis with Halogen Bond for Carbon–Carbon Bond Forming Reactions

Halogen bonds are attractive non-covalent interactions between terminal halogen atoms in compounds of the type R—X (X = Cl, Br, I) and Lewis bases LBs. It has been known that strong halogen bonds are realized when "R" is highly electronegative substituents such as perfluorinated alkyl or aryl substituents. We recently developed synthetic methodology for perfluorinated aryl compounds, and applied it for the development of chiral Brønsted acid catalysts. On the basis of our achievements, we have examined it to develop catalysis with halogen bond for carbon–carbon bond forming reactions.

We found that perfluorinated iodoaryls are able to catalyze the Mukaiyama Mannich-type reaction and allylation reaction.8)

References

1) C. Jongwohan, Y. Honda, T. Suzuki, T. Fujinami, K. Adachi and N. Momiyama, *Org. Lett.* **21**, 4991–4995 (2019).
2) N. Momiyama *et al.*, submitted.
3) N. Momiyama, H. Okamoto, J. Kikuchi, T. Korenaga and M. Terada, *ACS Catal.* **6**, 1198–1204 (2016).
4) N. Momiyama, T. Konno, Y. Furiya, T. Iwamoto and M. Terada, *J. Am. Chem. Soc.* **133**, 19294–19297 (2011).
5) N. Momiyama, K. Funayama, H. Noda, M. Yamanaka, N. Akasaka, S. Ishida, T. Iwamoto and M. Terada, *ACS Catal.* **6**, 949–956 (2016).
6) N. Momiyama, T. Narumi and M. Terada, *Chem. Commun.* **51**, 16976–16979 (2015).
7) N. Momiyama, H. Tabuse, H. Noda, M. Yamanaka, T. Fujinami, K. Yamanishi, A. Izumiseki, K. Funayama, F. Egawa, S. Okada, H. Adachi and M. Terada, *J. Am. Chem. Soc.* **138**, 11353–11359 (2016).
8) N. Momiyama *et al.*, Two manuscripts: Submitted; four manuscripts under preparation for submission.

Creation of Novel Photonic-Electronic-Magnetic Functions Based on Molecules with Open-Shell Electronic Structures

Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry

KUSAMOTO, Tetsuro
Associate Professor
[kusamoto@ims.ac.jp]

Education

2003	B.S. The University of Tokyo
2010	Ph.D. The University of Tokyo

Professional Employment

2005	Sony Corporation
2010	Postdoctoral Fellow, RIKEN
2012	Project Assistant Professor, The University of Tokyo
2013	Assistant Professor, The University of Tokyo
2019	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2019	Research Encouragement Award, Japan Society of Coordination Chemistry
2010	Research Award, Graduate School of Science, the University of Tokyo
2008	BCSJ Award, The Chemical Society of Japan

Member
Assistant Professor
MATSUOKA, Ryota
Graduate Student
KIMURA, Shun*
KATO, Soshi
ISHIHARA, Mei
FUJISAWA, Mayu
Secretary
MASUDA, Michiko

Keywords Radical, Open-Shell Electronic States, Photonic-Electronic-Magnetic Properties

The molecules with open-shell electronic states can exhibit unique properties, which are difficult to achieve for conventional closed-shell molecules. Our group develops new open-shell organic molecules (= radicals) and metal complexes to create novel photonic-electronic-magnetic functions.

While conventional closed-shell luminescent molecules have been extensively studied as promising components for organic light-emitting devices, the luminescent properties of radicals have been much less studied because of its rarity and low chemical (photo-)stability. We have developed a novel luminescent organic radical PyBTM, which is highly stable at ambient condition and in the photoexcited state. We have also discovered that (i) PyBTM-doped molecular crystals exhibit photoluminescence with a room-temperature emission quantum yield of 89%, which is exceptionally high in radicals, and (ii) the doped crystals show drastic changes in the emission spectra by applying a magnetic field. This is the first observation of the magnetoluminescence in organic radicals. Our studies provide novel and unique insights in molecular photonics, electronics, and spintronics, and also contribute to developing applied science for light-emitting devices.

Our group focuses on strongly-interacted spins in molecular crystals. The anisotropic assembly of open-shell molecules in crystalline states enables unique molecular materials with exotic electrical and magnetic properties, such as superconductors, ferromagnets, and quantum spin liquids.

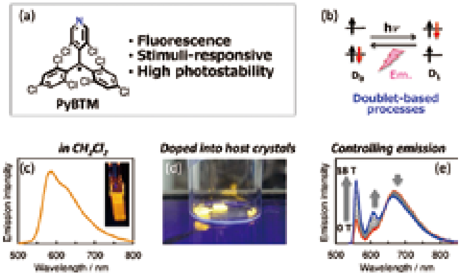


Figure 1. (a) Molecular structure of PyBTM and its characteristics. (b) Schematic photoexcitation-emission processes. (c) Emission in CH_2Cl_2. (d) Emission of PyBTM-doped molecular crystals. (e) Controlling emission by magnetic field.

Selected Publications

- S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, "Magnetoluminescence in a Photostable, Brightly Luminescent Organic Radical in a Rigid Environment," *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Enhanced Luminescent Properties of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical by Coordination to Gold," *Angew. Chem., Int. Ed.* **54**, 3731–3734 (2015).
- Y. Hattori, T. Kusamoto and H. Nishihara, "Luminescence, Stability, and Proton Response of an Open-Shell (3,5-Dichloro-4-pyridyl)bis(2,4,6-trichlorophenyl)methyl Radical," *Angew. Chem., Int. Ed.* **53**, 11845–11848 (2014).
- T. Kusamoto, H. M. Yamamoto, N. Tajima, Y. Oshima, S. Yamashita and R. Kato, "Bilayer Mott System with Cation···Anion Supramolecular Interactions Based on Nickel Dithiolene Anion Radical: Coexistence of Ferro- and Antiferro-Magnetic Anion Layers and Large Negative Magnetoresistance," *Inorg. Chem.* **52**, 4759–4761 (2013).

1. Construction of Supramolecular Two-Dimensional Network Mediated via Sulfur's σ-Holes in Conducting Molecular Crystals

Metal bis(dithiolato) complexes are attractive class of multi-functional molecular systems showing magnetic, conducting, and optical properties, such as superconductivity, ferromagnetism, quantum spin liquid, and NIR absorption. These properties depend highly on the arrangement of molecules in the solid state; therefore, controlling the arrangement (*i.e.*, crystal structure) plays a crucial role for achieving novel or desired properties. We have focused on a σ-hole bond as an efficient noncovalent supramolecular interaction to control the arrangement of metal bis(dithiolato) complexes, with a goal of developing exotic magneto-conducting phenomena in molecular system. The σ-hole bond is observed between electron-deficient region on an atomic surface, so-called σ-hole, and an electron-rich moiety in a molecule. Halogen and chalcogen atoms possess one and two σ-holes capable of forming supramolecular bonds with high directionality. We have developed novel conducting molecular solids based on platinum bis(dithiolato) complex anion radicals, $(\text{Et-4XT})_2[\text{Pt(mnt)}_2]_3$ (X = Br, I; Et-4BrT = ethyl-4-bromothiazolium, Et-4IT = ethyl-4-iodothiazolium, mnt = maleonitriledithiolato).[1,2] In their crystal structures, $\text{X}_{\text{cation}}\cdots\text{N}_{\text{anion}}$ and $\text{S}_{\text{cation}}\cdots\text{N}_{\text{anion}}$ σ-hole bonds (*i.e.*, halogen bond and chalcogen bond) were detected between the cation and the lone pairs of –CN moieties in the anion, forming a two-dimensional (2D) supramolecular network. The arrangement of the ions was similar in the two compounds (X = I and X = Br), while the orientation of the cations and the stacking manner of the anions along the direction perpendicular to the 2D supramolecular network were different (Figure 2). Such structural differences are attributed to the strength of the halogen bond, which is greater in iodine than in bromine, and resulted in distinct differences in their physical properties. For example, stronger trimerization of the anions in $(\text{Et-4IT})_2[\text{Pt(mnt)}_2]_3$ enhanced antiferromagnetic interaction between the spins on the anions. These results suggest that sulfur-mediated chalcogen bonds can be robust enough to dominate the primary arrangement of molecules and the resulted physical properties, even in the presence of the other noncovalent intermolecular interactions or even upon the atomic replacements. Sulfur-based chalcogen bonds would be effective to realize desired structures and properties in molecular materials, while understanding the hierarchy of the noncovalent interactions operated in the crystal would be important for the precise crystal engineering.

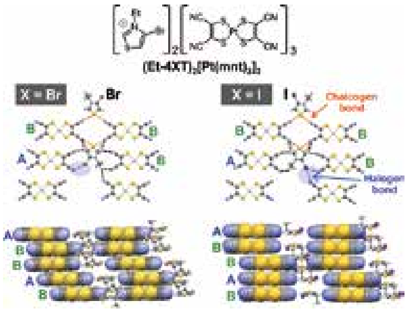


Figure 2. Chemical and crystal structures of $(\text{Et-4XT})_2[\text{Pt(mnt)}_2]_3$ (X = Br, I).

2. Magnetoluminescence as Unique Photofunctions of Open-Shell Molecules

Controlling the spin state of open-shell molecules is a promising strategy for developing unique photochemical and photophysical properties, which are difficult to realize with conventional closed-shell molecules. We have shown that PyBTM doped into α*H*-PyBTM molecular crystals demonstrates new luminescent properties for organic radicals attributed to interplay between spin and luminescence.[3] Crystals containing 10 wt% PyBTM displayed PyBTM monomer- and PyBTM excimer-centered emissions and magnetic-field-sensitive luminescence, *i.e.*, magnetoluminescence. We have revealed that changes in spin multiplicities of aggregated radicals contribute to the magnetic-field effect. To date, magnetoluminescence of stable radicals has been observed only in a few pure organic radicals. We are developing novel PyBTM-ligated metal complexes to expand the variety of materials showing magnetoluminescence behaviour, with a goal of realizing novel spin-sensitive photofunctions. We succeeded in observing excimer-like emission and magnetoluminescence behaviour in PyBTM-ligated zinc complexes doped into host crystals (Figure 3). Detailed investigations are in progress.

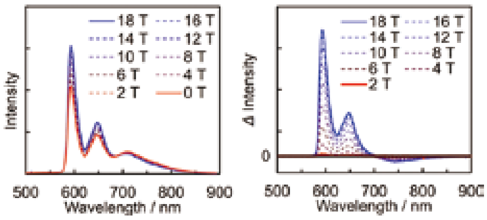


Figure 3. (left) Emission spectra of PyBTM-ligated zinc complex doped into host crystals at 4.2 K under magnetic fields. (right) Difference emission spectra (Δ intensity) under magnetic fields compared with the spectrum under 0 T.

References

1) C. Ohde, T. Kusamoto, K. Nakabayashi, S. Ohkoshi and H. Nishihara, *Cryst. Growth Des.* **17**, 2203–2210 (2017).

2) C. Ohde, T. Kusamoto and H. Nishihara, *J. Magn. Magn. Mater.* **497**, 165986 (2020).

3) S. Kimura, T. Kusamoto, S. Kimura, K. Kato, Y. Teki and H. Nishihara, *Angew. Chem., Int. Ed.* **57**, 12711–12715 (2018).

Award

KUSAMOTO, Tetsuro; Research Encouragement Award, Japan Society of Coordination Chemistry (2019).

---

* carrying out graduate research on Cooperative Education Program of IMS with the University of Tokyo

Design and Synthesis of Three-Dimensional Organic Structures

Department of Life and Coordination-Complex Molecular Science
Division of Functional Coordination Chemistry

SEGAWA, Yasutomo
Associate Professor
[segawa@ims.ac.jp]

Education

2005	B.S. The University of Tokyo
2007	M.S. The University of Tokyo
2009	Ph.D. The University of Tokyo

Professional Employment

2009	Assistant Professor, Nagoya University
2013	Designated Associate Professor, Nagoya University
2013	Group Leader and Project Coordinator, JST ERATO Itami Molecular Nanocarbon Project (until 2020)
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Award

2013	RSC PCCP Prize
2014	Akasaki Award
2017	Chemical Society of Japan Award for Young Chemists
2018	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2019	Nozoe Memorial Award for Young Organic Chemists

Member
Graduate Student
WATANABE, Kosuke*
Secretary
TANIWAKE, Mayuko

Keywords π-Conjugated Molecules, Molecular Topology, 3D Network Polymer

Aromatic compounds are potentially useful as functional electronic materials. However, the controlled synthesis and assembly of three-dimensional complex molecules are still very difficult, especially for the crystal engineering of organic molecules. This group aims to create novel topological and reticular organic structures by using synthetic organic chemistry and geometric insights.

To achieve our purpose, this group will start electron-diffraction crystallography (MicroED) for the rapid structure determination of organic compounds. While X-ray crystallography is a general and reliable method for structure determination, it requires ~0.1 mm single crystals and making such crystal sometimes needs tremendous times and efforts. Since electron beam have much higher diffraction intensity than X-ray, structural analysis can be performed even with ultra-small crystals (1 μm or less). There are many fields such as covalent organic crystals with a three-dimensional structure and molecules with complex molecular topologies, where structural analysis has not been sufficiently developed.

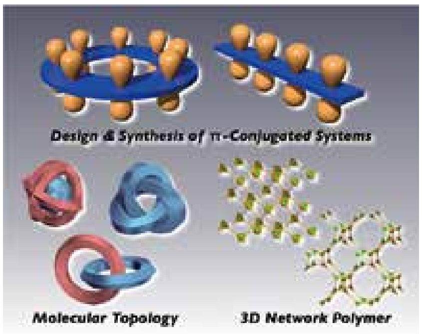


Figure 1. Design and synthesis of π-conjugated organic molecules (top); Development of novel molecular topology (bottom left); Construction of three-dimensional network polymers (bottom right).

Selected Publications

- Y. Saito, K. Yamanoue, Y. Segawa and K. Itami, "Selective Transformation of Strychnine and 1,2-Disubstituted Benzenes by C–H Borylation," *Chem* **6**, 985–993 (2020).
- Y. Segawa, D. R. Levine and K. Itami, "Topologically Unique Molecular Nanocarbons," *Acc. Chem. Res.* **52**, 2760–2767 (2019).
- Y. Segawa, M. Kuwayama, Y. Hijikata, M. Fushimi, T. Nishihara, J. Pirillo, J. Shirasaki, N. Kubota and K. Itami, "Topological Molecular Nanocarbons: All-Benzene Catenane and Trefoil Knot," *Science* **365**, 272–276 (2019).
- G. Povie, Y. Segawa, T. Nishihara, Y. Miyauchi and K. Itami, "Synthesis of a Carbon Nanobelt," *Science* **356**, 172–175 (2017).
- T. Yoshidomi, T. Fukushima, K. Itami and Y. Segawa, "Synthesis, Structure, and Electrochemical Property of a Bimetallic Bis-2-Pyridylidene Palladium Acetate Complex," *Chem. Lett.* **46**, 587–590 (2017).
- Y. Segawa and D. W. Stephan, "Metal-Free Hydrogenation Catalysis of Polycyclic Aromatic Hydrocarbons," *Chem. Commun.* **48**, 11963–11965 (2012).
- Y. Segawa, M. Yamashita and K. Nozaki, "Boryllithium: Isolation, Characterization, and Reactivity as a Boryl Anion," *Science* **314**, 113–115 (2006).

1. Synthesis and Reactivity of Highly Strained Belt-Shaped Polycyclic Aromatic Hydrocarbons

We performed the synthesis of novel π-conjugated molecules with high strain energies and the investigation of its structural properties.[2–4]

The synthesis of cycloiptycene derivatives was achieved in each one step from (6,6)carbon nanobelt (Figure 2).[3] It was revealed that the carbon nanobelt was reacted as a diene in the Diels–Alder reaction with arynes and alkynes. Structures of all products were identified by X-ray crystallography to confirm that the Diels–Alder reactions took place at the six central benzene rings of the carbon nanobelt. DFT calculations indicated that the release of strain energy is the driving force to proceed the Diels–Alder reaction. By using this method, we have successfully synthesized cyclotetracosiptycene, the largest iptycene ever synthesized.

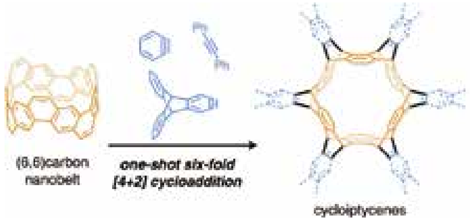


Figure 2. Diels–Alder reaction of (6,6)carbon nanobelt with alkynes and arynes for the formation of cycloiptycene derivatives.

The synthesis, structure, and properties of methylene-bridged [6]cycloparaphenylene ([6]CPP), a nonalternant aromatic belt, were investigated (Figure 3).[2] This belt-shaped methylene-bridged [6]CPP, in which each phenylene unit is tethered to its neighbors by methylene bridges, was constructed through 6-fold intramolecular nickel-mediated aryl–aryl coupling of triflate-functionalized pillar[6]arene in 18% isolated yield. As compared to the analogous [6]CPP, the methylene bridges coplanarize neighboring paraphenylene units and enhance the degree of π-conjugation, which results in a significant decrease in energy gap. Moreover, the incorporation of small molecules in the defined pocket of methylene-bridged [6]CPP makes it an attractive supramolecular architecture. Methylene-bridged [6]CPP is characterized by high internal strain energy reaching 110.2 kcal mol^{-1}, attributed to its restricted structure. This work not only exhibits an efficient strategy to construct a new family of aromatic belt, but also showcases their properties, which combine the merits of CPPs and pillararenes.

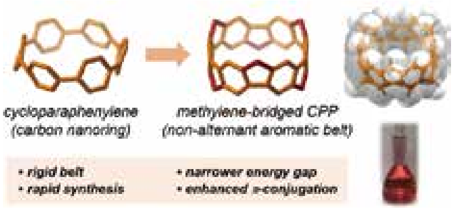


Figure 3. Synthesis of a nonalternant aromatic belt.

2. Development of a Direct Octagon-Forming Annulation Reaction by Palladium Catalyst

The discoveries of new forms of carbon have always opened doors to new science and technology. In 1991, three-dimensional (3D) periodic carbon crystals with negative Gaussian curvatures that consist of six- and eight-membered rings were proposed. To realize these 3D periodic carbon crystals, methods for creating polyaromatic structures embedding eight-membered rings must be developed. Here the two annulative coupling reactions that form an eight-membered ring through catalytic C–H functionalization are reported (Figure 4).[1] Bay-chlorinated polyaromatics undergo either annulative dimerization or cross-coupling with biphenylene in the presence of a palladium catalyst to form various hitherto inaccessible polyaromatics embedding an eight-membered ring. The threefold annulative cross-coupling of 1,5,9-trichlorotriphenylene allowed construction of a highly curved nanocarbon. The present work not only demonstrates the potential of annulative coupling for constructing octagonal nanocarbons but also provides a conceptual pathway for the synthetic realization of 3D periodic carbon crystals.

Based on this result, our group has started the Joint Research Program in IMS with Murakami group. Our group will support the rapid structural determination of targeted π-conjugated molecules, their synthetic intermediates, as well as active species of transition metal catalysts.

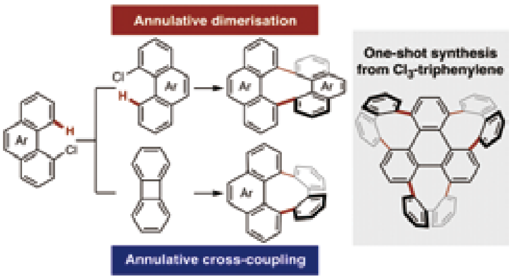


Figure 4. Palladium-catalyzed octagon-forming annulation reaction.

References

1) S. Matsubara, Y. Koga, Y. Segawa, K. Murakami and K. Itami, *Nat. Catal.* **3**, 710–718 (2020). doi: 10.1038/s41929-020-0487-0

2) Y. Li, Y. Segawa, A. Yagi and K. Itami, *J. Am. Chem. Soc.* **142**, 12850–12856 (2020).

3) H. Shudo, M. Kuwayama, Y. Segawa and K. Itami, *Chem. Sci.* **11**, 6775–6779 (2020).

4) K. Y. Cheung, Y. Segawa and K. Itami, *Chem. –Eur. J.* **26** (2020). doi: 10.1002/chem.202002316

---

* carrying out graduate research on Cooperative Education Program of IMS with Nagoya University

Visiting Professors

Visiting Professor
FUKAZAWA, Aiko *(from Kyoto University)*

Renaissance of Nonbenzenoid π-Conjugated Systems toward Functional Materials

The work of our group has focused on exploring functional organic compounds with unusual with superb optical and/or electronic properties, based on the molecular designs of novel π-conjugated scaffolds as well as unusual functional groups. In particular, we have recently proposed a rational design of stable yet unusual π-conjugated systems based on the characteristics of nonbenzenoid hydrocarbons, *i.e.*, dehydro-annulenes, non-alternant hydrocarbons, and fulvalenes, by the fusion of (hetero)arenes with small magnitude of aromaticity. In this year, we have succeeded in synthesizing several thiophene-fused antiaromatic π-systems, such as dithieno[*a*,*e*]pentalenes and their nitrogen-doped analogues. These thiophene-fused antiaromatics exhibit high thermal stability even without bearing bulky substituents while retaining pronounced antiaromatic character. These features give rise to characteristic long-wavelength absorption as well as aggregation behavior of these compounds.

Visiting Professor
WATANABE, Rikiya *(from RIKEN)*

Single Molecule Physiology

Our study aims to understand cellular functions using a bottom-up approach from the single molecule level. To achieve this, we are attempting to elucidate the mechanism by which individual biomolecules or their networks function in a precise manner, by developing novel single-molecule techniques using multidisciplinary approaches, including biophysics, bioMEMS, and chemical biology. In addition, we are developing a methodology to investigate correlations between genetic mutations, dysfunctions, and diseases with single molecule sensitivity, which would provide new insights for biological as well as pharmaceutical studies.

Visiting Associate Professor
UEDA, Akira *(from Kumamoto University)*

Development of Purely Organic Molecular Materials with Unique Structural/Electronic Properties

Design and synthesis of novel molecular materials have been a central issue for the development of molecular science. Our group has continuously focused on purely organic molecular materials with unique crystal/electronic structures and physical properties. Very recently, we have succeeded in the development of a novel neutral radical molecular conductor with a partially charge-transferred structure. Interestingly, this material forms a two-dimensional conducting layer like BEDT-TTF salts, resulting in a much higher electrical conductivity than that of the conventional neutral radical conductors. These results suggest that this material is a possible candidate of a purely organic single-component molecular metal or superconductor. The magnetic properties and phase transition behavior of this material are of interest and thus will be investigated in the near future.

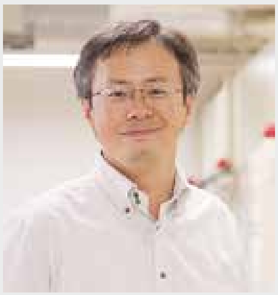
RESEARCH ACTIVITIES

Research Center of Integrative Molecular Systems

The mission of CIMoS is to analyze molecular systems in nature to find the logic behind the sharing and control of information between the different spatiotemporal hierarchies, with the ultimate goal of creating novel molecular systems on the basis of these findings.

Biological Rhythm and Dynamics through Chemistry

Research Center of Integrative Molecular Systems
Division of Trans-Hierarchical Molecular Systems



AKIYAMA, Shuji
Professor
[akiyamas@ims.ac.jp]

Education

1997	B.E. Kyoto University
1999	M.E. Kyoto University
2002	Ph.D. Kyoto University

Professional Employment

2001	JSPS Research Fellow
2002	JSPS Postdoctoral Fellow
2003	RIKEN Special Postdoctoral Researcher
2005	JST-PRESTO Researcher
2008	Junior Associate Professor, Nagoya University
2011	Associate Professor, Nagoya University
2012	Professor, Institute for Molecular Science Professor, The Graduate University for Advanced Studies

Awards

2016	The 13th (FY2016) JSPS PRIZE
2008	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Prize
2007	Young Scientist Prize, The Biophysical Society of Japan
2006	SAS Young Scientist Prize, IUCr Commission on Small-angle Scattering
2002	The Protein Society Annual Poster Board Award

Member

Assistant Professor
MUKAIYAMA, Atsushi
FURUIKE, Yoshihiko

Post-Doctoral Fellow
OUYANG, Dongyan

Graduate Student
SIMON, Damien

Technical Fellow
WASHIO, Midori
TAKAYA, Mari
SUGISAKA, Kanae
WADA, Kotoe

Secretary
SUZUKI, Hiroko

Keywords Biological Rhythm, Circadian Clock, Cyanobacteria

Living organisms on Earth evolved over time to adapt to daily environmental alterations, and eventually acquired endogenous time-measuring (biological clock) systems. Various daily activities that we perform subconsciously are controlled by the biological clock systems sharing three characteristics. First, the autonomic rhythm repeats with an approximately 24-hour (circadian) cycle (self-sustainment). Second, the period is unaffected by temperature (temperature compensation). Third, the phase of the clock is synchronized with that of the outer world in response to external stimuli (synchronization). We seek to explain these three characteristics, and consider the biological clock system of cyanobacteria to be an ideal experimental model.

The major reason that cyanobacteria are considered to be the ideal experimental model is that the core oscillator that possesses the three characteristics of the clock can be easily reconstructed within a test tube. When mixing the three clock proteins KaiA, KaiB, and KaiC with ATP, the structure and enzyme activity of KaiC change rhythmically during a circadian cycle. Taking advantage of this test tube experiment, we used an approach combining biology, chemistry, and physics to elucidate the means by which the clock system extends from the cellular to atomic levels.

Among the three Kai proteins, KaiC is the core protein of the oscillator. In the presence of KaiA and KaiB, KaiC revelas the rhythm of autophosphorylation and dephosphorylation; however, the cycle of this rhythm depends on the ATPase activity of KaiC independent of KaiA or KaiB. For example, when the ATPase activity of KaiC doubles as a result of amino acid mutations, the frequencies of both the *in vitro* oscillator and the intracellular rhythm also double (the cycle period is reduced to half). This mysterious characteristic is called a transmural hierarchy, in which the cycle (frequency) and even the temperature compensation both *in vitro* and *in vivo* are greatly affected (controlled) by the function and structure of KaiC.

How are the circadian activities and temperature compensation features encoded in KaiC and then decoded from it to propagate rhythms at the cellular level? We are committed to better understanding biological clocks and other dynamic systems through the chemistry of circadian ***rhythm***, ***structure***, and evolutionary ***diversity***.

Selected Publications

- D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
- A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
- A. Mukaiyama, Y. Furuike, J. Abe, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Rep.* **8**, 8803 (2018).
- J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
- Y. Murayama, A. Mukaiyama, K. Imai, Y. Onoue, A. Tsunoda, A. Nohara, T. Ishida, Y. Maéda, T. Kondo and S. Akiyama, *EMBO J.* **30**, 68–78 (2011).
- S. Akiyama, A. Nohara, K. Ito and Y. Maéda, *Mol. Cell* **29**, 703–716 (2008).

1. *Structure*: Atomic-Scale Origins of Clock Slowness in Cyanobacterial Circadian Clock System[1,2]

To identify the structural origins of slowness encoded in KaiC, its N-terminal ATPase domain was analyzed using high-resolution x-ray crystallography.[1] Water molecules are prevented from attacking into the ideal position (Figure 1) for the ATP hydrolysis by a steric hindrance near ATP phosphoryl groups. In addition, this hindrance is surely anchored to a spring-like structure derived from polypeptide isomerization. The ATP hydrolysis, which involves access of a water molecule to the bound ATP and reverse isomerization of the polypeptide, requires a much larger amount of free energy than for typical ATP hydrolysis. The atomic structure explains why the ATPase activity of KaiC is so much lower (by 100- to 1,000,000-fold) than that of typical ATPases.[2]

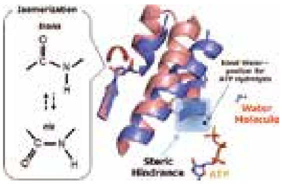


Figure 1. Structural basis for steady slowness. The steric barrier prevents access of a water molecule to the catalytic site (indicated by a black dot).

2. *Rhythm*: Transmural Hierarchy in Cyanobacterial Circadian Clock System[3–5]

KaiC ATPase is of particular interest here, as it finely correlates to the frequencies of *in vivo* as well as *in vitro* oscillations. This unique property has inspired us to develop an ATPase-based screening for KaiC clock mutants giving short, long, and/or temperature-dependent periods.[3] A developed HPLC system with a 4-channel temperature controller has reduced approximately 80% of time costs for the overall screening process (Figure 2).

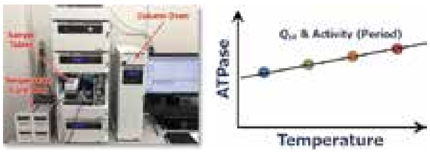


Figure 2. Development of a quick ATPase assay system.

How is the intra-molecular slowness encoded in KaiC (Figure 1) transmitted to the inter-molecular interactions with other Kai proteins? To address this question, a tryptophan residue was introduced in the N-terminal ring of KaiC as the fluorescent probe for KaiBC complex formation.[4] Our kinetic data indicated that KaiB exclusively selects the post-ATP-hydrolysis state of KaiC to form the KaiBC complex. This process follows a mechanism called conformational selection (CS), in which proteins (KaiC) first undergoes a structural change to form a specific intermediate. Ligands (KaiB) are then recognized specifically through the intermediate state to form a tight ligand-protein complex. The CS mechanism is elegantly designed in KaiC so that the slow intra-molecular ATPase reaction in KaiC can be the rate-liming step of the overall KaiBC complex formation.

We also collaborated with Drs. Ito-Miwa and Kondo (Nagoya University) to identify a series of KaiC mutations altering circadian periods dramatically, from 0.6 to 6.6 d.[5]

3. beyond Evolutionary *Diversity*[1,6]

In the presence of KaiA and KaiB, the ATPase activity of KaiC oscillates on a 24-hour cycle. KaiC is not capable of maintaining a stable rhythm on its own, but its activity was observed to fluctuate with reduced amplitude over time (Figure 3A). We have identified a signal component that is similar to damped oscillation, and propose that it encodes the specific frequency, equivalent to a 24-hour cycle.[1]

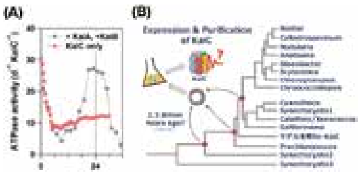


Figure 3. Damped oscillation of KaiC ATPase activity (**A**) and evolutionary diversity of cyanobacteria (**B**).

The habitats of cyanobacteria are diverse, so the space of their sequence is immense.[6] Furthermore, some KaiA and KaiB genes are missing in several strains of cyanobacteria. This is understandable to some extent if KaiC possesses the specific frequency. Given our current understanding of this phenomenon, *what specific frequencies are possessed by KaiC homologues in other species and ancestral cyanobacteria?* (Figure 3B) If you strain your ears, the rhythms of the ancient Earth may be heard from beyond evolutionary diversity.

4. Bio-SAXS Activity in IMS[7]

We have supported SAXS users so that they can complete experiments smoothly and publish their results.[7]

References

1) J. Abe, T. B. Hiyama, A. Mukaiyama, S. Son, T. Mori, S. Saito, M. Osako, J. Wolanin, E. Yamashita, T. Kondo and S. Akiyama, *Science* **349**, 312–316 (2015).
2) S. Akiyama, *Circadian Rhythms in Bacteria and Microbiomes*, in press (2020).
3) D. Ouyang, Y. Furuike, A. Mukaiyama, K. Ito-Miwa, T. Kondo and S. Akiyama, *Int. J. Mol. Sci.* **20**, 2789–2800 (2019).
4) A. Mukaiyama, Y. Furuike, J. Abe, E. Yamashita, T. Kondo and S. Akiyama, *Sci. Rep.* **8**, 8803 (2018).
5) K. Ito-Miwa, Y. Furuike, S. Akiyama and T. Kondo, *Proc. Natl. Acad. Sci. U. S. A.* **117**, 20926–20931 (2020). doi.org/10.1073/pnas.2005496117
6) A. Mukaiyama, D. Ouyang, Y. Furuike and S. Akiyama, *Int. J. Biol. Macromol.* **131**, 67–73 (2019).
7) I. Anzai, E. Tokuda, S. Handa, H. Misawa, S. Akiyama and Y. Furukawa, *Free Radical Biol. Med.* **147**, 187–199 (2020).

Protein Design Using Computational and Experimental Approaches

Research Center of Integrative Molecular Systems
Division of Trans-Hierarchical Molecular Systems

KOGA, Nobuyasu
Associate Professor
[nkoga@ims.ac.jp]

Education

2001	B.S. Kobe University
2006	Ph.D. Kobe University

Professional Employment

2003	JSPS Research Fellow
2006	Postdoctoral Fellow, Kobe University
2007	Postdoctoral Fellow, Kyoto Universtiy
2007	JSPS Postdoctoral Fellow for Research Abroad
2009	Postdoctoral Fellow, University of Washington
2014	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2014	JST-PRESTO Researcher (additional post) (–2017)
2018	Associate Professor, Exploratory Research Center on Life and Living Systems (ExCELLS)

Awards

2013	Young Scientist Award, The 13th Annual Meeting of the Protein Science Society of Japan
2013	Young Scientist Award, The 51st Annual Meeting of the Biophysical Society of Japan
2018	Morino Foundation for Molecular Science

Member
Assistant Professor
KOSUGI, Takahiro
JSPS Post-Doctral Fellow
KOBAYASHI, Naoya
Post-Doctoral Fellow
KOGA, Rie
KONDO, Minako
MINAMI, Shintaro
Graduate Student
SAKUMA, Kouya
MITSUMOTO, Masaya
YAMADA, Hiroko
KAIDA, Shingo
Secretary
SUZUKI, Hiroko

Keywords Protein Design for Structure and Function, Protein Folding, Structural Biology

Protein molecules spontaneously fold into unique three-dimensional structures specified by their amino acid sequences from random coils to carry out their functions. Many of protein studies have been performed by analyzing naturally occurring proteins. However, it is difficult to reach fundamental working principles of protein molecules only by analyzing naturally occurring proteins, since they evolved in their particular environments spending billions of years. In our lab, we explore the principles by computationally designing protein molecules completely from scratch and experimentally assessing how they behave.

Protein design holds promise for applications ranging from catalysis to therapeutics. There has been considerable recent progress in computationally designing proteins with new functions. Many of protein design studies have been conducted using naturally occurring protein structures as design scaffolds. However, since naturally occurring proteins have evolutionally optimized their structures for their functions, implementing new functions into the structures of naturally occurring proteins is difficult for most of cases. Rational methods for building any arbitrary protein structures completely from scratch provide us opportunities for creating new functional proteins. In our lab, we tackle to establish theories and technologies for designing any arbitrary protein structures precisely from scratch. The established methods will open up an avenue of rational design for novel functional proteins that will contribute to industry and therapeutics.

Selected Publications

- N. Koga, R. Tatsumi-Koga, G. Liu, R. Xiao, T. B. Acton, G. T. Montelione and D. Baker, “Principles for Designing Ideal Protein Structures,” *Nature* **491**, 222–227 (2012).
- Y.-R. Lin, N. Koga*, R. Tatsumi-Koga, G. Liu, A. F. Clouser, G. T. Montelione and D. Baker*, “Control over Overall Shape and Size in De Novo Designed Proteins,” *Proc. Natl. Acad. Sci. U. S. A.* **112**, E5478–E5485 (2015).
- P. Nordenfelt, T. Moore, S. Mehta, J. Kalappurakkal, V. S. Swaminathan, N. Koga, T. Lambert, D. Baker, J. Waters, R. Oldenbourg, T. Tani, S. Mayor, C. M. Waterman and T. Springer, “Direction of Actin Flow Dictates Integrin LFA-1 Orientation during Leukocyte Migration,” *Nat. Commun.* **8**, 2047 (2017).
- Y. Lin, N. Koga, S. M. Vorobiev and D. Baker, “Cyclic Oligomer Design with De Novo αβ-Proteins,” *Protein Sci.* **26**, 2187–2194 (2017).
- S. Basak, R. P. Nobrega, D. Tavella, L. M. Deveau, N. Koga, R. Koga, D. Baker, F. Massi and C. R. Matthews, “Networks of Electrostatic and Hydrophobic Interactions Modulate the Complex Folding Free Energy Surface of a Designed βα Protein,” *Proc. Natl. Acad. Sci. U. S. A.* **116**, 6806–6811 (2019).

1. Principles for Designing Ideal Protein Structures

We uncovered the principles for protein folding by designing "ideal" protein structures, which are stabilized completely consistent local and non-local interactions. We discovered a set of rules relating local backbone structures (secondary structure patterns) to tertiary motifs (Figure 1), which were identified using a combination of folding simulations and analyses of naturally occurring proteins. Building backbone structures according to the rules, and placing side chains stabilizing the backbone structures, we can readily design the proteins which have funnel-shaped folding energy landscapes leading into the target folded state. Using this approach, we have succeeded in designing ideal protein structures for five different topologies. These results suggest that the local backbone structures determine the tertiary folded structures rather than the details of amino acid sequences.

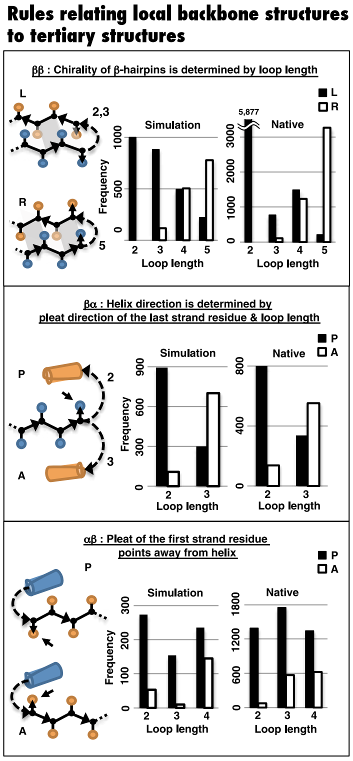


Figure 1. Rules relating local backbone structures to tertiary motifs.

2. Control over Overall Shape and Size in De Novo Designed Proteins

To achieve fine control over protein shape and size within a particular topology, we have extended the design rules by systematically analyzing the codependences between the lengths and packing geometry of successive secondary structure elements and the backbone torsion angles of the loop linking them. We demonstrated that the control is afforded by the resulting extended rule set by designing a series of proteins within the same fold but considerable variation in secondary structure length, loop geometry, β-strand registry, and overall shape. These extended design principles would provide the foundation for custom design of protein structures performing desired functions.

3. Robust Folding of De Novo Designed Ideal Protein Even with Most of the Core Filled with Valine

De novo designed ideal proteins, which are stabilized completely consistent local and non-local interactions, exhibit a remarkable property of extremely high thermal stability, compared with naturally occurring proteins. Whereas non-local interactions such as tight hydrophobic core packing have been traditionally considered to be crucial for protein folding and stability, the rules suggest the importance of local backbone structures in protein folding. We studied the robustness of folding of de novo designed proteins to the reduction of the hydrophobic core, by extensive mutation of large hydrophobic residues (Leu, Ile) to smaller ones (Val) for one of the designs. Surprisingly, even after 10-residue mutations from all of Leu and Ile to Val, a mutant with most of the core filled with Val was found to not be a molten globule and fold into the same backbone structure as the original design, with high stability. These results highlight the significance of local backbone structures for the folding ability and high thermal stability of designed proteins.

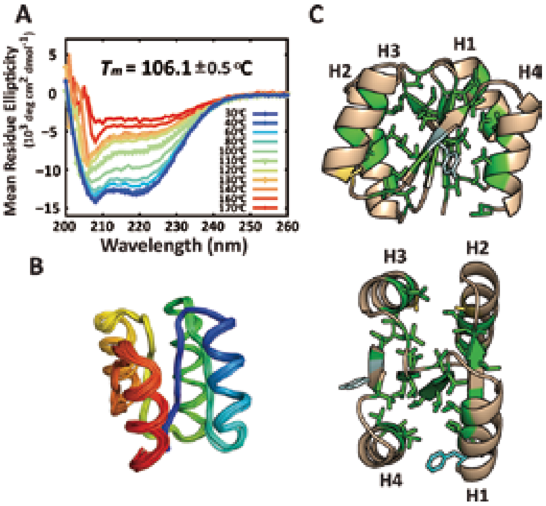


Figure 2. Experimental characterizations of the design with most of the core filled with Val.

References

1) R. Koga* and N. Koga*, *Biophys. Physicobiol.* **16**, 304–309 (2019).
2) R. Koga, M. Yamamoto, T. Kosugi, N. Kobayashi, T. Sugiki, T. Fujiwara and N. Koga, *Proc. Natl. Acad. Sci. U. S. A.* **117**, 31149–31156 (2020).

Elucidation of Function, Structure, and Dynamics of Condensed-Phase Molecular Systems by Advanced Ultrafast Laser Spectroscopy

Research Center of Integrative Molecular Systems
Division of Trans-Hierarchical Molecular Systems

KURAMOCHI, Hikaru
Associate Professor
[hkuramochi@ims.ac.jp]

Education

2007	B.S. Tokyo Institute of Technology
2013	Ph.D. Tokyo Institute of Technology

Professional Employment

2013	Special Postdoctoral Researcher, RIKEN
2016	Research Scientist, RIKEN
2017	JST-PRESTO Researcher
2020	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies

Awards

2017	The 8th Research Incentive Award of RIKEN
2017	The Spectroscopical Society of Japan Award for Young Scientists
2019	RSC PCCP Prize
2020	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award
2020	Morino Foundation for Molecular Science

Member
Secretary
ITO, Atsuko

Keywords Ultrafast Spectroscopy, Chemical Reaction Dynamics, Ultrashort Pulse Generation and Control

Chemical reactions of polyatomic molecular systems proceed on complex potential energy surfaces (PESs) with a vast degree of freedom of nuclear coordinates. For understanding molecular mechanisms underlying the chemical reactions, it is essential to map out the PESs and visualize how the molecules migrate and change its structure thereon. To this end, it is necessary to track the change of the electronic/vibrational structure of the molecule from the reactant all the way down to the product, with temporal resolution as high as possible.

We develop and apply advanced ultrafast laser spectroscopy based on state-of-the-art optical technology to study chemical reaction dynamics of the condensed-phase molecular systems. In particular, we exploit unique methodologies using sub-10-fs pulses (*e.g.*, ultrafast time-domain Raman spectroscopy and multidimensional electronic/vibrational spectroscopy), and track the molecular dynamics from the electronic and structural viewpoints, throughout the chemical reaction with an exquisite temporal resolution. Our particular interest rests on elucidating sophisticated molecular mechanisms that underlie the reactions of functional molecular systems such as photoreceptor proteins, molecular assemblies, and metal complexes. On the basis of new insights that can be gained from our unique spectroscopic tools, we aim to establish a new avenue for the study of chemical reaction dynamics.

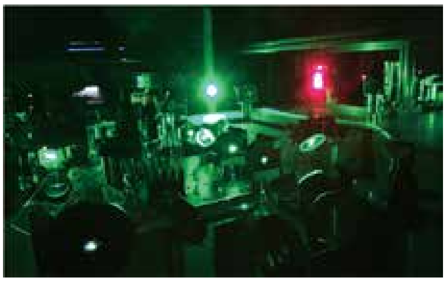


Figure 1. Setup for advanced ultrafast spectroscopy based on sub-10-fs pulses.

Selected Publications

- H. Kuramochi, S. Takeuchi and T. Tahara, "Femtosecond Time-Resolved Impulsive Stimulated Raman Spectroscopy Using Sub-7-fs Pulses: Apparatus and Applications," *Rev. Sci. Instrum.* **87**, 043107 (2016).
- T. Fujisawa, H. Kuramochi, H. Hosoi, S. Takeuchi and T. Tahara, "Role of Coherent Low-Frequency Motion in Excited-State Proton Transfer of Green Fluorescent Protein Studied by Time-Resolved Impulsive Stimulated Raman Spectroscopy," *J. Am. Chem. Soc.* **138**, 3942–3945 (2016).
- H. Kuramochi, S. Takeuchi, K. Yonezawa, H. Kamikubo, M. Kataoka and T. Tahara, "Probing the Early Stages of Photoreception in Photoactive Yellow Protein with Ultrafast Time-Domain Raman Spectroscopy," *Nat. Chem.* **9**, 660–666 (2017).
- H. Kuramochi, S. Takeuchi, H. Kamikubo, M. Kataoka and, T. Tahara, "Fifth-Order Time-Domain Raman Spectroscopy of Photoactive Yellow Protein for Visualizing Vibrational Coupling in Its Excited State," *Sci. Adv.* **5**, eaau4490 (2019).
- H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, "Tracking Photoinduced Au–Au Bond Formation through Transient Terahertz Vibrations Observed by Femtosecond Time-Domain Raman Spectroscopy," *J. Am. Chem. Soc.* **141**, 19296–19303 (2019).

1. Realtime Observation of the Structural Changes upon Photoinduced Tight Bond Formation

Realtime observation of chemical bond formation and subsequent nuclear rearrangements is one of the ultimate goals of chemical science. Nevertheless, such attempts have been long hampered by a technical difficulty to trigger bond formation at well-defined, desired timing. The dicyanoaurate complex trimer ($[Au(CN)_2^-]_3$) is the best suitable system in order to achieve this aim because the tight covalent Au–Au bonds are formed upon photoexcitation. Despite the apparent simplicity of the system, however, recent time-resolved studies failed to construct a consistent picture of its structural dynamics.

We used femtosecond time-resolved impulsive stimulated Raman spectroscopy to track ultrafast structural dynamics of the $[Au(CN)_2^-]$ trimer upon the photoinduced Au–Au bond formation. This ultrafast "time-resolved time-domain" Raman technique allows us to monitor the change of the vibrational structure on the femtosecond timescale by inducing and observing coherent molecular vibrations at arbitrary timings with ultrashort pulses. The obtained femtosecond time-resolved Raman data reveal that the Au–Au stretching vibration at ~90 cm^{-1} exhibits a gradual frequency upshift in a few picoseconds, demonstrating a continuous bent-to-linear structural change on the triplet-state potential energy surface upon the Au–Au bond formation. This comprehensive ultrafast spectroscopic study settles the controversy on this prototypical molecular assembly.1)

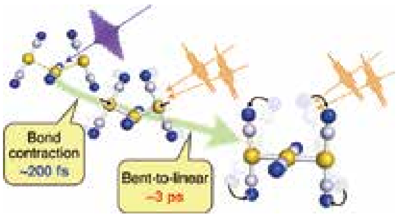


Figure 2. Schematic illustration of the structural changes in $[Au(CN)_2^-]_3$ upon photoinduced tight Au–Au bond formation.

2. Femtosecond Polarization Switching of the [CrCo] Dinuclear Complex Crystal

Polarization switching has been considered a promising key operating principle of next-generation sensors and memory devices. Ferroelectric compounds have been extensively studied as promising candidates because they exhibit polarization switching upon application of the external electric field or heating. However, the speed (and thus efficiency) of the polarization switching in these materials is often limited by the change in the molecular structure, which occurs on the picoseconds or longer time scale. Also, the polarization state of the ferroelectric compounds is, in many cases, dependent on their domain structure, making it difficult to realize large polarization at the macroscopic scale.

The crystal of the [CrCo] dinuclear complex has been shown to exhibit polarization switching upon the photoinduced phase transition.2) Because the molecular orientation is well defined inside the crystal and the phase transition is accompanied by the charge transfer that does not require the change in the molecular structure, it has potential to realize the fast polarization switching at the macroscopic scale.

We studied photoinduced polarization switching dynamics in the crystal of the [CrCo] dinuclear complex by ultrafast pump–probe spectroscopy in the visible and mid-infrared regions. Our data clearly show that the photoinduced polarization switching is an ultrafast process with a time constant of 280 fs, demonstrating itself as the fastest polarization switching material realized using the metastable state. Moreover, the pump–probe data in the visible region reveal pronounced appearance of coherent nuclear wavepacket motion with a frequency as low as 22 cm^{-1}, which we attribute to a lattice vibrational mode. The pronounced non-Condon effect for its resonance Raman enhancement implies that this mode couples the relevant electronic states, thereby facilitating the ultrafast polarization switching.3)

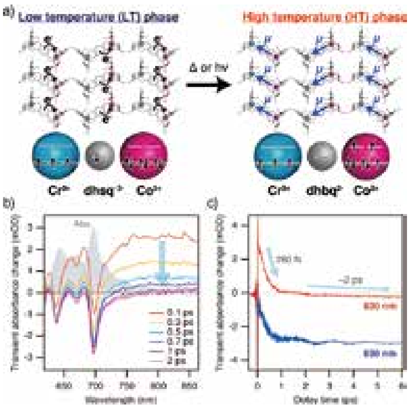


Figure 3. Schematic illustration of the change in the spin state associated with the phase transition. b) Time-resolved absorption spectra obtained after photoexcitation with the 9-fs pulse centered at 520 nm. c) Temporal profiles of the transient absorption signals.

References

1) H. Kuramochi, S. Takeuchi, M. Iwamura, K. Nozaki and T. Tahara, *J. Am. Chem. Soc.* **141**, 19296–19303 (2019).
2) S. Kanegawa, Y. Shiota, S. Kang, K. Takahashi, H. Okajima, A. Sakamoto, T. Iwata, H. Kandori, K. Yoshizawa and O. Sato, *J. Am. Chem. Soc.* **138**, 14170–14173 (2016).
3) H. Kuramochi, G. Aoyama, H. Okajima, A. Sakamoto, S. Kanegawa, O. Sato, S. Takeuchi and T. Tahara, *Angew. Chem., Int. Ed.* **59**, 15865–15869 (2020).

Awards

KURAMOCHI, Hikaru; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award (2020).

KURAMOCHI, Hikaru; Morino Foundation for Molecular Science (2020).

Open up Future Electronics by Organic Molecules

Research Center of Integrative Molecular Systems Division of Functional Molecular Systems

YAMAMOTO, Hiroshi
Professor
[yhiroshi@ims.ac.jp]

Education

1993 B.S. The University of Tokyo
1998 Ph.D. The University of Tokyo

Professional Employment

1998 Research Associate, Gakushuin University
1999 Special Postdoctral Fellow, RIKEN
2000 Research Scientist, RIKEN
2007 Senior Research Scientist, RIKEN
2012 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Awards

2009 RSC Publishing CrystEngComm Prize
2009 Young Scientist Awards, Japan Society for Molecular Science
2010 RIKEN-ASI Award for the Young Scientist
2019 The CSJ Award for Creative Work
2020 NAGAI Foundation for Science & Technology Academic Award

Member

Assistant Professor
SUDA, Masayuki
HIROBE, Daichi
IMS Research Assistant Professor
KAWAGUCHI, Genta
Visiting Scientist
SAENNAWA, Wiyada*
PACHARIYANGKUN, Anna
KUMSAMPAO, Jakkapan
Graduate Student
MORISHIMA, Masaki
AIZAWA, Hiroki
NABEI, Yoji
NAKAJIMA, Ryota
Technical Fellow
MURATA, Ryosuke
Secretary
SUZUKI, Ai

Keywords Organic Mott Insulator, Field Effect Transistors, Organic Spintronics

Organic molecules are attracting recent attention as new ingredients of electronic circuits. Our group focuses on the development of organic electronics in the next era by providing new mechanism and concepts of the device operation and fabrication. For example, an electronic phase transition is utilized for the ON/OFF switching of our field-effect-transistor (FET). This special FET is called an organic Mott-FET, where the conduction electrons in the organic semiconductor are solidified at the OFF state because of Coulomb repulsion among carriers. In the operation, these solidified electrons can be melted by applying a gate voltage, and show an insulator-to-metal transition so-called Mott-transition to be switched to the ON state. Because of this phase transition, a large electric response of the device can be achieved, resulting in the highest device mobility ever observed for organic FETs. In addition to this high performance, the Mott-FET is interesting in terms of superconductivity. Because the Mott-transition sometimes accompanies superconducting phase in between metal and insulator, modulation of gate electric field at low temperature may induce superconductivity. In fact, we have achieved first example of field-induced superconductivity in an organic FET. By combining a strain effect that can tune the bandwidth, this type of electric-field-induced superconducting transition can be utilized for mapping the phase diagram around the Mott-insulator as shown in Figure 1.

Another approach to the future electronics is the development of spintronic devices based on chirality of organic material. We aim to implement chirality-induced spin selectivity (CISS) effect into molecular devices that can generate spin-polarized current. This type of device is expected to realize spintronics devices without magnet or topological insulator.

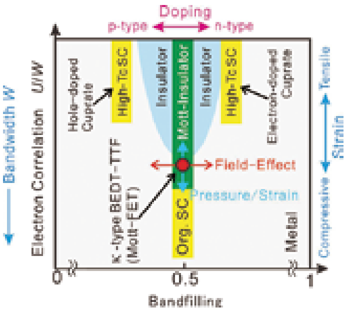


Figure 1. Phase diagram surrounding a Mott-insulator. SC denotes superconductor, while U and W are on-site Coulomb repulsion and bandwidth, respectively.

Selected Publications

- H. M. Yamamoto, M. Suda and Y. Kawasugi, "Organic Phase-Transition Transistor with Strongly Correlated Electrons," *Jpn. J. Appl. Phys.* **57**, 03EA02 (7 pages) (2018).
- Y. Kawasugi, K. Seki, S. Tajima, J. Pu, T. Takenobu, S. Yunoki, H. M. Yamamoto and R. Kato, "Two-Dimensional Ground-State Mapping of a Mott-Hubbard System in a Flexible Field-Effect Device," *Sci. Adv.* **5**, eaav7282 (9 pages) (2019).
- M. Suda, R. Kato and H. M. Yamamoto, "Light-Induced Superconductivity Using a Photo-Active Electric Double Layer," *Science* **347**, 743–746 (2015).
- H. M. Yamamoto, M. Nakano, M. Suda, Y. Iwasa, M. Kawasaki and R. Kato, "A Strained Organic Field-Effect Transistor with a Gate-Tunable Superconducting Channel," *Nat. Commun.* **4**, 2379 (7 pages) (2013).

1. Current-Induced Spin-Polarization in a Chiral Crystal $CrNb_3S_6$[1,2]

CISS effect has remarkable ability which generates highly polarized spin current even with light element molecules. However, its extension to inorganic chiral materials has not been well investigated. Moreover, detection of CISS effect in metals that show ohmic response is quite interesting because one can discuss the CISS-based spin polarization in terms of band theory if metallic CISS effect in linear response regime is observed. So far, however, CISS experiments have been investigated only in tunnelling conduction regime.

We detected CISS-based spin transport phenomena in a monoaxial chiral dichalcogenide $CrNb_3S_6$. This material has chiral structure and metallic conduction, so that we could perform CISS experiments with metallic conduction regime. Spin polarization was detected in this chiral bulk crystal under a charge current flowing along the principal c axis at room temperature without magnetic field. The detection was made by an inverse spin Hall signal which is induced on the tungsten electrode that absorbs polarized spin from the chiral crystal (Figure 2). An inverse response was also observed when applying the charge current into the detection electrode, which implied an inverse CISS effect. The signal sign reversed in the device with the opposite chirality, which is consistent with the symmetry required for CISS effect. Furthermore, the spin signals were found over micrometer length scale in a nonlocal configuration. Such a robust generation and protection of the spin-polarized state can be discussed based on a one-dimensional model with spin–momentum locking.

In addition to the above experiments, we also detected bulk magnetization generated by applying electric current to the crystal. When the current amplitude was swept from negative to positive, the current-induced magnetization changed linearly. Directly detecting such magnetization by magnetometry enables one to estimate the number of spin-polarized electrons. Using this number, we evaluated the spin polarization rate within the framework of Boltzmann's equation and found that spin polarization generated by CISS effect was enhanced by 10^5 times inside this material. It seemed that effective magnetic field generated by CISS could reach 10^3 T at high current density, which again confirmed the robustness of CISS effect. We also observed that the current-induced magnetization increased in the vicinity of the phase boundary between paramagnetic and forced ferromagnetic phases, which could be attributed to the spin fluctuation associated with the phase transition.

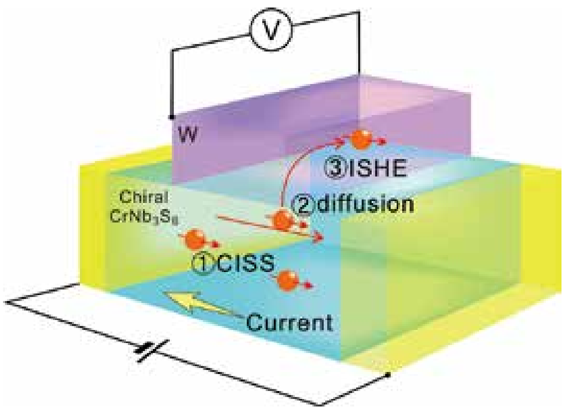


Figure 2. Detection of spin polarization in a chiral metal $CrNb_3S_6$. By applying electrical current (①), electron spins are polarized along the current direction by CISS effect. Then the spin current is diffused into W electrode (②) and generate a voltage by inverse spin Hall effect (③).

2. Anomalous Superconducting Phase in an Organic Field-Effect Device[3]

We have achieved simultaneous control of bandwidth and bandfilling for organic Mott-insulators by using field effect device that can control the lattice strain to the organic crystal to observe the phase diagram for superconducting state. A new superconducting field-effect transistor (FET) in the vicinity of bandwidth-controlled Mott transition has been developed using molecular strongly correlated system κ-$(BEDT\text{-}TTF)_2$ $Cu[N(CN)_2]Br$ laminated on CaF_2 substrate. This device exhibited significant cooling-rate dependence of resistance below about 80 K, associated with glass transition of terminal ethylene group of BEDT-TTF molecule, where more rapid cooling through glass transition temperature leads to the decrease in bandwidth. We demonstrated that the FET properties such as ON/OFF ratio and polarity can be changed by utilizing cooling rate. Therefore, this is another device that can control both bandwidth and bandfilling of an organic Mott-insulator simultaneously, to find phase diagram associated with superconducting and Mott-insulating phases. By analyzing the FET behaviors of the device at different cooling rates, an enhanced superconducting state at exactly half-filling was discovered.

[BEDT-TTF = bis(ethylenedithio)tetrathiafulvalene]

References

1) Y. Nabei, D. Hirobe, Y. Shimamoto, K. Shiota, A. Inui, Y. Kousaka, Y. Togawa and H. M. Yamamoto, *Appl. Phys. Lett.* **117**, 052408 (2020).
2) A. Inui, R. Aoki, Y. Nishiue, K. Shiota, Y. Kousaka, H. Shishido, D. Hirobe, M. Suda, J. Ohe, J. Kishine, H. M. Yamamoto and Y. Togawa, *Phys. Rev. Lett.* **124**, 166602 (2020).
3) G. Kawaguchi and H. M. Yamamoto, *Crystals* **9**, 605 (2019).

Award

YAMAMOTO, Hiroshi; NAGAI Foundation for Science & Technology Academic Award (2020).

---

* IMS International Internship Program

RESEARCH ACTIVITIES

Center for Mesoscopic Sciences

In the past few decades, great progress in experimental and theoretical methods to analyze structures, dynamics, and properties of single-component (or single hierarchical) molecules and nanomaterials has been made. Now we should also direct our attention to properties and functions of multi-hierarchical molecular systems. We develop innovative methods of measurements and analysis for molecular and materials systems to elucidate the processes that trigger the functions and reactions of the systems in the mesoscopic regime, that is the regime where micro and macroscopic properties influence each other.

Nano-Optical Imaging and Application to Nanomaterials

Center for Mesoscopic Sciences
Division of Supersensitive Measurements

OKAMOTO, Hiromi
Professor
[aho@ims.ac.jp]

Education
1983 B.S. The University of Tokyo
1991 Ph.D. The University of Tokyo

Professional Employment
1985 Research Associate, Institute for Molecular Science
1990 Research Associate, The University of Tokyo
1993 Associate Professor, The University of Tokyo
2000 Professor, Institute for Molecular Science
Professor, The Graduate University for Advanced Studies

Award
2012 The Chemical Society of Japan (CSJ) Award for Creative Work
2020 The Commendation for Science and Technology by the MEXT Awards for Science and Technology Research Category

Member
Assistant Professor
NARUSHIMA, Tetsuya
YOSHIZAWA, Daichi
Project Assistant Professor (NINS)
AHN, Hyo-Yong
Post-Doctoral Fellow
YAMANISHI, Junsuke
Visiting Scientist
WU, Yi-Ju*
Technical Fellow
ISHIKAWA, Akiko
Secretary
NOMURA, Emiko

Keywords Nano Optics, Plasmons, Chirality

Studies of local optical properties of molecular assemblies and materials are key to understanding nanoscale physical and chemical phenomena, and for construction of nanoscale functional devices. Nano-optical methods, such as scanning near-field optical microscopy (SNOM), enable optical imaging with spatial resolution beyond the diffraction limit of light. Combination of nano-optical techniques with various advanced spectroscopic methods may provide a methodology to analyze nanoscale functionalities and dynamics directly. It may yield essential and basic knowledge to understand origins of characteristic features of the nanomaterial systems. We have constructed nano-optical (near-field and far-field) spectroscopic and microscopic measuring systems, for the studies on excited-state properties of nanomaterials, with the feasibilities of nonlinear and time-resolved measurements. The developed apparatuses enable nano-optical measurements of two-photon induced emission, femtosecond time-resolved signals, and chiro-optical properties (as typified by circular dichroism), in addition to conventional transmission, emission, and Raman-scattering. Based on these methods, we are investigating the characteristic spatial and temporal behavior of various metal-nanostructure systems and molecular assemblies. Typical examples are shown in Figure 1. We succeeded in visualizing wave functions of resonant plasmon modes in single noble metal nanoparticles, confined optical fields in noble metal nanoparticle assemblies. In recent few years, we have succeeded in observing plasmon wave packet propagation dynamics with ultrafast time-resolved near-field imaging, local chiro-optical properties of chiral and achiral metal nanostructures, and so forth. We also developed far-field high-precision circular dichroism microscope that facilitate chirality analysis of materials in a wide range of research areas. The information on nano-optical properties of the materials are also relevant to exploration of novel optical manipulation principles, which is another research topic of the research group.

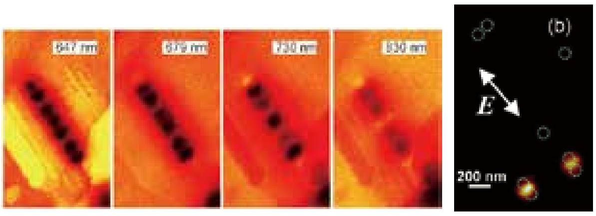


Figure 1. (Left four panels) Near-field transmission images of gold nanorod (20 nm^D × 510 nm^L). The wavelengths of observation were 647, 679, 730, and 830 nm from left to right. The spatial oscillating features were attributed to the square amplitudes of the resonant plasmonic wave functions. (Right) Near-field two-photon excitation image of dimers of spheric gold nanoparticles (diameter 100 nm) observed at 785 nm. The arrows indicates the incident light polarization. Dotted circles represent approximate positions of the particles.

Selected Publications

- H. Okamoto, "Local Optical Activity of Nano- to Microscale Materials and Plasmons," *J. Mater. Chem. C* **7**, 14771–14787 (2019).
- H. Okamoto, T. Narushima, Y. Nishiyama and K. Imura, "Local Optical Responses of Plasmon Resonance Visualized by Near-Field Optical Imaging," *Phys. Chem. Chem. Phys.* **17**, 6192–6206 (2015).
- H. Okamoto and K. Imura, "Visualizing the Optical Field Structures in Metal Nanostructures," *J. Phys. Chem. Lett.* **4**, 2230–2241 (2013).

1. Roles of Superchirality and Interference in Chiral Plasmonic Biodetection[1)]

Chiral plasmonic nanostructures enable ≤pg detection and characterization of biomaterials. The sensing capabilities are associated with the chiral asymmetry of the near fields, which locally can be greater than equivalent circularly polarized light, a property referred to as superchirality. However, sensing abilities do not simply scale with the magnitude of superchirality. We show that chiral molecular sensing is correlated to the thickness of a nanostructure. This observation is reconciled with a previously unconsidered interference mechanism for the sensing phenomenon. It involves the "dissipation" of optical chirality into chiral material currents through the interference of fields generated by two spatially separated chiral modes. The presence of a chiral dielectric causes an asymmetric change in the phase difference, resulting in asymmetric changes to chiroptical properties. Thus, designing a chiral plasmonic sensor requires engineering a substrate that can sustain both superchiral fields and an interference effect.

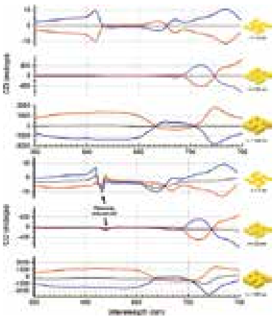


Figure 2. Simulated CD spectra for gammadions of h = 5 nm, 30 nm, and 100 nm when light is incident upon their top (blue) and bottom (red) faces. Top three: Encapsulated by an achiral layer. Their mean is shown in black and is ~0 in all cases. Bottom three: Encapsulated by a chiral layer. The mean of the two incidences is shown in black.

2. Spectral Properties of Chiral Electromagnetic Near Fields Created by Chiral Plasmonic Nanostructures[2)]

The surface-enhanced chiral-optical spectroscopy is based on the interaction of chiral molecules with chiral electromagnetic near field localized on a chiral plasmonic nanostructure. It is of fundamental importance to reveal the spectral characteristics of chiral near fields for maximizing the chiral interaction. We investigated relations between near field and far field polarization characteristics of the chiral plasmonic nanostructures, using electromagnetic simulations. We found that spectral features of chiral near fields created by the nanostructures intercorrelate with those of far field optical rotation. This finding may provide us a method to characterize and design the chiral near field.

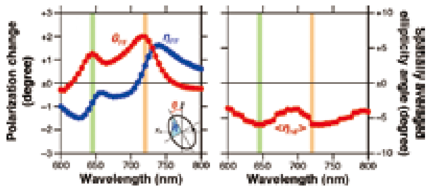


Figure 3. Simulated far-field circular dichroism η_{FF} (blue) and optical rotation θ_{FF} (red) spectra (top) and near-field circular dichroism η_{NF} spectrum (bottom) of a gold gammadion-shaped nanostructure (width 450 nm) by the finite-difference time-domain method.

3. Circularly Polarized Two-Photon-Induced Luminescence from Plasmonic Two-Dimensional Chiral Au Nanostructures[3)]

A chiral nanostructure, which exhibits optical activity, absorbs different amounts of left-handed circularly polarized (LCP) and right-handed circularly polarized (RCP) light. In this work, we report the observation of dissymmetry between two-photon-induced LCP and RCP photoluminescence from plasmonic two-dimensional (2D) chiral Au nanostructures. Under excitation by linearly polarized femtosecond pulses from a mode-locked Ti:sapphire laser with a low incident power of 3 mW, the 2D chiral plasmonic nanostructure yields circularly polarized two-photon-induced photoluminescence (TPIPL) due to resonance with a chiral multipolar plasmon mode of the nanostructure. The handedness of the circularly polarized TPIPL was dependent on the handedness of the chiral plasmonic nanostructure. The chiral nature of TPIPL may find potential applications in optical devices, sensing of chiral molecular environments in biological systems, and so forth.

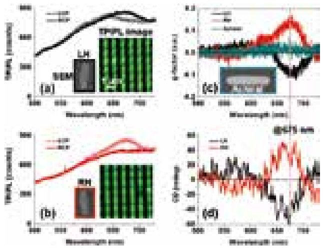


Figure 4. (a,b) Left- and right-circularly polarized TPIPL spectra of the chiral nanostructures. Insets: SEM and TPIPL microscopic images of the left- (a) and right-handed (b) chiral gold nanostructures. (c) Dissymmetry factor (g) spectra of TPIPL for the chiral and achiral nanostructures. (d) CD spectra of the chiral nanostructures.

References

1) C. Gilroy, S. Hashiyada, K. Endo, A. S. Karimullah, L. D. Barron, H. Okamoto, Y. Togawa and M. Kadodwala, *J. Phys. Chem. C* **123**, 15195–15203 (2019).
2) S. Hashiyada, K. Endo, T. Narushima, Y. Togawa and H. Okamoto, *J. Phys.: Conf. Ser.* **1220**, 012050 (2019).
3) K. Q. Le and H. Okamoto, *J. Phys.: Conf. Ser.* **1220**, 012004 (2019).

Award

OKAMOTO, Hiromi; The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology Awards for Science and Technology Research Category (2020).

---

* IMS International Internship Program (Graduate Student from National Chiao Tung University, Taiwan)

Center for Mesoscopic Sciences as an Interdepartmental Facility

OKAMOTO, Hiromi	Director, Professor
OHMORI, Kenji	Professor
IINO, Ryota	Professor
EHARA, Masahiro	Professor
SUGIMOTO, Toshiki	Associate Professor
MINAMITANI, Emi	Associate Professor
NARUSHIMA, Tetsuya	Assistant Professor
YOSHIZAWA, Daichi	Assistant Professor
NOMURA, Yutaka	Assistant Professor
OKANO, Yasuaki	Technical Associate
NOMURA, Emiko	Secretary

As the succeeding organization of former Laser Research Center for Molecular Science, Center for Mesoscopic Sciences continues development of new experimental apparatus and methods to open groundbreaking research fields in molecular science, in collaboration with other departments and facilities. Those new apparatus and methods will be served as key resources in advanced collaboration with the researchers from the community of molecular science. The targets cover:

- novel quantum-control schemes based on intense and ultrafast lasers
- novel optical imaging and nanometric microscopy and spectroscopy
- novel method of analysis for mesoscopic phenomena

and so forth.

The Center also possesses several general-purpose instruments for laser-related measurements (commercial as well as in-house developed), and lends them to researchers in IMS who conduct laser-based studies, so as to support and contribute to their advanced researches.

RESEARCH ACTIVITIES

Division of Advanced Molecular Science

The division consists of two sections. In the first one, scientists of the first water are invited as "distinguished professors," and the environment, in which they can devote themselves to their own research, is provided. The research in this section should be the last word in the field of molecular science.

In the second section, we invite researchers in the universities performing unique researches in the field of molecular science as cross-appointment faculty members, and provide the research environment to enable research activity with advanced facilities in IMS.

Self-Assembling Molecular Systems Based on Coordination Chemistry

Division of Advanced Molecular Science

FUJITA, Makoto
Distinguished Professor
[mfujita@ims.ac.jp]

Education

1980	B.S. Chiba University
1982	M.S. Chiba University
1987	Ph.D. Tokyo Institute of Technology

Professional Employment

1982	Researcher, Sagami Chemical Research Center
1988	Assistant Professor to Associate Professor, Chiba University
1997	Associate Professor, Institute for Molecular Science
1999	Professor, Nagoya University
2002	Professor, The University of Tokyo
2018	Distinguished Professor, Institute for Molecular Science
2019	Distinguished Professor, The University of Tokyo

Awards

1994	Progress Award in Synthetic Organic Chemistry, Japan
2000	Division Award of Chemical Society of Japan (Organic Chemistry)
2001	Tokyo Techno Forum 21 Gold Medal
2001	Japan IBM Award
2003	Nagoya Silver Medal
2004	Izatt-Christensen Award
2006	G. W. Wheland Award (Chicago University Lectureship Award)
2010	The Reona Esaki Award
2010	The JSCC Award
2011	3M Lectureship Award (University of British Columbia)
2012	Thomson Reuters Research Front Award 2012
2013	The Chemical Society of Japan (CSJ) Award
2013	Arthur C. Cope Scholar Award (ACS National Award)
2013	Merck-Karl Pfister Visiting Professorship (MIT Lectureship Award)
2014	ISNSCE 2014 Nanoprize
2014	Medal with Purple Ribbon
2014	Fred Basolo Medal (Northwestern University)
2018	Wolf Prize in Chemistry
2019	The Imperial Prize and the Japan Academy Prize
2020	The 73rd Chunichi Cultural Award

Member

IMS Research Assistant Professor
  MITSUHASHI, Takaaki
Post-Doctoral Fellow
  CHAN, Kwun Wa
Graduate Student
  ALBERTSMA, Jelco*
  CHEN, Jiazhuo[†]
  KAGEYAMA, Ko[†]
  YOUNGCHEOL, Jung[†]
  YU, Zhengsu[†]
  WADA, Naoki[†]
  ZHOU, Boyu[†]
Secretary
  MASUDA, Michiko

Keywords Self-Assembly, Nano-Space, Coordination Chemistry

We are designing new self-assembled molecular systems based on coordination chemistry, and apply the molecular system to various research fields. One of these examples is a molecular system called “crystalline sponge (CS).” The CS is a porous crystal, which can accommodate various kinds of small molecules, and align the accommodated molecules neatly in its inner space. Actually, we can observe the structure of the small molecules neatly aligned in the CS by the X-ray crystallography (Figure 1). Therefore, we can use the CS for the structure elucidation of the small molecules. This technique developed by us is called “CS method.” The CS method has a potential to accelerate the various kinds of researches, in which the structure elucidation of novel compounds is required.

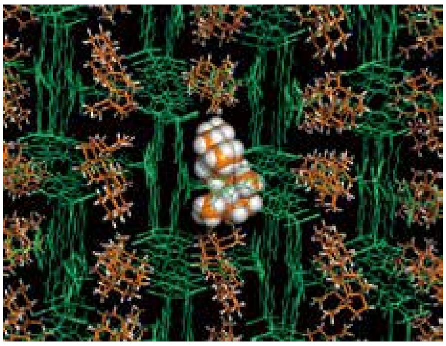


Figure 1. One example of the crystalline sponge method analysis result. Orange molecules are accommodated molecules, and green one is a framework of the crystalline sponge.

Selected Publications

- Y. Inokuma, S. Yoshioka, J. Ariyoshi, T. Arai, Y. Hitora, K. Takada, S. Matsunaga, K. Rissanen and M. Fujita, “X-Ray Analysis on the Nanogram to Microgram Scale Using Porous Complexes,” *Nature* **495**, 461–466 (2013).
- D. Fujita, Y. Ueda, S. Sato, N. Mizuno, T. Kumasaka and M. Fujita, “Self-Assembly of Tetravalent Goldberg Polyhedra from 144 Small Components,” *Nature* **540**, 563–566 (2016).

1. The CS Method Accelerates an Attempt to Create Artificial Natural Products

The natural products, compounds isolated from nature, exhibit great structural diversity and complexity. Such diversity and complexity of the natural products are generated by enzymatic reactions in organisms such as plants and bacteria. The enzymes can convert simple substrates into complex natural products. The natural products can be utilized for many kinds of purposes, such as medicines, industrial materials, and so on. Therefore, it can be said that the natural products are attractive resource for the exploration into useful compounds. However, recently, it becomes difficult to obtain new natural products with novel structures, because almost all types of natural products, which can be easily isolated, are considered to be already found through long history of natural product chemistry.

One way to solve this problem is a chemo-enzymatic approach. In this approach, we prepare unnatural synthetic substrates. Then, the substrates are converted into complex artificial molecules by enzymes, which is involved in the biosynthesis of natural products. In this way, we can expand the diversity of small molecules, using the biosynthetic mechanism of the natural products. One of the bottle-necks of this approach is the structural elucidation of the enzyme products, because the products often possess complex and unexpected structures. We consider that the CS method can solve this problem, since this method enables rapid structural elucidation of small molecules.

2. The CS Method Analysis of Artificial Indole-Containing Compound[1)]

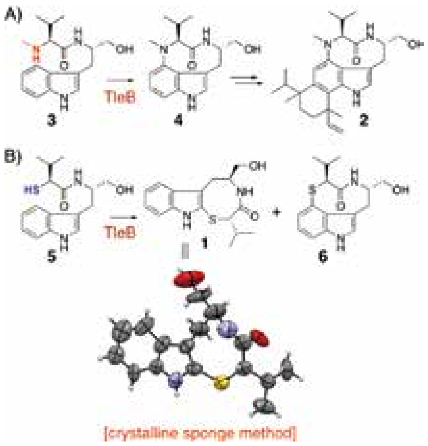


Figure 2. A) Reaction catalyzed by TleB in nature. B) Enzyme reaction to produce **1** and **6** from unnatural substrate **5**.

We elucidated a structure of a compound **1** generated by reaction using a biosynthetic enzyme, TleB, which is involved in a biosynthesis of **2** (Figure 2). In nature, TleB accepts **3** as a substrate and produce **4** (Figure 2A). However, it was found that unnatural substrate **5** could also be accepted by TleB, and **1** and **6** were generated (Figure 2B). Even though the structure elucidation of **6** could be accomplished by the NMR, MS, and single-crystal X-ray diffraction study, that of **1** could not be determined by the conventional methods. Therefore, we subjected **1** to the CS method, and succeeded in the structure elucidation.

3. The CS Method Analysis of Artificial Natural Products Produced by Enzymatic Cyclization Reaction[2)]

One of the important reactions to form basic skeletons of the natural products is a cyclization reaction. When a chemically synthesized unnatural substrate **7** was converted by an enzymatic cyclization reaction, **8** was generated (Figure 3). **8** has a novel structure, but its structure could not be determined by the NMR analysis. Thus, the structure of **8** was revealed by the CS method.

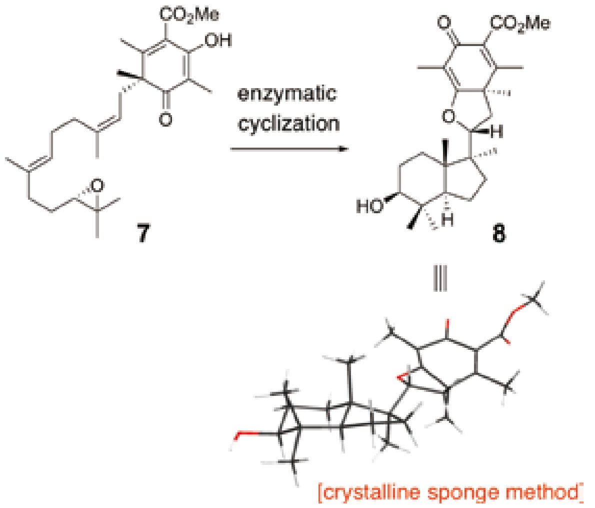


Figure 3. Enzyme reaction to produce **8** from **7**.

References

1) I. Morita, T. Mori, T. Mitsuhashi, S. Hoshino, Y. Taniguchi, T. Kikuchi, K. Nagae, N. Nasu, M. Fujita, T. Ohwada and I. Abe, *Angew. Chem., Int. Ed.* **59**, 3988–3993 (2020).

2) T. Mitsuhashi, L. Barra, Z. Powers, V. Kojasoy, A. Cheng, F. Yang, Y. Taniguchi, T. Kikuchi, M. Fujita, D. J. Tantillo, J. A. Porco and I. Abe, *Angew. Chem., Int. Ed.* **59**, in press (2020).

Award

FUJITA, Makoto; The 73rd Chunichi Cultural Award (2020).

---

* from the University of Twente

† carrying out graduate research on Cooperative Education Program of IMS with the University of Tokyo

Exploring Novel Physical Properties by Multi-Dimensional Spectroscopy

Division of Advanced Molecular Science (Department of Materials Molecular Science, Electronic Structure)

KIMURA, Shin-ichi
Professor
(Cross Appointment)
[kimura@ims.ac.jp]

Education

1988	B.S. Tohoku University
1990	M.S. Tohoku University
1991	Ph.D. Tohoku University

Professional Employment

1991	JSPS Postdoctoral Fellow, Tohoku University
1993	Research Associate, Kobe University
1993	Research Associate, Institute for Molecular Science
1998	Associate Professor, Kobe University
2002	Associate Professor, Institute for Molecular Science
2013	Professor, Osaka University
2020	Professor (Cross Appointment), Institute for Molecular Science

Awards

2001	Young Incentive Award, Japanese Society for Synchrotron Radiation Research
2008	The Commendation for Science and Technology by MEXT, Japan Science and Technology Prize (Research Field)
2008	Morita Memorial Prize

Member
Secretary
ISHIKAWA, Azusa

Keywords Condensed Matter, Biological Materials, Optical Property

Physical and chemical properties of solids, such as conductivity, magnetism, superconductivity and chemical reactions, and also life phenomena, such as redox and photosynthesis, originate from microscopic electronic and molecular vibrations and/or molecular movements based on quantum mechanics in materials and their interactions. To clarify the microscopic states provides us not only the knowledge of the origins of the physical properties and life phenomena but also the clarification of hidden functionalities. The information is useful for the creation of novel functional properties. To visualize the microscopic state, we also develop novel spectroscopic techniques using synchrotron radiation, high brilliant electron beams, and other so-called quantum beams. Recently, we have successfully developed a novel electron spectroscopy, namely resonant electron-energy-loss spectroscopy, as shown in Figure 1, to detect element-specific plasmons. Based on the obtained information of electronic structures, we are aiming to develop novel physical properties of new materials.

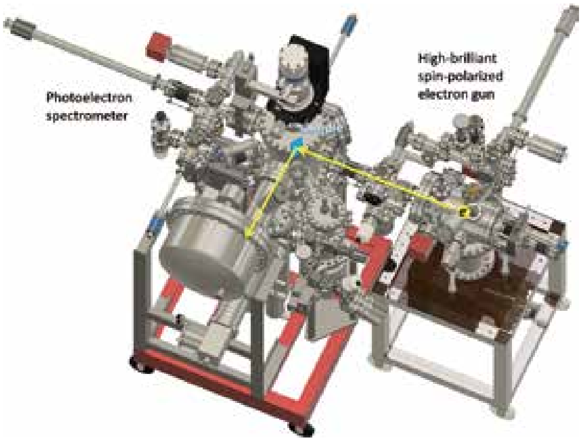


Figure 1. Resonant electron-energy-loss spectroscopy (rEELS) apparatus developed by our group. The apparatus consists of a high-brilliant spin-polarized electron gun and a photoelectron spectrometer.

Selected Publications

- S. Kimura, T. Ito, M. Sakai, E. Nakamura, N. Kondo, K. Hayashi, T. Horigome, M. Hosaka, M. Katoh, T. Goto, T. Ejima and K. Soda, "SAMRAI: A Variably Polarized Angle-Resolved Photoemission Beamline in the VUV Region at UVSOR-II," *Rev. Sci. Instrum.* **81**, 053104 (7 pages) (2010).
- S. Kimura, T. Iizuka, H. Miyazaki, A. Irizawa, Y. Muro and T. Takabatake, "Electronic-Structure-Driven Magnetic Ordering in a Kondo Semiconductor $CeOs_2Al_{10}$," *Phys. Rev. Lett.* **106**, 056404 (4 pages) (2011).
- S. Kimura and H. Okamura, "Infrared and Terahertz Spectroscopy of Strongly Correlated Electron Systems under Extreme Conditions," *J. Phys. Soc. Jpn.* **82**, 021004 (28 pages) (2013). [review]
- K. Hagiwara, Y. Ohtsubo, M. Matsunami, S. Ideta, K. Tanaka, H. Miyazaki, J. E. Rault, P. Le Fèvre, F. Bertran, A. Taleb-Ibrahimi, R. Yukawa, M. Kobayashi, K. Horiba, H. Kumigashira, K. Sumida, T. Okuda, F. Iga and S. Kimura, "Surface Kondo Effect and Non-Trivial Metallic State of the Kondo Insulator YbB_{12}," *Nat. Commun.* **7**, 12690 (7 pages) (2016).

1. Non-Trivial Surface States of Samarium Hexaboride at the (111) Surface[1)]

The peculiar metallic electronic states observed in the Kondo insulator, samarium hexaboride (SmB_6), has stimulated considerable attention among those studying non-trivial electronic phenomena. However, experimental studies of these states have led to controversial conclusions mainly to the difficulty and inhomogeneity of the SmB_6 crystal surface.

In this work, the detailed electronic structure of SmB_6 is revealed by angle-resolved photoelectron spectroscopy measurements of the three-fold (111) surface, where only two inequivalent time-reversal-invariant momenta (TRIM) exists. We observe the metallic two-dimensional state was dispersed across the bulk Kondo gap. Its helical in-plane spin polarization around the surface TRIM indicates that SmB_6 is topologically non-trivial, according to the topological classification theory for weakly correlated systems. Based on these results, we propose a simple picture of the controversial topological classification of SmB_6.

We expect that this discovery could provide a new, fertile playground for the following researches about the concert effect between electron correlation and topology. It would also be applicable for future spintronic technologies.

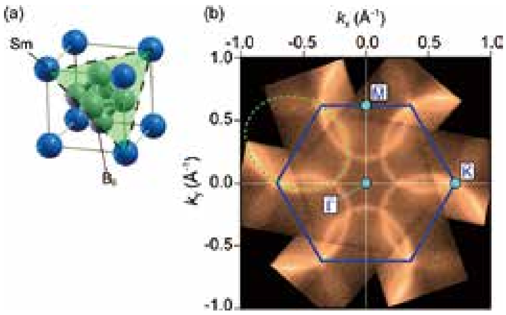


Figure 2. (a) Crystal structure of SmB_6. A shaded area is the (111) surface studied in the current work. (b) Surface electronic structure of SmB_6 obtained by angle-resolved photoelectron spectroscopy. Bright area represents the electrons with corresponding wavenumber (Fermi surface). A solid hexagon is the zone boundary determined from surface periodicity.

2. Relaxation Dynamics of $[Re(CO)_2(bpy)\{P(OEt)_3\}_2](PF_6)$ in TEOA Solvent Measured by Time-Resolved Attenuated Total Reflection Terahertz Spectroscopy[2)]

To reveal highly efficient photocatalytic properties of an artificial photosynthesis material $[Re(CO)_2(bpy)\{P(OEt)_3\}_2](PF_6)$, we have directly observed the photo-induced relaxation dynamics and reductive quenching process of the photo-excited state on a photosynthesis material in Triethanolamine (TEOA) solvent as an electron donor by time-resolved attenuated total reflection spectroscopy in the terahertz (THz) region. The spectrum of the complex in TEOA has an intermolecular vibrational mode between the complex and TEOA molecules, which reflects the precursor of the reductive quenching process. The intermolecular vibrational mode has three-step relaxation process in a picosecond timescale after photo-excitation, where firstly the triplet metal-to-ligand charge transfer excited state is vibrationally cooled down, secondly the distance between Re and TEOA is reduced by the rotation of TEOA molecules due to dipole–dipole interaction accelerated by heat transfer, and finally electrons transfer from TEOA to Re. These observations provide us the detailed information of the electron transfer process of photocatalytic properties of $[Re(CO)_2(bpy)\{P(OEt)_3\}_2](PF_6)$ in TEOA solvent.

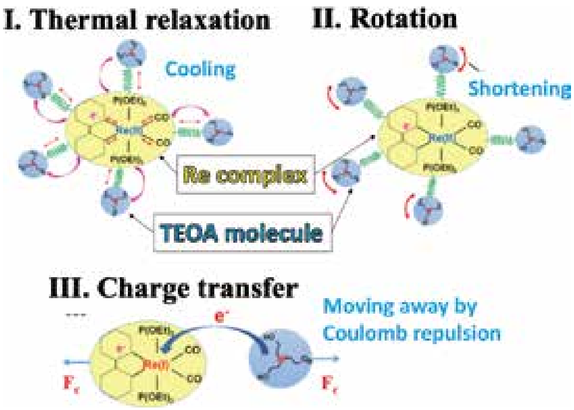


Figure 3. The schematic figures of the temporal evolution from I to III of the interaction between photocatalyst $[Re(CO)_2(bpy)\{P(OEt)_3\}_2]^+$ as a photocatalyst and TEOA molecules as reductants.

References

1) Y. Ohtsubo, Y. Yamashita, K. Hagiwara, S. Ideta, K. Tanaka, R. Yukawa, K. Horiba, H. Kumigashira, K. Miyamoto, T. Okuda, W. Hirano, F. Iga and S. Kimura, *Nat. Commun.* **10**, 2298 (7 pages) (2019).
2) P. N. Nguyen, H. Watanabe, Y. Tamaki, O. Ishitani and S. Kimura, *Sci. Rep.* **9**, 11772 (7 pages) (2019).

Innovative Catalysis Development Based on Radiant Right Spectroscopy

Division of Advanced Molecular Science (Department of Photo-Molecular Science, Photo-Molecular Science III)

TAKAYA, Hikaru
Associate Professor
(Cross Appointment)
[takaya@ims.ac.jp]

Education

1993	B.S. Osaka University
1995	M.S. Osaka University
1998	Ph.D. Osaka University

Professional Employment

1995	JSPS Research Fellow
1998	Assistant Professor, Osaka University
2002	Guest Scientist, Scripps Research
2008	Associate Professor, Kyoto University
2019	Associate Professor (Cross Appointment), Institute for Molecular Science

Awards

2001	N.E. CHEMCAT Award in Synthetic Organic Chemistry, Japan
2008	The 22nd Special Young Lecturer in the 88th CSJ Annual Meeting
2012	Theme Chemistry Journal Award
2015	BCSJ Award, The Chemical Society of Japan
2019	BCSJ Award, The Chemical Society of Japan

Member
Secretary
HAGIWARA, Hisayo

Keywords Organometallic Catalyst, Peptide-Based Material, X-Ray Spectroscopy

For future sustainable development, we promote research development of advanced catalysts based on element strategy criteria. Non-precious metal such as iron, nickel, cobalt, and cupper catalysts are investigated for synthetic transformation of various organic molecules related to pharmaceutical and photoelectronic materials. To elucidate the precise catalytic properties and mechanism, X-ray absorption spectroscopy (XAS) and various radiant right spectroscopies provided at UVSOR are used, where development of a solution-phase in situ XAS spectroscopic techniques and system will be intensively conducted for the study of homogeneous organometallic catalysts. Multidisciplinary research covered on DFT and XAS spectroscopy is also conducted to achieve an efficient structural determination technique being never accessible by the conventional XAS-based structural analysis. Using these cutting-edge spectroscopic technologies, we aim to promote innovative catalyst research which enable us highly efficient transformation of extremely unreactive organic molecules such as simple aromatic compounds, CO_2, and biomass into valuable functional materials.

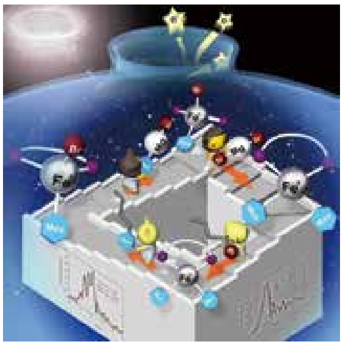


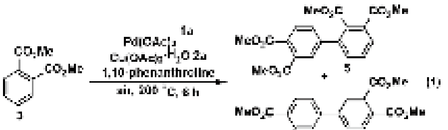
Figure 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAS analysis.

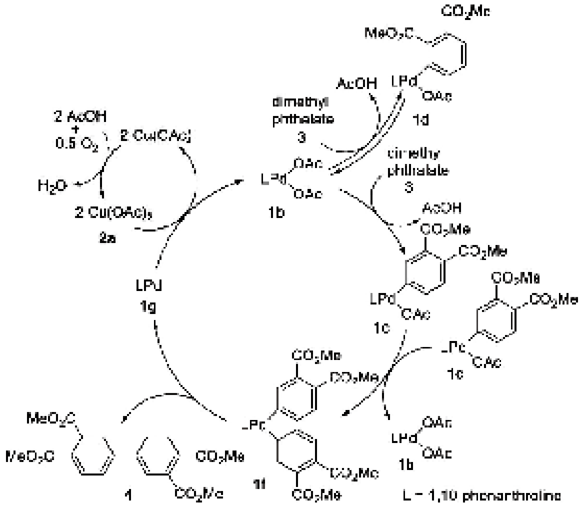
Selected Publications

- R. N. Dhital, A. Sen, T. Sato, H. Hu, R. Ishii, D. Hashizume, H. Takaya, Y. Uozumi* and Y. M. A. Yamada, "Activator-Promoted Aryl Halide-Dependent Chemoselective Buchwald-Hartwig and Suzuki-Miyaura Type Cross-Coupling Reactions," *Org. Lett.* **22**, 4797–4801 (2020).
- L. O. Benjamin, H. Takaya and T. Uemura, "Polymer Guest Directing the Solid-State Conversion of a Metal-Organic Framework," *J. Am. Chem. Soc.* **141**, 14549–14553 (2019).
- R. Agata, H. Takaya, T. Iwamoto, T. Hatakeyama, K. Takeuchi, N. Nakatani and M. Nakamura, "Iron-Catalyzed Cross Coupling of Aryl Chlorides with Alkyl Grignard Reagents: Synthetic Scope and Fe^{II}/Fe^{IV} Mechanism Supported by X-Ray Absorption Spectroscopy and Density Functional Theory Calculations," *Bull. Chem. Soc. Jpn.* **92**, 381–390 (2019).
- H. Takaya, S. Nakajima, N. Nakagawa, K. Isozaki, T. Iwamoto, R. Imayoshi, N. Gower, L. Adak, T. Hatakeyama, T. Honma, M. Takagi, Y. Sunada, H. Nagashima, D. Hashizume, O. Takahashi and M. Nakamura, "Investigation of Organoiron Catalysis in Kumada–Tamao–Corriu-Type Cross-Coupling Reaction Assisted by Solution-Phase X-Ray Absorption Spectroscopy," *Bull. Chem. Soc. Jpn.* **88**, 410–418 (2015).

1. DFT-XAS-Based Mechanistic Investigation of Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate[1,2]

Pd-catalyzed oxidative coupling reaction of phthalate esters is a well-known industrial process for the production of biphenyl compounds which can be readily converted into biphenyl tetracarboxylic dianhydride (BPDA), being an important monomer of polyimides. Equation 1 shows a typical procedure of the oxidative coupling, where dimethyl phthalate **3** readily couples in the presence of catalytic amounts of $Pd(OAc)_2$ **1a** and $Cu(OAc)_2$ **2a** to afford the corresponding biphenyls **4** and **5**. Despite the widespread use of this process, the precise reaction mechanism had still remained unclear due to the severe reaction condition and the complex Pd/Cu heterobimetallic catalyst system including paramagnetic Cu(II) species, both which hamper the conventional analysis based on solution-phase NMR. To solve such problems in mechanistic study of homogeneous catalysis, we conducted to use XAS which enables element specific analysis to determine the oxidation state and the geometry of catalytic species.[3,4] Recently, we have succeeded to elucidate the mechanism of Pd/Cu-catalyzed oxidative coupling of dimethyl phthalate as shown in Scheme 1. The oxidation states and the local coordination geometries of catalytic intermediates **1d**, **1c**, and **2a** were determined under the stoichiometric conditions of each reaction path. DFT- and single crystal X-ray structural analysis adequately provided the precise molecular structure of these intermediates. This research is first to provide a clear answer to the long-term debate on the reaction mechanism in the last three decades and demonstrated that XAS is the powerful tool for the mechanistic study on homogeneous transition-metal-catalyzed reactions, being difficult by means of the conventional solution-phase NMR analysis.





Scheme 1. Investigation of iron-catalyzed cross-coupling reactions based on DFT-XAFS analysis.

2. XAFS-Based Structural Study on Flexible Organometallic Systems[5–7]

Generally, organometallics bearing highly flexible molecular structure make it difficult to prepare a single crystal with sufficient size and quality for X-ray crystallography. We conducted DFT-XAS-based structural analysis of such flexible molecule. Recently, Prof. Uemura and Benjamin found a flexible MOF prepared from $[Zn_2(BDC)_2(DABCO)]_n$ and polystyrene which has a polymer-threaded multi-layered structure after removing the DABCO pillar ligand. The polymer-threaded extremely flexible molecular scaffolds showed no clear diffraction pattern except for a broad peak. To determine the molecular structure of this flexible MOF system, we carried out Zn K-edge and O K-edge XAS. A DFT-based simulation of both XAS spectra clearly demonstrated that $[Zn_2(BDC)_2]_n$-monolayer was preserved well in the turbostratic phase without DABCO pillar.

Another successful application was achieved in the structure determination of rotaxane-linked iron porpyrin dimer in which two units of iron-porpyrin or phtalocyanine were interlocked through highly flexble quadruplet axials. Fe K-edge XAS-based structural analysis supproted with DFT-MD-based simulation succefully provides the precise local coordionation geometry of iron centers in highly flexible supramolecular system.

References

1) H. Masafumi, K. Sano, Y. Kanazawa, N. Komine, Z. Maeno, T. Mitsudome and H. Takaya, *ACS Catl.* **8**, 5827–5841 (2018).

2) Y. Kanazawa, T. Mitsudome, H. Takaya and M. Hirano, *ACS Catal.* **10**, 5909–5919 (2020).

3) Y. Aoki, T. Toyota, H. Kawasaki, H. Takaya, A. K. Sharma, K. Morokuma and M. Nakamura, *Asian J. Org. Chem.* **8**, 1–6 (2019).

4) Y. Tanaka, Y. Kitamura, R. Kawano, K. Shoji, M. Hiratani, T. Honma, H. Takaya, H. Yoshikawa, T. Tsuruoka and D. Tanaka, *Chem. –Eur. J.* **26**, 1–9 (2020).

5) L. O. Benjamin, H. Takaya and T. Uemura, *J. Am. Chem. Soc.* **141**, 14549–14553 (2019).

6) N. Mihara, Y. Yamada, H. Takaya, Y. Kitagawa, K. Igawa, K. Tomooka, H. Fujii and K. Tanaka, *Chem. –Eur. J.* **25**, 3369–3375 (2019).

7) N. Mihara, Y. Yamada, H. Takaya, Y. Kitagawa, S. Aoyama, K. Igawa, K. Tomooka and, K. Tanaka, *Chem. –Eur. J.* **23**, 7508–7514 (2017).

RESEARCH ACTIVITIES

Division of Research Innovation and Collaboration

As the open innovation hub managed by IMS and companies, we conduct the research projects in collaboration with Academia, Industry and Government.

Micro Solid-State Photonics

Division of Research Innovation and Collaboration

TAIRA, Takunori
Project Professor
[taira@ims.ac.jp]

Education

1983	B.A. Fukui University
1985	M.S. Fukui University
1996	Ph.D. Tohoku University

Professional Employment

1985	Researcher, Mitsubishi Electric Corp.
1989	Research Associate, Fukui University
1993	Visiting Researcher, Stanford University (–1994)
1998	Associate Professor, Institute for Molecular Science Associate Professor, The Graduate University for Advanced Studies
2018	Group Director, RIKEN SPring-8 Center
2019	Project Professor, Institute for Molecular Science

Awards

2004	Persons of Scientific and Technological Research Merits, Commendation by Minister of Education, Culture, Sports, Science and Technology, Japan
2010	OSA Fellow Award, The Optical Society (OSA)
2012	SPIE Fellow Award, The International Society for Optical Engineering (SPIE)
2014	IEEE Fellow Award, The Institute of Electrical and Electronics Engineers (IEEE)
2018	IAPLE (The International Academy of Photonics and Laser Engineering) Fellow
2019	LSJ (The Laser Society of Japan) Fellow

Member

Program Manager
  SANO, Yuji
Visiting Professor
  KAWASE, Kodo
Visiting Associate Professor
  YOSHIDA, Mitsuhiro
Post-Doctoral Fellow
  TAKEYA, Kei
  ISHIZUKI, Hideki
  SATO, Yoichi
  ZHENG, Lihe*
  YAHIA, Vincent
  LIM, Hwanhong
Research Fellow
  KAUSAS, Arvydas
Technical Fellow
  MATSUDA, Miho
  KOBAYASHI, Jun
Secretary
  ONO, Yoko
  INAGAKI, Yayoi

Keywords Solid-State Lasers, Nonlinear Optics, Micro Solid-State Photonics

"Micro Solid-State Photonics" based on the micro domain structure and boundary controlled materials, opens new horizon in the laser science. The engineered materials of micro and/or microchip solid-state, ceramic and single-crystal, lasers can provide excellent spatial mode quality and narrow linewidths with enough power. High-brightness nature of these lasers has allowed efficient wavelength extension by nonlinear frequency conversion: The world first laser ignited car, highly efficiency broad frequency conversions from the wavelength of 118nm VUV until 300–500µm THz waves, and so on. In addition, the quasi phase matching (QPM) is an attractive technique for compensating phase velocity dispersion in frequency conversion. Lately, we propose a new architecture to realize a monolithic multi-disk laser by the surface activated bonding (SAB). This multiple thin-disk or chip gain medium for distributed face cooling (DFC) structure can manage the high-power and high-field laser with high-gain compact system. Besides, QPM-structured crystal quartz constructed by multi-plate stacking could be promising as a high-power and reliable VUV frequency conversion devices. These downsized and modularized **tiny integrated lasers** (TILA) promise the extremely high-brightness lasers to open up the new science, such as laser driven electron accelerator toward table-top XFEL, and innovation by the compact power laser (Figure 1).

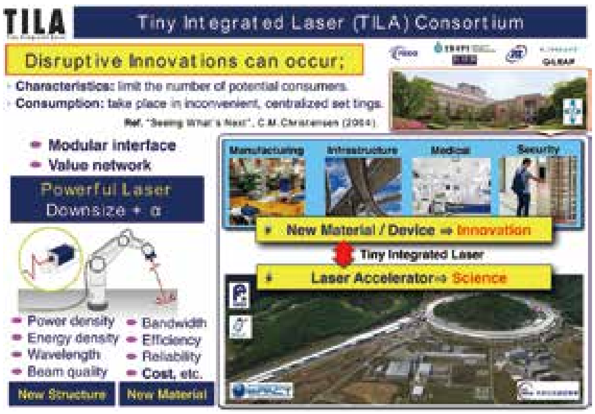


Figure 1. TILA consortium toward "Laser Science and Innovation" by micro solid-state photonics.

Selected Publications

- T. Taira *et al.*, *Opt. Lett.* **16**, 1955 (1991).
- T. Taira *et al.*, *IEEE J. Sel. Top. Quantum Electron.* **3**, 100 (1997).
- T. Taira, *IEEE J. Sel. Top. Quantum Electron.* **13**, 798 (2007).
- T. Taira, *Opt. Mater. Express* **1**, 1040 (2011).
- Y. Sato *et al.*, *Sci. Rep.* **7**, 10732 (2017).
- H. Sakai *et al.*, *Opt. Express* **16**, 19891 (2008).
- M. Tsunekane *et al.*, *IEEE J. Quantum Electron.* **46**, 277 (2010).
- T. Taira *et al.*, *The 1st Laser Ignition Conference '13, OPIC '13, Yokohama, April 23-26*, LIC3-1 (2013).
- R. Bhandari *et al.*, *Opt. Express* **21**, 28849 (2013).
- S. Hayashi *et al.*, *Sci. Rep.* **4**, 5045 (2014).
- L. Zheng *et al.*, *Opt. Mater. Express* **7**, 3214 (2017).
- H. Ishizuki *et al.*, *Opt. Mater. Express* **8**, 1259 (2018).
- N. H. Matlis *et al.*, *Nucl. Instrum. Methods Phys. Res., Sect. A* **909**, 27 (2018).
- S.W. Jolly *et al.*, *Nat. Commun.* **10**, 1 (2019).

1. Polarity Inversion of Crystal Quartz Using a Quasi-Phase Matching Stamp[1)]

Stress-induced polarity inversion of crystal quartz using a quasi-phase matching (QPM) stamp is proposed for a QPM frequency conversion quartz device (Figure 2). Fabrication of QPM structure in x-cut quartz plate could be realized using the periodically patterned QPM stamp. Also, second-harmonic 532 nm generation with 16.8 kW peak intensity was demonstrated using a QPM quartz device with QPM period of 124 μm (3rd-order QPM) to confirm its polarity-inverted structure (Figure 3).

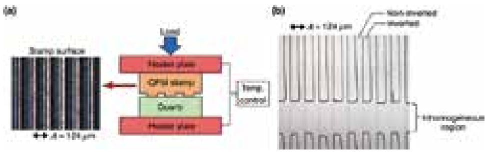


Figure 2. (a) Set up for the QPM stamp method, (b) Etched periodic pattern in *x*-cut plate.

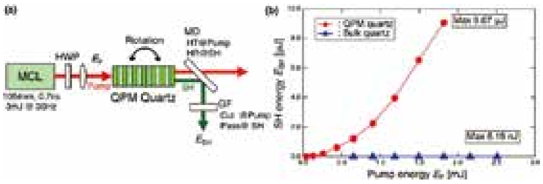


Figure 3. (a) Set up for SHG experiment, (b) SHG characteristics using a QPM quartz.

2. High Peak-Power Near-MW Laser Pulses by Third Harmonic Generation at 355 nm in $Ca_5(BO_3)_3F$ Nonlinear Single Crystals[2)]

In this work, the performance of $Ca_5(BO_3)_3F$ (CBF) single crystals (Figure 4) was investigated for the third harmonic generation at 355 nm. A high energy conversion efficiency of 16.9% at 355 nm was reached using a two-conversion-stage setup. First, using a high peak power, passively Q-switched Nd^{3+}:YAG/Cr^{4+}:YAG microlaser based gain aperture in micro-MOPA, the second harmonic at 532 nm was achieved with lithium triborate (LBO) crystal, reaching 1.35 MW peak power. On a second step, laser pulses at 355 nm were generated using a 5 mm-long CBF crystal growth by TSSG method with energy, pulse duration and peak power of 479 μJ, 568 ps and 0.843 MW, respectively (Figure 5). These results are currently the highest reported for CBF material.

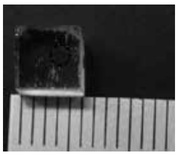


Figure 4. $Ca(BO_3)_3F$ crystal growth by TSSG method using 20 wt% LiF flux.

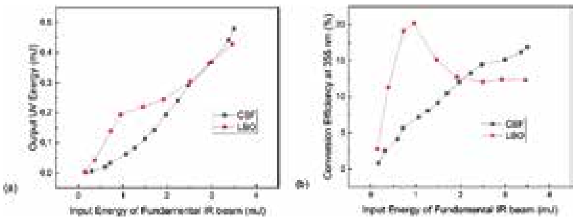


Figure 5. Experimental data on THG for uncoated CBF crystal and comparison with LBO crystal (anti-reflection coating) in terms of output UV energy (a) and of conversion efficiency (b).

3. Remote Laser Analysis Technique in Harsh Environment[3,4)]

In this study, a compact fiber-optic laser-induced breakdown spectroscopy (LIBS) system was developed using a microchip laser (MCL) with a monolithic Nd:YAG/Cr:YAG composite ceramic, for remote analysis of hazardous environments, such as nuclear reactor cores (Figure 6). Short duration laser pulses exhibiting a near-Gaussian beam profile were obtained. The output properties of the laser, such as pulse energy, repetition rate, temporal shape, and beam profile, were measured in view of their applicability to LIBS analysis and were found suitable for the purpose of this research (Figure 7). Spectra of zirconium metal were obtained, and signal intensity was further enhanced by applying multi-burst mode irradiation to the target. The results of this study reveal that the fiber-optic microchip-laser induced breakdown spectroscopy system is advantageous for efficient remote analysis of hazardous environments and is suitable for analyzing the inside of nuclear reactor cores.

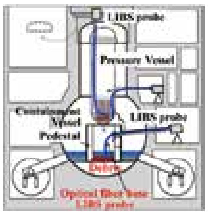


Figure 6. Concept of remote laser analysis technique (LIBS) in harsh environment, such as nuclear reactor cores of Fukushima.

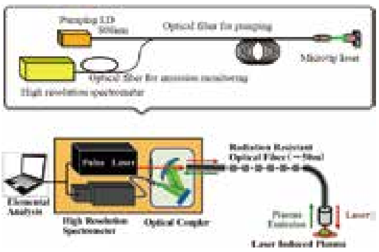


Figure 7. Instead of high power laser fiber delivering system, we have developed a fiber-optic microchip-laser induced breakdown spectroscopy system for efficient remote analysis of hazardous environments.

References

1) H. Ishizuki and T. Taira, *Opt. Express* **28**, 6505 (2020).
2) F. Cassouret, A. Kausas, V. Yahia, G. Aka, P. Loiseau and T. Taira, *Opt. Express* **28**, 10524 (2020). DOI: 10.1364/OE.384281
3) K. Tamura, H. Ohba, M. Saeki, T. Taguchi, H. H. Lim, T. Taira and I. Wakaida, *J. Nucl. Sci. Technol.* **57(10)**, 1189–1198 (2020). DOI: 10.1080/00223131.2020.1776648
4) H. Ohba, I. Wakaida and T. Taira., *ATOMOΣ (The Atomic Energy Society of Japan)*, **62(5)**, 263 (2020).

* Present Address; Yunnan University

RESEARCH FACILITIES

The Institute includes four research facilities, UVSOR Synchrotron Facility, Instrument Center, Equipment Development Center, and Research Center for Computational Science (Okazaki Research Facilities).

UVSOR Synchrotron Facility

KERA, Satoshi	Director, Professor
KATOH, Masahiro	Project Professor
TANAKA, Kiyohisa	Associate Professor
TAIRA, Yoshitaka	Associate Professor
MATSUI, Fumihiko	Senior Researcher
IWAYAMA, Hiroshi	Assistant Professor
OHIGASHI, Takuji	Assistant Professor
IDETA, Shin-ichiro	Assistant Professor
FUJIMOTO, Masaki	Assistant Professor
MATSUDA, Hiroyuki	Post-Doctoral Fellow
SALEHI, Elham	Post-Doctoral Fellow
HAYASHI, Kenji	Technical Associate
NAKAMURA, Eiken	Technical Assosiate
YAMAZAKI, Jun-ichiro	Technical Associate
KONDO, Naonori	Technical Associate
SAKAI, Masahiro	Technical Associate
TESHIMA, Fumitsuna	Technical Associate
YANO, Takayuki	Technical Associate
MAKITA,Seiji	Technical Associate
YUZAWA, Hayato	Technical Associate
OKANO, Yasuaki	Technical Associate
HORIGOME, Toshio	Specially Appointed Technical Associate
MINAKUCHI, Aki	Technical Fellow
INAGAKI, Itsuko	Secretary
ISHIHARA, Mayumi	Secretary

Outline of the UVSOR Synchrotron Facility

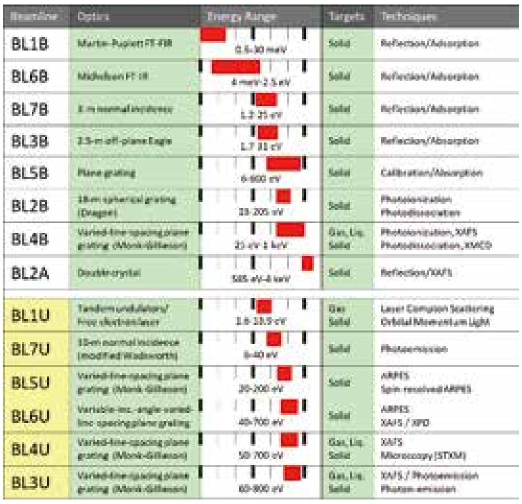
Since the first light in 1983, the UVSOR Synchrotron Facility has been successfully operated as one of the major synchrotron light sources in Japan. After the major upgrade of accelerators in 2003, UVSOR Synchrotron was renamed to UVSOR-II Synchrotron and became one of the world's brightest low energy synchrotron light sources. In 2012, it was upgraded again and has been renamed to be UVSOR-III Synchrotron. The brightness of the electron beam was increased further. Today, six undulators are installed in total, and the storage ring, that is approximately 53 meters in circumference, is regularly operated in the top-up mode, in which the electron beam current is kept constant, irrespective of multi bunches or single bunch.

The UVSOR accelerator complex consists of a 15 MeV injector LINAC, a 0.75 GeV booster synchrotron, and a 0.75 GeV storage ring. The magnet lattice of the storage ring consists of four extended double-bend cells with distributed dispersion function. The storage ring is normally operated under multi-bunch mode with partial filling. The single bunch top-up operation for time-resolved measurements or low current measurements is also conducted for two weeks per year.

Six undulators and eight bending magnets provide synchrotron radiation (SR). The bending magnet, its radius of 2.2 m, produces SR with the critical energy of 425 eV. There are eight bending magnet beamlines (Table. 1). Three of the six undulators are in- vacuum soft X-ray (SX) linear-polarized undulators (BL3U, BL4U, and BL6U) and the other three are vacuum/extreme ultraviolet (VUV/XUV or EUV) circular-polarized undulators (BL1U, BL5U, and BL7U). In total, fourteen beamlines are now operating. Two beamlines, BL1U and BL6U, are so-called "in-house beamlines," which are dedicated to strategic projects conducted by internal IMS groups in tight collaboration with domestic and foreign scientists. Other twelve beamlines are so-called "public beamlines," which are open to scientists from universities, governmental research institutes, public and private enterprises, and also to overseas scientists. Since 2018, BL1U is partly opened for using as public beamline.

From the viewpoint of photon energies, we have one SX station equipped with a double-crystal monochromator, seven SX stations with a grazing incidence monochromator, three VUV stations with a normal incidence monochromator, two IR/THz stations equipped with Fourier transform interferometers and one beamline for light source development without any monochromators.

Table 1. List of beamlines at UVSOR-III Synchrotron.



Beamline	Optics	Energy Range	Targets	Techniques
BL1B	Martin-Puplett FT-FIR	0.5-30 meV	Solid	Reflection/Adsorption
BL6B	Michelson FT-IR	4 meV-2.5 eV	Solid	Reflection/Adsorption
BL7B	3-m normal incidence	1.2-25 eV	Solid	Reflection/Adsorption
BL3B	2.5-m off-plane Eagle	1.7-31 eV	Solid	Reflection/Absorption
BL5B	Plane grating	6-600 eV	Solid	Calibration/Absorption
BL2B	18-m spherical grating (Dragon)	23-205 eV	Solid	Photoionization Photodissociation
BL4B	Varied-line-spacing plane grating (Monk-Gillieson)	25 eV-1 keV	Gas, Liq. Solid	Photoionization, XAFS Photodissociation, XMCD
BL2A	Double-crystal	585 eV-4 keV	Solid	Reflection/XAFS
BL1U	Tandem undulators/ Free electron laser	1.6-13.9 eV	Gas Solid	Laser Compton Scattering Orbital Momentum Light
BL7U	10-m normal incidence (modified Wadsworth)	6-40 eV	Solid	Photoemission
BL5U	Varied-line-spacing plane grating (Monk-Gillieson)	20-200 eV	Solid	ARPES Spin-resolved ARPES
BL6U	Variable-inc.-angle varied-line-spacing plane grating	40-700 eV	Solid	ARPES XAFS / XPD
BL4U	Varied-line-spacing plane grating (Monk-Gillieson)	50-700 eV	Gas, Liq. Solid	XAFS Microscopy (STXM)
BL3U	Varied-line-spacing plane grating (Monk-Gillieson)	60-800 eV	Gas, Liq. Solid	XAFS / Photoemission Photon emission

Inter-University and International Collaboration Programs

A variety of molecular science and related subjects have been carried out at UVSOR Synchrotron Facility by IMS and external/overseas researchers. The number of visiting researchers per year tops > 1200, whose come from > 60 different institutes. International collaborations are also pursued actively, and the number of visiting foreign researchers reaches ~70. UVSOR-III Synchrotron invites new/continuing research proposals twice a year. The proposals both for academic and public research (charge-free) and for private enterprises (charged) are acceptable. COVID-19 issue has a serious impact on user activity. The proposals of 63 % have been achieved so far. The fruits of the research activities using UVSOR-III Synchrotron are published as the UVSOR ACTIVITY REPORT annually.

Recent Developments

The UVSOR accelerators have been operated for 37 years. We have been upgrading and replacing the machine components, such as magnet power supplies or RF power amplifiers, to continue the stable operation. In these years, troubles occurred on some core components, such as the vacuum chambers and the magnets. We are carefully planning their replacements with short shutdown periods and under the limitation of the facility budget.

On the other hand, we are also putting effort into setting up state-of-the-art experimental stations that takes advantage of our unique beamline performance. A new photoelectron momentum microscope (PMM) station for 3D momentum-resolved photoelectron spectroscopy is constructed at beamline BL6U.1) The PMM, a combination of projection-type electron analyzer and photoelectron microscope, simultaneously realizes a microscope function for magnifying and observing minute parts of complicated- structured samples with element selectivity and a spectroscopy function for visualizing electron behavior (momentum) that determines the electronic properties of a functional materials. Microscopy with a spatial resolution of 50 nm and photoelectron spectroscopy (field of view: 2 μm) with energy/momentum resolutions of 20 meV / 0.01 Å^{-1} at 9 K are successfully demonstrated (Figure 1). The momentum microscope opens the door to direct observation of the Fermi surface and band structure of μm-sized targets such as surface atomic sites, thin films and interfaces, molecular adsorbates, and polycrystals, which was difficult with conventional electron energy analyzers.

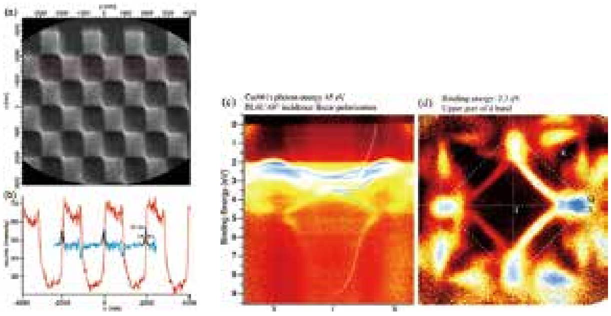


Figure 1. (a) A gold checkerboard pattern image obtained using Hg lamp. (b) Intensity profile indicating the spatial resolution of 50 nm was achieved.1) (c) Cu valence band dispersion and iso-energy cross section.

Research Highlights

One of the highlights of the UVSOR research activities this year is the discovery of the ability of synchrotron radiation to perform coherent control.2,3) Coherent control is a method to manipulate the populations and pathways in matters by light and is currently one of the most attractive research areas in optical physics and photochemistry. Lasers have been considered as unique light source enabling one to perform coherent control. Synchrotron radiation is usually considered as being of poor temporal coherence, therefore nobody thought that it has a hidden capability of coherent control. However, researchers have demonstrated the capability of synchrotron radiation on the coherent control using the double undulator system which is capable of producing light pulses with tailored waveform.

Figure 2 shows the schematic view of the double undulator system and the result of population control in the photoexcitation of helium atoms. The double undulator generated pairs of radiation wave packets in the extreme ultraviolet wavelength. The duration of each wave packet pair was a few femtoseconds and the time delay between them can be adjusted with attosecond precision. The individual excited states can be controlled by adjusting the interference between the electron wave packets produced in the atomic system. Moreover, the researchers succeeded also in controlling the shape and orientation of the electron cloud in a helium atom, formed as a coherent superposition state, by tuning the time delay between the circularly polarized radiation wave packets on the attosecond level.

In contrast to standard laser technology, there is no technical restriction on the extension of this method to shorter wavelengths. This new capability of synchrotron radiation not only advance the frontier of coherent control technology, but may also open up new applications in the development of functional materials and electronic devices in the future.

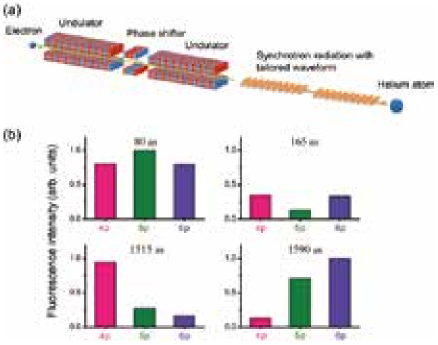


Figure 2. (a) Double undulator and produced pairs of radiation wave packets with tailored waveform. (b) Populations of 1snp states at four different time delays between the radiation wave packets.

References

1) F. Matsui *et al.*, *Jpn. J. Appl. Phys.* **59**, 067001 (2020).
2) Y. Hikosaka *et al.*, *Nat. Commun.* **10**, 4988 (2019).
3) T. Kaneyasu *et al.*, *Phys. Rev. Lett.* **123**, 233401 (2019).

Instrument Center

YOKOYAMA, Toshihiko	Director, Professor
SUZUKI, Toshiyasu	Team Leader
NAKAMURA, Toshikazu	Team Leader
MINATO, Taketoshi	Senior Researcher
TAKAYAMA, Takashi	Technical Associate
FUJIWARA, Motoyasu	Technical Associate
OKANO, Yoshinori	Technical Associate
MIZUKAWA, Tetsunori	Technical Associate
UEDA, Tadashi	Technical Associate
ASADA, Mizue	Technical Associate
URUICHI, Mikio	Technical Associate
OHARA, Mika	Project Manager
ISHIYAMA, Osamu	Project Manager
HASEGAWA, Hisashi	Project Manager
IKI, Shinako	Technical Fellow
NAGAO, Haruyo	Technical Fellow
FUJIKAWA, Kiyoe	Technical Fellow
TOYAMA, Aya	Technical Fellow
FUNAKI, Yumiko	Secretary
HYODO, Yumiko	Secretary
TOYAMA, Yu	Secretary
SHIBATA, Yuka	Secretary
ISHIKAWA, Azusa	Secretary
KATO, Kaori	Secretary
KUMITA, Machiko	Secretary
UCHIDA, Mariko	Secretary

Instrument Center was organized in April of 2007 by integrating the general-purpose and state-of-the-art facilities of Research Center for Molecular Scale Nanoscience and Laser Research Center for Molecular Science. The mission of Instrument Center is to support the in-house and external researchers in the field of molecular science, who intend to conduct their researches by utilizing general-purpose and state-of-the-art instruments. The staffs of Instrument Center maintain the best conditions of the machines, and provide consultation for how to use them. The main instruments the Center now maintains in Yamate campus are: Nuclear magnetic resonance (NMR) spectrometers (JNM-ECA 600 for solutions, JNM-ECS400 for solutions and Bruker AVANCE800 Cryoprobe for solutions), matrix assisted laser desorption/ionization time-of-flight (MALDI TOF) mass spectrometer (microflex LRF, Bruker Daltonics), powder X-ray diffractometer (Rigaku RINT-Ultima III), circular dichroism (CD) spectrometer (JASCO JW-720WI), differential scanning calorimeter (MicroCal VP-DSC), isothermal titration calorimeter (MicroCal iTC200), solid-state calorimeter (Rigaku DSC8231/TG-DTA8122), scanning electron microscope (SEM; JEOL JEM-6700F) and elemental analyzer (J-Science Lab Micro Corder JM10). In the Myodaiji campus, the following instruments are installed: Electron spin resonance (ESR) spectrometers (Bruker E680, E500, EMX Plus, ns pulsed laser for time resolved experiments), NMR spectrometer (Bruker AVANCE600 for solids), superconducting quantum interference devices (SQUID; Quantum Design MPMS-7 and MPMS-XL7), solution X-ray diffractometer (Rigaku NANO-Viewer), single-crystal X-ray diffractometers (Rigaku Mercury CCD-1, CCD-2, RAXIS IV, and Rigaku HyPix-AFC), molecular structure analysis using crystalline sponge method (Rigaku XtaLAB P200/PILATUS 200K, Rigaku SuperNova), operando multipurpose x-ray diffraction for powder and thin films (Panalytical Empyrean), thermal analysis instruments (Rigaku DSC8231/TG-DTA8122), fluorescence spectrometer (SPEX Fluorolog), X-ray fluorescence spectrometer (JEOL JSX-3400RII), UV-VIS-NIR spectrometer (Shimadzu UV-3600Plus), Raman microscope (Renishaw INVIA REFLEX 532), picosecond tunable laser system (Spectra Physics Tsunami/Quantronix Titan/Light Conversion TOPAS), low vacuum analytical SEM (Hitachi SU6600), electron spectrometers for chemical analysis (ESCA) (Omicron EA-125), angle resolved ultraviolet photoelectron spectroscopy (ARUPS) for functional band structures (VG-Scienta DA30), and FTIR spectrometer (Bruker IFS 66v/S). Recently, new equipment of high-performance *operando* scanning probe microscopes (Bruker Dimension XR Icon Nanoelectrical and Nanoelectrochemical, two sets) was just installed. In the fiscal year of 2019, Instrument Center accepted 102 applications from outside and the total user time amounted 2,424 days for outside and 610 days for in-house with 29 equipments. Instrument Center also maintains helium liquefiers in the both campus and provides liquid helium to users (48,827 L/year). Liquid nitrogen is also provided as general coolants used in many laboratories in the Institute (31,751 L/year). Instrument Center also organizes the Inter-University Network for Common Utilization of Research Equipments and the Molecule and Material Synthesis Platform in the Nanotechnology Platform Program supported by Ministry of Education, Culture, Sports, Science and Technology. These special programs are described in the other chapter of the booklet.

Equipment Development Center

YAMAMOTO, Hiroshi	Director
MIZUTANI, Nobuo	Technical Associate
AOYAMA, Masaki	Technical Associate
KONDO, Takuhiko	Technical Associate
TOYODA, Tomonori	Technical Associate
TAKADA, Noriko	Technical Associate
KIMURA, Sachiyo	Technical Associate
KIKUCHI, Takuro	Technical Associate
KIMURA, Kazunori	Technical Associate
MATSUO, Junichi	Technical Associate
SAWADA, Toshihiro	Technical Fellow
YOSHIDA, Hisashi	Technical Fellow
ISHIKAWA, Akiko	Technical Fellow
URANO, Hiroko	Secretary

Research and development of novel instruments demanded in the forefront of molecular science, including their design and fabrication, are the missions of this center. Technical staffs in the two work sections, mechanics and electronics, are engaged in developing state-of-the-art experimental instruments in collaboration with scientists. We expanded our service to other universities and research institutes since 2005, to contribute to the molecular science community and to improve the technology level of the center staffs. A few selected examples of our recent developments are described below.

Production of Detachable Models by 3D Printers

We are providing experimental tools and molecular/cellular models produced by 3D printers that use FDM (Fused Deposition Modeling), stereolithography, or binder jetting methods. The models are tools that are used by researchers to imagine molecular packing, cellular motion, *etc.* by holding them in hand. Since many researchers request to make the models detachable into multiple pieces, we have developed such models by using small magnets. 3D shape data is separated by Boolean processing so that there is no overlap between parts, and the magnets are embedded to allow each parts be reversibly detached.

A leaf primordium model in which each cell can be separated is shown in Figure 1. A Photosystem II protein model in which each subunit can be detached is shown in Figure 2.

Figure 1. Leaf Primordium model.

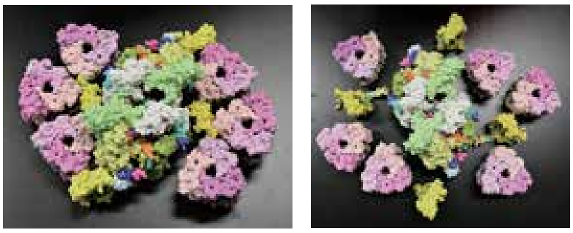


Figure 2. Photosystem II model.

NIM module Power Supply Adaptor

In experiments using a synchrotron light source or a laser, many NIM (Nuclear Instrument Modules) standard modules are used. Powers of NIM modules are supplied from BIN power supply which is expensive and heavy, even when one wishes only to put one or two NIM modules near a detector, for example.

We have developed a cheap and light-weight NIM module Power Supply Adaptor (Figure 3) which can provide power to up to two NIM modules using voltage regulator (Texas Instruments LM2941S/NOPB and LM2991S/NOPB) and AC power adaptors. It connects to NIM modules via cables and can supply maximum 1A at plus and minus 6, 12 and 24V d.c. from assigned connector pins based on the NIM standard. When it detects overcurrent, it protects own circuit and NIM modules by shutting off resettable fuses on circuit board.

Figure 3. Inside of a NIM module Power Supply Adaptor.

Award

KONDO, Takuhiko; The Chemical Society of Japan Award for Technical Achievements for 2019.

Research Center for Computational Science (Okazaki Research Facilities)

EHARA, Masahiro	Director, Professor
SAITO, Shinji	Professor
OKUMURA, Hisashi	Associate Professor
OONO, Hitoshi	Associate Professor
ISHIDA, Tateki	Assistant Professor
UCHIYAMA, Ikuo	Assistant Professor
IWAHASHI, Kensuke	Technical Associate
MIZUTANI, Fumiyasu	Technical Associate
NAITO, Shigeki	Technical Associate
SAWA, Masataka	Technical Associate
MATSUO, Jun-ichi	Technical Associate
NAGAYA, Takakazu	Technical Associate
KAMIYA, Motoshi	Technical Associate
KINOSHITA, Takamasa	Technical Associate
UNO, Akiko	Technical Fellow
ISHIHARA, Mayumi	Secretary
KONDO, Naoko	Secretary
KONDO, Noriko	Secretary

Research Center for Computational Science provides state-of-the-art computational resources to academic researchers in molecular science and related fields, *e.g.* solid state physics, biophysics, and physiology. Our systems consist of NEC LX (406Rh-2, 110-Rh1, 108Th-4G; since Oct. 2017). The NEC LX 406Rh-2 and 110-Rh1 combined system, named “Molecular Simulator,” is ranked 261st position in the TOP500 supercomputer list in June 2020. These massive computer resources have been used for various kinds of large-scale calculations, for example accurate electronic structure calculations of molecular systems and conformation searches using non-Boltzmann ensemble methods. We also provide a number of application programs to the users: Gaussian, GAMESS, Molpro, AMBER, Gromacs, and so on. The supercomputer systems had been used by 1,048 researchers from 268 groups in fiscal year 2019. Some of the computational resources are provided to the following projects: Post-K Supercomputer Priority Issues 5 and 7, Post-K Exploratory Challenge: Challenge of Basic Science—Exploring Extremes through Multi-Physics and Multi-Scale Simulations, Professional development Consortium for Computational Materials Scientists (PCoMS), and Elementary Strategy Initiative to Form a Core Research Center.

For fostering young generation, we organize the schools of quantum chemistry and molecular dynamics simulation every year. We also organize the RCCS supercomputer workshop focusing on the new trends of computational chemistry for the purpose of the research exchange and human resource development.

We also offer Quantum Chemistry Literature Database (QCLDB; http://qcldb2.ims.ac.jp/), Force Constant Database (FCDB; http://fcdb.ims.ac.jp/), and Segmented Gaussian Basis Set (SGBS; http://sapporo.center.ims.ac.jp/sapporo/) services. The latest release, QCLDB II Release 2016, containing 139,657 data of quantum chemical studies is available for the registered users. FCDB provides force constants of molecules collected from literature. SGBS service provides basis sets for atoms which efficiently incorporate valence and core electron correlations (also known as Sapporo basis sets) in various quantum chemistry package formats. Further details about the hardware, software, and the other services are available on our website (English: https://ccportal.ims.ac.jp/en/, Japanese: https://ccportal.ims.ac.jp/).

The center is jointly managed with National Institute for Physiological Sciences and National Institute for Basic Biology (both in the same campus).

Figure 1. NEC LX.

Safety Office

TANAKA, Shoji	Director
TOMURA, Masaaki	Research Assistant
SHIGEMASA, Eiji	Technical Associate
UEDA, Tadashi	Technical Associate
TAKAYAMA, Takashi	Technical Associate
SAKAI, Masahiro	Technical Associate
MAKITA, Seiji	Technical Associate
MIZUTANI, Nobuo	Technical Associate
TESHIMA, Fumitsuna	Technical Associate
TSURUTA, Yumiko	Secretary
KAMO, Kyoko	Secretary
ASAKURA, Yukiko	Secretary

The Safety Office was established in April 2004. The mission of the Office is to play a principal role in the institute to secure the safety and health of the staffs by achieving a comfortable workplace environment, and improvement of the working conditions. In concrete terms, it carries out planning, work instructions, fact-findings, and other services for safety and health in the institute. The Office is composed of the following staffs: The Director of the Office, Safety-and-Health Administrators, Safety Office Personnel, Operational Chiefs and other staff members appointed by the Director General.

The Safety-and-Health Administrators patrol the laboratories in the institute once every week, and check whether the laboratory condition is kept sufficiently safe and comfortable to conduct researches. The Office also edits the safety manuals and gives safety training courses, for Japanese and foreign researchers.

Research Enhancement Strategy Office

OKAMOTO, Hiromi	Head
YAMAMOTO, Hiroshi	Professor (in charge of Foreign Affairs)
AKIYAMA, Shuji	Professor (in charge of Personnel Affairs)
IINO, Ryota	Professor (in charge of Public Affairs)
ISHIZAKI, Akihito	Professor (in charge of Facilities/Buildings and Foreign Affairs)
KATAYANAGI, Hideki	Research Assistant (in charge of Public Affairs)
SHIGEMASA, Eiji	Technical Associate (in charge of General Affairs)
NAKAMURA, Toshikazu	Team Leader, Instrument Center
FUKUI, Yutaka	URA (Administrative Associate, Assistant to Head)
HARADA, Miyuki	URA (Technical Associate)
KAMETAKA, Ai	URA (Administrative Associate)
NAGASONO, Hisayo	URA (Administrative Associate)
NAKAMURA, Rie	Technical Fellow
YAZAKI, Toshiko	Technical Fellow
OHTA, Minori	Secretary
KAMIYA, Miho	Secretary
SUZUKI, Satomi	Secretary
SUGIYAMA, Kayoko	Secretary
SHIMODE, Ayako	Secretary
ISHIHARA, Mayumi	Secretary

In 2013, Research Enhancement Strategy Office was established in each research institute in NINS by support of the MEXT University Research Enhancement Project of 10 years 2013 to 2023. In this office, university research administrators (URA) and supporting staff members realize several strategic plans for the enhancement of international and inter-university collaborations, public relations, and research activities of young, female, and foreign scientists in collaboration with Head Office in NINS.

Technical Division

SHIGEMASA, Eiji	Head
UCHIYAMA, Koichi	Technical Associate
TANAKA, Kei	Secretary

Secretary for Director General

NOGAWA, Kyoko	Secretary

Information Office

TSURUTA, Yumiko	Secretary
KAMO, Kyoko	Secretary
ASAKURA, Yukiko	Secretary

The Technical Division was established in 1975 as an organization of technical staffs who technically support in-house and outside scientists. Each technical staff with professional skills belongs to individual research facilities or centers such as the UVSOR Synchrotron Facility, the Research Center for Computational Science, the Instrument Center, the Equipment Development Center, or the Center for Mesoscopic Sciences.

In addition, several members belonging to the Technical Division support administrative activities in IMS by managing the Safety Office, the Public Affairs Office, the Archives, and the Information Office.

The annual meeting for technical staff of research institutes and universities in Japan, was organized in 1975 and since then it has been regularly held every year. We aim toward higher technology and knowledge exchange concerning various technical problems related to our technology and engineering. Our best endeavors have been, and will be made, to promote the advanced research of IMS.

Special Research Projects

IMS has special research projects supported by national funds. Three projects in progress are:

(a) MEXT Nanotechnology Platform Program
Platform of Molecule and Material Synthesis

(b) Inter-University Network for Efficient Utilization of Research Equipments

These two projects are being carried out with close collaboration between research divisions and facilities. Collaborations from outside also make important contributions. Research fellows join these projects.

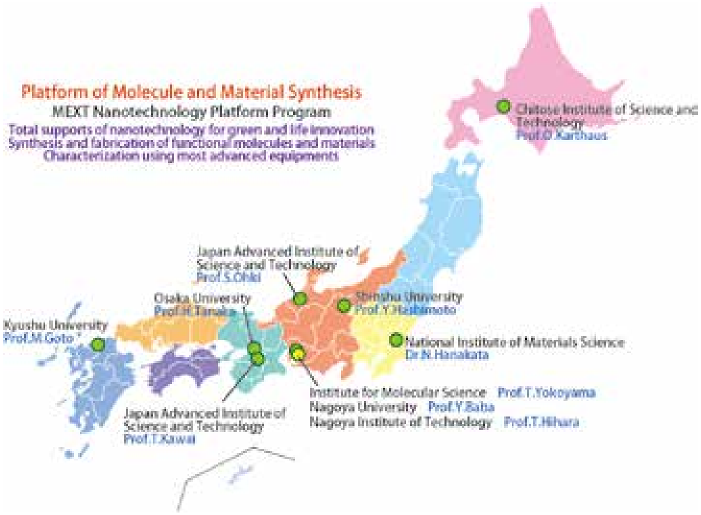
(a) MEXT Nanotechnology Platform Program Platform of Molecule and Material Synthesis

Since July 2012, Nanotechnology Platform Program supported by Ministry of Education, Culture, Sports, Science and Technology (MEXT) has been conducted in order to promote public usage of various nanotechnology facilities. This program will continue until March 2022 and consists of three platforms of nanostructure analysis, nanoprocessing, and molecule and material synthesis, together with the management center of the platforms. Each platform consists of about ten organizations all over Japan. IMS conducts a representative core organization of the Molecule and Material Synthesis Platform. All the organizations in this platform are shown in Figure. In this platform, to promote green and life innovation researches using nanotechnology related techniques not only for universities and government institutes but also for private companies, we will open various kinds of our facilities with total supports including molecular synthesis, materials fabrications, characterization, data analysis and scientific discussion. We will encourage applications not only to each element, but to combined usage of several supporting elements for biotechnology and green chemistry. In IMS, the number of accepted proposals in FY2019 amounted 155 (141 non-proprietary and 12 proprietary proposals, excluding inhouse applications from IMS) and the total number of days used for the supports is 2949 (2834 days for non-proprietary proposals and 116 days for proprietary ones).

List of Supports in IMS (FY2019)

Supporting Element		Responsible Persons	Charging Persons
Platform Management		T. Yokoyama	M. Ohara, Y. Toyama, Y. Shibata
Organization Management in IMS			Y. Hyodo, Y. Funaki
UVSOR Synchrotron Radiation	X-Ray Magnetic Circular Dichroism	T. Yokoyama	T. Koitaya, K. Yamamoto, O. Ishiyama
Microstructure Fabrication	Maskless Lithography with Step Gauge	H. Yamamoto	M. Aoyama, N. Takada, T. Kondo, S. Kimura, T. Kikuchi
	3D Optical Surface Profiler		
Equipment Development	Machine Shop		M. Aoyama, T. Kondo, T. Toyota, F. Mizutani, J. Mathuo
Electron Microscopy	Field Emission Scanning Electron Microscopy	T. Yokoyama	O. Ishiyama, A. Toyama
	Low Vacuum Analytical Scanning Electron Microscopy		
	Field Emission Transmission Electron Microscope		S. Iki, T. Ueda, M. Uruichi
X-rays	Single Crystal X-Ray Diffractometer		M. Fujiwara
	Low Temperature Single Crystal X-Ray Diffractometer for Microcrystals		Y. Okano
	Molecular Structure Analysis using Crystalline Sponge Method		M. Fujita, T. Mitsuhashi
	Powder X-Ray Diffractometer		M. Fujiwara
	X-Ray Fluorescence Analysis		T. Ueda
	Small Angle X-Ray Scattering for Solutions	S. Akiyama	A. Mukaiyama

Electron Spectroscopy	Electron Spectroscopy for Chemical Analysis	T. Yokoyama	S. Iki
	Angle Resolved Ultraviolet Photoelectron Spectroscopy for Functional Band Structures	S. Kera, K. Tanaka	S. Ideta
Electron Spin Resonance	Pulsed High Field ESR	T. Yokoyama, T. Nakamura	M. Asada, M. Fujiwara, S. Iki, T. Ueda
	X-Band CW ESR		
	X, Q-Band CW ESR		
SQUID	Superconducting Quantum Interference Device		M. Asada, M. Fujiwara, S. Iki
Thermal Analysis	Differential Scanning Calorimeter (Solutions)	T. Yokoyama	T. Mizukawa, M. Uruichi, H. Nagao
	Isothermal Titration Calorimeter (Solutions)		
	Calorimeter for solids		M. Fujiwara
Mass Spectrometer	Matrix Assisted Laser Desorption/Ionization Time of Flight Mass Spectrometer		T. Mizukawa, M. Uruichi, K. Fujikawa
Spectroscopy	Microscopic Raman Spectroscopy		M. Uruichi
	Fourier Transform Far Infrared Spectroscopy		
	Fluorescence Spectroscopy		T. Ueda
	Ultraviolet & Visible Absorption Spectroscopy		
	Circular Dichroism		T. Mizukawa, M. Uruichi, K. Fujikawa
Lasers	Picosecond Laser		T. Ueda
High Field NMR	800 MHz Solutions, Cryostat Probe	K. Kato	M. Yagi, S. Yanaka, Y. Isono
	600 MHz Solids	K. Nishimura	
	600 MHz Solutions	T. Yokoyama	T. Mizukawa, M. Uruichi, H. Nagao
Functional Molecular Synthesis and Molecular Device Fabrication	Organic Thin Film Solar Cells	M. Hiramoto	S. Izawa
	Organic Field Effect Transistors	H. Yamamoto	M. Suda, D. Hirobe
	Functional Organic Synthesis	N. Momiyama, T. Suzuki	A. Izumiseki, N. Ohtsuka
	Large Scale Quantum Mechanical Calculations	M. Ehara	
	Magnetic Thin Films	T. Yokoyama	T. Koitaya, K.Yamamoto
	Metal Complexes	T. Kusamoto	
	Inorganic Materials	G. Kobayashi	F. Takeiri
	Biomolecule System	S. Akiyama	A. Mukaiyama, Y. Furuike
	Supplementary Apparatus in Instrument Center	T. Yokoyama	



(b) Inter-University Network for Common Utilization of Research Equipments

It is highly important to improve instrumental supporting environments for research and education in the field of science and engineering. Nowadays, advanced research instruments are indispensable for conducting researches and educations with high standard quality. To install such sophisticated instruments, tremendous amount of budgets would be necessary. In 2007, for constructing a national-wide network to provide easy accesses to high-level equipments to researchers and students in universities all over Japan, the five-year project "Functioning of Inter-University Network for Efficient Utilization of Chemical Research Equipments" was launched. The network maintains an internet machine-time reservation and charging system by the help of equipment managers and accounting sections in each university. 72 national universities as well as Institute for Molecular Science (total 73 organizations) all over Japan have been participating in the network. They are grouped into 12 local regions and in each region the regional committee discusses and determines the operation of regional network systems with the hub university chairing. There is no barrier for every user to access to any universities beyond his/her regional group. From 2009, the registered equipments are open to the researchers and students of all the public (prefectural *etc.*) and private universities. Since 2010, the project has been renamed "Inter-University Network for Common Utilization of Research Equipments" still keeping the original strategy and stable functioning. Since 2018, the institutions that provide research facilities are open to public and private universities. Currently, the network is organized by 78 organizations. The number of registered users amounts to 14,000 in 431 universities/institutions/companies covering over 3,800 laboratories in Japan (June, 2020). Network usage reaches about 170,000 times a year, and the number continues to grow. Moreover, we have actively provided various opportunities where technical staffs and users can improve their technical skills and frankly communicate with each other.

Okazaki Conference

(a) The 81st Okazaki Conference
Forefront of Measurement Technologies for Surface Chemistry and Physics in Real-Space, *k*-Space, and Real-Time

(December 2–4, 2019)

Organizers: T. Sugimoto (*IMS*), T. Kumagai (*Fritz-Haber Institute*)

Invited Overseas Speaker: A. Paarmann (*Fritz-Haber Inst.*), A. Mazheika (*Technical Univ. Berlin*), A. Urakawa (*Delft Univ. of Tech.*), C. Kley (*Fritz-Haber Inst.*), H. Freund (*Fritz-Haber Inst.*), H. Ogasawara (*Stanford Linear Accelerator Cent.*), J. Stähler (*Fritz-Haber Inst.*), L. Grill (*Univ. of Graz*), M. Rossi (*Fritz-Haber Inst.*), N. Lin (*Hong Kong Univ. of Sci. and Tech.*), R. Ernstopher (*Fritz-Haber Inst.*), S. Wu (*Fudan Univ.*), T. Kumagai (*Fritz-Haber Inst.*), Y.-P. Chiu (*Natl. Taiwan Univ.*), Y. Tong (*Fritz-Haber Inst.*)

Surface/Interface science has contributed to a wide range of disciplines in heterogeneous catalysis,electrochemistry, and semiconductor science/technology. The development of surface characterization techniques and sophisticated experiments under atomically well-defined conditions played a central role, which have also been one of the driving forces for nanoscience and nanotechnology during the last few decades. The rapid advances of various laser sources, synchrotron facility, high-frequency electronic devices, scanning probe methods, nanoscale fabrication techniques, and computational science bring a new dimension to measurement science and technology, and a combination of different state-of-the-art techniques creates unprecedented measurement techniques for surface physics and chemistry in real-space, *k*-space, and real-time. In addition to the study of model systems, operand measurements have gained increasing attention to elucidate working principles of catalysts and electrochemistry. Low-dimensional materials, hybrid organic/inorganic interfaces, and molecular devices/machines are the scope of emerging measurement techniques. Theory and computational science provide indispensable tools to interpret elementary processes at the atomistic level and also pave the way for highly-efficient data analysis and material design. In the conference, we discuss the latest development of surface characterization techniques and how they can contribute to the innovation in material and energy conversion using heterogeneous catalysts and novel optoelectronic and electrochemical devices.

Joint Studies Programs

As one of the important functions of an inter-university research institute, IMS facilitates joint studies programs for which funds are available to cover the costs of research expenses as well as the travel and accommodation expenses of individuals. Proposals from domestic scientists are reviewed and selected by an interuniversity committee.

(1) Special Projects

(a) Construction of Synthetic Microdomains to Artificially Assemble Biological Polymers on Lipid Membranes Using Metal Complex Lipids

OHTANI, Ryo (*Kyushu Univ.*)
KAWANO, Kenichi (*Kyoto Univ.*)
KINOSHITA, Masanao (*Kyushu Univ.*)
YANAKA, Saeko (*IMS*)
KATO, Koichi (*IMS*)

Cell membranes are nonuniform entities characterized by heterogeneous molecular assemblies that mediate biological processes exemplified by signal transduction. Accumulating evidence has indicated that these microdomains comprise various lipid molecules including glycosphingolipids and cholesterol and serve as molecular platforms where specific biomolecules accumulate to perform sophisticated functions. To gain a deeper understanding of these complex membrane functions, we employed a multilateral approach in an attempt to artificially control membrane properties and their molecular assembly.

In this project, we created and applied *metal complex lipids* for (1) manipulating lipid membrane properties such as curvature and viscosity to construct synthetic domain architectures and (2) controlling assemblies of biological polymers thereon. The metal complex lipid consists of a metal complex moiety as its hydrophilic head and an alkyl chain as its hydrophobic tail. It exhibits different physical properties from those of natural lipid species, which further impacts lipid membrane properties. Through investigation of the influence of the metal complex lipids on phase-transition and molecular-assembling behaviors of both artificial and cell membranes, we successfully constructed an artificial phase separation system with micro-sized rigid domains consisting of metal complexes in living cell membranes. Furthermore, we succeeded in synthesizing a new metal complex lipid which could provide unique fluid–fluid phase separation in lipid membranes. The metal complex lipid not only exhibits such domain formation property but also offers a possibility to hybridize with biomolecules via the click chemistry approach due the head part incorporating an ethynyl substituent. We expect that this metal complex lipid will be applicable to assembling and accumulating biomolecules in lipid membranes, which is now underway.

We held three collaboration meetings in the 2019 to extensively discuss our research progress and future planning. All meetings were held at Yamate 3rd Bilding 2F small meeting room on June 10, September 11, and November 11, 2019. Moreover, collaborating experiments to synthesize the hybrid metal complex lipid with sugar chains were carried out at December 18th to 23rd, 2019 in the Kato lab.

(2) Research Symposia

(From Oct. 2018 to Sep. 2019)

Dates	Theme	Chair
Jul. 10, 2019	Design of Molecular Structure Change and Its Function Control Based on Coordination Chemistry	**KOSHIYAMA, Tomomi** **KUSAMOTO, Tetsuro**
Dec. 29, 2019	Joint Workshop on Molecular Science for Young Researcher: Exploring the Unexplored Field of Molecular Science	**KOMATSUBARA, Wataru** **SUGIMOTO, Toshiki**
Dec. 2– 4, 2019	Forefront of Measurement Technologies for Surface Chemistry and Physics in Real-Space, *k*-Space, and Real-Time	**KUMAGAI, Takashi** **SUGIMOTO, Toshiki**

(3) Numbers of Joint Studies Programs

Categories		Oct. 2019–Mar. 2020		Apr. 2020–Sep. 2020		Total		
		Regular	NanoPlat	Regular	NanoPlat	Regular	NanoPlat	Sum
Special Projects		1		1		2		2
Research Symposia		0		1		1		1
Research Symposia for Young Researchers		1		1		2		2
Cooperative Research		22	39	21	18	43	57	100
Use of Facility	Instrument Center		83		58		141	141
	Equipment Development Center	1	4	0	4	1	8	9
Use of UVSOR Facility		94	2	89	1	183	3	186
Use of Facility Program of the Computer Center						268*		268*

* from April 2019 to March 2020

Collaboration Programs

(1) MOU Partnership Institutions

IMS has concluded academic exchange agreements with overseas institutions.

The agreements encourage

- Exchange of researchers
- Internship of students and postdoctoral fellows
- Joint research workshops
- Joint research laboratories

Institution	Period	Accept*	Send*
The Korean Chemical Society, Physical Chemistry Division [Korea]	2006.12–2022.10	0	0
Institute of Atomic and Molecular Sciences (IAMS) [Taiwan]	2005. 1–2023. 1	8	0
Korea Advanced Institute of Science and Technology (KAIST) [Korea]	2008. 9–2020. 9	0	0
École Nationale Supérieure de Chimie de Paris (ENSCP) [France]	2009.10–2024.10	1	1
Freie Universität Berlin (FUB) [Germany]	2013. 6–2022. 6	3	0
Indian Institute of Science Education and Research Kolkata (IISER Kolkata) [India]	2015.10–2019.10	0	1
Indian Institute of Science (IISc) [India]	2015.10–2019.10	0	1
National Nanotechnology Center, National Science and Technology Development Agency (NANOTEC/NSTDA) [Thailand]	2017.10–2022.10	1	1
Sungkyunkwan University, Department of Chemistry (SKKU) [Korea]	2018. 4–2022. 3	0	0
University of Oulu [Finland]	2018. 5–2021. 5	5	0
National Chiao Tung University [Taiwan]	2018. 6–2023. 5	3	2
Peter Grünberg Institute, Forschungszentrum Jülich GmbH (FZJ) [Germany]	2018.10–2023. 9	0	3
State Key Laboratory of Physical Chemistry of Solid Surfaces (Xiamen University) [China]	2019.12–2024.12	0	10
Indian Institute of Technology Kanpur [India]	2020. 4–2024. 3	0	0

* No. of researchers during the period from Sep. 2019 to Aug. 2020

Academic Exchange Agreement with Overseas Universities/Institutes (SOKENDAI) as follows ;

Institution	Period	Accept*	Send*
Chulalongkorn University, Faculty of Science [Thailand]	2010. 4–2020. 3	1	2
Kasetsart University, Faculty of Science [Thailand]	2011. 3–2021. 4	3	5
University of Malaya, Faculty of Science [Malaysia]	2014. 3–2024.11	2	0
Vidyasirimedhi Institute of Science and Technology [Thailand]	2018. 9–2023. 9	3	0
Friedrich Schiller University Jena [Germany]	2020. 7–2023. 7	0	0

* No. of researchers during the period from Sep. 2019 to Aug. 2020

(2) International and Inter-Institutional Collaboration Symposia

Several international symposia and workshops in molecular science are held in IMS and in Japan. Some workshops are organized with our MOU partners for international collaboration in the MOU partner's country as well as in Japan:

Program	Coordinator	Date	Place
IMS-IAMS Joint Meeting	AKIYAMA, Shuji (IMS) TAKAHASHI, Kaito (IAMS)	2019.9.21	IAMS, Taiwan
IMS-PCOSS Bilateral Symposium	YAMAMOTO, Hiroshi (IMS) REN, Bin (PCOSS)	2019.12.21–24	PCOSS, China
SOKENDAI Asian Winter School "Challenges for New Frontiers in Molecular Science: From Basics to Advanced Researches"	NISHIMURA, Katsuyuki (IMS) MINAMITANI, Emi (IMS)	2020.1.16	IMS
The 2nd International Conference on Materials Research and Innovation (ICMARI)	YAMAMOTO, Hiroshi (IMS) PHONGPHANPHANEE, Saree (KU)	2019.12.16–18	Centara Grand Central Plaza Ladprao, Kasetsart University (KU), Thailand

(3) IMS International Internship Program and SOKENDAI International Lecture & Training Courses

Category	Number of People	
	Overseas	Domestic
IMS International Internship Program (IMS-IIP)	32*	–
SOKENDAI Asian Winter School (2020.1.16)	9†	1

* from Sep. 2019 to Aug. 2020, † include the IMS-IIP students

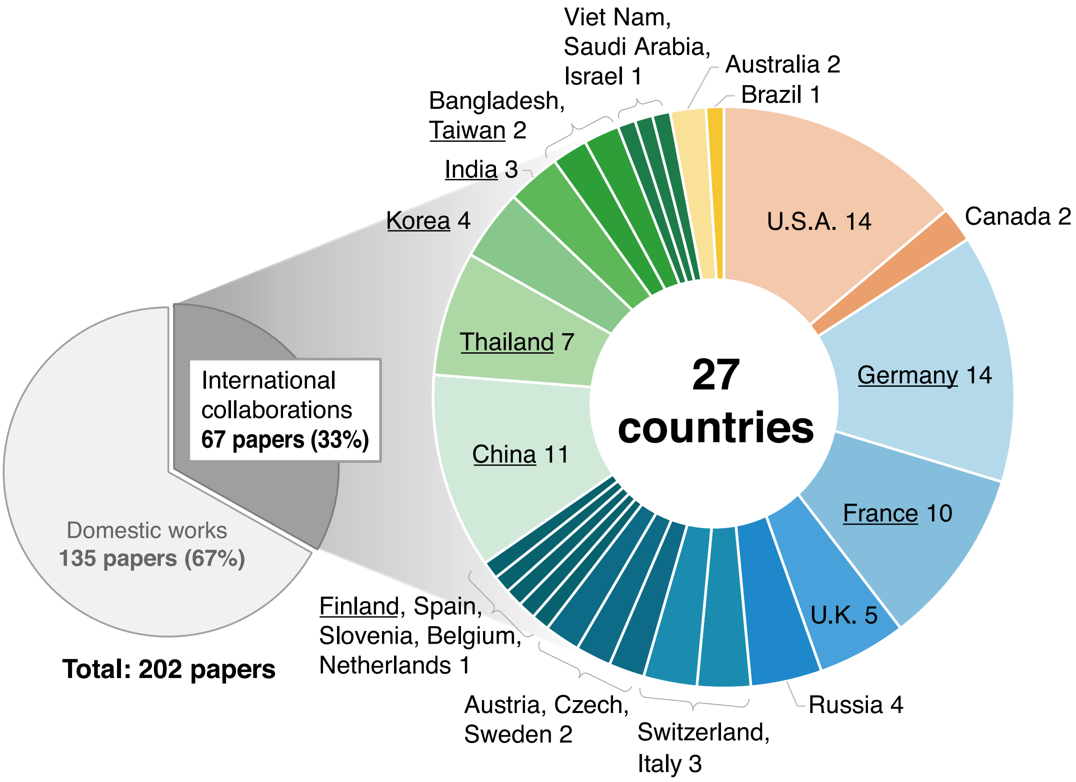
(4) IMS International Collaboration

Category	Number of People
International Joint Research Programs	50
International Use of Facilities Programs	24

from Sep. 2019 to Aug. 2020

Internationally Collaborated Publications

Articles and reviews published in 2019



Underlined countries include MOU Partnership Institutions
Scopus dataset, Nov. 2020

AWARDS

KAWAI, Maki Director General	The Japan Academy Prize "Single Molecule Spectroscopy Elucidating Chemical Reactions at Solid Surfaces"
FUJITA, Makoto Division of Advanced Molecular Science	The 73rd Chunichi Cultural Award "Creation and Applications of Self-Assembled Molecular Systems"
ISHIZAKI, Akihito Theoretical and Computational Molecular Science	The 16th JSPS Prize The 16th Japan Academy Medal "Theoretical Development of Quantum Dissipative Dynamics and Its Application to Primary Processes of Photosynthesis"
YAMAMOTO, Hiroshi Research Center of Integrative Molecular Systems	The NAGAI Foundation for Science & Technology Academic Award "Fabrication of Nano Scale Thin-Film Organic Conductors and Their Application to Electronic Materials"
OKAMOTO, Hiromi Center for Mesoscopic Sciences	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology Awards for Science and Technology Research Category "Development of Novel Nano-Optical Observation Methods and Studies on Spatial Characteristics of Plasmons"
SUGIMOTO, Toshiki Materials Molecular Science	The 12th Young Scientist Awards of the Japan Society for Molecular Science "Elucidation of Unique Functions and Hydrogen-Bonded Structures of the Water Molecular Aggregates by Sum-Frequency-Generation Vibrational Spectroscopy" The 14th Young Scientist Award of the Physical Society of Japan "Unveiling Unique Structures and Properties of Hydrogen Bonds of Water Molecules Induced by Inversion Symmetry Breaking at Solid Surfaces"
KOBAYASHI, Genki Materials Molecular Science	Morino Foundation for Molecular Science 2019 "Study on the Ionic Conductive Materials toward Developing the Next Generation Energy Devices"
KUSAMOTO, Tetsuro Life and Coordination-Complex Molecular Science	Research Encouragement Award, Japan Society of Coordination Chemistry "Development of Photofunctions of Open-Shell Molecules Based on Coordination Chemistry"
KURAMOCHI, Hikaru Research Center of Integrative Molecular Systems	The Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology The Young Scientists' Award "Studies on Ultrafast Structural Dynamics of Complex Molecules by Extreme Spectroscopy" Morino Foundation for Molecular Science 2020 "Study on the Femtosecond Structural Dynamics of Complex Molecular Systems by Extreme Time-Domain Raman Spectroscopy Using Few-Cycle Pulses"
IIDA, Kenji Theoretical and Computational Molecular Science	The 12th Young Scientist Awards of the Japan Society for Molecular Science "Elucidation of the Response Mechanism of Nano Interface Systems to Light and Voltage"
NGUYEN, Thanh Phuc Theoretical and Computational Molecular Science	The 9th Young Scientist Award of National Institutes of Natural Sciences "Theoretical Studies on Quantum Dynamics of Atoms and Molecules"
IZAWA, Seiichiro Materials Molecular Science	Kao Foundation for Arts and Sciences Award "Precise Control of Donor/Acceptor Interface for Efficient Organic Solar Cells"

AWARDS

NAKAMURA, Akihiko Life and Coordination-Complex Molecular Science	The 15th Early Career Award in Biophysics of the Biophysical Society of Japan “Crystalline Chitin Hydrolase Is a Burnt-Bridge Brownian Motor”
FUJIWARA, Motoyasu ASADA, Mizue IKI, Shinako Instrument Center	Nanotechnology Platform Japan The Best Technical Support Contribution Award “Technical Supporting of Electron Spin Resonance”
KONDO, Takuhiko Equipment Development Center	The Chemical Society of Japan Award for Technical Achievements for 2019 “Development of Experimental Equipment and Ultra-Precision Polishing Technology for Promoting Molecular Science”

LIST OF VISITING FOREIGN SCHOLARS

Visitors from abroad are always welcome at IMS and they have always played an important role in the research activities of the Institute. The foreign scientists who visited IMS during the past year (September 2019–August 2020) are listed below.

(1) Attendance at an Okazaki Conference

Prof. FREUND, Hans-Joachim	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. ERNSTORFER, Ralph	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Prof. STAHLER, Julia	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. TONG, Yujin	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. ROSSI, Mariana	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. KUMAGAI, Takashi	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. KLEY, Christopher	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. PAARMANN, Alexander	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Prof. GRILL, Leonhard	Univ. of Graz	Austria	Dec. ’19
Dr. NARITA, Akimitsu	Max Planck Inst. for Polymer Res.	Germany	Dec. ’19
Prof. CHIU, Ya-Ping	Natl. Taiwan Univ.	Taiwan	Dec. ’19
Prof. WU, Shiwei	Fudan Univ.,	China	Dec. ’19
Prof. LIN, Nian	The Hong Kong Univ. of Sci. and Tech.	China (Hong Kong)	Dec. ’19
Dr. MAZHEIKA, Aliaksei	Technical Univ. of Berlin	Germany	Dec. ’19
Dr. OGASAWARA, Hirohito	SLAC Natl. Accelerator Laboratory	U.S.A.	Dec. ’19
Prof. URAKAWA, Atsushi	Delft Univ. of Tech.	Netherlands	Dec. ’19
Dr. CIRERA, Borja	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. LIU, Shuyi	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. LIN, Chenfang	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Mr. LITMAN, Yair	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Mr. DEBNATH, Sreekanta	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Mr. LEWANDOWSKI, Adrian	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Ms. YOSHINO, Hiroko	Fritz-Haber Inst. of Max Planck Society	Germany	Dec. ’19
Dr. HSU, Hung-Chang	Natl. Taiwan Univ.	Taiwan	Dec. ’19

(2) IMS Councillor

Prof. NAAMAN, Ron	Weizmann Inst. of Sci.	Israel	Dec. ’19
Prof. ROSSKY, Peter Jacob	Rice Univ.	U.S.A.	Dec. ’19
Prof. PETEK, Hrvoje	Univ. of Pittsburgh	U.S.A.	Dec. ’19
Prof. LIST, Benjamin	Max Planck Inst. for Coal Res.	Germany	Dec. ’19

(3) IMS Visiting Scientist

Mr. GRZELAK, Dorota	Univ. of Warsaw	Poland	Sep. ’19
Prof. LEWANDOWSKI, Wiktor	Univ. of Warsaw	Poland	Sep. ’19
Mr. PARK, Heonjoon	Seoul Natl. Univ.	Korea	Sep. ’19 Nov. ’19 Feb. ’20
Mr. LEE, Suyoung	Seoul Natl. Univ.	Korea	Sep. ’19 Nov. ’19 Feb. ’20
Mr. OH, Dong Jin	Seoul Natl. Univ.	Korea	Sep. ’19 Nov. ’19 Feb. ’20
Prof. RÜHL, Eckart	Free Univ. of Berlin	Germany	Sep. ’19 Mar. ’20
Prof. FLESCH, Roman	Free Univ. of Berlin	Germany	Sep. ’19
Mr. GERMER, Gregor	Free Univ. of Berlin	Germany	Sep. ’19
Ms. SAENNAWA, Wiyada	Suranaree Univ. of Tech.	Thailand	Sep. ’19–Oct. ’19
Ms. PACHARIYANGKUN, Anna	VISTEC	Thailand	Sep. ’19–Dec. ’19
Mr. ALBERTSMA, Jelco	Univ. of Twente	Netherlands	Sep. ’19–Mar. ’20
Ms. WILASRI, Thunchanok	Kasetsart Univ.	Thailand	Sep. ’19–Mar. ’20
Prof. AKA, Gérard Philippe	École Nationale Supérieure de Chimie de Paris	France	Oct. ’19

LIST OF VISITING FOREIGN SCHOLARS

Dr. PRIESTLEY, Michael	Univ. of Gothenburg	Sweden	Oct. ’19
Mr. KONG, Xiangrui	Univ. of Gothenburg	Sweden	Oct. ’19
Prof. HE, Ruihua	Westlake Univ.	China	Oct. ’19
Mr. ZHAO, Geng	Westlake Univ.	China	Oct. ’19
Ms. WEN, Wei	Westlake Univ.	China	Oct. ’19
Mr. HONG, Caiyun	Westlake Univ.	China	Oct. ’19
Mr. SONG, Zhen	Westlake Univ.	China	Oct. ’19
Mr. WU, Yi-Ju	Natl. Chiao Tung Univ.	Taiwan	Oct. ’19–Dec. ’19
Ms. YANG, Ling	Natl. Chiao Tung Univ.	Taiwan	Oct. ’19–Feb. ’20
Mr. MADUWANTHA, kaveendra	Sabaragamuwa Univ. of Sri Lanaka	Sri Lanka	Oct. ’19–Mar. ’20
Mr. GOH, Ean Wai	Univ. of Malaya	Malaysia	Oct. ’19–Mar. ’20
Ms. HONSA, Monique	Ludwig Maximilian Univ. of Munich	Germany	Oct. ’19–Aug.. ’20
Mr. KUMSAMPAO, Jakkapan	VISTEC	Thailand	Oct. ’19–Sep. ’20
Dr. MAHATNIRUNKUL, Thanisorn	NANOTEC	Thailand	Nov. ’19
Ms. HOONG, Chang Yeet	Univ. of Malaya	Malaysia	Nov. ’19–Apr. ’20
Ms. LE LAN, Nguyen Ngoc	Chulalongkorn Univ.	Thailand	Dec. ’19–Mar. ’20
Dr. CHAN, Kwun Wa	Univ. of Hong Kong	China (Hong Kong)	Dec. ’19–Apr. ’20
Dr. HASIN, Panitat	Kasetsart Univ.	Thailand	Dec. ’19–Apr. ’20
Mr. MALATONG, Ruttapol	VISTEC	Thailand	Jan. ’20
Mr. URBON, Adrian	Univ. Münster	Germany	Jan. ’20
Prof. ZHAO, Xiang	Xi'an Jiaotong Univ.	China	Jan. ’20–Feb. ’20
Prof. CHUANG, Cheng-Hao	Tamkang Univ.	Taiwan	Jan. ’20–Feb. ’20
Mr. HUANG, Yu-Cheng	Natl. Chiao Tung Univ.	Taiwan	Jan. ’20–Feb. ’20
Dr. VELASCO VÉLEZ, Juan Jesús	Max Planck Inst. for Chemical Energy Conversion	Germany	Jan. ’20–Feb. ’20
Ms. ZHANG, Kaili	China Three Gorges Univ.	China	Jan. ’20–Mar. ’20
Mr. YOO, Han Young	Seoul Natl. Univ.	Korea	Feb. ’20
Dr. PATANEN, Minna	Univ. of Oulu	Finland	Feb. ’20
Mr. MANSIKKALA, Leo	Univ. of Oulu	Finland	Feb. ’20
Dr. PLUSKAL, Tomáš	Whitehead Inst. for Biomedical Res.	U.S.A.	Feb. ’20–Apr. ’20
Ms. MICHAILOUDI, Georgia	Univ. of Oulu	Finland	Mar. ’20
Dr. LIN, Jack	Univ. of Oulu	Finland	Mar. ’20
Mr. RAJ R, Kamal	Univ. of Oulu	Finland	Mar. ’20

(4) Visitor to IMS

Mr. TZENG, Sheng-Yuan	IAMS	Taiwan	Sep. ’19
Mr. YEH, Shou-Hao	IAMS	Taiwan	Sep. ’19
Dr. YOSHIDA, Daisuke	IAMS	Taiwan	Sep. ’19
Dr. HUANG, Qian-Rui	IAMS	Taiwan	Sep. ’19
Dr. HAYASHI, Michitoshi	IAMS	Taiwan	Sep. ’19
Dr. TAKAHASHI, Kaito	IAMS	Taiwan	Sep. ’19
Dr. KUO, Jer-Lai	IAMS	Taiwan	Sep. ’19
Dr. HSU, Liang-Yan	IAMS	Taiwan	Sep. ’19
Dr. NGUYEN, Phuong	Inst. of Physico-Chemical Biology	France	Oct. ’19
Prof. HÖFER, Ulrich	Philipps Univ. of Marburg	Germany	Nov. ’19
Dr. KLOTZBACH, Udo	Fraunhofer Inst. for Material and Beam Tech. IWS	Germany	Nov. ’19
Prof. WEIDEMÜLLER, Matthias	Ruprecht Karl Univ. of Heidelberg	Germany	Dec. ’19
Prof. LEITNER, David	Univ. of Nevada	U.S.A.	Dec. ’19
Prof. BORGUET, Eric	Temple Univ.	U.S.A.	Jan. ’20
Prof. QIU, Weihong	Oregon State Univ.	U.S.A.	Jan. ’20
Prof. LEE, Weontae	Yonsei Univ.	Korea	Jan. ’20
Dr. YUN, Ji-Hye	Yonsei Univ.	Korea	Jan. ’20
Mr. PARK, Jaehyun	Yonsei Univ.	Korea	Jan. ’20
Mr. HEO, Yoonseok	Yonsei Univ.	Korea	Jan. ’20
Ms. KIM, Taehee	Yonsei Univ.	Korea	Jan. ’20
Dr. YANG, Xu	Univ. of Groningen	Netherlands	Feb. ’20

Theoretical and Computational Molecular Science

Y. MORI, K. OKAZAKI, T. MORI, K. KIM and N. MATSUBAYASHI, "Learning Reaction Coordinates via Cross-Entropy Minimization: Application to Alanine Dipeptide," *J. Chem. Phys.* **153**, 054115 (8 pages) (2020).

Y. NAM, M. KALATHINGAL, S. SAITO and J. Y. LEE, "Tautomeric Effect of Histidine on β-Sheet Formation of Amyloid β 1−40: 2D-IR Simulations," *Biophys. J.* **119**, 831–842 (2020).

S.-I. KODA and S. SAITO, "An Alternative Interpretation of the Slow KaiB-KaiC Binding of the Cyanobacterial Clock Proteins," *Sci. Rep.* **10**, 10439 (7 pages) (2020).

T. MORI and S. SAITO, "Dissecting the Dynamics during Enzyme Catalysis: A Case Study of Pin1 Peptidyl-Prolyl Isomerase," *J. Chem. Theory Comput.* **16**, 3396–3407 (2020).

T. KATO, K. NOBUSADA and S. SAITO, "Inverse Kohn-Sham Equations Derived from the Density Equation Theory," *J. Phys. Soc. Jpn.* **89**, 024301 (15 pages) (2020).

S. SAITO, M. HIGASHI and G. R. FLEMING, "Site-Dependent Fluctuations Optimize Electronic Energy Transfer in the Fenna-Matthews-Olson Protein," *J. Phys. Chem. B* **123**, 9762–9772 (2019).

S. H. GAMOU, K. SHIMOSE, R. ENOKI, E. MINAMITANI, A. SHIOTARI, Y. KOTANI, K. TOYOKI, T. NAKAMURA, Y. SUGIMOTO, M. KOHDA, J. NITTA and S. MIWA, "Detection of Spin-Transfer from Metal to Molecule by Magnetoresistance Measurement," *Nano Lett.* **20**, 75–80 (2020). DOI: 10.1021/acs.nanolett.9b03110

K. SHIMIZU, W. LIU, W. LI, S. KASAMATSU, Y. ANDO, E. MINAMITANI and S. WATANABE, "First-Principles Study of Li-Ion Distribution at γ–Li_3PO_4/Metal Interfaces," *Phys. Rev. Mater.* **4**, 015402 (10 pages) (2020). DOI: 10.1103/PhysRevMaterials.4.015402

Z. NI, E. MINAMITANI, K. KAWAHARA, R. ARAFUNE, C.-L. LIN, N. TAKAGI and S. WATANABE, "Mechanically Tunable Spontaneous Vertical Charge Redistribution in Few-Layer WTe_2," *J. Phys. Chem. C* **124**, 2008–2012 (2020). DOI: 10.1021/acs.jpcc.9b10423

X. YANG, Y. YUAN, Y. PENG, E. MINAMITANI, L. PENG, J.-J. XIAN, W.-H. ZHANG and Y.-S. FU, "Observation of Short-Range Yu-Shiba-Rusinov States with Threefold Symmetry in Layered Superconductor 2H-$NbSe_2$," *Nanoscale* **12**, 8174–8179 (2020). DOI: 10.1039/d0nr01383h

K. IWATA, T. MIYAMACHI, E. MINAMITANI and F. KOMORI, "Sensing Surface Lattice Strain with Kondo Resonance of Single Co Adatom," *Appl. Phys. Lett.* **116**, 051604 (4 pages) (2020). DOI: 10.1063/1.5142064

P. MANO, E. MINAMITANI and S. WATANABE, "Straintronic Effect for Superconductivity Enhancement in Li-Intercalated Bilayer MoS_2," *Nanoscale Adv.* **3**, 3150–3155 (2020). DOI: 10.1039/D0NA00420K

N. H. SHIMADA, E. MINAMITANI and S. WATANABE, "Theoretical Prediction of Superconductivity in Monolayer h-BN Doped with Alkaline-Earth Metals (Ca, Sr, Ba)," *J. Phys.: Condens. Matter* **32**, 435002 (9 pages) (2020). DOI: 10.1088/1361-648X/aba674

T. P. NGUYEN and A. ISHIZAKI, Precise Determination of Excitation Energies in Condensed-Phase Molecular Systems Based on Exciton–Polariton Measurements," *Phys. Rev. Res.* **1**, 033019 (9 pages) (2019).

A. ISHIZAKI, "Prerequisites for Relevant Spectral Density and Convergence of Reduced Density Matrices at Low Temperatures," *J. Phys. Soc. Jpn.* **89**, 015001 (2 pages) (2020).

T. P. NGUYEN, Q. T. PHAM and A. ISHIZAKI, "Controlling the Nonadiabatic Electron-Transfer Reaction Rate through Molecular-Vibration Polaritons in the Ultrastrong Coupling Regime," *Sci. Rep.* **10**, 7318 (11 pages) (2020).

Y. FUJIHASHI, R. SHIMIZU and A. ISHIZAKI, "Generation of Pseudo-Sunlight via Quantum Entangled Photons and the Interaction with Molecules," *Phys. Rev. Res.* **2**, 023256 (7 pages) (2020).

A. ISHIZAKI, "Probing Excited-State Dynamics with Quantum Entangled Photons: Correspondence to Coherent Multidimensional Spectroscopy," *J. Chem. Phys.* **153**, 051102 (7 pages) (2020). [Editor's Pick]

H. TSUNOYAMA, A. OHNUMA, K. TAKAHASHI, A. VELLOTH, M. EHARA, N. ICHIKUNI, M. TABUCHI and A. NAKAJIMA, "Enhanced Oxygen Reduction Activity of Platinum Subnanocluster Catalysts through Charge Redistribution," *Chem. Commun.* **55**, 12603–12606 (2019).

Y.-X. ZHAO, M.-Y. LI, P. ZHAO, M. EHARA and X. ZHAO, "New Insight into U@C_{80}: Missing U@D_3(31921)-C_{80} and Nuanced Enantiomers of U@C_1(28324)-C_{80}," *Inorg. Chem.* **58**, 14159–14166 (2019).

Y. MAEDA, H. MURAKOSHI, H. TAMBO, P. ZHAO, K. KURODA, M. YAMADA, X. ZHAO, S. NAGASE and M. EHARA, "Thermodynamic Control of Quantum Defects on Single-Walled Carbon Nanotubes," *Chem. Commun.* **55**, 13757–13760 (2019).

T. YANG, C. KONG, S. YANG, Z. YANG, S. YANG and M. EHARA, "Reaction Mechanism, Norbornene and Ligand Effects, and Origins of Meta-Selectivity of Pd/Norbornene-Catalyzed C–H Activation," *Chem. Sci.* **11**, 113–125 (2020).

P. ZHAO, B. BOEKFA, T. NISHITOBA, N. TSUNOJI, T. SANO, T. YOKOI, M. OGURA and M. EHARA, "Theoretical Study on ^{31}P NMR Chemical Shifts of Phosphorus-Modified CHA Zeolites," *Microporous Mesoporous Mater.* **294**, 109908 (12 pages) (2020).

M.-Y. LI, Y.-X. ZHAO, Y.-B. HAN, K. YUAN, S. NAGASE, M. EHARA and X. ZHAO, "Theoretical Investigation of the Key Roles in Fullerene-Formation Mechanisms: Enantiomer and Enthalpy," *ACS Appl. Nano Mater.* **3**, 547–554 (2020).

S. HU, P. ZHAO, W. SHEN, M. EHARA, Y. XIE, T. AKASAKA and X. LU, "Crystallographic Characterization of Er_2C_2@$C_{80\text{-}88}$: Cluster Stretching with Cage Elongation," *Inorg. Chem.* **59**, 1940–1946 (2020).

H. YOSHIDA, M. EHARA, U. DEVA PRIYAKUMAR, T. KAWAI and T. NAKASHIMA, "Enantioseparation and Chiral Induction in Ag_{29} Nanoclusters with Intrinsic Chirality," *Chem. Sci.* **11**, 2394–2400 (2020).

S. SARTYOUNGKUL, M. EHARA and H. SAKURAI, "Time-Dependent Density Functional Theory Investigation of Excited State Intramolecular Proton Transfer in Tris(2-hydroxyphenyl)triazasumanene," *J. Phys. Chem. A* **124**, 1227–1234 (2020).

T. SADHUKHAN, A. JUNKAEW, P. ZHAO, H. MIURA, T. SHISHIDO and M. EHARA, "Importance of the Pd and Surrounding Site in Hydrosilylation of Internal Alkynes by Palladium-Gold Alloy Catalyst," *Organometallics* **39**, 528–537 (2020).

M.-Y. LI, Z.-B. GAO, Y.-B. HAN, Y.-X. ZHAO, K. YUAN, S. NAGASE, M. EHARA and X. ZHAO, "Potential Molecular Semiconductor Devices: Cyclo-C_n (n = 10 and 14) with Higher Stabilities and Aromaticities than Acknowledged Cyclo-C_{18}," *Phys. Chem. Chem. Phys.* **22**, 4823–4831 (2020).

M. PROMKATKAEW, S. SURAMITR, T. KARPKIRD, M. EHARA and S. HANNONGBUA, "DFT/TD-DFT Investigation on the Photoinduced Electron Transfer of Diruthenium and Viologen Complexes," *J. Lumin.* **222**, 117121 (9 pages) (2020).

Q. M. PHUNG, Y. KOMORI, T. YANAI, T. SOMMERFELD and M. EHARA, "Combination of a Voronoi-Type Complex Absorbing Potential with the XMS-CASPT2 Method and Pilot Applications," *J. Chem. Theory Comput.* **16**, 2606–2616 (2020).

B. ZHU, M. EHARA and S. SAKAKI, "Propene Oxidation Catalysis and Electronic Structure of M_{55} Particle (M = Pd or Rh): Differences and Similarities between Pd_{55} and Rh_{55}," *Phys. Chem. Chem. Phys.* **22**, 11783–11796 (2020).

H. YOSHIDA, J. KUMAR, M. EHARA, Y. OKAJIMA, F. ASANOMA, T. KAWAI and T. NAKASHIMA, "Impact of Enantiomeric Ligand Composition on the Photophysical Properties of Chiral Ag_{29} Nanoclusters," *Bull. Chem. Soc. Jpn.* **93**, 834–840 (2020).

T. SHIRAOGAWA and M. EHARA, "Theoretical Design of Photofunctional Molecular Aggregates for Optical Properties: An Inverse Design Approach," *J. Phys. Chem. C* **124**, 13329–13337 (2020).

M.-Y. LI, Y.-X. ZHAO, Y.-B. HAN, K. YUAN, K.-N. ZHANG, Y.-Q. CHEN, M. EHARA, S. NAGASE and X. ZHAO, "Covalent Interactions Depended on the Distances between Metals and Fullerenes for Thermodynamically Stable $M@C_{78}$ (M = La, Ce, and Sm)," *Inorg. Chem. Front.* **7**, 2538–2547 (2020).

H. OKUMURA and S. G. ITOH, "Molecular Dynamics Simulations of Amyloid-β(16-22) Peptide Aggregation at Air–Water Interfaces," *J. Chem. Phys.* **151**, 095101 (12pages) (2020).

M. YAMAUCHI and H. OKUMURA, "Replica Sub-Permutation Method for Molecular Dynamics and Monte Carlo Simulations," *J. Comput. Chem.* **40**, 2694–2711 (2019).

N. MURAKI, K. ISHII, S. UCHIYAMA, S. G. ITOH, H. OKUMURA and S. AONO, "Structural Characterization of HypX Responsible for CO Biosynthesis in the Maturation of NiFe-Hydrogenase," *Commun. Biol.* **2**, 385 (12 pages) (2019).

T. FUJITA, Y. NOGUCHI and T. HOSHI, "Revisiting the Charge-Transfer States at Pentacene/C_{60} Interfaces with the GW/Bethe–Salpeter Equation Approach," *Materials* **13**, 2728 (15 pages) (2020).

M. I. MAHMOOD, H. NOGUCHI and K. OKAZAKI, "Curvature Induction and Sensing of the F-BAR Protein Pacsin1 on Lipid Membranes via Molecular Dynamics Simulations," *Sci. Rep.* **9**, 14557 (11 pages) (2019).

J. WARNAU, D. WÖHLERT, K. OKAZAKI, Ö. YILDIZ, A. P. GAMIZ-HERNANDEZ, V. R. I. KAILA, W. KÜHLBRANDT and G. HUMMER, "Ion Binding and Selectivity of the Na^+/H^+ Antiporter MjNhaP1 from Experiment and Simulation," *J. Phys. Chem. B* **124**, 336–344 (2020).

K. OKAZAKI, A. NAKAMURA and R. IINO, "Chemical-State-Dependent Free Energy Profile from Single-Molecule Trajectories of Biomolecular Motors: Application to Processive Chitinase," *J. Phys. Chem. B* **124**, 6475–6487 (2020).

Y. MORI, K. OKAZAKI, T. MORI, K. KIM and N. MATUBAYASI, "Learning Reaction Coordinates via Cross-Entropy Minimization: Application to Alanine Dipeptide," *J. Chem. Phys.* **153**, 054115 (8 pages) (2020).

T. ISHIDA, "Theoretical Investigation of Dissolution and Decomposition Mechanisms of a Cellulose Fiber in Ionic Liquids," *J. Phys. Chem. B* **124**, 3090–3102 (2020).

S. SUMITA and Y. YANASE, "Superconductivity Induced by Fluctuations of Momentum-Based Multipoles," *Phys. Rev. Res.* **2**, 033225 (19 pages) (2020).

K. IMAMURA, T. YAMAZAKI, D. YOKOGAWA, M. HIGASHI and H. SATO, "Nuclear Magnetic Shielding of Molecule in Solution Based on Reference Interaction Site Model Self-Consistent Field with Spatial Electron Density Distribution," *J. Chem. Phys.* **152**, 194102 (11 pages) (2020).

H. NAKANO, M. HIGASHI and H. SATO, "Uniform Potential Difference Scheme to Evaluate Effective Electronic Couplings for Superexchange Electron Transfer in Donor–Bridge–Acceptor Systems," *J. Chem. Phys.* **152**, 224103 (13 pages) (2020).

Photo-Molecular Science

M. MIZOGUCHI, Y. ZHANG, M. KUNIMI, A. TANAKA, S. TAKEDA, N. TAKEI, V. BHARTI, K. KOYASU, T. KISHIMOTO, D. JAKSCH, A. GLÄTZLE, M. KIFFNER, G. MASELLA, G. PUPILLO, M. WEIDEMÜLLER and K. OHMORI, "Ultrafast Creation of Overlapping Rydberg Electrons in an Atomic BEC and Mott-Insulator Lattice," *Phys. Rev. Lett.* **124**, 253201 (7 pages) (2020).

H. KATSUKI, Y. OHTSUKI, T. AJIKI, H. GOTO and K. OHMORI, "Engineering Quantum Wave-Packet Dispersion with a Strong Non-Resonant Femtosecond Laser Pulse," *arXiv* 1910.08241 (2019).

H. SAKAI (Hamamatsu Photonics K.K.), K. OHMORI (NINS), T. ANDO (Hamamatsu Photonics K.K.), N. TAKEI (NINS), H. TOYODA, Y. OHTAKE, T. HYODO and Y. TAKIGUCHI (Hamamatsu Photonics K.K.), Patent Publication (15th Nov. 2018), "Quantum Simulator and Quantum Simulation Method."

H. SAKAI (Hamamatsu Photonics K.K.), K. OHMORI (NINS), T. ANDO (Hamamatsu Photonics K.K.), N. TAKEI (NINS), H. TOYODA, Y. OHTAKE, T. HYODO and Y. TAKIGUCHI (Hamamatsu Photonics K.K.), US Patent (3rd Nov. 2020), "Quantum Simulator and Quantum Simulation Method."

F. MATSUI, S. MAKITA, H. MATSUDA, T. YANO, E. NAKAMURA, K. TANAKA, S. SUGA and S. KERA, "Photoelectron Momentum Microscope at BL6U of UVSOR-III Synchrotron," *Jpn. J. Appl. Phys.* **59**, 067001 (9 pages) (2020). DOI: 10.35848/1347-4065/ab9184

F. MATSUI, S. MAKITA, H. MATSUDA, T. UEBA, T. HORIGOME, H. YAMANE, K. TANAKA, S. KERA and N. KOSUGI, "Bulk and Surface Band Dispersion Mapping of the Au(111) Surface by Acceptance-Cone Tunable PES System," *e-J. Surf. Sci. Nanotechnol.* **18**, 18–23 (2020). DOI: 10.1380/ejssnt.2020.18

G. D'AVINO, S. DUHM, R. DELLA VALLE, G. HEIMEL, M. OEHZELT, S. KERA, N. UENO, D. BELJONNE and I. SALZMANN, "Electrostatic Interactions Shape Molecular Organization and Electronic Structure of Organic Semiconductor Blends," *Chem. Mater.* **32**, 1261–1271 (2020). DOI: 10.1021/acs.chemmater.9b04763

J. YANG, S.-X. REN, T. YAMAGUCHI, M. MEISSNER, L. CHENG, L. ZHOU, S. IDETA, K. TANAKA and S. KERA, "Valence Band Dispersion Measured in the Surface Normal Direction of CH$_3$NH$_3$PbI$_3$ Single Crystals," *Appl. Phys. Express* **13**, 011009 (4 pages) (2020). DOI: 10.7567/1882-0786/ab6134

H. YAMANE, F. MATSUI, T. UEBA, T. HORIGOME, S. MAKITA, K. TANAKA, S. KERA and N. KOSUGI, "Acceptance-Cone-Tunable Electron Spectrometer for Highly-Efficient Constant Energy Mapping," *Rev. Sci. Instrum.* **90**, 093102 (7 pages) (2019). DOI: 10.1063/1.5109453

Y. NAKAYAMA, S. KERA and N. UENO, "Photoelectron Spectroscopy on Single Crystals of Organic Semiconductors: Experimental Electronic Band Structure for Optoelectronic Properties," *J. Mater. Chem. C* **8**, 9090–9132 (2020). DOI: 10.1039/D0TC00891E [Invited review]

Y. HIKOSAKA, T. KANEYASU, M. FUJIMOTO, H. IWAYAMA and M. KATOH, "Coherent Control in the Extreme Ultraviolet and Attosecond Regime by Synchrotron Radiation," *Nat. Commun.* **10**, 4988 (5 pages) (2019).

T. KANEYASU, Y. HIKOSAKA, M. FUJIMOTO, H. IWAYAMA and M. KATOH, "Controlling the Orbital Alignment in Atoms Using Cross-Circularly Polarized Extreme Ultraviolet Wave Packet," *Phys. Rev. Lett.* **123**, 233401 (5 pages) (2019).

L. GUO, H. YAMAGUCHI, M. YAMAMOTO, F. MATSUI, G. WANG, F. LIU, P. YANG, E. R. BATISTA, N. A. MOODY, Y. TAKASHIMA and M. KATOH, "Graphene as Reusable Substrate for Bialkali Photocathodes," *Appl. Phys. Lett.* **116**, 251903 (5 pages) (2020).

K. FUJIMORI, M. KITAURA, Y. TAIRA, M. FUJIMOTO, H. ZEN, S. WATANABE, K. KAMADA, Y. OKANO, M. KATOH, M. HOSAKA, J. YAMAZAKI, T. HIRADE, Y. KOBAYASHI and A. OHNISHI, "Visualizing Cation Vacancies in Ce:Gd$_3$Al$_2$Ga$_3$O$_{12}$ Scintillators by Gamma-Ray-Induced Positron Annihilation Lifetime Spectroscopy," *Appl. Phys. Exp*ress **13**, 085505 (4 pages) (2020).

K. ALI, H. OHGAKI, H. ZEN, T. KII, T. HAYAKAWA, T. SHIZUMA, H. TOYOKAWA, Y. TAIRA, V. IANCU, G. TURTURICA, C. ALEXANDRU UR, M. FUJIMOTO and M. KATOH, "Selective Isotope CT Imaging Based on Nuclear Resonance Fluorescence Transmission Method," *IEEE Trans. Nucl. Sci.* **67(8)**, 1976–1984 (2020).

T. KANEYASU, Y. HIKOSAKA, M. FUJIMOTO, H. IWAYAMA and M. KATOH, "Polarization Control in a Crossed Undulator without a Monochromator," *New J. Phys.* **22**, 083062 (8 pages) (2020).

K. FUJIMORI, M. KITAURA, Y. TAIRA, M. FUJIMOTO, H. ZEN, S. WATANABE, K. KAMADA, Y. OKANO, M. KATOH, M. HOSAKA, J. YAMAZAKI, T. HIRADE, Y. KOBAYASHI and A. OHNISHI, "Visualizing Cation Vacancies in Ce:Gd$_3$Al$_2$Ga$_3$O$_{12}$ Scintillators by Gamma-Ray-Induced Positron Annihilation Lifetime Spectroscopy," *Appl. Phys. Exp*ress **13**, 085505 (4 pages) (2020).

D. PINEK, T. ITO, K. FURUTA, Y. KIM, M. IKEMOTO, S. IDETA, K. TANAKA, M. NAKATAKE, P.L. FEVRE, F. BERTRAN and T. OUISSE, "Near Fermi Level Electronic Structure of Ti$_3$SiC$_2$ Revealed by Angle-Resolved Photoemission Spectroscopy," *Phys. Rev. B* **102**, 075111 (11 pages) (2020).

H. ANZAI, K. MORIKAWA, H. SHIONO, H. SATO, S. IDETA, K. TANAKA, T. ZHUANG, K. T. MATSUMOTO and K. HIRAOKA, "Temperature Dependence of the Kondo Resonance in the Photoemission Spectra of the Heavy-Fermion Compounds YbXCu$_4$ (X = Mg, Cd, and Sn)," *Phys. Rev. B* **101**, 235160 (7 pages) (2020).

F. MATSUI, S. MAKITA, H. MATSUDA, T. YANO, E. NAKAMURA, K. TANAKA, S. SUGA and S. KERA, "Photoelectron Momentum Microscope at BL6U of UVSOR-III Synchrotron," *Jpn. J. Appl. Phys.* **59**, 067001 (9 pages) (2020).

J. YANG, S.-X. REN, T. YAMAGUCHI, M. MEISSNER, L. CHENG, L. ZHOU, S. IDETA, K. TANAKA and S. KERA, "Valence Band Dispersion Measured in the Surface Normal Direction of CH$_3$NH$_3$PbI$_3$ Single Crystals," *Appl. Phys. Express* **13**, 011009 (4 pages) (2020).

S. IDETA, N. MURAI, M. NAKAJIMA, R. KAJIMOTO and K. TANAKA, "Experimental Investigation of the Suppressed Superconducting Gap and Double-Resonance Mode in Ba$_{1-x}$K$_x$Fe$_2$As$_2$," *Phys. Rev. B* **100**, 235135 (7 pages) (2019).

G. VINCINI, S. TAJIMA, S. MIYASAKA and K. TANAKA, "Multilayer Effects in Bi$_2$Sr$_2$Ca$_2$Cu$_3$O$_{10+z}$ Superconductors," *Supercond. Sci. Technol.* **32**, 113001 (12 pages) (2019).

M. HORIO, K. KOSHIISHI, S. NAKATA, K. HAGIWARA, Y. OTA, K. OKAZAKI, S. SHIN, S. IDETA, K. TANAKA, A. TAKAHASHI, T. OHGI, T. ADACHI, Y. KOIKE and A. FUJIMORI, "*d*-Wave Superconducting Gap Observed in Protect-Annealed Electron-Doped Cuprate Superconductors Pr$_{1.3-x}$La$_{0.7}$Ce$_x$CuO$_4$," *Phys. Rev. B* **100**, 054517 (5 pages) (2019).

Y. OHTSUBO, Y. YAMASHITA, J. KISHI, S. IDETA, K. TANAKA, H. YAMANE, J. E. RAULT, P LE. FEVRE, F. BERTRAN and S KIMURA, "Temperature-Driven Modification of Surface Electronic Structure on Bismuth, a Topological Border Material," *J. Phys. D: Appl. Phys.* **52**, 254002 (6 pages) (2019).

T. MATSUSHITA T. MURO, T. YOKOYA, K. TERASHIMA, Y. KATO, H. MATSUI, N. MAEJIMA, Y. HASHIMOTO and F. MATSUI, "Theory for High-Angular-Resolution Photoelectron Holograms Considering the Inelastic Mean Free Path and the Formation Mechanism of Quasi-Kikuchi Band," *Phys. Status Solidi B* **257**, 2000117 (5 pages) (2020).

L. GUO, H. YAMAGUCHI, M. YAMAMOTO, F. MATSUI, G. WANG, F. LIU, P. YANG, E. R. BATISTA, N. A. MOODY, Y. TAKASHIMA and M. KATOH, "Graphene as Reusable Substrate for Bialkali Photocathodes," *Appl. Phys. Lett.* **116**, 251903 (5 pages) (2020).

F. MATSUI, S. MAKITA, H. MATSUDA, T. YANO, E. NAKAMURA, K. TANAKA, S. SUGA and S. KERA, "Photoelectron Momentum Microscope at BL6U of UVSOR-III Synchrotron," *Jpn. J. Appl. Phys.* **59**, 067001 (9 pages) (2020).

LIST OF PUBLICATIONS

H. MATSUDA and F. MATSUI, "Principle and Basic Design of Omnidirectional Photoelectron Acceptance Lens," *Jpn. J. Appl. Phys.* **59**, 046503 (11 pages) (2020).

I. I. OGORODNIKOV, M. V. KUZNETSOV, F. MATSUI, D. Y. USACHOV and L. V. YASHINA, "Enhanced Surface Sensitivity of X-Ray Photoelectron Holography through the Example of Bi_2Te_3(111) Surface," *Appl. Surf. Sci.* **505**, 144531 (6 pages) (2020).

T. MATSUSHITA, T. MURO, F. MATSUI, N. HAPPO and K. HAYASHI, "Data Processing for Atomic Resolution Holography," *Jpn. J. Appl. Phys.* **59**, 020502 (10 pages) (2020).

F. MATSUI, S. MAKITA, H. MATSUDA, T. UEBA, T. HORIGOME, H. YAMANE, K. TANAKA, S. KERA and N. KOSUGI, "Bulk and Surface Band Dispersion Mapping of the Au(111) Surface by Acceptance-Cone Tunable PES System," *e-J. Surf. Sci. Nanotechnol.* **18**, 18–23 (2020).

F. MATSUI, S. MAKITA, H. MATSUDA, T. OHIGASHI, H., YAMANE and N. KOSUGI, "Identification of Twinning-Induced Edges on the Cleaved Graphite Crystal Surface," *J. Phys. Soc. Jpn.* **88**, 114704 (3 pages) (2019).

F. MATSUI, K. YASUDA, N. MAEJIMA, H. MATSUI, T. MATSUSHITA and H. DAIMON, "Chemical and Magnetic Properties of Polycrystalline Iron Surface Revealed by Auger Electron Holography, Spectroscopy, and Microscopy," *Jpn. J. Appl. Phys.* **58**, 110602 (8 pages) (2019).

H. YAMANE, F. MATSUI, T. UEBA, T. HORIGOME, S. MAKITA, K. TANAKA, S. KERA and N. KOSUGI, "Acceptance-Cone-Tunable Electron Spectrometer for Highly-Efficient Constant Energy Mapping," *Rev. Sci. Instrum.* **90**, 093102 (7 pages) (2019).

D. Y. USACHOV, A. V. TARASOV, F. MATSUI, M. MUNTWILER, K. A. BOKAI, V. O. SHEVELEV, O. Y. VILKOV, M. V. KUZNETSOV, L. V. YASHINA, C. LAUBSCHAT, A. COSSARO, L. FLOREANO, A. VERDINI and D. V. VYALIKH, "Decoding the Structure of Interfaces and Impurities in 2D Materials by Photoelectron Holography," *2D Mater.* **6**, 045046 (13 pages) (2019).

F. MATSUI and H. MATSUDA, "Electrostatic Lens, and Parallel Beam Generation Device and Parallel Beam Convergence Device which use Electroscatic Lens and Collimator," US 10614992, 2020.04.07 patented.

M. NAGASAKA and H. IWAYAMA, "Photoelectron Based Soft X-Ray Detector for Removing High Order X Rays," *Rev. Sci. Instrum.* **91**, 083103 (7 pages) (2020).

M. NAGASAKA, "Soft X-Ray Absorption Spectroscopy in the Low-Energy Region Explored Using an Argon Gas Window," *J. Synchrotron Radiat.* **27**, 959–962 (2020).

M. NAGASAKA, H. YUZAWA and N. KOSUGI, "Microheterogeneity in Aqueous Acetonitrile Solution Probed by Soft X-Ray Absorption Spectroscopy," *J. Phys. Chem. B* **124**, 1259–1265 (2020).

M. NAGASAKA, H. YUZAWA, N. TAKADA, M. AOYAMA, E. RÜHL and N. KOSUGI, "Laminar Flow in Microfluidics Investigated by Spatially-Resolved Soft X-Ray Absorption and Infrared Spectroscopy," *J. Chem. Phys.* **151**, 114201 (7 pages) (2019).

T. MANSIKKALA, M. PATANEN, A. KARKONEN, R. KORPINEN, A. PRANOVICH, T. OHIGASHI, S. SWARAJ, J. SEITOSONEN, J. RUOKOLAINEN, M. HUTTULA, P. SARANPAA and R. PIISPANEN, "Lignans in Knotwood of Norway Spruce: Localisation with Soft X-Ray Microscopy and Scanning Transmission Electron Microscopy with Energy Dispersive X-Ray Spectroscopy," *Molecules* **25**, 2997 (22 pages) (2020).

Y. R. LU, Y. F. WANG, Y. C. HUANG, J. L. CHEN, C. L. CHEN, Y. C. LIN, Y. G. LIN, W. F. PONG, T. OHIGASHI, N. KOSUGI, C. H. KUO, W. C. CHOU and C. L. DONG, "Effect of Fe_2Co_3 Coating on ZnO Nanowires in Photoelectrochemical Water Splitting: A Synchrotron X-Ray Spectroscopic and Spectromicroscopic Investigation," *Sol. Energy Mater. Sol. Cells* **209**, 110469 (7 pages) (2020).

M. NAGASAKA and H. IWAYAMA, "Photoelectron Based Soft X-Ray Detector for Removing High Order X Rays," *Rev. Sci. Instrum.* **91**, 083103 (7 pages) (2020).

A. FERTE, J. PALAUDOUX, F. PENENT, H. IWAYAMA, E. SHIGEMASA, Y. HIKOSAKA, K. SOEJIMA, K. ITO, P. LABLANQUIE, R. TAIEB and S. CARNIATO, "Advanced Computation Method for Double Core Hole Spectra: Insight into the Nature of Intense Shake-up Satellites," *J. Phys. Chem. Lett.* **11**, 4359 (11 pages) (2020).

Y. HIKOSAKA, H. IWAYAMA and T. KANEYASU, "Zeeman Quantum Beats of Helium Rydberg States Excited by Synchrotron Radiation," *J. Synchrotron Radiat.* **27**, 675 (6 pages) (2020).

S. KOSUGI, N. SUZUKI, KUMAGAI, H. IWAYAMA, E. SHIGEMASA, F. KOIKE and Y. AZUMA, "Dominance of Angular Momentum Exchange in the PCI Recapture of Photoelectrons Revealed by High Resolution Auger Electron Measurements of Kr," *J. Phys. B* **52**, 245002 (6 pages) (2019).

T. KANEYASU, Y. HIKOSAKA, M. FUJIMOTO, H. IWAYAMA and M. KATOH, "Controlling the Orbital Alignment in Atoms Using Cross-Circularly Polarized Extreme Ultraviolet Wave Packet," *Phys. Rev. Lett.* **123**, 233401 (5 pages) (2019).

Y. HIKOSAKA, T. KANEYASU, M. FUJIMOTO, H. IWAYAMA and M. KATOH, "Coherent Control in the Extreme Ultraviolet and Attosecond Regime by Synchrotron Radiation," *Nat. Commun.* **10**, 4988 (5 pages) (2019).

M. IMAI, Y. YOKOTA, I. TANABE, K. INAGAK, Y. MORIKAWA and K. FUKUI, "Correlation between Mobility and Hydrogen Bonding Network of Water at Electrified-Graphite Electrode Using Molecular Dynamics Simulation," *Phys. Chem. Chem. Phys.* **22**, 1767–1773 (2020).

D. OKAUE, I. TANABE, S. ONO, K. SAKAMOTO, T. SATO, A. IMANISHI, Y. MORIKAWA, J. TAKEYA and K. FUKUI, "Ionic-Liquid-Originated Carrier Trapping Dynamics at the Interface in Electric Double-Layer Organic FET Revealed by Operando Interfacial Analyses," *J. Phys. Chem. C* **124**, 2543–2552 (2020).

Y. MORINO, Y. YOKOTA, H. HARA, K. BANDO, S. ONO, A. IMANISHI, Y. OKADA, H. MATSUI, T. UEMURA, J. TAKEYA and K. FUKUI, "Rapid Improvements in Charge Carrier Mobility at Ionic Liquid/Pentacene Single Crystal Interfaces by Self-Cleaning," *Phys. Chem. Chem. Phys.* **22**, 6131–6135 (2020).

P. E. EVANS, T. KOMESU, L. ZHANG, D.-F. SHAO, A. J. YOST, S. KUMAR, E. F. SCHWIER, K. SHIMADA, E. TSYMBAL, X. HONG and P. A. DOWBEN, "Detection of Decoupled Surface and Bulk States in Epitaxial Orthorhombic $SrIrO_3$ Thin Films," *AIP Adv.* **10**, 045027 (5 pages) (2020).

D. GENG, K. YU, S. YUE, J. CAO, W. LI, D. MA, C. CUI, M. ARITA, S. KUMAR, E. F. SCHWIER, K. SHIMADA, P. CHENG, L. CHEN, K. WU, Y. YAO and B. FENG, "Experimental Evidence of Monolayer AlB_2 with Symmetry-Protected Dirac Cones," *Phys. Rev. B* **101**, 161407(R) (5 pages) (2020).

A. SINGH, S. KUMAR, M. SINGHA, P. SINGHA, R. SINGH, V. K. GANGWAR, A. LAKHANI, S. PATIL, E. F. SCHWIER, T. MATSUMURA, K. SHIMADA, A. K. GHOSH and S. CHATTERJEE, "Anomalous Hall Effect in Cu Doped Topological Insulator Bi_2Te_3," *J. Phys.: Condens. Matter* **32**, 305602 (11 pages) (2020).

A. G. RYBKIN, A. A. RYBKINA, A. V. TARASOV, D. A. PUDIKOV, I. I. KLIMOVSKIKH, O. YU. VILKOV, A. E. PETUKHOV, D. Y. USACHOV, D. A. ESTYUNIN, V. Y. VOROSHININ, A. VARYKHALOV, G. DI SANTO, L. PETACCIA, E. F. SCHWIER, K. SHIMADA, A. KIMURA and A. M. SHIKIN, "A New Approach for Synthesis of Epitaxial Nano-Thin Pt_5Gd Alloy via Intercalation Underneath a Graphene," *Appl. Surf. Sci.* **526**, 146687 (8 pages) (2020).

Y. ZHANG, K. DENG, X. ZHANG, M. WANG, Y. WANG, C. LIU, J.-W. MEI, S. KUMAR, E. F. SCHWIER, K. SHIMADA, C. CHEN and B. SHEN, "In-Plane Antiferromanetic Moments and Magnetic Polaron in the Axion Topological Insulator Candidate $EuIn_2As_2$," *Phys. Rev. B* **101**, 205126 (7 pages) (2020).

M. ZHENG, E. F. SCHWIER, H. IWASAWA and K. SHIMADA, "High-Resolution Angle-Resolved Photoemission Study of Oxygen Adsorbed Fe/MgO(001)," *Chin. Phys. B* **29**, 067901 (9 pages) (2020).

X. WU, J. LI, X.-M. MA, Y. ZHAN, Y. LIU, C.-S. ZHOU, J. SHAO, Q. WANG, Y.-J. HAO, Y. FENG, E. F. SCHWIER, S. KUMAR, H. SUN, P. LIU, K. SHIMADA, K. MIYAMOTO, T. OKUDA, K. WANG, M. XIE, C. CHEN, Q. LIU, C. LIU and Y. ZHAO, "Distinct Topological Surface States on the Two Terminations of $MnBi_4Te_7$," *Phys. Rev. X* **10**, 031013 (10 pages) (2020).

M. NURMAMAT, K. OKAMOTO, S. ZHU, T. V. MENSHCHIKOVA, I. P. RUSINOV, V. O. KOROSTELEV, K. MIYAMOTO, T. OKUDA, T. MIYASHITA, X. WANG, Y. ISHIDA, K. SUMIDA, E. F. SCHWIER, M. YE, Z. S. ALIEV, M. B. BABANLY, I. R. AMIRASLANOV, E. V. CHULKOV, K. A. KOKH, O. E. TERESHCHENKO, K. SHIMADA, S. SHIN and A. KIMURA, "Topologically Nontrivial Phase-Change Compound $GeSb_2Te_4$," *ACS Nano* **14**, 9059–9065 (2020).

P. SINGH, M. ALAM, S. KUMAR, K. ANAND, V. K. GANGWAR, S. GHOSH, M. SAWADA, K. SHIMADA, R. K. SINGH, A. K. GHOSH and S. CHATTERJEE, "Roles of Re-Entrant Cluster Glass State and Spin–Lattice Coupling in Magneto–Dielectric Behavior of Giant Dielectric Double Perovskite $La_{1.8}Pr_{0.2}CoFeO_6$," *J. Phys.: Condens. Matter* **32**, 445801 (9 pages) (2020).

P. E. EVANS, T. KOMESU, E. F. SCHWIER, S. KUMAR, K. SHIMADA and P. A. DOWBEN, "The Band Shifts in MoS_2(0001) and WSe_2(0001) Induced by Palladium Adsorption," *J. Phys.: Condens. Matter* **32**, 465001 (7 pages) (2020).

C. M. LAURIO, H. KATSUKI and H. YANAGI, "Numerical Simulations on Strong Coupling of Bloch Surface Waves and Excitons in Dielectric-Organic Multilayer Structures," *J. Phys.: Condens. Matter* **32**, 415003 (11 pages) (2020).

H. OKOCHI, H. KATSUKI, M. TSUBOUCHI, R. ITAKURA and H. YANAGI, "Photon Energy Dependent Ultrafast Photoinduced Terahertz Response in a Microcrystalline Film of $CH_3NH_3PbBr_3$," *J. Phys. Chem. Lett.* **11**, 6068–6076 (2020).

H. MIZUNO, T. JINJYO, C. LAURIO, H. KATSUKI, I. HIROMITSU, F. SASAKI and H. YANAGI, "Fabrication and Characterization of Vertical Microcavities Containing a Submicron Particle Film of 5,5'-di(4-biphenylyl)-2,2'-bithiophene," *Jpn. J. Appl. Phys.* **59**, SDDA14 (5 pages) (2020).

T. AKAZAWA, F. SASAKI, K. BANDO, H. MIZUNO, H. KATSUKI and H. YANAGI, "Fabrication of Low-Dimensional Microstructures with Distyrylbenzene Derivatives," *Jpn. J. Appl. Phys.* **59**, SDDA07 (5 pages) (2020).

Materials Molecular Science

A. ISHIHARA, T. NAGAI, K. UKITA, M. ARAO, M. MATSUMOTO, L. YU, T. NAKAMURA, O. SEKIZAWA, Y. TAKAGI, K. MATSUZAWA, T. NAPPORN, S. MITSUSHIMA, T. URUGA, T. YOKOYAMA, Y. IWASAWA, H. IMAI and K. OTA, "Emergence of Oxygen Reduction Activity in Zirconium Oxide-Based Compounds in Acidic Media: Creation of Active Sites for Oxygen Reduction Reaction," *J. Phys. Chem. C* **123**, 18150–18159 (2019).

T. NAKAMURA, Y. TAKAGI, S. CHAVEANGHONG, T. URUGA, M. TADA, Y. IWASAWA and T. YOKOYAMA, "Quick Operando Ambient Pressure Hard X-Ray Photoelectron Spectroscopy for Reaction Kinetic Measurements of Polymer Electrolyte Fuel Cells," *J. Phys. Chem. C* **124**, 17520–17527 (2020).

K. KAWAGUCHI, T. MIYAMACHI, T. IIMORI, Y. TAKAHASHI, T. HATTORI, T. YOKOYAMA, M. KOTSUGI and F. KOMORI, "Realizing Large Out-of-Plane Magnetic Anisotropy in L10-FeNi Films Grown by Nitrogen-Surfactant Epitaxy on Cu(001)," *Phys. Rev. Mater.* **4**, 054403 (7 pages) (2020).

Y. SONG, Q. SUN, T. YOKOYAMA, H. ZHU, Q. LI, R. HUANG, Y. REN, Q. HUANG, X. XING and J. CHEN, "Transforming Thermal Expansion from Positive to Negative: The Case of Cubic Magnetic Compounds of $(Zr,Nb)Fe_2$," *J. Phys. Chem. Lett.* **11**, 1954–1961 (2020).

Y. WAKISAKA, D. KIDO, H. UEHARA, Q. YUAN, F. E. FEITEN, S. MUKAI, S. TAKAKUSAGI, Y. UEMURA, T. YOKOYAMA, T. WADA, M. UO, O. SEKIZAWA, T. URUGA, Y. IWASAWA and K. ASAKURA, "Development of Surface Fluorescence X-Ray Absorption Fine Structure Spectroscopy Using a Laue-Type Monochromator," *Chem. Rec.* **19**, 1157–1165 (2019).

S. IKEMOTO, X. HUANG, S. MURATSUGU, S. NAGASE, T. KOITAYA, H. MATSUI, G. YOKOTA, T. SUDOH, A. HASHIMOTO, Y. TAN, S. YAMAMOTO, J. TANG, I. MATSUDA, J. YOSHINOBU, T. YOKOYAMA, S. KUSAKA, R. MATSUDA and M. TADA, "Reversible Low-Temperature Redox Activity and Selective Oxidation Catalysis Derived from the Concerted Activation of Multiple Metal Species on Cr and Rh-Incorporated Ceria Catalysts," *Phys. Chem. Chem. Phys.* **21**, 20868–20877 (2019).

K. YAMAMOTO, S. E. MOUSSAOUI, Y. HIRATA, S. YAMAMOTO, Y. KUBOTA, S. OWADA, M. YABASHI, T. SEKI, K. TAKANASHI, I. MATSUDA and H. WADATI, "Element-Selective Tracking Ultrafast Demagnetization Process in Co/Pt Multilayer Thin Films by the Resonant Magneto-Optical Kerr Effect," *Appl. Phys. Lett.* **116**, 172406 (5 pages) (2020).

T. SUGIMOTO and Y. MATSUMOTO, "Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces," *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020).
F. KATO, T. SUGIMOTO and Y. MATSUMOTO, "Direct Experimental Evidence for Markedly Enhanced Surface Proton Activity Inherent to Water Ice," *J. Phys. Chem. Lett.* **11**, 2524–2529 (2020).
K. HARADA, T. SUGIMOTO, F. KATO, K. WATANABE and Y. MATSUMOTO, "Thickness Dependent Homogeneous Crystallization of Ultrathin Amorphous Solid Water Films," *Phys. Chem. Chem. Phys.* **22**, 1963–1973 (2020).
Y. OTSUKI, K. WATANABE, T. SUGIMOTO and Y. MATSUMOTO, "Enhanced Structural Disorder at a Nanocrystalline Ice Surface," *Phys. Chem. Chem. Phys.* **21**, 20442–20453 (2019).

M. KIKUCHI, S. IZAWA, N. RAI and M. HIRAMOTO, "Very Low Activation Energy for Carrier Generation of Surface Doped Organic Single Crystals Observed by Hall Effects," *Appl. Phys. Lett.* **115**, 113301 (4 pages) (2019).
H. UENO, I. JEON, H. LIN, A. THOTE, T. NAKAGAWA, H. OKADA, S. IZAWA, M. HIRAMOTO, S. MARUYAMA and Y. MATSUO, "Li@C_{60} Endohedral Fullerene as Supramolecular Dopant for C_{60} Electron-transporting Layer Promoting Efficiency in Perovskite Solar Cells," *Chem. Commun.* **55**, 11837–11839 (2019).
S. IZAWA, N. SHINTAKU, M. KIKUCHI and M. HIRAMOTO, "Importance of Interfacial Crystallinity to Reduce Open-Circuit Voltage Loss in Organic Solar Cells," *Appl. Phys Lett.* **115**, 153301 (4 pages) (2019).
K. FUJIMOTO, S. IZAWA, Y. ARIKAI, S. SUGIMOTO, H. OUE, T. INUZUKA, N. UEMURA, M. SAKAMOTO, M. HIRAMOTO and M. TAKAHASHI, "Regioselective Bay-Functionalization of Perylenes toward Tailor-Made Synthesis of Acceptor Materials for Organic Photovoltaics," *ChemPlusChem* **85**, 285–293 (2020).
M. KATAYAMA, T. KAJI, S. NAKAO and M. HIRAMOTO, "Ultra-Thick Organic Pigment Layer up to 10 μm Activated by Crystallization in Organic Photovoltaic Cells," *Front. Energy Res. Section Solar Energy* **8**, 1–12 (2019).
J. LEE, A. PERROT, M. HIRAMOTO and S. IZAWA, "Photoconversion Mechanism at *pn*-Homojunction Interface in Single Organic Semiconductor," *Materials* **13**, 1727 (8 pages) (2020).
Y. NAKAMURA, M. IWASHITA, M. KIKUCHI, R. TSURUTA, K. YOSHIDA, Y. GUNJO, Y. YABARA, T. HOSOKAI, T. KOGANEZAWA, S. IZAWA and M. HIRAMOTO, "Electronic and Crystallographic Examinations of the Homoepitaxially-Grown Rubrene Single Crystals," *Materials* **13**, 1978 (11 pages) (2020).
Y. YABARA, S. IZAWA and M. HIRAMOTO, "Donor/Acceptor Photovoltaic Cells Fabricated on *p*-Doped Organic Single-Crystal Substrates," *Materials* **13**, 2068 (8 pages) (2020).
K. FUJIMOTO, M. TAKAHASHI, S. IZAWA and M. HIRAMOTO, "Development of Perylene-Based Non-Fullerene Acceptors," *Materials* **13**, 1978 (11 pages) (2020).

H. NAWAZ, T. TAKEIRI, A. KUWABARA, M. YONEMURA and G. KOBAYASHI, "Synthesis and H^- Conductivity of a New Oxyhydride Ba_2YHO_3 with Anion-Ordered Rock-Salt Layers," *Chem. Commun.* **56**, 10373–10376 (2020).
J. YANAGISAWA, T. HIRAOKA, F. KAOBAYASHI, D. SAITO, M. YOSHIDA, M. KATO, F. TAKEIRI, G. KOBAYASHI, M. OHBA, L. F. LINDOY, R. OHTANI and S. HAYAMI, "Luminescent Ionic Liquid Formed from a Melted Rhenium(V) Cluster," *Chem. Commun.* **56**, 7957–7960 (2020).
Y. MATSUDA, K. FUNAKOSHI, R. SEBE, G. KOBAYASHI, M. YONEMURA, N. IMANICHI, D. MORI and S. HIGASHIMOTO, "Arrangement of Water Molecules and High Proton Conductivity of Tunnel Structure Phosphates, $KMg_{1-x}H_{2x}(PO_3)_3 \cdot yH_2O$," *RSC Adv.* **10**, 7803–7811 (2020).
F. TAKEIRI, T. YAJIMA, S. HOSOKAWA, Y. MATSUSHITA and H. KAGEYAMA, "Topochemical Anion Insertion into One-Dimensional Bi Channels in Bi_2PdO_4," *J. Solid State Chem.* **286**, 121273 (2020).
H. UBUKATA, T. BROUX, F. TAKEIRI, K. SHITARA, H. YAMASHITA, A. KUWABARA, G. KOBAYASHI and H. KAGEYAMA, "Hydride Conductivity in an Anion-Ordered Fluorite Structure LnHO with an Enlarged Bottleneck," *Chem. Mater.* **31**, 7360–7366 (2019).

D. YOSHIZAWA, Y. SAWADA, Y. KOUSAKA, J. KISHINE, Y. TOGAWA, M. MITO, K. INOUE, J. AKIMITSU, T. NAKANO, Y. NOZUE and M. HAGIWARA, "Anomalous Spiked Structures in ESR Signals from the Chiral Helimagnet $CrNb_3S_6$," *Phys. Rev. B* **100**, 104413 (6 pages) (2019).
I. G. BOSTREM, E. G. EKOMASOV, J. KISHINE, A. S. OVCHINNIKOV and V. E. SINITSYN, "Discrete Magnetic Breathers in Monoaxial Chiral Helimagnet," *Chelyabinsk Phys. Math. J.* **5(2)**, 194–201 (2020).
A. INUI, R. AOKI, Y. NISHIUE, K. SHIOTA, Y. KOUSAKA, H. SHISHIDO, D. HIROBE, M. SUDA, J. OHE, J. KISHINE, H. M. YAMAMOTO and Y. TOGAWA, "Chirality-Induced Spin-Polarized State of a Chiral Crystal $CrNb_3S_6$," *Phys. Rev. Lett.* **124**, 166602 (6 pages) (2020).
G. W. PATERSON, A. A. TERESHCHENKO, S. NAKAYAMA, Y. KOUSAKA, J. KISHINE, S. MCVITIE, A. S. OVCHINNIKOV, I. PROSKURIN and Y. TOGAWA, "Tensile Deformations of the Magnetic Chiral Soliton Lattice Probed by Lorentz Transmission Electron Microscopy," *Phys. Rev. B* **101**, 184424 (12 pages) (2020).
J. KISHINE and A. S. OVCHINNIKOV, "Magnetic Response of a Highly Nonlinear Soliton Lattice in a Monoaxial Chiral Helimagnet," *Phys. Rev. B* **101**, 184425 (12 pages) (2020).
T. TAJIRI, M. MITO, Y. KOUSAKA, J. AKIMITSU, J. KISHINE and K. INOUE, "Spontaneous Magnetostriction Effects in the Chiral Magnet $CrNb_3S_6$," *Phys. Rev. B* **102**, 014446 (7 pages) (2020).

B. ADINARAYANA, D. SHIMIZU, K. FURUKAWA and A. OSUKA, “Stable Radical versus Reversible σ-Bond Formation of (Porphyrinyl) Dicyanomethyl Radicals,” *Chem. Sci.* **10**, 6007–6012 (2019).
K. SUDOH, Y. SATOH, K. FURUKAWA, H. NAKANO and Y. MATANO, “Synthesis and Optical, Magnetic, and Electrochemical Properties of 5,10,15,20-Tetraaryl-5,15-diazaporphyrin-tertiary Amine Conjugates,” *J. Porphyrins Phthalocyanines* **24**, 286–297 (2020).
B. ADINARAYANA, K. KATO, D. SHIMIZU, T. TANAKA, K. FURUKAWA and A. OSUKA, “Cyclophane-Type Chlorin Dimers from Dynamic Covalent Chemistry of 2,18-Porphyrinyl Dicyanomethyl Diradicals,” *Angew. Chem., Int. Ed.* **59**, 4320–4323 (2020).

K. GOTO, M. ASADA, T. NAKAMURA and F. TANI, “Switching Photomechanical Response by Structural Phase Transition and Evaluating Responsivity from Relaxation,” *ChemPhotoChem* **4**, 1–7 (2020).
T. INOUE, M. SHIBUTA, T. SUZUKI and A. NAKAJIMA, “Occupied and Unoccupied Levels of Half-Fluorinated and Perfluorinated Rubrene Thin Films Probed by One- and Two-Photon Photoemission,” *J. Phys. Chem. C* **124**, 12409–12416 (2020).

Life and Coordination-Complex Molecular Science

N. MURAKI, K. ISHII, S. UCHIYAMA, S. G. ITOH, H. OKUMURA and S. AONO, “Structural Characterization of HypX Responsible for CO Biosynthesis in the Maturation of NiFe-Hydrogenase,” *Commun. Biol.* **2**, 385 (12 pages) (2019).
N. MURAKI, C. KITATSUJI, Y. OKAMOTO, T. UCHIDA, K. ISHIMORI and S. AONO, “Structural Basis for Heme Transfer Reaction in Heme Uptake Machinery from Corynebacteria,” *Chem. Commun.* **55**, 13864–13867 (2019).

R. INOUE, T. NAKAGAWA, K. MORISHIMA, N. SATO, A. OKUDA, R. URADE, R. YOGO, S. YANAKA, M. YAGI-UTSUMI, K. KATO, K. OMOTO, K. ITO and M. SUGIYAMA, “Newly Developed Laboratory-Based Size Exclusion Chromatography Small-Angle X-Ray Scattering System (La-SSS),” *Sci. Rep.* **9**, 12610 (12 pages) (2019).
R. MURAKAMI, Y. YUNOKI, K. ISHII, K. TERAUCHI, S. UCHIYAMA, H. YAGI and K. KATO, “Cooperative Bbinding of KaiB to the KaiC Hexamer Ensures Accurate Circadian Clock Oscillation in Cyanobacteria,” *Int. J. Mol. Sci.* **20**, 4550 (10 pages) (2019).
C. CHO, J. JANG, Y. KANG, H. WATANABE, T. UCHIHASHI, S. J. KIM, K. KATO, J. Y. LEE and J.-J. SONG, “Structural Basis of Nucleosome Assembly by the Abo1 AAA+ATPase Histone Chaperone,” *Nat. Commun.* **10**, 5764 (13 pages) (2019).
M. L. A. DE LEOZ, D. L. DUEWER, A. FUNG, L. LIU, H. K. YAU, O. POTTER, G. O. STAPLES, K. FURUKI, R. FRENKEL, Y. HU, Z. SOSIC, P. ZHANG, F. ALTMANN, C. GRUBER, C. SHAO, J. ZAIA, W. EVERS, S. PANGELLEY, D. SUCKAU, A. WIECHMANN, A. RESEMANN, W. JABS, A. BECK, J. W. FROEHLICH, C. HUANG, Y. LI, Y. LIU, S. SUN, Y. WANG, Y. SEO, H. J. AN, N. C. REICHARDT, J. E. RUIZ, S. ARCHER-HARTMANN, P. AZADI, L. BELL, Z. LAKOS, Y. AN, J. F. CIPOLLO, M. PUČIĆ-BAKOVIĆ, J. ŠTAMBUK, G. LAUC, X. LI, P. G. WANG, A. BOCK, R. HENNIG, E. RAPP, M. CRESKEY, T. CYR, M. NAKANO, T. SUGIYAMA, P. A. LEUNG, P. LINK-LENCZOWSKI, J. JAWOREK, S. J. YANG, H. ZHANG, T. KELLY, S. KLAPOETKE, R. CAO, J. Y. KIM, H. K. LEE, J. LEE, J. S. YOO, S. R. KIM, S. K. SUH, N. DE HAAN, D. FALCK, G. S. M. LAGEVEEN-KAMMEIJER, M. WUHRER, R. J. EMERY, R. P. KOZAK, L. P. LIEW, L. ROYLE, P. A. URBANOWICZ, N. PACKER, X. SONG, A. EVEREST-DASS, E. LATTOVÁ, S. CAJIC, K. ALAGESAN, D. KOLARICH, T. KASALI, V. LINDO, Y. CHEN, K. GOSWAMI, B. GAU, R. AMUNUGAMA, R. JONES, C. J. M. STROOP, K. KATO, H. YAGI, S. KONDO, C. T. YUEN, A. HARAZONO, X. SHI, P. MAGNELLI, B. T. KASPER, L. K. MAHAL, D. J. HARVEY, R. M. O'FLAHERTY, P. RUDD, R. SALDOVA, E. S. HECHT, D. C. MUDDIMAN, J. KANG, P. BHOSKAR, D. MENARD, A. SAATI, C. MERLE, S. MAST, S. TEP, J. TRUONG, T. NISHIKAZE, S. SEKIYA, A. SHAFER, S. FUNAOKA, M. TOYODA, P. DE VREUGD, C. CARON, P. PRADHAN, N. C. TAN, Y. MECHREF, S. PATIL, J. S. ROHRER, R. CHAKRABARTI, D. DADKE, M. LAHORI, C. ZOU, C. W. CAIRO, B. REIZ, R. M. WHITTAL, C. LEBRILLA, L. D. WU, A. GUTTMAN, M. SZIGETI, B. G. KREMKOW, K. LEE, C. SIHLBOM, B. ADAMCZYK, C. JIN, N. G. KARLSSON, J. ÖRNROS, G. LARSON, J. NILSSON, B. MEYER, A. WIEGANDT, E. KOMATSU, H. PERREAULT, E. D. BODNAR, N. SAID, Y. N. FRANCOIS, E. LEIZE-WAGNER, S. MAIER, A. ZECK, A. J. R. HECK, Y. YANG, R. HASELBERG, Y. Q. YU, W. ALLEY, J. W. LEONE, H. YUAN and S. E. STEIN, “NIST Interlaboratory Study on Glycosylation Analysis of Monoclonal Antibodies: Comparison of Results from Diverse Analytical Methods,” *Mol. Cell. Proteomics* **19**, 11–30 (2020).
S. YANAKA, R. YOGO, H. WATANABE, Y. TANIGUCHI, T. SATOH, N. KOMURA, H. ANDO, H. YAGI, N. YUKI, T. UCHIHASHI and K. KATO, “On-Membrane Dynamic Interplay between Anti-GM1 IgG Antibodies and Complement Component C1q,” *Int. J. Mol. Sci.* **21**, 147 (12 pages) (2020).
M. YAGI-UTSUMI, A. SIKDAR, C. SONG, J. PARK, R. INOUE, H. WATANABE, R. N. BURTON-SMITH, T. KOZAI, T. SUZUKI, A. KODAMA, K. ISHII, H. YAGI, T. SATOH, S. UCHIYAMA, T. UCHIHASHI, K. JOO, J. LEE, M. SUGIYAMA, K. MURATA and K. KATO, “Supramolecular Tholos-Like Architecture Constituted by Archaeal Proteins without Functional Annotation,” *Sci. Rep.* **10**, 1540 (10 pages) (2020).
G. GEORGE, S. NINAGAWA, H. YAGI, T. SAITO, T. ISHIKAWA, T. SAKUMA, T. YAMAMOTO, K. IMAMI, Y. ISHIHAMA, K. KATO, T. OKADA and K. MORI, “EDEM2 Stably Disulfide-Bonded to TXNDC11 Catalyzes the First Mannose Trimming Step in Mammalian Glycoprotein ERAD,” *eLife* **9**, e53455 (19 pages) (2020).
H. YAGI, M. YAGI-UTSUMI, R. HONDA, Y. OHTA, T. SAITO, M. NISHIO, S. NINAGAWA, K. SUZUKI, T. ANZAI, Y. KAMIYA, K. AOKI, M. NAKANISHI, T. SATOH and K. KATO, “Improved Secretion of Glycoproteins Using an N-Glycan-Restricted Passport Sequence Tag Recognized by Cargo Receptor,” *Nat. Commun.* **11**, 1368 (9 pages) (2020).
K. YAMADA, Y. YAMAGUCHI, Y. UEKUSA, K. AOKI, I. SHIMADA, T. YAMAGUCHI and K. KATO, “Solid-State ^{17}O NMR Analysis of Synthetically ^{17}O-Enriched D-Glucosamine,” *Chem.Phys. Lett.* **749**, 137455 (5 pages) (2020).
T. SATOH, M. NISHIO, K. SUZUKI, M. YAGI-UTSUMI, Y. KAMIYA, T. MIZUSHIMA and K. KATO, “Crystallographic Snapshots of the EF-Hand Protein MCFD2 Complexed with the Intracellular Lectin ERGIC-53 Involved in Glycoprotein Transport,” *Acta Crystallogr., Sect. F: Struct. Biol. Commun.* **76**, 216–221 (2020).

LIST OF PUBLICATIONS

K. MORISHIMA, A. OKUDA, R. INOUE, N. SATO, Y. MIYAMOTO, R. URADE, M. YAGI-UTSUMI, K. KATO, R. HIRANO, T. KUJIRAI, H. KURUMIZAKA and M. SUGIYAMA, "Integral Approach to Biomacromolecular Structure by Analytical-Ultracentrifugation and Small-Angle Scattering," *Commun. Biol.* **3**, 294 (7 pages) (2020).

M. YAGI-UTSUMI, S. YANAKA, C. SONG, T. SATOH, C. YAMAZAKI, H. KASAHARA, T. SHIMAZU, K. MURATA and K. KATO, "Characterization of Amyloid β Fibril Formation under Microgravity Conditions," *NPJ Microgravity* **6**, 17 (6 pages) (2020).

M. HIRANYAKORN, S. YANAKA, T. SATOH, T. WILASRI, B. JITYUTI, M. YAGI-UTSUMI and K. KATO, "NMR Characterization of Conformational Interconversions of Lys48-Linked Ubiquitin Chains," *Int. J. Mol. Sci.* **21**, 5351 (12 pages) (2020).

K. OKAZAKI, A. NAKAMURA and R. IINO, "Chemical-State-Dependent Free Energy Profile from Single-Molecule Trajectories of Biomolecular Motor: Application to Processive Chitinase," *J. Phys. Chem. B* **124**, 6475–6487 (2020). DOI: 10.1021/acs.jpcb.0c02698

J. ANDO, T. SHIMA, R. KANAZAWA, R. SHIMO-KON, A. NAKAMURA, M. YAMAMOTO, T. KON and R. IINO, "Small Stepping Motion of Processive Dynein Revealed by Load-Free High-Speed Single-Particle Tracking," *Sci. Rep.* **10**, 1080 (11 pages) (2020). DOI: 10.1038/s41598-020-58070-y

A, VISOOTSAT, A. NAKAMURA, P. VIGNON, H. WATANABE, T. UCHIHASHI and R. IINO, "Single-Molecule Imaging Analysis Reveals the Mechanism of a High-Catalytic-Activity Mutant of Chitinase A from *Serratia marcescens*," *J. Biol. Chem.* **295**, 1915–1925 (2020). DOI: 10.1074/jbc.RA119.012078

J. ANDO, A. NAKAMURA, M. YAMAMOTO, C. SONG, K. MURATA and R. IINO, "Multicolor High-Speed Tracking of Single Biomolecules with Silver, Gold, Silver-Gold Alloy Nanoparticles," *ACS Photonics* **6**, 2870–2883 (2019). DOI: 10.1021/acsphotonics.9b00953

T. IIDA, Y. MINAGAWA, H. UENO, F. KAWAI, T. MURATA and R. IINO, "Single-Molecule Analysis Reveals Rotational Substeps and Chemo-Mechanical Coupling Scheme of *Enterococcus hirae* V_1-ATPase," *J. Biol. Chem.* **294**, 17017–17030 (2019). DOI: 10.1074/jbc.ra119.008947.

M. MATSUO, Y. HIRATA, K. KURIHARA, T. TOYOTA, T. MIURA, K. SUZUKI and T. SUGAWARA, "Environment-Sensitive Intelligent Self-Reproducing Artificial Cell with a Modification-Active Lipo-Deoxyribozyme," *Micromachines* **11**, 606 (18 pages) (2020).

A. OHTAKA, M. KAWASE, A. USAMI, S. FUKUI, M. YAMASHITA, K. YAMAGUCHI, A. SAKON, T. SHIRAKI, T. ISHIDA, S. NAGATA, Y. KIMURA, G. HAMASAKA, Y. UOZUMI, T. SHINAGAWA, O. SHIMOMURA and R. NOMURA, "Mechanistic Study on Allylic Arylation in Water with Linear Polystyrene-Stabilized Pd and PdO Nanoparticles," *ACS Omega* **4**, 15764–15770 (2019).

G. HAMASAKA, D. ROY, A. TAZAWA and Y. UOZUMI, "Arylation of Terminal Alkynes by Aryl Iodides Catalyzed by a Parts-per-Million Loading of Palladium Acetate," *ACS Catal.* **9**, 11640–11646 (2019).

H. OHTA, K. TOBAYASHI, A. KUROO, M. NAKATSUKA, H. KOBAYASHI, A. FUKUOKA, G. HAMASAKA, Y. UOZUMI, H. MURAYAMA, M. TOKUNAGA and M. HAYASHI, "Surface Modification of a Supported Pt Catalyst Using Ionic Liquids for Selective Hydrodeoxygenation of Phenols into Arenes under Mild Conditions," *Chem. –Eur. J.* **25**, 14762–14766 (2019).

S. ICHII, G. HAMASAKA and Y. UOZUMI, "The Hiyama Cross-Coupling Reaction at Parts Per Million Levels of Pd: In Situ Formation of Highly Active Spirosilicates in Glycol Solvents," *Chem. –Asian J.* **14**, 3850–3854 (2019).

H. HU, H. OTA, H. BAEK, K. SHINOHARA, T. MASE, Y. UOZUMI and Y. M. A. YAMADA, "Second-Generation meta-Phenolsulfonic Acid–Formaldehyde Resin as a Catalyst for Continuous-Flow Esterification," *Org. Lett.* **22**, 160–163 (2020).

T. OSAKO, J. SRISA, K. TORII, G. HAMASAKA and Y. UOZUMI, "Iterative Preparation of Platinum Nanoparticles in an Amphiphilic Polymer Matrix: Regulation of Catalytic Activity in Hydrogenation," *Synlett* **31**, 147–152 (2020).

H. BAEK, K. KASHIMURA, T. FUJII, S. TSUBAKI, Y. WADA, S. FUJIKAWA, T. SATO, Y. UOZUMI and Y. M. A. YAMADA, "Production of Bio Hydrofined Diesel, Jet Fuel, and Carbon Monoxide from Fatty Acids Using a Silicon Nanowire Array-Supported Rhodium Nanoparticle Catalyst under Microwave Conditions," *ACS Catal.* **10**, 2148–2156 (2020).

R. N. DHITAL, A. SEN, T. SATO, H. HU, R. ISHII, D. HASHIZUME, H. TAKAYA, Y. UOZUMI and Y. M. A. YAMADA, "Activator-Promoted Aryl Halide-Dependent Chemoselective Buchwald–Hartwig and Suzuki–Miyaura Type Cross-Coupling Reactions," *Org. Lett.* **22**, 4797–4801 (2020).

S. MIZUNO, H. TSUJI, Y. UOZUMI and M. KAWATSURA, "Synthesis of α-Tertiary Amines by the Ruthenium-catalyzed Regioselective Allylic Amination of Tertiary Allylic Esters," *Chem. Lett.* **49**, 645–647 (2020).

C. OHDE, T. KUSAMOTO and H. NISHIHARA, "Effects of Halogen Atom Replacement on the Structure and Magnetic Properties of a Molecular Crystal with Supramolecular Two-Dimensional Network Mediated via Sulfur's σ-Holes," *J. Magn. Magn. Mater.* **497**, 165986 (6 pages) (2020).

H. MAEDA, A. BAJPAYEE, T. KUSAMOTO and H. NISHIHARA, "Construction of Bis(2,6-bis(1-methylbenzimidazol-2-yl)pyridine)iron(II) Coordination Polymer for Incorporation of Magnetic Function," J. *Inorg. Organomet. Polym. Mater.* **30**, 147–152 (2020).

Y. LI, Y. SEGAWA, A. YAGI and K. ITAMI, "A Nonalternant Aromatic Belt: Methylene-Bridged [6]Cycloparaphenylene Synthesized from Pillar[6]arene," *J. Am. Chem. Soc.* **142**, 12850–12856 (2020).

H. SHUDO, M. KUWAYAMA, Y. SEGAWA and K. ITAMI, "Synthesis of Cycloiptycenes from Carbon Nanobelt," *Chem. Sci.* **11**, 6775–6779 (2020).

A. NAKA (FUKAZAWA), S. S. W. OEY (Kyoto University), "Diaryldithienophosphorines and Near-Infrared Absorbing Dyes Using These Compounds," JP2020/036443, 2020.

Research Center of Integrative Molecular Systems

K. ITO-MIWA, Y. FURUIKE, S. AKIYAMA and T. KONDO, "Tuning the Circadian Period of Cyanobacteria up to 6.6 Days by the Single Amino Acid Substitutions in KaiC," *Proc. Natl. Acad. Sci. U. S. A.* **117**, 20926–20931 (2020). doi.org/10.1073/pnas.2005496117
I. ANZAI, E. TOKUDA, S. HANDA, H. MISAWA, S. AKIYAMA and Y. FURUKAWA, "Oxidative Misfolding of Cu/Zn-Superoxide Dismutase Triggered by Non-Canonical Intramolecular Disulfide Formation," *Free Radical Biol. Med.* **147**, 187–199 (2020). doi.org/10.1016/j.freeradbiomed.2019.12.017

Y. KAWAKAMI, T. AMANO, H. OHASHI, H. ITOH, Y. NAKAMURA, H. KISHIDA, T. SASAKI, G. KAWAGUCHI, H. M. YAMAMOTO, K. YAMAMOTO, S. ISHIHARA, K. YONEMITSU and S. IWAI, "Petahertz Non-Linear Current in a Centrosymmetric Organic Superconductor," *Nat. Commun.* **11**, 4138 (6 pages) (2020).
Y. NABEI, D. HIROBE, Y. SHIMAMOTO, K. SHIOTA, A. INUI, Y. KOUSAKA, Y. TOGAWA and H. M. YAMAMOTO, "Current-Induced Bulk Magnetization of a Chiral Crystal $CrNb_3S_6$," *Appl. Phys. Lett.* **117**, 052408 (5 pages) (2020).
A. INUI, R. AOKI, Y. NISHIUE, K. SHIOTA, Y. KOUSAKA, H. SHISHIDO, D. HIROBE, M. SUDA, J. OHE, J. KISHINE, H. M. YAMAMOTO and Y. TOGAWA, "Chirality-Induced Spin-Polarized State of a Chiral Crystal $CrNb_3S_6$," *Phys. Rev. Lett.* **124**, 166602 (6 pages) (2020).
Y. KAWASUGI, K. SEKI, J. PU, T. TAKENOBU, S. YUNOKI, H. M. YAMAMOTO and R. KATO, "Non-Fermi-Liquid Behavior and Doping Asymmetry in an Organic Mott Insulator Interface," *Phys. Rev. B* **100**, 115141 (7 pages) (2019).
G. KAWAGUCHI and H. M. YAMAMOTO, "Control of Organic Superconducting Field-Effect Transistor by Cooling Rate," *Crystals* **9**, 605 (8 pages) (2019).
S. OGIKUBO, G. HASHIMOTO, T. UBE, M. SUDA, H. M. YAMAMOTO and T. IKEDA, "Photoinduced Deformation and Isomerization of Azobenzene Liquid-Crystalline Polymer Films at Cryogenic Temperature," *Mol. Cryst. Liq. Cryst.* **676**, 30–35 (2019).
T. CHOOPPAWA, S. NAMUANGRUK, H. M. YAMAMOTO, V. PROMARAK and P. RASHATASAKHON, "Synthesis, Characterization, and Hole-Transporting Properties of Benzotriazatruxene Derivatives," *J. Mater. Chem. C* **7**, 15035–15041 (2019).
Y. SHIOMI, J. LUSTIKOVA, S. WATANABE, D. HIROBE, S. TAKAHASHI and E. SAITOH, "Spin Pumping from Nuclear Spin Waves," *Nat. Phys.* **15**, 22–26 (2019).
M. KAMEDA, D. HIROBE, S. DAIMON, Y. SHIOMI, S. TAKAHASHI and E. SAITOH, "Microscopic Formulation of Nonlinear Spin Current Induced by Spin Pumping," *J. Magn. Magn. Mater.* **476**, 459–463 (2019).
N. ITO, T. KIKKAWA, J. BARKER, D. HIROBE, Y. SHIOMI and E. SAITOH, "Spin Seebeck Effect in Layered Ferromagnetic Insulators $CrSiTe_3$ and $CrGeTe_3$," *Phys. Rev. B* **100**, 060402(R) (6 pages) (2019).

Division of Advanced Molecular Science

Y. TAMURA, H. TAKEZAWA and M. FUJITA, "A Robust Double-Walled Knotted Cage Revealed Guest Binding through Adaptive Portal Expansion," *Chem. Lett.* **49**, 912–914 (2020). DOI: 10.1246/cl.200282
H. TAKEZAWA, K. SHITOZAWA and M. FUJITA, "Enhanced Reactivity of Twisted Amides Inside a Molecular Cage," *Nat. Chem.* **12**, 574–578 (2020). DOI: 10.1038/s41557-020-0455-y
Y. MORISHITA, T. SONOHARA, T. TANIGUCHI, K. ADACHI, M. FUJITA and T. ASAI, "Synthetic-Biology-Based Discovery of a Fungal Macrolide from Macrophomina Phaseolina," *Org. Biomol. Chem.* **18**, 2813–2816 (2020). DOI: 10.1039/D0OB00519C
Y. TAMURA, H. TAKEZAWA and M. FUJITA, "A Double-Walled Knotted Cage for Guest-Adaptive Molecular Recognition," *J. Am. Chem. Soc.* **142**, 5504–5508 (2020). DOI: 10.1021/jacs.0c00459
I. MORITA, T. MORI, T. MITSUHASHI, S. HOSHINO, Y. TANIGUCHI, T. KIKUCHI, K. NAGAE, N. NASU, M. FUJITA, T. OHWADA and I. ABE, "Exploiting a C–N Bond Forming Cytochrome P450 Monooxygenase for C–S Bond Formation," *Angew. Chem., Int. Ed.* **59**, 3988–3993 (2020). DOI: 10.1002/anie.201916269
Y. INOMATA, T. SAWADA and M. FUJITA, "Metal-Peptide Torus Knots from Flexible Short Peptides," *Chem* **6**, 294–303 (2020). DOI: 10.1016/j.chempr.2019.12.009
Y. DOMOTO, M. ABE, T. KIKUCHI and M. FUJITA, "Self-Assembly of Coordination Polyhedra with Highly Entangled Faces Induced by Metal–Acetylene Interactions," *Angew. Chem., Int. Ed.* **59**, 3450–3454 (2020). DOI: 10.1002/anie.201913142

Y. KANAZAWA, T. MITSUDOME, H. TAKAYA and M. HIRANO, "Pd/Cu-Catalyzed Dehydrogenative Coupling of Dimethyl Phthalate: Synchrotron Radiation Sheds Light on the Cu Cycle Mechanism," *ACS Catal.* **10**, 5909–5919 (2020).

Division of Research Innovation and Collaboration

T. KAWASAKI, V. YAHIA and T. TAIRA, "High Brightness Micro-MOPA (Master Oscillator Power Amplifier) with 100-Hz and 100-mJ Operation," *Rev. Laser Eng.* **47(4)**, 221–224 (2019). (in Japanese)
L. ZHENG, A. KAUSAS and T. TAIRA, ">30 MW Peak Power from Distributed Face Cooling Tiny Integrated Laser," *Opt. Express* **27**, 30217–30224 (2019). DOI: 10.1364/OE.27.030217
H. H. LIM and T. TAIRA, "High Peak Power Nd:YAG/Cr:YAG Ceramic Microchip Laser with Unstable Resonator," *Opt. Express* **27**, 31307–31315 (2019). DOI: 10.1364/OE.27.031307

T. SANO, T. EIMURA, A. HIROSE, Y. KAWAHITO, S. KATAYAMA, K. ARAKAWA, K. MASAKI, A. SHIRO, T. SHOBU and Y. SANO, "Improving Fatigue Performance of Laser-Welded 2024-T3 Aluminum Alloy Using Dry Laser Peening," *Metals* **9**, 1192 (13 pages) (2019). DOI: 10.3390/met9111192

H. ISHIZUKI and T. TAIRA, "Polarity Inversion of Crystal Quartz Using a Quasi-Phase Matching Stamp," *Opt. Express* **28**, 6505–6510 (2020). DOI: 10.1364/OE.386991

F. CASSOURET, A. KAUSAS, V. YAHIA, G. AKA, P. LOISEAU and T. TAIRA, "High Peak-Power Near-MW Laser Pulses by Third Harmonic Generation at 355 nm in $Ca_5(BO_3)_3F$ Nonlinear Single Crystals," *Opt. Express* **28**, 10524–10530 (2020). DOI: 10.1364/OE.384281

O. SAITO, E. SEN, Y. OKABE, N. HIGUCHI, H. ISHIZUKI and T. TAIRA, "Laser Wavelengths Suitable for Generating Ultrasonic Waves in Resin-Coated Carbon Fiber Composites," *ASME J. Nondestructive Evaluation*, **3**, 031103 (11 pages) (2020). DOI: 10.1115/1.4046719

K. TAMURA, H. OHBA, M. SAEKI, T. TAGUCHI, H. H. LIM, T. TAIRA and I. WAKAIDA, "Development of a Laser-Induced Breakdown Spectroscopy System Using a Ceramic Micro-Laser for Fiber-Optic Remote Analysis," *J. Nucl. Sci. Technol.* **57**, 1189–1198 (2020). DOI: 10.1080/00223131.2020.1776648

Y. SANO, "Quarter Century Development of Laser Peening without Coating," *Metals* **10**, 152 (11 pages) (2020). DOI: 10.3390/met10010152

Y. SANO, K. AKITA and T. SANO, "A Mechanism for Inducing Compressive Residual Stresses on a Surface by Laser Peening without Coating," *Metals* **10**, 816 (12 pages) (2020). DOI: 10.3390/met10060816

S. TOKITA, H. KOKAWA, S. KODAMA, Y. S. SATO, Y. SANO, Z. LI, K. FENG and Y. WU, "Suppression of Intergranular Corrosion by Surface Grain Boundary Engineering of 304 Austenitic Stainless Steel Using Laser Peening Plus Annealing," *Mater. Today Commun.* **25**, 101572 (7 pages) (2020). DOI: 10.1016/j.mtcomm.2020.101572

Theoretical and Computational Molecular Science

C. R. BAIZ , B. BŁASIAK, J. BREDENBECK, M. CHO, J.-H. CHOI, S. A. CORCELLI, A. G. DIJKSTRA, C.-J. FENG, S. GARRETT-ROE, N.-H. GE, M. W. D. HANSON-HEINE, J. D. HIRST, T. L. C. JANSEN, K. KWAC, K. J. KUBARYCH, C. H. LONDERGAN, H. MAEKAWA, M. REPPERT, S. SAITO, S. ROY, J. L. SKINNER, G. STOCK, J. E. STRAUB, M. C. THIELGES, K. TOMINAGA, A. TOKMAKOFF, H. TORII, L. WANG, L. J. WEBB and M. T. ZANNI, "Vibrational Spectroscopic Map, Vibrational Spectroscopy, and Intermolecular Interaction," *Chem. Rev.* **120**, 7152–7218 (2020).

C.-L. LIN, N. KAWAKAMI, R. ARAFUNE, E. MINAMITANI and N. TAKAGI, "Scanning Tunneling Spectroscopy Studies of Topological Materials," *J. Phys.: Condens. Matter* **32**, 243001 (24 pages) (2020). DOI: 10.1088/1361-648X/ab777d

M. EHARA and Y. MORISAWA, "Theoretical and Experimental Molecular Spectroscopy of Far-Ultraviolet Region," in *Molecular Spectroscopy: A Quantum Chemistry Approach*, Y. Ozaki, M. J. Wojcik and J. Popp, Eds., Wiley, pp. 119–145 (2019).
Y. MAEDA, M. YAMADA and M. EHARA, "Chemical Functionalization and Characterization of Carbon Nanotubes," *Carbon*, **290**, 183–194 (2019). (in Japanese)

A. NAKAMURA, K. OKAZAKI, T. FURUTA, M. SAKURAI and R. IINO, "Chitinase Moves on and Degradates Crystalline Chitin with Brownian Motion," *Seibutsubutsuri*, **59(6)**, 330–333 (2019). (in Japanese)
K. OKAZAKI, "Mechanism of Na^+/H^+ Antiporter from Molecular Simulations and Engineering of a Faster Transporte," *Seibutsubutsuri*, **60(2)**, 102–104 (2020). (in Japanese)

Photo-Molecular Science

F. MATSUI, T. MATSUSHITA and H. DAIMON, *Detailed Introduction to Photoelectron Spectroscopy*, Maruzen; Tokyo, pp. 1–298 (2020). (in Japanese)
T. KINOSHITA, T. MURO, T. MATSUSHITA, H. OSAWA, T. OHKOCHI, F. MATSUI, H. MATSUDA, M. SHIMOMURA, M. TAGUCHI and H. DAIMON, "Progress in Photoelectron Holography at SPring-8," *Jpn. J. Appl. Phys.* **58**, 110503 (11 pages) (2019).

M. NAGASAKA, H. YUZAWA and N. KOSUGI, "Soft X-Ray Absorption Spectroscopy of Liquids for Understanding Chemical Processes in Solution," *Anal. Sci.* **36(1)**, 95–105 (2020).
M. NAGASAKA and N. KOSUGI, "Soft X-Ray Liquid Absorption Spectroscopy in Transmission Mode Realized by Precise Thickness Control," *Butsuri*, **75(8)**, 496–503 (2020). (in Japanese)

K. SHIMADA, "Hiroshima Synchrotron Radiation Center at Hiroshima University," *AAPPS Bulletin* **30(4)**, 30–34 (2020).

Materials Molecular Science

T. YOKOYAMA and Y. IWASAWA, "*Operando* Observation of Sulfur Species that Poison Polymer Electrolyte Fuel Cell Studied by Near Ambient Pressure Hard X-Ray Photoelectron Spectroscopy," *SPring-8 Research Frontiers* **2019**, 64–65 (2020).
T. URUGA, M. TADA, O. SEKIZAWA, Y. TAKAGI, T. YOKOYAMA and Y. IWASAWA, "Status of Synchrotron Radiation X-Ray-Based Multi-Analytical Beamline BL36XU for Fuel Cell Electrocatalysis Research at SPring-8," *Synchrotron Radiation News* **33**, 26–28 (2020).
K. YAMAMOTO, "Report of the 40th International Conference on Vacuum Ultraviolet and X-Ray Physics (VUVX2019)," *J. Jpn. Soc. Synchrotron Radiat. Res.* **32**, 333–335 (2019). (in Japanese)
T. KOITAYA, S. YAMAMOTO, I. MATSUDA and J. YOSHINOBU, "Surface Chemistry of Carbon Dioxide on Copper Model Catalysts Studied by Ambient-Pressure X-Ray Photoelectron Spectroscopy," *e-J. Surf. Sci. Nanotechnol.* **17**, 169–178 (2019).

T. SUGIMOTO, "Peculiar Hydrogen-Bond Structure, Physical Properties and Function of Interfacial Water Molecules Elucidated by Nonlinear Laser Spectroscopy," *Mol. Sci.* **14**, A0112 (2020). (Award Accounts, 12th Young Scientist Award of the Physical Society of Japan) DOI: 10.3175/molsci.14.A0112
T. SUGIMOTO and Y. MATSUMOTO, "Orientational Ordering in Heteroepitaxial Water Ice on Metal Surfaces," *Phys. Chem. Chem. Phys.* **29**, 16435–17012 (2020). DOI: 10.1039/D0CP01763A
T. SUGIMOTO, "Unique Hydrogen-Bond Structures of Water Molecules at Ice Surface," *Chemistry and Chemical Industry* **73(6)**, 490 (2020). (in Japanese)
T. SUGIMOTO, "Observation of Proton Ordering in Crystalline-Ice Films Grown on Low-Temperature Substrate by Sum-Frequency Generation Spectroscopy," *Lot. Temp. Sci.* **78**, 61–70 (2020). DOI: 10.14943/lowtemsci.78.61

M. HIRAMOTO, M. KIKUCHI and S. IZAWA, "Lateral Junction for Single Crystalline Organic Solar Cells," in *Liquid and Single Crystals: Properties, Manufacturing and Uses*, J. Groosen, Ed., NOVA Science Publishers, Inc.; New York, Chap. 6, pp. 205–239 (2019).
S. IZAWA, K. FUJIMOTO, M. TAKAHASHI and M. HIRAMOTO, "Reduction of Voltage Loss of Organic Solar Cells—Toward the Realization of Organic Solar Cells Comparable to the High-Efficient Inorganic Solar Cells," *Clean Energy*, **29**, 42–48 (2020). (in Japanese)
M. HIRAMOTO and S. IZAWA, "New Phase of Organic Solar Cells—Close Up of the Suppression of Radiationless Recombination," *Kagaku*, **75**, 68–69 (2020). (in Japanese)

G. KOBAYASHI, “H$^-$ Conductors~Current State of Materials Development and Potential Applications for Batteries~,” *Denkikagaku*, **87**, 227–232 (2019). (in Japanese)

Life and Coordination-Complex Molecular Science

C. SATO, K. KATO, Y. YAMAGUCHI, D. KOHDA, R. KATO, K. G. N. SUZUKI, K. KIKUCHI, G. HIRAI, Y. KIZUKA, K. TANAKA, Y. NAKASHIMA and M. SETOU, “Structural Biology of Glycans,” in *Glycoscience: Basic Science to Applications*, N. TANIGUCHI, T. ENDO, J. HIRABAYASHI, S. NISHIHARA, K. KADOMATSU, K. AKIYOSHI and K. F. AOKI-KINOSHITA, Eds., Springer; Singapore, pp. 35–63 (2019).

T. SATOH and K. KATO, “Recombinant Expression and Purification of Animal Intracellular L-Type Lectins,” in *Lectin Purification and Analysis, Methods in Molecular Biology*, J. HIRABAYASHI, Ed., Humana Press; New York, **2132**, pp. 411–417 (2020).

S. YANAKA, R. YOGO and K. KATO, “Biophysical Characterization of Dynamic Structures of Immunoglobulin G,” *Biophys. Rev.* **12**, 637–645 (2020).

A. NAKAMURA, K. OKAZAKI, T. FURUTA, M. SAKURAI, J. ANDO and R. IINO, “Crystalline Chitin Hydrolase Is a Burnt-Bridge Brownian Motor,” *Biophys. Physicobiol.* **17**, 51–58 (2020). DOI: 10.2142/biophysico.BSJ-2020004

R. IINO, K. KINBARA and Z. BRYANT, “Introduction: Molecular Motors,” *Chem. Rev.* **120**, 1–4 (2020). DOI: 10.1021/acs.chemrev.9b00819

A. NAKAMURA, K. OKAZAKI, T. FURUTA, M. SAKURAI and R. IINO, “Chitinase Moves on and Degradates Crystalline Chitin with Brownian Motion,” *Seibutsubutsuri*, **59(6)**, 330–333 (2019). (in Japanese)

T. KUSAMOTO, “Development of Photofunctions of Open-Shell Molecules Based on Coordination Chemistry,” *Bull. Jpn. Soc. Coord. Chem.* **75**, 35–41 (2020). (in Japanese)

Research Center of Integrative Molecular Systems

S. AKIYAMA, K. AOKI and Y. KUBO, “Biophysical Research in Okazaki, Japan,” *Biophys. Rev.* **12**, 237–243 (2020). doi.org/10.1007/s12551-020-00633-4

S. AKIYAMA, “Treasurer’s Comments on the Financial Position of the Biophysical Society of Japan,” *Biophys. Rev.* **12**, 209–211 (2020). doi.org/10.1007/s12551-020-00623-6

R. KOGA and N. KOGA, “Consistency Principle for Protein Design,” *Biophys. Physicobiol.* **16**, 304–309 (2019).

M. SUDA and H. M. YAMAMOTO, “Reconfigurable Spin Filter Based on Molecular Motor,” *Ouyoubutsuri*, **89(4)**, 203–207 (2020). (in Japansese)

Center for Mesoscopic Sciences

H. OKAMOTO, “Local Optical Activity of Nano-to Microscale Materials and Plasmons,” *J. Mater. Chem. C* **7**, 14771–14787 (2019).

Division of Advanced Molecular Science

T. SAWADA and M. FUJITA, “Folding and Assembly of Metal-Linked Peptidic Nanostructures,” *Chem* **6**, 1861–1876 (2020). DOI: 10.1016/j.chempr.2020.07.002

H. TAKAYA, “Mechanistic Studies on Microwave-Assisted Organic Reactions,” *Chemistry and Chemical Industry* **73(3)**, 230–231 (2020). (in Japanese)

H. TAKAYAa, “No. 367: $FeHC_6Si_2$,” *Encyclopedia of Coordination Compounds*, 391 (2020).

Division of Research Innovation and Collaboration

Y. SANO, “Program Manager Role (ImPACT),” *OYO BUTURI*, **88(8)**, pp. 539–541 (2019). (in Japanese)

Y. SATO and T. TAIRA, “Transparent Ceramics Made of Non-Isometric Crystals,” *Rev. Laser Eng.* **47(8)**, pp. 442–447 (2019). (in Japanese)

Y. SATO and T. TAIRA, “Report on OPIC2019 the 7th Laser Ignition and Giant-Microphotonics Conference 2019 (LIC2019),” *Rev. Laser Eng.* **47(11)**, pp. 650–651 (2019).

T. TAIRA, “Micro Domain Control toward Tiny Integrated Power Lasers,” *CERAMICS JAPAN*, **55(2)**, pp. 113–116 (2020). (in Japanese)

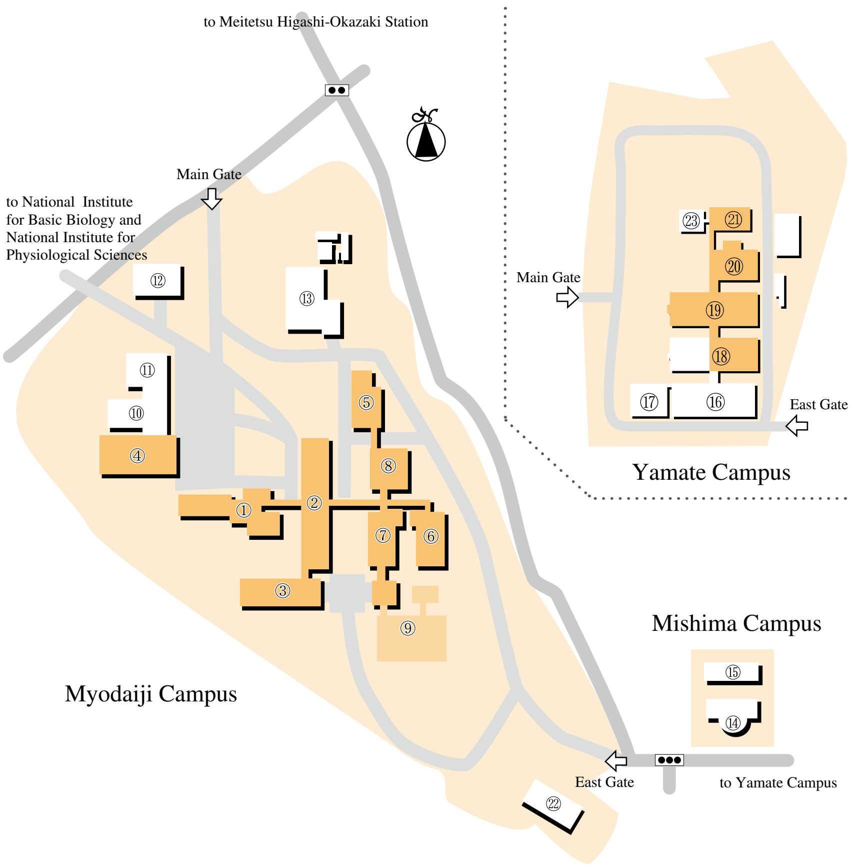
T. TAIRA, “Laser R&D for Processing Advantages,” *FORM TECH REVIEW 2019*, The Amada Foundation; Kanagawa, **29**, pp. 63–64 (2020). (in Japanese)

H. OHBA, I. WAKAIDA and T. TAIRA, “Remote Laser Analysis Technique in Harsh Environment,” *J. Atomic Energy Soc. Jpn.* **62(5)**, pp. 263–267 (2020). (in Japanese)

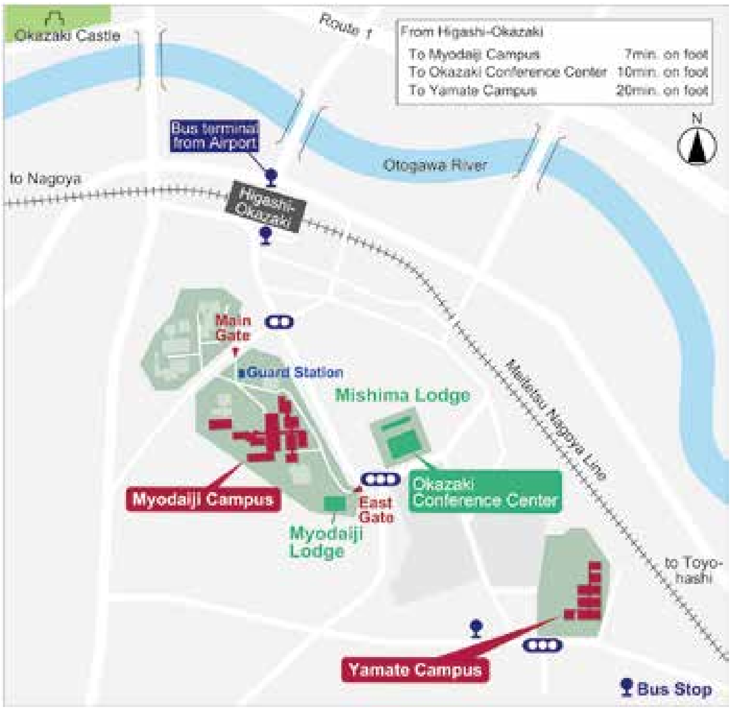
INDEX

to “Research Activities”

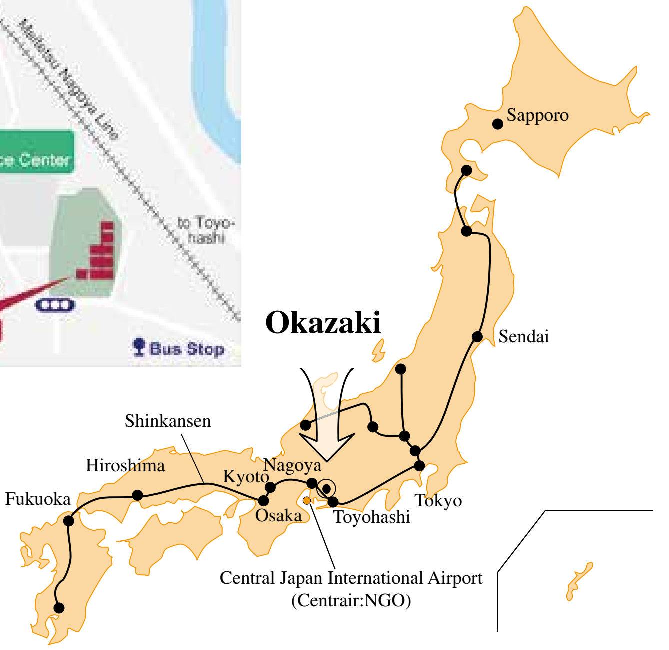
MAPS



1. Main Office Bldg.
2. Main Laboratory Bldg.
3. South Laboratory Bldg.
4. Computer Center Bldg.
5. Joint Research Bldg. A
6. Joint Research Bldg. D
7. Joint Research Bldg. C
8. Joint Research Bldg. B
9. Joint Research Bldg. UVSOR
10. Administration Bureau
11. Library
12. Faculty Club & Coop
13. Electricity Control Station
14. Okazaki Conference Center
15. Mishima Lodge
16. Yamate No.1 Bldg. A
17. Yamate No.1 Bldg. B
18. Yamate No.2 Bldg.
19. Yamate No.3 Bldg.
20. Yamate No.4 Bldg.
21. Yamate No.5 Bldg.
22. Myodaiji Lodge
23. NIBB Center of Interuniversity Bio-Backup Project



From Higashi-Okazaki	
To Myodaiji Campus	7min. on foot
To Okazaki Conference Center	10min. on foot
To Yamate Campus	20min. on foot



NATIONAL INSTITUTES OF NATURAL SCIENCES
Institute for Molecular Science
Since 1975