ISSN 1342-0321
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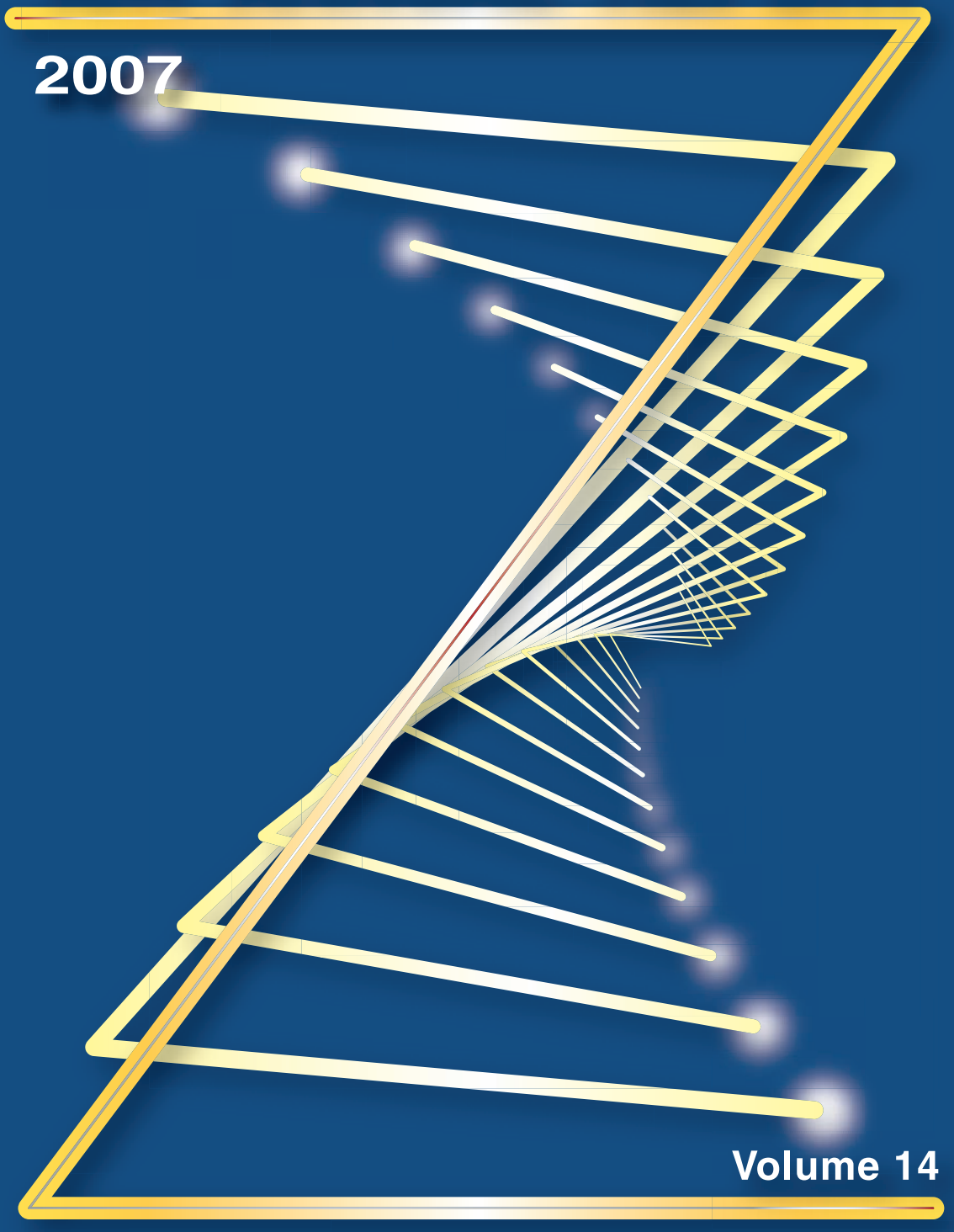
ICR ANNUAL REPORT

2007



Volume 14

Institute for Chemical Research
Kyoto University

ICR ANNUAL REPORT 2007 (Volume 14) - ISSN 1342-0321 -
This Annual Report covers from 1 January to 31 December 2007

Published and Distributed by:
Institute for Chemical Research (*ICR*), Kyoto University

Note: *ICR* Annual Report available from the *ICR* Office,
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Printed by:
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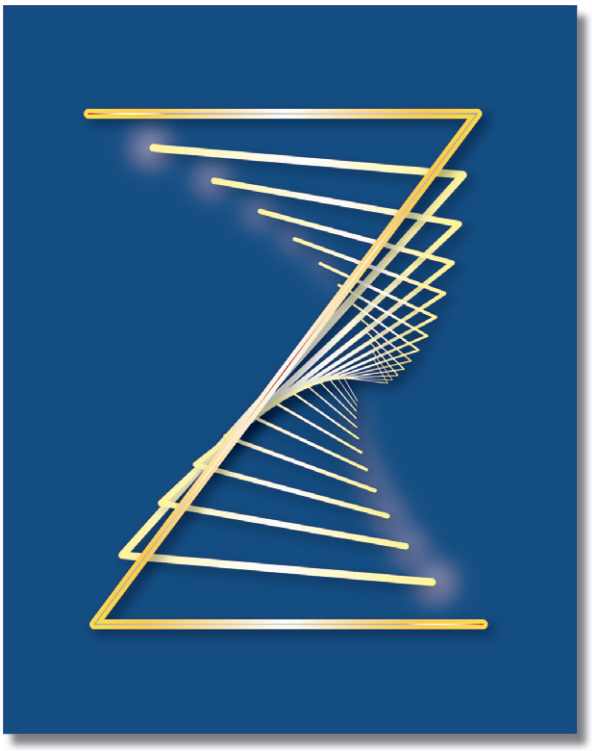


Institute for Chemical Research
Kyoto University
Volume 14

Preface

Institute for Chemical Research dates back to 1915 with the founding of the Specialized Center for Chemical Research at the Faculty of Science, Kyoto Imperial University. The formation of the Specialized Center was greatly influenced by historical events. In 1910, Dr. Sahachiro Hata developed salvarsan, a highly effective drug for syphilis, while conducting research with Dr. Paul Ehrlich. The effectiveness of this compound eventually became widely recognized, and its commercial production began in Germany. Although Japan was importing this drug, the outbreak of the World War I ceased the importation, and forced by circumstances the Japanese government requested that the University of Tokyo and Kyoto University produce salvarsan. The fourth Chancellor of Kyoto University, Professor Mitsuru Kuhara, who also happened to be a chemist, received this request. Facilities for salvarsan production were built with an investment of 20,000 yen, which is equivalent to about 200 million yen in today's market. Production went well, and as income was generated, faculty members, who had a passion for research in chemistry, gathered from across the University to form the Specialized Center for Chemical Research, which was later expanded and renamed as Institute for Chemical Research in 1926.

The newly established Institute soon began to produce outstanding research achievements: research on accelerators by Professor Bunsaku Arakatsu, research on synthesized petroleum oil production, and the development of vinylon, which is Japan's first synthetic fiber. Almost all the professors at the Institute, including the aforementioned, were also professors at the Faculty of Engineering or Science. However, over time, people began to recognize the importance of having professors dedicated solely to the Institute in order to operate the Institute with a clear responsibility, as well as the importance of the Institute's contribution in training researchers by providing guidance to graduate students. Thus, the Institute began accepting graduate students in 1962, and reorganization in 1964 saw the installation of the research division system where each division was led by one of our dedicated professors.

Since the Institute's founding in 1926, our basic principle has been to excel in the investigation of the basic principles of chemistry and chemical applications. Through several reorganizations, the Institute currently consists of the following five research divisions: Division of Synthetic Chemistry, Division of Materials Chemistry, Division of Biochemistry, Division of Environmental Chemistry, and Division of Multidisciplinary Chemistry as well as the following three research centers: Advanced Research Center for Beam Science, International Research Center for Elements Science, and Bioinformatics Center.

Today, the Institute spans 31 research fields (laboratories) with 104 faculty members and about 240 graduate students. Each laboratory belongs to one of the seven graduate schools, which encompass science, engineering, pharmaceutical science, agriculture, medicine, informatics, human and environmental studies. Our laboratories and the graduate schools work together to provide excellent graduate education.

The Institute strives to be the "central research center in chemistry" by achieving outstanding results in chemistry and related fields, and attracting motivated researchers in these fields. Chemistry is a fundamental science, which deals with materials, and its importance, including its contribution to physics and biology, cannot be overemphasized. One of our major strengths is our breadth and depth. In other words, our Institute is multidimensional, and is constantly widening and deepening our research activities. We intend to use our strengths to contribute to pioneering research as well as to expand the boundaries of chemical related fields and to promote research collaborations, which are difficult using conventional graduate schools. Moreover, we aim to utilize our strengths as an outstanding research center in education in order to produce excellent scientists and engineers who possess a broad perspective and can positively contribute to our global society.

The main body of the Institute belongs to the Department of Chemistry of the Graduate School of Science and the Department of Chemical Engineering of the Graduate School of Engineering. This basic structure of having these two departments at the core along with laboratories belonging to other graduate schools and departments, such as pharmaceutical science and agriculture, is a natural structure for a chemistry research center. Institute for Chemical Research is currently working towards establishing Global COE Programs in collaboration with the Graduate School of Engineering and the Graduate School of Science. This year, two programs have been selected from Kyoto University as Global COE Programs: International Center for Integrated Research and Advanced Education in Materials Science, which encompasses chemistry and materials science fields, and Center of Excellence for Education and Research on Photonics and Electronics Science and Engineering, which includes information science, electrical engineering, and electronics. We, at Institute for Chemical Research, would like to be a focal point in the Centers of Excellence by gathering chemists in our three campuses at Yoshida, Uji, and Katsura, and by serving as a bridge between science and engineering. Thus, we respectfully request your continued support and encouragement.

January 2008

ESAKI, Nobuyoshi
Director

ICR News 2007

Global COE Programs

Prof TOKITOH, Norihiro

The Global COE Program is an initiative by the Japanese Ministry of Education, Culture, Sports, Science and Technology (MEXT) to provide funding support for the development of internationally outstanding centers of education and research. The program aims to further improve and enrich the education and research capability of Japan's graduate schools and foster internationally outstanding, creative individuals through a research infrastructure of the highest global standard, promoting the development of internationally competitive universities.

The establishment of the Global COE Program was based on the assessment and evaluation of the 21st Century COE Program. In 2007, Kyoto University was honored with totally six COEs. Institute for Chemical Research is now making a great contribution to two of them, *"International Center for Integrated Research and Advanced Education in Materials Science"* and *"Center of Excellence for Education and Research on Photonics and Electronics Science and Engineering"*, as one of the main constituents.

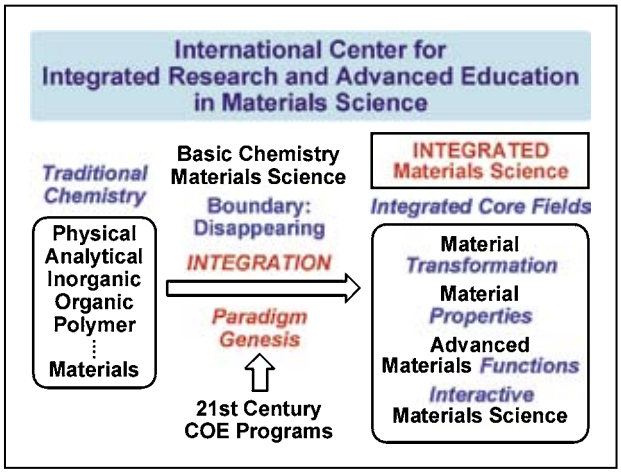
Global COE Joint Kick-off Symposium at FUNAI TETSURO Memorial Hall, Katsura Campus on 23 October 2007

The banquet of Global COE Joint Kick-off Symposium

International Center for Integrated Research and Advanced Education in Materials Science

Representative from ICR:
Prof TOKITOH, Norihiro

This Global COE project, granted in the area of *"Chemistry and Materials Science"* for fiscal 2007–2011, is intended to consolidate over 100 chemistry-related research groups of Kyoto University in Graduate School of Engineering, Graduate School of Science, and Institute for Chemical Research, covering virtually all the arenas of chemistry from basic to engineering and from molecules to materials, for the ultimate goal of "*Integrated Materials Science"* leading to *"a New Paradigm and a New Breed of Future Generation in Chemistry and Materials Science"*.

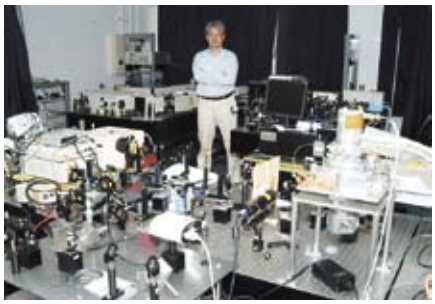


Integrated Materials Science: A new paradigm in chemistry and materials science

Center of Excellence for Education and Research on Photonics and Electronics Science and Engineering

Representative from ICR:
Prof KANEMITSU, Yoshihiko

In this program, we aim at establishing the COE for "photonics and electronics science and engineering", to investigate and develop innovative technologies, by which an arbitrary manipulation of photons (light) and an ultimate control of electrons will be achieved, as we hold the motto of "challenge the limitations of current technology and create new functionalities".



Developing a Network to Support Efficient Use of Chemistry Research Facilities

This nation-wide program is an attempt to share and maintain the research equipments among national universities and other public sectors. Nine major equipments in Kyoto University, primarily from Uji campus, are initially registered in the pilot program. Ms. Akiko Fujihashi is a research associate in charge of assisting the program in our institute.

Developing a Network to Support Efficient Use of Chemistry Research Facilities website (http://chem-eqnet.ims.ac.jp/)

The Alumni Association of Institute for Chemical Research is Inaugurated as "HEKISUIKAI"

Prof KANAYA, Toshiji
Prof SAKABE, Shuji

The general meeting for inauguration of ICR alumni association

HEKISUIKAI website
(http://www.kuicr.kyoto-u.ac.jp/ hekisuikai/)

Institute for Chemical Research (ICR) has been considering the inauguration of ICR alumni association, on the opportunity of the 80th anniversary last year. On the other hand, there already exists "HEKISUIKAI" association (HEKISUI means blue water) in ICR as an association of the faculty and students, which was founded in 1949. The alumni association inauguration preparation committee has decided to renew "HEKISUIKAI" so that both the incumbents and the alumnus become its members with the following goal: "The friendship between members is fostered, and the cooperation is encouraged among the members." The general meeting for the inauguration of ICR alumni association was held on July 27, 2007 and ICR alumni association was officially inaugurated as a part of HEKISUKAI at that time.

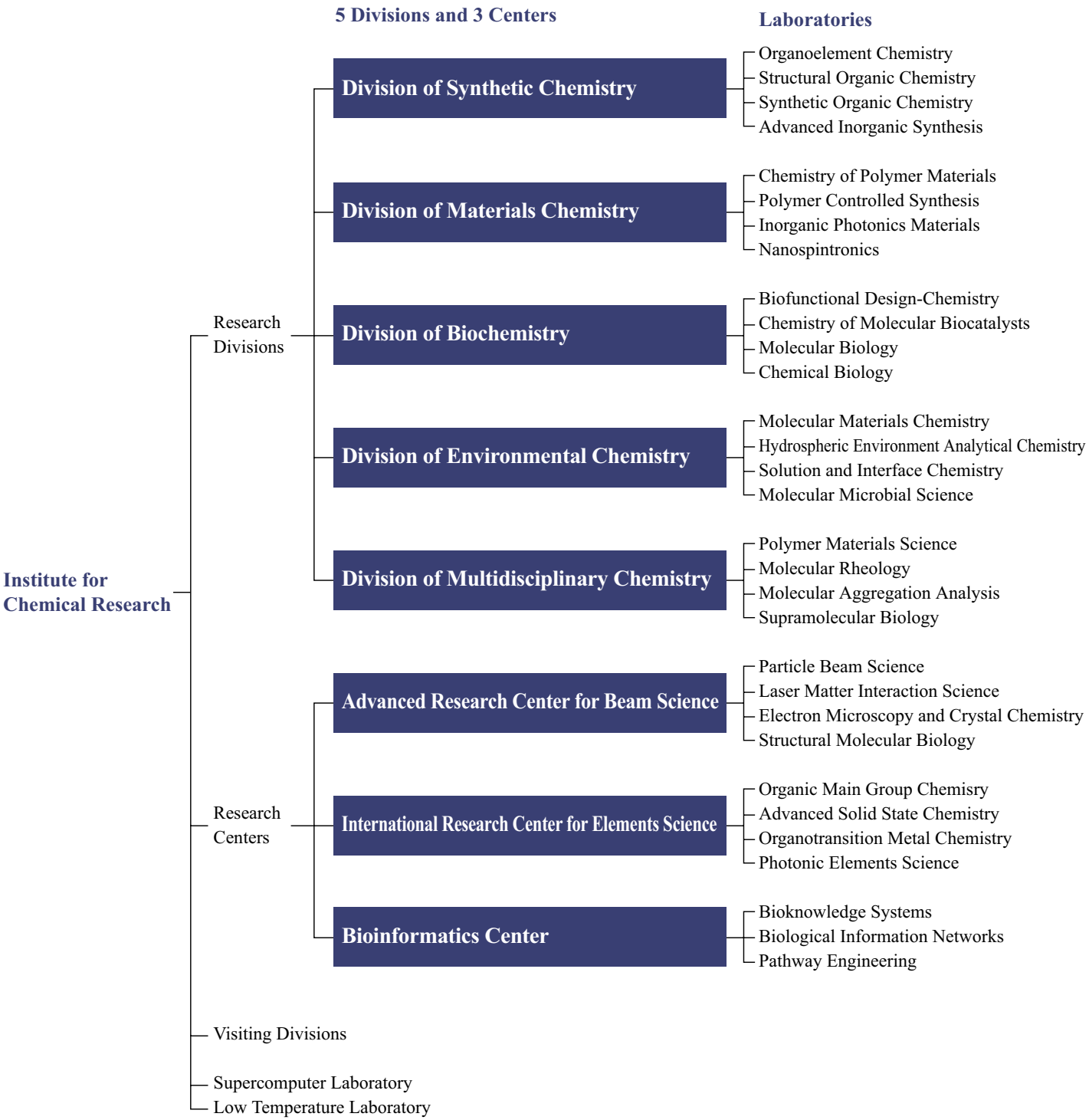
Take a look at website of ICR alumni association (http://www.kuicr.kyoto-u.ac.jp/hekisuikai/) to sign up for the membership. As a member of the alumni association, you will receive updated information about ICR. We would like to invite all the members to our annual summer beer party "RYOINKAI."

CONTENTS

Abbreviations used in the columns

Prof Em	Professor Emeritus	RF	Research Fellow
Prof	Professor	RS	Research Student
Vis Prof	Visiting Professor	D 1～3	Doctoral Course (Program) 1～3
Assoc Prof	Associate Professor	M1～2	Master's Course (Program) 1～2
Vis Assoc Prof	Visiting Associate Professor	UG	Undergraduate Student
Lect	Lecturer	D Sc	Doctor of Science
Assist Prof	Assistant Professor	D Eng	Doctor of Engineering
Vis Assist Prof	Visiting Assistant Professor	D Agr	Doctor of Agricultural Science
Res Associate	Research Associate	D Pharm Sc	Doctor of Pharmaceutical Science
Techn	Technician	D Med Sc	Doctor of Medical Science
Guest Scholar	Guest Scholar	D Inf	Doctor of Informatics
Guest Res Assoc	Guest Research Associate	Ph D	Doctor of Philosophy
PD	Post-Doctoral Research Fellow		
Res	Researcher	(SER)	Special Education and Research
A Res	Assistant Researcher	(AIGC)	Academic-Industry-Government Coalition
Proj Res	Project Researcher	(pt)	part-time

ORGANIZATION


5 Divisions and 3 Centers
Laboratories
Institute for Chemical Research
Research Divisions
Division of Synthetic Chemistry
Organoelement Chemistry
Structural Organic Chemistry
Synthetic Organic Chemistry
Advanced Inorganic Synthesis
Division of Materials Chemistry
Chemistry of Polymer Materials
Polymer Controlled Synthesis
Inorganic Photonics Materials
Nanospintronics
Division of Biochemistry
Biofunctional Design-Chemistry
Chemistry of Molecular Biocatalysts
Molecular Biology
Chemical Biology
Division of Environmental Chemistry
Molecular Materials Chemistry
Hydrospheric Environment Analytical Chemistry
Solution and Interface Chemistry
Molecular Microbial Science
Division of Multidisciplinary Chemistry
Polymer Materials Science
Molecular Rheology
Molecular Aggregation Analysis
Supramolecular Biology
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Advanced Research Center for Beam Science
Particle Beam Science
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Electron Microscopy and Crystal Chemistry
Structural Molecular Biology
International Research Center for Elements Science
Organic Main Group Chemisry
Advanced Solid State Chemistry
Organotransition Metal Chemistry
Photonic Elements Science
Bioinformatics Center
Bioknowledge Systems
Biological Information Networks
Pathway Engineering
Visiting Divisions
Supercomputer Laboratory
Low Temperature Laboratory

TOPICS AND INTRODUCTORY COLUMNS OF LABORATORIES

Division of Synthetic Chemistry
- Organoelement Chemistry -

http://boc.kuicr.kyoto-u.ac.jp/www/index-e.html

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Assist Prof
SASAMORI, Takahiro
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Assist Prof
MIZUHATA, Yoshiyuki
(D Sc)

Techn
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Proj Res*
NAGAHORA, Noriyoshi
(D Eng)

*Assist Prof (SER) of Institute of Sustainability Science

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OZAKI, Shuhei (D2)
TANABE, Taro (D2)
YUASA, Akihiro (D2)
INAMURA, Koji (D1)
MATSUMOTO, Teruyuki (D1)
TANABE, Yusuke (D1)
TSURUSAKI, Akihiro (D1)
HIRONAKA, Koji (M2)
HORI, Akimi (M2)
TAKEUCHI, Kosaku (M2)
KANEKO, Yoshikazu (M1)
SATO, Takahiro (M1)
YAMAMOTO, Osami (M1)

Visitor

Prof JUTZI, Peter University of Bielefeld, Germany, 23 October–26 November 2007

Scope of Research

Organic chemistry has been developed as that of second-row elements such as carbon, oxygen, and nitrogen so far, while the synthesis and isolation of the heavier congeners of typical organic molecules as stable compounds have been one of "dreams" for organic chemists. Our main research interest is the elucidation of the similarities and differences in structures and reactivity between organic compounds and the corresponding heavier congeners. These studies are interesting and important from the standpoints of not only fundamental chemistry but also opening the way to more extensive application of main group chemistry. Organic synthesis mediated by biocatalysts is also studied.

Research Activities (Year 2007)

Publications

Sasamori T, Matsumoto Te, Takeda N, Tokitoh N: Synthesis and Properties of a Rhodium Complex Having a Novel *β*-Ketophosphenato Ligand, a Heavier Congener of a *β*-Ketoiminato Ligand, *Organometallics*, **26**, 3621-3623 (2007).

Nagahora N, Sasamori T, Watanabe Y, Furukawa Y, Tokitoh N: Kinetically Stabilized 1,1'-Bis[(*E*)-diphosphenyl]ferrocenes; Syntheses, Structures, Properties, and Reactivity, *Bull. Chem. Soc. Jpn.*, **80**, 1884-1900 (2007).

Presentations

Synthesis and Characterization of the First Stable Stannanetellone, Tokitoh N, The 10th International Conference on the Chemistry of Selenium and Tellurium (ICCST-10), Łódź, Poland, 24 June 2007 (invited).

Recent Progress in the Chemistry of Multiply Bonded Germanium and Tin Compounds, Tokitoh N, Mizuhata Y, Sugiyama Y, Tajima T, Inamura K, Sasamori T, The 12th International Conference on the Coordination and Organometallic Chemistry of Germanium, Tin and Lead (ICCOC-GTL-12), Galway, Ireland, 13 July 2007 (invited).

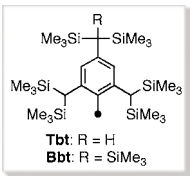
Grants

Tokitoh N, Sasamori T, Nagahora N, Mizuhata Y, The Chemistry of Unsaturated Compounds of Heavier Main Group Elements: Pursuit of Novel Properties and Functions, Grant-in-Aid for Creative Scientific Research, 1 April 2005–31 March 2009.

Sasamori T, Construction of Novel Extended π-Electron Conjugated Systems Containing Heavier Main Group Elements, Grant-in-Aid for Young Scientists (B), 1 April 2006–31 March 2008.

Sasamori T, Construction of Novel d-π Electron Conjugated Systems Containing Heavier Main Group Elements and Transition Metals and Elucidation of their Properties. Grant-in-Aid for Science Research on Priority Areas

Synthesis of Bis[(*E*)-diphosphenyl]ferrocenes



Low-coordinated species of heavier group 15 elements have attracted much interest due to their low-lying π* levels compared with diazenes (–N=N–) from two reasons: (i) their electrochemical properties and (ii) coordination ability toward transition metals. We have already reported the synthesis and isolation of many examples of "heavy" diazenes (–P=P–, –Sb=Sb–, –Bi=Bi–, and so on) by taking advantage of efficient steric protection groups, Tbt and Bbt, and revealed their unique characters based on their molecular structures, spectroscopic properties, and reactivities. Recently, we have succeeded in the syntheses, structural characterization, and properties of the first 1,10-bis[(*E*)-diphosphenyl]ferrocenes **1** kinetically stabilized by Tbt or Bbt groups. The ligand-exchange reactions of **1** with group 6 metal carbonyl complexes resulted in the formation of complexes **2** along with unique *E*-to-*Z* isomerization of the diphosphene moieties.

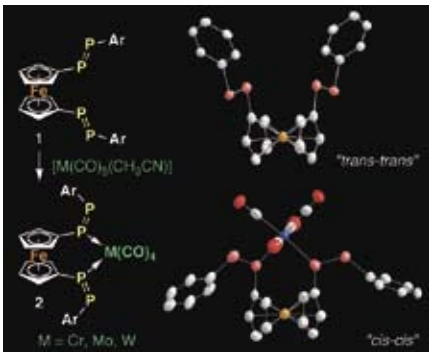


Figure 1. Complexation of **1** and the structures of **1** and **2** (M = W).

Generation of Silabenzene Anion Radical

The chemistry of aromatic compounds containing a heavier group 14 element, *i.e.*, "heavy aromatics," is important to understand the concept of "aromaticity", which has been one of the fascinating topics in organic chemistry. We have succeeded in the synthesis and isolation of kinetically stabilized sila-, germa-, and stannaaromatic compounds stabilized by Tbt group, and revealed their considerable aromaticity based on their molecular structures, spectroscopic properties, and reactivities. The comparison of redox properties between heavy aromatics and the corresponding aromatic hydrocarbons and the structural features of the corresponding radical species of heavy aromatics should be of great interest and importance in terms of their unique properties. An electrochemical study of kinetically stabilized silabenzene **3** revealed that the reduction potential of **3** is –2.96 V (vs. Cp_2Fe/Cp_2Fe^+) and lower than that of naphthalene. The anion radical species **4** was generated by the one-electron reduction using lithium naphthalenide and characterized by ESR spectroscopy.

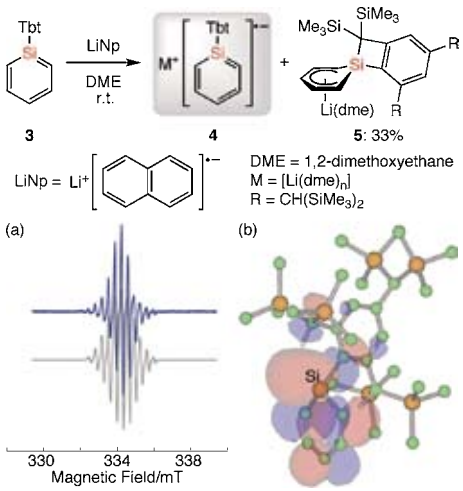


Figure 2. Generation of silabenzene anion radical **4**. (a) Observed (up) and simulated (below) ESR spectra of **4**. (b) Optimized structure of **4** and its SOMO.

"Synergy of Elements", 1 April 2007–31 March 2008.

Nagahora N, Study on Development of Novel Molecular Devices Bearing Metallocene and Double Bonds between Heavier Group 15 Elements, Kinki Invention Center, 1 April 2007–31 March 2008.

Mizuhata Y, Grant-in-Aid for Young Scientists (Kyoto Univ.), Synthesis and Properties of Novel Stannaaromatic Compounds by Taking Advantages of Kinetic Stabilization, 1 April 2006–31 March 2007.

Awards

Matsumoto Ta, The Best Poster Award, 2007 KAIST-Kyoto University Chemistry Symposium, 27 January 2007.

Mizuhata Y, Inoue Research Award for Young Scientists, 5 February 2007.

Sasamori T, Daiichi-Seiyaku Award in Synthetic Organic Chemistry, Japan, 22 February 2007.

Tanabe T, The Student Lecture Award, The 87th Annual Meeting of the Chemical Society of Japan, May 2007.

Hamaki H, The Student Lecture Award, The 87th Annual Meeting of the Chemical Society of Japan, May 2007.

Tanabe T, OMCOS Poster Prize in Organometallic Chemistry, The 14th IUPAC Symposium on Organometallic Chemistry Directed towards Organic Synthesis, 4 August 2007.

Nagahora N, Sasamori T, Tokitoh N, BCSJ Award (The Best Article of the Month), 15 October 2007.

Division of Synthetic Chemistry
- Structural Organic Chemistry -

http://hydrogen.kuicr.kyoto-u.ac.jp/K_eHP_F/main.html

Assoc Prof
MURATA, Yasujiro
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Assist Prof
MURATA, Michihisa
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PD
KUROTOBI, Kei
(D Sc)

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KATO, Keisuke (M1)

Lecturer (pt)

KITAGAWA, Toshikazu (D Eng) Mie University

Scope of Research

Fundamental studies are being conducted for creation of new functional π-systems with novel structures and properties. The major subjects are: organo-chemical transformation of fullerenes C_{60} and C_{70}, specifically organic synthesis of endohedral fullerenes by the technique of molecular surgery; generation of alkylated fullerene cations and their application for the synthesis of functional material; synthesis of new redox-active π-systems.

Research Activities (Year 2007)

Presentations

Fine Tuning of the Orifice Size: Synthesis and Properties of Selenium-Containing Open-Cage C_{60}, Murata Y, Chuang S-C, Murata M, Komatsu K, 211th Meeting of the Electrochemical Society, 7 May 2007, Chicago, USA.

Synthesis and Properties of Endohedral Open-Cage Fullerenes, Murata Y, The 2nd International Conference on Joint Project of Chemical Synthesis Core Research Institutions –Development of New Synthetic Methods and Creation of Functions–, 7 August 2007, Kyoto, Japan (invited).

The Outside Knows the Difference Inside: Trapping Helium by Immediate Reduction of Orifice Size of an Open-cage Fullerene and NMR Investigations of the Effect of Encapsulated Helium and Hydrogen to the Proton Directly Attached to the Open-cage Fullerene Sphere, Chuang S-C, Murata Y, Komatsu K, The 234th ACS National Meeting, 22 August 2007, Boston, USA.

Grants

Murata Y, PRESTO, Japan Science and Technology Agency, 1 October 2005–31 March 2009.

Murata Y, Grant-in-Aid for Scientific Research on Priority Areas, “Molecular Theory for Real Systems”, 1 April 2007–31 March 2008.

Murata M, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

An Orifice-Size Index for Open-Cage Fullerene

In the field of open-cage fullerenes, there was a lack of a universal standard that could correlate and quantify the orifice size of open-cage fullerenes. We estimated the corresponding effective areas *A(area)* for orifices of open-cage fullerenes by matching calculated activation energies *Ea(calcd)* for hydrogen release from open-cage fullerenes to the computed energies required for a hydrogen molecule passing through a cyclo[*n*]carbon ring. Then we defined an index *K(orifice)* based on experimental hydrogen release rate, where *K(orifice)* = ln *k*/*k*° (*k* is rate constant of hydrogen-release rate of any open-cage fullerenes taken for comparison at 160 °C; *k*° is the hydrogen release rate from the standard compound). A correlation of the index *K(orifice)* with the effective areas *A(area)* showed a good linear fit that demonstrated a good interplay between experiment and theory.

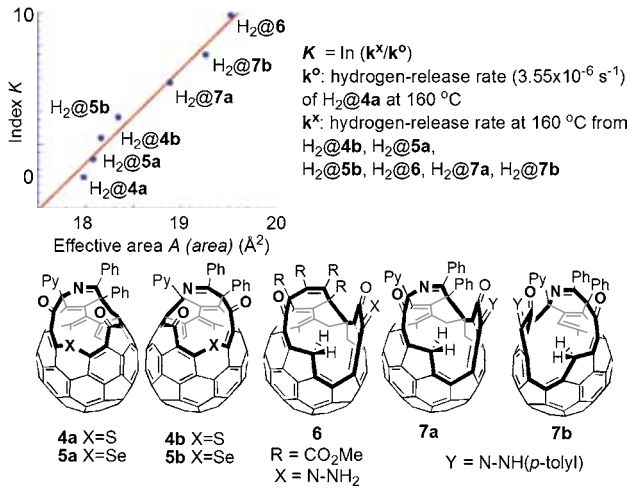

Figure 1. Correlation of the orifice-size index *K* with the effective area of orifice *A(area)* for open-cage fullerenes.

Communication of H_2 inside C_{60} with the Outside World

The quenching rate constants of singlet oxygen by C_{60}, $H_2@C_{60}$, $D_2@C_{60}$, H_2, and D_2 in solution were measured. The presence of a hydrogen ($H_2@C_{60}$) or deuterium ($D_2@C_{60}$) molecule inside the fullerene did not produce any observable effect based on triplet lifetime or EPR measurements. However, a remarkable effect was found for the $^1O_2$ quenching by C_{60}, $H_2@C_{60}$, $D_2@C_{60}$, H_2, and D_2. Singlet oxygen was generated by photo sensitization or by thermal decomposition of naphthalene endoperoxide derivatives. The comparison of the rate constants for quenching of $^1O_2$ by $H_2@C_{60}$ and $D_2@C_{60}$ demonstrate a significant vibrational interaction between oxygen and H_2 inside the fullerene. The quenching rate constant for H_2 is one order of magnitude higher than that of D_2, in agreement with the results observed for the quenching of $^1O_2$ with $H_2@C_{60}$ or $D_2@C_{60}$.

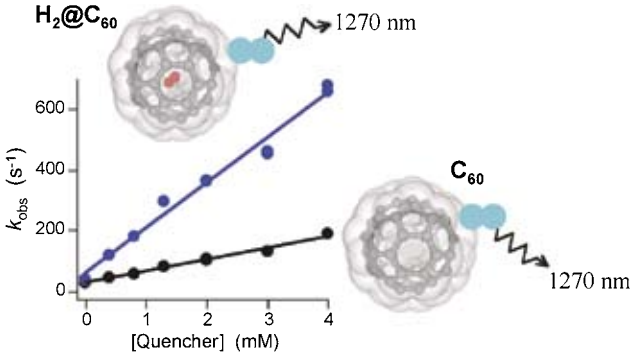

Figure 2. Singlet Oxygen quenching by $H_2@C_{60}$ and C_{60}.

The Outside Knows the Difference Inside

The size of orifice on open-cage fullerene **1** with a 13-membered ring was reduced to an 11-membered ring by reduction of the carbonyl group. This reaction can be used to entrap a He atom inside the fullerene cage by applying toward He@**1**. Interestingly, the chemical shifts of the methine protons in empty **2**, He@**2**, and H_2@**2** were dependent on the encapsulated species inside the cage. The ^1H NMR spectrum of the mixture of He@**2** and empty **2** showed two signals with a difference of 0.36 Hz. This notion suggested that the non-covalent interaction between helium and fullerene cage does exist. Furthermore, a clear downfield-shift of 1.9 Hz was observed for the methine proton signal of H_2@**2** as compared to that of empty **2**. The observed difference suggested that the encapsulated hydrogen molecule interacts more with the cage than helium.

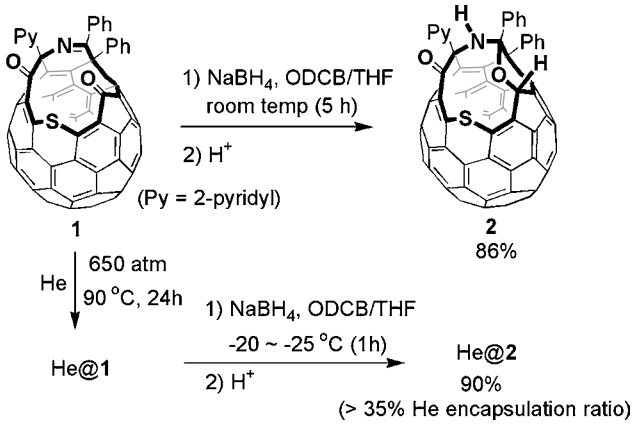

Figure 3. Synthesis of compound **2** and He@**2**.

Division of Synthetic Chemistry
- Synthetic Organic Chemistry -

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MISHIRO, Kenji (UG)
SAKAI, Hironori (UG)
TAKUWA, Masatoshi (UG)
UEDA, Yoshihiro (UG)

Visitors

Prof KAGAN, Henri — Université de Paris-Sud, France, 11 May 2007
Prof SMITH, Amos B — University of Pennsylvania, USA, 3 November 2007

Scope of Research

The research interests of the laboratory include the development of advanced molecular transformation, total synthesis of biologically active products, and molecular recognition. Programs are active in the areas of asymmetric alkylation of carbonyl compounds based on “memory of chirality”, nucleophilic catalysis for fine organic syntheses, synthesis of unusual amino acids and nitrogen heterocycles, visualization of molecular information by functional phenolphthaleins, synthesis and properties of homochiral oligonaphthalenes, and the structural and functional investigation of heterochiral oligomers.

Research Activities (Year 2007)

Publication

Kawabata T, Muramatsu W, Nishio T, Shibata T, Schedel H: A Catalytic One-Step Process for the Chemo- and Regioselective Acylation of Monosaccharides, *J. Am. Chem. Soc*., **129**, 12890-12895 (2007).

Presentations

Asymmetric Synthesis of Amino Acids with a Tetrasubstituted Carbon Center via Memory of Chirality, 233rd ACS National Meeting, Kawabata T, 26 March 2007.

Colorimetric Recognition of Spermidine and Spermine Based on Phenolphthalein Derivatives, Tsubaki K, 21st International Congress for Heterocyclic Chemistry, 17 July 2007.

Kinetic Resolution of (±)-1,1'-Binaphthyl-8,8'-diamines by Chiral PPY Organocatalysts, VALLURU R K, 12th International Symposium on Novel Aromatic Compounds, 23 July 2007.

Fine Molecular Transformation by Nucleophilic Catalysis, Kawabata T, ICCT-2007, 16 December 2007.

Grants

Kawabata T, Fine Organic Synthesis by Nucleophilic Catalysis, Grant-in-Aid for Scientific Research (A), 1 April 2006–31 March 2009.

Kawabata T, Advanced Molecular Transformation with Functional Carbanions, Grant-in-Aid for Scientific Research on Priority Areas, 1 October 2005–31 March 2009.

Kawabata T, Creation of Novel Binaphthyls with Inner Hydrogen Bonding, Grant-in-Aid for Exploratory Research, 1 April 2007–31 March 2009.

Synthesis and Determination of the Absolute Configuration of Chiral Tetracosanaphthalenes

Oxidative coupling of all-(*R*)-**1** and all (*R*)-**2** gave three diastereomeric 24-mers **3**. The mixture of diastereomers was purified by recycling preparative HPLC to give pure diastereomers (Figure 1, fractions 1-3). In order to determine the absolute configuration of the 24-mers with two unknown axes, tetraphenylporphyrin (TPP) was introduced into four phenolic hydroxy groups to give **4**. Based on the CD spectra of **4** (Figure 2), the diastereomer in fraction 1 with a large positive Cotton effect, the diastereomer in fraction 2 with a weak CD intensity, and the diastereomer in fraction 3 with a large negative Cotton effect were determined to be (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*), (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*S*,*R*,*R*,*R*,*R*,*R*,*R*,*R*), and (*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*,*R*), respectively.

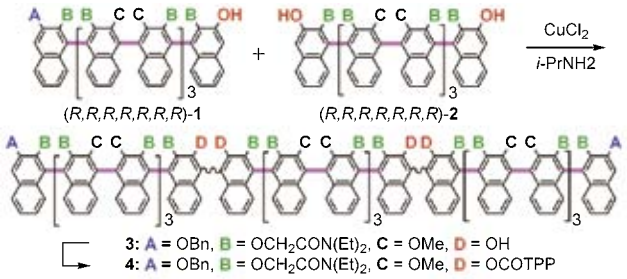

Figure 1.

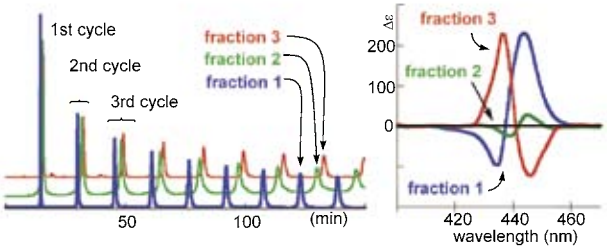

Figure 2.

A Novel Binaphtyl Analogue with Inner Hydrogen Bonding

Chiral binaphthyls have been exetensively utilized as ligands for asymmetric synthesis. A novel binaphtyl analogue **5** based on inner hydrogen bonding has been created. The N-H of **5** appears at 13.2 ppm in its ^{1}H NMR spectrum, indicating extremely strong hydrogen bonding. Enantiomers of **5** were stable at the ambient temperature and separable by HPLC with a chiral stationary phase. The half life of racemization of the enantiomer is ≥ six months at 20°C and the barrier for racemization is 27.4 kcal/mol. X-ray crystal analysis of **5** showes that the pseudo-naphthyl skeleton including C=N●●● H-N is almost completely planar, and the dihedral angle between the pseudo-naphthalene and naphthalene rings is 110°.

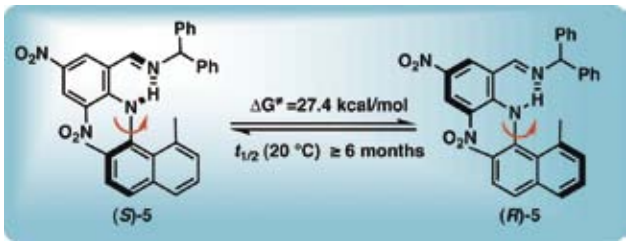

Figure 3. An enantiomerically stable binaphthyl analogue with Inner N-H-N hydrogen bonding.

Tsubaki K, Construction of Molecular Recognition System in Water and Rapid Quantification of Polyamines, Grant-in-Aid for Scientific Research (B), 1 April 2006–31 March 2009.

Tsubaki K, Synthesis and Properties of Optically Active Oligonaphthalene Deriveries, Grant-in-Aid for Exploratory Research, 1 April 2005–31 March 2007.

Awards

Takaishi K, Impressive Presentation Award, Synthesis of Higher Order Oligonaphthalenes and Optical Property of TPP, TPP-Zn Adducts, 2nd Host Guest Chemistry Symposium, 25 May 2007.

Tsubaki K, HGCS Japan Award of Excellence 2007, Colorimetric Recognition Using Functional Phenolphthalein Derivatives, 12 July 2007.

Moriyama K, Best Poster Award, Metal Hydroxide-Promoted Asymmetric Cyclization via Memory of Chirality at Room Temperature: Construction of Cyclic Amino Acids with a Tetrasubstituted Carbon Center, The 92nd Symposium on Organic Synthesis, Japan, 9 November 2007.

Tomohara K, Best Poster Award, Synthesis of Cyclic Ethers with a Tetrasubstituted Carbon Center via C-O Axially Chiral Enolates, The 27th Seminar on Synthetic Organic Chemistry for Young Scientists, 15 November 2007.

Muramatsu W, ICR Award for Graduate Students, A Catalytic One-Step Process for the Chemo-and Regioselective Acylation of Monosaccharides, 7 December 2007.

Imamura Y, Best Poster Award, Development of Highly Sensitive and Selective Molecules for Detection of Spermidine and Spermine, 1st Symposium on Organic π-Electron Systems, 8 December 2007.

Division of Synthetic Chemistry
- Advanced Inorganic Synthesis -

http://msk2.kuicr.kyoto-u.ac.jp/~shimak-lab/indexE.html

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SHIMAKAWA, Yuichi
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KOMATSU, Hiroshi (M2)
SHIRAKI, Hiroshi (M2)
HORIKAWA, Takenori (M1)
INOUE, Satoru (M1)

Visitors

Prof TAKEUCHI, Ichiro — University of Maryland, USA, 26 June 2007
Dr CHOU, Fangcheng — National Taiwan University, Taiwan, 3–7 September 2007

Scope of Research

Transition-metal oxides show lots of interesting and useful properties. They include ferroelectrics, ferromagnets, conductors, batteries, and so on. These materials are widely used in current electronic devices. The wide variety of their crystal structures gives rise to various electronic structures, which lead to interesting and useful physical and chemical properties. We are focusing on the fundamental physics and chemistry of these "functional oxides" and seeking new materials with new functions. We are conducting systematic studies of material synthesis based on phase equilibrium information. Precise crystal structures are analyzed by X-ray and neutron diffractions. Electronic and magnetic structures are discussed based on the results of electronic structure calculations and physical property measurements.

Research Activities (Year 2007)

Publications

Sakai M, Masuno A, Kan D, Hashisaka M, Takata K, Azuma M, Takano M, Shimakawa Y: Multiferroic Thin Film of Bi_2NiMnO_6 with Ordered Double-Perovskite Structure, *Appl. Phsy. Lett.*, **90**, [072903-1]-[072903-3] (2007).

Shiraki H, Saito T, Yamada T, Tsujimoto M, Azuma M, Kurata H, Isoda S, Takano M, Shimakawa Y: Ferromagnetic Cupreates $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$ with *A*-Site Ordered Perovskite Structure, *Phys. Rev. B*, **76**, [140403-1]-[140403-4] (2007).

Azuma M, Carlsson S, Rodgers J, Tucker M G, Tsujimoto M, Ishiwata S, Isoda S, Shimakawa Y, Takano M, Attfield J P: Pressure-Induced Intermetallic Valence Transition in $BiNiO_3$, *J. Am. Chem. Soc.*, **129**, 14433-14436 (2007).

Presentations

Complex Ordered Perovskites with Intriguing Physical Properties: Shimakawa Y, Gordon Research Conferences on Solid State Chemistry II, Oxford, UK, 2–7 September 2007.

High Pressure Synthesis of Functional Transition Metal Oxides: Azuma M, ICMR Workshop on Functional Oxide Materials, Santa Barbara, USA, 20–23 August 2007.

New Multi-Ferroic Compound Bi_2NiMnO_6: Shimakawa Y, 7th Pacific Rim Conference on Ceramic and Glass Technology, Shanghai, China, 11–14 November 2007.

Grants

Shimakawa Y, Strategic State-of-the-art Solid State Chemistry for New Functional Materials: Exploring for New Multi-functional Materials, Creative Scientific Research 1 April 2007–31 March 2012.

Deposition Rate Control on Defect Structure of Epitaxial Oxide Thin Films

Defect engineering for the epitaxial thin films have recently attracted much attention because strain fields and dislocations affect physical properties of the thin films. We prepared perovskite-type ferroelectric $BaTiO_3$ thin films grown on a $SrTiO_3$ (001) substrate by PLD, and found that their defect structures strongly depend on the growth rate The defect structures, which include structural strain and dislocations were examined by synchrotron radiation x-ray diffraction and cross-sectional HAADF-STEM observations. In a film grown at a low deposition rate (0.01 nm/s), misfit dislocations are found near the interface and a fully relaxed $BaTiO_3$ thin film grows epitaxially on the substrate. On the other hand, a film grown at a high deposition rate (0.04 nm/s) consists of strained and relaxed $BaTiO_3$ lattices. The results imply that the structures and strain states in the epitaxial thin films can be controlled by the growth rate.

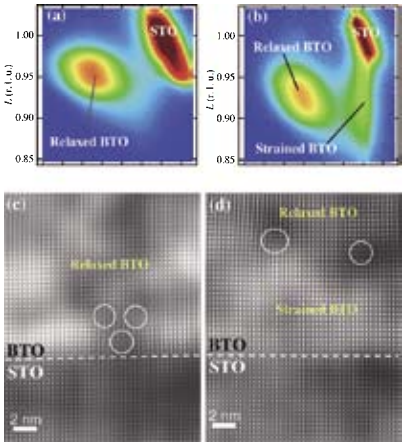

Figure 1. Synchrotron x-ray diffraction reciplocal space maps around the (301) Bragg reflection and cross-sectional HAADF-STEM images around the BTO/STO heterointerfaces for the $BaTiO_3/SrTiO_3$(001) epitaxial thin films grown at a low deposition rate (0.01 nm/s) ((a) and (c)) and high deposition rate (0.04 nm/s) ((b) and (d)).

Pressure-Induced Intermetallic Valence Transition in $BiNiO_3$

Charge ordering in oxides, drives many important phenomena such as the Verwey transition of Fe_3O_4. The melting of charge order often leads to exotic conducting phenomena near the insulator to metal boundary, such as colossal magnetoresistance in manganites. $BiNiO_3$ has the unusual charge distribution $Bi^{3+}_{0.5}Bi^{5+}_{0.5}Ni^{2+}O_3$ with ordering of Bi^{3+} and Bi^{5+} charges on the A sites of a highly distorted perovskite structure. High pressure neutron diffraction measurements and Bond valence sum calculations show that the pressure-induced melting of the charge disproportionated state leads to a simultaneous charge transfer from Ni to Bi, so that the high pressure phase is metallic $Bi^{3+}Ni^{3+}O_3$. This unprecedented charge transfer between A and B site cations coupled to electronic instabilities at both sites leads to a variety of ground states, and it is predicted that a Ni-charge disproportionated state should also be observable.

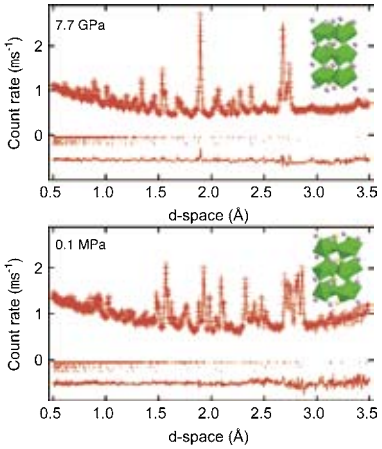

Figure 2. Time-of-flight powder neutron diffraction data for $BiNiO_3$ at variable pressures. (a) Rietveld fits of the triclinic structure to ambient pressure (0.1 MPa) data, and of the high pressure orthorhombic structure to 7.7 GPa data.

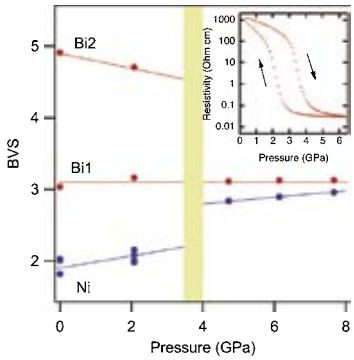

Figure 3. Bi and Ni bond valence sums (BVS) determined from the refined structures of $BiNiO_3$ at various pressures. The low pressure structure contains two distinct Bi sites, labeled Bi1 and Bi2 (red circles), corresponding respectively to Bi^{3+} and Bi^{5+}, and four Ni sites (blue circles) all containing Ni^{2+}. The high pressure structure contains single Bi and Ni sites, both with valences of 3+. The inset shows the resistivity of $BiNiO_3$ as a function of pressure exhibiting an insulator to metal transition at around 4 GPa.

Azuma M, Search for Anomalous Magnetic, Electric and Dielectric Phenomena in Transition Metal Oxides with Active *s*-electrons, Grant-in-Aid for Scientific Research (B), 1 April 2007–31 March 2010.

Award

Azuma M, Shimakawa Y and Takano M, Thomson Scientific Research Front Award 2007, Thomson Scientific, 19 September 2007.

Division of Materials Chemistry
- Chemistry of Polymer Materials -

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Assoc Prof
TSUJII, Yoshinobu
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OHNO, Kohji
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Assist Prof
GOTO, Atsushi
(D Eng)

PD
MA, Ying
(Ph D)

PD
MORINAGA, Takashi
(D Eng)

Students

OKAYASU, Kenji (D2)
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HIRAI, Norihiro (M2)
WAKADA, Tsutomu (M2)
KAYAMA, Yuzo (M1)
NAGASAWA, Koji (M1)
YOSHIOKA, Yuu (M1)
HSU, Sho Yao (RS)
AKASHI, Tatsuki (UG)

Visitors

Prof MA, Yung-Dae	Dankook University, Korea, 27–29 April 2007
Prof BUBACK, Michael	University of Göttingen, Germany, 10–14 June 2007
Prof MATYJASZEWSKI, Krzysztof	Carnegie Mellon University, USA, 10–14 June 2007
Prof ZHAO, Bin	University of Tennessee, USA, 10–14 June 2007
Ms MACEWAN, Maura E	University of Virginia, USA, 19 June–21 August 2007

Scope of Research

Kinetic and mechanistic analyses are made for better understandings of the chemical and physicochemical reactions occurring in polymerization systems and for better routes to the synthesis of well-defined polymers. By various polymerization techniques, in particular, living polymerizations, new well-defined polymers or polymer assemblies are prepared, and their structure/properties relationships are precisely analyzed. Projects in progress include: (1) kinetics and mechanisms of living radical polymerization (LRP). (2) Synthesis of new polymeric materials by living polymerizations and their structure/properties studies. (3) Synthesis, properties, and applications of concentrated polymer brushes (CPB).

Research Activities (Year 2007)

Publications

Fukuda T, Tsujii Y, Ohno K: Grafting and Polymer Brushes on Solid Surfaces; *In Macromolecular Engineering: Precise Synthesis, Materials Properties, Applications*, Wiley-*VCH*, 1137-1178 (2007).

Ohno K, Morinaga T, Takeno S, Tsujii Y, Fukuda K: Suspensions of Silica Particles Grafted with CPB: Effects of Graft Chain Length on Brush Layer Thickness and Colloidal Crystallization, *Macromolecules*, **40**, 9143–9150 (2007).

Goto A, Zushi H, Hirai N, Wakada T, Tsujii Y, Fukuda T: Living Radical Polymerizations with Ge, Sn, and P Catalysts - RTCPs, *J. Am . Chem. Soc*., **129**, 13347-13354 (2007).

Presentations

Tsujii Y, CPBs and Biointerfaces (invited): 29th Ann. Meeting of Jpn. Soc. Biomater. Osaka, 26–27 November 2007.

Fukuda T, New Development of CPBs (invited). And other 5 presentations: ICR Int. Symp. (ICRIS'07) Organized by Fukuda T, Kyoto, 11–13 June 2007.

15 Presentations, 56th Spring Meeting, Soc. Polym. Sci., Jpn., Kyoto, 29–31 May 2007.

10 Presentations, 56th Autumn Meeting, Soc. Polym. Sci., Jpn., Nagoya, 19–21 September 2007.

Grants

Fukuda T, Science and Technology of CPB, Grant-in-Aid for Specially Promoted Research, 1 April 2005–31 March 2009.

Tsujii Y, Creation of New Bio-Interfaces Based on CPB, Grant-in-Aid for Science Research (A), 1 April 2005–31 March 2008.

Thermo-responsive Lubrication of Concentrated Polymer Brushes in Water

Well-defined, concentrated poly(*N*-isopropylacrylamide) brushes were successfully fabricated on solid surfaces via surface-initiated atom transfer radical polymerization using a newly-designed immobilizable initiator. These brushes were demonstrated to be highly swollen, nearly to their full lengths $L_{c,w}$, in water at 5°C, gradually shrinking with increasing temperature down to an almost nonswollen state above 30°C. On the other hand, a dramatic change in frictional coefficient μ between brushes (more than 3 orders of magnitudes) was observed at around 30°C, below which it stayed at very low values ($< 10^{-3}$).

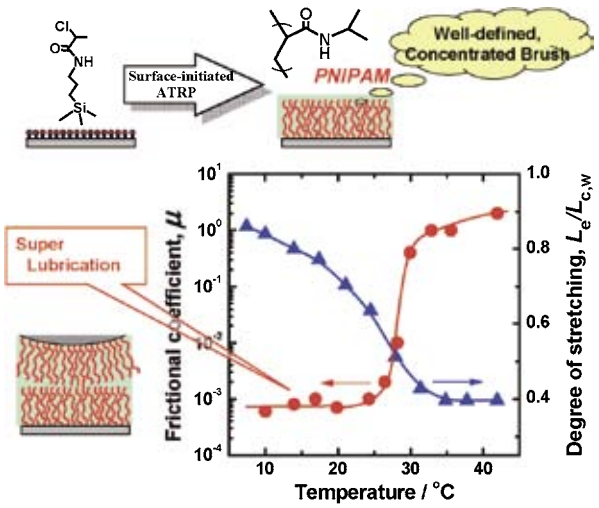

Figure 1. Swelling and frictional properties of concentrated PNIPAM brush in water.

Living Radical Polymerizations with Germanium, Tin, and Phosphorus Catalysts – Reversible Chain Transfer Catalyzed Polymerizations (RTCPs)

A novel class of living (controlled) radical polymerizations with germanium, tin, and phosphorus catalysts were developed. The polymerizations are based on a new mechanism, *Reversible chain Transfer (RT)* catalysis. Low-polydispersity polystyrene and polymethacrylates with predicted molecular weight were obtained with a fairly high conversion in a fairly short time. Attractive features of the catalysts include their *high reactivity*, *high solubility in organic media*, *insensitivity to air*, *minor color and smell*, *relatively low toxicity* (Ge and P catalysts), and *low cost* (P catalysts).

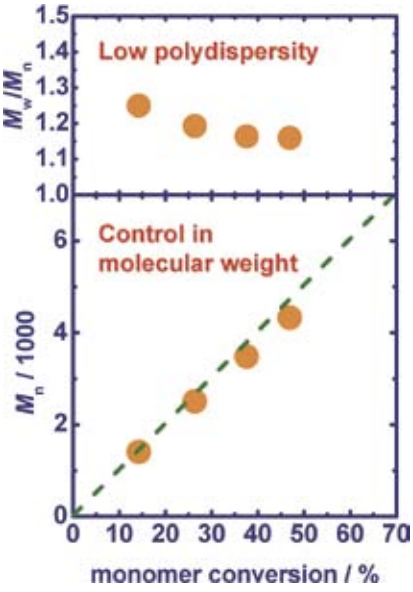

Figure 2. Plots of molecular weight (M_n) and molecular weight distribution (M_w/M_n) vs monomer conversion for the polymerization of styrene with GeI_4 (catalyst).

Tsujii Y, Patterning by Direct-Writing Graft Polymerization, Grant-in-Aid for Exploratory Research, 1 April 2005–31 March 2007.

Tsujii Y, Development of Ionic-Liquid Polymer-Based Electrolyte Membrane by Controlled Graft Polymerization, Strategic Development of PEFC Technologies for Practical Application Program by NEDO, 9 December 2005–20 March 2008.

Tsujii Y, Development of Novel Lithium Ion Battery with Network Channel of High Ionic-Conductivity, Development of High-Performance Battery System for Next-Generation Vehicles by NEDO, 1 July 2007–20 March 2008.

Ohno K, Science of Semi-Soft Colloidal Crystals, Grant-in-Aid for Young Scientists (A), 1 April 2005–31 March 2008.

Ohno K, Fundamentals and Applications of Semi-Soft Colloidal Crystals, Industrial Technology Research Grant Program by NEDO, 1 January 2005–31 December 2007.

Goto A, Non-Transition-Metal Catalyzed and Photo-Induced LRPs, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

Goto A, Development of Green LRP with Low Cost, Industrial Technology Research Grant Program by NEDO, 10 September 2007–31 August 2009.

Goto A, Fundamentals and Applications of Non-Transition-Metal Catalyzed LRP, Mitsubishi Chemical Corporation Fund, 1 November 2007–29 August 2008.

Division of Materials Chemistry
- Polymer Controlled Synthesis -

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Prof
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Students

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YAMAGUCHI, Katsuya (M1)
YANG, Junyue (RS)
UEKI, Kazuya (UG)
YAMADA, Hiroto (UG)

Visitors

Dr AUBERT, Corinne	Université Pierre et Marie Curie, France, 23 May 2007
Prof TERADA, Masahiro	Tohoku University, Japan, 26 September 2007
Prof SKRYDSTRUP, Troels	University of Aarhus, Denmark, 27 September 2007
Prof CHARLEUX, Bernadette	Université Pierre et Marie Curie, France, 11 December 2007

Scope of Research

Our research program focuses on development of new synthetic methods, which enable precise control of polymers in terms of their size and structure. Our attention is especially directed to control of reactive carbon species, such as carbon centered radicals and carbocations, with the aid of synthetic organic chemistry, element chemistry, computational chemistry, and so on. We also study various polymer condensed states by both static and dynamic methods to understand the relation of physical properties and structures.

Research Activities (Year 2007)

Publication

Kayahara E, Yamago S, Kwak Y, Goto A, Fukuda T: Optimization of Organotellurium Transfer Agents for Highly Controlled Living Radical Polymerization, *Macromolecules,* (in press).

Presentations

"Phase Imaging of Polymer Structure by TEM", Tosaka M, 56th SPSJ Symposium on Macromolecules, Nagoya, Japan, 19–21 September 2007 (invited).

"Effects of Heteroatoms in Highly Controlled Living Radical Polymerizations", Yamago S, 2007 Japan-Korea Joint Forum on Living/Controlled Polymerization and the Related Subjects, 3 May 2007, Gwanju, Korea (invited).

"Recent Advances in Organoheteroatom-Mediated Living Radical Polymerization", Yamago S, ICRIS'07, The Science and Technology of Well-Controlled Polymer Assembly, 11 June 2007, Kyoto (invited).

"Local Structures in Polymer Single Crystals Evidenced by High-Resolution Electron Microscopy", Tosaka M, Tsuji M, American Chemical Society 234th National Meeting & Exposition, Boston, USA, 19–23 August 2007 (invited).

Grants

Yamago S, Invention of New Radical Chemistry of "Heavy" Group 15 Heteroatom Compounds, Grant-in-Aid for Scientific Research, (A) (2), 1 April 2005–31 March 2008.

Yamago S, Precise Control of Radical Reactions Using Synergetic Effects of "Heavy" Heteroatom Compounds, Grant-in-Aid on Priority Areas, 1 October 2006–31 March 2010.

Yamago S, Precision Control of Organotellurium-

Optimization of Organotellanyl Group Transfer Agents for Highly Controlled Living Radical Polymerization

Living radical polymerization (LRP) has been recognized as one of the most efficient method for the controlled synthesis of macromolecules possessing a variety of polar functional groups with defined monomer sequences and architectures. We have recently developed organo*te*llurium-mediated living *r*adical *p*olymerization (TERP), which shows high versatility in polymerizing varieties of monomer families and gives living polymers with molecular weights predicated from the monomer/transfer agent ratio and with narrow molecular weight distributions. During the course to increase the control over the polymerization, we developed new organotellanyl group transfer agents which gave polymers with lower polydispersity indexes (PDIs); transfer agents possessing aryltellanyl groups, such as phenyltellanyl, *p*-methoxyphenyltellanyl, and *p*-trifluoromethylphenyltellanyl groups, showed higher PDI control than that bearing conventional methyltellanyl group. We also found that *n*-butyltellanyl-substituted transfer agent, which is higher cost efficiency than the conventional agent, exhibited similar control to the conventional one. Kinetic studies revealed that aryltellanyl groups underwent ca. 2~4 times faster tellanyl group transfer reaction than methyltellanyl group towards a polystyrene-end radical, and these results are consistent with the polymerization results.

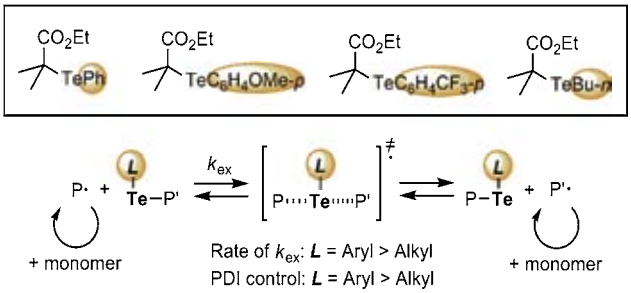

Figure 1. New transfer agents and the key mechanism for the PDI control.

Crystallization of Stretched Network Chains in Crosslinked Natural Rubber

Relatively fast kinetics of strain-induced crystallization (SIC) of crosslinked samples with various network-chain densities (ν) of natural rubber (NR) and its synthetic analogue (IR) was examined by the fast time-resolved wide angle X-ray diffraction and simultaneous tensile measurements. The lateral crystallite size was almost unchanged with elapsed time, though the crystallization proceeded considerably during the period. The rate of SIC was faster for the samples having the higher ν during the first tens of seconds. While the development of SIC obviously depends on ν, progress of relative stress relaxation with time was almost independent of ν. The different dependence of the experimental results on ν was explained by assuming coexistence of stretched and relaxed network chains. During SIC at fixed strain ratio, the intensity of crystalline reflections increased without reducing the intensity of anisotropic amorphous halo on the equator. Accordingly, rather relaxed chains that had shown the off-equatorial scattering were thought to be consumed for the crystal growth.

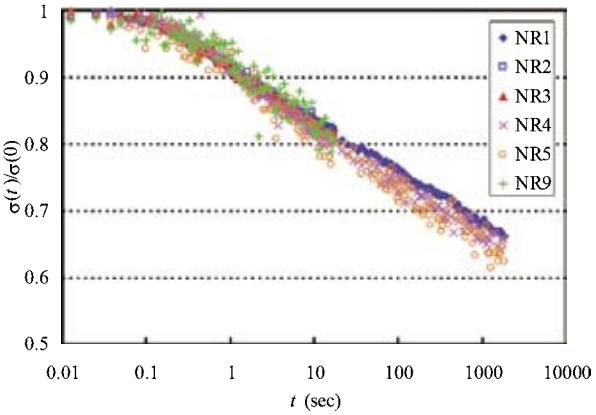

Figure 2. Tensile stress normalized by the maximum stress for NR samples, showing the relative stress relaxation. The smaller number in the sample code corresponds to the higher ν.

Mediated Living Radical Polymerization (TERP), Mitsubishi Foundation Grant, 1 October 2006–30 September 2007.

Yamago S, Creation of Functional Organic Materials by Organobismuthine-Mediated Living Radical Polymerization, Industry-University Joint Research for Innovative Seeds Program, Japan Science and Technology Agency, 1 September 2006–30 September 2007.

Tsuji M, Structure Analysis of Poly(dioxanone) Nanofibers Prepared by Electron-Spinning Method, Grant-in-Aid for Scientific Research, (C), 1 April 2007–31 March 2009.

Tosaka M, Near-Field Optical Effects of Self-Assembled Nanoparticle Chains on Oriented Polymer Layers, The Ogasawara Foundation for the Promotion of Science & Engineering Grant, 1 April 2007–31 March 2008.

Division of Materials Chemistry
- Inorganic Photonics Materials -

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TOKUDA, Yomei
(D Eng)

PD
IHARA, Rie
(D Eng)

Researcher
FUKUDA, Masaaki

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TANAKA, Yusuke (M2)
YAMAMOTO, Hideaki (M2)
OKA, Takanori (M1)
OKU, Satoshi (M1)
MIYAGAWA, Yuya (M1)
OHTA, Masayuki (UG)
KAWANISHI, Tomonori (UG)

Scope of Research

In this laboratory, amorphous and polycrystalline inorganic materials and organic-inorganic hybrid materials with various optical functions such as photorefractivity, optical nonlinearity, phptolumionescence and photocatalysis are the target materials, which are synthesized by sol-gel, melt-quenching and sintering methods and so on. Aiming at highly functional materials the structure-property relationship is investigated by X-ray diffraction techniques, high-resoluction NMR, thermal analysis, various laser spectroscopies and quantum chemical calculations.

Research Activities (Year 2007)

Publications

Takahashi M, Maeda T, Uemura K, Yao J, Tokuda Y, Yoko T, Kaji H, Marcelli A, Innocenzi P: Photo-induced Formation of Wrinkled Microstructures with Long-range Order in Thin Oxide Films, *Advanced Materials*, **19 (24)**, 4343-4346 (2007).

Menaa B, Takahashi M, Innocenzi P, Yoko T: Crystallization in Hybrid Organic-inorganic Materials Induced by Self-organization in Basic Conditions, *Chem. Mat.* **19 (8)**, 1946-1953 (2007).

Kakiuchida H, Takahashi M, Tokuda Y, Masai H, Yoko T: Effect of Organic Group on Structure and Viscoelastic Properties of Organic-inorganic Polysiloxane Hybrid System, *J. Phys. Chem. B*, **111**, 982-988 (2007).

Mizuno M, Takahashi M, Tokuda Y, Yoko T: Substituent Effect on the Formation of Organically-modified Silicophosphate through Nonaqueous Acid-base Reaction, *J. Sol-Gel Sci. Technol.*, **44**, 47-52 (2007).

Presentations

Takahashi M, *et al.*, Photopolymerisation-Initiated Formation of Ordered Microstructure in Oxide Thin Films from Photo Monomer-Oxide Precursor System Photopolymerisation-Initiated Formation of Ordered Microstructure in Oxide Thin Films from Photo Monomer-Oxide Precursor System, XIV International Sol-Gel Conference, 6 September 2007, Montpellier, France.

Tanaka Y, Tokuda Y, Takahashi M, Yoko T, Durable Organic-inorganic Hybrid Silicophosphate Glass Prepared through Nonaqueous Acid-base Reaction, The Ceramics Society of Japan Fall Meeting, Aichi, Japan, 12 September 2007.

Grants

Takahashi M, The Kyoto University Foundation, International Collaborative Work “Self Organized Nano/micro Fabrication of Thin Oxide Films”, 10 October 2006–9 October 2007.

Tokuda Y, Fabrication of Pb-free Sealing Glass, JST, Research for Promoting Technological Seeds, 13 September 2006–28 February 2007.

Tokuda Y, Quantitative Structure Analysis of Amorphous Materials Using Solid State NMR Spectroscopy, 1 December 2007–30 November 2008, CASIO Science Promotion Foundation.

Photo-induced Formation of Wrinkled Microstructures with Long-range Order in Thin Oxide Films

Formation of ordered microstructures via spontaneous organization is in principle one of the simplest routes to produce controlled patterns in thin films. Here we show that patterned structures of oxide materials are indeed obtained through controlled processing of sol-gel films. We have induced wrinkling, through UV curing, in hybrid organic-inorganic films containing acrylamide monomers and titania precursors. Figure 1 shows the fabrication process of the present method. We have successfully controlled the wrinkling process by suppressing the evaporation of solvents to obtain a wet and soft film even several hours after deposition. The faster polymerization of the film surface generates a buckling effect to create patterns in the films. The removal of the organic polymer by thermal treatment leaves titania microstructures having a long-range order. This method of producing the micropatterned structures as shown in Figure 2 will find several applications in photonics.

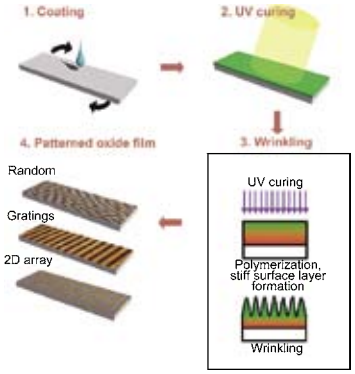

Figure 1. Schematic illustration of spontaneous formation of wrinkled patterns. 1. A hybrid acrylamide-titania film is deposited via spin-coating. 2. UV curing is applied to the film. 3. The formation of a stiff surface layer induces wrinkling on the films. 4. Thin oxide films with different wrinkled patterned structures are obtained by firing.

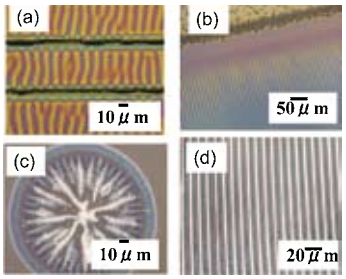

Figure 2. (a) ordered structure prepared on a patterned substrate (b) long range ordered structure fabricated by shaped UV light illumination, (c) dendrimer like structure fabricated by putting a droplet on the substrate, and (d) ordered structure fabricated by covering a part of the coating. Only black light (254nm, 5W) was used as a light source for fabricating these patterns.

Quantitative Structure Analysis of Quadrapolar Nuclei in Amorphous Material

MAS NMR is one of the powerful tools to obtain the structural information especially on dipolar nuclei (I = 1/2) in amorphous material. Unfortunately, quadrupolar nuclei (I ≥ 3/2) provide too broad MAS NMR spectra to be analyzed quantitatively, although half of the elements on earth have quadrupolar spin. Recently, Frydman et al. have developed MQMAS NMR for a better understanding of quadrupolar nuclei in a solid state material. However, it lacks quantitative information because the efficiency of multiquantum spin transition depends on the quadrupolar coupling constant.

In this work, we will provide a quantitative analysis of the local structure of quadrupolar nuclei in amorphous material based on the inverse analysis of MQMAS NMR spectroscopy and quantum chemical calculation. An observed spectrum and an inherent distribution of quadrupolar parameter, R, are related by the next equation

$$I(\varpi) = \int I_0(\varpi; R)\Pi(R)dR \qquad (1)$$

where $I(\varpi)$ is the observed spectrum, $I_0(\varpi;R)$ is the theoretical spectrum for R, $\Pi(R)$ is the distribution of R. Using equation (1), $\Pi(R)$ can be calculated based on the numerical approach with Tikhonov regularization (inverse analysis). The quantum chemical calculations make a direct correlation between R and structure parameter as follows,

$$C_q = e^2 Q(q_{zz})/h \qquad (2)$$

where C_q is the quadrupolar coupling constant and q_{zz} is the electric field gradient. We are now trying to establish inverse analysis to extract the inherent structure distribution in inorganic glass from the measured NMR spectra.

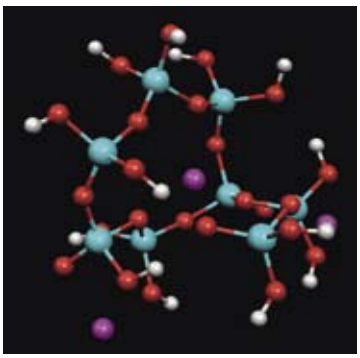

Figure 3. A model cluster of the local structure of sodium silicate glass. Quantum chemical calculation provides the electric field gradient tensor, q_{zz}, which is related to the quadrupolor coupling constant, C_q, as $C_q = e^2Q(q_{zz})/h$

Division of Materials Chemistry
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Visitors

Dr LETURCQ, Renaud — Solid State Physics Laboratory, ETH, Switzerland, 15–16 February 2007
Dr OHE, Junichiro — Hamburg University, Germany, 25 October 2007

Scope of Research

The conventional electronics utilizes only the "charge" of electrons, while the traditional magnetic devices use only "spin" degree of freedom of electrons. Aiming at the complete control of both charge and spin in single solid-state devices, a new field called *spintronics* is rapidly developing and impacting on information technology. By combining the atomic-layer deposition with nanofabrication, we focus on the development of spin properties of various materials and the control of quantum effects in mesoscopic systems for novel spintronics devices.

Research Activities (Year 2007)

Publications

Yamada K, Kasai S, Nakatani Y, Kobayashi K, Kohno H, Thiaville A, Ono T: Electrical Switching of the Vortex Core in a Magnetic Disk, *Nature Materials*, **6**, 269-273 (2007).

Tamada Y, Yamamoto S, Takano M, Nasu S, Ono T: Well-ordered $L1_0$-FePt Nanoparticles Synthesized by Improved SiO_2-nanoreactor Method, *Applied Physics Letters*, **90**, 162509 (2007).

Presentations

Excitation of Spin-structure in Nano-magnet by Electrical Current, Ono T, 7th Symposium on the Electron Spin Science and Engineering, 22–24 February 2007, Daemyung, Korea.

Excitation of Nano-spin-structure by Electric Current, Ono T, International Conference on Nanospintronics Design and Realization, 21–25 May 2007, Dresden, Germany.

Magnetic Vortex Excitation by Spin-polarized Currents, Kasai S, 6th International Symposium on Metallic Multilayers, 16 October 2007, Perth, Australia.

Grants

Ono T, Invention of Anomalous Quantum Materials, Grant-in-Aid for Scientific Research in Priority Areas, 1 April 2004–31 March 2010.

Ono T, Development of Writing Technology for Gbit-MRAM by Using Current-driven Domain Wall Motion, Industrial Technology Research Grant Program from NEDO, 1 January 2005–31 December 2007.

Ono T, Current-induced Spin Dynamics and Its Application to Spintronic Devices, Grant-in-Aid for Young Scientists (S), 1 October 2007–31 March 2012.

Kobayashi K, Generation and Detection of Quantum Correlation in Semiconductor Nanostructures, Grant-in-Aid for Young Scientists (S), 1 October 2007–31 March 2012.

Awards

Ono T, Ichimura Academic Award, Pioneering Research on the Nanoscopic Spin-structure Control in Nanofabricated Magnets, The New Technology Development Foundation, 27 April 2007.

Electrical Switching of the Vortex Core

A magnetic vortex is a curling magnetic structure realized in a ferromagnetic disk, which is a promising candidate for a memory cell for future non-volatile data-storage devices. Thus, an understanding of the stability and dynamical behavior of the magnetic vortex is a major requirement for developing magnetic data-storage technology. Since the publication of experimental proof for the existence of a nanometer-scale core with out-of-plane magnetization in a magnetic vortex, the dynamics of vortices have been investigated intensively. However, a way to electrically control the core magnetization, which is a key for constructing a vortex-core memory, has been lacking. Here, we demonstrate the electrical switching of the core magnetization by using the current-driven resonant dynamics of the vortex; the core switching is triggered by a strong dynamic field that is produced locally by a rotational core motion at a high speed of several hundred meters per second (Figure 1). Efficient switching of the vortex core without magnetic-field application is achieved owing to resonance. This opens up the potentiality of a simple magnetic disk as a building block for spintronic devices such as a memory cell where the bit data is stored as the direction of the nanometer-scale core magnetization.

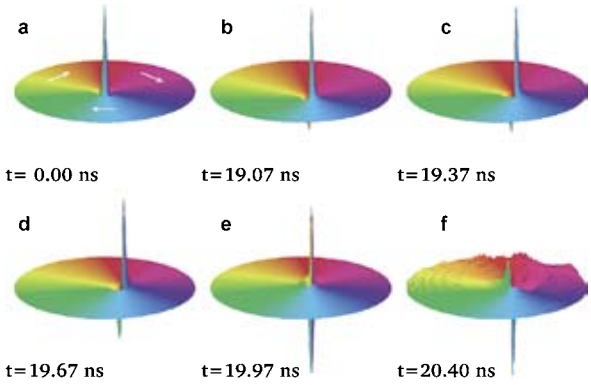

Figure 1. Perspective view of the magnetization with a moving vortex structure. After the electric pulse is applied to the initial status (a), the vortex core starts to rotate and finally reverses its direction in 20 ns (b-f).

Toward Pure Nanomagnets

Iron-Platinum (FePt) nanoparticles have been expected as a promising candidate for the future recording media with ultra-high densities beyond 1 Tbit/inch^2, as the FePt alloy with the $L1_0$ structure possesses high enough magnetic anisotropy to suppress super-paramagnetic fluctuation down to a particle size of about 3 nm. Recently, we have obtained the $L1_0$-FePt nanoparticles by developing a new synthetic "SiO_2-nanoreactor" method. However, the annealing condition in this method still suffered from the presence of the unconverted fcc-FePt nanoparticles that are super-paramagnetic at room temperature. For the practical applications in the magnetic recording media, it is highly desired that all nanoparticles possess well-ordered $L1_0$ structure. We have optimized the annealing condition and successfully achieved the well-ordered $L1_0$-FePt nanoparticles. The resultant room-temperature coercivity reaches an extremely large value of 28 kOe in spite of the very small particle size of 6.7 nm in diameter (Figure 2). Microscopic characterization by the Mössbauer spectroscopy proved that the synthesized $L1_0$-FePt nanoparticles have magnetic moments comparable to that of the bulk state even at the particle surface (Figure 3).

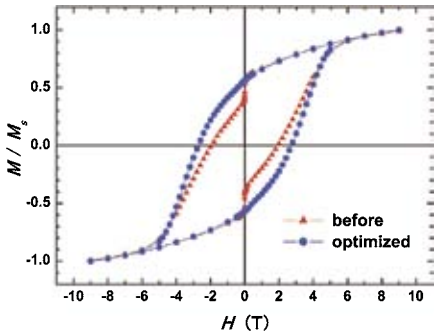

Figure 2. Hysteresis loops at 300 K of the FePt nanoparticles treated in the conventional and newly optimized annealing methods.

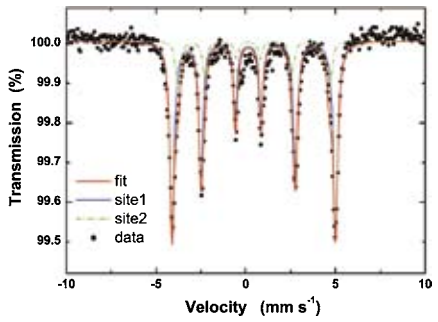

Figure 3. Mössbauer spectrum of the FePt nanoparticles treated in the optimized annealing method.

Ono T, MSJ Outstanding Research Award, "Research on the Current-driven Magnetic Domain Wall Dynamics", The Magnetic Society of Japan, 12 September 2007.

Morimoto Y, Tamada Y, Yamamoto S, Takano M, Ono T, MSJ Distinguished Paper Award "Detailed Study on the Structure and Magnetic Property of the Well-ordered $L1_0$-FePt Nanoparticles Synthesized by SiO_2-nanoreactor Method", The Magnetic Society of Japan, 12 September 2007.

Division of Biochemistry
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KONISHI, Yusuke (UG)
OTSUKA, Saori (UG)
TATSUTANI, Kazuya (UG)

Visitors

Ms PUJALS, Silvia R — University of Barcelona, Spain, 1 July–28 November 2007
Ms WATKINS, Catherine L — Cardiff University, UK, 16 November–10 December 2007

Scope of Research

The ultimate goal of our research is the regulation of cellular functions by designed peptides and proteins. Current research subjects include (1) development of novel intracellular delivery systems aiming at elucidation and control of cellular functions using designed membrane permeable peptide vectors, (2) elucidation of the DNA binding and recognition modes of C2H2-type zinc finger proteins and design of artificial transcription factors with various DNA binding specificities, and (3) design of stimulation-responsible artificial peptides and proteins.

Research Activities (Year 2007)

Presentations

"Creation of Zinc-Finger-Type Transcription Factors toward Gene Regulation and Analysis", Imanishi M, 127th Annual Meeting, The Pharmaceutical Society of Japan, Toyama, 29 March 2007.

"Cell Penetrating Peptides and Their Internalization Mechanisms", Futaki S, Special Lecture at Welsh School of Pharmacy, Cardiff, UK, 8 May 2007.

"Arginine-Rich Peptides and Their Internalization Mechanisms", Futaki S, Biochemical Society Focused Meeting Cell Penetrating Peptides, Telford, UK, 10 May 2007.

"Membrane Interaction and Internalization of Arginine-Rich Peptides", Futaki S, Stockholm University Neurochemistry Seminar, Stockholm, Sweden, 23 May 2007.

"Controlling Channel Peptide Assembly and Gating by Extramembrane Conformational Switch", Futaki S, Japanese-Swiss Symposium on Chemical Biology (JSCB), Lausanne, Switzerland, 25 June 2007.

"Efficient Cellular Uptake of Arginine-Rich Peptides", Nakase I, The Mini Peptide Symposium for Young Researchers, Toyama, 6 November 2007.

Grants

Futaki S, Chemical Biology in Translocation of Membrane Permeable Peptides into Cells, Grant-in-Aid for Scientific Research (A), 1 April 2007–31 March 2010.

Futaki S, Developing Methodologies of Efficient Intracellular Delivery for Cell Imaging and High-throughput Analysis, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2007–31 March 2009.

Futaki S, Cell Targeting Delivery Peptides: Functional Elucidation and Delivery Control, SORST Program, Japan Science and Technology Agency, 1 April 2006–31 March 2008.

Interaction of Arginine-rich Peptides with Membrane-Associated Proteoglycans Is Crucial for Induction of Actin Organization and Macropinocytosis

Arginine-rich peptides, including HIV-1 Tat (48-60), HIV-1 Rev (34-50), and octaarginine (R8), belong to one of the major classes of cell-permeable peptides that can deliver various membrane-impermeable molecules into cells. The importance of the endocytic pathways has recently been demonstrated in the cellular uptake of these peptides. We have previously shown that macropinocytosis is one of the major pathways for the peptides internalization, and that organization of F-actin accompanies this process. Using proteoglycan deficient Chinese hamster ovary cells, we have demonstrated that membrane-associated proteoglycans are indispensable for induction of the actin organization and the macropinocytic uptake of arginine-rich peptides. We have also shown that cellular uptake of Tat peptide is highly dependent on heparan sulfate proteoglycan (HSPG), whereas R8 peptide uptake is less dependent on HSPG. Additionally, activation of Rac protein and the actin organization has been observed a few minutes after the arginine-rich peptides treatment. These data strongly suggest the possibility that interaction of arginine-rich peptides with membrane-associated proteoglycans quickly activates intracellular signals and induces actin organization and macropinocytosis.

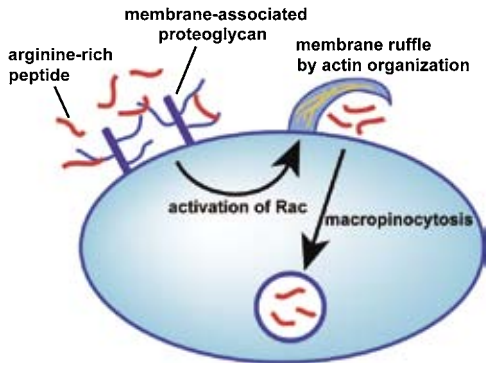

Figure 1. A possible pathway for cellular uptake of arginine-rich peptides. The interaction of the peptides with membrane-associated proteoglycans induces actin organization and macropinocytosis.

Alpha-Helical Linker of an Artificial 6-Zinc Finger Peptide Contributes to Selective DNA Binding to a Discontinuous Recognition Sequence

Although many zinc finger motifs have been developed to recognize specific DNA triplets, a rational way to selectively skip a particular non-recognized gap in the DNA sequence has never been established. We have now created a 6-zinc finger peptide with an alpha-helix linker, Sp1ZF6(EAAAR)$_4$, which selectively binds to the discontinuous recognition sites in the same phase (10 bp-gap) against the opposite phase (5 bp-gap) of the DNA helix. The linker peptide forms a helix structure stabilized by salt bridges, and the helical length is estimated to be about 30 Å, corresponding to that of 10 bp DNA. The gel shift assays demonstrate that Sp1ZF6(EAAAR)$_4$ preferably binds to the 10 bp-gapped target rather than the 5 bp-gapped target. The CD spectra show that the alpha-helical content of the linker is higher in the complex with the 10 bp-gapped target than with the 5 bp-gapped target. The present results indicate that the helical linker is suitable for binding to the recognition sites in the same phase, and that the linker induces the loss of binding affinity to the opposite phased recognition sites. The engineering of a helix-structured linker in the 6-zinc finger peptides should be one of the most promising approaches for selectively targeting discontinuous recognition sites depending on their phase situations.

Figure 2. Estimated DNA binding modes of an artificial 6-zinc finger peptides with (EAAAR)4 linker targeting discontinuous GC box sequences.

Imanishi M, Screening and Evaluation of Novel Clock-related Proteins Using Zinc-finger Technology, PRESTO program, Japan Science and Technology Agency, 1 October 2005–31 March 2009.

Imanishi M, Creation of Transcription Activation Peptides Based on Protein-protein Interaction between DNA Binding Zinc Finger Domains, Grant-in-Aid for Young Scientists (B), 1 April 2006–31 March 2008.

Nakase I, Development of New Cell-Targeting Peptides Having Functional Activities for Recognition of Various Proteoglycans on Cell Membrane, Grant-in-Aid for Young Scientist (B), 1 April 2007–31 March 2009.

Division of Biochemistry
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Scope of Research

Our research covers the comprehensive understanding of the physiological roles of biocatalysts (enzymes) as well as the reaction mechanism and specificity of each enzyme. 1) Studies on diglycosidases hydrolyzing the β-glycosidic bond between disaccharides and aglycons. 2) Development of intermediate analogue inhibitors of acyl-activating enzyme superfamily that plays pivotal roles in plant hormone homeostasis. 3) Design and synthesis of transition-state analogue and mechanism-based inhibitors of γ-glutamyltranspeptidase. 4) Directed evolutional studies of *Pseudomonas* lipase. 5) Studies on the activation/inactivation process of plant hormones. 6) Molecular mechanism of regulation of coumarin biosynthesis in plants.

Research Activities (Year 2007)

Publications

Han L, Hiratake J, Kamiyama A, Sakata K: Design, Synthesis and Evaluation of γ-Phosphono Diester Analogues of Glutamate as Highly Potent Inhibitors and Active Site Probes of γ-Glutamyl Transpeptidase, *Biochemistry*, **46**, 1432-1447 (2007).

Ahn Y O, Saino H, Mizutani M, Shimizu B, Sakata K: Vicianin Hydrolase is a Novel Cyanogenic β-Glycosidase Specific to β-Vicianoside (6-*O*-α-L-Arabinopyranosyl-β-D-Glucopyranoside) in Seeds of *Vicia angustifolia*, *Plant Cell Physiol*, **48**, 938-947 (2007).

Nakagawa Y, Hasegawa A, Hiratake J, Sakata K: Engineering of *Pseudomonas aeruginosa* Lipase by Directed Evolution for Enhanced Amidase Activity: Mechanistic Implication for Amide Hydrolysis by Serine Hydrolases, *Protein Eng Des Sel*, **20**, 339-346 (2007).

Presentation

The Campestanol-Independent Pathway of Brassinosteroid Biosynthesis, Mizutani M, 19th International Conference on Plant Growth Substances, Mexico, 22 July 2007.

Grants

Sakata K, Studies on Catalytic Mechanism of Disaccharide-Specific Glycosidases and Evolution of Plant β-Glucosidases, Grant-in-Aid for Scientific Research (B) (2), 1 April 2004–31 March 2007.

Hiratake J, Bio- and Organic Chemical Studies on Plant Glycosidases by Using β-Glycosylamidine Derivatives as Tools, Grant-in-Aid for Scientific Research (B) (2), 1 April 2004–31 March 2007.

Hiratake J, Development of Chemicals to Control Glutathione Metabolism and Oxidative Stress for Use in Chemical Biology, Grant-in-Aid for Scientific Research (B) (2), 1 April 2007–31 March 2010.

Mizutani M, Construction of Plant Oxygenase Library and its Functional Characterization, Grant-in-Aid for Scientific Research (C) (2), 1 April 2006–31 March 2008.

Mechanism of Disaccharide-Glycone Specificity in β-Primeverosidase Is Revealed by the Crystal Structure in Complex with β-Primeverosylamidine

β-Primeverosidase (PD) is a family 1 glycosidase catalyzing the hydrolysis of β-primeverosides (6-*O*-β-D-xylopyranosyl-β-D-glucopyranosides) to release a disaccharide primeverose (Figure 1a). To investigate how PD recognizes the disaccharide moiety of β-primeverosides, we determined the crystal structure of PD in complex with β-primeverosylamidine (Figure 1b) as a chemical probe at a resolution of 1.8 Å (Figure 1c). The shape of the substrate-binding pocket consisting of subsites –2, –1, and +1 is like a funnel approximately 18 Å deep, and its entrance is 14 Å long and 10 Å wide. In this pocket, the glycosidic nitrogen of β-primeverosylamidine interacts with the oxygen atom of Glu203 (acid/base) at a distance of 2.7 Å, and the oxygen atom of Glu416 (nucleophile) interacts with C1 of glucose at a distance of 3.2 Å. All the hydroxy groups on the primeverosyl moiety make hydrogen bonds with surrounding residues in subsites –2 and –1. The interaction with the glucose moiety in subsite –1 is almost identical to that in β-glucosidases. The subsite –2 is constituted of six amino acids, Val386, Phe389, Glu470, Ser473, Gln477, and Phe479, and these residues are crucial and responsible for the strict specificity of PD toward the xylosyl moiety of β-primeverosides.

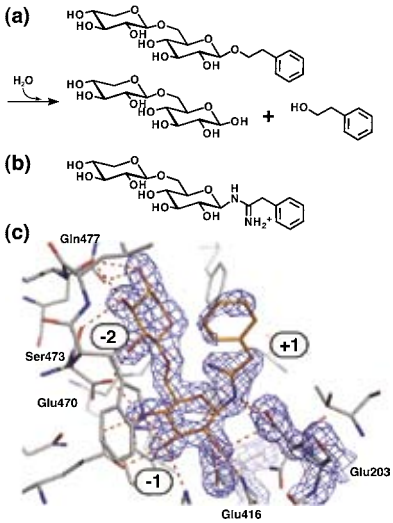

Figure 1. Crystal structure of PD in complex with β-primeverosylamidine. (a) The reaction scheme of PD. (b) β-primeverosylamidine. (c) Conformation of β-primeverosylamidine in the substrate-binding pocket of PD.

Biosynthetic Pathway of Coumarins in Plants

Coumarins are often found in the plant kingdom. They are involved in the plant defense due to their antimicrobial and antioxidative activities. They are originated from the phenylpropanoid pathway *via ortho*-hydroxylation of cinnamates, *cis-trans* isomerization of the side chain, and lactonization. The *ortho*-hydroxylation step is a key step, because it is the branching point from the general phenylpropanoid pathway. We explored coumarin biosynthesis using *Arabidopsis thaliana*, which accumulates scopolin, a glucoside of scopoletin (7-hydroxy-6-methoxycoumarin) in their roots. *Ortho*-hydroxylase of cinnamates was examined in the oxygenase families in Arabidopsis, and one of the candidate genes in the 2-oxoglutarate dependent dioxygenase family was designated as *F6'H1*. The T-DNA insertion mutants of F6'H1 exhibited severe reduction in the scopoletin/scopolin level in the roots. The recombinant F6'H1 protein exhibited *ortho*-hydroxylase activity for feruloyl-CoA to form 6'-hydroxyferuloyl-CoA. These results indicate that the 2-oxoglutarate dependent dioxygenase is the pivotal enzyme in *ortho*-hydroxylation of feruloyl-CoA in scopoletin biosynthesis. Adding to *F6'H1*, we also identified several genes involved in scopolin biosynthesis in Arabidopsis.

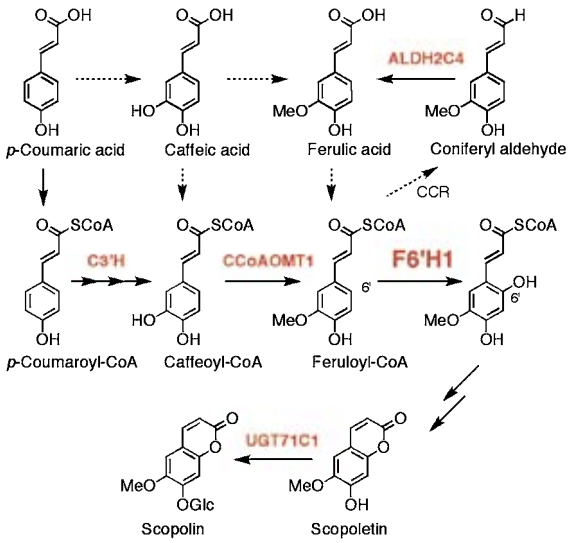

Figure 2. Biosynthetic pathway of scopoletin in *Arabidopsis thaliana.*

Awards

Ohnishi T, Watanabe B, Sakata K, Mizutani M, Paper Award, Award for Excellence to Authors Publishing in Bioscience, Biotechnology, and Biochemistry in 2006, "CYP724B2 and CYP90B3 Function in the Early C-22 Hydroxylation Steps of Brassinosteroid Biosynthetic Pathway in Tomato", Japan Society for Bioscience, Biotechnology, and Agrochemistry (NIPPON NOGEI-KAGAKU KAI), 24 March 2007.

Takeuchi Y, Poster Award, "Chemical Tools to Control IAA Homeostasis – IAA-Amino Acid Synthathase (GH3) Inhibitors and their *in vivo* Activiies –", The 42nd Annual Meeting of The Japanese Society for Chemical Regulation of Plants, Shizuoka, Japan, 30 October 2007.

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Guest Res Assoc
WANG, Wei

Guest Res Assoc
LI, Ruixi

Students

TANIGUCHI, Masatoshi (D3)
TANIGUCHI, Yukimi (D3)
NAKAMURA, Kinu (D2)
AKI, Shiori (D1)
KATAOKA, Mayuko (M1)

Visitors

Dr MELE, Giovanni	National Research Council of Italy, Italy, 7 February–6 March 2007
Prof SCHWECHHEIMER, Claus	University of Tübingen, Germany, 12–15 April 2007
Prof von ARNIM, Albrecht G	The University of Tennessee, USA, 4–7 July 2007
Prof GU, Hongya	College of Life Science, Peking University, China, 8–15 July 2007
Prof QU, Li-Jia	College of Life Science, Peking University, China, 11–24 July 2007
Mr WANG, Wei	College of Life Science, Peking University, China, 30 July 2007–31 January 2008
Ms LI, Ruixi	College of Life Science, Peking University, China, 30 July 2007–1 March 2008
Prof PETERS, Janny L	University of Nijmegen, The Netherlands, 3–17 September 2007

Scope of Research

This laboratory aims at clarifying the framework of regulatory network between genetic programs and environmental stress responses through the study on structure-function relationships of genetic materials and cellular proteins in higher plants. The current major subjects are the two-component response regulators involved in cytokinin signaling, HD-Zip proteins and phosphatidyl-inositol 4-phosphate 5-kinases required for phospholipid signaling, COP9 signalosome modulating protein degradation, and cyclins and CDKs controlling cell cycle.

Research Activities (Year 2007)

Presentations

Regulation of the COP9 Signalosome, a Repressor of Photomorphogenesis, Tsuge T, The 1st Workshop for Young Researchers – Scientific Research on Priority Areas "Plant Movement Regulation by LOV-Domain Photoreceptors", 17–18 January 2007 (Kyoto).

ARR1 Directly Activates Cytokinin Response Genes that Encode Proteins with Diverse Regulatory Functions, Taniguchi M, Tsuge T, Aoyama T, Oka A, Trends in Plant Hormones – RIKEN Plant Science Center International Symposium, 1–2 March 2007 (Yokohama).

Identifying Novel Regulation beyond Proteolysis of the COP9 Signalosome, Tsuge T, Aki S, Taniguchi M, Dohmae N, Menon S, Pick E, Wei N, Oka A; *Arabidopsis* CSN1 Binds SAP130, a Component of the mRNA Splicing Machinery, Aki S, Oka A, Tsuge T; *Arabidopsis AtPIP5K3* Gene Controlling Root-hair Morphogenesis, Kusano H, Yasuda K, Shimada H, Oka A, Aoyama T, 2007 Ann Meeting of Jpn Soc Plant Physiol, 28–30 March 2007 (Matsuyama).

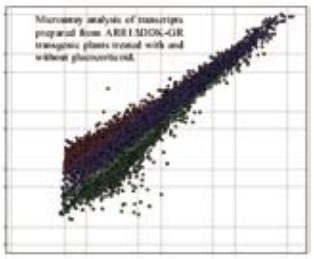
Towards Overall Architecture of Cytokinin Signaling and the Subsequent Responses

Cytokinin plays pivotal regulatory roles in plant development, including shoot regeneration from plant tissues, the release of axillary buds from apical dominance, leaf expansion, delay of senescence, vascular cell development, and the differentiation and proliferation of chloroplasts. In these processes, plant cells respond to the cytokinin signal by changing their gene expression patterns. Genome-wide analyses of *Arabidopsis* transcripts have revealed a number of genes responsive to exogenous cytokinin.

Intracellular signal transduction of cytokinin involves a histidyl-aspartyl phosphorelay among three components, *i.e.* sensor histidine kinases anchored at the plasma membrane, response regulators, and histidine-phosphotransfer (HPt)-type mediaotors. There are several paralogs with functional overlap for each component. Cytokinin triggers autophosphorylation of the histidine kinases whose phosphate is transferred to the response regulators *via* the mediators, and eventually activates the response regulators. The plant response regulators include two subtypes, type A and type B. Of 23 *Arabidopsis* response regulators (ARRs), 10 and 11 belong to types A and B, respectively. Type A ARRs lack known functional structures, except for the signal receiver domain, and constitute one clade in the phylogenic tree of plant response regulators. Exogenous cytokinin up-regulates steady-state levels of all type A transcripts examined, independent of *de novo* protein synthesis, suggesting that all type A *ARR* genes primarily respond to cytokinin. On the other hand, type B ARRs work as transcription factors. Although their gene themselves are not responsive to cytokinin, type B ARRs activate transcription of type A *ARR* genes upon cytokinin treatment.

Although molecular framework of phosphorelay signaling itself has become apparent, it is still hard to depict the overall architecture of the signal cascade leading to cytokinin-responsive phenomena in plant cells, mainly because the connections between the phosphorelay and downstream phenomena are unclear. Particularly, it is not known which of a number of genes immediately responsive to cytokinin are directly up-regulated by type B ARRs. To reveal events immediately downstream from the phosphorelay-mediated transcriptional activation, we searched for genes directly targeted by a type B ARR, ARR1, that has been most intensively studied in terms of both its molecular and biological functions [1]. Our approach used ARR1ΔDDK-GR, a chimeric transcription factor that is able to activate transcription of genes targeted by ARR1 in transgenic plants with treatment of glucocorticoid instead of cytokinin. We identified 23 such target genes, most of which were primarily responsive to cytokinin. Defect in the *ARR1* gene clearly affected the primary cytokinin response in at least 17 genes. This result imply that the majority of the genes primarily responsive to cytokinin are transactivated through the function of ARR1. The 17 genes encode proteins with diverse functions, including type A response regulators, cytokinin metabolic enzymes and putative disease resistance response proteins. The histidyl-aspartyl phosphorelay is thus connected to diverse regulatory levels of cytokinin-responsive phenomena through genes directly targeted by ARR1 and possibly its paralogs [2].

[1] Aoyama T, Oka A, *J. Plant Res.*, **116**, 221–231 (2003).
[2] Taniguchi M, Sasaki N, Tsuge T, Aoyama T, Oka A, *Plant Cell Physiol.*, **48**, 263–277 (2007).



Grants

Aoyama T, Development of Light Molecular Switch for Analyzing Intracellular Information Network, Grant-in-Aid for Exploratory Research, 1 April 2007–31 March 2009.

Tsuge T & Qu LJ, Molecular Mechanism Involved in Maintaining the Flatness of the Leaf Blade, Japan-China Scientific Cooperation Program (JSPS), 1 April 2007–31 December 2009.

Tsuge T, Novel Functions of COP9 Signalosome, the Key Signaling Component Is Conserved in both Human Carcinogenesis and Plant Photomorphogenesis, Research Grant (Research Foundation for Opto-Science and Technology), 1 April 2007–31 March 2009.

Tsuge T, Comparative Analysis of the Regulatory Mechanism Involved in Signal Transduction in Responses to Environmental Stimuli, among the Plant and Animal Kingdoms, Collaborative Research Grant (The Kyoto University Foundation), 1 April 2007–31 March 2008.

Aki S, Novel Functions of COP9 Signalosome, Plant Protein Analysis Research Project Graduate-Student-Grant (NAIST Science Research and Education Promotion Unit), 1 April 2007–31 March 2008.

Division of Biochemistry
- Chemical Biology -

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Prof
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Assist Prof
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PD
SATO, Ayato
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SHIRAKAWA, Takashi (D1)
YAMAZOE, Sayumi (D1)
TSUJIKAWA, Tomoko (M1)
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Visitor

PD JUNG, Hye Jin — Yonsei University, College of Engineering, Department of Biotechnology, Chemical Genomics Laboratory, Korea, 28 January–6 February 2007

Scope of Research

In human history, small organic molecules have been utilized for improving human health and for revealing secrets of life. Discovery or design of small organic molecules with unique biological activity permits small-molecule-initiated exploration of biology and further understanding of human diseases. Our laboratory has been discovering small organic molecules that modulate transcription or differentiation to use them as tools to explore biology. Such chemistry-initiated biology is recently called chemical biology, an emerging field of biology and medical sciences. Although our chemical biology is a basic one, it may "catalyze" future drug discovery.

Research Activities (Year 2007)

Publication

Sato S, Kwon Y, Kamisuki S, Srivastava N, Mao Q, Kawazoe Y, Uesugi M: Polyproline-rod Approach to Isolating Protein Targets of Bioactive Small Molecules: Isolation of a New Target of Indomethacin, *J. Am. Chem. Soc,* **129(4)**, 873-880 (2007).

Presentations

Chemical Biology of Gene Expression, Uesugi M, 32nd Lorne Conference on Protein Structure and Function, Australia, 4–8 February 2007.

Special Lecture: Chemical Biology of Gene Expression, Uesugi M, The University of Texas at Austin, TX, USA, 22 March 2007.

Chemical Biology of Gene Expression, Uesugi M, 87th Spring Meeting of the Chemical Society of Japan, Suita, Japan, 27 March 2007.

Special Lecture: Chemical Biology of Gene Expression, Uesugi M, School of Engineering, the University of Tokyo, Tokyo, Japan, 7 April 2007.

Chemical Biology of Gene Expression, Uesugi M, 19th FAOBMB Seoul Conference, Seoul, Korea, 27–30 May 2007.

Special Lecture: Chemical Biology of Gene Expression, Uesugi M, Ewha Womans University, Seoul, Korea, 30 May 2007.

Special Lecture: Chemical Biology of Gene Expression: Uesugi M, Kyung Hee University, Seoul, Korea, 31 May 2007.

Isolating and Identifying Protein Targets of Bioactive Small Molecules, Uesugi M, 4th Korea-Japan Young Scientist Meeting on Bioorganic and Natural Products Chemistry, Gyeongji, Korea, 29 August–1 September 2007.

Target Identification of Bioactive Small Molecules, Uesugi M, 2007 Chemical Genomics Symposium, Daejeon, Korea, 11 October 2007.

Small-molecule-initiated Biology

Knowledge about bioactive small molecules is a treasure of the humankind. Small organic compounds that the human being have discovered or synthesized from natural resources have been utilized for improving human health and for revealing secrets of life. The major goal of our research programs has been to expand the treasure by discovering and analyzing novel organic compounds with unique biological activities and to use them as tools to explore biology.

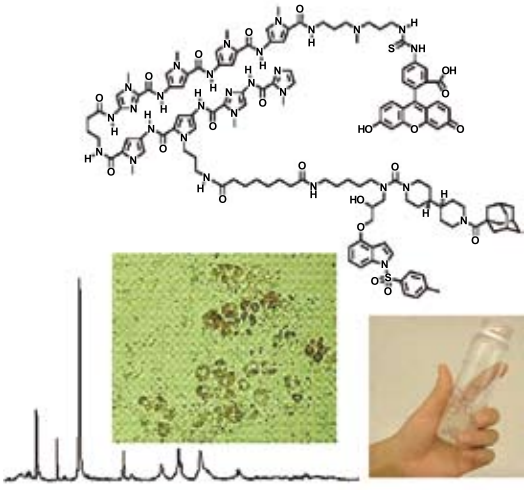
Our current research programs focus on discovering and using small organic molecules that modulate gene transcription or cell signaling. Regulation of gene transcription and cell signaling often induces drastic phenotypic changes in living organisms. Precise, external control over these endogenous processes through small organic molecules represents a challenge of chemistry to nature. The latest achievements are summarized below.

Discovery of synthetic small molecules that modulate transcription. Our group has discovered by screening chemical libraries a unique small-molecule modulator of transcription. The synthetic molecule we named "adamanolol" represents the first small molecules that modulate gene transcription by targeting transcription factor-coactivator interaction. Our group, as a collaboration with another laboratory, synthesized adamanolol and its derivatives and obtained structure-activity relationship, which enabled the design of the second-generation compound named "wrenchnolol." The wrench-shaped compound is now recognized in the field as a highly unique synthetic molecule that controls gene expression.

Wrenchnolol mimics an alpha-helical activation domain of transcription factor ESX: it may serves as a small-molecule activation module when coupled with a DNA binding molecule. Our group, as a collaboration with Prof. Dervan in Caltech, has recently succeeded in designing a completely organic, synthetic transcription factor that activates transcription. This work demonstrates that it is possible to generate a transcription factor out of organic compounds.

Discovery of small molecules that modulate cell signaling. Our group has developed an interesting method of screening chemical libararies for the discovery of bioactive molecules. In this unique method, synthetic small molecules were first profiled by their effects on phenotypic fat cell differentiation and pre-selected for more focused secondary assays. This approach enabled us to discover a number of bioactive compounds with a range of biological activities, including anti-proliferation of selective cell types and inhibition of lipogenesis. These molecules are now used for elucidation of new biological pathways in our group. For example, we recently discovered a new signaling pathway to control insulin/IGF pathways by utilizing the compound we call chromeceptin.

Our group also discovered small organic molecules that differentiate mouse embryonic stem (ES) cells into dopaminergic neurons. Our approach to discovering such molecules is rooted in the logic of asymmetric catalysts in chemistry. This work might be a good demonstration of applying the logic in chemistry to the biological field.



Chemical Biology of Gene Expression, Uesugi M, 4th Japanese-German Frontiers of Sciences (JGFoS) Symposium, Kanagawa, Japan, 2–4 November 2007.

Grants

Uesugi M, Small-molecule Initiated Analysis of Cellular Signaling, Grant-in-Aid for Scientific Research (B), 1 April 2006–31 March 2008.

Kawazoe Y, Small Molecules that Modulate Cell Differentiation, Grant-in-Aid for Young Scientists (B), 1 April 2006–31 March 2008.

Uesugi M, Methods for Isolating Target Proteins of Small Molecules, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2006–31 March 2008.

Uesugi M, Intracellular Imaging of Small Molecules, Industrial Technology Research Grant Program by NEDO, 1 June 2006–20 March 2008.

Uesugi M, Small Molecule Transcription Factors for Biological Investigations, PRESTO, Japan Science and Technology Agency, 1 October 2005–31 March 2009.

Division of Environmental Chemistry
- Molecular Materials Chemistry -

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Prof
HORII, Fumitaka
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Assoc Prof
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Techn
OHMINE, Kyoko

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SESEI, Takashi (M2)
IGARASHI, Yuki (M1)
KIUCHI, Yohei (M1)
YAMANE, Hiroaki (M1)
TAKAMI, Kosuke (UG)

Visitor

Prof LAUPRETRE, Francoise Laboratoire de Recherche sur les Polymeres CNRS, France, 9–16 June 2007

Scope of Research

The research activities in this subdivision cover structural studies and molecular motion analyses of highly organized polymer materials in the different states by high-resolution solid-state NMR, electron microscopy, X-ray diffractometry, and so on, in order to develop high-performance and high-functionality polymer materials such as organic electron luminiscence devices and different molecular hybrid materials. The structure formation process of bacterial cellulose is also characterized in detail and environmentally friendly cellulosic nanohybrid materials are examined to develop in different stages of the biosynthesis.

Research Activities (Year 2007)

Presentations

Disordered Structure of Polymer Materials as Revealed by High-Resolution Solid-State NMR Spectroscopy, Horii F, ICR International Symposium (ICRIS)'07, 11–13 June 2007 (Invited).

Molecular and Electronic Structure Analyses of N,N'-diphenyl-N,N'-di(m-tolyl)benzidine by Solid-State NMR and Quantum Chemical Calculations, Yamada T, Kaji H, Horii F, ICRIS'07, 11–13 June 2007.

Honored Lecture: New Developments in Solid-State NMR, Horii F, 46th Annual Meeting of NMR Society of Japan, 12 September 2007 (Invited).

Assembled and Hierarchical Structure of Native Cellulose, Horii F, International Cellulose Conference (ICC), 23 October 2007 (Invited).

Origin of the Different Emission Wavelengths in Alq_3 Analyzed by Solid-State NMR, Kaji H, SPIE Symposium on Photonic Devices + Applications, "Organic Light-Emitting Materials and Devices XI", 26 August 2007 (Invited).

Future Vision and Roadmap of Organic and Molecular Electronics/Bioelectronics, Kaji H, Special Program Symposium, "Future Vision of the Japan Society of Applied Physics", The 68th Annual Meeting of the Japan Society of Applied Physics, 29 March 2007.

Degradation and Structure of Materials in Organic LEDs Analyzed by Solution and Solid-State NMR, Kaji H, ATP Symposium, The 87th Spring Meeting of the Chemical Society of Japan, 26 March 2007 (Invited).

Effects of Added Electrolyte on the Magnetic Alignment of Bacterial Cellulose Microfibril Suspensions, Hirai A, Inui O, Horii F, Yamamoto S, Tsuji M, 56th Symposium on Macromolecules, Soc. Polym. Sci., Jpn., 20 September 2007.

Investigation of Dynamics of Poly(dimethylsilane) in the Mesophase by Solid-State ^{29}Si NMR: Evidence for Rotator Phase[1]

The characterization of the dynamics of materials is an important fundamental to understand their properties. For polymers, intermediate states, called "mesophases" often appear between the crystalline and liquid (or amorphous) states. The dynamics in the mesophases is closely related to important problems in polymer science, such as chain folding and (ultra)drawability. However, the dynamics of polymers with Si-Si backbones are not well characterized. In this study, the dynamics of poly(dimethylsilane) (PDMS) in the mesophase was studied.

Figure 1 shows the ^{29}Si cross polarization/chemical shift anisotropy (CP/CSA) spectra of PDMS. Below the transition temperature of 166ºC, which was observed by DSC measurements, we can observe typical CSA line shapes. The simulated CSA spectrum, shown on the experimental CSA spectrum at 23ºC by a green curve, agrees well with the experimental spectrum. Above the transition temperature of 166ºC, the observed CSA line shapes are found to be different from the typical CSA line shapes. The intensity near the isotropic chemical shift becomes small compared to the typical CSA line shapes. This intensity "hole" is experimental evidence of uniaxial rotational motion of the PDMS chains. Under the uniaxial rotation, the ^{1}H-^{29}Si dipolar interaction averages to be parallel to the direction of the rotation axis (see Figure 2). The ^{1}H-^{29}Si dipolar vector is then always directed to the polymer chain axis. The angular-dependence of the dipolar interaction is described by the second-order Legendre polynomial, P_2. Therefore, the signal intensity attenuation occurs during the CP process for polymers whose rotation axis is oriented near along the magic angle relative to the applied magnetic field, $\boldsymbol{B}_0$. The theoretical simulation considering the orientation-dependence of the CP efficiency, as shown on the experimental CSA spectrum at 240ºC by a pink curve in Figure 1, successfully explains the experimental spectrum with the "magic angle hole." This concept is confirmed by the ^{29}Si direct polarization (DP)/CSA and ultra-slow magic angle spinning (MAS) CP/CSA experiments. The change in the interchain packing from a monoclinic to a hexagonal lattice at 166ºC, which is analyzed by electron diffraction experiments, is therefore found to originate from the chain rotation dynamics around the molecular chain axis. From an analytical point of view, we provide an easy way to detect the rotational motion in solid materials.

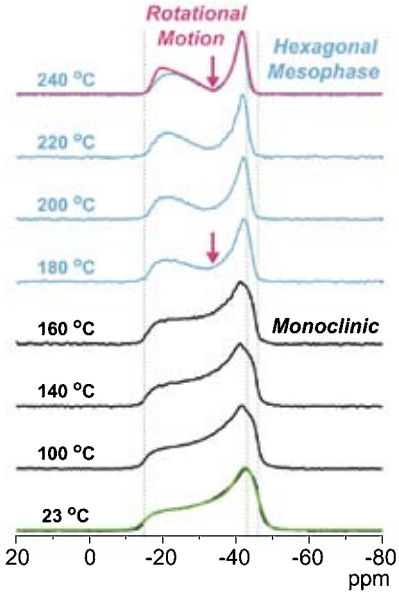

Figure 1. Temperature dependence of ^{29}Si CP/CSA spectra of PDMS from 23 to 240ºC. The arrow indicates the isotropic chemical shift, that is, the theoretical position of the magic angle hole. The simulated spectra for the experimental spectra of 23ºC and 240ºC are shown by the green curves.

[1] Kaji, H.; Horii, F. *Macromolecules* **2007**, *40*, 5420.

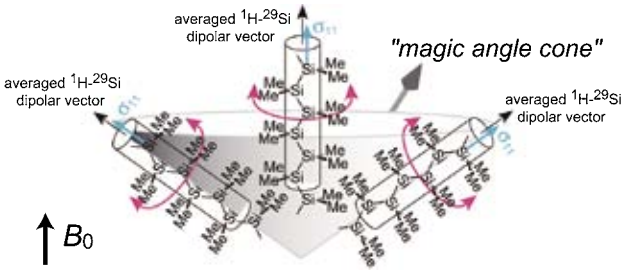

Figure 2. Rotational motion of PDMS in the mesophase.

Phase Separation Behavior of Aqueous Suspensions of Bacterial Cellulose Microfibrils, Hirai A, Inui O, Horii F, Tsuji M, 2nd International Cellulose Conference, 22 October 2007.

Grants

Kaji H, Science and Functions of Organic Amorphous Materials, Grant-in-Aid for Scientific Research (A), 1 April 2005–31 March 2008.

Kaji H, Electronic State Analysis of Organic Photoelectric Conversion Systems by Quantum Chemical Calculation and Nuclear Magnetic Resonance, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2007–31 March 2008.

Hirai A, Structure Control of Native Polymer Nano-Assemblies by Magnetic Field, Grant-in-Aid for Scientific Research, 1 April 2007–31 March 2010.

Division of Environmental Chemistry
- Hydrospheric Environment Analytical Chemistry -

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Prof
SOHRIN, Yoshiki
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UMETANI, Shigeo
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Assist Prof
NORISUYE, Kazuhiro
(D Sc)

Assist Prof*
FIRDAUS, Mochamad Lutfi
(D Sc)

Techn
MINAMI, Tomoharu
(D Eng)

Lecturer (pt)

SUZUKI, Yoshimi (D Sc) Shizuoka University

* Division of Environmental Chemistry, Laboratory of Trace Elemental Tomography

Students

KURAHASHI, Kensuke (D3)
NAKATSUKA, Seiji (D3)
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INADA, Keiko (M2)
KONO, Tomohiro (M2)
SHIMIZU, Akiyoshi (M2)
HIGO, Eri (M1)
NISHIDA, Shinsuke (M1)
OKABE, Taro (M1)

Visitor

Assoc Scientist SAITO, Mak Anderson Woods Hole Oceanographic Institution, USA, 3 July 2007

Scope of Research

Research activities are concerned with geochemistry, oceanography, limnology and analytical chemistry, which are important basic sciences in order to realize the sustainable society. Major research subjects are as follows: (i) Biogeochemistry of trace elements in the hydrosphere. The study also covers hydrothermal activity and deep biosphere. Major parts of these studies are based on field works. (ii) Iron uptake mechanism of phytoplankton. (iii) Ion recognition.

Research Activities (Year 2007)

Publications

Firdaus M L, Norisuye K, Sato T, Urushihara S, Nakagawa Y, Umetani S, Sohrin Y: Preconcentration of Zr, Hf, Nb, Ta and W in Seawater Using Solid-phase Extraction on TSK-8-hydroxyquinoline Resin and Determination by Inductively Coupled Prasma-mas Spectrometry, *Anal. Chim. Acta*, **583**, 296-302 (2007).

Norisuye K, Ezoe M, Nakatsuka S, Umetani S, Sohrin Y: Distribution of Bioactive Trace Metals (Fe, Co, Ni, Cu, Zn and Cd) in the Sulu Sea and Its Adjacent Seas, *Deep-Sea Res. II*, **54**, 14-37 (2007).

Nakatsuka S, Okamura K, Norisuye K, Sohrin Y: Simultaneous Determination of Suspended Particulate Trace Metals (Co, Ni, Cu, Zn, Cd and Pb) in Seawater with Small Volume Filtration Assisted by Microwave Digestion and Flow Injection Inductively Coupled Plasma Mass Spectrometer, *Anal. Chim. Acta*, **594**, 52-60 (2007).

Presentations

Simultaneous Determination of Key Trace Metals in Seawater, Sohrin Y, GEOTRACES Pacific Basin Workshop, 27 June 2007.

Development of Chelate Resin Column Preconcentration Method for Precise Isotope Analysis of Mo in Seawater, Nakagawa Y, Mochamad L F, Norisuye K, Sohrin Y, Irisawa K, Hirata T, 17th Annual V.M. Goldschmidt Conference 2007, 21 August 2007.

Physicochemical Speciation of Trace Metals during the Mesoscale Iron Enrichment (SEEDS II) in the Western North Pacific, Nakatsuka S, Sohrin Y, Norisuye K, Okamura K, Takeda S, Nishioka J, 17th Annual V.M. Goldschmidt Conference 2007, 23 August 2007.

Molecular Design of Extraction Reagents of High Selectivity Based on Steric Factors, Umetani S, Fukui Y, Sohrin Y, Uezu K, The 56th Annual Meeting of the Japan Society for Analytical Chemistry, 20 September 2007.

Simultaneous Determination of Trace Metals in Seawater Using NOBIAS CHLATE-PA1 and Its Application to the Bering Sea and the Arctic Ocean, Minami T, Urushihara S, Nakatsuka S, Higo E, Norisuye K, Sohrin Y, International Symposium on Metallomics 2007, 29 November 2007.

Development of Solid-phase Extraction Method Using Chelating Resin for Precise Isotope Analysis of Mo in Seawater

The behaviors of Mo in oxic environments are different from those in anoxic environments. The degree of isotopic fractionations in reactions of Mo in each environment is also different. Figure 1 shows reported Mo isotope ratios in natural samples. Using the isotopic information, the global material balance and circulation of Mo and the redox status of paleocean can be clearly estimated.

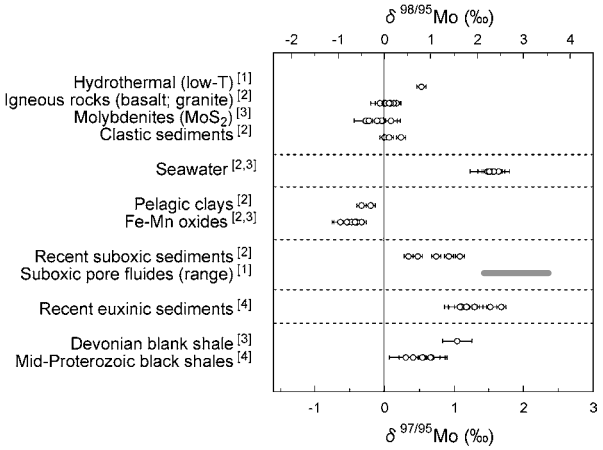

Figure 1. Summary of existing Mo isotope data from natural samples.

For geochemical studies, the isotope ratios in seawater are important reference values, and therefore precise and accurate analytical methods are required. In reported analytical methods, anion exchange resins have been used for separation and enrichment of Mo. These methods possess high procedure blank and low analytical precision and reliability, because the methods require complicated procedures with concentrated acid for elution. The methods give incomplete separation of major elements in seawater. Because of these reasons, although the reported isotopic ratios of Mo in seawater are scarce, they show a large variation. We have developed a solid-phase extraction method using chelating resin to resolve such problems.

TSK-8HQ [5] was used in a column to concentrate Mo. The sample solution that had been adjusted to pH 2.0 with HCl was passed through the column, and then the adsorbed Mo was eluted by the back flushing of 2 M NH_3. The eluate was then evaporated to dryness using a closed evaporation system, and then Mo was re-dissolved in 5 mL of 0.05% tetramethylammonium hydroxide solution. Mo isotope ratios were determined by multiple collector inductively coupled plasma mass spectrometry (MC-ICP-MS).

Seawater samples were collected from 3 stations in the western North Pacific Ocean during the MR05-01 cruise of R/V Mirai using a CTD carousel on which Niskin-X samplers were mounted. Seawater was filtered through a 0.2 μm Nuclepore filter and acidified to pH 2.2 with HCl.

Mo was quantitatively concentrated from 250 mL seawater with a 50-fold concentration factor through the column extraction and evaporation. Procedure blank was only 0.04% of the concentration of Mo in seawater. The residual ratios of major elements between the eluate and seawater were below 10^{-5}, and their matrix effects on Mo isotope analysis were negligible. The isobaric interference of ions of coexistent elements was also negligible.

The analytical precision of this method was higher than that of reported methods. Isotope ratios of Mo show uniform vertical profiles at all 3 stations. This is attributed to homogenization of Mo in the ocean, because Mo has a longer mean residence time (~10^5-10^6 years [6]) than ocean circulation time (~10^3 years). The overall variation of isotope ratios of Mo in seawater was smaller than previously reported.

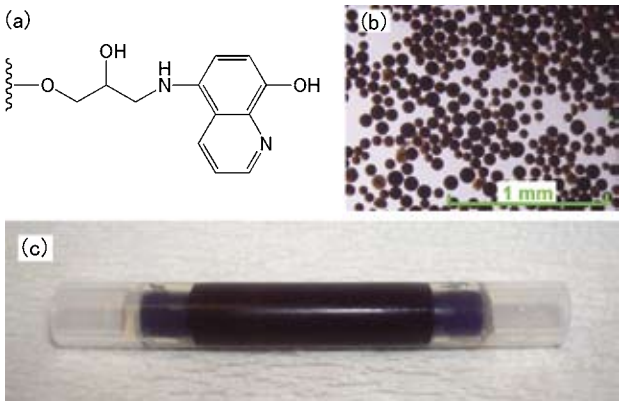

Figure 2. (a) Structure of TSK-8HQ (b) A micrograph of TSK-8HQ (c) A picture of TSK-8HQ column.

This is a joint research with associate professor Takafumi Hirata, Tokyo Institute of Technology.

[1] J. McManus *et al.*, Geochem. Geophys. Geosyst. 3, 10.1029/2002GC000356.
[2] C. Siebert *et al.*, *Earth Planet. Sci. Lett.* **211**, 159 (2003).
[3] J. Barling *et al.*, *Earth Planet. Sci. Lett.* **193**, 447 (2001).
[4] G. L. Arnold *et al.*, *Science* **304**, 87 (2004).
[5] H. Dierssen *et al.*, *Mar. Chem.* **73**, 173 (2001).
[6] J. L. Morford *et al.*, *Geochim. Cosmochim. Acta* **63**, 1735 (1999).

Grants

Sohrin Y, Interaction between Metallome and Proteome in the Marine Ecosystem, Grant-in-Aid for Scientific Research (A) (2), 1 April 2004–31 March 2007.

Norisuye K, Development of Analytical Method for Unstable Fe(II) in Seawater Based on in situ Preconcentration, Grant-in-Aid Young Scientists B, 1 April 2006–31 March 2008.

Division of Environmental Chemistry
- Solution and Interface Chemistry -

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Assist Prof
WAKAI, Chihiro
(D Sc)

PD
WANG, Jianyi
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Lecturer (pt)

TSUZUKI, Seiji (D Sc)
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MOROOKA, Saiko (D3)
YOSHIDA, Ken (D3)
YASAKA, Yoshiro (D1)
NISHIKAWA, Mayumi (M2)
KIMURA, Hiroshi (M1)
SHINTANI, Megumi (M1)

Visitors

Prof WEINGÄRTNER, Hermann — Ruhr-University Bochum, Germany, 10–13 August 2007
Dr Chau, Pak–Lee — Pasteur Institute, France, 30 November 2007

Scope of Research

Structure and dynamics of a variety of ionic and nonionic solutions of physical, chemical, and biological interests are systematically studied by NMR and computer simulations from ambient to extreme conditions. High pressures and high temperatures are employed to shed light on microscopic controlling factors for the structure and dynamics of solutions. Static and dynamic NMR of endocrine disruptors, anesthetics, peptides, and proteins in model and cell membranes are also investigated.

Research Activities (Year 2007)

Presentations

Free Energy of Solvation in the Energetic Perspective, Matubayasi N, Multiscale Dynamics of Biomolecules 2007, Taipei, Taiwan, 13–14 April 2007.

Free Energy of Solvation in the Energetic Perspective, Matubayasi N, International Mini-Symposium on Liquids, Okayama, Japan, 11 May 2007.

Free Energy of Solvation in the Energetic Perspective, Matubayasi N, ICCMSE (International Conference of Computational Methods in Sciences and Engineering), Yokohama, Japan, 25–30 September 2007.

Solution Chemistry of Supercritical Water through Development of High-Temperature NMR Spectroscopy and Solution Theory, Matubayasi N, Joint Conference of JMLG/EMLG Meeting 2007 and 30th Symposium on Solution Chemistry of Japan, Fukuoka, Japan, 21–25 November 2007.

Anion-field Effect on Rotational Dynamics of Water and Benzene in Ionic Liquids: 1-Butyl-3-methylimidazolium Chloride and Hexafluorophosphate, Wakai C, The 2nd International Congress on Ionic Liquids (COIL-2), Yokohama, Japan, 5–10 August 2007.

Structure and Dynamics of Molecules and Ions in Room-Temperature Ionic Liquids, Wakai C, Post Symposium of JMLG/EMLG Meeting 2007, Kyoto, Japan, 26 November 2007.

Grants

Nakahara M, Free-Energy Analysis of Nanoscale Aggregates of Molecules in the Method of Energy Representation, National Research Grid Initiative Project, 1 April 2003–31 March 2008.

Nakahara M, Development of Technology for Hydrogen Production, Storage, and Transportation of Hydrogen Using Hydrothermal Reactions of Formic Acid, ENEOS Hydrogen Trust Fund, 1 October 2006–30 September 2007.

Matubayasi N, Molecular Theory of the Solvation Effect on the Structural Formation and Fluctuation of Biomolecules and their Aggregates, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2003–31 March 2008.

Wakai C, NMR Study on Dynamics of Water Molecule, Organic Molecules, and Ions in Ionic Liquids, Grant-in-

Solvation Shell Dynamics Studied by Molecular Dynamics Simulation in Relation to the Translational and Rotational Dynamics of Supercritical Water and Benzene

The solvation shell dynamics of supercritical water is analyzed by molecular dynamics simulation with emphasis on its relationship to the translational and rotational dynamics. The relaxation times of the solvation number (τ^S), the velocity autocorrelation function (τ^D), the angular momentum correlation function (τ^J), and the second-order reorientational correlation function (τ^{2R}) are studied at a supercritical temperature of 400 ºC over a wide density region of 0.01–1.5 g cm^{-3}. The relaxation times are decomposed into those conditioned by the solvation number n, and the effect of the short-ranged structure is examined in terms of its probability P_n of occurrence. In the low to medium-density range of 0.01–0.4 g cm^{-3}, the time scales of water dynamics are in the following sequence,

$$\tau^D > \tau^S \gtrsim \tau^J \gtrsim \tau^{2R} \qquad (1)$$

This means that the rotation in supercritical water is of the "in-shell" type while the translational diffusion is not (see Figure 1). The comparison to supercritical benzene is also performed and the effect of hydrogen bonding is examined. The water diffusion is not of the in-shell type up to the ambient density of 1.0 g cm^{-3}, which is corresponding to the absence of the transition from the collision to the Brownian picture, whereas such transition is present in the case of benzene. The absence of the transition in water comes from the fast reorganization of the hydrogen bonds and the enhanced mobility of the solvation shell in supercritical conditions.

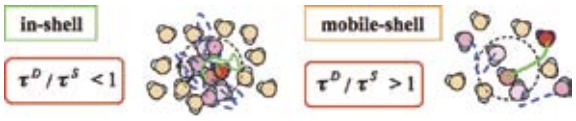

Figure 1. Schematic draw for the difference between in-shell and mobile-shell diffusions.

Rotational Dynamics of Water and Benzene Controlled by Anion Field in Ionic Liquids. 1-Butyl-3-methylimidazolium Chloride and Hexafluorophosphate

The rotational correlation time (τ_{2R}) is determined for D_2O (polar) and C_6D_6 (apolar) in 1-butyl-3-methylimidazolium chloride ([bmim][Cl]) and hexafluorophosphate ([bmim][PF_6]) by measuring ^{2}H (D) nuclear magnetic resonance spin-lattice relaxation time (T_1) in the temperature range from –20 to 110 °C. The τ_{2R} ratio of water to benzene ($\tau_{W/B}$) was used as a measure of solute-solvent attraction. The $\tau_{W/B}$ is 0.73 and 0.52 in [bmim][Cl] and [bmim][PF_6], respectively, whereas the molecular volume ratio is as small as 0.11. The slowdown of the water dynamics compared to the benzene dynamics in ionic liquids is interpreted by the Coulombic attractive interaction between the polar water molecule and the anion. As for the anion effect, the rotational dynamics of water solvated by Cl^- is slower than that solvated by PF_6^-, whereas the rotational dynamics of benzene is similar in the two ionic liquids (see Figure 2). This is interpreted as an indication of the stronger solvation by the anion with a larger surface charge density. The slowdown of the water dynamics via Coulombic solvation is actually significant only at water concentrations lower than ~9 mol dm^{-3} at room temperature, and it is indistinguishable at temperatures above ~100 °C. The quadrupolar coupling constants determined for D_2O and C_6D_6 in the ionic liquids were smaller by a factor of 2–3 than those in the pure liquid state.

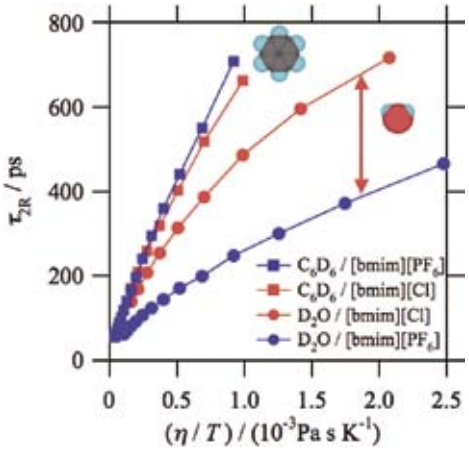

Figure 2. Plots of the rotational correlation times τ_{2R} for D_2O and C_6D_6 in ionic liquids against the solvent viscosity divided by temperature η/T.

Aid for Scientific Research on Priority Areas, 1 April 2006–31 March 2008.

Award

Matubayasi N, Award for Distinguished Achievement, The Japan Association of Solution Chemistry, 31 July 2007.

Division of Environmental Chemistry
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Visitor

Prof GLADYSHEV, Vadim N Nebraska Redox Biology Center, University of Nebraska, USA, 30 May–30 June 2007

Scope of Research

Structures and functions of biocatalysts, in particular, pyridoxal enzymes and enzymes acting on xenobiotic compounds, are studied to elucidate the dynamic aspects of the fine mechanism for their catalysis in the light of recent advances in gene technology, protein engineering and crystallography. In addition, the metabolism and biofunction of sulfur, selenium, and some other trace elements are investigated. Development and application of new biomolecular functions of microorganisms are also studied to open the door to new fields of biotechnology. For example, cold-adaptation mechanism and applications of psychrotrophic bacteria are under investigation.

Research Activities (Year 2007)

Presentations

Application of Cold-adapted Microorganisms and Cold-active Enzymes, Esaki N, Kurihara T, Kawamoto J, Miyake R, Yamamoto K, Wei Y, Kitayama K, International Conference on Biotechnology Engineering (ICBioE '07), 9 May 2007.

Strict Discrimination between Sulfur and Selenium by a Selenium-specific Enzyme, Selenocysteine Lyase, Esaki N, The 41st IUPAC World Chemistry Congress, 6 August 2007.

Physiological Role of Phospholipids Containing Eicosapentaenoic Acid in Cold Adaptation of an Antarctic Psychrotrophic Bacterium, *Shewanella livingstonensis* Ac10, Kurihara T, Kawamoto J, Sato S (Grad. Sch. Sci., Kyoto Univ.), Esaki N, Gordon Research Conference: Molecular and Cellular Biology of Lipids, 24 July 2007.

The Cellular Function of Selenocysteine Lyase in Selenoprotein Synthesis, Mihara H, Kurokawa S, Esaki N, TRACE ELEMENTS in DIET, NUTRITION, & HEALTH: Essentiality and Toxicity, 24 Octorber 2007.

Function of Selenium-specific Enzymes in Selenoprotein Biosynthesis, Mihara H, Kurokawa S, Omi R, Kurihara T, Miyahara I, Hirotsu K, Esaki N, International Symposium on Metallomics 2007, 1 December 2007.

Grants

Esaki N, Investigation of Organisms Carrying a Unique Selenium Metabolism and Its Application to Bioremediation, Grant-in-Aid for Scientific Research (B), 1 April 2006–31 March 2008.

Biosynthesis of Molybdopterin Requires Cysteine Desulfurase IscS

The persulfide sulfur formed on an active site cysteine residue of pyridoxal 5'-phosphate-dependent cysteine desulfurases is subsequently incorporated into the biosynthetic pathways of a variety of sulfur-containing cofactors and thionucleosides. It has been shown that three cysteine desulfurases IscS, CsdA (CSD) and SufS (CsdB) of *Escherichia coli* can transfer sulfur from L-cysteine to the C-terminal thiocarboxylate of the small subunit of molybdopterin (MPT) synthase in a defined *in vitro* system for the generation of the dithiolene group of MPT from precursor Z. Here we report that an *iscS*-deletion strain of *E. coli* accumulates compound Z, a direct oxidation product of precursor Z, to the same extent as a *ΔmoaD* strain. In contrast, analysis of the compound Z content of *ΔsufS* and *ΔcsdA* strains revealed no such accumulation. In addition, a genetic complementation experiment confirmed that the *in vivo* conversion of precursor Z to MPT requires IscS. These findings suggest that IscS but not SufS or CsdA is the physiological sulfur-donating enzyme for the generation of the thiocarboxylate of MPT synthase for the MPT biosynthesis (Figure 1). Furthermore, bioinformatic analysis shows that most of *moaD*/*moaE*-containing bacteria also carry at least one *iscS*-like group I cysteine desulfurase gene, suggesting that this type of system is widely distributed in bacteria.

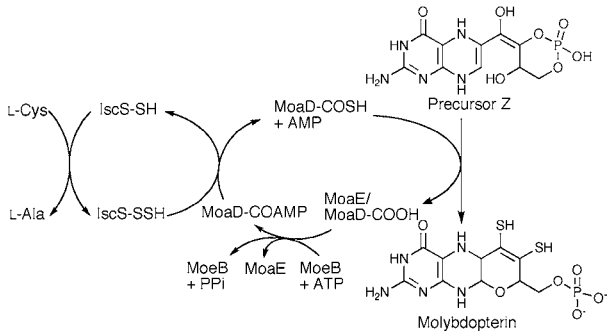

Figure 1. Proposed scheme for the biosynthesis of molybdopterin.

Physiological Role of Eicosapentaenoic Acid in a Cold-adapted Bacterium, *Shewanella livingstonensis* Ac10

Shewanella livingstonensis Ac10, a psychrotrophic Gram-negative bacterium isolated from Antarctic seawater, grows at a temperature range of 4˚C to 25˚C. The bacterium produces eicosapentaenoic acid (EPA) as a component of phosphatidylglycerol and phosphatidylethanolamine at low temperatures. EPA constitutes about 5% of the total fatty acids of the cells grown at 4˚C. We found that five genes termed *orf2*, *orf5*, *orf6*, *orf7*, and *orf8* are essential for the production of EPA by targeted disruption of the respective genes. The mutant cells lacking EPA exhibited significant growth retardation at 4˚C, whereas they grew normally at 18˚C. Microscopic observation revealed that the EPA-less strains became filamentous at 4˚C, suggesting that they have a defect in cell division (Figure 2). We analyzed the fluidity of the cell membrane at low temperatures by using pyrene as a fluorescence probe: the diffusion rate of pyrene is regarded as an index of the membrane fluidity. We found that the diffusion rate of pyrene in the membrane from the EPA-less strain was not significantly different from that in the membrane from the parent strain. The results suggest that EPA has a physiological function other than the function to maintain the membrane fluidity. Proteomic analysis of the membrane proteins revealed that the amounts of five proteins were decreased and the amounts of three proteins were increased by the absence of EPA. The cold-sensitive phenotype of the EPA-less strains may be ascribed to a defect in the function of these membrane proteins.

Figure 2. Fluorescence microscopic images of the EPA-less mutant of *S. livingstonensis* Ac10. DAPI and FM4-64 were used to stain DNA and the membrane, respectively.

Esaki N, Structure-Function Analysis of Selenium-specific Chemical Conversion System and Co-translational Insertion of Selenium into Protein, Grant-in-Aid for Scientific Research (B), 1 April 2007–31 March 2009.

Kurihara T, Conversion of Organofluorine Compounds with Microbial Enzymes: Mechanistic Analysis of the Enzyme Reactions and Their Application to Production of Useful Compounds and Bioremediation of Environments, Grant-in-Aid for Scientific Research (B), 1 April 2005–31 March 2008.

Kurihara T, Exploration of Novel Cold-adapted Microorganisms to Develop a System for the Production of Useful Compounds at Low Temperatures, Grant-in-Aid for Scientific Research (B), 1 April 2007–31 March 2009.

Mihara H, Studies on Mechanism of Selenium-specific Recognition and Selenoprotein Biosynthetic Machinery, Grant-in-Aid for Young Scientists (B), 1 April 2006–31 March 2008.

Division of Multidisciplinary Chemistry
- Polymer Materials Science -

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ITO, Tomoaki (UG)
KAWASHIMA, Kazuko (UG)

Visitors

Prof HU, Wenbing — Nanjing University, China, P.R., 27 March 2007
Dr ZORN, Reiner — Institut für Festkörperforschung Forscheungszentrum Jülich, Germany, 18 September 2007

Scope of Research

The structure and molecular motion of polymer substances are studied using mainly scattering methods such as neutron, X-ray and light with intension of solving fundamentally important problems in polymer science. The main projects are the mechanism of structural development in crystalline polymers from the glassy or molten state to spherulites; the dynamics in disordered polymer materials including low-energy excitation or excess heat capacity at low temperatures, glass transition and local segmental motions; formation processes and structure of polymer gels; the structure and molecular motion of polyelectrolyte solutions; the structure of polymer liquid crystals.

Research Activities (Year 2007)

Publication

Kanaya T, Matsuba G, Ogino Y, Nishida K, Hierarchic Structure of Shish-Kebab by Neutron Scattering in a Wide Q Range, *Macromolecules*, **40**, 3650-3654 (2007).

Presentations

Hierarchic Structure of Shish-Kebab by Neutron Scattering in a Wide Q Range, Kanaya T, Matsuba G, Ogino Y, Nishida K, 234th ACS Meeting, Boston, 20–22 August 2007.

Structural Formation Process of Polyethylene Blend with Ultra-high Molecular Weight Component, Matsuba G, Nishida K, Kanaya T, 3rd International Symposium on Engineering Plastics, Urumqi, 19–23 August 2007.

Glass Transition of Polymer Thin Films by Inelastic Neutron Scattering, Inoue R, Kanaya T, Nishida K, Tsukushi I, 56th SPSJ Symposium on Macromolecules, Nagoya, 19–21 September 2007.

Effect of Polylactide Stereocomplex Crystallites on Poly(L-Lactic Acid) Crystallization Behavior, Rahman N, Kawai T, Matsuba G, Nishida K, Kanaya T, International Symposium of Polymer Crystallization, Mishima, Japan, 22–24 September 2007.

Structure Formation of Isotactic Polystyrene under Shear Flow, Hayashi Y, Matsuba G, Nishida K, Kanaya T, 2007 Autumn Meeting in the Society of Fiber Science and Technology, Japan, Kyoto, 26–27 October 2007.

Annealing of Mesomorphic Phase of Isotactic Polypropylene, Yamamoto J, Konishi T, Nishida K, Kanaya T, 2007 Autumn Meeting in the Society of Fiber Science and Technology, Japan, Kyoto, 26–27 October 2007.

Crystallization Process of Poly(ethylene terephthalate) under Shear Flow, Tomohisa H, Matsuba G, Nishida K, Kanaya T, 2007 Autumn Meeting in the Society of Fiber Science and Technology, Japan, Kyoto, 26–27 October 2007.

Crystallization of Poly(L-lactic acid): Effect of the Addition of Poly(D-lactic acid) on Poly(L-lactic acid) Crystallization Behavior

Enhancement of crystallization rate of PLLA is a matter of concern when PLLA is utilized for various applications including industrial application. We have been studied the effect of incorporated of poly(D-lactic acid) (PDLA) on crystallization behavior of poly(L-lactide acid) (PLLA) using differential scanning calorimetry (DSC), optical microscope (OM), light scattering (LS), wide (WAXS) and small angle x-ray scattering (SAXS). Blend of PLLA and PDLA crystallizes as stereocomplex crystal. In the non-isothermal crystallization, the existence of stereocomplex crystallite was effective to accelerate PLLA crystallization rate in case of addition of high molecular weight PDLA (h-PDLA) but not in the addition of low molecular weight PDLA (l-PDLA). In the isothermal crystallization, we found that the crystal growth rate (G) value decreased with PDLA concentration for both l-PDLA/PLLA and h-PDLA/PLLA blends. On the other hand, PDLA concentration dependencies of nucleation rate (N) are well agreed with those of overall crystallization rate. It suggests that the effect of the addition of PDLA on PLLA crystallization is mainly due to the enhanced nucleation rate.

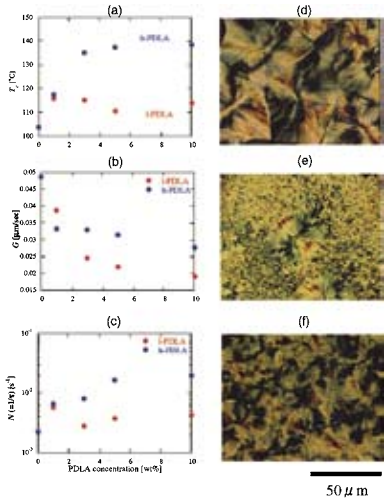

Figure 1. PDLA concentration dependence of crystallization temperature on non-isothermal crystallization (a), Growth rate (b) and Nucleation rate of PLLA spherulites on isothermal crystallization (c) (left) and OM final structure of PLLA (d), PLLA/l-PDLA3% (e) and PLLA/h-PDLA3% (f) after isothermal crystallization at 140°C (right).

Mesomorphic Phase of Poly(buthylene-2,6-naphthalate)

The structure formation of crystalline polymers when they are rapidly quenched from molten state is one of the main subjects in our laboratory. Some polymers are solidified in amorphous when quenched. Some other polymers are crystallized due to their rapid crystallizing nature even when quenched rapidly. However, in a few cases, polymers are solidified in an intermediate state between amorphous and crystal when quenched through a specific kinetic path. We found that a thin film of poly(buthylene-2,6-naphthalate) (PBN) is solidified in such an intermediate state when quenched into 0°C. Here, we refer to such a solid form of PBN as the "mesomorphic" phase of PBN. The mesomorphic PBN at room temperature shows a weak but sharp peak at q = 0.44 Å^{-1} and a strong broad peak at around q = 1.4 Å^{-1} in wide-angle X-ray diffraction (WAXD), where q is the absolute value of the scattering vector (Figure 2). The former and the latter peaks are the characteristics of a smectic structure and an amorphous structure, respectively. Also we found that the mesomorphic PBN has its own glass transition temperature at 71°C besides the glass transition temperature of normal isotropic glass at 48°C.

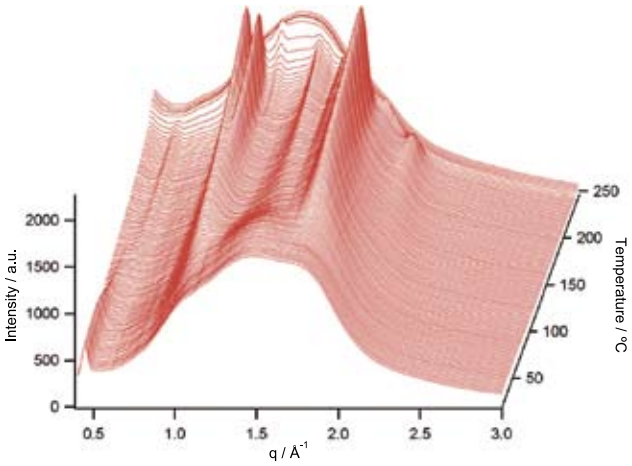

Figure 2. WAXD for the mesomorphic phase of PBN during a heating process.

Grants

Kanaya T, Higher Order Structure Formation in Induction Period of PLA Crystallization and External Fields, Collaboration Research with Toyota Motor Corporation and Toyota CRDL., INC, 15 January 2003–31 March 2008.

Nishida K, Kanaya T, Matsuba G, Control of Higher Order Structure by Crystallization via Mesomorphic Phase, Grant-in-Aid for Scientific Research (C), 1 April 2007–31 March 2009.

Matsuba G, Correlation between Phase Separation and Crystallization of Polyolefins, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

Awards

Kanaya T, The Award of the Society of Polymer Science, Japan, "Studies on Polymer Crystallization and Higher Order Structure", the Society of Polymer Science, Japan, 30 May 2007.

Kanaya T, The Award of the Japanese Society for Neutron Science, "Higher Order Structure and Dynamics of Polymer Systems by Neutron Scattering", The Japanese Society for Neutron Science, Japan, 27 November 2007.

Division of Multidisciplinary Chemistry
- Molecular Rheology -

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Dr PONNUSAMY, Karaichelvi National Institute of Technology, India, 23 April–22 May 2007

Scope of Research

The molecular origin of various rheological properties of material is studied. Depending on time and temperature, homogeneous polymeric materials exhibit typical features of glass, rubber, and viscous fluid while heterogeneous polymeric systems exhibit plasticity in addition to these features. For a basic understanding of the features, the molecular motion and structures of various scales are studied for polymeric systems in deformed state. Measurements are performed of rheological properties with various rheometers, of isochronal molecular orientation with flow birefringence, and of auto-correlation of the orientation with dynamic dielectric spectroscopy.

Research Activities (Year 2007)

Publications

Watanabe H, Matsumiya Y, Sawada T, Iwamoto T: Rheological and Dielectric Behavior of Dipole-Inverted (SIS)p-type Multiblock Copolymers: Estimates of Bridge/Loop Fractions for Respective I Blocks and Effect of Loops on High Extensibility of Bridges, *Macromolecules*, **40(19)**, 6885-6897 (2007).

Watanabe H, Matsumiya Y, Takada J, Sasaki H, Matsushima Y, Kuriyama A, Inoue T, Ahn K H, Yu W, Krishnamoorti R: Viscoelastic and Dielectric Behavior of a Polyisoprene/Poly(4-tert-butyl styrene) Miscible Blend, *Macromolecules*, **40(15)**, 5389-5399 (2007).

Matsumiya Y, Matsumoto M, Watanabe H, Kanaya T, Takahashi Y: Nonlinear Rheology and Structural Changes of (BS)n Multiblock Copolymers under Shear Flow, *Macromolecules*, **40**, 3724-3732 (2007).

Matsumiya Y, Inoue T, Watanabe H, Kihara S, Ohshima M: Dielectric Behavior of cis-polyisoprene in Carbon Dioxide under High Pressure, *J. Soc. Rheol. Japan*, **35**, 155-161 (2007).

Arai N, Yasuoka K, Masubuchi Y: Spontaneous Self-assembly Process for Threadlike Micelles, *J. Chem. Phys.*, **126 (24)**, 244905-244907 (2007).

Furuichi K, Nonomura C, Masubuchi Y, Ianniruberto G, Greco F, Marrucci G: Primitive Chain Network Simulations of Damping Functions for Shear, Uniaxial, Biaxial and Planar Deformations, *J. Soc. Rheol. Japan*, **35(2)**, 73-77 (2007).

Presentations

Masubuchi Y, "Molecular Rheology in DNA Solutions", Workshop in Ravello, Ravello, Italy, 15 April 2007 (invited).

Masubuchi Y, Ianniruberto G (Univ. Naples), Greco F (CNR-Italy) and Marrucci G (Univ. Naples), "Primitive Chain Network Simulations for Bidisperse Linear Polymers", AES-ATEMA, Montreal, Canada, 9 August 2007 (invited).

Watanabe H, Constraint Release in Star/Star Blends and

Molecular Rheology by Simulation and DNA

Molecular motion is main resource of polymer rheology since conformational entropy is dominant in free energy. Although for several simple cases such as monodisperse linear polymers description of the molecular motion has been established by the Rouse, Zimm and tube models, the polymer dynamics is still an open problem due to huge degree of freedom in material design of polymers with branching, molecular weight, molecular weight distribution, blends, copolymerization, etc., and hence challenges have been being in progress.

An interesting method to investigate the polymer dynamics is fluorescent microscopy with DNA. Although DNA is a rigid polyelectrolyte indicating distinguished characteristics from synthetic polymers, under certain conditions the observed DNA motion is consistent with the dynamics of synthetic polymers. In addition to the conventional analysis on the fluorescent images we have been developing a method to map the molecular configuration by means of a Monte Calro method where the observed fluorescence is converted to an effective potential field as shown in Figure 1.

If the polymer dynamics can be captured in a certain model, simulations would be achieved to predict the polymer dynamics and rheology. We have been developing a multi-body simulation for entangled polymers utilizing our primitive chain network model where the polymer dynamics is calculated in real 3D space similarly to ordinal molecular dynamics simulations and differently from tube theories. Figure 2 shows a typical snapshot and a result of the prediction.

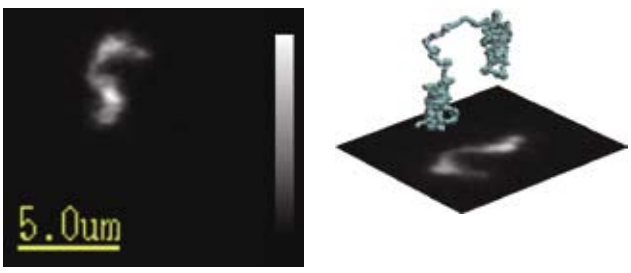

Figure 1. (a) A fluorescent image of a DNA molecule and (b) the constructed polymer configuration.

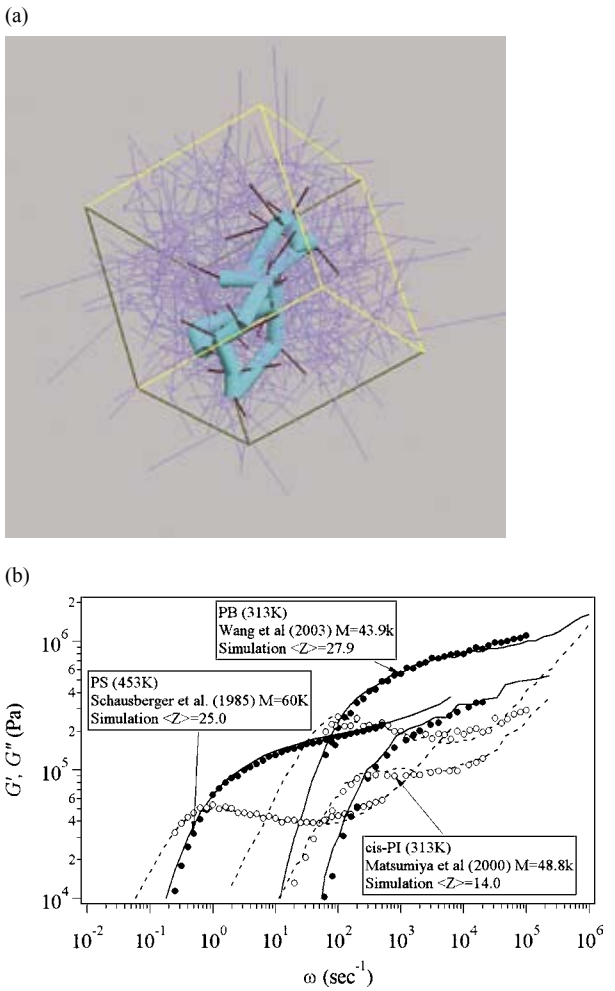

Figure 2. (a) A typical snapshot of the simulation and (b) the prediction of linear viscoelasticity for various polymer melts.

Dynamic Tube Dilation in Monodisperse Star Systems, Rheology of Complex Fluid: Courses and Workshop 2007, 8 July 2007 (invited).

Watanabe H, Rheology and Dynamics of Entangled Polymer Chains: Self-Consistent Coarse-Graining of Length and Time Scales, The 10th pacific Polymer Conference, 4 December 2007 (invited).

Grants

Watanabe H, Creation of Non-equilibrium Soft Matter Physics: Structure and Dynamics of Mesoscopic Systems, Grant-in-Aid for Scientific Research on Priority Areas, 1 October 2006–31 March 2011.

Masubuchi Y, Combined Digital and Analog Molecular Simulation of Polymer Dynamics, Precursory Research for Embryonic Science and Technology, Japan Science and Technology Agency, 1 October 2004–31 March 2008.

Masubuchi Y, Multi-scale Simulations for Soft Matters, Core Research for Evolutional Science and Technology, Japan Science and Technology Agency, 1 October 2006–31 March 2012.

Matsumiya Y, Dynamics of Ionic Liquids in Polymer Networks, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

Division of Multidisciplinary Chemistry
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TSUTSUMI, Jun'ya (D3)
SASAMURA, Tatsuya (M2)
FUKUHARA, Sho (M1)
UCHINO, Yosuke (M1)

Visitor

Prof BOUVET, Marcel — Ecole Supérieure de Physique et Chimie Industrielles de la ville de Paris, France, 4–17 November 2007

Scope of Research

The research at this subdivision is devoted to correlation studies on structures and properties of both natural and artificial molecular aggregates from two main standpoints: photoelectric and dielectric properties. The electronic structure of organic thin films is studied using photoemission and inverse photoemission spectrosocpies in connection with the former, and its results are applied to create novel molecular systems with characteristic electronic functions. The latter is concerned with heterogeneous sturcutres in microcapsules, biopolymers, biological membranes and biological cells, and the nonlinearity in their dielectric properties is also studied in relation to molecular motions.

Research Activities (Year 2007)

Publication

Yoshida H, Inaba K, Sato N: X-ray Diffraction Reciprocal Space Mapping Study of the Thin Film Phase of Pentacene, *Appl. Phys. Lett.*, **90**, 181930 (2007).

Presentations

Direct Observation of Electron and Hole Transport Levels in Organic Thin Films (in Japanese), Sato N, Research Meeting "Organic Electroluminescent Devices – New Developments from Now On" of Division of Molecular Electronics and Bioelectronics, The Japan Society of Applied Physics (Uji, Japan), 6 March 2007.

Dielectric Spectra of Biological Cell and Tissues Simulated by Three-dimensional Finite Difference Method, Asami K, The 13th International Conference on Electrical Bioimpedance Combined with the 8th Conference on Electrical Impedance Tomography (Graz, Austria) 29 August–2 September 2007.

Structures and Surface Electronic Properties of Evaporated Thin Films of a Series of Zwitterionic Molecules, Tsutsumi J, Yoshida H, Sato N, Kato S, The 4th Workshop on Advanced Spectroscopy of Organic Materials for Electronic Applications (Chiba, Japan), 8–12 October 2007.

The Crystallographic and Electronic Structures of Three Different Polymorphs of Pentacene, Yoshida H, Sato N, The 9th China-Japan Joint Symposium on Conduction and Photo-conduction in Organic Solids and Related Phenomena (Beijing, China), 27–29 October 2007.

Grants

Sato N, Development of Novel Electronic Systems Based on Hybridization of Characteristic Molecular

X-ray Diffraction Reciprocal Space Mapping Study of the Thin Film Phase of Pentacene

Pentacene thin films are extensively studied in connection with their application to organic field-effect transistors. To understand transport properties in those films, precise information on their structure is indispensable. On the other hand, pentacene thin films are known to show a few polymorphs usually distinguished by the interlayer spacing along the c^*-axis. Among them only the polymorph of "single crystal" phase (d_{001} = 1.41 nm) has so far disclosed the complete crystallographic data.

The "thin film" phase (d_{001} = 1.54 nm) is observed for a film in the thickness less than 100 nm vacuum-deposited on an insulating layer such as SiO_2; the structural information of this phase is particularly relevant, since this polymorph is often realized in the working layer in pentacene thin-film field effect transistors. Previous structural studies on this phase have been carried out using electron diffraction, grazing incidence X-ray diffraction (GIXD) as well as the θ-2θ scan of X-ray diffraction. The structural data obtained from these methods, however, are not enough to determine even the crystal system of the phase between monoclinic and triclinic ones. In this work we employed X-ray diffraction reciprocal space mapping (RSM) method to analyze the crystallographic structure of the thin film phase of pentacene. The obtained structure in comparison with that of the bulk phase is shown in Figure 1 and can be applied to the energy band calculation.

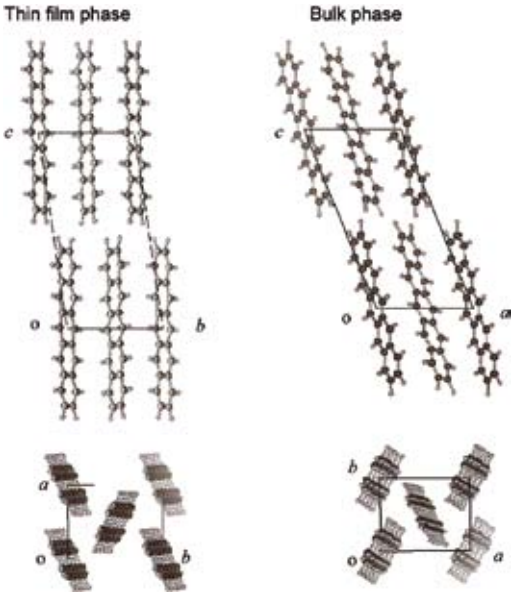

Figure 1. Structures of the thin-film and bulk phases of pentacene.

Dielectric Properties of Water in Triton X-100 (Nonionic Detergent) – Water Mixtures

Dielectric measurements were carried out for mixtures of Triton X-100 (TX, a nonionic detergent with a poly(ethylene oxide) chain) and water with or without electrolytes over a frequency range of 1 MHz to 10 GHz to study the structure and dynamics of water molecules in the mixtures (Figure 2). Dielectric relaxation was found above 100 MHz, being assigned to the dielectric relaxation of water. The intensity of the dielectric relaxation was proportional to the water content above 0 °C. Below the freezing temperature of bulk water, the relaxation intensity decreased at TX concentrations (C_{TX}) below 50 wt% at –10 °C and below 60 wt% at –20 °C because frozen water shifts the dielectric relaxation to a frequency region far below 1 MHz. This indicated that there is no bulk water at C_{TX} above 50 wt% and that at least two water molecules per ethylene oxide (EO) unit are tightly associated with the ethylene oxide chain. The low-frequency conductivity of the mixtures of TX and electrolyte solutions was well represented by Bruggeman's mixture equation at C_{TX} below 40 wt%, if two water molecules per EO unit form an insulating shell surrounding TX micelles.

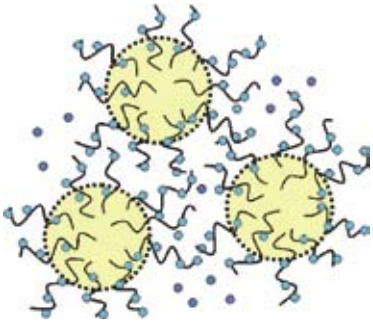

Figure 2. Schematic representation of TX micelles whose ethylene oxide chains are tightly associated with water molecules.

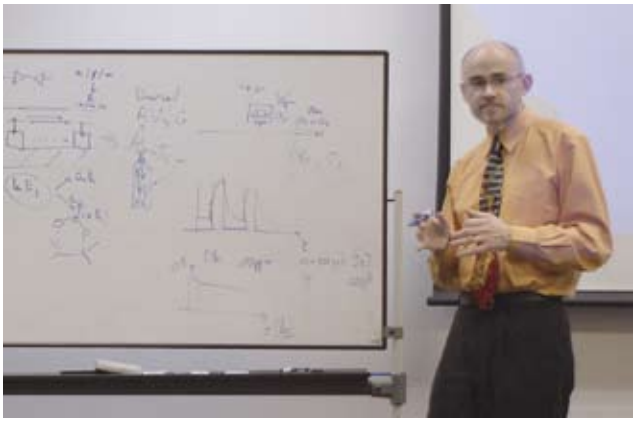

Figure 3. Professor Marcel Bouvet from ESPCI, France gave a stimulating seminar.

Properties and Specific Aggregate Structures, Grant-in-Aid for Scientific Research (2) on Priority Areas of Molecular Conductors, 17 October 2003–31 March 2008.

Asami K, Dielectric Monitoring of Cultured Cells Responding to External Stimuli, Collaboration Research with Sony Corporation (Life Science Laboratory, Material Laboratories), 28 June 2007–31 March 2008.

Division of Multidisciplinary Chemistry
- Supramolecular Biology -

http://www.scl.kyoto-u.ac.jp/~umeda/index.htm

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SUZUKI, Harumitsu (M1)

Scope of Research

We have undertaken the molecular biology, cell biology and behavioral genetics approaches to study the role of biological membrane systems in controlling animal morphogenesis and behavior. The membrane is a complex supramolecular complex formed by a noncovalent self-assembly of proteins, lipids, and carbohydrates. Our long term objective is to understand the fundamental principles underlying the dynamism of complex membrane systems and to provide a clue to reconstruct an artificial supramolecular membrane complex. Current research topics are as follows:

(1) Identification of a series of proteins that regulate molecular motion of lipid molecules and elucidation of their role in cellular and animal morphogenesis.

(2) Establishment of a series of *Drosophila* mutants with aberrant temperature preference (*atsugari, samugari*, etc) and elucidation of the molecular relationship between the temperature-responding membrane systems and animal behaviors.

Research Activities (Year 2007)

Publication

Saito K, Fujimura-Kamada K, Hanamatsu H, Kato U, Umeda M, Kozminski KG, Tanaka K: Transbilayer Phospholipid Flipping Regulates Cdc42p Signaling during Polarized Cell Growth via Rga GTPase-Activating Proteins, *Dev Cell.*, **13**, 743-751 (2007).

Presentations

Membrane Phospholipid Flip-flop and Its Role in Cell Motility. Kato U. The 10th Membrane Research Forum. 27 February–1 March 2007, Kyoto.

Regulation of Membrane Phospholipid Dynamics and Its Role in Control of Cell Migration. Kato U, Inadome H, Umeda M. The 112th Annual Meeting of the Japanese Association of Anatomists. 27–29 March 2007, Osaka.

The Present Bottom-up System of Grant-in-Aid for Scientific Research and Its Future. Umeda M. Special Symposium. 127th Annual Meeting of the Pharmaceutical Society of Japan, 28–30 March 2007, Toyama.

Requirement of ZO-1 for the Formation of Belt-like Adherens Junction and Tight Junction during Epithelial Cell Polarization. Ikenouchi J, Umeda K, Tsukita S, Furuse M, Tsukita S. The 59th Annual Meeting of the Japan Society for Cell Biology 28–30 May 2007, Fukuoka.

Defective Expression of Dystroglycan Causes Abnormal Energy Homeostasis via Ca^{2+} Handling in a *Drosophila* Cryophilic Mutant, *atsugari*. Takeuchi K, Takahara K, Kiyonaka S, Mori Y, Yamamoto D, Umeda M. BMB2007. 11–15 December 2007, Yokohama.

Membrane Phospholipid Flip-flop and Its Role in Cell Migration. Kato U, Inadome H, Umeda M. BMB2007. 11–15 December 2007, Yokohama.

Grants

Umeda M, Development of Two-dimensional Imaging Systems of Membrane Lipids Using Intense Femtosecond Laser Desorption/ionization Mass Spectrometory. Grant-in-Aid for Exploratory Research, 1 April 2006–31 March 2008.

Ikenouchi J, Grant-in-Aid for Scientific Research for JSPS Fellow, 1 April 2007–30 September 2007.

Ikenouchi J, Elucidation of Molecular Mechanisms Which Generate and Maintain Discrete Membrane Domains in Polarized Cells. PRESTO, Japan Science and Technology Agency, 1 October 2007–31 March 2011.

Regulation of Membrane Phospholipid Dynamics and Its Role in Control of Cell Motility

The basic structure of biological membranes is the lipid bilayer in which phospholipids distribute asymmetrically between the two leaflets of the bilayer. Although this asymmetry is regulated by the transbilayer movement of phospholipids, its physiological significance and molecular mechanisms are largely unknown. Previously we have identified a novel membrane protein, designated Ros3p, which is required for the transbilayer movement of phospholipids across the yeast plasma membrane. To investigate its biological functions, we have cloned mROS3, a mammalian homolog of Ros3p. In mammalian cells, mROS3 interacted with P-type ATPase (ATP8A1), a candidate enzyme responsible for the inward movement of aminophospholipids, and is essential for the recruitment of ATP8A1 to the plasma membrane. mROS3 knockdown cells were defective in inward movement of fluorescence-labeled analogs of aminophospholipids across the plasma membrane and exhibit decreased cell motility, while overproduction of mROS3 facilitated the membrane ruffling and cell migration in CHO cells. Cell migration was also inhibited by knockdown of ATP8A1 and the expression of dominant negative ATP8A1 (Figure 1 a). Furthermore, ATP8A1 localized at the leading edge of the serum-stimulated migrating cells and colocalized with actin cytoskleleton. These results suggest that organized movement of phospholipids plays an important role in regulation of cell motility by regulating actin reorganization and membrane ruffling.

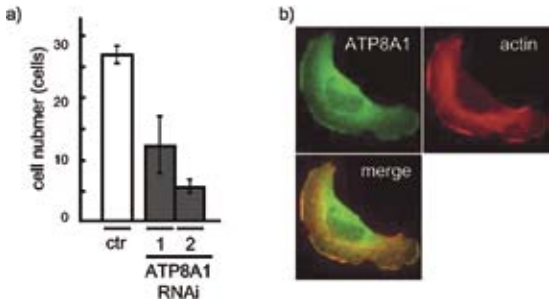

Figure 1. Aminophospholipid translocase ATP8A1 is required for the regulation of cell motility. a) Migration of ATP8A1 knockdown cells was studied by transwell assay and was quantitated by counting cells migrating across the membrane after 3h. b) Colocalization of ATP8A1 and actin cytoskeleton in the serum-stimulated migrating cell.

Elucidation of Molecular Mechanisms which Generate and Maintain Discrete Membrane Domains in Polarized Cells

The plasma membranes of cells are fundamental components of our body. They are composed of discrete membrane domains in which membrane proteins and lipids are differentially partitioned. Compared to plasma membrane proteins which have been investigated by many researchers, plasma membrane lipids are less well understood, even though they are the other main component of membranes. Using epithelial cells as an experimental model, we aim to clarify what kind of lipids and lipid metabolites are enriched in the apical as well as the basolateral membrane, and how these asymmetric membrane domains are maintained to be separated (Figure 2).

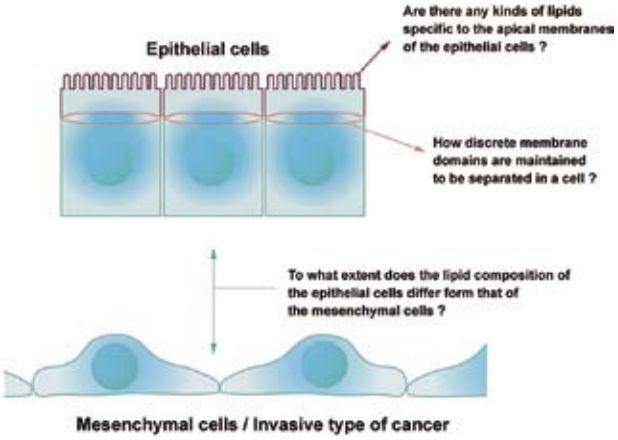

Figure 2.

Generation of the Transgenic Flies Expressing Delta 12 Fatty Acid Desaturase

Polynsaturated fatty acids (PUFAs) play an essential role in the biophysical characteristics of cell membrane. The proportion of PUFAs present in cell membrane, which regulates membrane fluidity and determines the proper function of membrane proteins, has been suggested to contribute to temperature adaptation in poikilothermic organisms. However, the precise mechanisms underlying the effect of PUFAs on thermal traits such as temperature preference and resistance of poikilotherms remain to be understood. To assess this problem, we have made a series of transgenic flies overexpressing fatty acid desaturases, which catalyze the fatty acid desaturation. Many eukaryotic organisms can synthesize dienoic fatty acid, but *Drosophila* can introduce only a single double bond at the delta 9 position. Here we generated the transgenic flies that express *C. elegans* delta 12 fatty acid desaturase, which is involved in biosynthesis of linoleic acid (C18:2). The analyses for fatty acid composition of phospholipids showed the content of linoleic acid was drastically increased in the transgenic flies. The transgenic flies expressing delta 12 fatty acid desaturase will provide important models understanding the molecular mechanisms of temperature preference and resistance of poikilothermic organisms.

Advanced Research Center for Beam Science
- Particle Beam Science -

http://wwwal.kuicr.kyoto-u.ac.jp/www/index-e.htmlx

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YAMADA, Masako (M1)
WAKITA, Akihisa (M1)

Visitors

Dr GRIESER, Manfred	Max-Planck-Institut für Kernphysik, Germany, 11–24 February 2007
Prof MESHKOV, Igor N	Joint Institute for Nuclear Research, Russia, 12–22 February 2007
Dr SMIRNOV, Alexander V	Joint Institute for Nuclear Research, Russia, 12 February–10 March 2007
Prof SYRESIN, Evgeny	Joint Institute for Nuclear Research, Russia, 11–29 March 2007
Dr WÜSTEFELD, Godehard	Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY), Germany, 2 October 2007
Prof SHEVELKO, Viatcheslav P	P. N. Lebedev Physical Institute, Russia, 19 October 2007

Scope of Research

The following subjects are being studied: Beam dynamics related to space charge force in accelerators: Beam handling during the injection and extraction processes of the accelerator ring: Electron cooling of a hot proton beam; Ultra-low emittance state of a proton beam created by the electron cooling; Laser cooling of Mg^+ ion beam; Compression of the energy spread of laser-produced ion beams by an rf cavity for phase rotation; Research and development of permanent quadrupole magnets for final focusing of International Linear Collider (ILC); Mitigation of power loss due to skin effect.

Research Activities (Year 2007)

Publications

Shirai T *et al.*, *Phys. Rev. Lett,* **98**, 204801 (2007).
Nakamura S *et al.*, *Jpn. J. Appl. Phys*, **46**, L717 (2007).
Iwashita Y *et al.*, *Int. J. Mod. Phys. B*, **21**, 600 (2007).

Presentations

Present Status and Recent Activity on Laser Cooling at S-LSR, Noda A, Invited Talk at The Workshop on Beam Cooling and Related Topics, COOL'07, 14 September 2007, Bad Kreuznach, Germany.

Experimental Approach to Ultra-Cold Ion Beam at S-LSR, Noda A, Particle Accelerator Conference 07 (PAC07), 27 June 2007, New Mexico, USA.

Rapid Cycling Variable Permanent Magnet Sextupole Lens for Pulsed Cold Neutrons, Iwashita Y, Invited Talk at ICANS-XVIII, 25–29 April 2007, Dongguan, Guangdong, China, P.R.

Electron Cooling Experiments at S-LSR, Shirai T, Invited Talk at the Workshop on Beam Cooling and Related Topics, COOL'07, 13 September 2007, Bad Kreuznach, Germany.

Grants

Noda A, Special Coordination Funds for Promoting Science and Technology, Creation of Innovation Centers for Advanced Interdisciplinary Research Areas: Photo-

Laser Cooling of a Mg^+ Ion Beam at S-LSR

Ion beams circulating in a storage ring usually have a high temperature. It has theoretically been predicted that ion beams are transferred to a crystalline state with a regular arrangement if a strong enough cooling force is applied. In 2006, we have succeeded to create a one-dimensional ordered state of 7 MeV protons by an electron cooling in the ion storage ring S-LSR at Institute for Chemical Research. For the purpose of realization of a crystalline beam, a stronger cooling force than the electron cooling such as a laser cooling, is required.

We have carried out a laser cooling experiment for a 40 keV $^{24}Mg^+$ ion beam. A transition; $3s^2S_{1/2}$-$3p^2P_{3/2}$, corresponding to a laser frequency at laboratory frame of 280 nm is utilized for the cooling. In addition to a co-propagating laser with the beam, an induction accelerator has been introduced to create a stable point of the cooling forces. A ring dye laser system pumped by a frequency stabilized Nd:YVO_4 laser, followed by a frequency doubling unit is used to produce the laser light of 280 nm (Figure 1).

Figure 2 shows the momentum spread before and after laser cooling. It was found that the momentum spread has been reduced from 1.7×10^{-3} to 2.9×10^{-4} by laser cooling when it is applied for the Mg ions with the intensity of 10^8. Up to now, temperature cooling down in the longitudinal direction is achieved. We will extend the laser cooling to a three-dimensional one by a resonant coupling method, to obtain an ultra-low temperature beam.

Radial Focusing/defocusing of a Laser Produced Protons by an rf Electric Field

Laser-plasma ion acceleration has possibility to downsize usual electromagnetic accelerators. However, such laser-produced ion beams had not been suitable for actual use, because they had almost 100 % energy spread. In order to compress the momentum spread of the laser-produced beam, we have proposed to combine laser-plasma acceleration and phase-rotation by a synchronous rf electric field. If the phase of the rf electric field is adjusted so that the faster ions are decelerated and the slower ions are accelerated, the ions can be collected into a certain energy region. We have succeeded to compress the energy spread less than 7% with this method [1]. In our experiment, it was also found that the radial component of the rf electric field gives focus or defocus effects on the motion of the protons in the transverse direction as shown in Figure 3. From the analysis, it was found that the ions included in the energy peak were defocused in a radial direction, and the focused ions in radial direction had an almost continuous energy spectrum.

[1] S. Nakamura *et al.*: Jpn. J. Appl. Phys. **46** (2007) L717.

Figure 1. A ring dye laser system (upper picture) and a frequency doubling unit (lower picture).

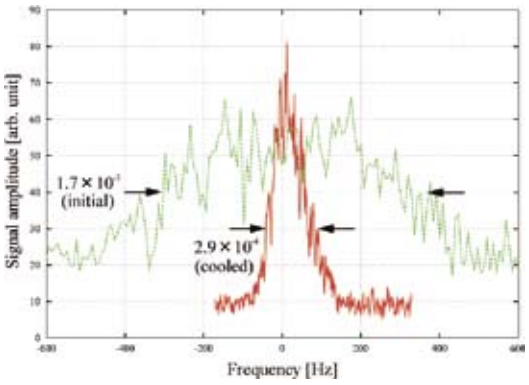

Figure 2. Momentum spread before and after the laser cooling.

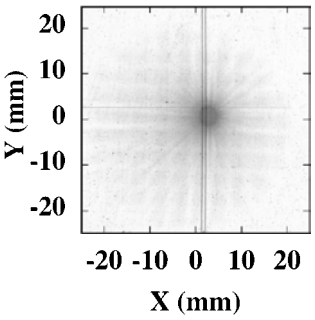

Figure 3. Radial distribution of the laser-produced proton beam after phase-rotation.

Medical Valley, 1 June 2007–31 March 2010.

Iwashita Y, Application and Development of Super Strong Permanent Magnet Especially for Linear Collider and Neutron Optics, Grant-in-Aid for Scientific Research, (A) (1), 1 April 2006–31 March 2009.

Shirai T, Realization of Ultra Low Emittance Ion Beam Using Phase Transition by Electron Cooling, Grant-in-Aid for Scientific Research (C), 1 April 2007–31 March 2009.

Iwashita Y, Development of Satellite Compact Pulse Neutron Source, Joint Development Research at High Energy Accelerator Research Organization (KEK), 1 April 2007–31 March 2008.

Advanced Research Center for Beam Science
- Laser Matter Interaction Science -

http://laser.kuicr.kyoto-u.ac.jp/e-index.html

Prof
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TOKITA, Shigeki
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Students

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NAMBA, Shin (M1)

Lecturer (pt)

YOSHIDA, Minoru (D Eng) Kinki University

Visitor

Dr TILLACK, Mark University of California, USA, 11 October 2007

Scope of Research

By making the physics of interaction between femtosecond laser and matters clear, possibility for new applications is being developed in such as laser processing and laser nuclear science. The interaction of femtosecond laser and matter differs from that of nanosecond laser in physics such as ionization and ablation process. Soft-ionization and ablation by the femtosecond laser can be applied to mass spectrometry and nano-scale structural formation and matter reforming, respectively. In addition, with the progress of short pulse lasers, even a small-sized equipment can create ultra-high optical field. In this strong electromagnetic field the motion of an electron becomes relativistic, and the electron is accelerated easily above MeV, emitting high energy pulse x-ray and ions. Laser produced radiation has the feature such as impulse, a point source and high intensity, and its potential to the new radiation source is expected. In our laboratory physics of intense laser matter interactions and its application are researched.

Research Activities (Year 2007)

Publications

Hashida M, Shimizu S, Sakabe S: Carbon Nanotubes Cathode Modified by Femtosecond Laser Ablation, *Journal of Physics: Conference Series*, **58**, 487-491 (2007).

Tokita S, Kawanaka J, Izawa Y, Fujita M, Kawashima T: 23.7-W Picosecond Cryogenic-Yb:YAG Multipass Amplifier, *Optics Express*, **15**, 3955-3961 (2007).

Presentations

Femtosecond Laser Ablation of Polytetrafluoroethylene, Hashida M, Mishima H, Shimizu S, Sakabe S, 27th Annual Meeting of The Laser Society of Japan, Miyazaki, 17–18 January 2007.

The Amount of Electrons Emitted from Solid Metal Plasmas Generated by Pulsed Laser, Masuno S, Hashida M, Sakabe S, 27th Annual Meeting of The Laser Society of Japan, Miyazaki, 17–18 January 2007.

Nano-ablation of Material with Femtosecond Laser Pulses, Hashida M, Shimizu S, Sakabe S, Research Meeting of the Japan Society of Plasma Science and Nuclear Research, Kyoto, 9 March 2007.

Prospect of Femtosecond Laser Processing, Hashida M, Laser Expo 2007, Yokohama, 25–27 April 2007.

Progress of Intense Short Pulse Lasers and Their Applications, Sakabe S, Optical Society of Japan, Lecture Meeting, 22 June 2007, Kyoto Japan. (Invited)

Mechanism of Femtosecond Laser Ablation of Polytetrafluoroethylene, Hashida M, Mishima H, Shimizu S, Tokita S, Sakabe S, The 3rd Meeting of Japan Intense Light Field Science Society, Osaka, 18 July 2007.

Femtosecond Laser Ablation of Polytetrafluoroethylene, Hashida M, Mishima H, Shimizu S, Tokita S, Sakabe S, The 68th Annual Meeting of the Japan Society of Applied Physics, Hokkaido, 4–8 September 2007.

Highly-efficient Low-repetition-rate Mode-locked Cryogenic Yb:YAG Laser, Tokita S, Kawanaka J, Fujita M, Kawashima T, Hashida M, Sakabe S, Izawa Y, The 68th Annual Meeting of the Japan Society of Applied

Femtosecond Laser Nano-ablation of Polytetrafluoroethyhlene

Laser ablation experiments were performed on polytetrafluoroethyhlene (PTFE, C_2F_4) with short pulse generated from T^6 laser system. Ablation threshold of PTFE was investigated from the crater surface diameter dependence on the laser fluence. It was found that the ablation threshold was approximately proportional to pulse duration to the power 0.39 in the range of 130fs-400ps. The released ions upon ablation were detected by time of flight mass spectrometer (TOF-MS) with 130fs and 400ps. The difference was shown in detected ions energy spectrum and maximum energy of C^{3+} between two pulses. It was suggested that the ablation of organic polymer such as PTFE might be due to coulomb explosion.

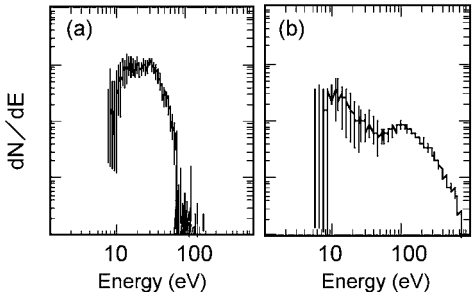

Figure 1. Energy spectra of detected ions. (a) 130fs, 0.78J/cm^2, (b) 400ps, 40J/cm^2.

Upgrade of the T^6 Laser System

The T^6-laser has been operated for the study of laser-matter interaction physics and its applications since 1987 (since 2004 at ICR), and lots of fruits were obtained by not only our laboratory members but also the collaboration with another universities and industrial enterprises. For future more advanced research complete renovation and upgrade of the laser system was done through June–September, 2007. The upgraded points are (1) higher stability of output energy, (2) stable protection of front-end stage from backward-reflected light from laser-matter interaction, (3) more safety for the laser users, and (4) more convenience of pulse monitors for users. Especially for the point (1) the highest stability has been achieved in our knowledge. (The detail will be published and patented in 2008). Here the system configuration is briefly described. Figure 2 shows a schematic of the T^6 laser system which consisted of four-pass pre-amplifier, four- and five-pass power amplifiers.

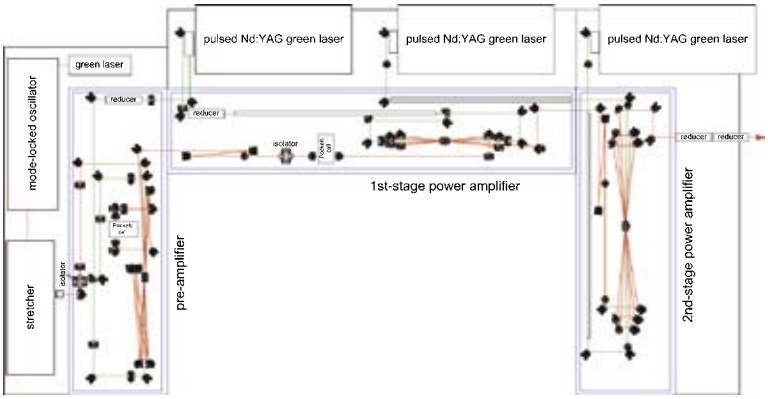

Figure 2. Schematic of the upgraded T^6 laser system.

Physics, Hokkaido, 4–8 September 2007.

Nano-ablation Processing with Femtosecond Laser Pulses, Hashida M, Mishima H, Shimizu S, Tokita S, Sakabe S, Optics & Photonics Japan 2007, Osaka, 26–28 November 2007.

Grants

Sakabe S, et al., Time Resolved Electron Microscope with Intense Femtosecond Laser Produced Electrons, Grant-in-Aid for Scientific Research (A), 1 April 2006–31 March 2009.

Hashida M, Advanced Material Processing with Femtosecond Lasers, Iketani Science and Technology Foundation, 20 July 2007–31 March 2008.

Hashida M, Improvement of Ablation Rate for Femtosecond Laser Processing, Amada Foundation for Metal Work Technology, 20 December 2007–31 March 2009.

Awards

Hashida M, Sakabe S, LSJ Award for Distinguished Achievements in Research, Carbon-nanotube Cathode Modified by Femtosecond Laser Ablation, The Laser Society of Japan, 31 May 2007.

Tokita S, Encouragement Prize, Sapphire-conductive End-cooling of High Power Cryogenic Yb:YAG Lasers, The Laser Society of Japan, 31 May 2007.

Advanced Research Center for Beam Science
- Electron Microscopy and Crystal Chemistry -

http://eels.kuicr.kyoto-u.ac.jp:8080/Root/English

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Res
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KOZAWA, Ryouhei (M2)
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SHINODA, Yasuhiro (M1)
UMEDA, Azumi (M1)

Visitors

Prof WEGNER, Gehnard	MPI for Polymer Science, Germany, 28 May 2007
Prof CHEN, Jen-Sue	Department of Materials Science and Engineering, National Cheng Kung University, Taiwan, 8–9 June 2007
Dr LO, Shen-Chuan	ITRI, Taiwan, 13–19 October 2007

Scope of Research

Crystallographic and electronic structures of materials and their transformations are studied through direct imaging of atoms or molecules by high-resolution spectromicroscopy which realizes energy-filtered imaging and electron energy-loss spectroscopy as well as high resolution imaging. It aims to explore new methods for imaging and also obtaining chemical information in thin films, nano-clusters, interfaces, and even in solutions. By combining this with scanning probe microscopy, the following subjects are urging: direct structure analysis, electron crystallographic analysis, epitaxial growth of molecules, structure formation in solutions, and fabrication of low-dimensional functional assemblies.

Research Activities (Year 2007)

Publications

Yoshida K, Minamikawa H, Kamiya S, Shimizu T, Isoda S: Formation of Self-Assembled Glycolipid Nanotubes with Bilayer Sheets, *J. Nanosci. Nanotechnol*., **7**, 960-964 (2007).

Koshino M, Kurata H, Isoda S: Stability of Peripheral Halogenation among Phthalocyanine Complexes, *Microsc. Microanal*., **13**, 96-107 (2007).

Minari T, Seto M, Nemoto T. *et al*.: Molecular-packing-enhanced Charge Transport in Organic Field-effect Transistors of Semiconducting Porphyrin Crystals, *APL*, **91**, 123501 (2007).

Presentations

Porphyrin Single-crystal Field-effect Transistors, Seto M, Nemoto T, Isoda S, et al., China NANO, 4–6 June 2007, Beijing, China.

Direct Observation of Iodine-doped C_{60} Crystal by Scanning Transmission Electron Microscopy, Haruta M, Kurata H, Yoshida K, Isoda S, IWFAC'2007, 2–6 July 2007, St. Petersburg, Russia.

Morphology-Controlled Titania Nanocrystals and Application for Dye-sensitized Solar Cells, Isoda S, Jiu J (Osaka Univ.), Adachi M (Doshisha Univ.), Yoshida K, Kurata H, KJF-2007, 27–29 September 2007, Seoul, Korea.

Nanostructuring of BTQBT Derivative Co-adsorbed

Development of Cold-FEG with a Nanotip for 200kV TEM/STEM

Electron energyloss spectroscopy (EELS) combining with an STEM makes it possible to extract local electronic structure as well as elemental information from a small area in solids. Because of the small inelastic scattering cross-section, however, it is still difficult to measure spectrum image data with an electron probe of atomic scale. Recent development of spherical aberration correctors is one of promised approaches to overcome this problem, because it can provide an increased probe current in addition to a sub-angstrom probe size. As another way to get a brighter electron source, we have developed a cold-FEG for a 200kV TEM/STEM (Figure 1) with a sharpened <111> orientation tungsten tip. The method producing a sharpened tip is to heat it under applying a strong electric field (thermal field, TF, treatment). It promotes the diffusion of surface atoms and the faceting of low index planes. The diffusing atoms gather around the edge region to gain the polarization energy due to the applied electric field, so that the protrusion is formed as a pyramid structure along the <111> direction with a few nm in height. The probe current at the specimen position is about 50–100 pA, which is almost one order higher than that of the Schottky type of FEG. If the bright electron gun is combined with a spherical aberration corrected STEM, one can expect the increased probe current at a sub-angstrom probe size, which will be promising to perform STEM-EELS analysis with a high efficiency.

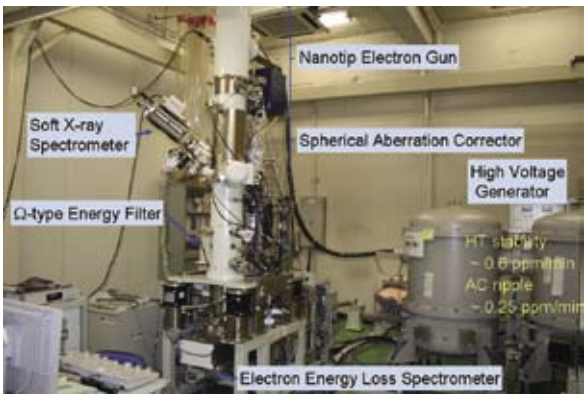

Figure 1. A 200kV TEM/STEM with nanotip electron gun.

Formation of Self-Assembled Glycolipid Nanotubes with Bilayer Sheets

Rolled-up morphology of bilayer sheets in a self-assembled glycolipid nanotube (LNT) in water was carefully examined by using a cryogenic transmission electron microscope (cryo-TEM) with a rapid-freezing specimen-preparation technique. The LNTs were obtained under a series of self-assembly conditions: boiling of an aqueous dispersion of glycolipid *N*-(11-*cis*-octadecenoyl)-*β*-D-glucopyranosylamine, subsequent gradual cooling, and incubation at room temperature for several days. Cryo-TEM images revealed that the LNT walls consist of a multilayer structure with interlayer distance of about 4.7 nm. (Figure 2) These layers correspond to constituent lipid bilayers. From the result of precise cryo-TEM observations and analyses, we confirmed the rolled-up morphology of the lipid bilayer sheets in a complete self-assembled glycolipid nanotube.

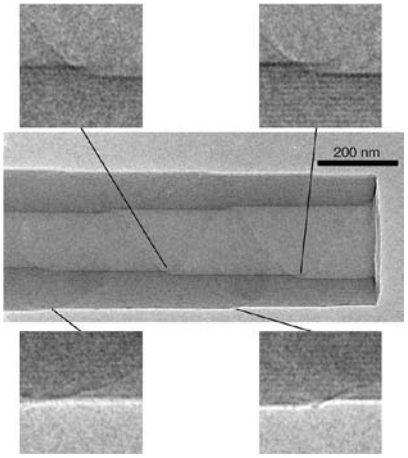

Figure 2. A cryo-TEM image of the LNT rolled up near its end.

with Solvents, Chiba Y, Nemoto T, Yamashita Y (Tokyo Inst. Tech.), Isoda S, ICSPM15, 6–8 December 2007, Atagawa, Japan.

Grants

Kurata H, Development of an EELS/XES Electron Microscope for Electronic Structure Analysis, Leading Project, The Ministry of Education, Science, Culture and Sports, Japan, 1 April 2004–31 March 2007.

Kurata H, Local State Analysis of Defects and Interface Regions by Spherical Aberration Corrected STEM and EELS, Grant-in-Aid for Scientific Research (B) 19310071, 1 April 2007–31 March 2010.

Isoda S, Nanotechnology Support Project, The Ministry of Education, Science, Culture and Sports, Japan, 1 April 2007–31 March 2011.

Award

Isojima S, Best Poster Awards, The 63rd Annual Meeting of the Japanese Society of Microscopy, “LAADF of Iron Oxide Nanowire”, The Japanese Society of Microscopy, 21 May 2007.

Advanced Research Center for Beam Science
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Visitor

Prof McLEOD, Cameron University of Sheffield, UK, 26–27 November 2007

Scope of Research

The research activities in this laboratory are performed for X-ray structural analyses of biological macromolecules and the investigation of the electronic state in materials as follows: The main subjects of the biomacromolecular crystallography are crystallographic studies on the reaction mechanism of enzymes, the relationship between the multiform conformation and the functional variety of proteins, and the mechanism of thermostabilization of proteins. In the investigation of the chemical state in materials, the characteristics of the chemical bonding in the atom and molecules are investigated in detail using a newly developed X-ray spectromator with a high-resolution in order to elucidate the property of materials. The theoretical analysis of the electronic states with DV-Xα and WIEN2k, and the development of new typed X-ray spectrometer with ultra high-resolution have also been carried out.

Research Activities (Year 2007)

Publication

Fujii T, Oikawa T, Muraoka I, Soda K, Hata Y: Crystallization and Preliminary X-ray Diffraction Studies of Tetrameric Malate Dehydrogenase from the Novel Antarctic Psychrophile *Flavobaterium frigidimaris* KUC-1, *Acta Cryst.*, F**63**, 983-986 (2007).

Presentations

Cold-adapting Structure of Psychrophilic MDH, Hata Y, Fujii T, Oikawa T, Muraoka I, Soda K, 2007 Annual Meeting of Japan Society for Bioscience, Biotechnology, and Agrochemistry, 27 March 2007, Tokyo, Japan.

Structural Features of Psychrophilic Malate Dehydrogenase Adapting to the Extreme Environment, Hata Y, Fujii T, Oikawa T, Soda K, The 8th Conference of Asian Crystallographic Association (AsCA'07 Taipei), 6 November 2007, Taipei, Taiwan.

Grant

Ito Y, Development of Basic Technologies for New Functional Particle Materials, Kyoto Prefecture Collaboration of Regional Entities for the Advancement of Technological Excellence, JST, 1 December 2004–31 December 2008.

X-Ray Crystallographic Analysis of Tetrameric Malate Dehydrogenase from Novel Antarctic Psychrophile

Various psychrophilic microorganisms, which grow at low temperatures unsuitable for most of other organisms, produce various psychrophilic and thermolabile enzymes in order to survive and grow effectively under such extreme environments. These enzymes have generated considerable interest, since they can be used to improve the efficiency of industrial processes and for environmental applications. In order to understand the structural basis of cold adaptation of psychrophilic enzymes, we have initiated X-ray structural studies on tetrameric malate dehydrogenase (MDH) from a novel psychrophilic bacterium *Flavobacterium frigidimaris* KUC-1, which was isolated from Antarctic seawater, as a model of structurally unknown psychrophilic enzyme. Malate dehydrogenase catalyzes the reversible oxidation of malate to oxaloacetate in the presence of NAD^+. The overall molecular weight of the present MDH is about 130 kDa as a tetramer and the subunit mass about 33 kDa. The subunit consists of 311 amino acid residues. The crystal structure of the tetrameric MDH is probably different in intersubunit organization and network of interactions from already determined crystal structure of dimeric MDH from a psychrophile *Aquaspirillium arcticum*. The structure determination of the present MDH and intensive comparisons tetrameric MDH structures of microorganisms living in different environments are expected to provide more detailed structural information on the mechanism of cold adaptation.

Crystallization was performed using the hanging-drop vapour-diffusion method. The protein concentration was adjusted to 17 mg ml^{-1} in 10 m*M* potassium phosphate buffer pH 7.0. Each of the drops was prepared by mixing 1 μl protein and 1 μl reservoir solutions. After extensive investigation of conditions, rod-shaped crystals of the enzyme with maximum dimensions of 1.1 × 0.15 × 0.05 mm were obtained at 288 K within 2–3 days by equilibrating the 2 μl protein drop against 500 μl reservoir solution (1.4 *M* $(NH_4)_2SO_4$, 5% (*v/v*) MPD, 2 m*M* NAD^+, 50 m*M* sodium citrate buffer pH 5.5) (Figure 1). The crystal belonged to trigonal space group $P3_221$ with unit cell dimensions of $a=b=147.8$ and $c=165.1$ Å. It contained one tetrameric molecule per asymmetric unit and a solvent content of 69.1%.

X-ray diffraction data collection was performed at the beamline BL-5A of Photon Factory, Tsukuba, Japan. A crystal with size of 0.35 × 0.15 × 0.05 mm was soaked in the reservoir solution containing 30% (*v/v*) glycerol for several ten seconds, then mounted in a nylon loop and flash-cooled in a nitrogen stream at 100 K. Diffraction data up to 1.8 Å resolution were collected at a wavelength of 1.000 Å using a Quantum 315 CCD detector (ADSC) set to the crystal-to-detector distance of 249.2 mm. The oscillation steps was 1.0° over a range of 180°. The exposure time was 1.5 seconds per frame. All diffraction images were processed with the program *MOSFLM* in the *CCP4* program suit. 2,099,880 observed reflections were merged to 192,407 independent reflections (completeness of 100%) with redundancy of 10.9. The *R*sym value was 8.0%.

Figure 1. Crystals of psychrophilic MDH from *F. frigidimaris* KUC-1. The dimensions of the largest crystal were 1.0 × 0.15 × 0.05 mm.

The structure determination of the enzyme was carried out by molecular replacement (MR) using the program *MOLREP* in *CCP4*. The structure of a hybrid consisting of a thermophilic and a mesophilic MDHs was used as a search model. MR calculations gave one solution for search model of the tetramer and four solutions for that of the subunit. These results coinside with the presence of one tetrameric MDH per asymmetric unit. The current structure of *F. frigidimaris* MDH is shown in Figure 2.

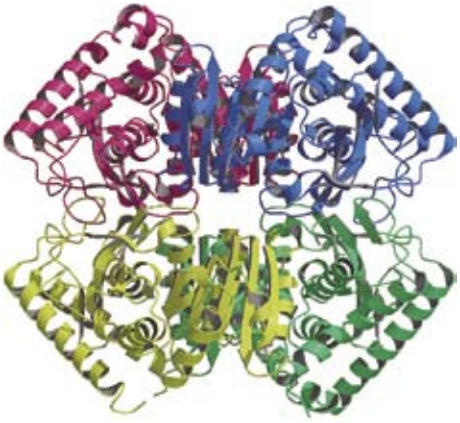

Figure 2. Ribon drawing of tetrameric MDH.

International Research Center for Elements Science - Organic Main Group Chemistry -

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TOMA, Gabriel (M2)
KAWAMURA, Shintaro (M1)
FUJIWARA, Yuichi (M1)
NAKAGAWA, Naohisa (M1)
HASHIMOTO, Sigma (UG)

Scope of Research

Our research activity is focused on the discovery, design and development of new molecular transformation reactions, which can provide new ways of efficient exploitation of chemical resources, such as haloalkanes, alkenes, alcohol etc. The present research subjects are (1) 3d-transition metal catalyzed controlled Carbon–Carbon bond forming reactions which exploit universal metals such as iron, magnesium and aluminum (2) understanding and design of synergistic effects of multi-element center interactions for the catalysis with the help of quantum chemical methods.

Research Activities (Year 2007)

Publications

Endo K, Hatakeyama T, Nakamura M, Nakamura E: Indium-Catalyzed 2-Alkenylation of 1,3-Dicarbonyl Compounds with Unactivated Alkynes, *J. Am. Chem. Soc.*, **129**, 5264-5271 (2007).

Hatakeyama T, Nakamura M: Iron-Catalyzed Selective Biaryl Coupling: Remarkable Suppression of Homocoupling by the Fluoride Anion, *J. Am. Chem. Soc.*, **129**, 9844-9845 (2007).

Tsuji H, Yamagata K-i, Itoh Y, Endo K, Nakamura M, Nakamura E: Indium-Catalyzed Cycloisomerization of ω-Alkynyl-β-ketoesters into Six- to Fifteen-Membered Rings, *Angew. Chem. Int. Ed.*, **46**, 8060-8062 (2007).

Presentations

Nakamura M, Asian Core Program (ACP) Lectureship Tour in Hong Kong (Chinese University of Hong Kong, Hong Kong Baptist University, Hong Kong University of Science and Technology, The University of Hong Kong), February 2007.

Nakamura M, The 99th National Meeting of Korean Chemical Society, Seoul, Korea, April 2007.

Nakamura M, ACP Lectureship tour in China, Shanghai Institute of Organic Chemistry, Fudan University, Shanghai Institute of Chemistry, Chinese Academy of Science, Beijing, China, May 2007.

Grants

Nakamura M, Development of Iron Catalyzed Reaction for Transformation of Polyvinylchloride, Grant-in-Aid for Exploratory Research, 1 April 2005–31 March 2007.

Nakamura M, Molecular Transformation of Unreactive Haloalkanes, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2006–31 March 2007.

Nakamura M, Design of Transition Metal/Main Group Elements Synergetic Reagent and Its Synthetic Application, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2006–31 March 2009.

Nakamura M, Exploratory Study on New Chemical Reactions Exploiting Biorenewable Carbon Resources, Kyoto University, ISS (Institute for Sustainability Science) Research Grant for Exploratory Studies, 1 April 2006–31 March 2008.

Hatakeyama T, Development of SN_2 Reaction of Carbon–Heteroatom Bond with Highly Reactive Metal Enolate, Grant-in-Aid for Young Scientists (Start), 1 April

Unsymmetrical Biaryl Syntheses

Transition metal-catalyzed cross-coupling reactions are one of the most powerful tools in organic synthesis. Palladium and nickel catalysts have been the dominant choice for such a purpose, and are widely used in academia as well as in industry. Whereas iron, a practically ideal transition metal, has been actively investigated as a catalyst in the field of cross-coupling reactions, iron-catalyzed aryl-aryl cross-coupling has remained a challenge because of competing homo-coupling reaction caused by oxidation with organic halides or iron-catalyzed halogen-metal exchange. We found a simple and highly selective iron-catalyzed cross-coupling reaction which selectively produced unsymmetrical biaryl compounds (Figure 1). The key to success is a novel combination of iron fluoride salts with an *N*-heterocyclic carbene (NHC) ligand, which specifically suppressed homo-coupling reactions (1–5% in most cases).

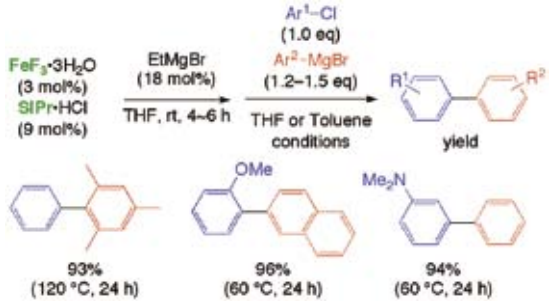

Figure 1. Selective Biaryl Cross-Coupling.

Cross-Coupling of Alkyl Tosylate

We sometime ago developed a new iron-catalyzed cross-coupling reaction of alkyl halides with aryl magnesium or zinc compounds in the presence of *N*, *N*, *N'*, *N'*-tetramethylethylenediamine (TMEDA). Whereas the alkyl halides are industrial feedstock and produced from corresponding alcohols, their preparative conditions are strongly acidic, and thus the overall yields are often low for certain substrates with functionalities. Cross-coupling of alkyl tosylates or triflates is, hence, more feasible and useful for the synthesis of fine chemicals. We found $FeCl_3$/TMEDA catalyst effect the cross-coupling of alkyl tosylates in the presence of zinc iodide, which converts *in-situ* the alkyl tosylates to corresponding iodides. With this one-pod method various secondary alkyl tosylates and arylzinc reagents possessing a variety of functional groups are available for the selective cross-coupling.

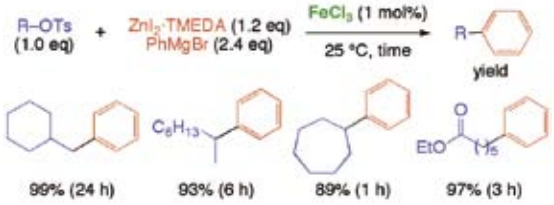

Figure 2. Cross-Coupling of Alkyl Tosylate.

Fluoroaromatic Coupling of Alkyl Halides

Fluoroaromatic rings are found as a key structural unit of numerous functional molecules, such as liquid crystals, drugs, agrochemicals, and dyes. Recent progress in the cross-coupling technology provided numbers of powerful methods for connecting fluoroaromatic rings with unsaturated (Csp^2 or Csp) substituents, but nonetheless few for introducing alkyl (Csp^3) substituents. Despite the fact that various cross-couplings of alkyl electrophiles and arylmetallic nucleophiles have been achieved, only a few fluoroaromatic couplings are available because of the low reactivity and instablity (e.g. undesired Csp^2-F bond cleavage) of polyfluorinated aryl metals under the reaction conditions. We have developed an effective and selective fluoroaromatic coupling of alkyl halides, which has been accomplished by combination of easily available fluoroaromatic metal reagents and 1,2-bis(diphenylphosphino)b enzene (DPPBz) as a ligand. The reaction can provide a concise synthetic route for the production of LC molecules (Figure 3).

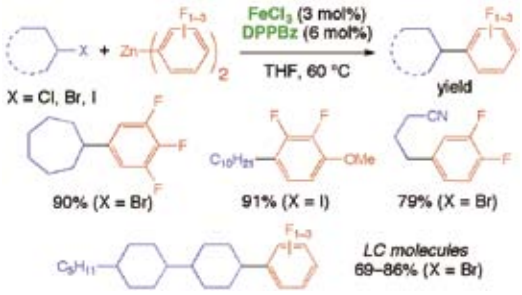

Figure 3. Fluoroaromatic Coupling of Alkyl Halides.

2006–31 March 2007.

Hatakeyama T, Refined Transformation of Biomass via S_N2 Reaction of Carbon–Heteroatom, Grant-in-Aid for Young Scientists (B), 1 April 2007–31 March 2009.

Award

Hatakeyama T, The ICR Award for Young Scientists, 7 December 2007.

International Research Center for Elements Science - Advanced Solid State Chemistry -

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Scope of Research

Novel inorganic crystalline materials that have new, useful or exotic features such as magnetoresistance, ferromagnetism and quantum spin ground state are synthesized. High pressure conditions are applied to obtain nonequilibrium materials with crystal structure and/or chemical composition unavailable at ambient pressures. Precise crystal structure analysis using X-ray or neutron beams as well as magnetic and electronic property measurements are performed to reveal and understand the physical properties of newly obtained materials.

Research Activities (Year 2007)

Publications

Saito T, Williams A, Attfield J P, Wuernisha T, Kamiyama T, Ishiwata S, Takeda Y, Shimakawa Y, Takano M: Neutron Diffraction Study of a Layered Cobalt Oxide $SrCo_6O_{11}$, *J. Mag. Mag. Mater.*, **310**, 1584-1586 (2007).

Ishiwata S, Terasaki I, Ishii F, Nagaosa N, Mukuda H, Kitaoka Y, Saito T, Takano M: Two-Staged Magnetoresistance Driven by the Ising-Like Spin Sublattice in $SrCo_6O_{11}$, *Phys. Rev. Lett.*, **98**, [217201-1]-[217201-4] (2007).

Shiraki H, Saito T, Yamada T, Tsujimoto M, Azuma M, Kurata H, Isoda S, Takano M, Shimakawa Y: Ferromagnetic Cuprates $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$ with *A*-site Ordered Perovskite Structure, *Phys. Rev. B*, **76**, [140403-1]-[140403-4] (2007).

Zhang W, Okubo S, Ohta H, Saito T, Takano M: High-frequency ESR Measurements of the Co Spinel Compound $SiCo_2O_4$, *J. Phys. Cond. Mat.*, **19**, [145264-1]-[145264-6] (2007).

Oba N, Kageyama H, Saito T, Yoshimura K: Synchrotron X-ray Diffraction Study on the Square-lattice Antiferromagnets $(CuCl)LaNb_2O_7$ and $(FeCl)LaNb_2O_7$, *J. Mag. Mag. Mater.*, **310**, 1337-1339 (2007).

Tsujimoto Y, Baba Y, Oba N, Kageyama H, Fukui T, Narumi Y, Kindo K, Saito T, Takano M, Ajiro Y, Yoshimura K: 1/3 Magnetization Plateau in Spin-1/2 Square Lattice Antiferromagnet $(CuBr)Sr_2Nb_3O_{10}$, *J. Phys. Soc. Jpn.*, **76**, [063711-1]-[063711-4] (2007).

Presentations

Magnetic Frustration in the Layered Cobalt Oxide $SrCo_6O_{11}$, Saito T, Williams A, Attfield J P, Wuernisha T, Kamiyama T, Ishiwata S, Takeda Y, Shimakawa Y, Takano M, Gordon Research Conference on Solid State Chemistry II, Oxford UK, 4 September 2007.

Magnetic Phase Diagram of $SrCo_6O_{11}$ with Magnetization Plateaux, Saito T, Williams A, Attfield J P, Wuernisha T, Kamiyama T, Ishiwata S, Takeda Y, Shimakawa Y, Takano M, Spring Meeting of the Physical Society of Japan, Kagoshima Japan, 20 March 2007.

High Pressure Synthesis and Magnetism Research of Transition Metal Oxides, Saito T, The Ceramic Society of Japan, Kansai Branch Seminar, Kyoto Japan, 26 November 2007.

Grant

Takano M, Chemistry and Physics of 3d Transition Metal Oxides Equipped with Deep 3d Levels: Search for New Materials and New Functions, Grant-in-Aid for Scientific Research (S), 1 April 2005–31 March 2010.

Stepwise Magnetoresistance and Magnetic Frustration in $SrCo_6O_{11}$

$SrCo_6O_{11}$ is a layered cobalt oxide with unique magnetic and electronic properties, first synthesized using a high pressure technique in our group. Its magnetization process shows a plateau region at the 1/3 of the saturated magnetization M_0, which is concomitant with the negative and stepwise magnetoresistance effect. It was found that $SrCo_6O_{11}$ comprises itinerant electrons and Ising-like local spins of S = 2 on separate crystallographic sites, having strong interactions with each other. The spin structure at the 1/3 magnetization plateau state was found to be ferromagnetic in the *ab*-plane and like ↑-↑-↓-↑-↑-↓ along the *c*-axis. The quick reorientation of the ferromagnetic layers from the ↑-↑-↓ (M/M_0=1/3; M = magnetization) manner to the ↑-↑-↑ (M/M_0=1) manner under magnetic field should result in a major decrease of the magnetic scattering of conduction electrons penetrating through the ferromagnetic layers, which explains the negative, sharp and two-stepped magnetoresistance. The ↑-↑-↓ magnetic structure in the 1/3 magnetization plateau state implies the existence of competing magnetic interactions along the *c*-axis, forbidding simple antiferromagnetism or ferromagnetism. Such a competition in the magnetic interactions produce magnetic frustration in $SrCo_6O_{11}$, resulting in rather complex magnetic phase diagram. Large magnetostriction is also observed at low temperatures. Spin, charge and orbital degree of freedom is strongly coupled with each other in $SrCo_6O_{11}$, giving rise to the unique physical properties.

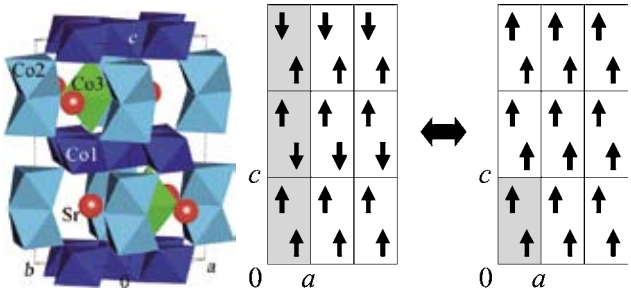

Figure 1. The crystal structure and spin structures of $SrCo_6O_{11}$. Up and down arrows represent Co(3) spins.

Magnetism of $CaCu_3B_4O_{12}$ (B = Ge, Ti, Sn) Perovskites

A-site ordered perovskites $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$, which are isostructural to a well-known antiferromagnet (AFM) $CaCu_3Ti_4O_{12}$, were found to be ferromagnets (FM). $CaCu_3Sn_4O_{12}$ was newly synthesized under high pressure of 8 GPa. Though the crystal structure (*e.g.* lattice parameters, bond angles, bond lengths, *etc.*) of these materials changes systematically from $CaCu_3Ge_4O_{12}$ to $CaCu_3Ti_4O_{12}$ to $CaCu_3Sn_4O_{12}$, their magnetism changes in different manner, i.e. from FM to AFM to FM. Crystal structure analysis, magnetic measurements and electronic structure calculations were done to understand the origin of their magnetism. The special alignment of the CuO_4 planes in the crystal structure plays an important role in the magnetic properties of Cu^{2+} spins. Direct exchange interaction gives rise to the ferromagnetic behavior in $CaCu_3Ge_4O_{12}$ and $CaCu_3Sn_4O_{12}$, whereas involvement of Ti-3*d* orbitals produces the antiferromagnetic superexchange interaction in $CaCu_3Ti_4O_{12}$. This finding demonstrates that either ferromagnetic or antiferromagnetic behavior can appear within the same structural framework.

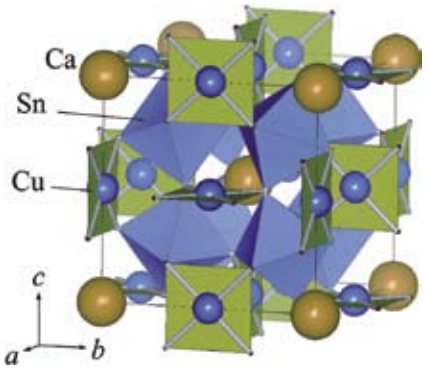

Figure 2. The crystal structure of $CaCu_3Sn_4O_{12}$.

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TAKADA, Yuko (M2)
YAMAMOTO, Yasutaka (M2)
MUKAIHARA, Yoko (M1)
SHIRAISHI, Yu (UG)

Scope of Research

This laboratory aims at establishment of new synthetic methodologies and new functional materials by designing well-defined catalysts based on transition metal chemistry. New concepts and ideas of molecular-based catalysts are accumulated by mechanistic investigations using kinetic techniques on the reaction intermediates and elementary processes. The research subjects include: (1) development of novel ligand systems for catalysis, (2) creation of functional metal complexes based on synergistic effects, (3) construction of π-conjugation system including transition-metals, and (4) development of functional molecules including redox-active transition-metal clusters.

Research Activities (Year 2007)

Publications

Jensen R S, Umeda K, Okazaki M, Ozawa F, Yoshifuji M: Synthesis and Catalytic Properties of Cationic Palladium(II) and Rhodium(I) Complexes Bearing Diphosphinidenecyclobutene Ligand, *J. Organomet. Chem.,* **692**, 286-294 (2007).

Hayashi A, Ishiyama T, Okazaki M, Ozawa F: Cationic Iridium(III) Complexes Bearing Phosphaalkene and 2-Pyridylphenyl Ligands, *Organometallics*, **26**, 3708-3712 (2007).

Hayashi A, Okazaki M, Ozawa F, Tanaka R: Synthesis, Structures, and Catalytic Properties of Late-Transition-Metal 2,6-Bis(2-phosphaethenyl)pyridine Complexes, *Organometallics*, **26**, 5246-5249 (2007).

Presentations

Construction of Novel Reaction Sites on Transition-Metal Complexes Enhanced by Low-Coordinated Phosphorus Compounds, Ozawa F, The 87th Annual Meeting of the Chemical Society of Japan, 25–28 March 2007, Osaka, Japan (Invited).

Electron-Induced Structural Changes in [4Fe–4C] Cluster Core, Okazaki M, Takano M, Ohtani T, Yoshimura K, Ozawa F, Ogino H, The 1st Asian Conference on Coordination Chemistry, 30 July 2007, Okazaki, Japan.

Construction of Functional Molecules Possessing [4Fe–4C] Core, Okazaki M, The 56th Symposium on Coordination Chemistry of Japan, 16 September 2007, Nagoya, Japan (Invited).

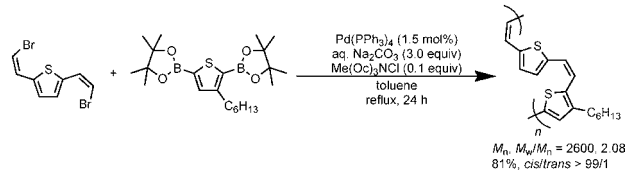
Stereocontrolled Synthesis of All-cis Poly(arylene vinylene)s: Effects of Primary Structures on Photo-Induced Insolubilization in Thin Films, Yamamoto Y, Wakioka M, Mutoh Y, Takita R, Katayama H, Ozawa F, The 10th Pacific Polymer Conference, 4–7 December 2007, Kobe, Japan.

Grants

Ozawa F, Okazaki M, Takita R, Synergistic Effects of Transition Metals and Heavier Main Group Elements in Functional Organometallic Complexes, Grant-in-Aid for Priority Area "Synergy of Elements", 1 September 2006–31 March 2010.

Syntheses and Characteristics of All-cis Poly(arylene vinylene)s Containing Thienylene Groups in Main Chains

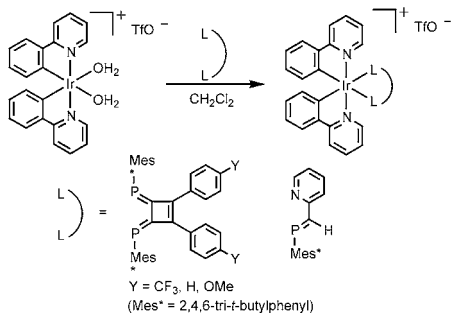
All-cis poly(arylene vinylene)s (PAV) containing thiophene derivatives have been prepared in a highly stereocontrolled manner based on Suzuki-Miyaura coupling according to a procedure we previously developed. It has been found that thin films of all-cis PAVs are insolubilized and well immobilized under UV-irradiation, along with cis-to-trans one-way photoisomerization. This phenomenon has been successfully applied to construction of novel carrier transfer materials showing great enhancement of carrier mobility upon photo-induced insolubilization.



Scheme 1. Synthesis of all-cis PAV containing thiophene in main chain.

Cationic Iridium(III) Complexes Bearing Phosphaalkenes and 2-Phenylpyridine Ligands

We have synthesized a new series of cationic iridium(III) complexes bearing phophaalkene and 2-pyridylphenyl ligands and examined their electrochemical and photophysical properties. It has been confirmed that the metal t_{2g} levels can be tuned by chemical modification of the phosphaalkene ligands. The DPCB-CF_3 ligand in **1** serves as a particularly effective π-acceptor to cause bluish-green luminescence at 492 nm.



Scheme 2. Synthesis of Ir(III) complexes bearing phosphaalkene and 2-pyridylphenyl ligands.

Synthesis and Property of Phosphine Ligands Possessing Redox-Active [4Fe–4C] Core Substituents

Treatment of $[Cp'_4Fe_4(HCCH)_2]$ (**1**, Cp' = η^5-C_5H_4Me) with 2 equiv. NBS resulted in the exclusive formation of $[Cp'_4Fe_4(HCCH)(HCC–Br)]^+$ ($[\mathbf{2}]^+$). The generated bromoacetylene part on the tetrairon core is highly electrophilic and reacted with $HPPh_2$ in the presence of NEt_3 to give $[Cp'_4Fe_4(HCCH)(HCC–PPh_2)]^+$ ($[\mathbf{3}]^+$). Reaction of $[\mathbf{3}]^+$ with $[Cp_2Co]$ afforded the neutral form **3**. To estimate the *s* character of the lone pair of **3**, the NMR coupling constant ^1J(P–Se) of the phosphine selenide **4** was measured. The ^1J(P–Se) value of **4** (693 Hz) is significantly smaller than those in $Se{=}PR_3$ [R = Ph (755 Hz), ^{t}Bu (708 Hz), Cy (706 Hz)], indicating the exceptionally electron-releasing character of **3**. Complexation of **3** with Pd(II) and Pt(II) metals have been achieved under the mild conditions.

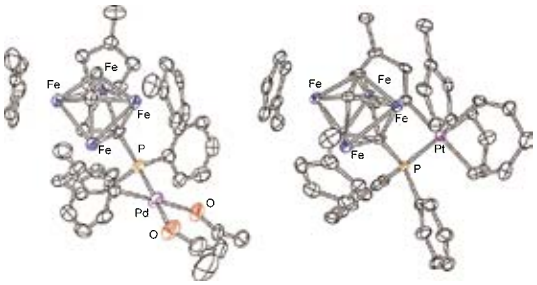


Figure 1. Molecular structure of Pd(II) and Pt(II) complexes having cluster ligands.

Okazaki M, Mihara H, Construction of Novel Functional Molecules by Hybridization of Biomolecules with Transition Metal Clusters, Grant-in-Aid for Exploratory Research, 1 April 2007–31 March 2009.

Okazaki M, Mihara H, Construction of Novel Catalysts Based on Flexible Structural Changes of Multimetallic Cores, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2007–31 March 2008.

Okazaki M, Chemistry of Nonplanar Carbocations Bridged over Transition Metals, Mitsubishi Chemical Corporation Fund, 1 April 2007–31 March 2008.

Takita R, Development of Catalytic Reactions Using Low Coordinate Phosphine Ligands, Grant-in-Aid for Young Scientists (Start-up), 1 August 2007–31 March 2009.

International Research Center for Elements Science - Photonic Elements Science -

http://www.scl.kyoto-u.ac.jp/~opt-nano/index-e.html

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Scope of Research

Our research interest is to understand optical and quantum properties of nanometer-structured materials and to establish opto-nanoscience for creation of innovative functional materials. Optical properties of semiconductor quantum nanostructures and strongly-correlated electron systems in low-dimensional materials are studied by means of space- and time-resolved laser spectroscopy. The main subjects are as follows: (1) Investigation of optical properties of single nanostructures through the development of high-resolution optical microscope, (2) Development of nanoparticle assemblies with new optical functionalities, and (3) Ultrafast optical spectroscopy of excited states in semiconductor nanostructures.

Research Activities (Year 2007)

Publications

Ito Y, Matsuda K, Kanemitsu Y: Mechanism of Photoluminescence Enhancement in Single Semiconductor Nanocrystals on Metal Surfaces, *Phys. Rev. B*, **75**, [033309-1]-[033309-4] (2007).

Matsuda K, Nair S V, Ruda H E, Sugimoto Y, Saiki T, Yamaguchi K: Two-exciton State in GaSb/GaAs type II Quantum Dots Studied Using Near-field Photoluminescence Spectroscopy, *Appl. Phys. Lett.*, **90**, [013101-1]-[013101-4] (2007).

Tamada Y, Yamamoto S, Nasu S, Takano M, Ono T: Well-Ordered $L1_0$-FePt Nanoparticles Synthesized by Improved SiO_2-Nanoreactor Method, *Appl. Phys. Lett.*, **90**, [162509-1]-[162509-4] (2007).

Presentations

Nano-imaging Spectroscopy of Semiconductor Quantum Structures, Matsuda K, 3rd Handai Nano Symposium, 26–28 October 2007, Osaka, Japan (Invited).

Optical Probing of a Single Carbon Nanotube, Matsuda K, JSPS 2nd Japan-Germany Nanophotonics Seminar, 24–28 October 2007, Yonago, Japan (Invited).

Dynamics of Electron-Hole Plasmas in Highly Excited GaN-based Ternary Alloys, Hirano D, Kanemitsu Y, 16th International Conference on Dynamical Processes in Excited States of Solids (DPC07), 17–22 June 2007, Segovia, Spain.

Grants

Kanemitsu Y, Study of Highly Excited State in Semiconductor Nanostructures by Means of Time and Spatially Resolved Spectroscopy, Grant-in-Aid for Scientific Research (B), 1 April 2006–31 March 2008.

Matsuda K, Explorer of Optical Properties and Application of Quantum Optical Devices in an Individual Carbon-Nanotube by Optical Nanoprobing, Grant-in-Aid for Young Scientists (A), 1 April 2005–31 March 2008.

Awards

Matsuda K, Explorer of Nanoimaging Spectroscopy: Wavefunction Mapping of Semiconductor Quantum Structures, Award for Research Promotion, Marubun Research Promotion Foundation, 5 March 2007.

Matsuda K, Electronic States Mapping of Semiconductor Quantum Structures by Near-field Nanoimaging Spectroscopy, 1st Physical Society of Japan Award for Young Scientist, 21 September 2007.

Dynamics of Nonlinear Photoluminescence from $SrTiO_3$

Transition metal oxides have attracted a great deal of attention as new device materials due to their wide variety of fascinating and multifunctional properties. With its unique electrical and optical properties, $SrTiO_3$ is one of the most important oxide materials. We studied the behavior and dynamics of polarons in non-doped and electron-doped $SrTiO_3$. The photoluminescence (PL) decay dynamics are dependent on both the photogenerated and the chemically doped carrier density in $SrTiO_3$ (Figure 1). The PL dynamics are well explained using a simple model that includes radiative bimolecular recombination and nonradiative Auger recombination processes of polarons.

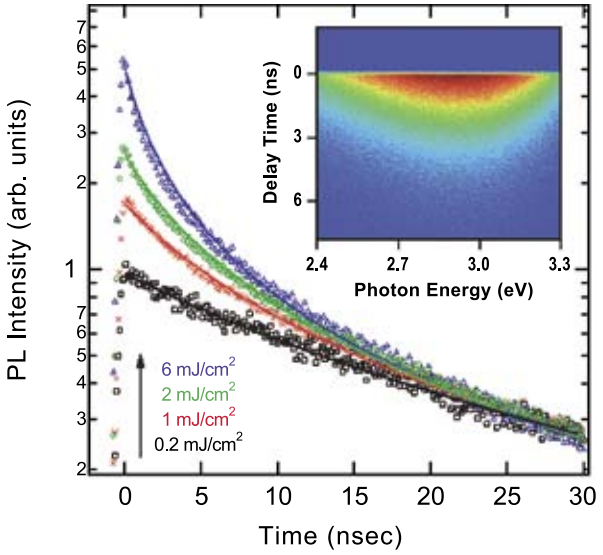

Figure 1. Excitation density dependence of PL dynamics in $SrTiO_3$. The inset shows streak image of PL decay.

Multiexciton Recombinations in a Single Carbon Nanotube

Electronic and optical properties of single-walled carbon nanotubes (SWNTs) have attracted much attention from the fundamental physics viewpoint. The recent discovery of efficient PL from isolated semiconducting SWNTs has stimulated considerable efforts in understanding optical properties of SWNTs. We studied the temperature and excitation intensity dependence of exciton luminescence in single SWNTs. The linear temperature dependence of the PL linewidth in a single SWNT implies that the exciton dephasing is dominated by the interaction between the exciton and the phonon mode with very low energies under lower excitation conditions. Saturation of the PL intensity and broadening of the PL linewidth in a single SWNT occur simultaneously with an increase in the excitation laser intensity. Our findings show that the rapid exciton-exciton annihilation through multiparticle Auger recombination broadens the homogenous PL linewidth.

Photoluminescence Enhancement and Quenching of Single CdSe/ZnS Nanocrystals on Metal Surfaces

Colloidal semiconductor nanocrystals with high PL quantum efficiencies have been extensively studied both from the viewpoint of fundamental physics and with consideration for the potential applications to electronics and biotechnology. The interfaces between metals and nanocrystals play complex and essential roles in the optical responses of semiconductor nanocrystals on metals. The detailed understanding of interactions between nanocrystals and metal surfaces are very important to enhance the PL intensity of nanocrystals in conjunction with the improvement of the PL efficiency of nanocrystals. We studied the mechanism of the PL enhancement and quenching of CdSe/ZnS nanocrystals on rough Au surfaces in Figure 2. Single nanocrystal spectroscopy revealed that the PL enhancement depends strongly on the excitation wavelength and liner-polarization angle due to the localized plasmon excitation. The simulated electric-field distribution was shown in the inset of Figure 2. The observed PL enhancement and quenching are sensitive to the nanocrystal size. The polarization- and size-dependent PL enhancement and quenching are determined by the balance between the resonant energy transfer from the nanocrystal to the Au surface and the electric field enhancement.

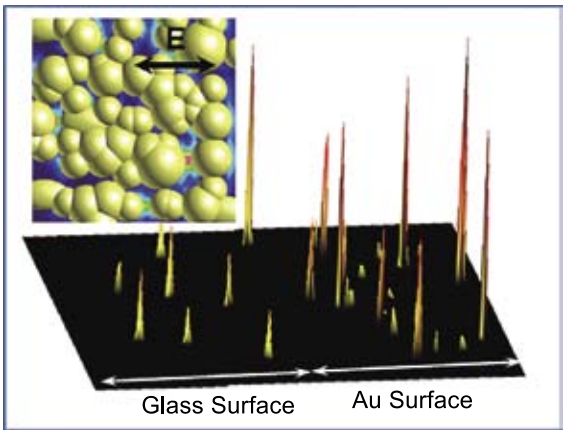

Figure 2. PL image of single CdSe/ZnS nanocrystals on glass (left side) and metal substrate (right side). Inset shows simulated electric-field distributions induced by surface plasmon.

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Scope of Research

DNA, RNA, and proteins are the basic molecular building blocks of life, but the living cell contains additional molecules, including water, ions, small chemical compounds, glycans, lipids, and other biochemical molecules, without which the cell would not function. Because the proteins responsible for biosynthesis, biodegradation, and transport of these additional molecules are encoded in the genome, one may assert that all cellular functions are specified by the genomic DNA sequence. In practice, however, it is not possible to infer higher-level systemic functions of the cell or the organism simply from the molecular sequence infomation alone. We are developing bioinformatics methods to integrate different types of data and knowledge on various aspects of the biological systems towards basic understanding of life as a molecular interaction/reaction system and also for practical applications in medical and pharmaceutical sciences.

Research Activities (Year 2007)

Grants

Kanehisa M, Education and Research Organization for Genome Information Science, MEXT.

Kanehisa M, Knowledge Information Infrastructure for Genome Information Science, Kyoto University 21st Century COE Program, MEXT.

KEGG RPAIR Database and Prediction of Biodegradation Pathways

In this study, we focus on the biodegradation pathways of xenobiotics in bacteria. First, we perform a systematic survey of the KEGG RPAIR database containing chemical structure alignments of substrate-product pairs and chemical structure transformation patterns in all known enzyme-catalyzed reactions. Biochemical structure transformations are described by what we call RDM patterns, which represent KEGG atom type changes at the reaction center atom (R) and its neighbouring atoms on the different region (D) and the matched region (M). Second, we present a method to predict potential biodegradation pathways of xenobiotics. The RDM patterns presumably represent the reaction specificity of enzymes, but not the substrate specificity. Therefore, in our prediction system a new compound is first compared against all known substrate and product structures, and then possible RDM patterns are selected by considering the similarity scores of matched compounds. By limiting the dataset to bacterial reactions appearing in the "Xenobiotics Biodegradation and Metabolism" category of the KEGG PATHWAY database, this prediction system can be adjusted to microbial biodegradations.

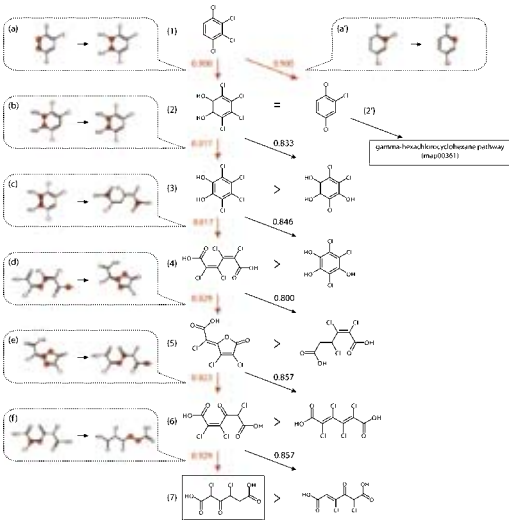

Figure 1. The prediction of 1,2,3,4-tetrachlorobenzene biodegradation pathway. The query compound (1) is transformed to compounds (2)–(7) with the transformation patterns of matching compounds (a)–(f). The reactions in the dotted boxes show the transformation patterns of the best matching compounds (a)-(f), where the reaction center atoms are marked with red circles.

The Commonality of Protein Interaction Networks Determined in NDDs

Neurodegenerative disorders (NDDs) are progressive and fatal disorders, which are commonly characterized by the intracellular or extracellular presence of abnormal protein aggregates. Here, we first investigated the commonality among the six NDDs from the molecular point of view. By reviewing published literatures in PubMed, we created pathway maps in KEGG for binary relations in six NDDs: Alzheimer's disease (AD), Parkinson's disease (PD), amyotrophic lateral sclerosis (ALS), Huntington's disease (HD), dentatorubral-pallidoluysian atrophy (DRPLA) and prion disease (PRION). We also collected data on 201 interacting proteins and 13 compounds with 282 interactions from the literature. We found 19 proteins common to these six NDDs. These common proteins were mainly involved in the apoptosis and MAPK signaling pathways. We also expanded the interaction network by adding protein interaction data from the Human Protein Reference Database and gene expression data from the Human Gene Expression Index Database and finally we found 174 common proteins and 202 common interactions. We then carried out domain analysis on the extended network and found the characteristic domains, such as 14-3-3 protein, phosphotyrosine interaction domain and caspase domain, for the common proteins. Moreover, PD and HD showed the highest correlation in terms of domain distributions and we found the commonality in the tight junction pathway, which has not previously been associated with the mechanism of either disease.

Figure 2. 174 common proteins and 202 common interactions found in the extended network of NDDs.

Kanehisa M, Backbone Database for Analysis of the Biological Systems and Environment, Grant-in-Aid for Scientific Research on Priority Areas, MEXT.

Kanehisa M, Deciphering Systemic Biological Functions by Integration of Genomic and Environmental Information, Bioinformatics Research and Development, JST.

Kanehisa M, Hierarchical Structuring and Integration of Knowledge in Life Sciences, Integrated Database Project, MEXT.

Kanehisa M, Integration of Genomics and Chemistry in Glycome Informatics, NIH, USA.

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Assoc Prof DAI, Yang — University of Illinois at Chicago, USA, 23 April 2007
TAN, Hao — Monash University, Australia, 7 December 2007–1 March 2008

Scope of Research

Due to rapid progress of the genome projects, whole genome sequences of organisms ranging from bacteria to human have become available. In order to understand the meaning behind the genetic code, we have been developing algorithms and software tools for analyzing biological data based on advanced information technologies such as theory of algorithms, artificial intelligence, and machine learning. We are recently studying the following topics: systems biology, scale-free networks, protein structure prediction, inference of biological networks, chemo-informatics, discrete and stochastic methods for bioinformatics.

Research Activities (Year 2007)

Publications

Takemoto K, Nacher JC, Akutsu T: Correlation between Structure and Temperature in Prokaryotic Metabolic Networks, *BMC Bioinformatics*, **8**, [303-1]-[303-11] (2007).

Akutsu T, Hayashida M, Ching WK, Ng MK: Control of Boolean Networks: Hardness Results and Algorithms for Tree Structured Networks, *Journal of Theoretical Biology*, **244**, 670-679 (2007).

Tamura T, Akutsu T: Subcellular Location Prediction of Proteins Using Support Vector Machines with Alignment of Block Sequences Utilizing Amino Acid Composition, *BMC Bioinformatics*, **8**, 466 (2007).

Presentations

An $O(1.787^n)$-time Algorithm for Detecting a Singleton Attractor in a Boolean Network Consisting of AND/OR Nodes, Tamura T, Akutsu T, The 16th International Symposium on Fundamentals of Computation Theory, 30 August 2007.

A Grammatical Approach to RNA-RNA Interaction Prediction, Kato Y, Akutsu T, Seki H (Nara Institute of Science and Technology), International Symposium on Computational Models for Life Sciences, 17 December 2007.

Grants

Akutsu T, Kawabata T, Nagamochi H, Hayashida M, A Novel Approach to Computational Drug Design Based on Graph Theory and Kernel Methods, Grant-in-Aid for Scientific Research (A), 1 April 2007–31 March 2010.

Akutsu T, Goto S, Mochizuki A, Tokita K, Mathematical Analysis of Structure and Dynamics of Biological Information Networks, Grant-in-Aid for Scientific Research on Priority Areas, 1 April 2005–31 March 2010.

Awards

Akutsu T, Contribution Award, Special Interest Group on Mathematical Modeling and Problem Solving, Information Processing Society of Japan, 3 March 2007.

Tamura T, FIT Award for Young Researchers, Approximation Algorithms for Optimal RNA Secondary Structures Common to Multiple Sequences, IPSJ and IEICE, 6 September 2007.

Structural Difference with Temperature in Prokaryotic Metabolic Networks

Organisms grow in the environment of different temperatures. Since heat-loving organisms are believed to be primeval forms of life, elucidation of differences with temperature is a major topic in evolutionary biology. Up until now, the adaptive differences as a result of temperature have been revealed in structural and sequence properties of transcriptomes and proteomes. However, temperature-dependent differences in metabolism are still unclear.

We here represent the metabolism as a network (graph) in which nodes and edges correspond to metabolites and substrate-product relationships between them, respectively, and investigate a relationship between structure and optimal growth temperature in metabolic networks of 113 prokaryotes using graph-theoretical metrics. As a result, we find significant correlations between structural properties and optimal growth temperature in the metabolic networks (e.g. see Figure 1A). The metabolic networks become less dense and low modular with increasing temperature. Furthermore, the connectivity of the networks becomes homogenous. This result implies that metabolic networks undergo a change from ordered structures such as clustered scale-free networks to disordered structures such as random networks with increasing temperature (Figure 1B). Our finding might suggest that the temperature plays an important role in design principles of metabolic networks.

Takemoto K, Nacher J C, Akutsu T, *BMC Bioinformatics*, **8**, 303 (2007).

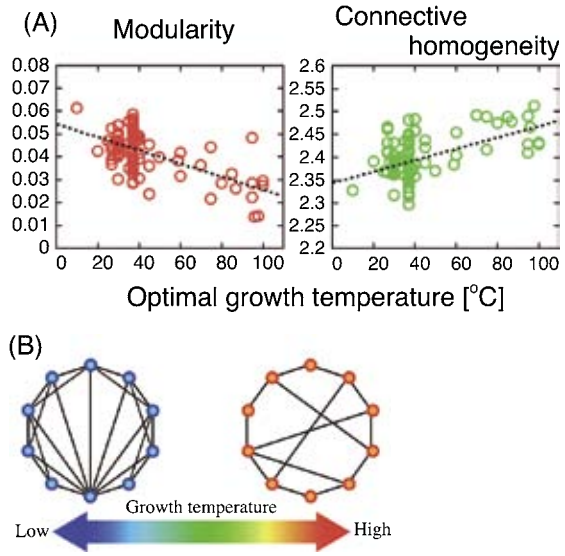

Figure 1. (A) Major example of statistically significant correlations between structure properties and optimal growth temperature. (B) Schematic diagram of a structural transition of metabolic networks with temperature.

Subcellular Location Prediction of Proteins Using Support Vector Machines with Alignment of Block Sequences Utilizing Amino Acid Composition

Subcellular location prediction of proteins is an important and well-studied problem in bioinformatics.

This is a problem of predicting which part in a cell a given protein is transported to, where an amino acid sequence of the protein is given as an input. This problem is becoming more important since information on subcellular location is helpful for annotation of proteins and genes and the number of complete genomes is rapidly increasing. Since existing predictors are based on various heuristics, it is important to develop a simple method with high prediction accuracies.

In this work, we propose a novel and general predicting method by combining techniques for sequence alignment and feature vectors based on amino acid composition. We implemented this method with support vector machines on plant data sets extracted from the TargetP database.

Through fivefold cross validation tests, the obtained overall accuracies and average MCC were 0.9096 and 0.8655 respectively. We also applied our method to other datasets including that of WoLF PSORT.

Although there is a predictor which uses the information of gene ontology and yields higher accuracy than ours, our accuracies are higher than existing predictors which use only sequence information. Since such information as gene ontology can be obtained only for known proteins, our predictor is considered to be useful for subcellular location prediction of newly-discovered proteins. Furthermore, the idea of combination of alignment and amino acid frequency is novel and general so that it may be applied to other problems in bioinformatics. Our method for plant is also implemented as a web-system and available on [http://sunflower.kuicr.kyoto-u.ac.jp/~tamura/slpfa.html].

Tamura T, Akutsu T: *BMC Bioinformatics*, **8**, 466 (2007)

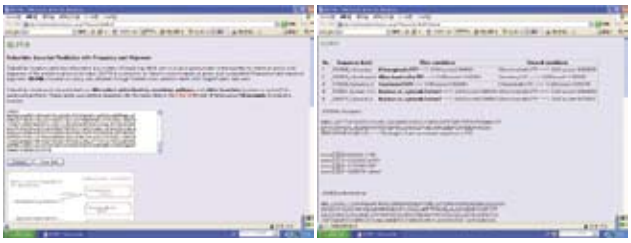

Figure 2. (Left) SLPFA prediction server. (Right) Result of an example.

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Dr MATTHIAS, E Futschik	Humboldt University, Germany, 6 August 2007
Prof KASKI, Samuel	Helsinki University of Technology, Finland, 20 September 2007
Dr HORTON, Paul	National Institute of Advanced Industrial Science and Technology, Japan, 30 October 2007

Scope of Research

With the recent advancement of experimental techniques in molecular biology, research in modern life science is shifting to the comprehensive understanding of a biological mechanism consisting of a variety of molecules. Our focus is placed on molecular mechanisms in biological phenomena, represented by biological networks such as metabolic and signal transduction pathways. Our research objective is to develop techniques based on computer science and/or statistics to systematically understand biological entities at the cellular and organism level.

Research Activities (Year 2007)

Publications

Shiga M, Takigawa I, Mamitsuka H: A Spectral Clustering Approach to Optimally Combining Numerical Vectors with a Modular Network, *Proceedings of the Thirteenth ACM SIGKDD International Conference on Knowledge Discovery and Data Mining (KDD 2007)*, 647-656 (2007).

Shiga M, Takigawa I, Mamitsuka H: Annotating Gene Function by Combining Expression Data with a Modular Gene Network, *Bioinformatics*, **23** (13) (*Proceedings of the Fifteenth International Conference on Intelligent Systems for Molecular Biology (ISMB 2007)*) , i468-i478 (2007).

Presentations

Random Field, Network Modularity, Spectral Clustering and Beyond, Mamitsuka H, Keynote Speech, *3rd International Conference on Intelligent Computing (ICIC 2007)*, Academic Exchange Center, Ocean University of China, Qingdao, China, 22 August 2007.

An Integrative Approach for Gene Annotation Based on Spectral Clustering and Network Modularity, Mamitsuka H, Invited Talk, AASBi (Association of Asian Societies of Bioinformatics) Symposium 2007, Biopolis, Singapore, 2 December 2007.

Clustering Genes with Expressions and Network Modularity

Recent progress in genome sciences has led to the development of DNA microarray technology which allows to monitor the expression of thousands of genes simultaneously. A current popular approach to annotate gene function from gene expression data is clustering genes by expression values based on the assumption that genes with similar expression patterns can be clustered into a group with the same gene function. However, microarray expression data is inevitably noisy, making the clustering result by the above methods unstable. A promising solution for this issue in current bioinformatics research is to combine microarray expression data with the existing knowledge of gene annotation derived from literature. This type of combination is of interest, since dynamic behavior of genes which would be observed from microarray data can be integrated with the literature-derived biological data which is obviously static information. However, existing approaches are not methodologically sophisticated enough in combining the two data, i.e. real-valued expression data and literature-derived data, especially gene networks. In addition, the focus of current approaches is placed on the rather local information, such as neighboring genes, of gene networks, and incorporating global information of gene networks might find more appropriate gene clusters. In light of the above, we develop two new methods based on the idea of network modularity which allow to consider the global property of gene networks. We emphasize that our methods are general for combining two different types of data: structured (microarray expressions) and unstructured (gene networks) data, and one method is probabilistic model learning and the other is based on spectral clustering. Interested readers should refer the publications raised on the left-hand side page. We show some examples of results obtained by applying one of our methods to real data. Figure 1 shows the clustering results obtained in three cases in which we use a. only gene expressions, b. both expressions and networks, and c. only networks. This figure shows that combining two data information sources is very useful for clustering genes, since the color distribution of the middle network is the closest to the standard color distribution. Figure 2 shows the enlargement of each of the squares in Figure 1. As shown in this figure, two colors, red and green, were merged in b. while more than two colors were merged in a. and the two colors were clearly separated in c. We then checked orange colored genes in b. by using the KEGG database and found that they all correspond to those categorized in "metabolism of cofactors and vitamins", more precisely those in the folate biosynthesis pathway.

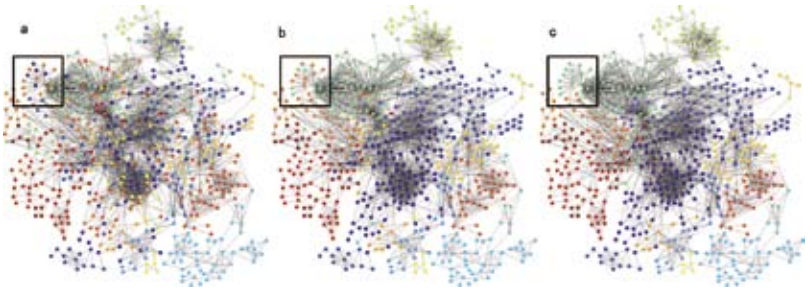

Figure 1. Clustering results where we used a. only gene expressions, b. both expressions and networks, and c. only networks.

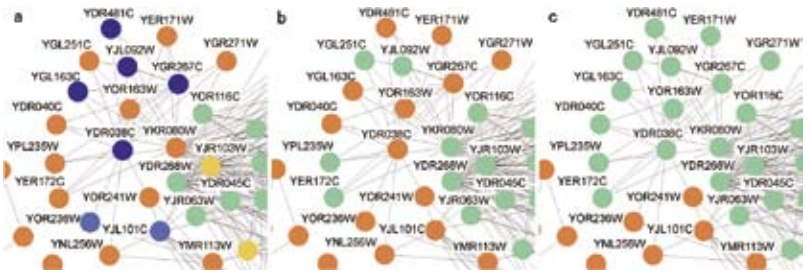

Figure 2. Enlargement of the corresponding squares in Figure 1.

Grants

Mamitsuka H, Integrative Data Mining Approaches for Unstructured Data in Life Sciences, Research Grant from BIRD (BioInformatics Research and Development) of JST (Japan Science and Technology Agency), 15 October 2007–30 September 2010.

Takigawa I, Large-Scale Biological Information Processing Based on Computational Geometric Structures and Adaptive Sampling, Grant-in-Aid for Young Scientist (B), 1 April 2006–31 March 2008.

VISITING PROFESSORS' ACTIVITIES IN ICR

Vis Prof
ISHIHARA, Kazuaki
(D Eng)

Laboratory of Synthetic Organic Chemistry
Professor, Graduate School of Engineering, Nagoya University
(Furo-cho, Chikusa, Nagoya 464-8603)

Lectures at *ICR*
"Design of Environmentally Benign Catalysts Based on Acid-Base Combination Chemistry"
"Design of Asymmetric Catalysts Based on Acid-Base Combination Chemistry"

Vis Prof
NAITO, Satoshi
(D Sc)

Laboratory of Molecular Biology
Professor, Laboratory of Molecular Biology, Graduate School of Advanced Life Science, Hokkaido University
(Kita-ku, Sapporo 060-8589)

Lecture at *ICR*
"Molecular Mechanisms of Gene Expression Control in Higher Plants"

Vis Prof
SUZUKI, Akemi
(D Med Sc)

Laboratory of Supramolecular Biology
Professor, Establishment of a Genuinely International Glycoscience Center, Tokai University
(1117 Kitakaname, Hiratsuka, Kanagawa Japan)

Lecture at *ICR*
"Glycobiology"

Vis Prof
FUJITA, Makoto
(D Eng)

Laboratory of Organic Main Group Chemistry
Professor, School of Engineering, The University of Tokyo,
(7-3-1, Hongo, Bunkyo-ku, Tokyo 113-8656)

Lecture at *ICR*
"Self-Assembling Molecular System"

Vis Prof
FEJFAR, Antonin
(Ph D)

Laboratory of Photonic Elements Science
Researcher, Institute of Physics, Academy of Sciencies of the Czech Republic
(Cukrovarnicka 10, 162 53 Prague, Czech Republic)

Lecture at *ICR*
"Mapping Electronic Properties with Nanometer Resolution"

Vis Assoc Prof
FUJINO, Shigeru
(D Eng)

Laboratory of Inorganic Photonics Materials
Associate Professor, Department of Materials Process Engineering, Graduate School of Engineering, Kyushu University
(744 Motooka, Nishi-ku, Fukuoka 819-0395)

Lecture at *ICR*
"A Rheological Approach for Developing a New Family of Low-Melting Glasses"

Vis Assoc Prof
KUROSU, Hiromichi
(D Eng)

Laboratory of Molecular Materials Chemistry
Associate Professor, School of Natural Science and Ecological Awareness, Graduate School of Humanities and Sciences, Nara Women's University
(Kitauoya-Nishimachi, Nara 630-8506)

Lectures at *ICR*
"Introduction of Molecular Orbital Theory"
"Higher-order Structure of Polymers Studied by Solid-state NMR and Quantum Chemistry"
"Quantum Chemical Calculations of NMR Shieldings"

Vis Assoc Prof
SHIBUYA, Shinji
(D Eng)

Laboratory of Particle Beam Science
Accelerator Engineering Corporation
(4-9-1 Anagawa, Inage, Chiba 263-8555)

Lecture at *ICR*
"Present Status and Progress of Devices for Hadron Cancer Therapy"

Vis Assoc Prof
TSUDA, Koji
(D Eng)

Laboratory of Pathway Engineering
Research Scientist/Group Leader, Max Planck Institute for Biological Cybernetics, Dept. Schölkopf
(Spemannstraße 38, 72076 Tübingen, Germany)

Lecture at *ICR*
"Mathematical Programming Methods for Learning from Structured Data"

Vis Assoc Prof
SUN, Ling-Dong
(Ph D)

Laboratory of Advanced Solid State Chemistry
Associate Professor, The State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University
(Beijing 100871, China, P. R.)

Lecture at *ICR*
"Fabrication of Oxide Nanoparticles with Various Shapes"

Prof Em FUKUDA, Takeshi (D Eng)

Appointed as Res (pt) at ICR,
1 April 2007–31 March 2008

Prof Em TAKANO, Mikio (D Sc)

Appointed as Res (pt) at ICR,
1 April–15 November 2007

PERSONAL

Retirement

Professor OKA, Atsuhiro
Division of Biochemistry
— Molecular Biology —

On March 31st, 2008, Dr. Atsuhiro Oka retired from Kyoto University after 33 years of service and was honored with the title of Professor Emeritus of Kyoto University. Dr. Oka was born in Hyogo Prefecture on March 14th, 1945. He graduated from Department of Biology, Faculty of Science, Osaka University in 1967 and subsequently entered Graduate School of Science, Osaka University, where he studied molecular genetics of *Escherichia coli* phages under the supervision of late Professor Haruo Ozeki. In 1972, he was granted a doctoral degree with a thesis entitled "Molecular mechanisms of genetic recombination in coliphage lambda". After completing the doctoral program, he joined Sumitomo Chemical Co., Ltd. in Takarazuka to study agricultural chemicals. On leave from the company from 1973 to 1974, he returned to the basic biology field and studied on the replication of the *E. coli* plasmid ColE1 under Professor Joseph Inselburg at Department of Microbiology, Dartmouth Medical School in Hanover, New Hampshire as a postdoctoral fellow. In 1975, he was appointed Assistant Professor of Institute for Chemical Research, Kyoto University, and promoted to Associate Professor in 1984, and to Professor in 1994, directing the Laboratory of Molecular Biology. Meanwhile, from 1996 to 1998, he served concurrently as the head of Research Facility of Nucleic Acids.

During his academic carrier, Dr. Oka has devoted himself to molecular biology, focusing on structures and functions of genes and genetic elements. He started his study from bacterial molecular genetics focusing on genetic recombination and DNA replication. He determined functional structures of many genetic elements including the entire structure of transposable element Tn*903* and the structure required for the replication of the plasmid ColE1. He also defined a small region of 245-base-pair length as the replication origin of the *E. coli* chromosomal. These early works in his study have contributed to the progress of not only basic biology but also recombinant DNA techniques. Notably, the kanamycin resistance gene that Tn*903* contains is known as one of standard marker genes in both prokaryotic and eukaryotic systems today.

In late 1980's, he extended the field of his study to plant pathogenic bacteria and investigated the structure and function of the Ri plasmid pRiA4b, which mediates the hairy root formation on the plants surface by *Agrobacterium rhizogenes*. He determined the entire structure of the Ri plasmid, defined the region essential for the plasmid replication, and clarified the molecular mechanism of the plant-bacteria signal transduction through the His-Asp phosphorelay system composed of VirA and VirG.

In 1990's, he further extended his field of studies to plant molecular biology, focusing on regulatory mechanisms for plant morphogenesis and responses to environmental stimuli. He identified genes encoding proteins with a wide variety of regulatory functions, including protein kinases, protein phosphatases, transcription factors, phospholipid metabolizing enzymes. Among them, *Arabidopsis thaliana* ARR1 and ARR2 were identified as the first transcription factor-type response regulators in plants, and revealed to be the intracellular signal transducers of cytokinins. This finding lead to the first comprehensive understanding of phytohormone signaling at the molecular level, connecting the cytokinin signal pathway to the expression of cytokinin responsive genes. Throughout his carrier, Dr. Oka has frequently published his work in high profiled international journals that include Nature and Science.

His contribution to Kyoto University and the Institute through his scientific and educational activities is hereby greatly acknowledged. His strong motivation towards revealing the truth in nature and his warm and sincere personality will remain deep in the hearts of those who have known him.

Retirement

Professor HORII, Fumitaka
Division of Environmental Chemistry
— Molecular Materials Chemistry —

On 31 March, 2008, Dr. Fumitaka Horii retired from Kyoto University after 31 years of service and he was honoured with the title of Professor Emeritus of Kyoto University.

Dr. Horii was born in Shiga on 24 June, 1944. He graduated from the Department of Polymer Chemistry, Faculty of Engineering, Kyoto University, in 1967 under the supervision of the late Professor Ichiro Sakurada. He studied the structure and properties of graft copolymers at the Graduate School of Engineering under the supervision of Professor Yoshito Ikada and he was awarded the doctoral degree for the thesis entitled "Characterization of Graft Copolymers and Their Emulsifying Behavior" in 1975. In 1977, he held the post of Research Associate at the Institute for Chemical Research (ICR), Kyoto University; he was appointed Assistant Professor in 1981, Associate Professor in 1987, and Full Professor in 1992 at ICR. As Full Professor, he directed the Laboratory of Molecular Dynamic Characteristics (presently re-named as Laboratory of Molecular Materials Chemistry).

Throughout his academic career, Dr. Horii devoted himself mainly to studies on the structure, structure formation and structure control of polymers, including native cellulose, and made a number of notable findings. His main achievements are as follows. (1) By introducing a high-resolution solid-state NMR spectrometer at the initial stage of the progress, he developed new methods to characterise the solid structure for many crystalline and liquid crystalline polymers. In particular, he contributed to the elucidation of the crystalline-amorphous interfacial component and the oriented noncrystalline chains in polymer materials. He also characterised intra- and inter-molecular hydrogen bondings for different poly(vinyl alcohol) materials on the basis of statistical and quantum chemistry calculations. (2) He contributed to further developments in the solid-state NMR characterisation of the dynamics and local structure of noncrystalline polymers on different temporal or spatial scales. (3) He developed a new solid-state NMR method for analysing the surface structure of polymer materials as a function of the distance (in Å) from the surface. He expects to combine dynamic nuclear polarization (DNP) with this method for increasing the sensitivity by 100–1000 times. (4) He has made pioneering contributions to the establishment of the composite crystal model for native cellulose, which was assumed to comprise two allomorphs, cellulose I_α and I_β, by the discoveries of a new crystal transformation for native cellulose and the wide distribution in the fractions of cellulose I_α and I_β in nature. He also clarified the liquid-crystal-like structure of the basic assembly for bacterial cellulose and proposed a structural model for the formation of the hierarchical structure, including the crystallisation process.

These notable findings of Dr. Horii were published in over 260 scientific publications. He was presented with the Award of the Society of Fiber Science and Technology, Japan, in 1992 and the Anselme Payen Award by the Cellulose and Renewable Materials Division of American Chemical Society in 2007.

Dr. Horii has contributed to various scientific societies. He has been an associate editor with international journals including *Polymer Journal* and *Cellulose*. He has served as President and Vice-President of the Cellulose Society, Japan, and as Representative of the Society of Solid-State NMR for Materials.

He has also greatly contributed to the establishment of the organisation for safety and health in Uji campus as General Safety and Health Manager and as Director of the Center for Environment and Safety Managements in Uji campus after Kyoto University changed from a national university to a national university corporation.

Dr. Horii's contribution to Kyoto University through his scientific, educational and administrative activities is gratefully acknowledged.

Awards

SASAMORI, Takahiro

Daiichi-Seiyaku Award in Synthetic Organic Chemistry, Japan

"Development of Novel π-electron Conjugated Systems Containing Heavier Main Group Elements"

The Society of Synthetic Organic Chemistry, Japan

22 February 2007

MIZUHATA, Yoshiyuki

Inoue Research Award for Young Scientists

"Syntheses and Properties of Kinetically Stabilized Tin—Carbon Double-bond Compounds"

Inoue Foundation for Science

5 February 2007

HAMAKI, Hirofumi

The Student Lecture Award

The 87th Annual Meeting of the Chemical Society of Japan
"Reactivity of *β*-Diketimianto and Azabutadienyl Complexes of Group 4 Metals"

The Chemical Society of Japan

May 2007

TANABE, Taro

The Student Lecture Award

The 87th Annual Meeting of the Chemical Society of Japan
"Syntheses of Silanedichalcogenolato Complexes Utilizing Stable Silanedichalcogenols and Elucidation of Their Structures and Reactivities"

The Chemical Society of Japan

May 2007

TSUBAKI, Kazunori

HGCS Japan Award of Excellence 2007

"Colorimetric Recognition Using Functional Phenolphthalein Derivatives"

The Society of Functional Host-Guest Chemistry, Japan

12 July 2007

MURAMATSU, Wataru

ICR Award for Graduate Students

"A Catalytic One-Step Process for the Chemo- and Regioselective Acylation of Monosaccharides"

Institute for Chemical Research, Kyoto University

7 December 2007

AZUMA, Masaki
SHIMAKAWA, Yuichi
TAKANO, Mikio

Thomson Scientific Research Front Award 2007

Thomson Scientific Academic Symposium Honoring Excellence in Emerging Japanese Research Fronts
"The Search for Magnetic Ferroelectrics in Bi-based Perovskites"

Thomson Scientific, Thomson Corporation

19 September 2007

OHNO, Kohji

ICR Award for Young Scientists

"A New Family of Colloidal Crystal Constructed by Concentrated Polymer Brush-afforded Fine Particles"

Institute for Chemical Research, Kyoto University

7 December 2007

ONO, Teruo

Ichimura Academic Award

"Pioneering Research on the Nanoscopic Spin-structure Control in Nano-fabricated Magnets"

The New Technology Development Foundation

27 April 2007

MSJ Outstanding Research Award

"Research on the Current-driven Magnetic Domain Wall Dynamics"

The Magnetic Society of Japan

12 September 2007

MATUBAYASI, Nobuyuki

Award for Distinguished Achievement

The 30th Symposium on Solution Chemistry of Japan
"Solution Chemistry of Supercritical Water through Developments of High-temperature NMR Spectroscopy and Theory of Solutions"

The Japan Association of Solution Chemistry

24 November 2007

KANAYA, Toshiji

The Award of the Society of Polymer Science, Japan

The 56th Annual Meeting of the Society of Polymer Science, Japan
"Studies on Polymer Crystallization and Higher Order Structure"

The Society of Polymer Science, Japan

30 May 2007

The Award of the Japanese Society for Neutron Science

The 7th Annual Meeting of the Japanese Society for Neutron Science
"Higher Order Structure and Dynamics of Polymer Systems by Neutron Scattering"

The Japanese Society for Neutron Science

27 November 2007

HASHIDA, Masaki
SAKABE, Shuji

LSJ Award for Distinguished Achievements in Research

"Carbon-nanotube Cathode Modified by Femtsecond Laser Ablation"

The Laser Society of Japan

31 May 2007

TOKITA, Shigeki

Encouragement Prize

"Sapphire-conductive End-cooling of High Power Cryogenic Yb:YAG Lasers"

The Laser Society of Japan

31 May 2007

HATAKEYAMA, Takuji

ICR Award for Young Scientists

"Iron-Catalyzed Selective Biaryl Coupling: Remarkable Suppression of Homocoupling by the Fluoride Anion"

Institute for Chemical Research, Kyoto University

7 December 2007

AKUTSU, Tatsuya

Contribution Award

"Special Interest Group on Mathematical Modeling and Problem Solving"

Information Processing Society of Japan

3 March 2007

MATSUDA, Kazunari

Award for Research Promotion

"Explorer of Nanoimaging Spectroscopy: Wavefunction Mapping of Semiconductor Quantum Structures"

Marubun Research Promotion Foundation

5 March 2007

1st Physical Society of Japan Award for Young Scientist

"Electronic States Mapping of Semiconductor Quantum Structures by Near-field Nanoimaging Spectroscopy"

Physical Society of Japan

21 September 2007

TAMURA, Takeyuki

FIT Award for Young Researchers

The 5th Forum on Information Technology
"Approximation Algorithms for Optimal RNA Secondary Structures Common to Multiple Sequences"

Information Processing Society of Japan (IPSJ), and The Institute of Electronics, Information and Communication Engineers (IEICE)

6 September 2007

Paper Awards

NAGAHORA, Noriyoshi
SASAMORI, Takahiro
TOKITOH, Norihiro

BCSJ Award (The Best Article of the Month)

"Kinetically Stabilized 1,1'-Bis[(*E*)-diphosphenyl]ferrocenes: Syntheses, Structures, Properties, and Reactivity"
The Chemical Society of Japan

15 October 2007

MORIMOTO, Yasumasa
TAKANO, Mikio
TAMADA, Yoshinori
ONO, Teruo
YAMAMOTO, Shinpei

MSJ Distinguished Paper Award

"Detailed Study on the Structure and Magnetic Property of the Well-ordered $L1_0$-FePt Nanoparticles Synthesized by SiO_2-nano-reactor Method"
The Magnetic Society of Japan 12 September 2007

OHNISHI, Toshiyuki
SAKATA, Kanzo
WATANABE, Bunta
MIZUTANI, Masaharu

Award for Excellence to Authors Publishing in Bioscience, Biotechnology, and Biochemistry in 2006

"CYP724B2 and CYP90B3 Function in the Early C-22 Hydroxylation Steps of Brassinosteroid Biosynthetic Pathway in Tomato"
Japan Society for Bioscience, Biotechnology, and Agrochemistry (NIPPON NOGEIKAGAKU KAI) 24 March 2007

Poster Awards

HIRANO, Toshiko

Poster Prize

The 24th Joint Symposium (The 74th Meeting of the Association of Organic Micro-Analysts in the Japan Society for Analytical Chemistry/ The 74th Meeting of the Technical Committee on Measurment of Mechanical Quantities in the Society of Instrument and Control Engineers)
"History of the Conference on Organic Elemental Microanalysis ~Results of the Activity and Prospect in the Future~"
Organizing Committee of the 24th Joint Symposium
25 May 2007

TANABE, Taro

OMCOS Poster Prize in Organometallic Chemistry

The 14th IUPAC Symposium on Organometallic Chemistry Directed towards Organic Synthesis
"Direct Observation of β-Aryl Elimination from Metal Siloxide"
OMCOS-14 Organizing Committee
4 August 2007

MATSUMOTO, Takeshi

The Best Poster Award

2007 KAIST-Kyoto University Chemistry Symposium
"Electrochemical Properties of Kinetically Stabilized Silaaromatic Compounds"
21st Century COE on Kyoto University Alliance for Chemistry
27 January 2007

MORIYAMA, Katsuhiko

Best Poster Award

The 92nd Symposium on Organic Synthesis, Japan
"Metal Hydroxide-Promoted Asymmetric Cyclization via Memory of Chirality at Room Temperature: Construction of Cyclic Amino Acids with a Tetrasubstituted Carbon Center"
The Society of Synthetic Organic Chemistry, Japan
9 November 2007

TAKAISHI, Kazuto

Impressive Presentation Award

2nd Host Guest Chemistry Symposium
"Synthesis of Higher Order Oligonaphthalenes and Optical Property of TPP, TPP-Zn Adducts"

The Society of Functional Host-Guest Chemistry, Japan

25 May 2007

IMAMURA, Yoko

Best Poster Award

1st Symposium on Organic π-Electron Systems
"Development of Highly Sensitive and Selective Molecules for Detection of Spermidine and Spermine"

The Society of Cyclophane Chemistry, Japan

8 December 2007

TOMOHARA, Keisuke

Best Poster Award

Seminar on Synthetic Organic Chemistry for Young Scientists
"Synthesis of Cyclic Ethers with a Tetrasubstituted Carbon Center via C-O Axially Chiral Enolates"

The 27th Seminar on The Society of Synthetic Organic Chemistry, Japan, Kinki Branch

15 November 2007

TAMADA, Yoshinori

Best Poster Award

The 1st International Symposium on Advanced Magnetic Materials and Applications (ISAMMA)
"Composition-Dependent Magnetic Properties of $L1_0$-FePt Nanoparticles Synthesized by the SiO_2-Nanoreactor Method"

The Organizing Committee of ISAMMA 2007

1 June 2007

TAKEUCHI, Yoshinori

Best Poster Award

The 42th Annual Meeting of the Japanese Society for Chemical Regulation of Plants
"Chemical Tools to Control IAA Homeostasis – IAA-Amino Acid Synthathase (GH3) Inhibitors and Their *in vivo* Activiies –"

The Japanese Society for Chemical Regulation of Plants

30 October 2007

ISOJIMA, Seiichi

Best Poster Awards

The 63rd Annual Meeting of the Japanese Society of Microscopy
"LAADF of Iron Oxide Nanowire"

The Japanese Society of Microscopy

21 May 2007

YAMAMOTO, Yasutaka

2007 PPF Young Scientist Poster Award

The 10th Pacific Polymer Conference
"Stereocontrolled Synthesis of All-cis Poly(arylene vinylene)s: Effects of Primary Structures on Photo-Induced Insolubilization in Thin Films"

The Pacific Polymer Federation

6 December 2007

Obituary

Professor Emeritus

Dr. KOIZUMI, Naokazu (1921–2007)

Dr. Naokazu Koizumi, Professor Emeritus of Kyoto University, passed away in Yokohama on July 4, 2007.

Dr. Koizumi was born in Kyoto on July 12, 1921. He graduated from Kyoto Imperial University with a major in Chemistry in 1945. In 1946, he joined Institute for Chemical Research (ICR), Kyoto University, and started his studies on the dielectric properties of materials under the supervision of Professor Rempei Gotoh. In 1953, he was appointed to an Associate Professor of ICR. In 1958, he was awarded a Ph D (Doctor of Science) for his studies on the dielectric properties of polar liquids in the microwave region. In 1959, he had an opportunity to spend for two years at Purdue University, U.S.A., where he worked on the physical properties of organotin compounds and metal carbonyls in co-operation with Professor W. F. Edgell.

In 1961, Dr. Koizumi was promoted to full professorship, in charge of the overall direction of the Laboratory of Dielectrics. He conducted extensive research on the development of dielectric spectroscopy and the dielectric behaviour of a variety of materials. He designed and constructed various kinds of research instrument for dielectric measurements such as waveguide and coaxial equipment in a microwave region and a milli-hertz bridge circuit for the very low frequency region. From his experiments with these instruments over a very wide range of frequency, he elucidated a variety of dielectric behaviour of pure liquids, solutions, solid polymers, and colloidal dispersions. He especially focused on hydrogen-bonded polar liquids and discussed the liquid structure from their dielectric properties. Moreover, he also performed systematic studies on the dielectric and ferroelectric properties of fluorocarbon polymers, which gave us great insight into the electric polarization of the polymers and participated in their applications to electric and audio devices.

His effort to extend the range of dielectric measurement to both lower and higher frequencies was rewarded by important results and contributed to the recent development of broadband dielectric spectroscopy. He had a strict attitude toward accuracy of measurement data and expected his students to do so, thereby his experimental data having been trusted by many related researchers.

Dr. Koizumi gave lectures on advances in dielectric investigations into electrical properties of matter at the Graduate School of Science, Kyoto University, and he was also in charge of supervising the dissertation work of many graduate students. He also gave lectures on selected topics as well as physical chemistry as a visiting professor at several different universities.

Dr. Koizumi is respected by his students and loved by his colleagues for his amicable, sincere and thoughtful personality. In 1996, the Government made public recognition of his achievements by the Third Class of the Order of the Rising Sun.

PUBLICATIONS
INTERNATIONAL RESEARCH COLLABORATIONS
THESES

PUBLICATIONS

DIVISION OF SYNTHETIC CHEMISTRY
— Organoelement Chemistry —

Nakanishi W, Nakamoto T, Hayashi S, Sasamori T, Tokitoh N: Atoms-in-Molecules Analysis of Extended Hypervalent 5c6e C_2Z_2O Interactions at the 1,8,9-Positions of Anthraquinone and 9-Methoxyanthracene Systems, *Chem. Eur. J.*, **13**, 255-268 (2007).

Hamaki H, Takeda N, Yamasaki T, Sasamori T, Tokitoh N: Synthesis and Properties of Alkaline Metal Complexes with New Overcrowded *β*-Diketiminato Ligands, *J. Organomet. Chem.*, **692**, 44-54 (2007).

Sasamori T, Kobayashi M, Nagahora N, Sugiyama Y, Tokitoh N: Synthesis and Characterization of Functionalized Ferrocenylsilanes Bearing a Bulky Substituent, *Silicon Chem.*, **3**, 199-207 (2005).

Hamaki H, Takeda N, Tokitoh N: Nucleophilic Attack toward Group 4 Metal Complexes Bearing Reactive 1-Aza-1,3-butadienyl and Imido Moieties, *Inorg. Chem.*, **46**, 1795-1802 (2007).

Tokitoh N, Nakata N, Shinohara A, Takeda N, Sasamori T: Coordination Chemistry of a Kinetically Stabilized Germabenzene: Syntheses and Properties of Stable η^6-Germabenzene Complexes Coordinated with Transition Metals, *Chem. Eur. J.*, **13**, 1856-1862 (2007).

Tsubaki K, Tanima D, Sasamori T, Tokitoh N, Kawabata T: Colorimetric Recognition of the Length of *α*,*ω*-Diamines in Water, *Tetrahedron Lett.*, **48**, 2135-2138 (2007).

Tanabe T, Takeda N, Tokitoh N: First Structural Characterization of Silanedithiol and Its Application toward the Synthesis of Silanedithiolato Complexes, *Eur. J. Inorg. Chem.*, 1225-1228 (2007).

Sasamori T, Ozaki S, Tokitoh N: Unexpected Reaction of an Overcrowded 9,10-Dihydroanthrylchlorosilane Leading to the Formation of a Dibenzo-7-silanorbornadiene Derivative, *Chem. Lett.,* **36**, 588-589 (2007).

Shimizu D, Takeda N, Tokitoh N: Synthesis of Mono- and Trinuclear Palladium(II) Complexes via Oxidative Addition of a Bulky Hexathioether Containing a Disulfide Bond to Palladium(0), *J. Organomet. Chem.*, **692**, 2716-2728 (2007).

Matano Y, Matsumoto K, Terasaka Y, Hotta H, Araki Y, Ito O, Shiro M, Sasamori T, Tokitoh N, Imahori H: Synthesis, Structures, and Properties of Meso-Phosphorylporphyrins: Self-organization through P-oxo-to-Zinc Coordination, *Chem. Eur. J.*, **13**, 891-901 (2007).

Tajima T, Sasamori T, Takeda N, Tokitoh N: Synthesis and Structure of a Kinetically Stabilized Stannanethione, *Bull. Chem. Soc. Jpn.*, **80**, 1202-1204 (2007).

Takeda N, Isobe T, Tokitoh N: Synthesis of an Acyclic Diselenodithioether Its Application to the Synthesis of a Distorted Ligand Tethered with Bulky Substituents and Octahedral Palladiurn(II) Complex, *Heteroatom Chem.,* **18**, 549-556 (2007).

Sasamori T, Matsumoto T, Takeda N, Tokitoh N: Synthesis and Properties of a Rhodium Complex Having a Novel *β*-Ketophosphenato Ligand, a Heavier Congener of a *β*-Ketoiminato Ligand, *Organometallics*, **26**, 3621-3623 (2007).

Katoh K, Sasamori T, Tokitoh N, Sato N: Synthesis of a Donor Molecule with Metal Coordination Sites toward Multifunctional Complexes, *Chem. Lett.*, **36**, 1122-1123 (2007).

Tokitoh N, Shinohara A, Matsumoto T, Sasamori T, Takeda N, Furukawa Y: Synthesis and Properties of a Kinetically Stabilized 9-Silaphenanthrene, *Organometallics*, **26**, 4048-4053 (2007).

Takeda N, Isobe T, Sasamori T, Tokitoh N: [1,2-Bis(phenylseleno)benzene] dichloridopalladium(II), *Acta Cryst. E*, **63**, M2546 (2007).

Takeda N, Tokitoh N: A Bulky Silylene Generated under Mild Conditions: Its Application to the Synthesis of Organosilicon Compounds, *Synlett*, 2483-2491 (2007).

Nagahora N, Sasamori T, Watanabe Y, Furukawa Y, Tokitoh N: Kinetically Stabilized 1,1'-Bis[(*E*)-diphosphenyl]ferrocenes: Syntheses, Structures, Properties, and Reactivity, *Bull. Chem. Soc. Jpn.*, **80**, 1184-1900 (2007).

Sasamori T, Mieda E, Tokitoh N: Chalcogenation Reactions of Overcrowded Doubly Bonded Systems between Heavier Group 15 Elements, *Bull. Chem. Soc. Jpn.*, **80**, 2425-2435 (2007).

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THESES

FIRDAUS, Mochamad Lutfi
D Sc, Kyoto University
"Determination of Zr, Hf, Nb, Ta, Mo and W in Seawater and Its Oceanic Distribution"
Supervisor: Prof SOHRIN, Yoshiki
25 September 2007

FUJIMOTO, Shinji
D Sc, Kyoto University
"Beam Commissioning and Suppression of Transverse Coherent Instability at S-LSR"
Supervisor: Prof NODA, Akira
23 March 2007

FUJITA, Masashi
D Sc, Kyoto University
"In Search for Genes Related to Stop Codon Readthrough and Novel Amino Acids"
Supervisor: Prof KANEHISA, Minoru
26 November 2007

GIORDANI, Cristiano
D Sc, Kyoto University
"Structural and Dynamic NMR Studies on Distribution and Aggregation of Cholesterol in Solution and in Phospholipid Bilayer"
Supervisor: Prof NAKAHARA, Masaru
25 September 2007

HAMAKI, Hirofumi
D Sc, Kyoto University
"Synthesis, Structure, Reactivity and Catalytic Activities of Group 4 Metal Complexes with Novel β-Diketiminato Ligands Bearing Bulky Substituents"
Supervisor: Prof TOKITOH, Norihiro
23 March 2007

HIMENO, Atsushi
D Sc, Kyoto University
"Dynamical Behavior of the Magnetic Domain Wall in the Structure-Controlled Ferromagnetic Nanowires"
Supervisor: Prof ONO, Teruo
23 March 2007

IKEDA, Yasunori
D Sc, Kyoto University
"Phase Equilibrium of Cupper Oxide Superconductors and Related Compounds"
Supervisor: Prof SHIMAKAWA, Yuichi
23 March 2007

ITOH, Masumi
D Sc, Kyoto University
"Evolutionary History and Functional Implications of Protein Domains and Their Combinations in Eukaryotes"
Supervisor: Prof KANEHISA, Minoru
26 November 2007

KAI, Kosuke
D Agr, Kyoto University
"Biosynthesis of Coumarins in Arabidopsis thaliana"
Supervisor: Prof SAKATA, Kanzo
23 March 2007

KASHIMA, Hisashi
D Inf, Kyoto University
"Machine Learning Approaches for Structured Data"
Supervisor: Prof AKUTSU, Tatsuya
23 March 2007

LIMVIPHUVADH, Vachiranee
D Sc, Kyoto University
"The Commonalities of Neurodegenerative Disorders Characterized by Protein-protein Interaction Network Analysis"
Supervisor: Prof KANEHISA, Minoru
26 November 2007

MINOWA, Yohsuke
D Sc, Kyoto University
"Comprehensive Analysis of Distinctive Polyketide and Non-ribosomal Peptide Structural Motifs Encoded in Microbial Genomes"
Supervisor: Prof KANEHISA, Minoru
26 November 2007

MONGUCHI, Daiki
D Pharm Sc, Kyoto University
"Studies on Intramolecurar Conjugate Addition Based on Memory of Chirality"
Supervisor: Prof KAWABATA, Takeo
23 March 2007

MORINAGA, Takashi
D Eng, Kyoto University
"Synthesis and Applications of Silica Particles Grafted with Concentrated Polymer Brush"
Supervisor: Prof FUKUDA, Takeshi
23 March 2007

NAKAMURA, Shu
D Sc, Kyoto University
"Real-Time Time-of-Flight Measurement of Proton Beam Produced by an Intense Short-Pulse Laser"
Supervisor: Prof NODA, Akira
23 March 2007

OH, Mina
D Pharm Sc, Kyoto University
"Prediction of Biodegradation Pathways Using Knowledge Base of Enzymatic Reactions"
Supervisor: Prof KANEHISA, Minoru
23 March 2007

OKUDA, Shujiro
D Sc, Kyoto University
"Characterization of Relationships between Transcriptional Units and Operon Structures"
Supervisor: Prof KANEHISA, Minoru
23 May 2007

OOHASHI, Hirofumi
D Sc, Kyoto University
"Au Lβ X-ray Satellites from Multi-hole States"
Supervisor: Assoc Prof ITO, Yoshiaki
23 March 2007

SATO, Tetsuya
D Sc, Kyoto University
"Analysis of Protein-Protein Interactions by Using Co-Evolutionary Information"
Supervisor: Prof KANEHISA, Minoru
23 March 2007

SHIRAI, Toshiyuki
D Sc, Kyoto University
"One-dimensional Beam Ordering of Protons at Ion Storage Ring, S-LSR"
Supervisor: Prof NODA, Akira
23 July 2007

TANIGUCHI, Masatoshi
D Sc, Kyoto University
"ARR1 Directly Activates Cytokinin Response Genes that Encode Proteins with Diverse Regulatory Functions"
Supervisor: Prof OKA, Atsuhiro
23 March 2007

TANIMA, Daisuke
D Pharm Sc, Kyoto University
"Development of Phenolphthalein-Based Functional Molecules"
Supervisor: Prof KAWABATA, Takeo
23 March 2007

YAMAZAKI, Daisuke
D Eng, Kyoto University
"Structural and Mechanistic Studies on Cyclic π-Conjugated Systems Annelated with Bicyclo[2.2.2]octane Units"
Supervisor: Prof OZAWA, Fumiyuki
23 March 2007

YOSHIZAWA, Akiyasu
D Sc, Kyoto University
"Extracting Sequence Motifs and the Phylogenetic Features of SNARE-dependent Membrane Traffic"
Supervisor: Prof KANEHISA, Minoru
23 May 2007

THE 107TH ICR ANNUAL SYMPOSIUM

SEMINARS

MEETINGS AND SYMPOSIA

THE 107TH ICR ANNUAL SYMPOSIUM

(7 December 2007)

ORAL PRESENTATIONS

MASUBUCHI, Yuichi (Molecular Rheology)
"Molecular Rheology of Polymers"

SHIRAI, Toshiyuki, et al. (Particle Beam Science)
"One-dimensional Ordering of Proton Beam in the Storage Ring"

HIRATAKE, Jun (Chemistry of Molecular Biocatalysts)
"Molecular Design and Applications of γ-Glutamyl Transpeptidase (GGT) Inhibitors as Chemical Probes to Understand the Physiological Roles of GGT"

KAMISUKI, Shinji, et al. (Chemical Biology)
"A Small Molecule That Blocks Fat Synthesis"

SATO, Naoki (Molecular Aggregation Analysis)
"Studies on Correlation among Structure, Electronic Structure and Properties of Organic Thin Films"

– ICR Award for Young Scientists –
OHNO, Kohji (Chemistry of Polymer Materials)
"A New Family of Colloidal Crystal Constructed by Concentrated Polymer Brush-afforded Fine Particles"

HATAKEYAMA, Takuji (Organic Main Group Chemistry)
"Iron-Catalyzed Selective Biaryl Coupling: Remarkable Suppression of Homocoupling by the Fluoride Anion"

– ICR Award for Graduate Students –
MURAMATSU, Wataru (Synthetic Organic Chemistry)
"A Catalytic One-Step Process for the Chemo-and Regioselective Acylation of Monosaccharides"

– ICR Grants for Young Scientists –
KOBAYASHI, Kensuke (Nanospintronics)
"Development of Magnetic Switch Devices by Using FePt Nanoparticles"

MIHARA, Hisaaki (Molecular Microbial Science)
"Construction of Novel Functional Molecules by Hybridization of Transition Metal Clusters with Biomolecules"

KATO, Utako (Supramolecular Biology)
"Regulation of Cell Polarity in Static Magnetic Fields"

AZUMA, Masaki (Advanced Inorganic Synthesis)
"Search for New Lead-free Ferroelectric Piezoelectric Materials by Means of First Principle Calculations and High-pressure Synthesis"

POSTER PRESENTATIONS

LW : Laboratory Whole Presentation
LT : Laboratory Topic
GE : General Presentation

— Organoelement Chemistry —

LW "Synthesis and Properties of Novel Organic Compounds Containing Heavier Elements"

GE KAWAI, Masahiro; SASAMORI, Takahiro; TOKITOH, Norihiro
"Syntheis of Stable Platinum Complexes Bearing Overcrowded Primary Phosphine Ligands and Its Deprotonation Reaction"

GE YUASA, Akihiro; SASAMORI, Takahiro; TOKITOH, Norihiro
"Synthesis and Structure of the First Stable 1,2-Diferrocenyldisilene"

GE TANABE, Taro; MIZUHATA, Yoshiyuki; TOKITOH, Norihiro
"Syntheses of Silanedichalcogenolato Complexes Utilizing Stable Silanedichalcogenols and Elucidation of Their Structures and Reactivities"

GE OZAKI, Shuhei; SASAMORI, Takahiro; TOKITOH, Norihiro
"Synthesis and Properties of a Kinetically Stabilized 1-Hydrosilene and Its Unique [6+6]-Dimerization"

— Structural Organic Chemistry —

LT MURATA, Michihisa; OCHI, Yuta; TANABE, Fumiyuki; KOMATSU, Koichi; MURATA, Yasujiro
"NMR Studies of Dianions of Fullerene C_{60} and Its Cage-Opened Derivatives Encapsulating Molecular Hydrogen"

GE KATO, Keisuke; MURATA, Michihisa; KOMATSU, Koichi; MURATA, Yasujiro
"Synthesis and Properties of Novel Open-Cage Fullerenes Having a Lactone Group"

GE KUROTOBI, Kei; MURATA, Michihisa; MURATA, Yasujiro
"The Reaction and Property of Open-cage C_{60} Having an 8-membered-ring Orifice"

— Synthetic Organic Chemistry —

GE WATANABE, Toshihide; KAWABATA, Takeo
"Asymmetric Aldol Reaction via Memory of Chirality: Synthesis of β-hydroxy-α-amino Acids with a Tetrasubstituted Carbon Center"

GE KAN, Keizo; SHIBATA, Takeshi; KAWABATA, Takeo
"Asymmetric Lactonization with C_2-Symmetric Chiral Nucleophilic Catalysts"

— Advanced Inorganic Synthesis —

LW "Recent Research Topics from Advanced Inorganic Synthesis"

GE NISHIMURA, Kousuke; AZUMA, Masaki; TAKANO, Mikio; SHIMAKAWA, Yuichi
"Synthesis and Physical Properties of Double Perovskite PPb_2FeReO_6"

GE TENG, Yonghong; AZUMA, Masaki; SHIMAKAWA, Yuichi
"Size-controlled Synthesis of Transition Metal Oxides Particles and Their Catalytic Activity"

— Chemistry of Polymer Materials —

LT GOTO, Atsushi; HIRAI, Norihiro; WAKADA, Tsutomu; FUKUDA, Takeshi; TSUJII, Yoshinobu
"A New Class of Living Radical Polymerizations with Non-Transition Metal Catalysts—Reversible Chain Transfer Catalyzed Polymerization (RTCP)"

GE OKAYASU, Kenji; NOMURA, Akihiro; KURAMOTO, Mamoru; OHNO, Kohji; FUKUDA, Takeshi; TSUJII, Yoshinobu
"Tribological Properties of Concentrated Polymer Brushes"

GE MA, Ying; OHNO, Kohji; FUKUDA, Takeshi; TSUJII, Yoshinobu
"Living Radical Polymerization of Phenylboronic Acid-Carrying Monomer"

— Polymer Controlled Synthesis —

GE HAMANO, Tsubasa; TOSAKA, Masatoshi; TSUJI, Masaki; YAMAGO, Shigeru
"Formation of Stacked-lamella-like Structure in Aromatic Polyester Nanofibers"

GE KAYAHARA, Eiichi; YAMAGO, Shigeru
"Precision Control of Living Radical Polymerization by Using Organobismuthine Co-catalyst"

— Inorganic Photonics Materials —

LW "Research Activity at Inorganic Photonics Materials"

GE UEMURA, Koji; TAKAHASHI, Masahide; TOKUDA, Yomei; YOKO, Toshinobu
"Photopolymerisation-Initiated Formation of Ordered Microstructure in Oxide Thin Films from Photo Monomer-Oxide Precursor System"

GE YAMAMOTO, Hideaki; TOKUDA, Yomei; TAKAHASHI, Masahide; YOKO, Toshinobu
"Fundamental Studies on the Organic-inorganic Hybrid Glass Prepared through Two Phase Solution Treatment"

— Nanospintronics —

GE TANIGAWA, Hironobu; KONDOU, Kouta; KASAI, Shinya; ONO, Teruo
"Domain Wall Motion Induced by a Pulsed-current under an External Magnetic Field"

GE KONDOU, Kouta; TANIGAWA, Hironobu; KASAI, Shinya; OHSHIMA, Norikazu; NAKATANI, Yoshinobu; KOBAYASHI, Kensuke; ONO, Teruo
"Dynamics of a Magnetic Domain Wall in Submicron Magnetic Wires"

GE TAMADA, Yoshinori; INOUE, Takanori; YAMAMOTO, Shinpei; TAKANO, Mikio; NASU, Saburou; ONO, Teruo
"Mossbauer Spectroscopy of Easy-axis Aligned $L1_0$-FePt Nanoparticles"

GE NAKAMURA, Shuji; HASHISAKA, Masayuki; YAMAUCHI, Yoshiaki; KASAI, Shinya; KOBAYASHI, Kensuke; ONO, Teruo
"Measurement of Conductance in Quantum Point Contacts at Low Temperature"

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LT KOBAYASHI, Sachiko; NAKASE, Ikuhiko; FUTAKI, Shiroh
"Internalization of Protein by the pH-sensitive Peptide in the Presence of Cationic Lipids"

GE NOSHIRO, Daisuke; ASAMI, Koji; FUTAKI, Shiroh
"Metal-assisted Stabilization of the His-containing Alamethicin Derivative Assembly"

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GE TAKEUCHI, Yoshinori; LIZ, Tai; MIZUTANI, Masaharu; SIMIZU, Bun-ichi; HIRATAKE, Jun
"Chemical Tools to Inhibit Auxin Inactivation—Design, Synthesis and *in vivo* Activities of IAA-amino Acid Conjugate Synthetases (GH3)—"

GE KAI, Kosuke; YAMAMOTO, Ryotaro; KAWAMURA, Naohiro; MIZUTANI, Masaharu; SAKATA, Kanzo; SHIMIZU, Bun-ichi
"*Ortho*-hydroxylation of Cinnamate Unit and Coumarin Biosynthesis in Plants"

GE NAKAJIMA, Mado; HAN, Riyou; HIRATAKE, Jun
"Substrate Recognition of γ-glutamyl Transpeptidase Probed by Using Transition-state Analogue Inhibitors"

— Molecular Biology —

LT KUSANO, Hiroaki; TESTERINK, Christa; VERMEER, Joop E M; YASUDA, Keiko; TSUGE, Tomohiko; SHIMADA, Hiroaki; OKA, Atsuhiro; MUNNIK, Teun; AOYAMA, Takashi
"The *Arabidopsis* Phosphatidylinositol Phosphate 5-kinase PIP5K3 Is a Key Regulator for Root Hair Tip Growth"

LT TANIGUCHI, Yukimi; AOYAMA, Takashi; OKA, Atsuhiro
"Functional Analysis of AtPLDξ2"

— Chemical Biology —

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LT KUSAKA, Masafumi; QING, Luo; KANIE, Yasumasa; IWATA, Daiki; HIRAI, Asako; HORII, Fumitaka
"Surface High Resolution NMR - Observations of the Surface Structure of Different Polymer Materials and Their Mechanisms"

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"Molecular and Electronic Structure Analyses of TPD, a Hole Transport Material in Organic LEDs"

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"Liquid Crystal Formation in Aqueous Suspensions of Bacterial Cellulose Microfibrils and Effects of Added Electrolytes on Phase Behavior of the Suspensions"

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LT NORISUYE, Kazuhiro; MINAMI, Tomoharu; NAKATSUKA, Seiji; SOHRIN, Yoshiki; FIRDAUS, Mochamad Lutfi
"Method for Determination of Trace Elements in Seawater and Its Application to Observation of Their Distributions in the Oceans"

GE NAKAGAWA, Yusuke; FIRDAUS, Mochamad Lutfi; NORISUYE, Kazuhiro; SOHRIN, Yoshiki
"Development of Chelate Resin Column Preconcentration Method for Precise Isotope Analysis of Mo in Seawater"

— Solution and Interface Chemistry —

LT YASAKA, Yoshiro
"Slowdown of H/D Exchange Reaction Rate and Water Dynamics in Ionic Liquid: Deactivation of Solitary Water Solvated by Small Anions in 1-Butyl-3-Methylimidazolium Chloride"

GE YOSHIDA, Ken; MATUBAYASI, Nobuyuki; NAKAHARA, Masaru
"High-temperature NMR and MD Simulation Study on the Self-diffusion and Rotation in Supercritical Water in Relation to the Solvation Shell State and Lifetime"

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LT KAWAMOTO, Jun; KURIHARA, Tatsuo; ESAKI, Nobuyoshi
"Physiological Role of Eicosapentaenoic Acid in High-pressure Adaptation of *Shewanella violacea* DSS12"

LT ZHANG, Wanjiao; MIHARA, Hisaaki; KURIHARA, Tatsuo; ESAKI, Nobuyoshi
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— Polymer Materials Science —

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GE TOMOHISA, Hiroshi; MATSUBA, Go; NISHIDA, Koji; KANAYA, Toshiji
"Crystallization Process of Poly(ethylene terephthalate) under Shear Flow"

GE RAHMAN, Nelly; KAWAI, Takahiko; MATSUBA, Go; NISHIDA, Koji; KANAYA, Toshiji
"Effect of Polylactide Stereocomplex Crystallites on Poly(L-Lactic Acid) Crystallization Behavior"

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GE IWASHIGE, Tomohito; MATSUMIYA, Yumi; WATANABE, Hiroshi; INOUE, Tadashi
"Dielectric Relaxation and Dynamics of Poly(lactic acid) in Carbon Dioxide at High Pressure"

GE HORIO, Kazushi; MASUBUCHI, Yuichi; WATANABE, Hiroshi; KHALIULLIN, Renat; SCHIEBER, Jay D
"A Free Energy of Entangled Polymers on Segment Interaction"

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"Rheological and Dielectric Behavior of Dipole-Inverted $(SIS)_p$-Type Multiblock Copolymers"

GE SATO, Hiroki; MASUBUCHI, Yuichi; WATANABE, Hiroshi
"Direct Observation of DNA Dynamics in Suspensions with Various Micro-sphere Concentrations"

GE NAOI, Azusa; MASUBUCHI, Yuichi; WATANABE, Hiroshi; TSUKAHARA, Noboru; KOJIMA, Yuya; YOSHIKAWA, Hideo; TATSUMI, Masanori
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"Contribution of Electronic Polarization to Lattice Energies and Permittivities of Organic Molecular Crystals"

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"Death of Biological Cells Monitored by Dielectric Spectroscopy"

— Supramolecular Biology —

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GE KATO, Utako
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LT IKEGAMI, Masahiro; NODA, Akira; IWASHITA, Yoshihisa; SHIRAI, Toshiyuki; SOUDA, Hikaru; TAJIMA, Yujiro; TONGU, Hiromu; TANABE, Mikio; DAIDO, Hiroyuki
"Quality Improvement of Laser Produced Proton Beam by Synchronous RF Field"

GE SOUDA, Hikaru; TANABE, Mikio; ISHIKAWA, Takehiro; NAKAO, Masao; IKEGAMI, Masahiro; TONGU, Hiromu; SHIRAI, Toshiyuki; NODA, Akira
"Laser Cooling of Mg^+ Beam at Storage Ring S-LSR"

— Laser Matter Interaction Science —

GE HASHIDA, Masaki; MISHIMA, Hidehiko; TOKITA, Shigeki; MASUNO, Shinichro; NAMBA, Shin; SAKABE, Shuji
"Femtosecond Laser Ablation of Polytetrafluoroethylene"

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LT ISOJIMA, Seiichi; KURATA, Hiroki; CHOU, Li-Jen; ISODA, Seiji
"LAADF Observation of Iron Oxide Nanowire"

— Structural Molecular Biology —

GE TOCHIO, Tatsunori; OHASHI, Hirofumi; HORIGUCHI, Daisuke; SAKAKURA, Shusuke; ITO, Yoshiaki; FUKUSHIMA, Sei; SHOJI, Takashi
"Quantitative Chemical Analysis of Cr Compounds Using Cr Kα Emission Lines"

GE IDE, Junko; HANDA, Katsumi; TOCHIO, Tatsunori; ITO, Yoshiaki
"Chemical State Analysis of Si in Menerals Using X-ray Spectroscopy"

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GE ITOH, Takuma; ITO, Shingo; NAKAMURA, Eiichi; NAKAMURA, Masaharu
"Iron-Catalyzed Asymmetric Carbozincation of Oxabicyclic Alkenes"

GE KONDO, Yoshiyuki; HATAKEYAMA, Takuji; FUJIWARA, Yuichi; ITO, Shingo; NAKAMURA, Eiichi; NAKAMURA, Masaharu
"Polyfluoroarylation of Haloalkanes via the Selective Iron-Catalyzed Cross-Coupling"

GE YOSHIMOTO, Yuya; HATAKEYAMA, Takuji; TOMA, Gabriel; NAKAMURA, Masaharu
"Iron-Catalyzed Eneyne Cross-Coupling Reaction"

— Organotransition Metal Chemistry —

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GE TAKADA, Yuko; JENSEN, Rader S; TAKITA, Ryo; OKAZAKI, Masaaki; OZAWA, Fumiyuki
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GE HASHIMOTO, Kosuke
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LT SHIGA, Motoki; TAKIGAWA, Ichigaku; MAMITSUKA, Hiroshi
"A New Method for Clustering Genes by Optimally Combining Expression Data with a Modular Gene Network"

— Research Center for Low Temperature and Materials Sciences —

LT TERASHIMA, Takahito; SHISHIDO, Hiroaki; IZAKI, Manabu; KATO, Tomonari; SHIBAUCHI, Takasada; MATSUDA, Yuji
"Preparation and Characterization of Two-dimensional Heavy-Fermion Superlattices"

SEMINARS

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Graduate School of Engineering, Kyoto University, Kyoto, Japan
"Nanosecond Dynamics of Concentrated Polymer Brush"
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Department of Biochemistry Cell and Molecular Biology, The University of Tennessee, Knoxville, USA
"Translational Research in *Arabidopsis*: Close Encounters of the Complex Kind"
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"Hydrazine, Hydrazine Radical Cation Electron Transfer"
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"The World of Colloidal Crystals"
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Department of Chemistry,University of Florida, USA
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Center for Plant Molecular Biology, Developmental Genetics Department, University of Tübingen, Tübingen, Germany
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"Total Synthesis Exploiting Anion Relay Chemistry (ARC)"
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The State Key Laboratory of Rare Earth Materials Chemistry and Applications, College of Chemistry and Molecular Engineering, Peking University, China, P. R.
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"Cross-Coupling Reactions of Organoboron Compounds"
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Department of Bioengineering, Nagaoka University of Technology, Niigata, Japan
"Researches in ICR"
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Institute for Materials Chemistry and Engineering, Kyusyu University, Fukuoka, Japan
"Structure and Dynamics of Network System Formed by Transient Crosslinks"
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University of Maryland, USA
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Department of Chemistry, Tohoku University, Sendai, Japan
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Department of Physical Chemistry II, Ruhr-University Bochum, Germany
"Structure and Dynamics of Ionic Liquids as Seen by Microwave Dielectric Spectroscopy"
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Berliner Elektronenspeicherring-Gesellschaft für Synchrotronstrahlung m.b.H. (BESSY), Berlin, Germany
"Coherent THz Generation at the BESSY II and MLS Storage Rings"
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Graduate School of Natural Science and Technology, Kanazawa University, Ishikawa, Japan
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Merck Research Insitute, USA
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Graduate School of Science and Engineering, Kinki University, Osaka, Japan
"Basis and Element Technology of Fiber Lasers, I"
14 June 2007
"Basis and Element Technology of Fiber Lasers, II"
9 July 2007

Dr ZORN, Reiner
Institut für Festkörperforschung, Forschungszentrum Jülich, Germany
"What Neutron Scattering Can Tell Us about Nanoscopically Confined Liquids and Polymers"
18 September 2007

MEETINGS AND SYMPOSIA

The 2nd Symposium on Joint Project of Chemical Synthesis Core Research Institutions
"Chemical Synthesis toward Creation of Functional Materials"
Organized by OZAWA, Fumiyuki
15–16 January 2007 (Kyoto, Japan)

The 2nd International Workshop for Far East Asian Young Rheologists
Organized by WATANABE, Hiroshi (Kyoto University); SAKURAI, Shinichi (Kyoto Institute of Technology); AHN, Kyung Hyun (Seoul National University); YU, Wei (Shanghai Jiao Tong University)
26–28 January 2007 (Kyoto, Japan)

Mini-workshop on Ion Beam Cooling/Low Energy Storage Ring and Related Topics
Organized by NODA, Akira
13–14 February 2007 (Kyoto, Japan)

The Pharmaceutical Society of Japan 127th Annual Meeting
"Drug Discovery Driven by Chemical Biology"
Organized by UESUGI, Motonari
28–30 March 2007 (Toyama, Japan)

ICR Mini Workshop
"Phase Separation in Thin Films of Polymer Blends"
Organized by KANAYA, Toshiji
3 April 2007 (Kyoto Japan)

The ICR International Symposium 2007 (ICRIS'07)
"The Science and Technology of Well-Controlled Polymer Assemblies"
Organized by FUKUDA, Takeshi
11–13 June 2007 (Kyoto, Japan)

Oral Presentations
Prof BUBACK, Michael
Institute for Physical Chemistry, University of Goettingen, Germany
"Pulsed Laser Experiments for Detailed Studies into Free-Radical Polymerization Kinetics"

Prof YAMAGO, Shigeru
Institute for Chemical Research, Kyoto University, Kyoto, Japan
"Recent Advances in Organoheteroatom-Mediated Living Radical Polymerization"

Prof YUSA, Shin-ichi
Graduate School of Engineering, University of Hyogo, Hyogo, Japan
"Thermo-responsive Diblock Copolymers Synthesized via Organotellurium-mediated Controlled Radical Polymerization (TERP)"

Prof ASANDEI, D. Alexandru
Institute of Materials Science and Department of Chemistry, University of Connecticut, USA
"Complex Polymer Synthesis by Late and Early Transition Metal Catalyzed Living Radical and Ring Opening Polymerizations"

Prof FUKUDA, Takeshi
Institute for Chemical Research, Kyoto University, Kyoto, Japan
"New Development of Concentrated Polymer Brushes"

Prof ZHAO, Bin
Department of Chemistry, University of Tennessee, USA
"Synthesis and Nanoscale Phase Separation of Well-defined Mixed Homopolymer Brushes on Silica Particles"

Prof KIMURA, Tsunehisa
Department of Forest and Biomaterials Science, Kyoto University, Kyoto, Japan
"Magnetic Alignment and Patterning of Feeble Magnetic Materials"

Prof TANIGUCHI, Takashi
Department of Polymer Science and Engineering, Yamagata University, Yamagata, Japan
"Orientation Dynamics of Lamellae of Block Copolymer under an Electric Field"

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