Message from ICPAC 2018 Chairman

The International Congress on Pure & Applied Chemistry, or ICPAC 2018, is a joint effort of Institut Kimia Malaysia (IKM) and the Cambodian Chemical Society (CCV) with the collaboration and support of Asia Chem Corporation (ACC) and Foundation for Interaction between Science and Technology (FIST) Japan. This is the second time that IKM and CCS have worked together, the first being the Cambodia Malaysia International Chemical Conference (CMICCC) in 2012 in Siem Reap, Cambodia. CMICCC is so successful that we decide to organise ICPAC 2018 in the same place, Siem Reap, Cambodia.

The main objective of ICPAC 2018 is to promote the advancement of chemical sciences, especially in Asia. With the theme, “Chemistry for Fourth Industrial Revolution and Beyond”, we are looking at how chemistry and chemical research can contribute further to the socio-economic transformation of the world population. We are very fortunate to have a large group of top Japanese and European scientists participating in ICPAC 2018 to share their knowledge, skill and expertise. We hope that ICPAC 2018 will also promote research collaboration and networking among the scientists from various countries taking part in ICPAC 2018. This will augur well for the advancement of chemical sciences in this part of the world.

As Co-Chair of ICPAC 2018 Organising Committee, I would like to record my sincere appreciation to all the participants of ICPAC 2018 including the Plenary Speakers, Keynote and Invited Lecturers. Your active participation has definitely contributed to the success of ICPAC 2018. I must also thank my Co-Chair, Dr Sieng Huy, and members of the ICPAC 2018 Organising Committee including IKM/ICPAC Secretariat staff for their hard work in putting ICPAC 2018 together. I must especially convey my sincere gratitude and appreciation to Prof Tamotsu Takahashi for his effort in bringing such a big group of top Japanese and overseas scientists to participate in ICPAC 2018. This has contributed to a big success of ICPAC 2018.

I hope that you have good deliberation and exchange of ideas at ICPAC 2018. I am sure that ICPAC 2018 will be an excellent scientific meeting and wonderful experience for all. Also don’t forget to visit Angkor Wat, the world renown historical site of the Khmer Empire.

Best wishes.

Soon Ting Kueh
Chairman, ICPAC 2018 Organising Committee
Date: 28th February 2018
Message from Executive Director
Cambodian Chemical Society (CCS)

On behalf of Cambodian Chemical Society (CCS) and on behalf of the Conference co-organizer, I would like to warmly welcome all of you to the International Congress on Pure & Applied Chemistry (ICPAC) 2018, which will be held on 07-10 March 2018 at Sokhalay Angkor Resort & Spa, Siem Reap, Cambodia.

This ICPAC is a jointly organizing by The Institut Kimia Malaysia (IKM) and the Cambodian Chemical Society (CCS), together with the Foundation for Interaction between Science and Technology (FIST) Japan and Asia Chem Corporation (ACC) Japan.

This is the second time that Cambodian Chemical Society (CCS) has had honor to cooperate with the Institut Kimia Malaysia (IKM). I would like to sincerely thank and appreciate very much to the Institut Kimia Malaysia (IKM) for giving us the opportunity to work together for a closer collaboration and networking, especially, I would like to record our sincere appreciation to Datuk Dr. Soon Ting Kueh, former President of Institut Kimia Malaysia (IKM) and Prof. Dr. Tamotsu TAKAHASHI, President of Foundation for Interaction between Science and Technology (FIST) Japan for their greatness support for ICPAC 2018 happened. I would also like to thank the Royal Academy of Cambodia (RAC) and Asia Chem Corporation (ACC) Japan for their support and endorsement.

I would like to thank all the participants for attending our international conference and bringing your expertise to our forum and sharing.

Special thanks go to the all organizing Committee staffs, and student volunteers without whom this conference would not have been possible. We look forward to thought-provoking discussions that will effect meaningful change.

My personal respect and thanks goes out to all of you and wish you all by having a fruitful and rewarding deliberation at ICPAC 2018 and memorable time in Cambodia.

Sincerely yours,

Dr. SIENG Huy
Executive Director
Cambodian Chemical Society (CCS)
Message from IKM President

On behalf of the Institut Kimia Malaysia (IKM), I would like to extend a very warm welcome to all the participants to the International Congress on Pure & Applied Chemistry 2018 (ICPAC 2018), which is jointly organised by the Institut Kimia Malaysia (IKM) and the Cambodian Chemical Society (CCS) with the collaboration and strong support of Asia Chemical Corporation (ACC) and Foundation for Interaction between Science and Technology (FIST) Japan.

IKM, through the spirit of ASEAN and the established ASEAN Economic Community (AEC) in 2015, has since organised International Chemical Congress in Cambodia and Vietnam jointly with the respective National Chemical Society. Through this collaboration, we hope to stimulate a free flow of research ideas and collaboration among our ASEAN chemists and to create an equitable economic development in Chemical industry and services in the region. Hopefully, this second collaboration of IKM and CCS will help to achieve this target.

As we move towards the era of Industry 4.0, we need to learn from experts from developed nations. We are not only aiming at “Chemistry for Fourth Industrial Revolution and Beyond”, which is the theme of our conference, we also want to implement digital transformation in our chemical laboratories. We are fortunate to have experts and top scientists from Japan, Europe and other developed and developing nations among the participants, whom we can look up to for advice. They will be able to show us how to integrate and standardise laboratory data in a digital laboratory, and to leverage the Internet of Things (IoT) for the laboratory, besides sharing their knowledge in their respective disciplines.

I must once again record my appreciation to the President and the council members of the Chemical Society of Cambodia, the Asian Chemical Corporation, Foundation for Interaction between Science and Technology (FIST) Japan, especially Prof Tamotsu Takahashi, for without their support, encouragement and commitment, the organisation of ICPAC 2018 will not materialise.

I would also like to thank the Chairman of ICPAC 2018 organising committee Datuk Dr Soon Ting Kueh, his Co-Chair, Dr Sieng Huy and members of organising committee, supported by the IKM/ICPAC Secretariat staff for the excellent effort in organising the conference. They have through their hard work attracted a vast pool of speakers with enviable experience and international fame. To all the Plenary Speakers, Keynote and invited lecturers, thank you for your contributions and your willingness to share with us your research findings.

I am confident that with the active deliberations and exchange of ideas among the esteem speakers and participants, we will have a successful ICPAC 2018. Thank you.

Dato Dr Ong Eng Long
President, Institut Kimia Malaysia
Advisor: Dato’ Dr. Ong Eng Long (IKM)
               Dr. Neth Barom (CCS)
Chairman:   Datuk Dr. Soon Ting Kueh (IKM)
Co-Chairman: Dr. Sieng Huy (CCS)
Vice-Chairman: Dato’ Chang Eng Thuan
Secretary:  Assoc. Prof. Dr. Juan Joon Ching (IKM)
Co-Secretary: Dr. Sotha Chek (CCS)
Treasurer:  Assoc. Prof. Dr. Chan Chin Han
Committee: Datuk Haji Ismail Bin Talib (IKM)
               Mr. Chang Hon Fong (IKM)
               Prof. Datin Dr. Zuriati Zakaria (IKM)
               Dr. Malarvili Ramalingam (IKM)
               Assoc. Prof. Dr. Sharon Teh Geok Bee (IKM)
               Prof. Dr. Mansor Ahmad (IKM)
               Dr. Jenny Lee Nyuk Len (IKM)
               Dr. It Putherary (CCS)
               Mr. Heng Savouen (CCS)
               Mrs. Mey Sovuthy (CCS)
               Dr. Phan Kong Kea (CCS)
               Mr. Khin Bora (CCS)
               Dr. Eap Bunna (CCS)
Message from Minister of Education, Youth and Sport (MoEYS), Cambodia

On behalf of the Ministry and myself, I would like to cordially welcome you all to the International Congress on Pure and Applied Chemistry (ICPAC) 2018 jointly organized by the Cambodian Chemical Society (CCS), the Institut Kimia Malaysia (IKM), the Foundation for Interaction between Science and Technology (FIST), and the Asia Chem Corporation Japan (ACC-Japan) from 07th-10th March 2018 in our Kingdom of Wonder, Cambodia. On its fundamental theme “Chemistry for Sustainable Development Goals 2030”, this ICPAC 2018 marks an auspicious occasion for all prominent and young scientists, researchers, academics and students, scholars, practitioners, and key actors of the government agencies, academic communities, research institutions, development partners, private industries, and civil society organizations including science and technology relevant societies and innovation-based bodies to meet up, share and exchange knowledge, experiences, skills, and especially, our progresses towards sustainable development through pure and applied chemistry.

It is my earnest hope that, through our concerted endeavors, we will be able to sharpen the fortunes and prosperities of our nations, regions, and the globe using the advantages of Science, Technology and Innovation (STI). Our existing national and regional STEM and STI policies and strategies aim at providing impactful frameworks for stimulating innovation in the economy and the society without compromising sustained, inclusive and equitable growth. We all are here with either our firm mandate or ultimate intention to promote STEM and STI application in our societies, particularly through practices in chemistry and chemistry-embedded fields, and to generate conditions and enabling environment for chemistry-supported innovations and sustainable development to genuinely occur and matter for good.

While we are moving forward with confidence and progress in chemistry-related theory generation and application in pursuit of sustainable multi-sectoral progression, featuring our finest research practices in pure and applied chemistry, this ICPAC 2018 presents an opportunity for us to rededicate ourselves to contribute to the realization of our national and global sustainable development goals as well as millennium development goals through STEM and STI. With no doubt, this crucial event will generate not only research papers, but also provide a platform for interactive and proactive learning, sharing and partnership building, and especially, new scientific findings will be mainstreamed into future policy and planning for the betterment of our society and the environment.

I thank the co-organizing committee, sponsoring bodies, scientists, scholars, researchers, students and all participants for supporting and making this ICPAC 2018 come into existence. You and your scientific communities deserve my wholehearted appreciation and veneration. Let me congratulate you all and wish this event productive and successful to its mission and goal.

Sincerely yours,

H.E. Academician Hang Chuon Naron
Minister of MoEYS
ICPAC 2018 Opening Ceremony

Wednesday, 7th March 2018
Sokhalay Angkor Resort & Spa, Siem Reap, Cambodia

Programme

0830   Arrival of ICPAC 2018 Delegates & Invited Guests

0845   Arrival of Guest of Honour
        H.E. Mr Youk Ngoy
        Vice Minister
        Representative of H.E. Academician Dr Hang Chuon Naron, Minister of Education, Youth and Sport, Cambodia

0900   Opening Ceremony

        Welcome Address
        Datuk Dr Soon Ting Kueh
        Chairman, ICPAC 2018 Organising Committee

        Address
        Dr Neth Barom
        President, Cambodian Chemical Society

        Address
        Dato’ Dr Ong Eng Long
        President, Institut Kimia Malaysia

        Opening Address
        H.E. Mr Yok Ngoy
        Vice Minister
        Representative of H.E. Academician Dr Hang Chuon Naron, Minister of Education, Youth and Sport, Cambodia

        Presentation of Souvenirs

1000   End of Opening Ceremony / Refreshments
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<td>1030 – 1245</td>
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<td>Malaysian Institute of Chemistry, Malaysia</td>
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<td>Chairman II: Dr Neth Barom</td>
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<td></td>
<td>Title: Adventures with Catalytic [2+2+2]Cyclotrimerizations: Synthesis and Application of Various Aromatic compounds</td>
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<td></td>
<td>Professor Kotora Martin</td>
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<td>Charles University in Prague, Czech Republic</td>
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<td>Plenary Lecture 2: Award Lecture</td>
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<td></td>
<td>Title: Phosphoroselenoic Acid Derivatives with a Binaphthyloxy Group as Chiral Molecular Tools</td>
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<td>Professor Toshiaki Murai</td>
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<td>Plenary Lecture 3:</td>
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<td>Title: Synthesis of Sequence-Controlled Terpolymer directed by Self-Sorting Behaviors</td>
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<td>Professor Takeharu Haino</td>
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ICPAC 2018 – Full Programme

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**Saturday, March 10, 2018**

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<td><strong>Refreshments</strong></td>
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<td>1630</td>
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Martin Kotora obtained his MsC degree in 1986 from Charles University in Prague under the supervision of Vladimir Sváta and a PhD degree in 1991 from the Institute of Chemical Process Fundamentals, the Czech Academy of Sciences under the supervision of Milan Hájek. Then he carried out postdoctoral work with Tamotsu Takahashi (1993-1995) at the Institute for Molecular Science (Okazaki, Japan) as a JSPS fellow and later with Ei-ichi Negishi at Purdue University (Indiana, USA). In 1996 he joined the faculty at the Catalysis Research Center, Hokkaido University (Sapporo, Japan) in the rank of associate professor. In autumn 2000 he joined the faculty of Charles University in Prague as an assistant professor of chemistry and subsequently was promoted to rank of associate professor (2003) and full professor (2006). In 2013 he received Rudolf Lukeš Prize for Achievements in Organic Chemistry from the Czech Chemical Society. His group’s research interests are centered around transition metal complex catalyzed or mediated reactions (e.g. cyclotrimerization, cycloisomerization, the C-C bond activation), enantioselective organocatalysis, and Dewar benzenes. The essential part of these endeavors also include applications of the above mentioned methodologies on syntheses of natural and biologically active compounds. Recently his current interests have also focused on development of new approaches to various complex polyaromatic hydrocarbon molecules. He has authored and co-authored over 160 publications.
Adventures with Catalytic [2+2+2]Cycotrimerizations: Synthesis and Application of Various Aromatic compounds

Martin Kotora*
Department of Organic Chemistry, Faculty of Science, Charles University, Hlavova 8, 128 43 Prague, Czech Republic
*Corresponding author: martin.kotora@natur.cuni.cz

Abstract

Benzene and pyridine rings can be efficiently accessed by using catalytic [2+2+2]cyclotrimerization of alkynes or alkynes with nitriles. In this respect the proper choice of a transition metal based catalysts depends on specific decoration of the reacting substrates (alkynes and nitriles). In a similar manner, aromatic rings could be accessed by using the C-C or C-H bond cleavage. Combination of these methods allows synthesis of complex aromatic compounds with designed substitution.

In the last 15 years we have used alkyne and nitrile cyclotrimerization processes in syntheses of many aromatic compounds and their application spans across areas of biologically active compounds (arylated steroids), new types of ligands (chiral bipyridines), organocatalysts (N,N'-dioxides), and potential application in material science (fluorenes and indenofluorenes). Hence cyclotrimerization and related reactions as well as their combination offer almost endless possibilities for synthesis of plethora of aromatic compounds that can application in various branches of chemistry.

Keywords: catalysis, cyclotrimerization, alkynes, nitriles, aromatic compounds

References
Plenary Lecture 2

Award Lecture

Professor Dr Toshiaki Murai
Gifu University, Japan

Name: Murai, Toshiaki
Date of Birth: 23 December 1957
Present address: Department of Chemistry, Faculty of Engineering, Gifu University, Yanagido, Gifu 501-1193, Japan
E-mail: mtoshi@gifu-u.ac.jp

Education:
1976-1980 Department of Petroleum Chemistry, Faculty of Engineering, Osaka University Awarded the degree of B.Sc. in Chemistry
1980-1982 Department of Petroleum Chemistry, Faculty of Engineering, Osaka University, Awarded the degree of M.Sc in Chemistry
1986 Awarded the degree of Ph.D. in Chemistry. Work supervised by Professor Noboru Sonoda and Shinji Murai

Research and professional experience:
1983-1990 Research Associate at the Department of Chemistry, Gifu University
1986-1988 The postdoctoral fellow at Professor Jonathan L. Sessler group at the Department of Chemistry, University of Texas, Austin
1990-2001 Associate Professor at the Department of Chemistry, Gifu University
2001- Full Professor at the Department of Chemistry, Gifu University
2014- 2016 Section editor of the Chemistry Letters
2016- Vice dean of Faculty of Engineering, Gifu University

Awards: Progress Award in Synthetic Organic Chemistry, Japan (1997, 2)
Gifu Shimbun Grand Prize

Research Interest Synthetic Organic Chemistry, Main Group Chemistry
Phosphoroselenoic Acid Derivatives with a Binaphthyloxy Group as Chiral Molecular Tools

Toshiaki Murai*

Department of Chemistry and Biomolecular Science, Faculty of Engineering, Gifu University, Japan
*Corresponding author: mtoshi@gifu-u.ac.jp

Abstract
Organophosphorus compounds having a binaphthyl group such as BINAPs, phosphoric acids and their derivatives are one of highly powerful tools for asymmetric catalytic reactions. Compounds belonging to these categories can be designed by replacing some of elements in the known compounds with heavier elements, and the designed compounds can also be chiral molecular tools. For example, the replacement of the hydroxyl group (OH) in phosphoric acids with SH or SeH can give rise to the generation of acids with higher acidity. In this regards, we have developed a wide range of synthetic methods for chiral optically active compounds starting from the compounds having a binaphthyloxy group, and P=S or P=Se group.

The reaction of PCl₃, elemental selenium, and binaphthol proceeded smoothly to give phosphoroselenyl chloride in high yields. The chloride is stable under neutral conditions and purified through the column chromatography, whereas it reacts with carbon, nitrogen and oxygen nucleophiles to give the corresponding phosphoroselenoic and phosphonoselenoic acid derivatives. The reaction does not show good diastereoselectivity, but the resulting diastereomers were clearly distinguished through ³¹P and ⁷⁷Se NMR spectra. In contrast, the deprotonation and alkylation of phosphoroselenoic acid esters give the corresponding products with high diastereoselectivity. Fluorinative hydrolysis of phosphorothioic acid esters and hydrolysis of phosphonothioic acid esters also took place with high diastereoselectivity via axis-to-center chirality transfer.

Keywords: chiral molecular tools, phosphoric and phosphonic acid esters, binaphthyloxy groups, axis-to-center chirality transfer, main group chemistry

References
Plenary Lecture 3

Professor Dr Takeharu Haino
Hiroshima University, Japan

Professional Address:
Department of Chemistry, Graduate School of Science, Hiroshima University,
1-3-1 Kagamiyama, Higashi-Hiroshima 739-8526 Japan
Phone: +81-82-424-7427; FAX: +81-82-424-0724
E-mail: haino@hiroshima-u.ac.jp

Education:
1983–1987, B. Sc. (Hiroshima University)
1987-1989, M. Sc. (Hiroshima University)
1989-1992, Ph. D. (Hiroshima University)

Employment:
1992–1993, Postdoctoral Fellow, Sagami Chemical Research Center, Kanagawa, Japan
1993–2000, Research Associate, Department of Chemistry, Faculty of Science, Hiroshima University.
1999–2000, Postdoctoral Fellow, The Scripps Research Institute, La Jolla, CA.
2000–2007, Associate Professor, Department of Chemistry, Graduate School of Science, Hiroshima University
2007–, Professor, Department of Chemistry, Graduate School of Science, Hiroshima University

Honor:
2017 Matsuura Award of an Alumni Association of Chemistry, Hiroshima University
2016 Guest Editor for a Special Issue of Polymer, entitled “Supramolecular Polymer.”
2016 The Award of the Society of Polymer Science, Japan
2009 Visiting Lectureship of the Chemistry Research Promotion Center, Taiwan
2005 Bulletin of the Chemical Society of Japan Award.
2004 Incentive Award in Chugoku-Shikoku Branch of The Society of Synthetic Organic Chemistry.

Research Interests:
Our research interests are mainly in supramolecular chemistry. Supramolecular polymers based on fullerene and porphyrins are recent achievements. Linear and networked fullerene organization in nanospace is developed. Self-standing supramolecular polymer films are fabricated. The helical supramolecular stacks of phenylisoxazolyl systems are also developed, which produce uncommon CPL and CD responses. Chemistry in the confined space of cavitation-based coordination capsules is ongoing projects in our lab. Unique heterodimeric molecular dimers as well as molecular encapsulation are formed in the confined space. Recently, the enatiopure coordination capsule is constructed. Graphene chemistry has started in our lab. We have discovered white-light-emitting graphene nano dots.

Recent Selected Publications:
Synthesis of Sequence-Controlled Terpolymer directed by Self-Sorting Behaviors

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Abstract

Precise manipulation of primary monomer sequence is established in Nature. But, in synthetic polymer sequences, this precision has been hardly given because of the lack of polymerization techniques for conventional polymer synthesis. Thus, the development of the primary monomer sequence in a polymer main chain is a formidable challenge in polymer science. Here, we will report the development of sequence-controlled supramolecular terpolymerization by taking advantage of a self-sorting behavior among three sets of monomers possessing mismatched host-guest pairs. Complementary pairs of biscalix[5]arene-C60, and bisporphyrin-trinitrofluorenone (TNF) have been developed in our lab. To establish the ABC-sequence, one more additional host-guest pair is required; therefore, Hamilton’s bis(acetamido pyridinyl)isophthalamide-barbiturate hydrogen-bonding host-guest complex is used for the self-sorting. These host-guest pairs are separately combined into heteroditopic monomers, which then generate an ABC-sequence-controlled supramolecular terpolymer. The polymeric nature of the supramolecular terpolymer is established both in solution and in the solid state. Our synthetic methodology may pave an avenue for constructing polymers with tailored sequences that are associated with advanced functions.

Keywords: Supramolecular Polymer, Host-Guest Chemistry, Calixarene, Fullerene

References

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Abstract

Electrophilic aromatic substitution of calixarenes is well known procedure for derivatization of the para-positions of macrocyclic skeleton. Recently, we described\textsuperscript{1} an unprecedented regioselectivity of direct mercuration (reaction with mercury(II) trifluoroacetate) leading to the meta-substituted organomercurial products. This unexpected reaction represents the most straightforward way for derivatization of calix[4]arenes in the meta position as documented by meta-arylation\textsuperscript{2} or by the formation of meta-bridged calixarenes.\textsuperscript{3}

Due to their inherent chirality the meta-substituted calixarenes represent very attractive building blocks for construction of chiral receptors.\textsuperscript{4} Moreover, these compounds exhibit very unusual dynamic behaviour in solution as shown by RDC measurements.\textsuperscript{5} The rigid and highly distorted calix[4]arenes bearing single bond bridge possess significantly different chemical behaviour,\textsuperscript{6} demonstrated by their easy cleavage or the rearrangement of basic calixarene skeleton.

Keywords: calix[4]arene, mercuration, inherent chirality, bridged macrocycle.

References


Acknowledgement

This work was supported by Czech Science Foundation (reg. No. 16-13869S).
Natural Products Research: Chemical Synthesis and Ionic Liquid

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Abstract

The lecture highlights recent progress of natural products research in our laboratory. The topics include: 1) chemical synthesis of elastin crosslinker/COPD biomarker desmosines and its application in the clinical samples; 2) novel extraction/isolation techniques of natural products from plant materials utilizing ionic liquids that dissolve cellulose.

Desmosine and isodesmosine are tetrasubstituted pyridinium amino acids and are crosslinking amino acids of elastin. Desmosines are expected as useful biomarkers of chronic obstructive pulmonary disease (COPD), which is the fourth leading cause of death worldwide. In this study, chemical syntheses of desmosine, isodesmosine, isotopically labeled desmosines, and cyclic desmosines were successfully achieved. The syntheses lied on palladium-catalyzed cross-coupling reactions as well as praseodymium triflate-promoted Chichibabin pyridinium synthesis. Synthetic desmosine-d4 was contributed as a peerless internal standard for the precise liquid chromatography-tandem mass spectrometry (LC-MS/MS) analysis of clinical samples of COPD patients. Thus, synthetic study of desmosines contributed the clinical and medicinal application.

The second topic presents novel extraction and isolation of naturally occurring organic compounds from plant materials utilizing cellulose-dissolving ionic liquids such as 1-butyl-3-methylimidazolium chloride ([C4mim]Cl) and 1-ethyl-3-methylimidazolium methylphosphonate ([C2mim][MeO(H)PO2]). Ionic liquid-mediated extraction yields of shikimic acid and bilobalide from Ginkgo biloba leaves were improved comparing to conventional methods. Meanwhile, essential oil citral and polyphenols caffeoylquinic acids were efficiently extracted from lemon myrtle and sweet potato leaves, respectively. The present method may be applicable to the efficient extraction/isolation of other plant natural products.

Keywords: natural product chemistry, amino acid, desmosine, ionic liquid, extraction

References
Efficient Photocatalysts for H₂ and O₂ Evolution from Water under Solar Light Irradiation

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Abstract

Hydrogen (H₂) is a zero carbon emission fuel, and is forecast to be an ideal source of energy in the future. In the past decades, great efforts have been devoted to realize efficient solar-to-hydrogen, since the first report of photoelectrochemical splitting of water into H₂ and O₂ in 1972. Although H₂ can be produced from direct splitting of water using semiconductor photocatalysts under solar light irradiation, the present energy conversion efficiency of solar-to-hydrogen (STH) is too low for the technology to be economically sound. The main barriers are the rapid charge recombination as well as no absorption of traditional semiconductors such as TiO₂ in the visible and near-infrared (NIR) regions. In view of solar energy utilization, the search for suitable materials as photocatalysts that not only can harvest the broad wavelength solar light, from UV to near-infrared (NIR) region, but also can achieve high efficient STH is one of the most challenging missions. Recently, among the numerous photocatalysts, layer-structured semiconductors have received extensive attention owing to their layered structures which separate out the H₂ and O₂ evolution sites.

Recently we found that two dimensional (2D) black phosphorous (BP) nanoflakes can harness visible and NIR light for H₂ evolution. A binary nanohybrid (BP/CN) of BP and graphitic carbon nitride (CN), was designed and used as a metal-free photocatalyst for the first time. During irradiation of BP/CN in water with >420 and >780 nm light, H₂ gas was generated. Owing to the interfacial interaction between BP and CN, efficient charge transfer occurred and thereby enhanced the photocatalytic performance. Spontaneously solar-driven water splitting to produce H₂ and O₂ is always a dream for mankind to convert solar energy to chemical energy. Drawing inspiration from nature, we successfully prepared a new artificial Z-scheme photocatalytic system based on 2D heterostructure of BP/BiVO₄.

Keywords: photocatalyst, H₂ Evolution, O₂ Evolution, water splitting, solar light

References

Physico-chemical Properties of Mesoporous Material for Biofuel Production

J.C. Juan\textsuperscript{a,*}, H.V. Lee\textsuperscript{a}, M.Y. Choo\textsuperscript{a}, L.E. Oi\textsuperscript{a}, S. Zulkelpi\textsuperscript{a}, N. Asikin-Mijan\textsuperscript{a}, T.C. Ling\textsuperscript{b}, E-P Ng\textsuperscript{c}, N.A. Rahman\textsuperscript{d}, G. Centi\textsuperscript{e}, D. Tungasmita\textsuperscript{f}

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Abstract

There are raising environmental concern owing to greenhouse gas emission through combustion of fossil fuel and depletion of fossil fuel urged the need for sustainable biofuel production\textsuperscript{1}. The high oxygen content of fatty acid methyl ester (FAME) used as biodiesel hinders the direct application as a fuel substitute\textsuperscript{1,2}. Therefore, catalytic deoxygenation under hydrogen free condition is a technology of increasing relevance for the production of hydrocarbon from seed oils and fats. By avoiding the use of hydrogen, the carbon footprint largely decreases. In general, the catalytic deoxygenation of plant oils involves two major routes: i) hydrodeoxygenation (HDO) and ii) DCO (decarboxylation and decarbonylation). The DCO pathway is more preferable in principle due to the cost and environmental impact. In addition, the major product of DCO reaction are unsaturated hydrocarbons which can be used as an octane enhancer for gasoline.

Generally, the plant oil which mainly comprised of triglycerides (an ester formed from glycerol and three fatty acid groups) is considered as large molecules\textsuperscript{3}. This large molecules will encounter diffusional limitations inside the pores of the catalyst and thus the pore size plays a critical role on the catalytic behaviour. To increase the performances, we have synthesized many types of mesoporous material such as mesoporous titania, mesoporous silica (HMS and MCM-41), mesoporous zeolite, etc. It is interesting to observe, the mesoporous catalyst demonstrate a remarkable catalytic acidity which contributed to more than 85% of hydrocarbon yield This study suggested that the effect of surface area, porosity, and acidity have play an important role in determining deoxygenation activities. This finding shows that mesoporous type of catalysts are a potential candidate in producing sustainable hydrocarbon like biofuel from non-edible oil.

Keywords: Mesoporous, catalysis, deoxygenation, hydrodeoxygenation, biofuel

References

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2. LE Oi, MY Choo, HV Lee, HC Ong, SBA Hamid, JC Juan. RSC Advances 2016, 6, 108741-108754.
Designing Earth Abundant Organometallic Complexes for Greener Catalytic Processes

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Abstract

Due to high natural abundance, benign environmental impact, and low cost, iron has emerged as an interesting potential surrogate in catalytic processes for classical precious transition metals. During the last decade, iron-catalysed reactions, and peculiarly in reduction area were intensively studied.[1] The reduction of carbonyl derivatives is now well established, but iron-catalysed hydrosilylation of carboxylic derivatives is far less developed.

This presentation will be devoted to the use of well-defined iron complexes bearing N-heterocyclic carbene, mono- or diphosphine ligands as efficient catalysts for chemoselective transformations such as hydrosilylation reactions of aldehydes, ketones[2,3] or amides,[3] and carboxylic acid derivatives.[4,5] Furthermore, iron complexes can be efficiently used as catalysts on hydroboration of alkenes and arenes[8] and on hydrogen borrowing reactions. [9]

Keywords: Iron; catalysis; reduction; hydrosilylation; hydroboration

References

Synthesis of functional nanocarbon molecules by surface-induced conformation-controlled mechanism

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Abstract

The mechanism that underlies heterogeneous catalysis is believed to involve the electronic interactions between the reactants and the metal surface. Recently, we found that the surface conformation of adsorbed organic molecules on a metal surface plays a critical role on the mechanism of chemical reactions. Herein, we would like to introduce our recent findings, 1) acene-type graphene nanoribbon synthesis via homochiral polymerization on Au(111),1 2) strain-induced skeletal rearrangement of polycyclic aromatic hydrocarbon on Cu(001).2

Graphene nanoribbons (GNRs) with a controlled width and edge structure have been attracted much attention because of their structure-dependent unique optoelectric properties. We have developed new bottom-up synthesis, two-zone chemical vapor deposition method(2Z-CVD) which enabled systematic production of armchair-edged GNRs in high yield. Herein, we have designed the “Z-bar linkage” precursor, which has flexibility that allows it to adopt asymmetrical conformation on a Au(111). Under 2Z-CVD condition, Z-bar linkage precursor afforded self-assembled homochiral polymer arrays, resulting in the efficient formation of acene-type GNRs.

Designed “spring” polycyclic aromatic hydrocarbon molecule, which adopt helical structure to avoid intramolecular repulsion, were flatten on Cu(001) surface. Upon annealing to 250 °C, its azulene moiety (fused 5 and 7 membered rings) were rearranged to fulvalene moiety (two 5 membered rings connected with a double bond). This class of skeletal rearrangement is never reported before and presumed to proceed by releasing molecular torsion as a driving force of chemical reaction.

In conclusion, we found a new chemistry of surface conformation-controlled mechanism. These finding will pave the way for the production of a new class of functional nanocarbon materials that conventional synthetic technique cannot attain.

Keywords: nanocarbon molecules, graphene nanoribbons, surface synthesis, conformation-controlled mechanism

References
2-electron-3-center bonds as a tool for hydrogen storage

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Abstract

From the first complex described by G. Kubas in 1984 with one H\(_2\) coordinated without H-H bond breaking, so-called σ--bond complex, many σ--dihydrogen complexes have been characterized\(^1\). Complexes bearing more than one σ--dihydrogen remain scarce. I will present the reactivity of the first bis dihydrogen complex characterized by neutron structures\(^2\). This ruthenium complex is a good model for reversible hydrogen release systems and may open new routes to hydrogen storage studies\(^3\). I will present our last results obtained in that domain based on NMR, Neutrons and DFT studies.

**Keywords:** hydrogen storage, ruthenium, dihydrogen complexes, neutrons, NMR.

References

Psychology and STEM: Pathways to a Neuroscience Approach to Career Choice

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Abstract

Science, technology, engineering and mathematics (STEM) are recognised widely as pathways for leveraging a nation’s better economic competitiveness, political and military security as well as mental health for its people. In this direction the United Nations’ Sustainability Development Goals 2030 focus on sustainable development and improving the quality of life as well as social well-being of people (United Nations, 2017). The universality of sustainable development, improving the quality of life and social well-being of people extend from an individual’s decision in making a career choice. A career choice is made to attain psychological success which enables the individual to enjoy satisfaction at the workplace and at home and it comes from achieving career and life goals. And with rapid changes in technology and global competitiveness that impact on people’s working life and daily living, it is recognised that determining a career choice is a crucial decision that is expected to meet individuals’ self-developmental needs as well as national needs for sustainable development. In the Malaysian context, governmental efforts in promoting the transformation of Malaysia (Transformation 2050) toward a sustainable nation emphasises on STEM careers to leverage on individuals’ creativity and innovation for sustainable development (Academy of Sciences Malaysia, 2017). Success in attaining the Sustainability Development Goals 2030, requires a concerted effort to identify pathways for facilitating individuals to make STEM their career choice so as to embrace creativity and innovation; as well as to lead research and development (R&D) toward attainment in new technologies and high performance work system that can enhance sustainable development, improve quality of life and social well-being of people (Malaysia Productivity Corporation, 2017). Career psychology provides a pathway to obtain evidence-based data in scientific studies on career choice decisions including STEM career choice (Lent & Brown, 2013; 2017; Quek, 2005; 2011 2016; Strauss, Griffin, & Parker, 2012). More importantly, neuroscience opens pathways to career psychology for understanding brain functioning in the decision making process of an individual which can outcome in attaining career and life goals. Career psychology in a neuroscience approach upholds that cognition, affect and behaviour are synchronised by an individual’s brainwaves. As such, career choice decision making by an individual can be scientifically analysed by EEG spectral changes in response to stimulation by using the event-related spectral perturbation techniques (Cona et al., 2009).

This is a novel pathway for career psychologists to apply a neuroscience approach on studying career choice of individuals. This keynote lecture addresses: (1) the scope of career choice, (2) career choice and psychological success, (3) psychology and STEM disciplines for insights into scientific research on career choice and (4) recommending pathways to a neuroscience approach to career choice in Malaysia and outside Malaysia.

Keywords: STEM, career choice, psychological success, neuroscience
Abstract

Stimuli-responsive polymers are a promising class of functional materials with switchable properties. In this presentation the synthesis of stimuli-responsive copolymers by Reversible Addition Fragmentation Transfer Polymerisation (RAFT) is discussed. Besides the possibility to tune the lower critical solution temperature (LCST) in water by controlled copolymerisation of different acrylamides\textsuperscript{1,2}, such copolymers also display interesting cononsolvency properties in water/alcohol mixtures.\textsuperscript{1} Variation of the chemical structure of the alcohols leads to either increase or decrease of the cloud point. The results are discussed in terms of polymer–additive as well as additive–water interactions and help to gain a more detailed understanding of water interactions with amphiphilic additives and, hence, of cononsolvency phenomena. Furthermore, the influence of different anions (salting-out (kosmotropic) and salting-in (chaotropic) along the Hofmeister series) on the solubility properties is presented.\textsuperscript{3} Of particular interest is to take advantage of changing the LCST by adding of an organic solvent to water in the synthesis of rather high molecular weight block copolymers with a large hydrophobic block and a shorter hydrophilic block by so-called Polymerization Induced Self-Assembly (PISA).\textsuperscript{4} Finally we demonstrate the possibility to perform RAFT polymerization without using typical radical initiators by just taking advantage of some impurities in some organic solvents which are typically used for such polymerisations.\textsuperscript{5}

**Keywords:** RAFT polymerisation, copolymer, stimuli-responsiveness, LCST

**References**

Fabrication of Single Crystal Thin Films and Tunneling Junctions using MgB$_2$ and Iron-based Superconductor SmFeAs(O,F)

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Abstract

Superconducting electronic devices are required for bioinstrumentation, radio-astronomy, and measurement of magnetic properties. Since now, superconducting devices have been fabricated using niobium, which works by using liquid helium or power-consuming cryocoolers. MgB$_2$ and iron-based superconductor SmFeAs(O,F) have superconducting transition temperatures ($T_c$) which is higher than 20 K. Therefore, they have a great potential to realize the superconducting electronic devices operating without liquid helium nor heavy cryocoolers. We have challenged to establish the fabrication method of SIS (Superconductor/Insulator/Superconductor) Josephson junctions on MgB$_2$ and SmFeAs(O,F), which are the electrical elements for superconducting devices. In the presentation, we report the preparation of high-quality thin films of MgB$_2$ and SmFeAs(O,F) by molecular beam epitaxy (MBE) method, and also the fabrication of tunneling superconducting junctions based on the thin films.

Thin films of MgB$_2$ and SmFeAs(O,F) were prepared on Al$_2$O$_3$, CaF$_2$, and LaAlO$_3$ substrates. We measured the X-ray diffraction, and the temperature dependence of the electrical resistivity for the characterization of superconducting performance. Next, the tunneling junctions were fabricated via depositing various materials of barrier layer (MgO, AlO$_x$, CaF$_2$) and counter electrodes in-situ. Subsequently, the multi-layer films were delineated into tunneling junctions using standard photolithography and Ar ion-milling. We measured the current-voltage characteristics of the junctions using a standard DC and AC four probe method.

We were successful to fabricate thin films on SmFeAs(O,F) which reproducibly show the high-$T_c$ over 50 K. In the talk, we will present a series of data which include the process from high-quality thin films to superconducting tunneling junctions on MgB$_2$ and SmFeAs(O,F).
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1990.4-1994.3 B. Sci., Department of Chemistry, Faculty of Science, Tokyo University of Science
1994.4-1996.3 M. Sci., Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology
1996.4-1999.3 D. Sci., Department of Electronic Chemistry, Interdisciplinary Graduate School of Science and Engineering, Tokyo Institute of Technology

Professional Carrier:
1998.4-1999.3 Research Fellow (DC2), Japan Society for the Promotion of Science (JSPS), Chemical Resources Laboratory, Tokyo Institute of Technology
1999.4-2003.9 Researcher, Surface Chemistry Laboratory, Kanagawa Academy of Science and Technology (KAST)
2003.10-2010.8 Assistant Professor, Catalysis Research Center, Hokkaido University
2010.8-present Associate Professor, Toyota Technological Institute
2006.6-2006.8 Visiting Researcher, Department of Chemical Physics of Fritz-Haber-Institute der Max-Planck-Gesellschaft, Berlin, Germany
2011.10-2017.3 PRESTO Researcher, Japan Science and Technology Agency (JST)

Awards:
2004.11 Young Researcher Award, the Surface Science Society of Japan
2009.11 Young Researcher Award, the Spectroscopical Society of Japan
2010.1 Young Researcher Award, Hokkaido branch of Chemical Society of Japan
2012.10 Outstanding Education Award, Toyota Technological Institute
2013.10 Outstanding Education Award, Toyota Technological Institute
2014.3 Young Researcher Award, Toyota Technological Institute
2015.3 The Academic Award, The NAGAI Foundation for Science and Technology
2017.10 Outstanding Education Award, Toyota Technological Institute

Research Interests:
Time-resolved laser spectroscopy, photocatalysis, electrochemistry, surface science.

I am studying the reaction mechanism of photocatalytic reactions on semiconductors. I have developed original spectrometers and elucidated many elementary steps such as electron & energy transfer to the reactant molecules and their structural changes toward the products. I believe that the elucidation of reaction mechanism is indispensable for the development of highly efficient catalysts. I wish to design original and highly active photocatalysts.
Trapping-Induced Enhancement of Photocatalytic Activity on TiO$_2$ Powders

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Abstract

Photocatalysts have attracted considerable attention due to their potential application to the water splitting reaction and degradation of pollutants using solar energy. TiO$_2$ is one of the most often used materials for photocatalysts because it is non-toxic and chemically stable during photocatalytic reactions. For TiO$_2$, anatase and rutile are the primary crystal structures, and their differences in photocatalytic activity have been well studied. In many reactions, anatase TiO$_2$ exhibits higher activity than rutile TiO$_2$, but rutile TiO$_2$ exhibits higher activity for water oxidation. However, the mechanism responsible for the difference in their photocatalytic activity had been a longstanding question for more than 40 years. In this work, the mechanism that determines the difference in photocatalytic activities between anatase and rutile TiO$_2$ powders have been studied by femtosecond to millisecond time-resolved visible to mid-IR absorption spectroscopy [1,2]. We found for the first time that the principal difference is in the depth of the electron traps that are associated to oxygen vacancies. In the case of anatase TiO$_2$, the depth of the electron trap is shallower than 0.1 eV and considerable number of free electrons survives longer than 1 ms. However, in the case of rutile TiO$_2$, the depth is deeper than 0.9 eV and most of the electrons are trapped within a few picoseconds. The longer lifetime of free electrons causes the higher activity for reduction on anatase TiO$_2$. However, deep electron-trapping in rutile TiO$_2$ drastically elongates the lifetime of holes, and enhances the multi-hole processes such as water oxidation. These peculiar behaviors of photogenerated electrons and holes are induced by defects on the powder particles, which are absent in defect-free single crystals: the behaviors of carriers are totally different in powder and defect-free single crystals.

Keywords: TiO$_2$ photocatalysts, photogenerated charge carriers, recombination, powder defects,

References

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Birth: Nagoya, Japan; February 19, 1956

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Bachelor: Nagoya University, 1978
Master: Nagoya University, 1980
Ph.D.: Nagoya University (Professors T. Goto and M. Isobe), 1983
Postdoctoral Fellow: Columbia University (Professor G. Stork), 1983

Appointments:
Assistant Professor, Department of Chemistry, Nagoya University
1990–1996
Associate Professor, Department of Chemistry, Nagoya University
1996–1998
Associate Professor, Research Center for Materials Science, Nagoya University
1998–2012
Professor, Research Center for Materials Science, Nagoya University
2012–
Professor, Graduate School of Pharmaceutical Sciences, Nagoya University

Awards:
The Chemical Society of Japan Award for Young Chemists in 1989
Asian Core Program Lectureship Award 2006
The Award of the Society of Synthetic Organic Chemistry in 2012,

Field of Research:
Research interests mainly span three areas of synthetic organic chemistry in view of the creation of organic materials that show useful chemical, physical, or biological functions: (1) Development of new synthetic methods. Especially establishment of selective catalytic systems. (2) Mechanistic study on catalysis. (3) Application of new methodology to the strategical synthesis of terpenes, alkaloids, antibiotics, prostaglandins, peptides, and related unnatural compounds.
Structural Analyses of *fac*-Ruthenium Complexes Bearing an sp\(^3\)P/sp\(^3\)NH/sp\(^2\)N Linear Tridentate Ligand (PN(H)N)

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Abstract

A PN(H)N–Ru complex catalyzes asymmetric hydrogenation of both chelatable and non-chelatable sterically demanding ketones in CH\(_2\)OH–DMSO mixed solvent. DMSO is responsible for the high-performance catalysis. The linear and flexible PN(H)N ligand sterically prefers the mer geometry over the fac isomer in the formation of octahedral Ru complexes. DMSO changes the situation. The highly □-acceptive S=O group coordinates to the soft Ru atom by use of the soft sulfur atom, and is forced to locate cis each other, resulting in the selective formation of fac-[Ru(PN(H)N)(dmso)]\(_2\)BF\(_4\) \(2\) (A). In order to deepen understanding for the mechanism, structures of the related ruthenium complexes were investigated. The time-course \(^1\)H-NMR analysis of A determined the dissociation rate ratio of sp\(^3\)P-trans, sp\(^3\)N-trans, and sp\(^2\)N-trans DMSO to be >37:2:1. The rate difference leads to stereoselective generation of fac-RuH(CH\(_2\)O)(PN(H)N)(dmso) \(2\) (B) by the action of 2 mol amount of t-BuOK in CH\(_2\)OH–DMSO. The complex B can exist only in CH\(_2\)OH–DMSO, and the amide complex fac-RuH(PNN)(dmso) \(2\) (C) is generated by removal of the solvent. Small \(^2\)J\(_\text{NP}\) values (2–5 Hz) of A–C with PN(H)\(15\)N confirmed the fac geometry. With a Ph-substituted ligand Ph-PN(H)N, a dihydride complex fac-RuH\(_2\)(Ph-PN(H)N)(dmso) (Ph-D) was generated in high yield from Ph-B but not from Ph-C (THF, 1 atm H\(_2\), 1 mol amount t-BuOK). A series of structural analyses have given an important information for the catalysis, where the hydrogenation proceeds in the H–Ru–N–H reaction site of the sp\(^3\)P-trans region. The sp\(^3\)N-trans DMSO, which is stabilized by a strong Ru □/O=S □* interaction, fixes the conformation through a PyC(6)H---O=S hydrogen bond, endowing the reaction site with a clear chiral circumstance. In this chiral reaction site, the difference in the steric demand of the C=O substituents is discriminated to produce nearly optically pure alcohols.

Keywords: asymmetric hydrogenation; mechanistic study; ruthenium; hydride complex

Graphical abstract

References

Yasuhiro Ohki received Bachelor degree from Department of Applied Chemistry at Tokyo Institute of Technology in 1995 and Master degree from the same institute in 1997, under the guidance of Prof. Hiroharu Suzuki. After working for a year at the research center of TOTO co. ltd., he joined the Suzuki group again as a researcher of CREST, Japan Science and Technology Corporation. He was appointed to an assistant professor in 2000 and was promoted to an associate professor in 2008 at Department of Chemistry, Nagoya University, where he has worked with Prof. Kazuyuki Tatsumi until 2013. His Ph.D. degree was given in 2002 from Tokyo Institute of Technology. In 2006, he took a sabbatical leave at the University of British Columbia, Canada, where he worked with Prof. Michael D. Fryzuk.

Professor Ohki’s research interests include organometallic chemistry and bioinorganic chemistry with emphasis on inorganic synthesis. He has been active in making synthetic analogues of the active sites of metallo-enzymes and in activation of small molecules mediated by organometallic and bio-mimetic inorganic compounds.

**Awards**
- Japan Society of Coordination Chemistry Award for Young Chemists (2004)
- The Chemical Society of Japan Award for Young Chemists (2009)
- The Young Scientists’ Prize (Minister Award) (2009)
- International Symposium on Pure & Applied Chemistry (ISPAC) 2016 Symposium Prize

**Recent Publications**
Bio-Inspired [Mo\textsubscript{2}Fe\textsubscript{2}] Hydride Clusters: Synthesis and Application in the Catalytic Silylation of N\textsubscript{2}

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Abstract

The biological reduction of N\textsubscript{2} is catalyzed by the nitrogenase FeMo-cofactor, which is a complex Mo-Fe-S cluster. Recent biochemical studies have suggested the intermediary formation of two Fe-H-Fe hydrides followed by the release of these hydrides as H\textsubscript{2} concomitant to the activation of N\textsubscript{2}. The postulated importance of hydride intermediates in the biological reduction of N\textsubscript{2}, as well as previously reported examples on the activation of N\textsubscript{2} by hydride complexes of transition metals, prompted us to synthesize hydride-supported Mo-Fe clusters. Here we report the [Mo\textsubscript{2}Fe\textsubscript{2}] hydride clusters and a [Mo\textsubscript{2}Mn\textsubscript{2}] congener, which were found to serve as catalytic precursors for the silylation of N\textsubscript{2}.

We have recently established a new synthetic protocol for Fe and Co hydride clusters based on the metathesis-type reactions of M-N(SiMe\textsubscript{3})\textsubscript{2} moiety and pinacolborane (HBpin) in the presence/absence of phosphines,\textsuperscript{1,2} however this protocol is not applicable for the selective synthesis of hetero-metallic clusters. To selectively link Mo and Fe with hydrides, we designed an acid-base type reaction, where the high-valent Mo(VI) hydride Cp*Mo(PMe\textsubscript{3})(H)\textsubscript{5} (1, Cp* = \eta\textsuperscript{5}-C\textsubscript{5}Me\textsubscript{5}) is used as a Brønsted acid and the Fe(II) amide complex Fe{N(SiMe\textsubscript{3})\textsubscript{2}}\textsubscript{2} is used as a base. This reaction resulted in the formation of the [Mo\textsubscript{2}Fe\textsubscript{2}] hydride cluster 2a in ca. 70% yield as crystals. Similarly, crystals of the [Mo\textsubscript{2}Mn\textsubscript{2}] congener (2b) were obtained from 1 and Mn{N(SiMe\textsubscript{3})\textsubscript{2}}\textsubscript{2} in ca. 70% yield (Fig. 1).\textsuperscript{1} Upon treatment with bulky thiols (HSR), the amide ligands in 2a were replaced by thiolates, furnishing the crystals of [Mo\textsubscript{2}Fe\textsubscript{2}](SR)\textsubscript{2} hydride clusters (3a-b) in ca. 50% yield.

The [Mo\textsubscript{2}Fe\textsubscript{2}] clusters serve as catalyst precursors for the reductive silylation of N\textsubscript{2}, yielding 65–69 equiv of N(SiMe\textsubscript{3})\textsubscript{3} per [Mo\textsubscript{2}Fe\textsubscript{2}] cluster. Details of the catalytic reactions will be discussed in the lecture.

Keywords: N\textsubscript{2} fixation, Fe, Mo, hydrides, silylation
Yasuyuki Yamada is an Associate Professor of Research Center for Materials Science, Nagoya University, Japan. He received his B.S. (1998) (under the direction of Prof. Renji Okazaki), M.S. (2000) (under the direction of Prof. Hiroshi Nishihara), and Ph.D. (2003) (under the direction of Prof. Mitsuhiko Shionoya) from The University of Tokyo. From 2003 to 2004, he was a post-doc researcher in the group of Prof. Jean A. Chmielewski at Purdue University, USA. He began his academic career at Tokyo University of Science as an Assistant Professor in the group of Prof. Shin Aoki. He moved to Nagoya University as an Assistant Professor (Prof. Kentaro Tanaka’s group) in 2007, and promoted to an Associate Professor in 2014. His current research interests are 1) Development of Bio-Inspired Supramolecular Catalysts, 2) Design of Molecular Assembly, and 3) Development of Molecular Machines and Molecular Devices.

Supramolecular Enhancement of Catalytic Ethane Oxidation Activity of \( \mu \)-Nitride-Bridged Iron Porphyrinoid Dimer

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Abstract

Low temperature catalytic conversion of light alkanes such as ethane and methane into more valuable chemical raw materials is of great interest due to the increasing social demands for efficient use of natural gases. However, on the other hand, C-H activation of light alkanes at low temperature is well recognized as a long-standing challenge in the field of catalytic chemistry since their C-H bond dissociation energies are quite high. Oxo species of \( \mu \)-nitrido-bridged iron porphyrinoid dimers, which can be generated by treating \( \mu \)-nitrido-bridged iron porphyrinoid dimers with \( \text{H}_2\text{O}_2 \), are one of the most promising candidates for direct C-H activation of light alkanes at low temperature.\textsuperscript{ref1} In this paper, we report on enhancement of the ethane oxidation activity of a \( \mu \)-nitrido-bridged porphyrinoid dimer via formation of a supramolecular stacked assembly with an additive porphyrin.

We prepared a \( \mu \)-nitrido-bridged dinuclear Fe(IV) complex of a cofacial supramolecular heterodimer\textsuperscript{ref2} of a porphyrin and a phthalocyanine connected through fourfold rotaxane structure 1 and its stacked assembly 2 with a tetraanionic Cu(II)-porphyrin (Fig. 1) It was revealed that ethane was catalytically oxidized into \( \text{EtOH}, \text{CH}_3\text{CHO}, \text{CH}_3\text{COOH}, \) and \( \text{HCOOH} \) in an acidic aqueous solution including absorbed on \( \text{SiO}_2 \) in the presence of excess amount of \( \text{H}_2\text{O}_2 \) at 60 °C. Importantly, 2 was found to have enhanced ethane oxidation ability compared to that of 1 at the same reaction condition (Fig. 2). The possible explanation of this enhancement will be reported in the presentation.

References


Fig. 1 Structures of the catalysts 1 and 2.

Fig. 2 Results of catalytic oxidation of ethane by 1 or 2.
Award Lecture of ISPAC 2017

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1987–1991 B.Sc. The University of Tokyo (Advisor: Prof. Masaji Ohno)
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1997–1999 Postdoctoral fellow, The Scripps Research Institute
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1999–2005 Assistant Professor, Graduate School of Pharmaceutical Sciences, The University of Tokyo
2005–2010 Associate Professor, Department of Chemistry, Graduate School of Engineering Science, Osaka University
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Research Interests:
Development of New Catalysis, Green & Sustainable Chemistry, Natural Product Synthesis, Flow Chemistry, Medicinal Chemistry

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2001 Fujisawa Award in Synthetic Organic Chemistry
2004 The Pharmaceutical Society of Japan Award for Young Scientists
2010 Green Sustainable Chemistry Award with MEXT Award
2012, 2013, 2015, 2016, 2017 Asian Core Program Lectureship Award
2014 The Pharmaceutical Society of Japan Award for Divisional Scientific Promotions
2017 ISPAC 2017 Lecture Award
Direct Catalytic Asymmetric Addition of Various Nucleophiles to N-Unprotected Ketimines

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Abstract

Enantioselective nucleophilic addition to ketimines is one of the most straightforward approaches to synthesize optically active tetrasubstituted amines. Recently, several direct catalytic additions to N-protected ketimines were reported including our Rh-catalysis.1 To obtain N-unprotected amines, however, they require additional deprotection steps, which limit their synthetic utilities. Although a prominent way to address these issues is using N-unprotected ketimines, there are only limited success using N-unprotected ketimines as an electrophile. Herein, we disclose direct catalytic asymmetric addition of terminal alkynes and 1,3-dicarbonyl compounds, to N-unprotected ketimines.

By proper choice of catalysts for each of reactions, the reaction of various nucleophiles proceeded smoothly to afford the corresponding N-unprotected tetrasubstituted amines in high yield.2,3 Very surprisingly, under our reaction conditions, Zn-catalyzed alkynylation selectively proceeded with N-unprotected ketimines over the N-PMP-protected ketimines and aldimines.2 It is notable that alkynylation of N-PMP-protected aldimine predominantly proceeded in the presence of Cu(I) catalyst, which is commonly used for alkynylation of imines. Our recent studies on direct catalytic asymmetric Mannich-type reactions to N-unprotected ketimines for direct access to N-unprotected α- and/or β-tetrasubstituted amino acid esters3 and direct catalytic asymmetric Friedel-Crafts-type alkylation4 will also be presented.

Keywords: N-protected ketimines; alkynylation, Mannich-type reaction, Friedel-Crafts-type alkylation, tetrasubstituted amino acid

References

Award Lecture of ISPAC 2017

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Prof. Joe Otsuki earned a Ph.D. in chemistry from the University of Tokyo in 1991. He then worked as a research associate at the Institute of Industrial Science, University of Tokyo until 1999. In 1993, he worked as a postdoctoral research fellow in the laboratory of Jean-Marie Lehn at Université Louis Pasteur (presently, Université de Strasbourg). He then moved to College of Science and Technology, Nihon University, where he currently works as a professor. His research focuses on photo/electroactive (supra)molecular devices and materials. He received the Lecture Award in ISPAC 2017, which this lecture in ICPAC 2018 is for, and was selected as Outstanding Reviewer from the Materials Chemistry Frontiers, Royal Society of Chemistry in 2016. More information at http://www.chem.cst.nihon-u.ac.jp/~otsuki/otsuki.html.
Coordination-Directed Supramolecular Assemblies: Light-Harvesting and Metal-Metal Interactions

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Abstract

The coordination bonding is one of the favorite interactions of chemists who are interested in preparing supramolecular assemblies owing to its directionality and a wide choice of the combinations of metal ions and organic ligands. In this presentation, we report some examples of coordination-directed assemblies from our laboratory.

Porphyrrins and chlorophylls constitute one of the most important and interesting classes of compounds for their photo/electro-activity. The chlorophylls, which are aptly called "the pigments of life" are the major components of natural photosynthesis. Highly efficient energy and electron transfer processes of photosynthesis are realized by the supramolecular organization of chlorophylls and other chromophore components. We have modified the structure of chlorophylls such that they self-assemble via the axial coordination involving the central Zn ion and a pyridyl moiety introduced on the periphery. These molecules form polymeric structures in the crystalline states, while they form cyclic oligomers in solutions\textsuperscript{1,2}. In the cyclic assemblies in solutions, efficient energy transfer has been demonstrated. Introducing an electron accepting unit, C\textsubscript{60}, into the assemblies gives a coupled light-harvesting and charge-separation systems.

Another example was found serendipitously in the course of searching Cu-based electrochemical catalysts. A mixture of acetylacetonedioxime and Cu(NO\textsubscript{3})\textsubscript{2} in water gave a metallacrown complex composed of five copper ions and four organic ligands\textsuperscript{3}. Surprisingly, the ligand is not an intact acetylacetonedioxime but it is nitrosated (NO) at the central carbon. Thus, a spontaneous reaction and self-assembly occur simultaneously in this case.

Keywords: artificial photosynthesis, chlorophyll, coordination, metallacrown complex, self-assembly

References

Dr. Daisuke Onoshima is a Unit Leader of Institute of Innovation for Future Society at Nagoya University. He is also a member of ImPACT Research Center for Advanced Nanobiodevices at Nagoya University. Dr Onoshima received his Ph.D. in Applied Chemistry from Nagoya University. Following his postdoctoral research in Creation of Innovation Centers for Advanced Interdisciplinary Areas Program by Japan Ministry of Education, Culture, Sports, Science and Technology (MEXT), and Funding Program for World-Leading Innovative R&D on Science and Technology by Japan Cabinet Office, he joined Institute of Innovation for Future Society at Nagoya University, the newly organized institute for business-academia collaboration at Nagoya University with Center of Innovation Program by MEXT. His current research interests are in the areas of nanobioscience based on lab-on-a-chip technology. Specifically, Dr. Onoshima’s work aims towards addressing challenging problems associated with the performance of cancer diagnostics and bacteriological testing. Some of Dr. Onoshima’s more current research has been focused on pattern analysis using machine learning. Dr. Onoshima was recently awarded New Chemical Technology Research Encouragement Award from Japan Association for Chemical Innovation (2015), Wakashachi Award Best Proposal Award from Aichi Prefecture (2016), and Lecture Award at International Symposium on Pure & Applied Chemistry (ISPAC) 2017.

Research Topics:
Nanobioscience, lab-on-a-chip, cancer diagnostics, bacteriological testing, machine learning
A Microfiltration Device for Cancer Detection by Circulating Tumor Cells in Blood

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Abstract

We present a study of blood microfiltration system towards optimal approach of non-invasive liquid biopsy for cancer detection by circulating tumor cells (CTCs). Filtration behavior of a microfilter was experimentally analyzed for tumor cell isolation from leukocytes in whole blood. This approach achieved an average of >96% recovery of spiked tumor cells and >99% total leukocytes depletion.

The purity of CTCs is important for oncogene mutation analysis using technologies with less contamination tolerance such as RT-PCR or next generation sequencing[1]. Previously, our group had developed a size-exclusive microfiltration device for tumor cell isolation[2]. The isolation of CTCs by size exclusion is helpful due to the advantage of capturing cells without depending on cell surface expression markers. However, the size-based approach is susceptible to the overlapping of size and density between CTCs and leukocytes. Here, we demonstrate an application of our device to leukocyte depletion and size-based enrichment of tumor cells with filtration pressure sensing. Filter-hole pattern and pressure drop were investigated as filtration parameters for influencing CTCs enrichment.

Keywords: liquid biopsy, circulating tumor cells, microfiltration device, single cell analysis

References

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Award Lecture of ISPAC 2017

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April 2012-March 2016: Lecturer, Keio University, Department of Applied Chemistry
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3. Young Scientist's Research Award in Natural Product Chemistry (2014)
4. BCSJ award
   "Total Synthesis of (±)-Gephyrooxin and (±)-Perhydroggephyrotoxin" (2015)
   "Reductive Approach to Nitrone from N-Siloxymides and N-Hydroxymides" (2017)
5. Incentive Award in Synthetic Organic Chemistry, Japan (2017)
   "Unified Total Synthesis of Stemoamide-Type Alkaloids"
Unified Total Synthesis of Madangamine Alkaloids

Takaaki Sato*

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Abstract

A skipped diene is an important functional group widely distributed in biologically active natural products such as madangamines, corallopyronins and ripostatins. The skipped dienes in these natural products exist as various types of stereoisomers derived from the two olefins. An ideal method to construct the skipped dienes must be stereodivergent, i.e., start from the same compound and give all four possible stereoisomers, as well as be highly convergent for the efficient synthesis of complex molecules. Although a number of synthetic methods have been reported, the development of approaches to provide all four possible stereoisomers of a skipped diene still remains a major challenge in synthetic organic chemistry. In this talk, we report a practical stereodivergent strategy involving hydroboration of allenes and the Migita/Kosugi/Stille coupling. The method was successfully applied to a unified total synthesis of the madangamine alkaloids.

Keywords: allene, hydroboration, madangamine, skipped diene, total synthesis

References
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2001.12 – 2006.11  Lecturer, Tohoku University
1997.9 – 2001.11  Research Associate; Tohoku University
1996.6 – 1997.8  Frontier Researcher, Riken, Photodynamic Centre (Prof. M. Kira)
1995.3 – 1996.5  Postdoctoral Research Associate (Prof. T. P. Fehlner at University of Notre Dame, USA)
1992.4 – 1995.3  Research Fellow, Japan Society for the Promotion of Science (JSPS)

Recent Publications:

Scientific Activities and Honors
2017. 6 Oral Presentation Award from International Symposium on Pure & Applied Chemistry (ISPAC 2017)
2006.11 Encouragement Award from the Society of Silicon Chemistry, Japan

Research interest: Transition-metal complexes having metal□heavier Group 14 element (Si, Ge) multiple bonds (double bonds; triple bonds), electron-deficient bonds, and multi-centered bonds
Synthesis and Some Peculiar Properties of a Transition-Metal Complex Having a Metal–Silicon Triple Bond

Hisako Hashimoto\textsuperscript{a,}\textsuperscript{*}, Takashi Yoshimoto\textsuperscript{a}, Tetsuya Fukuda\textsuperscript{a}, Naoki Hayakawa\textsuperscript{b}, Tsukasa Matsuo\textsuperscript{b}, Hiromi Tobita\textsuperscript{a}

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Abstract

The chemistry of transition-metal complexes bearing triple bonds between metals and heavier Group 14 elements has made considerable progress in the last two decades.\textsuperscript{1} Although metal-silicon triple bonded complexes, silylyne complexes, have been the most challenging synthetic targets, nearly 10 examples have been recently reported and their structures have been characterized. Despite this progress, reactivity of silylyne complexes remains largely unexplored yet.

Our group recently succeeded in synthesizing silylyne complexes of tungsten by developing a new synthetic strategy.\textsuperscript{2,3} The one bearing a very bulky aryl group (Eind) on silicon, 1, was isolated in good yield as a dimeric form in the solid state.\textsuperscript{3} The dimer is in rapid dissociation equilibrium with its monomer in solution and hence is suitable for reactivity study of the monomeric silylyne complex. As expected, the silylyne complex reacted with several unsaturated organic compounds such as carbodiimide, aldimines, aldehydes, and diaryl ketones at the polarized metal-silicon triple bond via [2+2] cycloaddition to give four-membered metallacycles as the initial products. These [2+2] cycloaddition reactions are essentially important because of their relevance to metathesis reactions. Indeed, in the case of aldehydes, the four-membered metallacycles subsequently underwent metathesis-like fragmentation into W≡C and Si=O species. This is the first example of such reactions involving silicon. In contrast, similar reactions with diarylketones resulted in ketone-coupling.

Keywords: triple bond, tungsten, silicon, synthesis, [2+2] cycloaddition

References

Award Lecture

Professor Masamichi Ogasawara
The University of Tokushima, Japan

1985 - 1989  Undergraduate Studies at The University of Tokyo
1989 - 1994  PhD Studies at The University of Tokyo (Supervisor: Prof. Masahiko Saburi)
1994 - 1996  Postdoc at Indiana University (Supervisor: Prof. Kenneth G. Caulton)
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1997 - 2002  Assistant Professor at Kyoto University (working with Prof. Tamio Hayashi)
2002 - 2016  Associate Professor at Hokkaido University (working with Tamotsu Takahashi)
2016 - Present  Professor at Tokushima University
2003  Daicel Award in Synthetic Organic Chemistry
2006  Incentive Award in Synthetic Organic Chemistry, Japan

Research interests: catalytic asymmetric synthesis, organometallic chemistry, homogeneous catalysis, coordination chemistry of phospholes/phospholides.
Atropisomeric Chiral Dienes in Asymmetric Catalysis

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Abstract

"Atropisomerism" is the phenomenon of chirality by virtue of restricted rotation about a single bond. The most common atropisomeric compounds are properly substituted biaryls, and they have been utilized as useful chiral scaffolds in organic synthesis. On the other hand, atropisomerism in 1,3-dienes is very rare, because the energy barrier of such rotation in the dienic system is generally low. We have recently found that incorporation of the C-C single bond of a conjugated diene into a proper ring system reduces conformational flexibility of the molecule, which results in induction of conformationally stable atropisomeric chirality. Based on these findings, we have designed and synthesized various atropisomeric chiral 1,3-dienes and applied them as chiral catalysts or chiral ligands in asymmetric synthesis.

Tetralin-fused diene-phosphine 1 was prepared utilizing a Zr-mediated reaction, and subsequent oxidation of 1 afforded phosphine oxide 2. While 2 showed conformational stability at 135 °C, 1 gradually racemized even at room temperature. On the other hand, analogous phosphate derivatives 3 could be separated into conformationally stable enantiomers. Likewise, tetralin-fused 1,4-diido-1,3-dienes 4 were found to be atropisomeric and resolvable. Enantiomerically pure 3 were utilized in various transition-metal-catalyzed asymmetric reactions as chiral ligands and display promising performances as shown below. Applications of 2 and 4 as chiral organocatalysts were also examined. In the Lewis base-catalyzed allylation, (M)-2 was an excellent catalyst in both enantioselctivity and catalytic activity. Single-enantiomeric 4 were applied in the asymmetric dearomatizing spirolactonization as chiral organocatalysts to show good enantioselectivity in up to 73% ee. The results shown below have demonstrated potential usefulness of the diene-based atropisomeric-chiral molecules in asymmetric synthesis.

Keywords: atropisomer; 1,3-diene; chiral; phosphine; organocatalyst

References


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Keywords: atropisomer; 1,3-diene; chiral; phosphine; organocatalyst

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Keywords: atropisomer; 1,3-diene; chiral; phosphine; organocatalyst

References

### Wednesday, 7 March 2018

#### Thematic Session: Organic and Biomolecular Chemistry (OBC)

**Venue:** Sophanith Ballroom 1st Floor, Lobby Level

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<td>Pavel Lhoták</td>
<td>UCT Prague, Czech Republic</td>
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<td>Hokkaido University, Japan</td>
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<td>Hiroyuki Asanuma</td>
<td>Nagoya University, Japan</td>
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<td><strong>OBC 07 (Invited Lecture)</strong> Amide base generated in situ from TMAF and N(TMS)3 catalyzed deprotonative functionalization</td>
<td>Masanori Shigeno</td>
<td>Tohoku University, Japan</td>
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<td>Satoshi Hayashi</td>
<td>Meiji Pharmaceutical University, Japan</td>
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<td><strong>OBC 09 (Invited Lecture)</strong> Total Synthesis of Phaeosphaerides A and B</td>
<td>Kenichi Kobayashi</td>
<td>Meiji Pharmaceutical University, Japan</td>
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<td>1440</td>
<td><strong>OBC 07 (Invited Lecture)</strong> A Versatile Synthesis of Renieramycin Marine Natural Products.</td>
<td>Masashi Yokoya</td>
<td>Meiji Pharmaceutical University, Japan</td>
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<td>1500 – 1520</td>
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<td>1520 – 1540</td>
<td>OBC 11 (Invited Lecture)</td>
<td><strong>Synthesis of 3,4-Fused Tricyclic Indoles Using Transition Metal Catalysis</strong>&lt;br&gt;Tetsuhiro Nemoto&lt;br&gt;Chiba University, Japan</td>
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<td>1540 – 1600</td>
<td>OBC 12 (Invited Lecture)</td>
<td><strong>Construction of “metathesase” with Protein Scaffold and Potential Application of Olefin Metathesis as a Biochemical Tool</strong>&lt;br&gt;Takashi Matsuo&lt;br&gt;Nara Institute of Science and Technology, Japan</td>
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<td>Session Ic Chairperson: Prof Dr Yang Farina Abdul Aziz&lt;br&gt;National University of Malaysia, Malaysia</td>
<td><strong>Mechanistic Insight of Asymmetric Autocatalysis of Pyrimidyl Alkanol by Structure Analysis of Zinc Alkoxide Complexes</strong>&lt;br&gt;Arimasa Matsumoto&lt;br&gt;Nara Women's University, Japan</td>
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<td>1650 – 1710</td>
<td>OBC 14 (Invited Lecture)</td>
<td><strong>Heme Uptake Proteins from Pathogenic Vibrio cholera</strong>&lt;br&gt;Takeshi Uchida&lt;br&gt;Hokkaido University, Japan</td>
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<td>1710 – 1730</td>
<td>OBC 15 (Invited Lecture)</td>
<td><strong>C(sp3)–H Bond Functionalization Mediated by Hydride Shift/Cyclization System</strong>&lt;br&gt;Keiji Mori&lt;br&gt;Tokyo University of Agriculture and Technology, Japan</td>
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<td>OBC 47 (Invited Lecture)</td>
<td><strong>Hypervalent Iodine-Induced Silyl Enolate Coupling for New C-C Bond-Forming Reaction</strong>&lt;br&gt;Toshifumi Dohi&lt;br&gt;Ritsumeikan University, Japan</td>
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<td>1750 - 1810</td>
<td>OBC 72 (Award Lecture)</td>
<td><strong>Atropisomeric Chiral Dienes in Asymmetric Catalysis</strong>&lt;br&gt;Masamichi Ogasawara&lt;br&gt;Tokushima University, Japan</td>
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| Session Ig | Chairperson: Prof Pavel Lhoták  
UCT Prague, Czech Republic |
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| 0900 – 0930 | OBC 31 (Keynote Lecture)  
**Natural Products Research: Chemical Synthesis and Ionic Liquid**  
Toyonobu Usuki  
Sophia University, Japan |
| 0930 – 0950 | OBC 32 (Invited Lecture)  
**Optically Active Conjugated Compounds Based on Planar Chirality**  
Yasuhiro Morisaki  
Kwansei Gakuin University, Japan |
| 0950 – 1010 | OBC 62 (Invited Lecture)  
**Drug Discovery of Vancomycin Dimer against Vancomycin-Resistant Enterococcal Infections**  
Kaori Itto  
Tohoku University, Japan |
| 1000 – 1030 | Refreshments |
| 1030 – 1245 | Plenary Lectures 1, 2, & 3  
Venue: Sophanith Ballroom 1st Floor, Lobby Level |
| 1245 – 1400 | Lunch |
| Session Ih | Chairperson: Dr. Neth Barom  
Cambodian Chemical Society, Cambodia |
| 1400 – 1420 | OBC 33 (Invited Lecture)  
**Niobium-catalyzed [2+2+2] Cycloaddition of Alkynes, Nitriles, and Alkenes**  
Yasushi Obora  
Kansai University, Japan, Japan |
| 1420 – 1440 | OBC 34 (Invited Lecture)  
**Ladder-Type Fused Benzofurans and Indoles Synthesized by Transition-Metal-Catalyzed Intramolecular Cascade Cyclization**  
Takanori Matsuda  
Tokyo University of Science, Japan |
| 1440 – 1500 | OBC 35 (Invited Lecture)  
**Acceleration of Catalytic Site-Selective Acylation of Carbohydrates by in Situ Counteranion Exchange of Acylpyridinium Intermediates**  
Yoshihiro Ueda  
Kyoto University, Japan |
| 1500 – 1520 | OBC 36 (Invited Lecture)  
**Functionalized CpRh(III) Complexes; Preparation and Catalytic Activity toward C–H Functionalization**  
Yu Shibata  
Tokyo Institute of Technology, Japan |
| 1520 – 1540 | OBC 37 (Invited Lecture)  
**Proximity-Dependent Tyrosine Chemical Labeling**  
Shinichi Sato  
Tokyo Institute of Technology, Japan |
| 1540 – 1600 | OBC 38 (Invited Lecture)  
**QM/MM Studies of the Reaction Mechanisms of Metalloenzymes**  
Megumi Kayanuma  
University of Tsukuba, Japan |
| 1600 – 1630 | Refreshments |
### Session II

**Chairperson:** Dr. Neth Barom  
**Cambodian Chemical Society, Cambodia**

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<td>The Proton NMR Spectra of the Glyceride CH2 and CH Groups of Triacylglycerols in Edible Oils. Application to the Analysis of the Fatty Acid Composition at the sn-2 position of the Triacylglycerols in the Oils</td>
<td>Ng Soon</td>
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<td>New Insights of Naturally Occurring O2-tolerant [NiFe]hydrogenase</td>
<td>Ki-Seok Yoon</td>
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<td>Total Synthesis of Ustiloxin D</td>
<td>Yoko Yasuno</td>
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<td>Jianrong Zhou</td>
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<td>Development of Crystalline Photochromic Compounds Involving Intramolecular Hydrogen Bond</td>
<td>Masatsugu Taneda</td>
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<td>Optical Properties of 1-[(3,6-Di-tert-butyl-1-carbazolyl)azo]-4-nitrobenzene Involving N-H···N Intramolecular Hydrogen Bond</td>
<td>Mai Morimoto</td>
<td>Osaka Kyoiku University, Japan</td>
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### Saturday, 10 March 2018

**Thematic Session:**  
**Organic and Biomolecular Chemistry (OBC)**  
**Venue:** Sophanith Ballroom 1st Floor, Lobby Level

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<td>Unified Total Synthesis of Madangamine Alkaloids</td>
<td>Takaaki Sato</td>
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<td>Direct Catalytic Asymmetric Addition of Various Nucleophiles to N-Unprotected Ketimines</td>
<td>Takashi Oshshima</td>
<td>Kyushu University, Japan</td>
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<td>0940 – 1000</td>
<td>OBC 47 (Invited Lecture)</td>
<td>PEG Hydrogels Utilizing DNA Quadruplexes as Crosslinking Points</td>
<td>Akinori Kuzuya</td>
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<td>OBC 48 (Oral Presentation)</td>
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<td>Mai Morimoto</td>
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<td>1030 – 1050</td>
<td>Ick</td>
<td>Assoc Prof Dr Sharon Teh</td>
<td>Nickel-Catalyzed Oxysulfonylation of Alkenes Using Sodium Sulfinates</td>
<td>Nobukazu Taniguchi</td>
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<td>Assoc Prof Dr Sharon Teh</td>
<td>Regioselective C-H Trifluoromethylation of 6-Membered Heteroaromatic Compounds</td>
<td>Yoichiro Kuninobu</td>
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<td>Assoc Prof Dr Sharon Teh</td>
<td>Synthetic assembly of sugar moieties using biotin-avidin interaction</td>
<td>Koji Matsuoka</td>
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<td>1130 – 1150</td>
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<td>Assoc Prof Dr Sharon Teh</td>
<td>Development of Cellulose-Based Chiral Fluorescent Sensors</td>
<td>Tomoyuki Ikai</td>
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<td>Assoc Prof Dr Sharon Teh</td>
<td>Direct Benzyne Generation from Phenol Derivatives:Synthesis of Aromatic Primary Amines</td>
<td>Takashi Ikawa</td>
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<td>The Enhanced Enantio-recognition of Chiral Secondary Alcohols with Chiral Acyltriazolium by Formation of Alcohol–Carboxylate Complexes</td>
<td>Ken-ichi Yamada</td>
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<td>Takashi Ohshima</td>
<td>Synthesis of Iodinated-Organic Salts and Diversity of Iodine-Iodine Interaction in Their Crystal Structures</td>
<td>Shoji Matsumoto</td>
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<td>Cholesterol Interaction with Steroidal Saponins in Bilayer Membrane</td>
<td>Shinya Hanashima</td>
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<td>Elastic Organic Single Crystals based on Fluorescent Molecules</td>
<td>Shotaro Hayashi</td>
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<td>1030</td>
<td>PCC 01</td>
<td>Assoc Prof Dr Juan Joon Ching</td>
<td>Efficient Photocatalysts for H₂ and O₂ Evolution from Water under Solar Light Irradiation</td>
<td>Tetsuro Majima</td>
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<td>Assoc Prof Dr Akira Yamakata</td>
<td>Trapping-Induced Enhancement of Photocatalytic Activity on TiO₂ Powders</td>
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<td>Yuta Tsuji</td>
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<td>Assoc Prof Dr Takashi Kamachi</td>
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<td>Takashi Kamachi</td>
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<td>Assoc Prof Dr Hideki Nabika</td>
<td>Liesegang phenomenon: Chemical Model for Pattern Formations in Nature</td>
<td>Hideki Nabika</td>
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<td>Assoc Prof Dr Takatoshii Fujita</td>
<td>Exciton Dynamics in Organic Optoelectronic Materials</td>
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<td>Theoretical Study on Conversion of Methane to Higher Hydrocarbons by Liquid-Metal Indium</td>
<td>Yuhki Ohtsuka</td>
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<td>(Invited Lecture) In-Silico Ammonia Synthesis Using Heterogeneous Catalysts. A First-Principles Molecular Dynamics Study</td>
<td>Manabu Sugimoto</td>
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<td>(Invited Lecture) SMASH: Massively Parallel Software for Quantum Chemistry Calculations</td>
<td>Kazuya Ishimura</td>
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<td>Masayoshi Nishiyama</td>
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<td>Yoshikiyo Hatakeyama</td>
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<td>Kenichiro Saita</td>
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<td>Yu Harabuchi</td>
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<td>Shintaro Ida</td>
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<td>Yoshihiro Sohtome</td>
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<td>Shin-ya Takizawa</td>
<td>The University of Tokyo, Japan</td>
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### Session IIf
**Chairperson:** Assoc Prof Dr Juan Joon Ching  
**University of Malaya, Malaysia**

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<td>(Invited Lecture) Highly Active and Selective Electrocatalysts based on Covalent Organic Frameworks Modified with Single Metal Atoms</td>
<td>Kazuhide Kamiya</td>
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<td>(Invited Lecture) Thermal Decomposition Behavior of Supported Platinum Salt for Catalyst Preparation</td>
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<td>Akira Nakayama</td>
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### Session IIg
**Chairperson:** Prof Tan Guan Huat  
**University of Malaya, Malaysia**

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<td>Kaoru Yamazaki</td>
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<td>Hirotoshi Mori</td>
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### Session IIh
**Chairperson:** Prof Tan Guan Huat  
**University of Malaya, Malaysia**

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<td>(Invited Lecture) Development of Plasmonic Cu₂O/Cu Composite Arrays as Plasmonic Photocatalysts</td>
<td>Kosuke Sugawa</td>
<td>Nihon University, Japan</td>
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<td>1110</td>
<td>PCC 32</td>
<td>(Invited Lecture) Effect of Ultraviolet Light Irradiation on Solution Processed ZnO Films</td>
<td>Hajime Wagata</td>
<td>Meiji University, Japan</td>
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<tr>
<td>1130</td>
<td>PCC 33</td>
<td>(Invited Lecture) Recent Advance in Nitride Photocatalyst for New Hydrogen Energy Source</td>
<td>Tomoaki Watanabe</td>
<td>Meiji University, Japan</td>
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<td>1150 - 1210</td>
<td>PCC 34</td>
<td>(Invited Lecture)</td>
<td><strong>Utilizing the Space of Molecular Nanocarbon Assemblies</strong></td>
<td>Hirotoshi Sakamoto</td>
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<tr>
<td>1210 - 1230</td>
<td>PCC 35</td>
<td>(Invited Lecture)</td>
<td><strong>Theoretical Investigation on Structural Stability and Catalytic Activity of Platinum Clusters of Low Atomicity</strong></td>
<td>Naoki Haruta</td>
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<tr>
<td>1230 - 1400</td>
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<td>1300 - 1400</td>
<td>Session III</td>
<td>Chairperson: Prof Takaaki Sato</td>
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<td>1400 - 1420</td>
<td>PCC 36</td>
<td>(Invited Lecture)</td>
<td><strong>Controlling Selective Hydrogenation Performances on Ru Nanocluseter / K-Al₂O₃ Catalyst</strong></td>
<td>Satoshi Muratsugu</td>
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<td>1420 - 1440</td>
<td>PCC 37</td>
<td>(Invited Lecture)</td>
<td><strong>Infrared-Emissive Luminescent Mechanochromism of Anthryl Gold Isocyanide Complex</strong></td>
<td>Tomohiro Seki</td>
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<td>1440 - 1500</td>
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<td>FMC 05 (Invited Lecture)</td>
<td><strong>MGeND: A new Integrated Database of Clinical and Genomic Information developed in Japan</strong></td>
<td>Masahiko Nakatsui</td>
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<td>1600 - 1630</td>
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| 1030 – 1100 | ICC 01 (Keynote Lecture)  
Designing Earth Abundant Organometallic Complexes for Greener Catalytic Processes  
Christophe Darcel  
UMR 6226-CNRS-Université de Rennes, France | VIP Grand II, G Floor Level                    |
| 1100 – 1120 | ICC 02 (Invited Lecture)  
Tailoring Spin Crossover Probed by X-ray Absorption Spectroscopy and Monte-Carlo Simulation  
Jun Okabayashi  
The University of Tokyo, Japan |                                |
| 1120 – 1140 | ICC 03 (Award Lecture)  
Supramoeulcular Enhancement of Catalytic Ethane Oxidation Activity of  
=Nitride-Bridged Iron Porphyrinoid Dimer  
Yasuyuki Yamada  
Nagoya University, Japan |                                |
| 1140 – 1200 | ICC 04 (Invited Lecture)  
Properties of SrTiO\(_3\)/TiO\(_2\) Heterojunction Photocatalyst Prepared by Acid Treatment of SrTiO\(_3\)  
Sayaka Yanagida  
University of Yamanashi, Japan |                                |
| 1200 – 1220 | ICC 05 (Invited Lecture)  
Development of Useful Molecules Based on Bioinspired Metal Complexes  
Yutaka Hitomi  
Doshisha University, Japan |                                |
| 1220 – 1240 | ICC 06 (Invited Lecture)  
Photochemical and Electrochemical Water Oxidation Mechanisms of Cobalt porphyrins  
Takashi Nakazono  
Rikkyo University, Japan |                                |
| 1240 – 1400 | Lunch / Posters                                |                                |
| 1400 – 1420 | ICC 07 (Award Lecture of ISPAC2016)  
Bio-Inspired [Mo\(_2\)Fe\(_2\)] Hydride Clusters : Synthesis and Application in the Catalytic Silylation of N\(_2\)  
Yasuhiro Ohki  
Nagoya University, Japan |                                |
| 1420 – 1440 | ICC 08 (Award Lecture of ISPAC2017/ Award Lecture)  
Synthesis and Some Peculiar Properties of a Transition-Metal Complex Having a Metal-Silicon Triple Bond  
Hisako Hashimoto  
Tohoku University, Japan |                                |
| 1440 – 1500 | ICC 09 (Invited Lecture)  
Structural Analyses of fac-Ruthenium Complexes Bearing an sp3P/sp3NH/sp2N Linear Tridentate Ligand (PN(H)N)  
Shinji Tanaka  
Nagoya University, Japan |                                |
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<tr>
<td>1500 – 1520</td>
<td>ICC 10 (Invited Lecture)</td>
<td><strong>Stimuli-Responsive Helical Metal Complexes: Helicity Inversion, Expansion/Contraction, and Memorization</strong></td>
<td>Hiroyuki Miyake</td>
<td>Osaka City University, Japan</td>
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<td>1520 – 1540</td>
<td>ICC 11 (Invited Lecture)</td>
<td><strong>Fabrication of Plasmonic Array of Metallic Nanocylinders and Its Optical Properties</strong></td>
<td>Shunsuke Murai</td>
<td>Kyoto University, Japan</td>
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<tr>
<td>1540 – 1600</td>
<td>ICC 12 (Invited Lecture)</td>
<td><strong>Humidity-responsive Switching of Gas Inclusion by using Cooperative Opening and Closing of Heterogeneous Nano-cavities in a Crystalline Peptide Ni(II)-macrocycle</strong></td>
<td>Ryosuke Miyake</td>
<td>Ochanomizu University, Japan</td>
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<td>1630 – 1650</td>
<td>Session IIIc</td>
<td><strong>Chairperson:</strong> Dr. Malarvilli Ramalingam</td>
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<td>1630 – 1650</td>
<td>ICC 13 (Invited Lecture)</td>
<td><strong>Transition-Metal Complexes with Silyl(2,2'-Bipyridine) Pincer Ligands: Synthesis and Catalysis for Functionalization of C–H/C–D Bonds</strong></td>
<td>Takashi Komuro</td>
<td>Tohoku University, Japan</td>
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<td>1650 – 1710</td>
<td>ICC 14 (Invited Lecture)</td>
<td><strong>Dinitrogen Activation by an Iron Complex of 1,1′-Bis(arylamido)vanadocene</strong></td>
<td>Tsubasa Hatanaka</td>
<td>Osaka University, Japan</td>
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<td>1710 – 1730</td>
<td>ICC 15 (Invited Lecture)</td>
<td><strong>Surface Modification of Nano-carbon Materials by Metal Complexes or Metal-organic Network Films</strong></td>
<td>Hiroaki Ozawa</td>
<td>Chuo University, Japan</td>
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<td>1730 – 1750</td>
<td>ICC 29 (Invited Lecture)</td>
<td><strong>Metal Complexes with Bistability</strong></td>
<td>Hiroki Oshio</td>
<td>University of Tsukuba, Japan</td>
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<td>IIId</td>
<td>0900 – 0930</td>
<td>ICC 16 (Keynote/Award Lecture)</td>
<td>Synthesis of Functional Nanocarbon Molecules by Surface-induced Conformation-controlled Mechanism&lt;br&gt;Takahiro Nakae&lt;br&gt;Kyoto University, Japan</td>
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<td>0930 – 0950</td>
<td>ICC 24 (Invited Lecture)</td>
<td>Interface Engineering of Transition Metal Oxides as a New Route for Exploring Functional Properties&lt;br&gt;Daisuke Kan&lt;br&gt;Kyoto University, Japan</td>
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<td>1245 – 1400</td>
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<td>1400 – 1420</td>
<td>ICC 18 (Invited Lecture)</td>
<td>Syntheses of Heterometallic Clusters based on Cubane Type Cores Supported by Macrocyclic Triazacyclononane Complexes&lt;br&gt;Keisuke Kawamoto&lt;br&gt;Kanazawa University, Japan</td>
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<td>1420 – 1440</td>
<td>ICC 34 (Invited Lecture)</td>
<td>Function Integrated Space Based on Liposome and Metal Complexes&lt;br&gt;Masaaki Ohba&lt;br&gt;Kyushu University, Japan</td>
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<td>1440 – 1500</td>
<td>ICC 20 (Invited Lecture)</td>
<td>Photoluminescence Switching of Rhenium(V) Complexes with Nitrido by Mechanochemical Reactions and Exposure of Water&lt;br&gt;Takashi Yoshimura&lt;br&gt;Osaka University, Japan</td>
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<td>1500 – 1520</td>
<td>ICC 21 (Invited Lecture)</td>
<td>Rare-earth Metallacyclopentadienes: Synthesis, Structure and Reactivity&lt;br&gt;Wen-Xiong Zhang&lt;br&gt;Peking University, China</td>
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<td>1520 – 1540</td>
<td>ICC 22 (Award Lecture of ISPAC2017)</td>
<td>Coordination-Directed Supramolecular Assemblies: Light-Harvesting and Metal-Metal Interactions&lt;br&gt;Joe Otsuki&lt;br&gt;Nihon University, Japan</td>
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<td>1540 – 1600</td>
<td>ICC 23 (Invited Lecture)</td>
<td>Size-dependent Polymorphism in Aluminum Carbide Cluster Anions AlnC2&lt;br&gt;Kiichiro Koyasu&lt;br&gt;The University of Tokyo, Japan</td>
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<td>1600 – 1630</td>
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</table>
| Session IIIf | Chairperson: Prof. Takahiro Nakae  
Kyoto University, Japan |
|-------------|--------------------------------------------------|
| 1630 – 1650 | ICC 17 (Invited Lecture)  
PTRF-XAFS Study of Single Metal Dispersion on an Oxide Single Crystal Surface by Premodification with a Functional Organic Molecule  
Satoru Takakusagi  
Hokkaido University, Japan |
| 1650 – 1710 | ICC 25 (Invited Lecture)  
Synthesis and Characterization of Pd-supported Fluoro-dodecavanadates  
Miftahul Khair  
Universitas Negeri Padang |
| 1710 – 1730 | ICC 26 (Invited Lecture)  
Crystalline Sponge Method: X-ray Structural Analysis in the Porous Coordination Network  
Shota Yoshioka  
Hokkaido University, Japan |
| 1730 - 1750 | ICC 31 (Invited Lecture)  
Single Molecule Conductance Studies of Organometallic Molecular Wires with Ruthenium Acetylide Units  
Yuya Tanaka  
Tokyo Institute of Technology, Japan |
| 1750 | End |

**Saturday, 10 March 2018**  
**Thematic Session:**  
**Inorganic and Coordination Chemistry (ICC)**  
**Venue:** VIP Grand II, G Floor Level

| Session IIIg | Chairperson: Prof. Masato Kitamura  
Nagoya University, Japan |
|-------------|--------------------------------------------------|
| 0900 – 0930 | ICC 27 (Keynote Lecture)  
2-electron-3-center Bonds as a Tool for Hydrogen Storage  
Mary Grellier  
Université Toulouse III, France |
| 0930 – 0950 | ICC 28 (Invited Lecture)  
Synthesis and Chemical Characteristics of the Freebase Forms of Quadruply Fused Porphyrins  
Tomoya Ishizuka  
University of Tsukuba, Japan |
| 1000 – 1030 | Refreshments |
| Session IIIh | Chairperson: Prof. Masato Kitamura  
Nagoya University, Japan |
| 1050 – 1110 | ICC 30 (Invited Lecture)  
Excited-state Dynamics and Photophysical Properties of Blue-emissive Dicyanoaurate Oligomers  
Koichi Nozaki  
University of Toyama, Japan |
| 1130 – 1150 | ICC 19 (Invited Lecture)  
Elemental Allotropes in Interactive Porous Coordination Networks  
Hiroyoshi Ohtsu  
Tokyo Institute of Technology, Japan |
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<th>Time</th>
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| 1150 – 1210 | ICC 33 (Invited Lecture)  
**Cold Crystallisation of Alkyl Substituted Nickel(II) Complexes Capable of Storing Heat Energy**  
Kazuo Miyamura  
Tokyo University of Science, Japan |
| 1210 – 1230 | ICC 32 (Invited Lecture)  
**Photochemical Hydrogen Evolution Assisted by Nonprecious Metal Complexes Bearing Redox-active Ligands**  
Tsuyoshi Matsumoto  
Chuo University, Japan |
| 1230 – 1400 | Lunch / Posters  
Thematic Session:  
**ICPAC General Session (IGS)** |
| Session VIIc | Chairperson:  
Prof Mary Grellier  
Université Toulouse III, France |
| 1400 – 1420 | IGS 01 (Invited Lecture)  
**Measure of Regression Model Accuracy for Quantitative Structure-Activity(Property) Relationship Considering Applicability Domains**  
Hiromasa Kaneko  
The University of Tokyo, Japan |
| 1420 – 1440 | IGS 11 (Award Lecture)  
**Donor-Acceptor Bifunctional Catalyst From DAIB–Zn to Ru/Brønsted Acid Combined Catalyst**  
Masato Kitamura  
Nagoya University, Japan |
| 1440 – 1500 | IGS 12 (Invited Lecture)  
**Recent Advances in Materials Simulations and Informatics**  
Kenta Hongo  
Japan Advanced Institute of Science and Technology, Japan |
| 1600 – 1630 | Refreshments |
| 1630 | End |
| Session Id | Chairperson: Assoc Prof Dr Chan Chin Han
Universiti Teknologi MARA, Malaysia |
|------------|--------------------------------------------------------------------------------|
| 1030 – 1050| OBC 16 (Invited Lecture) Cobalt-Catalyzed Allylic C(sp³)–H Additions to Low Reactive Carbonyl Compounds, CO₂ and Ketones
Tsuyoshi Mita
Hokkaido University, Japan |
| 1050 – 1110| OBC 17 (Invited Lecture) The First Synthesis of Meso-dicyclopophylenes and their Photofunctions
Toshikazu Ono
Kyushu University, Japan |
| 1110 – 1130| OBC 18 (Invited Lecture) Enantioselective Alkynylation of Ketones Catalyzed by Chiral Pincer Rh Complexes
Jun-ichi Ito
Nagoya University, Japan |
| 1130 – 1150| OBC 19 (Invited Lecture) Radical Reactions of Alkynes with N-Heterocyclic Carbene Boranes
Tsuyoshi Taniguchi
Kanazawa University, Japan |
| 1150 – 1210| OBC 20 (Invited Lecture) Synthesis, Characterization, and Inclusion Behavior of Bisporphyrin with Two BCOD Units
Shigeki Mori
Ehime University, Japan |
| 1210 – 1230| OBC 21 (Invited Lecture) Two-Step Synthesis of 1,10-Phenanthroline-Derived Polyaza-[7]helicenes
Takashi Otani
National Institute of Technology, Anan College, Japan |
| 1230 – 1250| OBC 52 (Invited Lecture) Total Synthesis and Structure-Activity Relationship Study of Cyclodepsipeptide Destruxin E
Masahito Yoshida
Tohoku University, Japan |
| 1250 – 1400| Lunch / Posters |
| Session Ie | Chairperson: Dr. Chek Sotha
Cambodian Chemical Society, Cambodia |
| 1400 – 1420| OBC 22 (Invited Lecture) Simple β-Amino Alcohol Organocatalyst for Asymmetric Reactions
Hiroto Nakano
Muroran Institute of Technology, Japan |
| 1420 – 1440| OBC 48 (Invited Lecture) Total Synthesis of (+)-Haplophytine
Hiroyuki Ueda
Tohoku University, Japan |
| 1440 – 1500| OBC 67 (Invited Lecture) Recent Development of Halogen Dance
Kentaro Okano
Kobe University, Japan |
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<tr>
<td>1500 – 1520</td>
<td>OBC 25 (Invited Lecture)</td>
<td>Hiromitsu Maeda</td>
<td>π Electronic Ion-Pairing Materials That Exhibit Stimuli-Responsive</td>
<td>Ritsumeikan University, Japan</td>
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<tr>
<td>1520 – 1540</td>
<td>OBC 26 (Oral Presentation)</td>
<td>Nikola Topolovcan</td>
<td>Synthesis of 1,2-Disubstituted Cyclopentadienes and Polarization and Chelation Effect on Regioselectivity of Haloallylation of Internal Alkynes</td>
<td>Charles University</td>
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<tr>
<td>1540 – 1600</td>
<td>OBC 27 (Oral Presentation)</td>
<td>Nikola Topolovcan</td>
<td>Direct Synthesis of Allene from Propargyl Alcohol via Oxaphosphetane Intermediate</td>
<td>Charles University</td>
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<td>1600 – 1630</td>
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<td>Chairperson: Dr. Chek Sotha</td>
<td>Cambodian Chemical Society, Cambodia</td>
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<td>1630 – 1650</td>
<td>OBC 61 (Invited Lecture)</td>
<td>Yuichiro Mutoh</td>
<td>Ruthenium-Catalyzed Cycloisomerization of 2-Alkynylanilides Leading to 3-Substituted Indoles via 1,2-Carbon Migration</td>
<td>Tokyo University of Science, Japan</td>
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<td>1650 – 1710</td>
<td>OBC 29 (Oral Presentation)</td>
<td>Masashi Shimomura</td>
<td>Total Synthesis of (−)-Lepadiformine A via Diastereoselective Radical Translocation-Cyclization Reaction</td>
<td>Tohoku University, Japan</td>
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<td>1710 – 1730</td>
<td>OBC 30 (Oral Presentation)</td>
<td>Haruka Sannabe</td>
<td>β-Amino Alcohol Organocatalyst for Asymmetric Michael Addition of Active Methylene Compounds to Nitroalkens</td>
<td>Muroran Institute of Technology, Japan</td>
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<tr>
<td>1730 - 1750</td>
<td>OBC 70 (Invited Lecture)</td>
<td>Yusuke Sasano</td>
<td>Chemoselective and Environmentally Benign Alcohol Oxidation Using Nitroxyl Radical/Copper Cooperative Catalysis</td>
<td>Tohoku University, Japan</td>
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<td>0900 – 0930</td>
<td>PMC 01</td>
<td>Volker Abetz</td>
<td>Venue: VIP Grand I, 1st Floor, Lobby Level</td>
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<td>PMC 02</td>
<td>Igor Potemkin</td>
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<td>1400 – 1420</td>
<td>PMC 03</td>
<td>Chin Han Chan</td>
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<td>1420 – 1440</td>
<td>PMC 04</td>
<td>Domagoj Vrsaljko</td>
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<td>PMC 05</td>
<td>Mansor Ahmad</td>
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<td>1500 – 1520</td>
<td>PMC 06</td>
<td>Olga Philippova</td>
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<td>PMC 07</td>
<td>Valentina Vasilevskaya</td>
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<td>1540 – 1600</td>
<td>PMC 08</td>
<td>Katsuhiro Maeda</td>
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**Thursday, 8 March 2018**

**Thematic Session:**

**Polymer and Materials Chemistry (PMC)**

**Venue:** VIP Grand I, 1st Floor, Lobby Level

**Session IVa**

**Chairperson:** Prof. Yasuhiro Ohki  
Nagoya University, Japan

- **0900 – 0930**  
  **PMC 01** (Keynote Lecture)  
  *Synthesis and Properties of Stimuli-responsive Copolymers*  
  Volker Abetz  
  University of Hamburg, Germany

- **0930 – 0950**  
  **PMC 02** (Invited Lecture)  
  *Polyelectrolyte and Polyampholyte Microgels. Swelling, Collapse and Interaction with Guest-Molecules*  
  Igor Potemkin  
  Physics Department, Lomonosov Moscow State University, Russian Federation

**Session IVb**

**Chairperson:** Prof Christophe Darcel  
UMR 6226-CNRS-Université de Rennes1, France

- **1400 – 1420**  
  **PMC 03** (Invited Lecture)  
  *Effect of Selective Localization of Salt and Filler on Thermal and Dielectric Properties of Poly(Ethylene Oxide)/Polyacrylate-Based Composite Polymer Electrolytes*  
  Chin Han Chan  
  Universiti Teknologi MARA, Malaysia

- **1420 – 1440**  
  **PMC 04** (Oral Presentation)  
  *Influence of ICP Etching on Hydrophobicity of Polymer Blend Surfaces*  
  Domagoj Vrsaljko  
  University of Zagreb, Faculty of Chemical Engineering and Technology, Croatia

- **1440 – 1500**  
  **PMC 05** (Invited Lecture)  
  *Development of Hyaluronic Acid-based Hydrogel Nanocomposites using Gold Nanoparticles and Seaweed*  
  Mansor Ahmad  
  Universiti Putra Malaysia, Malaysia

- **1500 – 1520**  
  **PMC 06** (Oral Presentation)  
  *Soft Nanocomposites with Tunable Matrix*  
  Olga Philippova  
  Moscow State University, Russia

- **1520 – 1540**  
  **PMC 07** (Oral Presentation)  
  *Parking-Garage Structure in Densely Grafted Polymer Brushes*  
  Valentina Vasilevskaya  
  Nesmeyanov Institute of Organoelement Compounds Russain Academy of Sciences, Russia

- **1540 – 1600**  
  **PMC 08** (Invited Lecture)  
  *Macromolecular Helicity Control in Helical Polymer Brushes through Long-range Communication of Sterechemical Information*  
  Katsuhiro Maeda  
  Kanazawa University, Japan

**Session IVc**

**Chairperson:** Prof Christophe Darcel  
UMR 6226-CNRS-Université de Rennes1, France
### Session IVd
**Chairperson:** Dr Jenny Lee
Malaysian Institute of Chemistry, Malaysia

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<td>0900 – 0930</td>
<td>PMC 12 (Keynote Lecture)</td>
<td>Fabrication of Single Crystal Thin Films and Tunneling Junctions using MgB₂ and Iron-based Superconductor SmFeAs(O,F)</td>
<td>Masahito Sakoda</td>
<td>Tokyo University of Agriculture and Technology, Japan</td>
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### Session IVe
**Chairperson:** Prof. Masahito Sakoda
Tokyo University of Agriculture and Technology, Japan

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<td>1030 – 1050</td>
<td>PMC 14 (Invited Lecture)</td>
<td>Enhanced Electroluminescence from Delayed-Fluorescence Emitters by Suppressing Nonradiative Decay</td>
<td>Katsuyuki Shizu</td>
<td>Kyoto University, Japan</td>
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<td>1050 – 1110</td>
<td>PMC 15 (Invited Lecture)</td>
<td>Peptide Ligands Immobilization via Single-step Tyrosine Oxidation for Biologically Active Cardiovascular Devices</td>
<td>Sachiro Kakinoki</td>
<td>Kansai University, Japan</td>
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<td>1110 – 1130</td>
<td>PMC 16 (Invited Lecture)</td>
<td>Supramolecular Liquid-Crystalline Materials for Ion and Electron Transport and Stimuli-Responsive Emission</td>
<td>Masafumi Yoshio</td>
<td>National Institute for Materials Science, Japan</td>
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<td>1130 – 1150</td>
<td>PMC 17 (Invited Lecture)</td>
<td>Molecular Computing by Tetranuclear Mixed-Valence Complexes: A Theoretical Study on Relationship between Molecular Structure and Device Operation of Molecular</td>
<td>Ken Tokunaga</td>
<td>Kogakuin University, Japan</td>
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1150 – 1210  
**PMC 18 (Invited Lecture)**  
**Self-Assembling Organic-Inorganic Hybrid Dendrimers with a Monodispersed Functional Nanoparticle-Core**  
Kiyoshi Kanie  
Tohoku University, Japan

1210 – 1230  
**PMC 19 (Invited Lecture)**  
**Organic Long Persistent Luminescence**  
Ryota Kabe  
Kyushu University, Japan

1230 – 1400  
**Session IVf**  
Chairperson: Prof. Masahito Sakoda  
Tokyo University of Agriculture and Technology, Japan

1400 – 1420  
**PMC 20 (Invited Lecture)**  
**Development of Functional Nanoparticles Based on RAFT Polymerization**  
Kazuhiro Nakabayashi  
Yamagata University, Japan

1420 – 1440  
**PMC 21 (Invited Lecture)**  
**Incorporating a TiOx Shell in Single-Walled Carbon Nanotube/Fullerodendron Coaxial Nanowires**  
Tomoyuki Tajima  
Okayama University, Japan

1440 – 1500  
**PMC 22 (Invited Lecture)**  
**Synthesis and Gas Permeability of Poly(substituted acetylene)s and their Mixed Matrix Membranes with Metal Chlorides**  
Toshikazu Sakaguchi  
University of Fukui, Japan

1500 – 1520  
**PMC 23 (Invited Lecture)**  
**Synthesis and Properties of a p-Stacked Antioxidant Polymer**  
Tamaki Nakano  
Hokkaido University, Japan

1520 – 1540  
**PMC 24 (Invited Lecture)**  
**Preferred Crystal Orientation of Melt-crystallized Biobased Polyesters in Thin Films on Si Substrates**  
Sono Sasaki  
Kyoyo Institute of Technology, Japan

1540 – 1630  
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<td>1050</td>
<td>FMC 02 (Invited Lecture)</td>
<td>Synthesis of Minor Flavonoids and Their Effects on Prostaglandin E2 and Nitric Oxide Production in LPS/IFN-γ Stimulated Murine RAW 264.7 and Human U937 Cell Kamal Rullah University of Malaya, Malaysia</td>
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<td>1100</td>
<td>FMC 03 (Invited Lecture)</td>
<td>Effects of Water Blanching on Biological and Physicochemical Properties of Sweet Potato Slide Chhe Chinda Royal University of Agriculture, Cambodia</td>
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<td>1130</td>
<td>FMC 04 (Invited Lecture)</td>
<td>Organometallic Antitumor Compounds: A new generation of Ferrociphenols Siden Top Cambodian Chemical Society, Phnom Penh, Cambodia</td>
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<td>1400</td>
<td>IGS 10 (Keynote Lecture)</td>
<td>Psychology and STEM: Pathways to a Neuroscience Approach to Career Choice Quek Ai-Hwa HELP University Malaysia, Malaysia</td>
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<td>1420</td>
<td>IGS 02 (Invited Lecture)</td>
<td>Creation of High Activity Water-Splitting Photocatalyst using Au25 cluster Cocatalyst Wataru Kurashige Tokyo University of Science, Japan</td>
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<td>1440</td>
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<td>Triphosphasumanenes: Janus-Type p-Conjugated Molecules and Their Out-of-Plane Anisotropy Shunsuke Furukawa Saitama University, Japan</td>
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<td>1500</td>
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<td>Engineering of Phosphorus Metabolic Pathway: A Safeguard Strategy for Greater Use of Genetically Modified Microorganisms Ryuichi Hirota Hiroshima University, Japan</td>
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<td>1520</td>
<td>IGS 05 (Invited Lecture)</td>
<td>Symmetry Projection Approach for Strongly Correlated System Motoyuki Uejima Kobe University, Japan</td>
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<td>IGS 06 (Invited Lecture)</td>
<td>Design and Syntheses of Ion-Conducting Metal-Organic Frameworks Masaaki Sadakiyo Kyushu University, Japan</td>
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| Session VIIb | Chairperson: Dr. Kamal Rullah  
University of Malaya, Malaysia |
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| 1630 – 1650 | IGS 07 (Invited Lecture)  
**Rule Extraction and prediction for Ignition Point using Decision Tree and Random Forest**  
Ryoko Hayashi  
Kanazawa Institute of Technology, Japan |
| 1650 – 1710 | IGS 08 (Invited Lecture)  
**Nucleophilic-Type Ring Transformation: A Powerful Synthetic Tool**  
Nagatoshi Nishiwaki  
Kochi University of Technology, Japan |
| 1710 – 1730 | IGS 09 (Invited Lecture)  
**Psychological Well-being of Students in context of Education and Career**  
QUEK Ai-Hwa  
HELP University Malaysia, Malaysia |
| 1730- 1750 | IGS 13 (Invited Lecture)  
**Synthesis of Nanosheet Photocatalysts and Their Applications**  
Ken-ichi Katsumata  
Tokyo University of Science, Japan |
| 1750        | End |

**Thursday, 8 March 2018**  
**Thematic Session:**  
**Analytical and Environmental Chemistry & Engineering (AEC)**  
Venue: Sophamith Ballroom, 3rd Floor

| Session Va | Chairperson: Prof Dr Mansor Ahmad  
Universiti Putra Malaysia, Malaysia |
|-------------|--------------------------------|
| 0900 – 0920 | AEC 01 (Invited Lecture)  
**Laser Ionization Time-of-Flight Mass Spectrometry for the Analysis of Emulsions**  
Tomohiro Uchimura  
University of Fukui, Japan |
| 0920 – 0940 | AEC 02 (Invited Lecture)  
**Remediation of 2,4,6-trichlorophenol Contaminated Wastewater Using TiO₂ Photocatalysis: Parametric & Kinetic Studies**  
Collin Joseph  
Universiti Malaysia Sabah, Malaysia |
| 0940 – 1000 | AEC 03 (Invited Lecture)  
**Adsorption Behavior of Organoarsenic Compounds in Soils**  
Masato Tanaka  
The University of Tokyo, Japan |
| 1000 –1030  | Refreshments |
| 1030 – 1245 | Plenary Lectures 1, 2, & 3  
*Venue: Sophanith Ballroom 1st Floor, Lobby Level* |
| 1245 – 1400 | Lunch |

**Session Vb**  
Chairperson: Dr. Collin Joseph  
Universiti Malaysia Sabah, Malaysia

| 1400 – 1420 | AEC 04 (Invited Lecture)  
**Orientation Dependent FRET as a Tool to Analyze DNA Structures**  
Hiromu Kashida  
Nagoya University, Japan |
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<td>Yang Farina</td>
<td>Universiti Kebangsaan Malaysia, Malaysia</td>
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<td>Oral Presentation: Classification of Bird’s Nest by State Using Isotope Ratio Mass Spectrometry</td>
<td>Malarvili Ramalingam</td>
<td>Jabatan Kimia Malaysia, Malaysia</td>
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<td>1500 – 1520</td>
<td>AEC 07</td>
<td>Oral Presentation: Electrochemical Detection of Antioxidants BHA, BHT and TBHQ in food samples using Graphite Nanocomposite Green Electrochemical Sensors</td>
<td>Tan Guan Huat</td>
<td>University of Malaya, Malaysia</td>
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<td>AEC 08</td>
<td>Award Lecture of ISPAC2017: A Microfiltration Device for Cancer Detection by Circulating Tumor Cells in Blood</td>
<td>Daisuke Onoshima</td>
<td>Nagoya University, Japan</td>
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<td>AEC 09</td>
<td>Invited Lecture: Assessing Arsenic Health Issues in the Mekong River Basin of Cambodia</td>
<td>Kongkea Phan</td>
<td>Cambodian Chemical Society, Cambodia</td>
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<td>Invited Lecture: Seasonal Variation of Metals (Cd, Cu, Fe, Pb and Zn) in Surface Water of Tropical Riverine System, Cambodia</td>
<td>Sorya Proum</td>
<td>Royal University of Phnom Penh, Cambodia</td>
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<td>Invited Lecture: Electrochemical remediation of prazosin using Graphite-PVC composite as anode</td>
<td>Zuriati Zakaria</td>
<td>Malaysia Institute of Chemistry, Malaysia</td>
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**Saturday, 10 March 2018**

**Thematic Session:**

**Organic and Biomolecular Chemistry (OBC)**

**Venue:** Sophamith Ballroom, 3rd Floor

**Session Im**

**Chairperson:** Dr. Phan Kong Kea  
Cambodian Chemical Society, Cambodia

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<td>0900 – 0920</td>
<td>OBC 57</td>
<td>Invited Lecture: Asymmetric Desymmetrization of meso-Aliphatic Dials through Intramolecular Aldol Reaction</td>
<td>Takumi Furuta</td>
<td>Kyoto University, Japan</td>
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<td>0920 – 0940</td>
<td>OBC 58</td>
<td>Invited Lecture: Palladium-Catalyzed Direct Allylic Substitution by Using Phosphine-Borane Ligand</td>
<td>Gen Onodera</td>
<td>Nagasaki University, Japan</td>
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| Session In | Chairperson: Dr. Phan Kong Kea  
Cambodian Chemical Society, Cambodia |
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| 1030 – 1050 | OBC 68 (Invited Lecture)  
Amino Acids as Precursors for Efficient Synthesis of Oxindoles, Pyrroloindolines and Dihydroquinoxalinones via C-H Functionalization  
Kyalo Stephen Kanyiva  
Waseda University, Japan |
| 1050 – 1110 | OBC 60 (Invited Lecture)  
Synthesis of Azadirachtin  
Naoki Mori  
The University of Tokyo, Japan |
| 1150 – 1210 | OBC 63 (Invited Lecture)  
Large Scale Synthesis and Conductivities of [10]Cycloparaphenylene and Its Tetraalkoxy Derivatives  
Eiichi Kayahara  
Kyoto University, Japan |
| 1210 – 1230 | OBC 64 (Invited Lecture)  
Catalytic Stereoselective Formation of C-C Bond in Target-Oriented Synthesis  
Andrei Malkov  
Loughborough University, UK |
| 1230 – 1250 | OBC 65 (Invited Lecture)  
Coexistence of a Li Moiety and a Pd Moiety on Dihydropentacene  
Song Zhiyi  
Hokkaido University, Japan |
| 1250 – 1400 | Lunch / Posters |
| Session Io | Chairperson: Dr Jenny Lee  
Malaysian Institute of Chemistry, Malaysia |
| 1400 – 1420 | OBC 66 (Invited Lecture)  
Copper-Catalyzed Defluoroborylation of Fluoroarenes  
Takashi Niwa  
Institute of Physical and Chemical Research, Japan |
| 1420 – 1440 | OBC 24 (Invited Lecture)  
Electrochemical Synthesis of Heterocycles through Radical Cyclizations  
Hai-chao Xu  
Xiamen University, China |
| 1500 – 1520 | OBC 69 (Invited Lecture)  
Amino-halogenation of Indoles as Dual Functionalization Using I–N Bonding Hypervalent Iodine Compounds  
Katsuhiko Moriyama  
Chiba University, Japan |
| 1600 – 1630 | Refreshments |
| 1630 | End |
### Thematic Session: Organic and Biomolecular Chemistry (OBC)

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<td>Monosulfide-Disulfide-based Lubricant Additives: Synthesis and Tribology Performance for Metalworking Fluid</td>
<td>Ong Chiu Ling</td>
<td>University of Malaya, Malaysia</td>
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<td>OBC 74P</td>
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<td>Synthesis of Asymmetric Disulfide Derivatives as Potential Multifunctional Lubricant Additives</td>
<td>Lim Shi Teng</td>
<td>University of Malaya, Malaysia</td>
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### Thematic Session: Polymer and Materials Chemistry (PMC)

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<td>Investigation of Electron Density Distribution Imaging by Maximum Entropy Method for Paracrystal Structure of Polyamide</td>
<td>Miho Nagao</td>
<td>Kyoto Institute of Technology, Japan</td>
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<td>PMC 25P</td>
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<td>Characterization and Properties of Polymer Thin-Film Based on Poly(acrylic acid) and Lithium Perchlorate</td>
<td>Koh Sing Ngai</td>
<td>University of Malaya, Malaysia</td>
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<td>PMC 26P</td>
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<td>Additive manufacturing of polymeric microreactors for continuous flow synthesis</td>
<td>Igor Dejanović</td>
<td>University of Zagreb, Croatia</td>
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The Abstracts

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Datuk Dr Soon Ting Kueh
on behalf of the ICPAC2018 Organising Committee
Date: 26 February, 2018
Story of SF5-Pyridines

Norio Shibata\textsuperscript{a,b,*}

\textsuperscript{a}Department of Nanopharmaceutical Sciences  
\textsuperscript{b}Department of Life Science and Applied Chemistry  
Nagoya Institute of Technology, Gokiso, Showa-ku, Nagoya 466-8555, Japan  
\textsuperscript{*}Corresponding author: nozshiba@nitech.ac.jp

Abstract

Chemistry of SF\textsubscript{5}-substituted compounds has gained attention due to the unique property of SF\textsubscript{5}-group. Recent substantial efforts in synthetic SF\textsubscript{5} chemistry have made simple SF\textsubscript{3} aromatics easily available. However, the preparation of SF\textsubscript{5} pyridines remains a challenge. Unlike SF\textsubscript{5}-benzenes, which can be prepared at an industrial scale by direct fluorination of aryl disulfides or by Umemoto’s procedure by the oxidative chloro-tetrafluorination of aryl disulfides to arene-sulfur chlorotetrafluorides (SF\textsubscript{4}Cl-arenes) followed by a chloride/fluoride exchange reaction with fluoride, heteroaromatic systems were difficult to follow this pathway and different strategies are used. In 2015, Dolbier and co-workers reported the first general method for the synthesis of ortho-SF\textsubscript{5}-substituted pyridines using Umemoto’s method in which 2,2’-dipyridyl disulfides interacted with the KF/Cl\textsubscript{2}/MeCN system to afford SF\textsubscript{4}Cl pyridines. For further transformation of these sulfur chlorotetrafluorides to SF\textsubscript{5} pyridines, silver fluoride (AgF) was found to be the principal reagent. Despite this, m- and p-pyridine disulfides failed to form SF\textsubscript{4}Cl-pyridines under same conditions. Herein we disclose a general method for the preparation of m- and p-SF\textsubscript{5}-pyridines for the first time. First, at least one fluorine atom in the pyridine ring effectively reduces the basicity of nitrogen, inhibiting it from entering a decomposition pathway. Second, fluorine induces greater stability of the SF\textsubscript{4}Cl moiety. Moreover, the C-F bond at the ortho-position of pyridine can be easily activated towards nucleophilic aromatic substitutions under suitable conditions selected.

Keywords: SF\textsubscript{5}, fluorine, pyridine, sulfur

References

Microarray and NMR Study of Core M1 Glycan Modified α-Dystroglycan Fragments

Hiroshi Hinou*, Seiya Kikuchi

Graduate School of Life Science, Hokkaido University
*Corresponding author: hinou@sci.hokudai.ac.jp

Abstract

Congenital disorders of the O-mannose type glycan synthesis on α-dystroglycan cause some forms of muscular dystrophy called dystroglycanopathy. Protein O-linked mannose β1,2-N-acetylgalactosaminyltransferase 1 (POMGnT1), a glycosyltransferase that catalyzes β1,2-linkage formation of N-acetylgalactosamine (GlcNAc) to mannose (Man) on threonine or serine residues of protein, was reported as a causative gene for muscle-eye-brain (MEB) disease, however, the function of the POMGnT1-related glycans, assigned as core M1, is still unclear. In this study, structural and functional effects of the core M1 type glycan modification were investigated using a synthetic glycopeptide library focused on an α-dystroglycan fragment, 372TRGAIIQTPTLGPIQPTRV390. A microarray study displaying the core M1 modified glycopeptide library revealed some characteristic binding pattern of lectins. In NMR study, core M1 glycan modification specific changes in amide bond chemical shift of peptide backbone were found. Conformational analysis based on NMR (NOE) signals revealed structural change of the peptide backbone at the core M1 modified region, Thr381 and Thr388, from extended to turn-like conformation.

Keywords: microarray, conformation, NMR, dystroglycan, POMGnT1
**Detailed Mechanism and Application of Selective Lithium-Bromine Exchange on the Hexaphenylbenzene Framework**

**Tatsuo Kojima**

*Department of Basic Science, Graduate School of Arts and Sciences, The University of Tokyo, Japan*

*Corresponding author: ckojima@mail.ecc.u-tokyo.ac.jp*

**Abstract**

Hexaphenylbenzene (HPB) is a versatile scaffold for various materials and a useful precursor of graphene fragments such as hexa-\textit{peri}-benzocoronene. While HPB derivatives with various substituents have been prepared through metal-catalyzed cyclotrimerization of diarylacetylenes or through Diels-Alder reaction of tetraphenylcyclopentadienone derivatives and diarylacetylenes, both of the methods can achieve limited substitution patterns in a selective manner.

We recently developed selective alternate trilithiation through lithium-bromine exchange of brominated HPB derivatives (Scheme).\(^1,2\) This lithiation reaction can selectively and efficiently afford HPB derivatives with \(C_3\) or \(C_{2v}\)-symmetric substitution patterns. This selectivity was found to derive from a two-stage mechanism through the monitor of the lithiation process of a hexabrominated HPB derivative. In the first stage, solubility-controlled lithiation affords the mixture mainly comprised of the completely lithiated species and the starting HPB derivative due to the low solubility of the starting HPB derivative. In the second stage, the reversible ArBr/ArLi exchange, halogen dance, affords the alternately trilithiated species selectively under thermodynamic control. In some cases, addition of mesityl bromide (MesBr) or \(p\)-(dimethylamino)phenyl bromide (MapBr) was crucial because \textit{in situ} generated MesLi or MapLi should complete the lithiation of the HPB derivatives at a high temperature in THF instead of \(t\)-BuLi, which is unstable in such a condition. Through the mechanistic study with partially brominated HPB derivatives, we experimentally confirmed that the thermodynamic preference of the alternate lithiation pattern results from the strong through-space interaction between adjacent aryl groups, especially from the strong electronic repulsion between adjacent lithiophenyl groups.

**Keywords:** lithium, hexaphenylbenzene, lithium-bromine exchange, self-assembly

**References**

Total Synthesis of Antrimycin A and D

Yoko Yasuno, Akito Nishimura, Akira Sawai, Ai Sekihara, Tetsuro Shinada*  
Graduate School of Science, Osaka City University, Japan  
*Corresponding author: shinada@sci.osaka-cu.ac.jp

Abstract

Antrimycins 1–4 were isolated from Streptomyces bacteria by Umezawa et al.1 and Otake et al.2 These natural products are rich in characteristic unusual amino acids: dehydropiperazic acid, α,β-dehydroamino acid, 2,3-diaminobutyric acid, and α-hydroxymethylserine, and display a unique spectrum of antimicrobial activities for Lactobacillus casei and some strains of Streptococci and Mycobacterium sp. The structural and biological features made antrimycins attractive targets for total synthesis aiming to develop a new lead of antimicrobial agents. Schmidt3 and Shin4 independently achieved total synthesis of antrimycin Av (2) and Dv (4) bearing a dehydrovaline (Δ-Val) moiety. On the other hand, total synthesis of antrimycin A (1) or D (3) in which Δ-Val of 2 or 4 is replaced with E-dehydroisoleucine (Δ-Ile) has not been achieved yet. In this presentation, we report the first total synthesis of 1 and 3 by fragment coupling of 5, 6, and 7 via the stereoselective construction of E-ΔIle.5

Keywords: peptide, natural product, total synthesis, dehydroamino acid, antimicrobial activity

References

Azobenzene-tethered DNA for the photo-regulation of DNA functions

Hiroyuki Asanuma*
Graduate School of Engineering, Nagoya University, Japan
*Corresponding author: asanuma@chembio.nagoya-u.ac.jp

Abstract

DNA has not only a genetic carrier but various physical and chemical functions as a supramolecule. These roles and functions are mainly based on the spontaneous hybridization of two strands that are complementary each other. If one can photo-regulate formation and dissociation of the duplex, scope of the application should be extended, such as artificial regulation of gene expression, DNA computer, as well as molecular machine. For this purpose, we have synthesized modified DNA tethering azobenzenes via D-threoninol as a scaffold, and hybridization with its complementary strand has been successfully photo-regulated (Fig.(a)).

Azobenzene derivatives are the most popular photo-responsive molecules for versatile applications, because of its availability and chemical stability. A planar trans-form can be obtained upon visible light irradiation (λ > 400 nm) and a nonplanar cis-form is obtained by UV light irradiation (300 nm < λ < 400 nm). The photo-isomerization between trans- and cis-form is totally reversible without side reaction. We introduced multiple azobenzenes into DNA as base-surrogates designed with D-threoninol as a scaffold. In trans-form, planar azobenzenes are intercalated and stabilize the DNA duplex by stacking interaction. In cis-form, however, non-planar structure interferes with base-pairing of adjacent nucleobases, resulting in dissociation of the duplex (Fig.(a)). With this photoresponsive DNA, we successfully achieved various functional molecular machines that are operated by light irradiation (Fig. (b-d)).

Keywords: azobenzene, DNA, photoregulation, threoninol

References
A Versatile Synthesis of Renieramycin Marine Natural Products

Masashi Yokoya, Mitsuhiro Sato, Kento Monden, Kei-ichiro Kobayashi, Naoki Saito*

Graduate School of Pharmaceutical Sciences, Meiji Pharmaceutical University, Japan
*Corresponding author: naoki@my-pharm.ac.jp

Abstract

Following the discovery of renieramycins A-D from the Pacific Ocean blue sponge Reniera sp. in 1982,¹ about 30 marine natural renieramycins have been isolated from several kinds of marine organisms. The structure of renieramycins were almost similar to that of ecteinascidin 743 (3, Yondelis®, trabectedin), which has been approved and marketed in 80 countries worldwide for the treatment of human soft tissue sarcoma. Some of these alkaloids show antitumor activity with respect to several human cancer cell lines.² However a detailed biological activities about them are little explored, because these marine natural products are available in very minute quantities. As a number of pioneering researchers have published the total synthesis of renieramycins, but most syntheses were targeted on only an individual natural products. Herein, we describe a versatile and practical synthesis of seven renieramycin congeners from a common pentacyclic intermediate 5, which was effectively synthesized from 4 over 12 steps.³ Renieramycins H and I (1H, 1I) having unsaturated bond at C-3,4 were prepared through a bis-quinone 6. Other renieramycins 1M, 1G, 1S, 1T and 2 were synthesized, through 7, which was obtained from 5 by the action of hydrogen (1.5 MPa) on Raney nickel stereoselectively. A detail results in effective synthesis of renieramycins will be discussed.

Keywords: renieramycin, total synthesis, isoquinoline, marine natural product, antitumor agent

References

Total Synthesis of Phaeosphaerides A and B

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Abstract

Phaeosphaerides A (proposed structure 1) and B (2) are nitrogen-containing bicyclic natural products that were isolated from the endophytic fungus FA39 (Phaeosphaeria avenaria) by Clardy and co-workers in 2006. Phaeosphaeride A is an inhibitor of STAT3-DNA binding with an IC\(_{50}\) of 0.61 mM and also inhibits cell growth in STAT3-dependent U266 multiple myeloma cells with an IC\(_{50}\) of 6.7 μM, whereas its stereoisomer phaeosphaeride B (2) has no STAT3 inhibitory activity. In 2011, we accomplished the first total synthesis of the proposed structure of phaeosphaeride A (1), however, \(^1\)H and \(^13\)C NMR spectra of the synthetic compound were not identical to those of the natural product.\(^1\) The result suggested that the structure of natural phaeosphaeride A was misassigned, and implied that the correct structure of phaeosphaeride A was the C-7 epimer 3 of the originally proposed structure or its enantiomer 4.

We have recently finished the total synthesis of 3\(^2\) and 4\(^3\), and spectroscopic data of these compounds correspond to the literature data for natural phaeosphaeride A. The optical rotations of 4 and the natural product have the same signs; therefore, phaeosphaeride A was assigned as compound 4. Thus, we established the relative and absolute configurations of natural phaeosphaeride A.

Additionally, we identified the remarkable biomimetic transformation from phaeosphaeride A (4) to phaeosphaeride B (2) by trifluoroacetylation with inversion at the C-6 stereocenter followed by basic hydrolysis.\(^3\) This work confirmed the hypothetical biosynthesis of phaeosphaeride B (2) from phaeosphaeride A (4).

Keywords: Phaeosphaeride A, Phaeosphaeride B, STAT3, natural product synthesis

References

Determining Nonempirical Absolute Configuration of Chiral Mono-alcohols Using Bis(zinc porphyrin) as a CD-Sensitive Bidentate Host Molecule

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Abstract

Absolute configuration determination of chiral organic molecules remains an important and challenging task in the life and material sciences fields. Recently, supramolecular chirality induction (supramolecular chirogenesis) utilizing a circular dichroic (CD)-sensitive host molecule possessing two or more chromophores with known electronic transitions has been attracted interest for a highly sensitive, non-empirical, microscale determination of absolute configuration of chiral organic molecules. However major problematic issue is their insufficient binding affinity for weakly ligating substrates, particularly simple chiral mono-alcohols.

Herein we report a newly designed bis(zinc porphyrin) BP1 bearing a splayed cofacial structural motif as an unprecedented bidentate CD-sensitive host molecule, which can effectively capture both of the hydroxyl lone pair through simultaneous coordination with two central metals of the porphyrin subunits (Figure 1). The combination of BP1 as a chirality probe and the simple working model depicted in Figure 2 is effective for method to determine the nonempirical absolute configuration of chiral mono-alcohols. We have developed a facile and direct determination of absolute configurations for chiral mono-alcohols using a CD-sensitive BP1 host system.

Keywords: CD-Sensitive, bis(zinc porphyrin), mono-alcohols, absolute configuration, nonempirical,

Figure 1. Structure of BP1.

Figure 2. Working model and CD spectra of BP1 in the presence of chiral mono-alcohols.

References

Total Synthesis of Brasilicardins A and C

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Abstract

Brasilicardins A–D (1-4), isolated from the cultured broth of the pathogenic actinomycete Nocardia brasiliensis and characterized by Kobayashi et al., are tricyclic metabolites containing a highly strained trans/syn/trans-perhydrophenanthrene skeleton with a mono- or disaccharide moiety and an amino acid side chain attached. 1 Of these congeners, Brasilicardin A (1) has been shown to exhibit the most potent immunosuppressive activity in a mouse mixed lymphocyte reaction assay (IC50 = 0.057 μg/mL) and to exhibit cytotoxic activity against adriamycin-resistant murine lymphoma cells (IC50 = 0.078 μg/mL). Owing to its great potential as a new drug lead for immunosuppressants and its unprecedented hybrid molecular architecture prompted us to embark on the total synthesis. Herein, we report the first total synthesis of Brasilicardins A (1) and C (3).

Diels–Alder reaction of α-cyano-α,β-enone 5 with silyloxydiene 6 in a sealed tube at 140 °C proceeded uneventfully to give the target cycloadduct 7 as a single diastereomer in 98% yield. Sequential treatment of tricyclic α-cyano ketone 7 with lithium naphthalenide in a 6:1 mixture of ether/DME at −78 °C and CH3I provided the desired C-methylated ketone 8 as a single diastereomer, which was uneventfully transformed to aldehyde 9 in 10 steps. Upon employing a procedure reported by Solladié-Cavalló group, aldol reaction using a titanium enolate generated from a chiral iminoglycinate 10 proceeded with complete diastereoselectivity to give anti-aldol product 11 in 86% yield. Functional group manipulations, stereoselective glycosylations and a one-pot, two-step global deprotection sequence completed total synthesis of Brasilicardins A (1) and C (3).

Keywords: Brasilicardin A, total synthesis, Diels–Alder cycloaddition/reductive angular methylation sequence, anti-selective aldol reaction, glycosylation

References


Synthesis of 3,4-Fused Tricyclic Indoles Using Transition Metal Catalysis

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Abstract
3,4-Fused tricyclic indole skeletons are found in various bioactive natural products and pharmaceuticals. Most of these molecules possess a functionalized medium-size ring bridging the C3 and C4 positions of the indole. This class of compounds is an attractive target in synthetic organic chemistry due to the ubiquity of the structural motif in bioactive molecules, as well as their characteristic structures. In this presentation, two-types of synthetic method of this structural motif will be discussed.

Allenes generally react with an aryl halide in the presence of a Pd(0) catalyst to give the corresponding π-allylpalladium(II) species through a Heck insertion process. We hypothesized that treatment of allenes tethered to ortho-iodoaniline derivatives at the meta-position with a Pd(0) catalyst in the presence of base would lead to the formation of 3,4-fused tricyclic 3-alkylidene indoline derivatives, which would be isomerized to 3,4-fused tricyclic indole skeletons. The corresponding substrates were reacted with 5–10 mol % of Pd catalyst and 4 equiv of K2CO3 in DMSO at 90 °C, producing 3,4-fused tricyclic 3-alkylidene indoline derivatives in moderate to excellent yield. The products were divergently transformed into three types of 3,4-fused tricyclic indole derivatives.

Difficulty in preparing multi-substituted iodoaniline derivatives limited the flexibility to synthesize 3,4-fused tricyclic indoles with additional substituents on the aromatic ring using the developed Pd catalysis. Therefore, a novel Pt-catalyzed cascade cyclization reaction was developed by intramolecular Friedel-Crafts-type C–H coupling of aniline derivatives with a propargyl carbonate unit–allylic amination sequence. Treatment of various propargyl carbonates tethered to meta-aniline derivatives with a Pt(dba)3/DPEphos catalyst system afforded the corresponding 3,4-fused tricyclic 3-alkylidene indolines, which could be transformed into the target compounds in excellent yield.

Keywords: Cascade catalysis, Indole, Palladium, Platinum.

References
Construction of “metathesase” with protein scaffold and potential application of olefin metathesis as a biochemical tool

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Abstract

Recently, a variety of artificial enzymes with protein scaffold have been constructed by genetic mutation and synthetic approaches to aim at chemical materials conversion under mild conditions. Most of artificial enzymes reported so far mediate oxidation, reduction and hydrolysis. On the other hand, C–C bond formation is a popular and important reaction type in organic syntheses. However, C–C bond formation is a rather minor type of reaction in biological systems. And thus, artificial enzymes mediating C–C bond formations have become attractive. In this context, we have prepared a Hoveyda-Grubbs complex-containing enzyme and have attempted to conduct ring-closing metathesis inside of the protein. In order to regioselectively conjugate the complex to the structural cleft of α-chymotrypsin, a natural hydrolase, protease inhibitor 1-L was designed. The inhibitor is expected to bind to the protein through molecular recognition of the protein to alkylate the histidine residue of the active site.

The ring-closing metathesis activity of the chymotrypsin with 1-L depends on the charge state of substrates. A glucose-pendant diallylamine compound showed the higher turnover number compared to a cationic diallylammonium or a hydrophobic N-tosylated diallylamine. The low activities in the latter two substrates are due to electronic repulsion between the substrate and the protein and preferential hydration, because chymotrypsin has a highly positive charge surface under the conditions (pI = 8.1). Furthermore, we found throughout this work that the addition of KCl into the reaction mixture is effective to enhance the metathesis activity in aqueous media. This stems from the suppression of ligand exchange of Cl– with H2O or OH– on the metal center. The knowledge is an important insight on the optimization of reaction conditions for olefin metathesis under neutral conditions in water. Namely, the finding may indicate a possibility of olefin metathesis as a biochemical tool.

Keywords: Artificial enzyme; Olefin metathesis; Biochemical reaction

References

Mechanistic Insight of Asymmetric Autocatalysis of Pyrimidyl Alkanol by Structure Analysis of Zinc Alkoxide Complexes

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Abstract

Asymmetric amplification phenomena are highly interesting topics for scientists due to their usefulness in synthetic application and possible relation to the origin of biological homochirality. In 1995, the first and the only example of asymmetric amplification during the asymmetric autocatalytic reaction was revealed. Thus, in the addition reaction of diisopropylzinc to pyrimidine-5-carbaldehyde, the product alkanol act as an asymmetric autocatalyst, which afforded a product with the same structure and absolute configuration (Scheme 1). The most remarkable point of this reaction is significant amplification of ee. Even when the initial catalysts only have trace amount of ee, the reaction can amplify the ee to detectable level and the reaction affords almost enantiopure products at the end of the reaction. To obtain the mechanistic insights of this unique reaction, we examined single crystal X-ray diffraction analysis and revealed that the key of this significant amplification of ee was attributed to the formation of oligomeric structure of zinc alkoxides (Fig. 1). The crystallization of enantiopure and racemic alkoxide give the tetramer structures by 12-memberd macrocycle formation between two Zn-O-Zn-O square alkoxide dimers. By changing the amount of diisopropylzinc, higher oligomeric structure of zinc alkoxide was also observed. Furthermore, CD spectrum analysis of alkoxide solution suggests that this tetramer complexes exist in equilibrium with Zn-O-Zn-O square dimer complexes. The key of amplification of ee is attributed to these complex equilibria of various oligomeric structures.

Keywords: Asymmetric Autocatalysis, Asymmetric Amplification

References

Heme Uptake Proteins from Pathogenic *Vibrio cholerae*

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Abstract

Almost all bacteria require iron for their survival and have developed sophisticated mechanism by which they solubilize, sequester, and release iron within the cell. Most bacterial pathogens have evolved to take advantage of heme-containing proteins as a source of iron. Based on the genome sequence of *Vibrio cholerae* and bioinformatics-based predictions, putative genes coding heme acquisition have been discerned and called as Hut *(Heme Utilization)* (Fig. 1). Among the Hut proteins, HutZ and HutW were predicted as a heme-degrading enzyme and heme-transport proteins, respectively. In this study, we constructed *Escherichia coli* expression system of HutZ and HutX, and confirmed the function of both proteins. HutZ was overexpressed in *E. coli* and purified to homogeneity. By addition of H$_2$O$_2$ to the purified heme-HutZ, absorbance at the Soret band diminished with a concomitant increase in the absorbance at 644 nm (Fig. 2)\(^1\). This spectral change suggests the formation of verdoheme, one of the reaction intermediates observed in human heme degrading enzyme, heme oxygenase (HO). In the reaction with ascorbic acid, we identified oxyferrous heme using rapid mixing apparatus combined with resonance Raman spectroscopy, *meso*-hydroxyheme, and biliverdin using mass spectroscopy. Accordingly, we concluded that HutZ degrades heme in a manner similar to mammalian heme oxygenase, despite their low sequence and structural homology\(^2\).

HutX was purified as an apoprotein without any pigment. However, absorption spectral analysis demonstrated that HutX binds heme at a ration of 1:1 with $K_d$ of 7.4 nM. The crystal structure of HutX (Fig. 3) and resonance Raman spectra of heme-bound HutX suggest that the axial ligand of the ferric heme is Tyr90, present at the dimer interface\(^3\). Surface plasmon resonance experiments confirmed that HutX interacts with HutZ with the dissociation constant of about 400 $\mu$M. These results suggest that heme is transferred from HutX to HutZ via specific protein-protein interaction. Therefore, it can be concluded that HutX is a cytoplasmic heme transport protein to HutZ.

Keywords: heme, enzyme, iron, pathogen

References

C(sp³)–H Bond Functionalization Mediated by Hydride Shift/Cyclization System

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Abstract

The development of methods for the direct functionalization of unreactive C–H bonds has now become a major topic in synthetic organic chemistry. These methods have enabled the formation of C–C and/or C–Y bonds (Y = O, N, etc.) without pre-functionalization to C–X bonds (X = halogens, OSO₂CF₃, etc.). Recently, we have developed novel type of C–H bond functionalization methodology based on hydride shift involved internal redox system. The key feature of this transformation is the hydride shift of the C(sp³)–H bond to the heteroatom. Subsequent endo-type cyclization to a cationic species affords heterocycle.

In addition to the unique reaction system, synthetic utility of this reaction was worthy to emphasize. Various synthetically useful skeletons, such as quinazoline, benzopyran, isoquinoline, and tetralin could be constructed based on this method. Challenging, enantioselective C(sp³)–H bond functionalization was also attainable by means of chiral phosphoric acid. Further interesting feature of this reaction was that it could be extended to unprecedented, double C(sp³)–H bond functionalization by sequential utilization of hydride shift process. In the presentation, I want to talk about double C(sp³)–H bond functionalization involving [1,4]-, [1,5]-, [1,6]-hydride shift composite sequential system, which leading to congested, polycyclic framework such as bicyclo[3.2.2]nonanes and linear tricyclic compounds.

Keywords: C(sp³)–H bond functionalization, hydride shift, internal redox, polyheterocycles, trifluoromethyl group

References

Cobalt-Catalyzed Allylic C(sp\(^3\))-H Additions to Low Reactive Carbonyl Compounds, CO\(_2\) and Ketones

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Abstract

The C–H activation reaction has become a powerful tool, especially for the construction of C–C bonds directly from poorly reactive C–H bonds (the pKa values are usually more than ca. 30) without using a strong base or acid. Of particular interest is the functionalization of C(sp\(^3\))-H bonds because of its high potential for the synthesis of three-dimensional complex molecules from simple aliphatic compounds. In this regard, we have been focusing on allylic C(sp\(^3\))-H functionalization. Two catalytic allylic C(sp\(^3\))-H additions to low reactive carbonyl electrophiles (CO\(_2\) and simple ketones) have been developed, thus far. In the presence of Co(acac)$_2$/Xantphos and AlMe$_3$, allylic C(sp\(^3\))-H carboxylation of allylarenes and 1,4-dienes with CO\(_2\) smoothly proceeded to afford linear $\beta,\gamma$-unsaturated carboxylic acids in high yields with good functional group tolerance. This is the first example of catalytic C(sp\(^3\))-H carboxylation with CO\(_2\) without UV irradiation. In addition, C(sp\(^3\))-H additions to various simple ketone electrophiles were achieved, affording homoallylic alcohols in high yields. The branch/linear selectivity depended on the steric and electronic factors of the ketone electrophiles: sterically compact and/or reactive ketones were favoured for branch selectivity, whereas sterically crowded ketones were favoured for linear selectivity. The intermediate in these C(sp\(^3\))-H addition reactions is thought to be an allylcobalt(I) species, which exhibits high nucleophilicity toward CO\(_2\) and ketones.

Keywords: C(sp\(^3\))-H activation, CO\(_2\), ketones. cobalt, allylic compounds

References

The first synthesis of *meso*-dicycloalkylporphycenes and their photofunctions

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Abstract

Porphycenes, which was first prepared by Vogel and co-workers in 1986, is a constitutional isomer of porphyrin with two direct bonds between neighboring pyrroles and two ethenyl bridges. Because of their unique optical properties, porphycene derivatives have been investigated as potential photosensitizers for photodynamic therapy, mimicity of proteins, near-IR theranostic agents, catalysts, and various functional materials. However, owing to the synthetic challenges involved, the growth of porphycene chemistry is much slower than that of its parent isomer porphyrin. In terms of synthetic strategies to obtain porphycene derivatives, two synthetic protocols have been envisioned as shown in below: reductive cyclization of two 5,5’-diacyl-2,2’-bipyrroles (Method a.) and oxidative cyclization of two dipyrroethanes (Method b.). The first approach has been recognized as the standard synthesis, as proposed by Vogel et al. in 1986.\textsuperscript{1} The alternative strategy was devised in 2008 by Srinivasan and co-workers.\textsuperscript{2} Inspired by the alternative strategy, our group have reported two step synthesis of 9,10,19,20-tetraalkylporphycenes (TMPc) by oxidative coupling reaction of 5,6-dialkyldipyrroethenes in 2017.\textsuperscript{3} The above findings motivated us to further exploration of unique *meso*-alkylporphycene derivatives using alternative synthetic method. Here, we report two novel *meso*-dicycloalkenylporphycenes, namely *meso*-dicyclopentyl- (Cy\textsubscript{5}Pc) and *meso*-dicyclohexylporphycenes (Cy\textsubscript{6}Pc) for the first time in porphycene chemistry.\textsuperscript{4} The solution fluorescence maxima of Cy\textsubscript{5}Pc are more than 400 times as intense as that of Cy\textsubscript{6}Pc. The results suggested that photoluminescence switching is achieved through the ring strain perturbation of the *meso*-substituted cycloalkyl groups on the porphycene cavity.

**Keywords:** porphycenes, fluorescence, oxidative coupling, hypervalent iodine (III)

References


Enantioselective Alkynylation of Ketones Catalyzed by Chiral Pincer Rh Complexes

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Abstract

Enantioselective alkynylation of carbonyl compounds is one of the most efficient methods to synthesize chiral propargylic alcohol derivatives. Generally, metal acetylides generated by terminal alkynes with stoichiometric amounts of alkyl lithium and alkyl zinc reagents were used as a nucleophile in this transformation. While this method is reliable and highly enantioselective in various ketones including acetophenone derivatives, it requires a stoichiometric amount of metal reagents for generation of metal alkynyl species. In contrast, direct alkynylation of terminal alkynes by using a metal catalyst is considered to provide an atom-economical process. Here we reported enantioselective direct alkynylation of activated ketones catalyzed by new pincer Rh catalysts.\(^1\)

The pincer Rh complexes were prepared by three steps. First, reaction of imidazolium salts with [Rh(cod)(OH)]\(_2\) yielded NHC-Rh(I) complexes. Successive oxidation by NIS promoted cyclometalation to give the corresponding CCN pincer Rh(III) complexes. Finally, the desired acetate complexes were obtained by the ligand exchange reaction with AgOAc.

The CCN pincer Rh catalysts were found to serve as an efficient catalyst in the reaction of trifluoroacetophenone derivatives with terminal alkynes to give the corresponding alcohols in high yield with high enantioselectivity. In this reaction, aromatic and aliphatic alkynes were used to show good to high enantioselectivity. Control and kinetic experiments suggested a bis(alkynyl) Rh intermediate as the active species for the C-C bond-forming step.

Keywords: Asymmetric Catalyst, alkynylation, pincer complex, rhodium, ketone

\[ \text{PhCF}_3 \text{O} + \text{Ph} \equiv \text{C}=\text{H} \xrightarrow{\text{Rh cat. (5 mol\%), 60 \text{\degree C}}} \text{Ph} \text{HO} \text{CF}_3 \]

up to 93% ee

References
Radical Reactions of Alkynes with N-Heterocyclic Carbene Boranes

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Abstract

N-heterocyclic carbene boranes (NHC-boranes) are surprisingly stable whereas they cause various radical, ionic and metal-catalyzed reactions.\textsuperscript{1} In this presentation, we report new radical reactions between alkynes and NHC-boranes.

NHC-boranes can become good precursors of boryl radicals. The NHC-boryl radicals formed in the presence of an appropriate initiator cause addition reactions to alkynes to form the corresponding β-boryl alkenyl radicals. These radicals induce interesting reactions such as \textit{trans}-hydroboration and unusual cyclization reactions\textsuperscript{2} to provide unique organoboron compounds.

Keywords: alkynes, borylation, cyclization, NHC-boranes, radical reactions

\begin{center}
\begin{tikzpicture}
\node (a) at (0,0) {NHC-borane};
\node (b) at (2,0) {NHC-boryl radical};
\node (c) at (4,0) {β-boryl alkenyl radical};
\node (radical_initiator) at (1.5,-1) {radical initiator};
\node (R1) at (2.5,-1.5) {R\textsuperscript{1}};
\node (R2) at (3.5,-1.5) {R\textsuperscript{2}};
\draw [->] (a) -- (b) node [midway, above] {\textbf{Me}} node [midway, below] {\textbf{Me}};
\draw [->] (b) -- (c) node [midway, above] {\textbf{Me}} node [midway, below] {\textbf{Me}};
\draw [->] (radical_initiator) -- (b) node [midway, below] {\textbf{Me}};
\draw [->] (R1) -- (R2) node [midway, right] {\textbf{R\textsuperscript{1}}} node [midway, left] {\textbf{R\textsuperscript{2}}};
\end{tikzpicture}
\end{center}

References

Synthesis, Characterization, and Inclusion Behavior of Bisporphyrin with Two BCOD Units

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Abstract
Porphyrins are macrocyclic molecules consisting of four pyrrolic moieties and characterized by their large \(\pi\)-conjugation system. Retro Diels-Alder reaction of bicyclo[2.2.2]octadiene (BCOD) framework is a promising method for constructing a novel \(\pi\)-conjugation network. We have developed the preparation of highly pure \(\pi\)-extended porphyrins and related compounds based on thermal conversion of BCOD moieties on the precursor.\textsuperscript{1,2} BCOD skeleton can work as a bridging unit and thermal conversion affords two \(\pi\)-system-fused macrocyclic material.\textsuperscript{3} Non-covalent interaction by \(\pi\)-conjugated compound is of special importance due to the construction of host molecule. We have also reported the synthesis of bisporphyrin connected by two BCOD unit as a spacer, which makes a cavity with defined size and shape.\textsuperscript{4} In the cavity, the porphyrin can be expected to interact strongly with electron-acceptable molecules such as fullerenes.\textsuperscript{5} In this study, we designed \textit{syn}-oriented bisporphyrin with chrysene-like bridge unit. The inclusion behavior with \(\text{C}_{60}\) and \(\text{C}_{70}\) was examined by means of UV-Vis and fluorescent titration. We will discuss synthesis and properties of this bisporphyrin.

Keywords: porphyrins, bicyclic framework, fullerene, inclusion complex

References
Two-Step Synthesis of 1,10-Phenanthroline-Derived Polyaza-[7]helicenes

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Abstract

Helicenes have attracted continuing attention regarding their synthesis and their unique photophysical properties arising from the helical chiral $\pi$-electron system. Since the pioneering helicene synthesis by Newman in 1955, various efficient approaches have been developed. However, the synthesis of [7]helicene derivatives requires more than five steps. Helicenes have potential applications in organic luminescent materials, such as a circularly polarized luminescence (CPL)-emitting material, because some helicenes show a large dissymmetry factor $g_{\text{lum}}$ (normalized difference in the emission of right-handed and left-handed circularly polarized light). However, inherent curved $\pi$-systems promote rapid intersystem crossing from the singlet to the triplet states. Thus, the fluorescence quantum yields of helicenes, and especially of more than [7]helicenes, are generally low. Therefore, easily accessible fluorescent helicenes with high quantum yields and $g_{\text{lum}}$ have been anticipated.

We report a facile two-step synthesis of aza[7]helicenes possessing a 6-5-6-6-5-6 skeleton from commercially available 2,9-dichloro-1,10-phenanthroline (1) via double amination with aniline derivatives followed by hypervalent iodine reagent-mediated intramolecular double-NH/CH couplings.1 Polyazahelicenes 2 are highly fluorescent among the helicenes reported to date. The quantum yield of tetrazahelicene 2a is enhanced up to 0.80 by the addition of TFA. Helicene 2a displayed strong CPL activity with $g_{\text{lum}}$ values that reached 0.008 under both neutral and acidic conditions.

Keywords: helicene, hypervalent iodine reagent, aza[7]helicenes, fluorescence, circularly polarized light

Reference

Simple β-Amino Alcohol Organocatalyst for Asymmetric Reactions

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Abstract

The design of a chiral organocatalyst is very important for obtaining a chiral product with a high optical purity in a catalytic asymmetric reaction. Recently, we developed chiral β-amino alcohol organocatalysts A and this catalyst showed high levels of catalytic activity in some asymmetric reactions. β-Amino alcohol is stable in air, and has two advantageous features of easy preparation and desirable structural characteristics. Thus, it can be derived easily from the corresponding amino acid ester and contains both amino group acting as covalent or basic sites and hydroxyl group acting as hydrogen bonding site in the single molecule. Furthermore, the steric influences of both the α- and β-position substituents also might be effective for control the enantioselective reaction course.

I will introduce our recent works that simple primary β-amino alcohol acts as an efficient chiral organocatalyst for the asymmetric reactions such as the Diels-Alder (DA) reactions of 1,2-dihydropyridines or 3-hydroxy-2-pyridones as dienes with dienophiles, the asymmetric 1,3-dipolar cycloaddition of some nitrones with α,β-unsaturated aldehydes, the aldol reaction of isatins with carbonyl compounds, and the Michael addition of 1,3-dicarbonyl compounds with nitroalkenes.

Keywords: β-amino alcohol, organocatalyst, Diels-Alder reaction, 1,3-dipolar cycloaddition, aldol reaction

References


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Simple β-Amino Alcohol Organocatalyst for Asymmetric Reactions

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Abstract

The design of a chiral organocatalyst is very important for obtaining a chiral product with a high optical purity in a catalytic asymmetric reaction. Recently, we developed chiral β-amino alcohol organocatalysts A and this catalyst showed high levels of catalytic activity in some asymmetric reactions. β-Amino alcohol is stable in air, and has two advantageous features of easy preparation and desirable structural characteristics. Thus, it can be derived easily from the corresponding amino acid ester and contains both amino group acting as covalent or basic sites and hydroxyl group acting as hydrogen bonding site in the single molecule. Furthermore, the steric influences of both the α- and β-position substituents also might be effective for control the enantioselective reaction course.

I will introduce our recent works that simple primary β-amino alcohol acts as an efficient chiral organocatalyst for the asymmetric reactions such as the Diels-Alder (DA) reactions of 1,2-dihydropyridines or 3-hydroxy-2-pyridones as dienes with dienophiles, the asymmetric 1,3-dipolar cycloaddition of some nitrones with α,β-unsaturated aldehydes, the aldol reaction of isatins with carbonyl compounds, and the Michael addition of 1,3-dicarbonyl compounds with nitroalkenes.

Keywords: β-amino alcohol, organocatalyst, Diels-Alder reaction, 1,3-dipolar cycloaddition, aldol reaction

References


7 - 10th March 2018, Sokhalay Angkor Resort & Spa, Siem Reap, Cambodia
Development of Cellulose-Based Chiral Fluorescent Sensors

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Abstract

Chiral sensing using fluorescent responses as output signals is an attractive technique for enantiodifferentiation in terms of its rapidity, simplicity, high sensitivity, and high-throughput ability. However, because the reported sensors can only be applied to a limited type of chiral molecule (mainly compounds with a chiral center), it is still a great challenge to develop a powerful fluorescent sensor applicable to various types of chirality. Herein, we synthesized a novel chiral fluorescent sensor (Ce-1) containing a benzo [1,2-b:4,5-b']dithiophene-based π-conjugated group as a fluorescent signaling unit using microcrystalline cellulose as a starting material. The enantioselective fluorescence response of this modified cellulose to aromatic nitro compounds was investigated in solution and in the film state. Ce-1 exhibited enantioselective fluorescence quenching for a wide range of aromatic nitro compounds with central, axial and planar chirality. Visual chiral detection based on a change of the visible emission color was also achieved with Ce-1 in conjunction with anthracene as an achiral fluorescent dye. A corresponding model molecule did not show any marked sensing ability, suggesting that the regular higher-order structure of Ce-1 plays an important role in this efficient chiral sensing.

Keywords: chirality, fluorescence, helical polymers, polysaccharides, sensing

References

Electrochemical Synthesis of Heterocycles through Radical Cyclizations

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Abstract

The research of my group focuses on the development of sustainable organic synthesis using organic electrochemistry. Particularly, we are interested in the preparation of radical intermediates via the electrooxidative activation of easily available X–H bonds (X = N, S, P, C) and application of these reactive species in the construction of C–C as well as C-heteroatom bonds. Heterocyclic structural moieties are prevalent in natural products, pharmaceuticals, agrochemicals and organic materials. As a result, the preparation of heterocycles is one of the major focuses of organic chemistry. We have been involved in the preparation of heterocycles through dehydrogenative cyclization or annulation reactions. In the lecture, our recent progress on the electrochemical generation of radical intermediates and their synthetic applications in the preparation of several classes heterocycles will be discussed. The use of electric current obviates the need for oxidizing reagents for the dehydrogenative processes.

Key words: Electrochemistry, heterocycle, radical, cyclization

Reference

**π-Electronic Ion-Pairing Materials That Exhibit Stimuli-Responsive Behaviors**

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**Abstract**

π-Electronic ions with appropriate geometries and peripheral substituents would provide assemblies through interactions between building subunits, resulting in fascinating electronic properties. Diverse ionresponsive π-electronic systems and π-electronic ions were prepared, affording dimension-controlled ionpairing assemblies as crystals, supramolecular gels, and thermotropic liquid crystals (LCs).[1] Structures and properties of the assemblies can be controlled by the combined negatively and positively charged species in the assemblies. Highly ordered arrangement of charged species, not only the ion complexes but also charged π-systems, has been found to be a key factor to exhibit the enhanced performance as fascinating electronic materials.[2] Recently, ion pairs based on porphyrin–AuIII complexes as π-electronic cations were prepared with the combination of various anions including a π-electronic anion. Porphyrin–AuIII complexes possessing aliphatic alkyl chains formed dimension-controlled ion-pairing assemblies as thermotropic liquid crystals, whose ionic components were highly organized by electrostatic and π–π stacking interactions [3]. Ion-pairing assemblies, consisting of oppositely charged species, can include various building units such as stimuli-responsive π-electronic ions. For example, the azobenzene carboxylates possessing aliphatic chains were prepared as photo-responsive anions that promote the formation of ion-pairing dimension-controlled assemblies, including mesophases, when used in conjunction with a tetrabutylammonium (TBA) cation. The photo-responsive properties of the ion pairs and the precursory carboxylic acids in the bulk state were examined by POM and XRD, demonstrating that LC–liquid and crystal–liquid phase transitions occurred depending on the number and lengths of the aliphatic chains of each assembly. It is noteworthy that an ion pair exhibited photo-induced crystal–crystal phase transitions upon switching by two irradiation wavelengths (365/436 nm) (Figure 1) [4].

**Keywords:** π-electronic ions, ion binding, ion pairing, self-assemblies, soft materials, stimuli-responsive behaviors

![Figure 1](https://example.com/figure1.png)

**Figure 1** Photo-induced crystal–crystal phase transitions of the ion pair comprising azobenzene carboxylate and TBA cation.

**References**

Synthesis of 1,2-Disubstituted Cyclopentadienes and Polarization and Chelation Effect on Regioselectivity of Haloallylation of Internal Alkynes

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Abstract

Design of new synthetic approaches to substituted cyclopentadienes has been in a great demand due to their ability to function either as substrates in organic synthesis\textsuperscript{1} or as ligands in organometallic complexes.\textsuperscript{2} In this respect, we have developed a three-step approach to the 1,2-disubstituted cyclopentadienes and its implementation for the synthesis of various metallocenes. The described method is based on i) Pd-catalyzed haloallylation of internal alkynes as a pivotal step, ii) Pd-catalyzed cross-coupling and iii) Ru-catalyzed ring-closing metathesis.\textsuperscript{3} Bromoallylation of various symmetrically and unsymmetrically substituted alkynes 1 was catalyzed by PdCl\textsubscript{2}(PhCN)\textsubscript{2} providing stereoselectively 1-bromo-1,4-dienes 2 in good yields (53-95\%). Then PEPPSI-IPr\textsuperscript{\circledast}-catalyzed Suzuki or Stille cross-coupling of vinyl metals with bromodienes 2 gave rise to the 1,3,6-trienes 3 (50-92\% yields). Finally, ring-closing metathesis of 3 catalyzed by Ru-catalysts (Grubbs 1\textsuperscript{st} and 2\textsuperscript{nd} generation catalysts) provided 1,2-disubstituted cyclopentadienes 4 (58-83\%). Metallation of the formed cyclopentadienes with n-BuLi was followed by reactions with anhydrous FeCl\textsubscript{2} or bromopentacarbonylmetals (M = Mn or Re) providing the ferrocene 5 or cymantrenes and cyrhetrenes 6. In addition, effect of polarization of the triple bond in unsymmetrical alkynes on regioselectivity of the haloallylation step was investigated in detail. Two classes of internal alkynes 7 and 8 were prepared and with an aid of simple NMR experiments (\textsuperscript{13}C, HMBC, HSQC) direction and an extent of polarization were measured. The prepared internal alkynes were subjected to the haloallylation reaction and obtained results clearly indicate that the regioselectivity of haloallylation of unsymmetrically substituted alkynes 7 is greatly affected by the polarization of the triple bond. On the other hand the regioselectivity can be reversed by introducing the chelating group in the side chain of alkynes 8.

Keywords: cyclopentadienes, haloallylation, cross-coupling, ring-closing metathesis, regioselectivity

References

Direct Synthesis of Allene from Propargyl Alcohol 
via Oxaphosphetane Intermediate

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Abstract

The allene framework is often found as an important motif in natural products. A lot of synthetic protocols for allenes have been developed, among which the Wittig reaction via phosphaoxetane intermediate is straightforward synthetic strategy. However, this method requires the reaction of unstable ketenes with reactive phosphorous ylide under basic conditions, which prevents the practical use of this method. In other words, allenes are promisingly synthesized if oxaphosphetane is constructed by alternative route. From this viewpoint, we paid attention to propargyl alcohol because the oxygen atom and an electrophilic triple bond are considered to form an oxaphosphetane framework upon treatment with an oxaphilic and nucleophilic phosphine. According to this strategy, reaction of propargyl alcohol with PBu3 was conducted. As a result, desired allene 2 and 1,3-diene 3 were successfully obtained1. Interestingly, product ratio of 2 and 3 could be controlled by changing solvent. Allene 2 predominantly formed in 70% yield in non-polar solvent, and 1,3-diene was obtained as a main product in 69% yield in polar solvent. In addition, this reaction shows good tolerance with functional groups. Indeed, formyl and pyridyl substituted allene could be prepared without any protection. Moreover, this reaction was applicable to propargyl alcohol possessing no substituent at the propargyl position. Furthermore, synthesized 2-pyridylallene could be converted into indolizinone by copper-catalyzed cyclization.

Keywords: Allene, Propargyl alcohol, Phosphine, Oxaphosphetane, Pseudo-Wittig reaction

References

Optical Properties of 1-[(3,6-Di-tert-butyl-1-carbazolyl)azo]-4-nitrobenzene Involving N-H···N Intramolecular Hydrogen Bond

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Abstract

N-Salicylideneanilines (SAs) are well-known compounds to exhibit photochromism in solid-state upon irradiation with UV. The photo-coloration processes involve excited state intramolecular proton transfer (ESIPT) from the o-hydroxy group to the imine nitrogen atom followed by framework changes in the molecule. In order to exhibit solid-state photochromism, formation of intramolecular hydrogen bond and securing reaction room for the isomerization in the crystal lattice are important. In this study, 1-[(3,6-di-tert-butyl-1-carbazolyl)azo]-4-nitrobenzene (BCAN) was designed as a compound which satisfy these condition.

BCAN involves intramolecular hydrogen bond between a hydrogen atom attached to a nitrogen atom included in hetero cyclic ring (carbazole) and a nitrogen atom bonding to a nitrophenyl moiety. The bulky tert-butyl substituents in BCAN are effective to act as a spacer opener, which maintain room for the photoisomerization. Since carbazole is an electron rich heterocyclic aromatic ring and nitrophenyl moiety is an electron poor substituent, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) would be distributed on carbazole ring and nitrophenyl ring, respectively. Density functional theory (DFT) calculations suggested such distribution of the molecular orbitals of BCAN. The HOMO is distributed on the nitrogen atom of carbazole ring, whereas a distribution of the LUMO on the nitrogen atom is small. It indicate that the electron density (basicity) of two nitrogen atoms connected through the intramolecular hydrogen bond would inverse by excitation from HOMO to LUMO.

In this work, BCAN was synthesized and its optical properties were investigated. 1-Amino-3,6-di-tert-butylcarbazole was synthesized as a precursor of BCAN from carbazole through 3 step. The precursor was coupled with p-nitroaniline to obtain BCAN. The absorption spectra of BCAN in dichloromethane before and after UV irradiation were measured and no spectral change was observed. It suggest that cis-to-trans isomerization of azobenzene moiety was quenched by intramolecular hydrogen bond.

Keywords: intramolecular hydrogen bond, ESIPT, photochromism, carbazole, azobenzene

Acknowledgement
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Total Synthesis of (−)-Lepadiformine A via Diastereoselective Radical Translocation-Cyclization Reaction

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Abstract

(−)-Lepadiformine A (1), isolated from a tunicate Clavelina lepadiformis by Biard and co-workers in 1994, exhibits potent antitumor and antiarrhythmic activity.1 Intrigued by the potential biological activities as well as the complex molecule architecture possessing the unique aza-spirocyclic motif embedded in tricyclic core, we initiated synthetic studies to develop an efficient synthetic route of 1. In this paper, we report an asymmetric total synthesis of 1 featuring the diastereoselective radical translocation-cyclization reaction developed in our laboratory as the key step.2,3

First, we prepared substrate 4 bearing chiral butenolide in the side chain (97:3) for the key radical reaction. Catalytic asymmetric allylation of racemic alcohol 2 by Krische’s protocol4 provided homoallylic alcohol 3 in an excellent selectivity, which was then converted to substrate 4 through several steps. Upon heating of 4 with AIBN and n-Bu3SnH in benzene at reflux the spirocyclization proceeded diastereoselectively through generation of sp2 radical 5, 1,5-hydrogen atom transfer, rapid inversion of sp3 radical center, and finally 6-exo-trig radical cyclization via the favorable chair-like conformer 6. The high optical purity of 7 (94% ee) determined by HPLC analysis indicated that the configuration of aza-spirocyclic framework (C5, C10) was completely controlled by the C6-stereocenter. After C ring formation, we accomplished the total synthesis of (−)-1.

Keywords: natural product, total synthesis, aza-spirocyclic compound, radical cyclization

References
β-Amino Alcohol Organocatalyst for Asymmetric Michael Addition of Active Methylene Compounds to Nitroalkens

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Abstract

Asymmetric Michael addition of active methylene compounds to nitroalkens afford the Michael adducts having quaternary carbon stereogenic center in the molecules and the adducts are useful chiral synthetic intermediates for biologically active compounds including drugs. Several effective metal catalysts and organocatalysts have been developed for this reaction. Particularly, organocatalyst is cheaper and environmentally friendly catalyst, and therefore the organocatalyzed asymmetric Michael addition has been explored intensively in recent years. From these reasons, we attended this reaction using β-amino alcohol organocatalyst 1. Amino alcohol 1 is stable in air, and has the two advantageous features of easy preparation and desirable structural characteristics. Thus, it can be derived easily from the corresponding amino acids and contains both an amino basic site and a hydroxyl bonding site in a single molecule. Furthermore, the steric influences of both the α- and β-position substituents also might be effective for control the enantioselective reaction course [1-3]. We examined the asymmetric catalytic activity of the amino alcohol organocatalyst 1 in this reaction.

Herein, we will present that simple primary amino alcohol organocatalyst 1 acts an efficient chiral organic base for the enantiointroselective Michael addition of active methylene compounds 2 with nitroalkenes 3 affording the chiral Michael adduct in satisfactory chemical yield (up to 99%), an excellent enantioselectivity (up to >99% ee) and a diastereoselectivity (up to 99:1). Furthermore, it was observed that the corresponding enantiomeric chiral Michael adducts 4a or 4a’ can be separately made by the reaction of 2a with 3a using catalyst 1b under different temperatures.

Keywords: asymmetric Michael addition, β-amino alcohol, organocatalyst, active methylene compounds

References

Optically Active Conjugated Compounds Based on Planar Chirality

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Abstract

Planar chirality is one of the unique features of mono- and polysubstituted [2.2]paracyclophane compounds. The potential applications of the [2.2]paracyclophane derivatives in materials chemistry necessitate the further development of practical optical resolution methods for planar chiral [2.2]paracyclophanes. Recently, we achieved the optical resolutions of 4,12-disubstituted [2.2]paracyclophane\(^1\) and 4,7,12,15-tetrasubstituted [2.2]paracyclophane compounds.\(^2\) By using the optically pure 4,12-disubstituted and 4,7,12,15-tetrasubstituted [2.2]paracyclophanes, we have prepared various planar chiral [2.2]paracyclophane building blocks\(^3\) to synthesize optically active conjugated compounds. Herein, their optical resolution methods as well as subsequent transformations to the enantiopure conjugated compounds will be shown. As a representative example of the optically active conjugated compounds based on planar chirality, cyclic compounds will be introduced (Figure 1). These compounds comprise optically active higher-ordered structures such as propeller-shaped structure (left in Figure 1),\(^2\) double helical structure (right in Figure 1),\(^3\) and so on. They exhibit excellent chiroptical properties, i.e., large molar ellipticity in the ground state and intense circularly polarized luminescence (CPL) with large dissymmetry factors \((g_{\text{lum}})\) in the exited state. The results suggest that planar chiral [2.2]paracyclophane-based optically active higher-ordered structures (propeller-shaped and double helical structures in this study) are promising scaffolds for efficient CPL, and appropriate modifications can enhance the CPL properties.

Keywords: circularly polarized luminescence, [2.2]paracyclophane, planar chirality

Figure 1. Optically active conjugated compounds based on planar chirality.

References

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Niobium-catalyzed [2+2+2] Cycloaddition of Alkynes, Nitriles, and Alkenes

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Abstract

Transition-metal-catalyzed intramolecular cycloaddition to form cyclohexadiene derivatives is an useful methodology. However, the chemo- and regio-selective preparation of cyclohexadienes from alkenes and alkynes is difficult because aromatization of cyclohexadiene or double-bond migration via 1,5-hydrogen shift may occur. In this presentation, we report our recent examples of inter- and intramolecular [2+2+2] cycloaddition of alkynes with alkenes, or diynes with alkenes catalyzed by low-valent niobium-catalyst to afford cyclohexadienes and bicyclic cyclohexadienes in good yields with high chemo and regioselectivities without C=C bond migration. We also report low-valent niobium-catalyzed three-component intermolecular cycloaddition of internal alkynes, terminal alkynes, and alkenes resulting in 1,3,4,5-tetrasubstituted-1,3-cyclohexadiene derivatives in high yields. In this study, we achieved selective intermolecular cycloaddition to 1,3-cyclohexadienes by using various efficient niobium catalysts such as NbCl₃(DME), NbCl₅, and low-valent Nb species generated from NbCl₅ and (TMS)₃SiH. In addition, we found cycloaddition of diynes and simple alkenes catalyzed by low-valent Nb species generated from NbCl₅ combined with Zn and tricyclohexylphosphine to give bicyclic cyclohexadienes in high yields with high regioselectivities.

Furthermore, pyridines and pyrimidines are important scaffolds in numerous natural products and bioactive products. The [2+2+2] cycloaddition of nitriles with alkynes would provide efficient methods in terms of atom and step economy for preparing multi-substituted pyridine and pyrimidine derivatives. In this presentation, we also report low-valent niobium-catalyzed and NbCl₅-mediated/catalyzed [2+2+2] cycloaddition of nitriles with alkynes to form pyridine and pyrimidine derivatives, respectively. During the course of our study, we found independent Lewis acid functions of NbCl₅ and FeCl₃ enables to catalytic version of the NbCl₅-catalyzed cycloaddition of alkynes with nitriles to give pyrimidines.

Keywords: niobium, cycloaddition, cyclohexadiene, pyridine, pyrimidine

References

Ladder-Type Fused Benzofurans and Indoles Synthesized by Transition-Metal-Catalyzed Intramolecular Cascade Cyclization

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Abstract

Ladder-type polycyclic aromatic compounds have attracted considerable interest because of their potential applications in organic electronic materials. Several ladder-type π-conjugated aromatic compounds and their heterocyclic analogues have been synthesized.\textsuperscript{1-3} As such, intramolecular cascade cyclization of 2,2′-difunctionalized diphenylacetylenes as the precursors allows the formation of bis-bridged ladder-type stilbenes. Herein, we report on two transition-metal-catalyzed cascade cyclization reactions of 2,2′-difunctionalized diphenylacetylenes, which produce ladder-type polycyclic heteroaromatic compounds under mild, redox-neutral conditions.

When substrates 1 containing both hydroxy and acyl groups were reacted in the presence of a rhodium (I) catalyst, consecutive intramolecular C–O and C–C bond formations occurred to produce 10H-indeno[1,2-b]benzofuran-10-ols 2 in 70–89% yields. The cyclization in the presence of a chiral Rh(I)–SEGPHOS catalyst afforded indenobenzofuranols bearing chiral tertiary alcohol moieties in 77–91% enantiomeric excess. Indenoindolols were also obtained in good yields from the corresponding 2-alkynylaniline derivatives. Moreover, a linear heptacyclic benzo[1,2-b:4,5-b′]difuran derivative was synthesized via the cascade process.

Cyclization of 2-[2-(azidophenyl)ethynyl]anilines 3 involves an initial indole cyclization with the aniline moiety catalyzed by gold(I), and a following C–H amination with the azide group catalyzed by rhodium(II). Various 5,10-dihydroindolo[3,2-b]indoles 4 with two different nitrogen substituents were obtained (62–72% yields) via the two-fold C–N bond formation of 3. The corresponding cyclization of phenol derivatives under identical conditions resulted in a complex mixture of products. The reaction in the presence of K\textsubscript{2}CO\textsubscript{3} and Rh\textsubscript{2}(esp)\textsubscript{2} furnished benzofuroindoles (45–79% yields) through base-promoted benzofuran cyclization and subsequent C–H amination.

Keywords: rhodium, gold, cyclization, benzofuran, indole

References
Acceleration of Catalytic Site-Selective Acylation of Carbohydrates by in Situ Counteranion Exchange of Acylpyridinium Intermediates

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Abstract

Site-selective molecular transformation has attracted increasing attention due to its utility for direct diversification of bioactive natural products and medicinally important compounds with multiple functional groups. Especially, development of catalysts that realize catalyst-controlled selectivity is challenging in current organic synthesis. We previously reported organocatalytic secondary C(4)-OH selective acylation of a glucose derivative 2 with four free hydroxy groups, including primary C(6)-OH. During course of its application to efficient total synthesis of natural glycosides, the relatively high catalyst loading and long reaction time have been a fundamental problem, because many natural glycosides contain substituted benzoyl groups with less electrophilicity. Here we report a new catalytic system that enables reducing catalyst loading and reaction time (<0.1 mol%, <1 h) for site-selective acylation of glucose derivatives.

Acylpyridinium ions have been widely accepted as catalytically reactive species in acylation reactions catalyzed by 4-dialkylaminopyridines. NMR analysis of formation of acylpyridinium intermediates and kinetic studies of acylation of an alcohol catalyzed by 4-pyrrolidinopyridine (PPY) revealed that the relative reactivities of acylpyridinium ions depend on the counteranions: acylpyridinium carboxylates were assumed to be 1000 times more reactive than the corresponding acylpyridinium chlorides. Based on the results, we developed a new catalytic system, in which acylpyridinium carboxylates were generated by in-situ counteranion-exchange from the acylpyridinium chlorides generated quantitatively from the catalysts and acyl chlorides. High catalyst turnover number of up to 6700 was achieved by the present catalytic system for site-selective acylation of glucose derivatives.

Keywords: site-selective, organocatalyst, acylation, carbohydrates

References

Functionalized CpRh(III) Complexes; Preparation and Catalytic Activity toward C–H Functionalization

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Abstract

\(\eta^5\)-Cyclopentadienyl-rhodium(III) (CpRhIII) complexes are known as highly active catalysts for C–H bond functionalization.\(^1\) A commercially available pentamethylcyclopentadienyl (Cp*)-rhodium(III) complex has largely been employed for this purpose. In order to improve catalytic activity and selectivity, rhodium(III) complexes with several sterically and electronically tuned Cp ligands were developed recently. We recently developed the electron-deficient cyclopentadienyl-rhodium(III) complex (Cp\(^{\text{E}}\)Rh)\(^2\) and cyclopentadienyl-rhodium(III) complexes with the pendant amide moiety (Cp\(^{\text{A}}\)Rh)\(^3\) by the reductive complexation functionalized fulvenes with RhCl\(_3\) using ethanol as a reducing agent. We also found that thus obtained modified CpRh complexes showed significantly higher catalytic activity than Cp*Rh complex in the oxidative C–H coupling reactions of acetanilides,\(^4,5\) benzyl alcohols,\(^6\) and benzoic acids\(^7\) with alkynes and alkenes.\(^8,9\) For example, the oxidative [3+2] annulation of acetanilides with internal alkynes catalyzed by Cp\(^{\text{E}}\)Rh proceeded at room temperature under air which afforded indoles in high yields.\(^4\) Herein, we disclose that the modified CpRh complexes show not only high but also characteristic catalytic activity toward coupling reactions involving C–H bond cleavage.\(^10\)

Keywords: C–H Bond Functionalization, Cyclopentadienyl Complexes, Reductive Complexation, Rhodium

References

Proximity-Dependent Tyrosine Chemical Labeling

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Abstract

Techniques for the visualization of target proteins in living systems are highly important to investigate the function, dynamics, localization, and crosstalk of individual proteins. The chemical labeling of proteins with small-molecule probes has received much interest as a powerful method for the study of individual proteins in their native environments. The key to this chemical labeling is a bioorthogonal chemical reaction that enables the rapid and selective bioconjugation of proteins with nonnatural functional groups under physiological conditions. The most widely utilized bioorthogonal chemical reactions rely on electrophilic reagents that target nucleophilic amino acids. On the other hand, we developed radical type protein labeling reaction. Herein, we report the development of tyrosine labeling method based on local single-electron transfer (SET) catalyst such as ruthenium tirs(2,2'-bipyridyl) complex ([Ru(bpy)]^2+), and the application for target selective protein labeling in complex protein mixture using a ligand-directed method.

Tyrosine, an aromatic amino acid, is known to be oxidized by SET and tyrosyl radical species generate. We trapped tyrosyl radical by redox active small molecules named tyrosyl radical trappers (TRTs) under the physiological reaction condition. Since SET occurs at a few nanometers under physiological reaction condition, it is considered that target protein selective labeling is possible by trapping tyrosyl radical species generated in the proximity environment of SET catalyst. We found several types of TRTs that selectively function in the catalyst proximity environment. In this presentation, we will report the catalyst-proximity dependency and the labeling efficiency of these labeling agents and their application to target protein selective chemical labeling.

Keywords: bioconjugation, protein, tyrosine, proximity-dependent labeling

References
OBC 38- Invited Lecture

QM/MM Studies of the Reaction Mechanisms of Metalloenzymes

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Abstract

Metal ions play an important role in many biological functions, especially in biochemical reactions of metalloenzymes. Enzymes are very effective catalysts, and some of them are applied in chemical industry and environmental remediation, because they usually require relatively mild conditions and demonstrate high turnover numbers and structural selectivities. However, the catalytic mechanisms of many metalloenzymes are not yet fully understood. We report our theoretical studies of the reaction mechanisms of two metalloenzymes, Nitrile Hydratase (NHase) and organophosphate-degrading enzyme from Agrobacterium radiobacter (OpdA) using Quantum Mechanics/Molecular Mechanics (QM/MM) method.

NHase is an important biocatalyst widely used in the chemical industry, which catalyzes hydration of nitriles to the corresponding amides. The coordination structure at the active site of NHase is very unique, which includes a metal ion (Fe(III) or Co(III)) coordinated by two nitrogen atoms of deprotonated main-chain amide and three sulfur atoms of one normal and two post-translationally modified cysteine residues (i.e., one Cys-S, one Cys-SO\textsuperscript{-}, and one Cys-SO\textsuperscript{2-}). We investigated the reaction mechanism of NHase containing an Fe(III) ion. First, we examined the initial steps of the catalytic mechanism and showed that the formation of a cyclic intermediate is the most probable one, which is consistent with previous experimental and theoretical studies. Then, we analyzed the reaction mechanisms subsequent to the cyclic intermediate and revealed the details of the catalytic reactions of NHase. We also shed light on the effect of protein environment on the active site, which had been considered as PCM in previous theoretical studies using cluster models.

OpdA is one of metalloenzymes which are expected to be applied for bioremediation by degrading toxic organophosphate compounds. OpdA is a promiscuous enzyme in terms of substrate and metal ions at active (Fe\textsuperscript{2+}-Zn\textsuperscript{2+}, di-Co\textsuperscript{2+}, di-Mn\textsuperscript{2+}, or di-Cd\textsuperscript{2+}). We analyze the reaction mechanism of phosphotriester hydrolysis catalyzed by di-Co\textsuperscript{2+} OpdA.

Keywords: QM/MM, enzyme, metal, reaction, catalysis

References

OBC 39- Invited Lecture

The Proton NMR Spectra of the Glyceride CH\(_2\) and CH Groups of Triacylglycerols in Edible Oils. Application to the Analysis of the Fatty Acid Composition at the sn-2 position of the Triacylglycerols in the Oils.

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Abstract

The glyceride backbone in triacylglycerols (TAG) consists of two CH\(_2\) groups, a CH group and three ester head groups. The two glyceride methylene groups are equivalent (having the same chemical shift) on the NMR time-scale, but the methylene protons are non-equivalent, and are classified as an AB spin system, with chemical shift (\(\Delta_{AB}\)). The AB protons are each spin-coupled to the methine (X) proton, forming an ABX spin system. The vicinal coupling constants (\(J\)) are found to be invariant among the various species of TAG. The magnitude of the dihedral angles in the ABX spin system is derived from the observed vicinal coupling constants by application of the Karplus equations. The new discovery is that the fatty acid (FA) at the sn-2 position which has one or more double bonds enhances the chemical shift (\(\Delta_{AB}\)) in the CH\(_2\) protons. This phenomenon is the result (1) of the effect of the electric field that is generated by the olefinic electrons in the FA at the sn-2 position on the glyceride CH\(_2\) protons, and (2) of the dihedral angles in the glyceride backbone. The chemical shift (\(\Delta_{AB}\)) is calculated by applying the results of the quantum mechanics of the AB spin system on the observed proton NMR spectrum. Because of the long time-scale of NMR spectroscopy, the observed \(\Delta_{AB}\) is a weighted average of the contributions to the \(\Delta_{AB}\) from the various FA at the sn-2 position, saturated and unsaturated FA. The contribution from each of these FA has been obtained from selected TAG and from the palm oil fractions whose positional distribution of FA have been determined previously. Thus by obtaining the chemical shift (\(\Delta_{AB}\)) in the glyceride CH\(_2\) protons of a sample of an edible oil, palm oil in particular, it is possible to obtain a reliable composition of the FA at the sn-2 position in terms of mole fractions\(^1\). The real advantage is that the proton NMR spectrum can be acquired in a short time (possibly less than a minute). To obtain the same information from the carbonyl carbon-13 NMR spectrum requires six hours or more of spectrometer time, although the carbonyl carbon spectrum provides a complete profile of the FA distribution at the sn-1,3 positions and sn-2 position.\(^2,3,4\) It is known that the composition of the FA at the sn-2 position in edible oils has special nutritional significance.

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**New insights of naturally occurring O2-tolerant [NiFe]hydrogenase**

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**Abstract**

[NiFe]hydrogenases catalyze the reversible reaction of the cleavage and production of H\(_2\), harboring a NiFe center for H\(_2\) activation in a large subunit and iron-sulfur clusters for electron transfer in a small subunit. The H\(_2\)-catalyzing biocatalysts and their mimic model complexes have received much attention due to their potential applications in H\(_2\)-based fuel cell technology. However, most hydrogenases found in microorganisms are highly sensitive to O\(_2\), leading to inactivation of catalytic activity after air oxidation. We recently reported a number of new O2-tolerant [NiFe]hydrogenases, such as membrane-bound [NiFe] hydrogenase (MBH\(_1,2\)) and soluble NAD+−reducing [NiFe]hydrogenase (SH\(_3\)), which have special structural features to protect the [NiFe] catalytic site against oxidative stress. MBH found in hydrogen-oxidizing bacteria contains a novel iron-sulfur cluster in a small subunit\(_1\), which plays an essential role in the O2-tolerant mechanism. On the other hand, SH localized in the cytosol has a unique intramolecular system\(_3\), which functions as a redox sensor to protect the NiFe center by attacking O2 molecule. Additionally, a new type of the MBH purified from *Citrobacter* sp. S-77 displays excellent performance as an anode catalyst in the H\(_2\)-based polymer electrolytic fuel cells\(_2\). On the basis of these findings, I will present the new insights into the structure and function of O2-tolerant [NiFe]hydrogenase.

**Keywords:** Hydrogen, H\(_2\)-activation, O2-tolerant, biocatalyst, membrane-bound [NiFe]hydrogenase, soluble NAD+−reducing [NiFe]hydrogenase

**References**

Total Synthesis of Ustiloxin D

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Abstract

Ustiloxin D (1), isolated from Ustilaginoidea virens, is known to be a potent antimitotic natural product which binds to tubulin to inhibit microtubule assembly. The structure of 1 is featured by the constrained 13-membered cyclophane ring consisted of two unusual amino acids, β-hydroxy-DOPA and β-hydroxy isoleucine, and valine. Ustiloxin D has received much attention as a synthetic target due to the structural and biological features. In this presentation, we would like to report the total synthesis of ustiloxin D by coupling of fragments 2–5. The key fragments 2 and 3 were prepared from D-serine. Fragments 2–4 were combined to a cyclization precursor which was subjected to macrocyclization under the high dilution condition to furnish the 13-membered cyclophane ring. The cyclization product was successfully transformed to the target natural product via coupling of glycine (5).

Keywords: ustiloxin D, microtubule polymerization, non-proteinogenic amino acid, cyclophane, total synthesis

References

PEG Hydrogels Utilizing DNA Quadruplexes as Crosslinking Points

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Abstract

DNA is a water-soluble and biodegradable polymer, which forms right-handed double helices and carries genetic information in life. Because of its high structure regularity and sequence programmability, DNA has been used as a key component in development of functional nanomaterial. Despite such success in nanoscience, reports on application of DNA to typical material, i.e. hydrogels, are very few, except for some excellent achievements, because preparation of DNA in gram scales usually requires unreasonable costs. One solution for this problem is liquid-phase DNA synthesis method developed by Bonora et al. They used PEG as soluble polymeric support, which enables coupling reaction of phosphoramidite monomers in liquid phase and can be easily precipitated by ether addition for product separation.

We have applied this system to synthesize DNA-PEG-DNA tri-block copolymer in grams, and successfully prepared biodegradable PEG hydrogels by using higher-order DNA structures, such as G-quadruplexes, for cross-linking points. Aqueous solution of a tri-block copolymer bearing multiple guanosines at the ends, for example, immediately turns into gel upon addition of Na+ or K+ ions. Introduction of toehold sequence to the DNA portion enabled sequence-selective dissolution of a hydrogel bead and resulting release of guest micro particles into the solution. Employment of another DNA quadruplex, i-motif, realized construction of pH responsive hydrogels as well.

Keywords: DNA, quadruplexes, PEG, hydrogels, biomaterials

References

Radical Reactions of Alkynes with N-Heterocyclic Carbene Boranes

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Abstract

N-heterocyclic carbene boranes (NHC-boranes) are surprisingly stable whereas they cause various radical, ionic and metal-catalyzed reactions.\textsuperscript{1} In this presentation, we report new radical reactions between alkynes and NHC-boranes.

NHC-boranes can become good precursors of boryl radicals. The NHC-boryl radicals formed in the presence of an appropriate initiator cause addition reactions to alkynes to form the corresponding $\beta$-boryl alkenyl radicals. These radicals induce interesting reactions such as trans-hydroboration and unusual cyclization reactions\textsuperscript{2} to provide unique organoboron compounds.

Keywords: alkynes, borylation, cyclization, NHC-boranes, radical reactions

References

Regioselective C-H Trifluoromethylation of 6-Membered Heteroaromatic Compounds

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Abstract

Many important drugs, agrochemicals and their lead compounds contain trifluoromethyl group(s). Most processes currently used to access trifluoromethyl group-containing molecules are performed by substitution of the carboxy or trichloromethyl groups using hazardous fluorinating reagents under harsh reaction conditions. Cross-coupling reactions between organohalides or boronic acids/esters and trifluoromethylation reagents are also used. Direct C-H trifluoromethylation of organic molecules, however, is the ideal method of introducing trifluoromethyl group(s). Despite the recent advances in C-H trifluoromethylation of N-heteroaromatic compounds, regioselective C-H trifluoromethylation of six-membered heteroaromatic compounds was not achieved. We developed a general and reliable method for the synthesis of trifluoromethyl group-containing N-heteroaromatics through highly regioselective addition of a trifluoromethyl nucleophile to pyridine, quinoline, isoquinoline and two or three heteroatom-containing N-heteroaromatic N-oxides activated by trifluoromethyldifluoroborane (eq 1).1 The C-H trifluoromethylation proceeds under mild conditions in gram scale with high functional group tolerance. This method will be useful in both laboratory and industrial processes.

We also succeeded in the development of the first 4-2 and benzylic-3 position selective C−H perfluoroalkylation and perfluoroarylation of six-membered heteroaromatic compounds. The two reactions proceeded in good yield, even in gram scale, and by a sequential reaction without isolating the intermediates. This reaction could be applied to late-stage trifluoromethylation of bioactive compounds.

**Keywords:** C-H transformation, Lewis acid-base interaction, regioselective, trifluoromethylation

References

Hypervalent Iodine-Induced Silyl Enolate Coupling for New C-C Bond-Forming Reaction

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Abstract

Nowadays, hypervalent iodine reagent in organic synthesis has gained status as a safe alternative to toxic heavy-metal oxidants by taking advantage of their user-friendly characteristics. The researches in hypervalent iodine chemistry for synthetic uses that appeared in the early stages are in line with this objective, and these reagents were frequently used during the total syntheses of natural products and construction of complex molecules. In the 21st century, this position has dramatically changed, and one of the significant advances in recent years is their utilizations for oxidative couplings that can create new C-C bond between molecules under metal catalyst-free conditions.

One of the important contributions in this area is the single-electron-transfer (SET) oxidation ability of hypervalent iodine(III) reagent for selective activation of aromatic rings, which has enabled a series of metal-free oxidative couplings of aryl C-H bonds with nucleophiles.1 In 2008, we first realized the effective metal-free C-H cross-biaryl-coupling based on the hypervalent iodine-induced SET oxidation strategy toward aromatic rings.2 These oxidative couplings between the two C-H bonds using hypervalent iodine reagent3 are advantageous in view of the metal catalyst-free methods, mild reaction conditions (no use of hazardous oxidant), high yields and selectivities of the products, and no over-oxidations. By utilizing the unique SET oxidation reactivity of hypervalent iodine reagent, we now report our new developments of oxidative coupling reactions between silyl enolates and electron-rich aromatics to form synthetically-useful α-aryl ketones. It is found that the SET activation strategy of nucleophiles is even applicable to the nitrogen-containing molecules, and hence the cross-coupling of two different enol equivalents, i.e., silyl enolates and enamines, can be realized to afford valuable 1,4-diketone compounds in good yields. These recent developments of the reactions are presented with brief introduction of our research background.

Keywords: hypervalent iodine, oxidation, silyl enolate, C-C coupling, single-electron-transfer (SET)

References

Total Synthesis of (+)-Haplophytine

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Abstract

Since dimeric indole alkaloids possess architectural diversities and a wide range of biological activities, development of new synthetic strategies for construction of these structures has been one of the important topics in synthetic chemistry. In particular, development of new synthetic method, which enables the connection of two different indole segments at a late stage of the synthesis, is crucial for convergent and efficient synthesis of these dimeric compounds. In this presentation, our recently completed total synthesis of a dimeric indole alkaloid (+)-haplophytine (1) based on AgNTf₂-mediated coupling reaction and late-stage oxidation will be discussed.

(+)-Haplophytine (1) was isolated from the leaves of Haplophyton cimicidum by Snyder in 1952, and the structure was elucidated by Cava and Yates in 1973. In 2009, we achieved the first total synthesis of 1 via construction of the dimeric skeleton by Fischer indole synthesis. Very recently, we have achieved the second-generation total synthesis of 1, which is more convergent and efficient than the first-generation synthesis of 1. We will present the second-generation total synthesis of 1 featuring a AgNTf₂-mediated direct coupling between iodoindolenine 2 and pentacyclic compound 3 and sequential thiol-induced air oxidation of 1,2-diaminoethene moiety and skeletal rearrangement of substrate 5 at the late stage of the synthesis.

Keywords: alkaloid, indole, dimeric compound, oxidation, cascade reaction

References
Direct Benzyne Generation from Phenol Derivatives: Synthesis of Aromatic Primary Amines

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Abstract

Various benzyne reactions have been developed in the last two decades. These are particularly useful for the synthesis of a wide variety of substituted aromatic compounds in fewer steps under mild reaction conditions. However, there still remain several issues such as low regioselectivities of unsymmetrical benzyne and relatively harsh reaction conditions for the synthesis of substituted benzyne precursors. Against such background, we have been working on developing methods to control orientations of benzyne reactions, and methods to generate benzyne from easily available compounds.1

On the other hand, aromatic primary amines are important skeleton present in biologically active compounds. The traditional synthesis of primary arylamines is to hydrogenate nitro compounds. However, starting nitro compounds have to be synthesized under strongly acidic conditions. Buchwald group and Hartwig group reported synthetic methods of primary arylamines through Pd- and Ni-catalyzed coupling reactions of aryl halides using ammonia equivalents and even molecular ammonia.2 These are extremely useful because aryl primary amines can be synthesized from aryl halides under mild conditions. The nucleophilic amination of benzyne should be a potential method for the synthesis of aromatic primary amines. Although there are many nucleophilic benzyne amination producing secondary and tertiary aromatic amines, only a few syntheses of primary anilines through benzyne have been reported.

In this symposium we are going to present a new benzyne generation from phenol derivatives for the selective synthesis of aromatic primary amines (Scheme). The substrates, phenols were in-situ nonaflated by nonafluorobutanesulfonyl fluoride (NfF) in the presence of KHMDS and the produced nonaflates generated benzyne by the ortho deprotonation of sulfonyloxy group. The nucleophilic additions of KHMDS to benzyne and following acid hydrolysces produced aryl primary amines. The highly selective additions of bulky KHMDS enabled the selective synthesis of various meta-substituted primary amines.

Keywords: aryl amine, benzyne, nucleophilic addition, meta-selective, phenol

References


The Enhanced Enantio-recognition of Chiral Secondary Alcohols with Chiral Acyltriazolium by Formation of Alcohol–Carboxylate Complexes

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Abstract

Recently, we have been interested in the complex formation of a substrate and a co-catalyst to enhance enantioselectivity of reactions\cite{1}. We herein report a new method for the kinetic resolution of α-hydroxy thioamides, versatile building blocks for the synthesis of pharmaceuticals, via acylation using an NHC catalyst and a carboxylate cocatalyst.

A mixture of chiral NHC precursor 1 (0.5 mol%), racemic α-hydroxy thioamide (±)-2, and proton sponge (1.0 equiv) in chloroform was stirred for 10 min at room temperature. Then, the mixture was cooled in an ice–water bath, and 2-bromo aldehyde 3 (0.6 equiv) was added to the mixture. After 7 h, ester (S)-4 was produced in 10% yield with 95% ee, and slightly enantiomerically enriched (R)-2 with 10% ee was recovered in 90% yield. The selectivity factor \( s \), the relative reaction rate of (S)-2 to (R)-2 was calculated to be 44. The selectivity factor jumped to 94 when the reaction was conducted in the presence of 4-dimethylaminobenzoic acid (0.1 equiv).

Keywords:

References

Amide base generated in situ from TMAF and N(TMS)$_3$ catalyzed deprotonative functionalization

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Abstract

Stilbene is one of the core motifs of biologically active molecules and functional organic materials. Conventionally, Wittig, Horner-Wadsworth-Emmons, or Peterson olefination using prefunctionalized toluene derivatives were used for its synthesis. Direct condensation of toluene and carbonyl derivatives were also reported. However, the reaction required stoichiometric amounts of strong bases such as $n$-BuLi and LDA, and functional group tolerance is relatively limited. Then, development of efficient construction methodologies of stilbenes bearing a high functional group tolerance is of great importance in organic synthetic chemistry.

We have been studying catalytic deprotonative functionalizations by amide bases generated in situ from fluoride sources and aminosilanes. In this study, it was found that the condensation reaction of 1 and 2 is catalyzed by tetramethylammonium fluoride (TMAF) and N(TMS)$_3$ in DMF to form stilbene derivative 3 in 80% yield. Benzylic positions of heteroarenes such as pyridine, benzothiophene, and benzofuran can also be applied to the transformation. Details of substrate scope and reaction mechanism will be discussed in the presentation.

Keywords: catalytic deprotonative functionalization, amide base generated in situ, stilbene

References
Total Synthesis and Structure-Activity Relationship Study of Cyclodepsipeptide Destruxin E

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Abstract

Middle-size molecules are expected to cover novel chemical space for next-generation drug discovery, and macrocyclic molecules such as macrolides and cyclic peptides are recognized as typical middle-size molecules. In addition, middle-size molecules are categorized into out of ‘Rule of five (Ro5)’, therefore the molecules categorized in ‘extended or beyond Rule of five (bRo5)’ is a promising chemical space to develop novel drug candidates.[1] Among several compound classes in the bRo5, we focus on cyclic peptide derivatives. Generally, linear peptides are known to be unstable under metabolic conditions, however recent studies reveal that cyclization or introduction of unnatural amino acids may adopt the stability and cell permeability, for example, cyclosporine A is a highly permeable molecule even its molecular weight is more than a thousand. Because of unique structural feature and biological activity of cyclic peptides, we became interested in elucidation of the mode of action of the cyclic peptides.

Destruxin E, isolated from \textit{Metarhizium anisopliae} by Païs \textit{et al.} in 1981, is a middle-size cyclodepsipeptide consisting of five amino acids (\(\beta\)-Ala, MeAla, MeVal, Ile and Pro) and an epoxide-containing derivative of \(\alpha\)-hydroxy acid \[2\], and is known to exhibit potent V-ATPase inhibitory activity (IC\(_{50}\) 0.4 \(\mu\)M) among destruxin analogues [3]. Intriguingly, destruxin E reversibly induces morphological changes in osteoclast-like multi-nuclear cells (OCLs) under concentrations lower than those affecting the V-ATPase activity to inhibit bone-resorption without causing cell death [4]. V-ATPase in osteoclasts is known to be a drug target for osteoporosis therapeutics; therefore destruxin E is a novel candidate in the development of anti-resorptive agent. In this talk, combinatorial synthesis and biological evaluation of destruxin analogues based on the total synthesis will be discussed [5]. The results presented would lead us to develop a molecular probe for target identification in the osteoclasts, and to discover a novel anti-resorptive agent for osteoporosis therapeutics.

Keywords: Total Synthesis, SARs, Cyclodepsipeptide

References

Synthesis of Iodinated-Organic Salts and Diversity of Iodine-Iodine Interaction in Their Crystal Structures

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Abstract

Iodine-induced cyclization reaction is one of the powerful method to construct heterocyclic compounds bearing iodine substituent. Recently, iodine atom in organic compounds is focused on halogen bond. Especially, iodine atom bearing cationic moiety gave the strong halogen bond called as “charge-assisted halogen bond”.\textsuperscript{1} We synthesized various iodinated-organic salts by the reaction of thioamides, benzimidazoles, and thiazoles bearing \textit{o}-ethynylphenyl group with molecular iodine. The cyclization reaction proceeded in good to excellent yields to give corresponding heterocyclic cations with iodide (I\textsubscript{\textsuperscript{-}}) and/or triiodide (I\textsubscript{3\textsuperscript{-}}) as a counter anion. Thioamide derivatives gave five-membered cyclic compounds with I\textsubscript{\textsuperscript{-}}.\textsuperscript{2} Benzimidazole\textsuperscript{3} and thiazole derivatives formed six-membered ones, and the counter anion of I\textsubscript{3\textsuperscript{-}} was mainly observed. Furthermore, we revealed that the ring system to be constructed was influenced on ethynyl moiety.

Focused on the interaction at iodine atom on cationic part by the single-crystal X-ray analysis, we found that the various interactions could be possible. In the case of the compounds having I\textsubscript{3\textsuperscript{-}} anion, no interaction as well as the strong halogen bond between cationic iodine and counter I\textsubscript{3\textsuperscript{-}} were observed. Two types of the positions of I\textsubscript{3\textsuperscript{-}} were found in the crystal structure of some thiazole derivatives. One was interacted with iodine atom on the cationic part, and the other approximated hydrogen atom on benzene ring. And we also found that the halogen bond was formed with greater preference than the electrostatic interaction between the cationic atom and I\textsubscript{3\textsuperscript{-}}.

Keywords: cyclization, iodine, halogen bond, heterocyclic compound, crystal structure

References

**Cholesterol Interaction with Steroidal Saponins in Bilayer Membrane**

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**Abstract**

Cholesterol (Chol) is one of the abundant lipid molecule in plasma membrane. Chol is essentially required for controlling membrane fluidities and assisting formation of the functional domains called as lipid rafts, together with sphingolipids and raft proteins. However, membrane distribution of the intact Chol particularly localizing at the raft domain remains unclear. We have been studying on the lipid interactions occurring in lipid rafts, and developed a deuterated Chol probe for solid state $^2\text{H}$ NMR to determine partition of Chol in membrane model. Selective deuteration fully maintains membrane properties of the Chol, and the sets of NMR signals clearly demonstrate the amount of Chol in ordered and disordered domains, respectively.

OSW-1 is a structurally unique steroidal saponin isolated from the bulbs of *Ornithogalum saundersiae*. Although OSW-1 has potent and selective cytotoxic activities to tumor cell lines, membrane disrupting activity was not well studied. Therefore, we investigated the membrane action mechanism of OSW-1 in comparison with digitonin, a potent membrane disrupting saponin. OSW-1 as well as digitonin showed potent hemolytic activity in Chol dependent manner. Solid state $^2\text{H}$ NMR using 3-d-Chol probe suggested that OSW-1 interacts with membrane Chol without forming large aggregates, while digitonin forms Chol-containing aggregates. The results suggest that OSW-1/Chol interaction is likely to cause membrane permeabilization and pore formation without destroying the whole membrane integrity, which could partly be responsible for its highly potent cell toxicity.

**Keywords:** membrane, lipid rafts, cholesterol, saponin, NMR

**References**

Development of Crystalline Photochromic Compounds Involving Intramolecular Hydrogen Bond

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Abstract

The crystalline photochromism of N-Salicylideneaniline (SA) and its analogues is of interest owing to the usefulness for a model system to elucidate molecular tautomerism in the solid state. There is general agreement that the coloration process involve excited state intramolecular proton transfer (ESIPT) from the o-hydroxy group to the imine nitrogen atom followed by framework changes in the molecular. Considerable structure of photocolored species of SAs are trans-keto form and cis-keto form. Ohashi et al. reported that the isomerization processes to afford trans-keto form involve pedal motion of two phenyl rings of the molecule. In contrast with this result, Taneda and Kawato et al. reported the photochromism of cyclic N-salicylideneanilines (CSAs) in which the pedal motion is prevented. The photocolored species was reasonably assigned to a cis-keto form and CSAs are the first example of photochromic SAs which have no azomethine hydrogen atom. To investigate optical properties of the novel photochromic compounds, CSAs including oxygen, nitrogen, and sulfur in its heterocycles were synthesized.

In order to discover new class of solid-state photochromic compounds, carbazolylazobenzene (CAB) was designed. CAB involves intramolecular hydrogen bond between a hydrogen atom attached to a nitrogen atom included in hetero cyclic ring (carbazole) and a nitrogen atom bonding to a phenyl moiety. The intramolecular hydrogen bond is important factor for ESIPT. Since carbazole is an electron rich heterocyclic aromatic ring, the highest occupied molecular orbital (HOMO) and the lowest unoccupied molecular orbital (LUMO) would be distributed on carbazole ring and phenyl ring, respectively. It indicate that the electron density (basicity) of two nitrogen atoms connected through the intramolecular hydrogen bond would inverse by excitation from HOMO to LUMO. Thus ESIPT occur by light irradiation and CABs would exhibit photochromism in solid state.

Keywords: N-salicylideneanilines, intramolecular hydrogen bond, ESIPT, photochromism

Graphical abstract

References

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Elastic Organic Single Crystals based on Fluorescent Molecules

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Abstract

Organic single crystals assembled by π-conjugated molecules are highly important in material science because of their characters such as densely packed 3D morphology and anisotropy. However, the organic single crystals are brittle (no flexibility) due to densely packed structure. On the one hand, polymers in the solid state (films and fibers) are typical flexible materials. However, in polymer science, the amorphous polymer materials are flexible, but the increasing of crystalline state in polymer matrix decreases flexibility. Flexibility vs. crystallinity of the materials is often a noticeable problem in the solid-state materials science. Fabrication of highly flexible and crystalline materials based on π-conjugated molecules is a next stage of challenges. The organic crystals with elastic bending flexibility, namely elastic crystals, are an important point to capture such ideal material. However, the crystal with optical functionality is extremely rare. From these viewpoints, we have been searched for the elastic and fluorescence single crystals by a “trial and error” approach using of new designs. We have successfully demonstrated an elastic organic single crystal based on π-conjugated oligomer in recent years. The crystal also showed fluorescence (λfl = 500 nm, Φ = 25%) based on the π-conjugated structure. Elastic (flexible) single crystal (densely packed and anisotropic material) with solid-state fluorescence (optical functionality) may use as a variety of flexible optical devices in the near future.1-3

During our recent studies of π-conjugated molecules for functional elastic crystals, we noticed that a commercially available molecule, 4,7-dibromo-2,1,3-benzothiadiazole, gave a centimeter-scale crystal. This material showed solid-state fluorescence and elastic bending flexibility.4 Unlike common organic crystals, a centimeter-scale needle-shaped single crystal of the molecule bent under applied stress and quickly reverted to its original shape upon relaxation. Namely, the material is elastic organic single crystal. Moreover, the crystal showed greenishblue colored fluorescence (λ = 513 nm, Φ = ca. 9%). The crystal shows a reversible fluorescence change via mechanical bending–relaxation that can be performed many times (Figure 1). The unique mechanical and fluorescent properties of the crystal include mechanofluorochromism based on mechanical bending–relaxation cycles. This work turns the next page of materials chemistry for “flexible crystals with optical functionality.” Further studies of these molecules and their derivatives are now in progress.

Keywords: elastic organic crystals, π-conjugated molecules, fluorescence, mechanochromism

Figure 1. (A) Illustration and photograph of the setup for fluorescence measurements of the crystals. (B) Fluorescence spectra of original, bent, and relaxed crystals. (C) Photograph of original (relaxed) and bent crystals. (D) Spectral change induced by the bending–relaxation cycles.

References
Asymmetric Desymmetrization of meso-Aliphatic Dials through Intramolecular Aldol Reaction

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Abstract

Chiral cyclopentane derivatives are promising core framework in natural products and pharmaceuticals. Iloprost and neplanocin A are typical examples of this class of compounds. Direct asymmetric desymmetrization of meso-dials 1 through intramolecular aldol reaction is one of the promising ways for preparing these cyclic compounds 2 and 3 having contiguous stereogenic centers.

We have developed regio- and stereoselective intramolecular cross-aldol reaction of unsymmetric aliphatic dial by virtue of the mild reactivity of aniline-type acid base catalyst \((R)-4a\). With this successful achievement, we extended the aniline-type catalysts to the asymmetric desymmetrization of meso-aliphatic dials through intramolecular aldol reaction.

The intramolecular aldol reaction of dial 1a proceeded smoothly in the presence of cat. \((S)-4b\) at 0 °C to give the aldol adducts having four contiguous stereogenic centers in 87% total yield after Wittig reaction. The relative stereochemistry and the ratio of diastereomers were determined to be \(1,2\)-syn-2,3-\(\text{anti}\)-2a, \(1,2\)-anti-2,3-\(\text{anti}\)-2b, and \(1,2\)-\(\text{anti}\)-2,3-\(\text{syn}\)-2c in 4.1 : 2.0 : 1. The enantiomeric excesses of each diastereomer were determined to be 97%, 80%, and 99% ee, respectively. Furthermore, cyclopentene 3a was obtained in 89% with 85% ee by raising the reaction temperature to 20 °C.

Keywords: Asymmetric desymmetrization, aldol reaction, chiral cyclopentane, aniline

Reference

Palladium-Catalyzed Direct Allylic Substitution by Using Phosphine-Borane Ligand

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Abstract

Catalytic allylic substitution starting from the Tsuji-Trost reaction is one of the most useful processes for organic synthesis. In the original Tsuji-Trost reaction, various allylic electrophiles, derived from allyl alcohols, could be used to give the allylated products. From the viewpoint of the step-economy synthesis and the reduction of waste, the development of highly efficient direct allylic substitution of allyl alcohols is in demand in the field of organic synthesis. The direct allylic substitution gives the corresponding allylic compound in one step along with only 1 equiv of water as a byproduct. In our laboratory, we have been studying the direct allylic substitution by use of a palladium catalyst and organoborane reagent. The direct allylic substitution catalyzed by a palladium species and BEt₃ is shown in Scheme 1 (a). In this reaction, allylic alcohol was activated by Lewis acidic BEt₃ to give π-allylpalladium species via an oxidative addition. This π-allylpalladium was an electrophilic species and attacked by a nucleophile to give the product and water. We have now thought that the modification of this intermolecular oxidative addition to intramolecular process should be effective for the acceleration of the direct allylic substitution. To execute the intramolecular oxidative addition, we designed a palladium catalyst bearing a Lewis acid moiety. The phosphine-borane compound was expected to be a suitable ligand for this idea. Our working hypothesis is shown in Scheme 1 (b). Boryl group of the Pd/phosphine-borane catalyst acts as Lewis acid to activate the hydroxy group of allyl alcohols. Successive oxidative addition proceeds intramolecularly to give the π-allylpalladium intermediate which can be attacked by a nucleophile. We have investigated the direct allylic amination and alkylation by using various phosphine-borane ligands prepared according to the literature, and found the structure of the best ligand for these reactions.

Keywords: allylic amination, allylic alkylation, phosphine-borane, palladium

References

2. For a recent review, see: Bouhadir, G.; Bourissou, D. Chem. Soc. Rev. 2016, 45, 1065.
Reaction Discovery with Nickel Catalysts

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Abstract

In recent years, there is renewed interest in replacing rare noble metals with abundant late transition metals in catalytic organic transformations. We have used homoenzyme nickel catalysts in several interesting reactions. They often employ different key steps in catalytic process from those promoted by 4d and 5d metal complexes. Some examples are illustrated below.

1) In recent years my lab reported enantioselective hydrogenation of olefins, enamides and hydrazones, using formic acids as safe hydrogen source. Mechanistically, after hydride insertion, the resulting nickel enolates were quenched by protonation to release products, rather than C-H reductive elimination as in Rh and Ir catalyzed hydrogenation. Later, we extended the reactivity to reductive amination of ketones with arylamines, acylhydrazines and tosylamines in good enantiomeric ratios.

2) In 2017, we published nickel catalyzed arylation of various ketones that afforded aryl alkenes under neutral conditions. The reaction tolerates acidic protons and base sensitive structures.

3) Asymmetric reductive Heck cyclization of indoles. We found that after aryl insertion into the pedant indole ring, the resulting nickel-carbon bond was quenched by water to release products, unlike C-H reductive elimination as in Rh catalyzed hydrogenation. Later, we extended the reactivity to reductive amination of ketones with arylamines, acylhydrazines and tosylamines in good enantiomeric ratios.

4) In 2017, we published nickel-catalyzed arylation of various ketones that afforded aryl alkenes under neutral conditions. The reaction tolerates acidic protons and base-sensitive structures. Recently, the reactivity was extended to arylation of aldehydes that bear enolizable hydrogens to afford aryl ketones (Lei and Zhou, unpublished results).

Keywords: nickel catalysis, hydrogenation, reductive Heck reaction

References

Synthesis of Azadirachtin

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Abstract

Azadirachtin is a complex natural product, which possesses sixteen contiguous stereogenic centers as well as various oxygen-containing functional groups. Following the first synthesis of azadirachtin by Ley in 2007, we achieved the second synthesis of azadirachtin in 2015. In this presentation, I will discuss the details of our synthetic studies on azadirachtin.

Keywords: azadirachtin, insect antifeedant, total synthesis, natural products, radical cyclization

References

Ruthenium-Catalyzed Cycloisomerization of 2-Alkynylanilides Leading to 3-Substituted Indoles via 1,2-Carbon Migration

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Abstract

Indole skeleton is found in many natural products, and various synthetic methods for indoles have been explored. Among those, the cycloisomerization of 2-ethynylanilines into indoles with the formation of vinylidene complexes by 1,2-hydrogen migration was achieved by transition-metal catalysis. A cationic rhodium/H$_8$-BINAP complex catalyzed cycloisomerization of 2-silylthynylanilines leading to 3-silylindoles via 1,2-silicon migration. In contrast, the formation of vinylidenes from internal alkynes via 1,2-carbon migration has been limited to stoichiometric reactions, and no catalytic process that involves the rearrangement of internal alkynes has been reported. Herein, we describe ruthenium-catalyzed cycloisomerization of 2-alkynylanilides leading to 3-substituted indoles via 1,2-carbon migration.

In the presence of the cationic ruthenium catalyst [CpRu(dppe)]$^+$, various 2-alkynylanilides were converted into the corresponding 3-substituted indoles in high yields. Anilides with aryl, heteroaryl, acyl, and alkyl groups participated in the cycloisomerization. The reactions proceeded through the disubstituted vinylidene complex from 2-alkynylanilides by 1,2-carbon migration, which was confirmed by the stoichiometric reaction of 2-phenylethenylenebenzanilide and [CpRu(dppe)]$^+$.

Keywords: Rearrangement, Vinylidene, Alkyne, Indole, Ruthenium

References

Drug Discovery of Vancomycin Dimer against Vancomycin-Resistant Enterococcal Infections

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Abstract

Infections due to multidrug-resistant bacteria have widespread over the past two decades, affecting strongly health care for human. Among these bacteria, Enterococcal infection is one of nosocomial pathogens. Glycopeptide antibiotics show antibiotic activity against gram positive bacterial infection including enterococcus bacteria. Especially, vancomycin is known as the most effective antibiotics against methicillin-resistant Staphylococcus aureus (MRSA). However, vancomycin-resistant MRSA (VRSA) and enterococcus (VRE) were clinically isolated in 1990’s and this is of grave concern for the security in the world. Vancomycin inhibits cell wall synthesis in bacteria by binding tightly to the C-terminal D-Ala-D-Ala of peptidoglycan. On the other hand, in resistant bacteria, vancomycin does not bind to the C-terminal peptidoglycan because resistant bacteria form the C-terminal D-Ala-D-Lac instead of D-Ala-D-Ala.1 Recently, we reported that vancomycin dimer has potent antibiotic activity against vancomycin-resistant bacteria.2 Our experimental results indicated that vancomycin dimer inhibits an enzyme in cell wall synthesis of resistant-bacteria. Investigating the target of vancomycin dimer makes promising for novel treatment of vancomycin-resistant enterococcal infections. We will present our current research result about mode of action and drug design of vancomycin dimer.

Keywords: enterococcal infections, vancomycin dimer, cell wall synthesis, drug design

References

Large Scale Synthesis and Conductivities of [10]Cycloparaphenylenes and Its Tetraalkoxy Derivatives

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Abstract

Cycloparaphenylenes (CPPs) represent a growing interest because of their availability by bottom-up organic synthesis. The synthetic endeavors not only enabled to synthesize different sizes of CPPs and several derivatives but also provided the opportunity to unveil physical properties of CPPs. Despite these developments, however, the quantity of CPPs and their derivatives that has been synthesized is quite limited. Here we report a new, scalable synthesis for [10]CPP and its tetraalkoxy derivatives. The key steps involve the highly cis-selective bis-addition of 4-bromo-4’-lithiobiphenyl to the quinones to produce a five-ring unit containing cyclohexa-1,4-diene-3,6-diol moiety, the platinum-mediated dimerization of the five-ring unit, and the H₂SnCl₄-mediated reductive aromatization of cyclohexadienediol. The tetraalkoxy substituents increased the solubility of [10]CPP in common organic solvents. The carrier-transport properties of thin films of [10]CPP and its derivatives were measured for the first time and indicated that [10]CPP derivatives could rival phenyl-C₆₁-butyric acid methyl ester, which is used widely as an n-type active layer in bulk heterojunction photovoltaics.

Keywords: Cycloparaphenylenes, Platinum, Tin, Thin film device, Carrier transport

References

Catalytic Stereoselective Formation of C-C Bond in Target-Oriented Synthesis

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Abstract

Carbon-carbon bond formation remains one of the cornerstones of synthetic chemistry. We shall present our recent achievements in developing efficient catalytic methods for crotylation of carbonyl compounds and application of this methodology in target-oriented synthesis. Asymmetric allylation of aldehydes with allyltrichlorosilane reagents in recent years has become a powerful synthetic tool [1]. We shall discuss novel strategies and new developments in organocatalytic, highly stereo- and enantioselective synthesis of branched and linear homoallylic alcohols, including design of new catalysts.

The synthetic application part will focus on a series of secondary metabolites isolated from marine soft coral \textit{Pseudopterogorgia elisabethae} exhibit a wide range of useful biological properties, which include anti-tubercular, anti-inflammatory, antimicrobial and analgesic activities [2].

Keywords: Lewis bases, crotylation, stereoselectivity, total synthesis

References

Coexistence of a Li Moiety and a Pd Moiety on Dihydropentacene

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Abstract

Introduction of substituents to an organic molecule is a basic topic in organic synthesis. Numerous methods have been developed by metalation and then coupling reactions of the organic molecules. In this regard, metalation with Li or Pd is commonly-employed for induction of substituents from electrophiles or nucleophiles. However, introduction of substituents from both of electrophiles and nucleophiles is unknown since there is no precedent of organic compounds bearing both of Pd and Li moieties.

In this work, dibromodihydropentacene compound was palladated and then lithiated to give lithiated-palladated intermediate. Both of lithium moiety and palladium complex moiety on dihydropentacene unexpectedly survived in solution. The Li moiety and Pd moiety reacted with electrophiles and nucleophiles respectively to give the substituted dihydropentacene products. Aromatization of these dihydropentacenes gave substituted pentacene derivatives. As mentioned above, this work provides a fundamentally new methodology for introduction of substituents from both of nucleophiles and electrophiles.

Keywords: Pentacene, Electrophile, Nucleophile
Copper-Catalyzed Defluoroborylation of Fluoroarenes

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Abstract

Fluoroarenes are often found in a wide spectrum of molecules, including pharmaceuticals, agrochemicals, and organic functional materials. Further transformation of these readily available fluorinated molecules to a diverse range of compounds would expedite development of new drugs and organic materials. In this context, we previously developed a transformation method of fluoroarenes to corresponding borylarenes via Ni/Cu-cocatalyzed C–F bond cleavage in the presence of bis(pinacolato)diboron. During the course of this research, we unexpectedly found that the defluoroborylation also proceeded by using only a copper catalyst. Whereas Cu-catalyzed borylation of haloarenes other than fluoroarenes has been well investigated, to the best of our knowledge, this is the first case for Cu-catalyzed borylative C–F bond cleavage of unactivated fluoroarenes.

We found that an air-stable PCy$_3$-precoordinated copper complex, CuCl(PCy$_3$)$_2$, effectively catalyzed the reaction to afford a wide range of borylated arenes in good to excellent yields. The use of tricyclohexylphosphine (PCy$_3$) and cesium fluoride was crucial to achieve the transformation. The reaction was scalable and applicable to polyfluoroarenes, which furnished polyborylbenzenes that would be useful building blocks for organic synthesis and supramolecular chemistry. Mechanistic studies suggested that the Cu-catalyzed defluoroborylation involved a single electron transfer process, which differed from that of the Ni/Cu-cocatalytic system. Furthermore, we recently found that the precoordinated copper complex also efficiently catalyzed trans-selective defluoroborylation of gem-difluoroalkenes to afford boryl(fluoro)alkenes, which served as useful synthetic intermediates for monofluoroalkenes. In this presentation, details on the substrate scope, mechanistic considerations, and synthetic applications of these defluoroborylation reactions will be discussed.

Keywords: copper catalyst, defluoroborylation, fluoroarene, gem-difluoroalkene

References

Recent Development of Halogen Dance

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Abstract

Multiply substituted heteroaromatic compounds are structural constituents of biologically active natural products, pharmaceuticals, and functional organic materials. The regiocontrolled synthesis of these heteroaromatic compounds remains important because classical Paal–Knorr synthesis and Gewald thiophene synthesis require preparation of functionalized acyclic dicarbonyl compounds before cyclization under heating conditions in the presence of a strong acid, resulting in limited substrate scope. Alternatively, stepwise installation of functional groups onto a heterocyclic skeleton involves regiochemical issues. The base-mediated halogen dance\(^1\) allows forming two chemical bonds in one pot, which renders reduction of a number of reaction pots; however, synthetic application of the halogen dance as well as regiochemical control in the migration have not been fully investigated.

We first controlled the reactivity of transient thienyl lithium species by transmetalation and achieved regiocontrolled synthesis of multiply arylated thiophenes through Negishi coupling.\(^2\) During the studies exploring substrate scope, a benzoxazole proved to be a superior directing group for a novel 1,3-migration of the bromo group.\(^3\) These results provided a reliable and direct access to functionalized thiophenes, furans, pyrroles in a regioselective manner, which was applied to short-step syntheses of several important compounds. In this presentation control of the deprotonation step by flash chemistry and selective trapping of several transient anion intermediates will be also discussed.

Keywords: halogen dance, one-pot reaction, cross coupling, palladium, heteroaromatic compounds

Regiocontrolled Synthesis of Multiply Arylated Thiophenes\(^2\)

![Regiocontrolled Synthesis of Multiply Arylated Thiophenes](image)

Benzoxazole-Directed Halogen Dance of Bromofuran\(^3\)

![Benzoxazole-Directed Halogen Dance of Bromofuran](image)

References

Amino Acids as Precursors for Efficient Synthesis of Oxindoles, Pyrroloindolines and Dihydroquinoxalinones via C-H Functionalization

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Abstract

Oxindoles, pyrroloindolines and dihydroquinoxalinones are core motifs in numerous significant pharmaceuticals and natural products, and are versatile intermediates for the synthesis of complex organic molecules. On the other hand, amino acids are attractive building blocks and precursors for the synthesis of diverse molecules because of their ready availability and structural complexity. Amino acids are also useful as organocatalysts and ligands to tune reactivity and control selectivity in modern organic chemistry.

We established a silver-catalyzed decarboxylative $\alpha$-aminoalkylation reaction for the synthesis of oxindoles from inexpensive and readily available materials in moderate to high yields.\textsuperscript{1} The reaction tolerated a broad scope of $N$-arylacrylamides and amino acid derivatives. The obtained oxindoles were readily transformed into densely functionalized pyrroloindolines by deprotection and cyclization in one pot. We also developed a metal-free reaction for the synthesis of dihydroquinoxalinones via intramolecular N-H/C-H coupling using hypervalent iodine.\textsuperscript{2} The starting materials were prepared from readily available aniline and amino acids. Various functional groups were tolerated to give multisubstituted dihydroquinoxalinones in moderate to excellent yields. The chirality of the amino acid was transferred to the desired target compound without a loss of enantiomeric excess. Noteworthy, the $\alpha$-aminoalkylation and intramolecular N-H/C-H coupling proceeded via direct C-H functionalization, and therefore the starting materials did not require preactivations such as halogenation.

Keywords: oxindole, pyrroloindoline, dihydroquinoxalinone, amino acid, C-H activation

\begin{center}
\begin{tikzpicture}
\node (1) at (0,0) {$R^1$};
\node (2) at (1,0) {$R^2$};
\node (3) at (2,0) {$R^3$};
\node (4) at (0,-1) {$N$};
\node (5) at (1,-1) {$O$};
\node (6) at (2,-1) {$N$};
\node (7) at (0,-2) {$R^4$};
\node (8) at (1,-2) {$R^5$};
\node (9) at (2,-2) {$NPG$};
\node (10) at (0,-3) {$R^1$};
\node (11) at (1,-3) {$R^2$};
\node (12) at (2,-3) {$R^3$};
\node (13) at (-2,-1) {$R^1$};
\node (14) at (-1,-1) {$R^2$};
\node (15) at (0,-1) {$R^3$};
\node (16) at (1,-1) {$R^4$};
\node (17) at (2,-1) {$R^5$};
\node (18) at (-2,-2) {$R^1$};
\node (19) at (-1,-2) {$R^2$};
\node (20) at (0,-2) {$R^3$};
\node (21) at (1,-2) {$R^4$};
\node (22) at (2,-2) {$R^5$};
\node (23) at (-2,-3) {$R^1$};
\node (24) at (-1,-3) {$R^2$};
\node (25) at (0,-3) {$R^3$};
\node (26) at (1,-3) {$R^4$};
\node (27) at (2,-3) {$R^5$};
\draw [->] (1) -- (2) -- (3);
\draw [->] (4) -- (5) -- (6);
\draw [->] (7) -- (8) -- (9);
\draw [->] (10) -- (11) -- (12);
\draw [->] (13) -- (14) -- (15);
\draw [->] (16) -- (17) -- (18);
\draw [->] (19) -- (20) -- (21);
\draw [->] (22) -- (23) -- (24);
\draw [->] (25) -- (26) -- (27);
\end{tikzpicture}
\end{center}

References

Amino-halogenation of Indoles as Dual Functionalization Using I–N Bonding Hypervalent Iodine Compounds

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Abstract

Environmentally friendly hypervalent iodine compounds have been utilized in oxidative transformations in lieu of transition metal reagent. [(Diacetoxy)iodo]benzene (PhI(OAc)₂), 2-iodoxybenzoic acid (IBX), Dess-Martin periodinane, [(hydroxyl)(tosyloxyl)iodo] benzene (Koser’s reagent), and diaryliodonium salts are the most popular oxygen-combined hypervalent iodine compounds, which have oxygen and iodine (O–I) bond, and these compounds have been used in a number of unique transformations. On the other hand, nitrogen-combined hypervalent iodine compounds, in which the nitrogen atom of the amine group forms a bond with the iodine atom of the iodine compound (N–I), have been used as organic reagents for the direct installation of a nitrogen group. We also succeeded in the preparation of heteroaromatic(phenyl)iodonium imides (1) as a novel nitrogen-combined hypervalent iodine compound useful for the regioselective amination of heteroarenes. Furthermore, we developed the transition metal-free regioselective Csp2–H dual functionalization underlying the bromo-amination via 1,3-migration of the imide groups on indolyl(phenyl)iodonium imides, which were prepared from electron-withdrawing-group-protected indoles. This dual-functionalization provided the corresponding 2-bis(sulfonyl)amino-3-bromo-indole derivatives (2) in high yields.

Keywords: dual functionalization, halo-amination, hypervalent iodine, indole, iodine

References
Chemoselective and Environmentally Benign Alcohol Oxidation Using Nitroxyl Radical/Copper Cooperative Catalysis

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Abstract

The oxidation of alcohols is one of the most reliable reactions to obtain carbonyl compounds, which play pivotal roles in organic synthesis, and thus numerous selective alcohol oxidation methods have been developed. Nevertheless, the direct oxidation of alcohols having oxidation-labile functional groups, such as unprotected amino, sulfide, and dithiane groups, into their corresponding carbonyl compounds often suffers from poor yield owing to either the nonproductive or destructive interaction between the oxidation-labile functional groups and oxidants. In our recent report, 2-azaadamantane N-oxyl (AZADO)/copper catalysis promoted the highly chemoselective aerobic oxidation of unprotected amino alcohols into amino carbonyl compounds.¹

Herein, we investigated the extension of the promising AZADO/copper-catalyzed aerobic oxidation of alcohols to other types of alcohol. During close optimization of the reaction conditions by using various alcohols, we found that the optimum combination of nitroxyl radical, copper salt, and solution concentration was dependent on the type of substrate. Various alcohols, including highly hindered and heteroatom-rich ones, were efficiently oxidized into their corresponding carbonyl compounds under mild conditions with lower amounts of the catalysts.²

In the presentation, we will also report applicability of the aerobic alcohol oxidation using the AZADO/copper catalysis to alcohols with oxidation-labile-sulfur-containing functional groups.

Keywords: alcohols, oxidation, copper, nitroxyl radical, sulfide

References

Synthetic assembly of sugar moieties using biotin-avidin interaction

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Abstract

It is well known that sugar chains of glycoconjugates specifically interact with carbohydrate-binding proteins and lectins. However, the affinities of naturally obtainable sugar chains against the proteins are not so high (~mM range). In order to enhance the binding affinities, various cluster-type carbohydrate derivatives have been prepared. We have also reported glycopolymers and glycodendrimers as multivalent-type substrates for the proteins and the substrates showed remarkable enhancement of the binding affinities against the proteins.\textsuperscript{1)} Since these glyoclusters typically showed positive glyocluster effect, this strategy can be applicable for the preparation of cluster-type bioactive compounds. Therefore, in this presentation, design, syntheses, and biological evaluation of a new class of glyocluster,\textsuperscript{2)} which is constructed by means of biotin-avidin interaction system, will be discussed

Keywords: glyoclusters, lectins, biotin, avidin, glycoconjugates

Graphical abstract

References

Photocatalytic and photoelectrochemical water oxidation using oxynitrides

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Abstract

Photocatalytic water splitting gathers much attention because of its potential for applications of solar hydrogen production. Oxynitride are promising candidates for visible-light-driven photocatalysts due to valence bands located at shallower positions than those in general oxides such as TiO$_2$, SrTiO$_3$, and NaTaO$_3$. We have demonstrated that tuning of valence band potentials by control of nitrogen contents is a useful method to obtain high activity for water oxidation (oxygen evolution). According to our results, excessively shallow potentials of valence bands are not favorable for water oxidation although valence bands at shallow positions are essential for the visible light response of oxynitrides.

We have discovered that La$_{0.5}$Sr$_{0.5}$Ta$_{0.5}$Ti$_{0.5}$O$_2$N, which is one composition in the solid solution between LaTaON$_2$ and SrTiO$_3$, is highly active for water oxidation. Such an oxynitride photocatalyst possessing high ability for water oxidation is regarded to be a candidate for photoanode materials. Indeed, we confirmed that La$_{0.5}$Sr$_{0.5}$Ta$_{0.5}$Ti$_{0.5}$O$_2$N showed anodic photoresponse under visible light although the photocurrent density was very low, 0.03 µA cm$^{-2}$ at 0.8 V$_{RHE}$. The photocurrent density was improved to 3 µA cm$^{-2}$ by necking treatment and modification with CoOx further improved the current density, 8 µA cm$^{-2}$. When the oxide precursor was annealed in air at 1500 ºC prior to nitriding treatment, particle size of obtained La$_{0.5}$Sr$_{0.5}$Ta$_{0.5}$Ti$_{0.5}$O$_2$N was increased. La$_{0.5}$Sr$_{0.5}$Ta$_{0.5}$Ti$_{0.5}$O$_2$N composed of large particles showed high photocurrent (40 µA cm$^{-2}$) with modification of necking and the CoOx cocatalyst.

Keywords: photocatalyst, oxynitride, solid solution, band potential, water oxidation

References

Role of the Acid-Base and Redox Sites on Catalytic Reactions at the Liquid/CeO$_2$ Interface

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Abstract
A detailed understanding of the interface between liquid and metal-oxide is fundamental due to its relevance to the broad range of physicochemical phenomena and technological applications. Chemical reactions occurring at the liquid/metal-oxide interface are very complex, and the probing of the microscopic nature of the interface remains a formidable task for experiments. In this work, we focus on the catalytic reactions at the water/CeO$_2$ and methanol/CeO$_2$ interface and investigate the role of acid-base and redox sites over CeO$_2$ by employing the first-principle molecular dynamics simulations. We will present the following topics: (1) Structure and dynamical properties of water molecules at the water/CeO$_2$ interface. (2) Substrate-specific adsorption of 2-cyanopyridine and hydration reaction over CeO$_2$ explored by the free energy landscape with the aid of metadynamics simulations. (3) Self-assembled hybrid catalysis of 2-cyanopyridine and CeO$_2$ and a formation of strong base site by hybridization. (4) The reaction mechanism for the direct synthesis of dimethyl carbonate (DMC) from methanol and CO$_2$ over CeO$_2$.

Keywords: Cerium Oxide, Hydration, 2-cyanopyridine, DMC

References
Conformational Analysis of Enantioselective Mukaiyama–Mannich Reaction by Cyclopentadiene-Based Brønsted Acid

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Abstract

Chiral Brønsted acid catalysts are useful for a wide variety of enantioselective transformations. Among them, a chiral phosphoric acid (CPA) derived from binaphthol (BINOL) is the most frequently used catalyst for a number of enantioselective reactions. The reactivity and selectivity can be modulated by varying the 3,3’-substituents. The major drawback of CPA is the lengthy, laborious, and expensive protocol required for its synthesis, which complicates catalyst optimization and limits its application on scale. Recently, a fundamentally new strategy on the design of chiral Brønsted acid catalysts was reported by Lambert and co-workers.\textsuperscript{1} The new catalyst class is based on 1,2,3,4,5-pentacarboxycyclopentadiene (PCCP), which preferably exists in the enol form 1 and its deprotonation leads to the stable aromatic cyclopentadienyl anion 2, as shown in Figure 1. Its acidity is comparable to mineral acids. This catalyst is readily prepared in one step using naturally occurring (–)-menthol as a chiral pool compound. PCCP catalyzes the addition of silyl ketene acetal 4 to imine 3 in ethyl acetate at –78°C in 1 hour to give an optically active product 5 in 97% yield and 97% enantiomeric excess. The catalyst loading could be reduced to 0.01 mol% and the organocatalytic reaction is successful on gram scale. Thus, the new catalyst system has a potential to become valuable alternatives to the established Brønsted acid catalysts. In this study, we performed a systematic conformational search of the stereo-controlling transition states for the reaction to uncover the origin of the enantioselectivity.

Keywords: organocatalysts, enantioselectivity, conformational analysis, DFT computation

References

Liesegang phenomenon: Chemical model for pattern formations in nature

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Abstract

Nature has a wealth of beautiful and spatiotemporal periodic patterns, some of which has an essential role to maintain the robustness and flexibility of life such as circadian rhythms of the Nobel Prize in Physiology or Medicine 2017. Understanding the mechanism underlying such spatiotemporal periodicity is important for multidisciplinary research ranging from chemistry, biology, physics, mathematics, and social science. In chemical viewpoint, most powerful approach to understand the pattern formation in nature is the use of model chemical reactions that can reproduce spatial and temporal patterns in vitro.

The Liesegang phenomenon is one of the major mechanisms that can mimic static self-organized patterns in nature, e.g., the concentric patterns of mycelial growth and agates. Since the discovery of the Liesegang phenomenon in chemistry, many researchers have attempted to identify the inherent mechanism to enable the engineering of desired patterns by chemical reactions. We will discuss recent developments in the controlled construction of Liesegang patterns with the aid of nanoscience, surface chemistry, and polymer chemistry. Our finding yields a new chemical and mathematical model to reproduce spatial patterns in nature.

Keywords: Liesegang, reaction-diffusion, nonequilibrium, self-organization

Concentric pattern formation in nature

Chemical reaction (Liesegang pattern)

Biological reaction (mycelial growth)

Geological reaction (agate rock)

References

Exciton Dynamics in Organic Optoelectronic Materials

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Abstract

There has been a growing interest in electronic and optical properties of organic semiconductors because of their potential applications for optoelectronic devices. However, it is difficult to theoretically study the excited states and photophysical processes. First, computation of large number of excited states in large molecular systems is still a challenging issue in quantum chemistry. Second, to investigate the photophysical processes such as electronic energy transfer or charge separation, one has to simulate real-time dynamics with exciton-phonon interaction being incorporated. We have been developing the simulation method based on the fragment-based electronic structure method and quantum dynamics theory. The model exciton Hamiltonian is constructed by the ab initio electronic structure calculations utilizing the fragment molecular orbital method. Exciton dynamics coupled to the nuclear vibrations is modeled by the stochastic Schrödinger equation, which allows to describe ultrafast coherent dynamics and subsequent thermal relaxation.

In this talk, we present optical properties and exciton dynamics in the dinaphtho[2,3-b:2',3']-thieno[3,2-b]-thiophene (DNTT), a p-type organic semiconductor molecule. The calculated absorption spectrum based on the first principle is in qualitative agreement in the experiment; it is composed of main excitations of Frenkel-dominant states with partial admixture of CT states and CT-dominant states with slight admixture of Frenkel states. Next we show exciton dynamics in a DNTT thin film. The localized Frenkel and CT excitons is relaxed to the lowest exciton state in about 1.5 and 2.5 ps, respectively. We observe the mixing of CT excitons with Frenkel state in 50 fs after the excitation. Accordingly, electron- hole separation increases and shows an oscillation pattern as a result of delocalization of electron and hole and electron-hole Coulomb interactions. We discuss the roles of charge delocalization and localization in the Frenkel-CT mixings.

Keywords: organic semiconductor, electronically excited states, exciton dynamics,

References

Theoretical Study on Conversion of Methane to Higher Hydrocarbons by Liquid-Metal Indium

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Abstract
Conversion of methane to valuable hydrocarbons is desired to utilize abundant natural gas effectively. Recently, Prof. Yamanaka’s group of Tokyo Institute of Technology reported direct dehydrogenative conversion of methane to higher hydrocarbons by liquid-metal indium\textsuperscript{1}. They examined 20 transition and post-transition metals as the catalyst and found that indium gives the best yields. Indium has the low melting point, 430K, and is liquid in the experimental condition of 1173K. To investigate the mechanism of catalytic reaction by liquid indium theoretically, we calculated the reaction energies and activation energies using the density functional theory (DFT). To consider geometrical change of liquid indium, we also performed the ab-initio molecular dynamics (MD) calculations. In this study, we considered only ethane formation from methane because it is suggested experimentally that the first product is ethane, and higher hydrocarbons are formed from ethane in gas phase. From the calculation results, we suggested the mechanism as shown in the figure below. (1) C-H bond activation reaction is endothermic and unlikely to occur on a clean indium surface. (2) On the disordered surface of liquid indium, this activation reaction becomes exothermic by the row coordinated atoms. The reaction and activation energies become especially low when methane interacts with two indium atoms. In the transition state structure, one indium forms a bond with H, and another indium with C. (3) CH\textsubscript{3} diffuses on the liquid indium surface. When two CH\textsubscript{3} encounter, ethane is formed. The geometrical change of liquid indium surface is crucial in the present reaction.

Keywords: Methane, C-H bond activation, Liquid-metal indium, DFT calculation, ab-initio MD

Reference
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In-Silico Ammonia Synthesis Using Heterogeneous Catalysts.  
A First-Principles Molecular Dynamics Study 

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Abstract  
In this presentation, I will report first-principles molecular dynamics (FPMD) simulations on ammonia synthesis from nitrogen and hydrogen molecules using supported metal catalysts. Ammonia is considered to be one of the important “energy carriers” because of the two reasons: (i) it is considered to carry H\textsubscript{2} molecule, and (ii) ammonia itself can be used as a fuel for direct combustion and for ammonia-based fuel cells. For mass production of ammonia, the well-known Haber-Bosch process has been still used in industry. This process is operated in high temperature at very high pressure. Therefore, more reactive catalysts that can perform the synthesis in a much milder condition has been strongly demanded.  
The present research aims at revealing reaction mechanisms of ammonia synthesis on Ru nano catalyst supported of MgO. In order to provide useful information for catalyst design, we try to reveal important sites on surface by carrying the FPMD simulations. Through various trials in the simulations, we were successful to reproduce the ammonia formation in various models. In the presentation, I will discuss about important reaction sites in this catalytic reaction and will suggest some design principles for supported metal catalysts for ammonia synthesis in a mild condition.  

Keywords: ammonia synthesis, heterogeneous catalyst, catalysis, first-principles calculation, molecular dynamics  

Graphical abstract
SMASH: Massively Parallel Software for Quantum Chemistry Calculations

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Abstract

The performance of computer systems continues to be improved by increasing the numbers of nodes and CPU cores because of heat and power problems. The trend is for not only supercomputers but also computers in laboratories. On the other hand, nano-sized molecules are one of the attractive and promising targets, and their computational costs are considerably high. Therefore, parallel computing is significant to treat large molecular systems using present and future computers.

Scalable Molecular Analysis Solver for High-performance computing systems (SMASH) is open-source software for massively parallel quantum chemistry calculations written in the Fortran 90/95 language with MPI and OpenMP parallelization techniques.1,2 The software is distributed under the Apache 2.0 open source license since 2014, and Hartree-Fock, Density Functional Theory (DFT), and second-order Møller-Plesset perturbation theory (MP2) calculations are available. All the large data of electronic correlation calculations are distributed and stored in memory, not on disk. Frequently used calculation routines such as two-electron repulsion integrals are modularized, making it possible to reduce development costs and making it easy to port to other programs. The DFT (B3LYP) energy calculation of (C_{150}H_{30})_2 (the cc-pVDZ basis set (4500 dimensions)) on the K Supercomputer (2.0GHz, 8 cores/node) achieved a speed-up of 50,000 and a CPU efficiency of 13% on 100,000 cores, which took 154 seconds.3 It is now easy to calculate electronic structures of nano-sized molecules routinely.

Keywords: quantum chemistry, supercomputers, massive parallelization, open source software

References

High-pressure microscopy for controlling molecular machines in living cells.

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Abstract  
The bacterial flagellar motor is a molecular machine that converts an ion flux to the rotation of a helical flagellar filament. Counterclockwise rotation of the filaments allows them to join in a bundle and propel the cell forward. Loss of motility can be caused by environmental factors such as temperature, pH, and solvation. Hydrostatic pressure is also a physical inhibitor of bacterial motility, but the detailed mechanism of this inhibition is still unknown. Here, we developed a high-pressure microscope that is optimized both for the best image formation and for the stability to hydrostatic pressure up to 150 MPa. We also characterized the pressure dependence of the motility of swimming Escherichia coli cells and the rotation of single flagellar motors. The fraction and speed of swimming cells decreased with increased pressure. At 80 MPa, all cells stopped swimming and simply diffused in solution. After the release of pressure, most cells immediately recovered their initial motility. Direct observation of the motility of single flagellar motors revealed that application of >120 MPa pressure induces a reversal from counterclockwise to clockwise rotation. Application of pressure generally promotes the formation of clusters of ordered water molecules on the surfaces of proteins. It is possible that hydration of the switch complex of motors at high pressures induces structural changes similar to those caused by the binding of switch-inducing protein CheY.

Keywords: High-pressure microscope, molecular machines, bacterial flagellar motors

References
Preparation of Metal Nanoparticles in Low Vapor Pressure Liquids and Their Applications

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Abstract
The sputter deposition of metals onto ionic liquids (ILs) is a simple and elegant method for preparing nanoparticles without any chemical reaction [1]. Although there have been some reports on the size determination factors for Au nanoparticles (Au NPs) prepared using this method, the effects with respect to the type of IL used have not been clearly elucidated. This is because there are some complicating factors, some of which have been revealed by previous systematic studies [2,3].

In the present study, Au NPs are prepared in nine types of imidazolium-based IL to examine the size determination effects of the type of anion involved, the length of the alkyl chain of the cation, and the preparation temperature for each IL, while keeping other factors constant. For most of the capture media ILs, the sizes of the Au NPs increase with an increase in temperature. The Au NPs prepared in ILs containing different types of anions exhibit distinctly different particle sizes and temperature dependences. Conversely, the alkyl chain is regarded as a secondary stabilizer that works only at higher preparation temperatures.

It is concluded that the sizes of Au NPs prepared by this method may be determined by the competition between the collision frequency of the ejected Au atoms and the stabilizing capability of the anions that form the first coordination shell around the Au NPs [4]. The Au NP sizes are closely related to the volume of anions. A new method that combines sputter deposition of Au and the use of a capture medium of poly(ethylene glycol) (PEG) has developed for preparing Au NPs based on the knowledge [5]. We are now studying to use metal NPs prepared in ILs and PEG as catalyst for hydrogen absorption and lithium-air batteries.

Keywords: metal nanoparticle, ionic liquid, poly(ethylene glycol)

Acknowledgements
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References
Theoretical study on the geometry and size effect on the catalytic activity of gold clusters

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Abstract

Catalysis by nanoscaled particles (nanocatalysis) is one of the most exciting fields of modern nanoscience. The enormous interest in nanocatalysis is stipulated by the fact that the catalytic activity of nanoparticles is strongly dependent on their size, structure, morphology, charge state, type of the support material, etc., and hence can be controlled and tuned by these factors. However, despite intensive theoretical and experimental studies, the clear understanding of the morphology effects in nanocatalysis is still lacking. Metal clusters are structural flexible, which leads that they can possess different geometrical structures and different reactivity for the same sized cluster. This property makes the investigation of catalytic activity for metal clusters relatively difficult. Recently, we systematically investigated the catalytic activity of small metal clusters by considering all the possible metal clusters isomers (Figure 1).\textsuperscript{[1-3]} This study is based on the global reaction route mapping [4] technique by using the artificial force-induced reaction method. It is shown that the most stable structure of metal clusters are not always highly reactive and the most stable adsorption configurations of reactants on metal clusters do not necessarily lead to the low-energy dissociation pathways (Figure 1). Therefore, in order to investigate the activity of metal clusters, the contribution of all the possible reaction sites and low-energy isomers are highly required. The detailed results and method will be shown in the presentation.

Keywords: Metal Cluster, Catalytic Activity, Isomers, Size

Figure 1 All the reaction paths for H\textsubscript{2} dissociation Au\textsubscript{7} and the reaction scheme of H\textsubscript{2} dissociation path on Au\textsubscript{8}

References

Theoretical Study on Photoreactivity and Phosphorescence Capabilities: Systematic Search of Intersystem Crossing Pathways

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Abstract

Intersystem crossing (ISC) often plays a key role in photochemical reaction, and the ISC effectively occurs at a crossing point between two potential energy surfaces. We have been developing the method for systematic search of the such crossing points, minimum-energy seams of crossings (MESXs).\textsuperscript{1}

The mechanism of the CO ligand dissociation of \textit{fac}-[Re\textsuperscript{I}(bpy)(CO)\textsubscript{3}P(OMe)\textsubscript{3}]\textsuperscript{+} has theoretically been investigated,\textsuperscript{2} as the dominant process of the photochemical ligand substitution (PLS) reactions of \textit{fac}-[Re\textsuperscript{I}(bpy)(CO)\textsubscript{3}PR\textsubscript{3}]\textsuperscript{+}, by using the (TD-)DFT method. The PLS reactivity can be determined by the topology of the T\textsubscript{1} potential energy surface, since the photoexcited complex is able to decay into the T\textsubscript{1} state by internal conversions (through conical intersections) and intersystem crossings (via crossing seams) with sufficiently low energy barriers.\textsuperscript{3} The T\textsubscript{1} state has a character of the metal-to-ligand charge-transfer (\textsuperscript{3}MLCT) around the Franck-Condon region, and it changes to the metal-centered (\textsuperscript{3}MC) state as the Re–CO bond is elongated and bent. The equatorial CO ligand has a much higher energy barrier to leave than that of the axial CO, so that the axial CO ligand selectively dissociates in the PLS reaction. The single-component artificial force induced reaction (SC-AFIR) search\textsuperscript{3} reveals the CO dissociation pathway in photostable \textit{fac}-[Re\textsuperscript{I}(bpy)(CO)\textsubscript{3}Cl] as well, however, the dissociation barrier on the T\textsubscript{1} state is substantially higher than that in \textit{fac}-[Re\textsuperscript{I}(bpy)(CO)\textsubscript{3}PR\textsubscript{3}]\textsuperscript{+} and the minimum-energy seams of crossings (MESXs) are located before and below the barrier. The MESXs have also been searched in \textit{fac}-[Re(bpy)(CO)\textsubscript{3}PR\textsubscript{3}]\textsuperscript{+} and no MESXs were found before and below the barrier.

Keywords: photochemical reaction, intersystem crossing, TD-DFT, artificial force induced reaction (AFIR)

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{diagram.png}
\end{figure}

References


Theoretical study of decay paths in photoreactions based on automated exploration of minimum energy conical intersection and seam of crossing geometries

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Abstract

In a photo reaction, a photo-excited molecule eventually decays to the ground state by four processes, i.e. internal conversion via conical intersection (CI) regions, intersystem crossing via seam of crossing (SX) regions, fluorescence, and phosphorescence. By considering the four decay processes, it will be possible to discuss all photoreactions. Internal conversion can occur quickly if an accessible CI region exists. If there is a high barrier between the Franck-Condon (FC) and CI regions, intersystem crossing, fluorescence, phosphorescence processes are in competition. Thus, an exploration of non-radiative decay paths, i.e. internal conversion and intersystem crossing paths, is required to investigate photo-reactions. However, the estimation of CIs and SXs is not trivial. To search for CI and SX geometries automatically, a method with a combination of gradient projection (GP) and single component artificial force induced reaction (SC-AFIR) method \cite{1,2} was developed \cite{3} and implemented in the GRRM program \cite{4}. By using this method with time dependent density functional theory (TDDFT) or spin-flip TDDFT (SF-TDDFT), it is possible to systematically explore CI and SX region which consists of singlet and triplet states, i.e. singlet/singlet-CI, triplet/triplet-CI and singlet/triplet-SX regions. The method is applicable to molecules containing up to 40 atoms even with a small PC cluster. Automated search methods have been applied to more than 30 aromatic compounds \cite{5,6}. The details of methods and the applications to photoreactions will be discussed in the presentation.

Keywords: Conical intersection, Seam of crossing, GRRM, artificial force induced reaction

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{potential_energy_curves.png}
\caption{Schematic potential energy curves for photoreactions.}
\end{figure}

References

2-Dimensional Nanocarbons for Catalytic Organic Reactions

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Abstract
2-Dimensional materials like graphene has a great potential as a catalyst component. We have utilized graphene oxide (GO) in catalysis for organic reactions.

1. Application for support materials
GO is a carbon nanosheet with a one carbon atom-thickness (ca. 0.8 nm), good solubility in water and polar solvents, high surface area (>1000 m\textsuperscript{2}/g), and high strength. GO possesses a variety of different oxygen-containing functionalities, such as hydroxyl, epoxy, and carboxyl groups, and these groups would be able to coordinate to metal species and prevent them from aggregating and leaching.

We have developed a simple method to deposit Pd nanoparticles on single-layer GO, and used as a catalyst in cross coupling reactions.

2. Application for metal-free reactions
Metal-free oxidations using carbon-based materials as catalysts have attracted much attention. Unfortunately, the reaction mechanism was not adequately elucidated because of the complexity of the active sites on the carbon catalyst. Therefore, any guideline to improve the catalytic activity of the carbon materials has not been proposed. Through our investigations, we found that reduced graphene oxide (rGO) can activate O\textsubscript{2}, but graphene oxide (GO) cannot. In contrast, stoichiometric amount of GO could promote oxidation reactions even in the absence of O\textsubscript{2}.\textsuperscript{2, 3} In addition, the electron transfer from graphene to a diazonium salt facilitated the formation of aryl radicals, which underwent coupling reaction with an aromatic compound.\textsuperscript{4}

Keywords: graphene, oxidation, C-H transformation, reduction, cross coupling

References
Relativistic quantum Monte Carlo methods

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Abstract

Quantum Monte Carlo (QMC) methods are quantum mechanical methods to obtain highly accurate wave functions and their energies. Especially, QMC methods can treat wave functions with explicit two electron terms, which are hard to analytically integrate, and naturally describe electron correlation effects. Additionally, QMC methods are based on the stochastic treatment of the electronic wave equations and suitable for massively parallel computers. However, conventional QMC methods for molecular calculations are derived from the non-relativistic Schrödinger equation and relativistic effects are treated only as the perturbation. In order to obtain accurate wave function of molecular systems containing heavier elements, non-perturbative extensions to the QMC methods are required.

In this presentation, we introduce relativistic extensions to the QMC methods using two-component relativistic theories developed in the molecular orbital theory. The zeroth-order regular approximation (ZORA) Hamiltonian has very simple structure and relativistic QMC methods – relativistic variational Monte Carlo (VMC)\textsuperscript{1} and relativistic diffusion Monte Carlo (DMC)\textsuperscript{2} – can be derived from the ZORA equation. Using these relativistic QMC methods, we can overwrite conventional non-relativistic counterparts with a few additional computational costs. For better description of the relativistic effects, extensions with more accurate infinite-order regular approximation (IORA) equation are also investigated.

Keywords: quantum Monte Carlo, relativistic effect, regular approximation

References

Oxide Nanosheet Photocatalysts for Water Splitting

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Abstract

Hydrogen production from water using photocatalyst is an ultimate goal in a renewable energy research. However, there are several issues such as the quantum efficiency in visible light region is still low for the practical application. One factor that causes a decrease in the photocatalytic activity is a recombination reaction between electron and hole. When the photocatalyst is illuminated by light with a energy greater than the bandgap energy, the photo-excited electron and hole are generated within the powder. For these carriers generated within the powder to react with water, they have to travel long distance to the surface from within. During the long trip to the surface, they may be recombined or get trapped at the defect sites. One of the ideal materials that can suppress the recombination and give short travel distance is a two-dimensional material without inner and surface defects. Specifically, two-dimensional crystal (nanosheet) prepared by exfoliation of layered compound is a single crystal with a homogeneous ultrathin thickness, and has a lateral dimension from several hundred nanometer to several micrometer. Therefore, the travel distance of the photo-excited carriers is short, and many photons can be absorbed by nanosheet in a remarkably short time under low photon flux density due to its large section area. In this study, we have focused on the characteristic performance of nanosheet photocatalysts. For instance, it is well known that a photocatalyst without co-catalyst loading has poor photocatalytic activity for water splitting. However, a particular type of oxide nanosheet shows a high photocatalytic activity for hydrogen evolution from water without co-catalyst loading. Thus, the two-dimensional structure is expected to contribute to the development of photocatalysts for water splitting in the future. In this presentation, we report the characteristic performance of nanosheet photocatalysts and nanosheet p-n junction photocatalysts.

Keywords: Photocatalyst, hydrogen, nanosheet, p-n junction, reaction site

References
MRI-based gel dosimeter for heavy ion beam cancer therapy

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Abstract
An energetic heavy-ion beam has the advantages of a localized dose distribution and an enhanced radiobiological effectiveness in the Bragg peak region compared with X-rays and gamma rays. Exploiting these features, heavy-ion cancer therapy has established its effectiveness for solid cancers. The evaluating and adjusting of 3D dose distributions in advance are essential for the aim of which is to avoid unnecessary damage to healthy tissue and to concentrate the dose on only tumor target. The 3D dosimeter is necessary to verify a treatment plan exactly.

Gel dosimeters, including radiation sensitive chemicals, are nearly tissue-equivalent and are capable of imaging 3D dose distributions by using magnetic resonance imaging (MRI) because radiation-induced chemical products shift the relaxation time of proton nuclear magnetic resonance in gels. There is two major gel dosimeter that are Fricke type \cite{1} and polymer type \cite{2} gels, utilizing the radiation induced oxidation and polymerization, respectively for record of absorbed dose mapping. Recently, we have developed new type chemical 3D dosimeter prepared by mixing aqueous chemical dosimeter and nano-sized clay gel matrix, which is able to measure the heavy ion beam dose distribution\cite{3,4,5}. We present recent results and application of 3-D gel dosimeter in the radiation therapy.

Keywords: chemical dosimeter, radiation measurement, 3D dose distribution, irradiation, gel

References
Centralochiral transition metal complexes
for catalytic asymmetric [3+2] cycloaddition of α-ketoester enolates

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Abstract

Optimization in asymmetric metal catalysis often requires trial-and-error approaches. Considering that cooperative activation of two reaction components in asymmetric space is a common key strategy to attain high rate acceleration and selectivity, it is important to understand the electron density distribution (EDD) of the chiral catalyst. Here we will present our empirical approaches for providing insights into the catalytic activation process in the distorted Ni(II)-catalyzed asymmetric [3+2] cycloaddition of α-ketoesters 1 with (E)-nitrone 2. We characterize the bonding properties of the Ni(II) catalyst by means of EDD analysis, showing that the distortion around the Ni(II) center makes the dz^2 orbital partially “naked”, wherein the labile acetate ligand is masked with weak electrostatic interaction. A series of structural analyses in the solution state, together with DFT calculations, supported that the exposed nature of the dz^2 orbital allows it to interact with α-ketoester 1 as a Lewis acid and the labile acetate ligand acts as a Brønsted base, leading to the formation of (Λ)-Ni(II)-enolate. The observed intermolecular H-bonding interaction in the X-ray structure analysis also suggests that the H-bonding activation of the nitrone 2 would be a key driving force for fixing the two reaction components in close proximity. The model presented herein can explain the obtained absolute stereochemistry of 3. Another variant of the asymmetric [3+2] cycloaddition between nitrile oxides and α-ketoesters catalyzed by a chiral Cu(II)-diamine complex will be also discussed.

Keywords: nickel, copper, enolates, α-ketoesters, [3+2] cycloadditions

References

Visible Light-Driven Hydrogen Generation Using Ir(III) Photosensitizers Incorporated in Vesicles

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Abstract

The demand for clean energy sources, such as hydrogen produced from water and solar energy, has increased in recent years. Thus we have developed cationic iridium (Ir) complexes comprising coumarin 6 and 2,2'-bipyridine (bpy) derivatives as effective photosensitizers in visible light-driven hydrogen (H\textsubscript{2}) generation.\textsuperscript{1,2} These complexes possess important photophysical features including strong visible-light absorption and long-lived phosphorescence. However, the system requires a significant amount of acetonitrile so that the Ir(III) complexes can become soluble in the reaction mixture.

In this presentation, we report on a new photochemical H\textsubscript{2}-generating system using spherical bilayer-membrane compartments, so-called vesicles, that form as a result of self-organization of amphiphiles in aqueous medium. As the first step in this study, cationic Ir(III) complexes 1–4 embedded in the vesicle membranes were examined for their phosphorescent properties. While all the complexes were successfully incorporated into the vesicles, the phosphorescence lifetimes of complexes 1–3 with bpy ancillary ligands (ca. 4 \(\mu\)s) were much shorter after incorporation into the membrane than in dichloromethane (ca. 30 \(\mu\)s). By contrast, complex 4 having 2-(1-pyrazolyl)pyridine exhibited a remarkably long lifetime (31 \(\mu\)s) as well as high phosphorescence quantum yield (32\%) even in the vesicles. These results can be interpreted by different excited-state deactivation pathways and/or location of the complexes in the membranes. The relatively long-lived excited states in vesicles (i. e. 4–31 \(\mu\)s) make these Ir(III) complexes promising photosensitizers in the new H\textsubscript{2}-generating system. Indeed, visible-light irradiation of the vesicle solutions resulted in H\textsubscript{2} production when electron-donating sodium ascorbate and a water-soluble Ni molecular catalyst were present in the outer aqueous phase. For the reaction with complex 3, turnover numbers of the photosensitizer and catalyst were determined to be 867 and 145, respectively, which demonstrated that H\textsubscript{2} was photocatalytically generated in this reaction.

Keywords: iridium complex, photosensitizer, phosphorescence, visible light, hydrogen

References

Highly active and selective electrocatalysts based on covalent organic frameworks modified with single metal atoms

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Abstract

Covalent triazine frameworks (CTFs) have attracted a keen attention as novel catalyst platforms because of their unique physicochemical properties, including their nano-porous structure, mechanical robustness and high design flexibility. Recently, we successfully developed a CTF-based electrocatalyst by hybridizing CTFs with conductive carbon particles, although CTFs are non-conductive. As CTFs possess abundant nitrogen atoms with an electron lone pair, various metals can be loaded onto CTFs by coordination bonds with nitrogen. Using this approach, we demonstrated that electrocatalysts composed of atomic metal-loaded CTFs exhibit unique reaction activity and selectivity [1-6]. For example, a single Pt-atom-modified CTF showed the methanol tolerance during oxygen reduction reaction and the efficient activity for hydrogen oxidation reaction. In this presentation, we introduce our recent studies on the unique electrocatalytic activities of single-metal atoms modified CTFs.

Keywords: Electrocatalysts, Covalent triazine frameworks, single-metal catalysts

Graphical abstract

References

Thermal Decomposition Behavior of Supported Platinum Salt for Catalyst Preparation

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Abstract

Supported platinum catalysts are widely utilized for practical use such as automobile exhaust gas, hydrogenation/dehydrogenation, reforming, and electrode catalysts for PEFC. It is well known that preparation procedure would influence on the catalytic performance remarkably, but relatively few studies have been reported on formation of platinum particles in the initial step. In the present study, transformation of platinum salt on silica and $\gamma$-alumina upon calcination and was investigated by in-situ XAFS spectroscopic technique.

Catalyst samples were prepared by impregnation of silica or $\gamma$-alumina with aqueous solution of H$_2$PtCl$_6$ or Pt(NH$_3$)$_2$Cl$_2$ at 353 K, followed by drying at 383 K. Pt L-edge XAFS spectra were recorded using a laboratory–type spectrometer in a transmission mode\textsuperscript{1}. Oxidation states of supported platinum species was evaluated with the d-orbital occupancy\textsuperscript{2} by analyzing L2,3 XANES spectra. Supported H$_2$Pt$^{VI}$Cl$_6$ species were gradually reduced until 573 K on both silica and alumina. Further increment of calcination temperature up to 773 K little influenced on the oxidation states on silica; however, re-oxidation proceeded on alumina. Pt$^{II}$(NH$_3$)$_2$Cl$_2$ of cationic precursor was also re-oxidized on alumina above 523 K. EXAFS characterization demonstrated that the number of coordinated Cl atoms for supported H$_2$PtCl$_6$ species decreased upon calcination until 573 K. Formation of Pt-Pt pair proceeded on silica after calcination at 773 K. In contrast, Pt-O and Pt-(O)-Al pairs were detected on H$_2$PtCl$_6$/Al$_2$O$_3$ calcined at 773 K whereas no Pt-Pt pairs were confirmed. It shows that isolated Pt species formed on both supports at around 573 K under air stream accompanied by elimination of chlorine atoms. The isolated species would aggregate to form Pt particle on the surface of silica above 573 K, whereas cation-vacant site on $\gamma$-alumina captures the isolated Pt atoms. The adjacent oxygen atoms would cause re-oxidation.

Keywords: supported platinum salt, decomposition behavior, XAFS, Al$_2$O$_3$, SiO$_2$

References

Frontier Orbital Perspective for Electron Transport in Alternant and Nonalternant Hydrocarbons

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Abstract

Exploring charge transport properties through single molecules is an active theoretical and experimental area not only in molecular electronics but also in molecular sensing. One of the most striking quantum effects in molecular conductance is destructive quantum interference (QI), where conductivity is significantly suppressed. Recently, growing attention has been devoted to QI because it has the potential to open doors to many new applications, such as thermoelectric devices, molecular switches, and spin filters. Predicting QI in both alternant and non-alternant hydrocarbons is a goal of theoretical work in molecular electronics.

A significant challenge to be addressed in molecular electronics is to further develop chemical intuition to understand and predict QI features. In this study, an orbital rule is markedly ameliorated so that it can capture the manifestation of QI not only in alternant hydrocarbons but also in non-alternant ones. The orbital-based prediction about the occurrence of QI in a non-alternant hydrocarbon shows good agreement with experimental results. A simple perturbation theoretic line of reasoning suggests that frontier orbital phase and splitting play a pivotal role in QI phenomena.\textsuperscript{1}

Keywords: quantum interference, molecular conductance, frontier orbitals

References

Different Photoisomerization Routes in the Structural Isomers of Cinnamate Based Sunscreens

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Abstract

Cinnamate derivatives are widely used molecules in the nature and industry: the chromophore of photoactive yellow protein, sunscreens of many plants to protect their DNA, UV absorber of sunscreen cosmetics etc. Understanding their nonradiative decay (NRD) mechanisms should realize new effective sunscreens and other photofunctional materials. In this study, we investigated the NRD pathways of jet-cooled para-methoxy methylcinnamate (p-MMC) and para-methoxy ethylcinnamate (p-MEC), ortho-, meta- and para-hydroxy methylcinnamate (o-, m- and p-HMC, respectively) by picosecond and nanosecond pump-probe spectroscopy, and low-temperature matrix-isolation FTIR spectroscopy. The possible NRD pathways were calculated by the single component artificial force induced reaction (SC-AFIR) method\textsuperscript{1} combined with time-dependent density functional theory.

We found that the all investigated cinnamate based sunscreens undergo trans $\rightarrow$ cis photoisomerization under UV irradiation but differ in the isomerization pathway\textsuperscript{2-4}. p-MMC, p-MEC, and p-HMC are isomerized via multistep intersystem crossing (ISC) from the bright \textit{1}ππ* state to the \textit{3}ππ* state mostly via stepwise ISC followed by the internal conversion (IC) from \textit{1}ππ* to the dark \textit{1}nπ* state\textsuperscript{3,4}. On the other hand, m-, o-HMC are directly isomerized by twisting along the C=C double bond to 90° on the \textit{S}_1 state and subsequent IC to the \textit{S}_0 state\textsuperscript{3}. These results suggest that controlling the substitution position is essential to design the cinnamate based photofunctional materials.

Acknowledgement: We are grateful for the coauthors of refs. 2-4.

Keywords: trans $\rightarrow$ cis photo-isomerization, nonradiative decay, picosecond and nanosecond pump-probe spectroscopy, low-temperature matrix-isolation FTIR spectroscopy, single component artificial force induced reaction (SC-AFIR) method

References

Design of Functional Liquids based on \textit{ab initio} Materials Informatics

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Abstract

Materials science has played a large role in the advancement of human civilization through the ages, its involvement starting as far back as the Stone Age and continuing its influence in the Carbon Age. With the rapid growth of computer technology and advancements in mathematical algorithms, materials science has reached a new era of advancement with the collaboration of information science. More specifically, large amounts of material data are available for use, yet accelerating the process of discovering new materials urgently requires access to a database that houses all of the available data in an organized manner. The most successful example of the collaboration between natural science and information science is the field of bioinformatics, where patterns are identified within the human genome. The success found within bioinformatics has inspired similar movements in areas such as catalysis and drug discovery. With these precedents in motion, a new way of materials discovery and development can be proposed by successfully combining information science and materials science. In this talk, a set of \textit{ab initio} Materials Informatics studies to search for functional liquid materials (e.g. azeotropes for mixed refrigerants, ionic liquids for CO$_2$ capture and storage (CCS), etc.) will be introduced.

Keywords: Materials informatics, Functional Liquids, Refrigerants, CCS, Electronic structure

Acknowledgments

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Crystal structure prediction by Artificial Force Induced Reaction method: A case study on carbon crystal

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Abstract

Properties of materials depend not only on their composition but also on their crystal structure. For example, both of diamond and graphite are made from carbon only, but their properties are dramatically different. Not only these structures, there are various carbon allotropes such as fullerene and carbon nanotube, etc. Furthermore, many carbon crystal structures have been predicted theoretically: M-carbon and Cco-C\textsubscript{8} (or Z-carbon), etc. are one of the famous ones. Until now, more than 500 allotropes are recorded in the database\textsuperscript{1}. As shown here, prediction of crystal structures has been a great challenge in computational science.

On the other hands, in our group, an efficient method, artificial force induced reaction (AFIR),\textsuperscript{2,3} has been developed for automated exploration of chemical reaction pathways. This method has been applied to various chemical reactions in the gas phase and in the solution phase.

In this study, we extended the AFIR method for periodic system by combining this method with periodic boundary conditions (PBCs)\textsuperscript{4}. By using this method, we perform global search for low-lying carbon crystal structures described by a small unit-cell (eight carbon atoms in a unit-cell). Then, we obtained 274 structures of carbon crystals including famous structures such as graphite, diamond, M-carbon and Cco-C\textsubscript{8}. About 200 unreported ones are also included in the obtained structures\textsuperscript{4}. These results suggest that the AFIR method is effective not only in molecular systems but also for the global exploration of low-lying crystal structures of a given atomic composition.

Keywords: Crystal structure prediction, Carbon crystal, AFIR method, GRRM

References

Development of Plasmonic Cu$_2$O/Cu Composite Arrays as Plasmonic Photocatalysts

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Abstract

The activity of photocatalysts consisting of metal oxides has been enhanced by hybridizing with metal nanoparticles showing localized surface plasmon resonance (LSPR). It has been reported that complicated mechanisms including LSPR-mediated local electromagnetic (LEMF), direct electron transfer (DET), and plasmon-induced resonance energy transfer (PIRET) leads to the expansion of photocatalytic active wavelength as well as the activity enhancement. However, these plasmonic photocatalysts are not practical because the plasmonic nanoparticles have been composed of expensive metallic species of Au, Ag, and Pd. In this study, we report the characteristic photocatalytic activity of plasmonic arrays consisting of Cu$_2$O/Cu hierarchical structures.

The Cu$_2$O/Cu arrays (Cu$_2$O/CuHS(D), D: silica diameter / nm) were fabricated by a colloidal lithography. Typically, the arrays were prepared by thermally-depositing Cu (thickness: 50 nm) on the two-dimensional silica colloidal crystals (diameter: 224 and 543 nm). And then, ultrathin films of Cu$_2$O (thickness: ca. 3 nm) were formed on the arrays by spontaneous oxidation of Cu surfaces in an oxygen atmosphere. Consequently, the Cu$_2$O/CuHS(224 and 543) showed an LSPR in a visible and a NIR regions, respectively. Note that the LSPR of Cu$_2$O/CuHS(543) is generated in the region, far from absorption wavelengths of Cu$_2$O. The photocatalytic activity was evaluated using a photodegradation of methyl orange. The rate of photodegradation of Cu$_2$O/Cu arrays was enhanced up to 84 times, as compared with that of nonplasmonic planar Cu plate with Cu$_2$O/Cu composite layers. In addition, the activity was maximally enhanced at the generating region of LSPR. We demonstrate from these results that our developed Cu$_2$O/Cu arrays can effectively be driven by the irradiation of NIR light.

Keywords: localized surface plasmon resonance, Cu arrays, photocatalyst, methyl orange, Cu$_2$O

References

Effect of Ultraviolet Light Irradiation on Solution Processed ZnO Films

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Abstract

Thin film fabrication techniques for functional metal oxides can be generally classified into vapor phase and liquid phase syntheses. Some of these methods require substrate heating and/or post-preparation heating of above several hundred °C for the crystallization of target materials. Although the heat-treatment has offered high quality metal oxide films, the development of a low-temperature syntheses is valuable for not only lower environmental load and energy consumption but also applying to flexible electronics utilizing functional polymers which are not tolerable to high-temperature.

Transparent conductive films have been widely used in industrial field as application for liquid crystal displays, thin film transistors and solar cells. In general, sputtered tin-doped indium oxide (ITO) has been used as transparent conductive films due to their high transparency in visible region and high conductivity about 1×10⁻⁴ Ω·cm⁻¹. Since there is a drawback as high cost of indium and its drastic change in price, various alternative materials for ITO have been researched. For example, thin films fabricated by carbon nanotube, graphene, metal nanowires have intensively researched in addition to various metal oxides. In particular, ZnO films have been extensively studied due to its high transparency and high electron conductivity. ZnO films mainly fabricated by physical vapor deposition (PVD), such as sputtering. The sputtering process requires expensive and mass energy-consuming facilities. In contrast, aqueous solution route is one of promising candidates to overcome the difficulties of PVD because of facile equipment without vacuum system, and low temperatures below 100°C. In this viewpoint, our group have developed an aqueous solution process for ZnO films. ¹⁻³)

ZnO films prepared by a solution process were constructed from needle-shaped crystals. They were not transparent because the needle-shaped crystals could easily scatter light. In contrast, addition of trisodium citrate to starting solution changed the microstructure from needle array to dense film. The dense film is transparent in visible region due to decreasing light scattering at the interface. UV light irradiation on the prepared ZnO films drastically decreased their resistivity from several tens Ω·cm⁻¹ up to ca. 4×10⁻³ Ω·cm⁻¹ and increase of carrier concentration was observed at the same time. The detail of UV-enhanced electrical conductivity will be shown and discussed in ICPAC2018.

Keywords: Zinc Oxide, Thin Film, Transparent Conductive Oxides, Aqueous Solution Process, Electrical Properties

References

Recent advance in nitride photocatalyst for new hydrogen energy source

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Abstract

Metal nitrides have received much attention owing to various applications in electronic devices because of their unusual dielectric and optical properties and ionic conductivity as well as their catalytic activity, and show particular potential as photocatalysts for the splitting of water. They have a number of other intriguing properties as well. Particularly intriguing are the recent findings that some Ta-based oxynitrides can serve as visible-light-driven photocatalysts because of their narrow band gaps. For example, Domen et al. reported recently that Ta-based oxynitrides show high activity for water reduction and oxidation in aqueous solutions containing sacrificial reagents under visible-light irradiation. Despite these promising findings, transition metal oxynitrides have been much less investigated in terms of syntheses, properties, and applications, than have the corresponding oxides. For example, transition metal oxynitrides are still generally synthesized by the conventional but rather difficult routes of calcining oxide or reactive oxide precursors with flowing ammonia at high temperatures. However, the products so obtained rarely exhibit the expected properties, but rather tend to exhibit low crystallinity, slow reaction rates, and significant structural defects because of the long duration and high temperature of calcination. Among the new methods for synthesizing oxynitrides, the use of supercritical ammonia shows promise. Important advantages of this method compared with the conventional methods are that it gives well-crystallized nitrides such as GaN[1], CaAlSiN3[2], LaTaON5[3], SrAlSiN3[4], Ta3N5[5] at relatively low temperatures and it suppresses defect formation because the reaction scheme is not so much a solid-state reaction as it is a liquid-state reaction. However, there are a few reports about nitride photocatalyst synthesized by supercritical ammonia. Thus, in the present talk, we will demonstrate (1) the synthesis of well-crystallized nitrides and oxynitrides powders at low temperature by reacting metal precursors in ammonia under supercritical conditions, and (2) direct fabrication of nitride photoelectrode with the nitride on metal plate.

Keywords: Nitride, Ammonothermal, Photocatalyst, photoelectrode

References

Utilizing the Space of Molecular Nanocarbon Assemblies

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Abstract

Molecular nanocarbons, which we define as molecules with structures of nanocarbon fragments or pure nanocarbons with uniform chemical formulae, have been studied intensively. Vigorous synthetic works have afforded us a variety of fascinating nanocarbon-associated molecules, such as carbon nanorings, carbon nanocages, nanographenes and carbon nanobelts.

Since some of these molecules have internal cavities which should be interconnected to give uniform nanopores with an all-benzene surface, when they assemble into solids. These features of CPP are significantly fascinating from the viewpoint of porous materials, and we have been investigating the nanospace to discover unique functionalities.

In this presentation, we will show some unique nanospace-associated properties derived from carbon nanorings, cycloparaphenylenes (CPPs), which consist of solely benzene rings interconnected circularly at their para positions: gas/vapor adsorption behavior with structural deformation,\(^1\) polymorphism depending on a crystallization process,\(^2\) and stimuli-responsive property changes of their iodine complexes.\(^3\)

Keywords: molecular nanocarbon, carbon nanoring, cycloparaphylene, nanoporous material, host-guest chemistry

References

Theoretical Investigation on Structural Stability and Catalytic Activity of Platinum Clusters of Low Atomicity

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Abstract

Sub-nanoscale metal clusters (ca. 1 nm) possess completely different physical and chemical properties as compared to bulk and nanoscale materials. Their size-sensitive unique spectroscopic properties and catalytic activities have been reported\textsuperscript{1-4}. Recently, we have successfully synthesized platinum clusters with precise numbers of atoms by the low-temperature calcination of well-defined platinum thiolate complexes in a hydrogen stream\textsuperscript{5}. The synthesized clusters have been characterized by the atomic resolution HAADF-STEM studies. Furthermore, we have observed that a 10-atom platinum cluster (Pt\textsubscript{10}) among small clusters exhibits a specific high catalytic activity in the hydrogenation of styrene. In order to elucidate the origin of the specific activity, we theoretically investigated the structural stabilities and electronic states of platinum clusters with various sizes, combining DFT-based global optimization techniques\textsuperscript{6} and simple mathematical models. Thereby, we found that the Pt\textsubscript{10} cluster of \textit{T\textsubscript{d}} symmetry shows the anomalous stability and uneven distribution of electron density. In this congress, we will discuss the effect of these geometrical and electronic properties on the catalytic activity on the basis of transition state calculations.

Keywords: cluster, platinum, hydrogenation, density functional theory, global optimization

Graphical abstract

![Graphical abstract](image)

References

Controlling selective hydrogenation performances on Ru nanocluster / K-Al₂O₃ catalyst

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Abstract
A Ru nanocluster catalyst (Ru/K-Al₂O₃) was prepared by the attachment of Ru₃(CO)₁₂ complex on a potassium-doped Al₂O₃ surface. XRD, TEM, and Ru K-edge EXAFS analysis revealed that Ru nanoparticles whose average diameter was smaller than 2 nm were formed on the support. The formation process of the Ru nanoclusters was investigated by in-situ FT-IR and in-situ XAFS, and we found out that there are three stages for the nanocluster formation. The K-doped Al₂O₃ supported Ru nanoparticle catalyst exhibited high selectivity toward primary amine on nitrile hydrogenation under hydrogen at atmospheric pressure, and the favorable structures of adsorbed nitriles and mono-hydrogenated intermediate on the catalyst surface for the primary amine selectivity were investigated by DFT calculations.

The direct impregnation of free N-heterocyclic carbenes (NHCs, dicyclohexylimidazolyldiene (1) and dimesitylimidazolylidene (2)) on Ru/K-Al₂O₃ yielded NHC-modified Ru/K-Al₂O₃ catalysts (1@Ru/K-Al₂O₃ and 2@Ru/K-Al₂O₃). The existence of NHC ligands on Ru/K-Al₂O₃ was confirmed by FT-IR, N 1s XPS, and TGA. The existence of the metal-carbene bond, the direct evidence that NHCs were coordinated to the surface of Ru nanoclusters, was characterized by the chemical shift of the carbene carbon atom in ¹³C SS-NMR. Chemoselective hydrogenation performance of phenyl acetylene that contains two different functional groups (benzene ring and triple bond) was fully investigated on the NHC-functionalized Ru/K-Al₂O₃ catalysts.

Keywords: Ruthenium, nanocluster, hydrogenation, in-situ characterization, N-heterocyclic carbene

References
Infrared-Emissive Luminescent Mechanochromism of Anthryl Gold Isocyanide Complex

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Abstract

Tunable solid-state emissive organic compounds attract considerable interest owing to potential applications in recording and sensing devices. Among them, luminescent mechanochromic compounds are one of the emerging functional materials and their solid-state emission colors can be switched in response to mechanical stimulation, such as grinding, pressing and ball-milling. So far, luminescent mechanochromic properties of various organic and organometallic compounds have been reported. However, only limited examples of the luminescent mechanochromism with emissions in the long wavelength regions, including infrared, have been known. In this report, anthracene-based gold(I) isocyanide complex 3, which exhibits a mechano-induced red-shift of its emission color from the visible to the infrared region will be described. Unprocessed as-prepared polymorphs of 3, 3α and 3β, exhibit emission maximum wavelength (λem,max) at 448 and 710 nm, respectively, upon excitation with UV light. After mechanical stimulation, ground powder 3α ground and 3β ground were obtained, respectively, and they both show broad emission spectra with λem,max of 900 nm. Thus, 3α and 3β represent the first examples of mechanochromic luminescent compounds with λem,max in the infrared region. The underlying mechanism of the mechanochromism of 3 was investigated by single-crystal X-ray diffraction analyses and theoretical calculations.

Keywords: Luminescent mechanochromism, Gold complex, Phase transition, Infrared photoluminescence

Graphical abstract

References

Tailoring spin crossover probed by X-ray absorption spectroscopy and Monte-Carlo simulation

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Abstract

Bimetallic assemblies with transition-metal complexes bridged by ligand molecules have attracted much attention for their cooperative interactions caused by transitions between high-spin and low-spin states, which results in interesting physical and chemical phenomena. The controlling of ligand field strength via external perturbations that change the coordinating ligand polymers is also one of the most fascinating subjects in molecular magnetochemistry. The complex compounds such as Fe(pyridine)$_2$Ni(CN)$_4$, possessing two-dimensional networks bridged by cyanides with Fe$^{2+}$ (3$d^6$) SCO compounds, are interesting in the synthesis of self-assemblies of new kinds of SCO molecules. However, the element-specific electronic structures, including the information about the local structural environments around Fe or Ni sites, have not been investigated explicitly. In this talk, the changes in electronic and structural properties across the SCO transition in novel magnetic complexes are discussed by means of x-ray absorption fine structure spectroscopy$^1$ and Monte-Carlo simulation$^2$.

Keywords: Spin crossover, XAFS, Monte-Carlo simulation

References


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Abstract
Semiconductor-based photocatalysis attracts wide attention because it applicable to environmental purification, hydrogen generation, and recycle CO2 into fuels. However, fast recombination of photogenerated electrons and holes is an intrinsically limits the photocatalytic activity, therefore heterojunction photocatalysts have been studied as one of the approach to prevent the fast recombination. For the design of heterojunction photocatalysts, not only band structure but also contact between the materials is important for effective electron and hole migration. In fact, Kudo et al. reported that the contact condition of mixed two photocatalysts is critically affected the efficiency of water splitting1. To achieve high photocatalytic activity in heterojunction system, combination of photocatalysts in micro- or nano-scale with stable contacts is desired.

We report the preparation of SrTiO$_3$/TiO$_2$ heterojunction photocatalyst by nitric acid treatment of SrTiO$_3$ particles. When 1M of HNO$_3$ was used, SrTiO$_3$ particles were partly dissolved and TiO$_2$ (anatase) nanoparticles were precipitated on the SrTiO$_3$. SEM image and EDS mapping clearly shows SrTiO$_3$ was surrounded by precipitated TiO$_2$ particles. The phase of precipitated TiO$_2$ was changed from anatase to rutile by both increase of HNO$_3$ concentration and increase of SrTiO$_3$ particle size. These results indicate that pH and supersaturation degree of Ti$_4^+$ species in the solution affects the phase of TiO$_2$ precipitated by acid treatment. Photocatalytic activity of the SrTiO$_3$/TiO$_2$ photocatalysts and references were examined by methylene blue decomposition under UV illumination. The SrTiO$_3$/TiO$_2$ photocatalysts exhibited higher photocatalytic activity than the starting SrTiO$_3$ and commercial anatase particles (ST-01, Ishihara Sangyo Kaisha, Ltd.).

Keywords: heterojunction photocatalyst, TiO$_2$, SrTiO$_3$, water purification

References

![Diagram: SrTiO$_3$ to SrTiO$_3$/TiO$_2$ composite after acid treatment]

Acid treatment
- Partial dissolution of SrTiO$_3$
- Precipitation of TiO$_2$
Development of Useful Molecules Based on Bioinspired Metal Complexes

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Abstract

Superoxide anion ($O_2^{•−}$) is a by-product of the mitochondrial respiratory chain and plays a role in a number of medical issues, including inflammation and ischemia-reperfusion injuries. Superoxide dismutase (SOD) catalyzes the disproportionation of $O_2^{•−}$ to $H_2O_2$ and dioxygen to protect cells from oxidative damage caused by $O_2^{•−}$. Therefore, malfunctioning SODs and the over-production of $O_2^{•−}$ beyond the catalytic capacity of SODs are suspected to be related to certain neurological diseases or ischemia-reperfusion injuries. Metal complexes that can show SOD-like activity in vivo may have potential as pharmaceuticals for the neurological diseases. However, despite recent advances in the field, creating SOD mimics that possess high activity and bio-compatibility remains a great challenge. Most SOD mimics reported thus far are manganese complexes, such as a manganese-based SOD mimic, EUK-134.

We recently reported that a carboxylamidoiron(III) complex, $[Fe^{III}(dpaq^H)]Cl$ ($dpaq^H = 2\text{-}[\text{bis}(2\text{-pyridinylmethyl})\text{-amino}]\text{-N\text{-}8\text{-quinolinylacetylamido}$), is stable in buffers at pH values ranging from 3 to 9, but did not catalyze oxidation reactions of external substrates such as guaiacol (2-methoxyphenol), which use $H_2O_2$ as an oxidant.\textsuperscript{1} Additional experiments to further explore the bio-related catalytic activity of $Fe^{III}(dpaq^H)$ in aqueous solutions disclosed that it has a higher SOD-like activity than EUK-134. Furthermore, we found that the introduction of electron-withdrawing groups at the 5-position of the quinoline moiety of the pentadentate ligand\textsuperscript{2,3} enhances its SOD activity as well as its antioxidant activity, which protects cultured cells from menadione-mediated oxidative stress.\textsuperscript{4}

Keywords: functional model, hydrogen peroxide, iron, oxidation, SOD

References

Photochemical and Electrochemical Water Oxidation Mechanisms of Cobalt porphyrins

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Abstract

In nature, water oxidation plays a crucial role of an electron source in photosynthesis, in which the Mn$_4$CaO$_5$ core serves as an efficient water oxidation catalyst (WOC). Similarly, splitting of water (2H$_2$O + 4hv $\rightarrow$ 2H$_2$ + O$_2$) also needs to rely on the use of a highly active WOC. As artificial models of WOCs, we demonstrated that iron and copper complexes are highly active WOCs.\textsuperscript{1,2} We have also reported on the water oxidation activity of three water-soluble cobalt porphyrin complexes (CoTMPyP, CoTCPP and CoTPPS). The water oxidation activity was examined using the photochemical system made up of [Ru(bpy)$_3$]$^{2+}$ (photosensitizer) and Na$_2$S$_2$O$_8$ (sacrificial electron accepter).\textsuperscript{3} Furthermore, we have also noted that these cobalt porphyrins decompose into several less catalytically active porphyrin ring opened species upon reaction with singlet oxygen (1$^1$O$_2$). In an attempt to inhibit this attack by 1$^1$O$_2$, CoFPS was developed as a new WOC that was modified with fluorine atoms at the 2 and 6 positions of the aryl groups as blocking substituents. As expected, the stability of CoFPS is significantly improved compared with none fluorinated analogues.\textsuperscript{4} Recently, we have developed CoCIPS, which is chlorinated Co-porphyrin, as a new WOC. CoCIPS shows high activity and stability for WO. The maximum TOF and TON are 1.7 s$^{-1}$ and 836 respectively.\textsuperscript{5} Cares should be paid to avoid contamination of the system with CoO$_x$ nanoparticles, as pointed out by Finke et al.[4] However, the result of dynamic light scattering experiments revealed that no colloid particles form during the photolysis.\textsuperscript{6} We also show the electrochemical water oxidation properties of Co-porphyrins modified electrodes. We observed reaction intermediate species using In situ Raman spectroscopy.\textsuperscript{7}

Keywords: water oxidation, cobalt porphyrin, homogeneous catalysis

References

Structural Analyses of *fac*-Ruthenium Complexes Bearing an sp³P/sp³NH/sp²N Linear Tridentate Ligand (PN(H)N)

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Abstract

A PN(H)N–Ru complex catalyzes asymmetric hydrogenation of both chelatable and non-chelatable sterically demanding ketones in CH₃OH–DMSO mixed solvent. DMSO is responsible for the high-performance catalysis. The linear and flexible PN(H)N ligand sterically prefers the mer geometry over the fac isomer in the formation of octahedral Ru complexes. DMSO changes the situation. The highly π-acceptive S=O group coordinates to the soft Ru atom by use of the soft sulfur atom, and is forced to locate cis each other, resulting in the selective formation of *fac*-[Ru(PN(H)N)(dms)]₂(BF₄)₂ (A). In order to deepen understanding for the mechanism, structures of the related ruthenium complexes were investigated. The time-course ¹H-NMR analysis of A determined the dissociation rate ratio of sp³P-trans, sp²N-trans, and sp²N-trans DMSO to be >37:2:1. The rate difference leads to stereoselective generation of *fac*-RuH(CH₃O)(PN(H)N)(dms) (B) by the action of 2 mol amount of t-BuOK in CH₃OH–DMSO. The complex B can exist only in CH₃OH–DMSO, and the amide complex *fac*-RuH(PNN)(dms)₂ (C) is generated by removal of the solvent. Small ²Jₚₚ values (2–5 Hz) of A–C with PN(H)N confirmed the fac geometry. With a Ph-substituted ligand Ph-PN(H)N, a dihydride complex *fac*-RuH₂(Ph-PN(H)N)(dms) (Ph-D) was generated in high yield from Ph-B but not from Ph-C (THF, 1 atm H₂, 1 mol amount t-BuOK). A series of structural analyses have given an important information for the catalysis, where the hydrogenation proceeds in the H–Ru–N–H reaction site of the sp³P-trans region. The sp²N-trans DMSO, which is stabilized by a strong Ru δ/O=S σ* interaction, fixes the conformation through a PyC(6)H---O=S hydrogen bond, endowing the reaction site with a clear chiral circumstance. In this chiral reaction site, the difference in the steric demand of the C=O substituents is discriminated to produce nearly optically pure alcohols.

Keywords: asymmetric hydrogenation; mechanistic study; ruthenium; hydride complex

Graphical abstract

![Graphical abstract](image)

References

Stimuli-Responsive Helical Metal Complexes: Helicity Inversion, Expansion/Contraction, and Memorization

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Abstract

Stimuli-responsive helical molecules have gained increasing attention because of their potential to develop sophisticated molecular switching systems.\textsuperscript{1} Labile metal-organic hybrid materials offer one of the promising strategies due to their characteristic coordination geometry, redox activity and other unique spectroscopic properties as well as their rapid ligand exchanging. We have demonstrated selective helicity induction and a dynamic helicity inversion process ($\Lambda \rightarrow \Delta$) in a labile metal complex consisting of Co($\text{ClO}_4$)\textsubscript{2}•6H\textsubscript{2}O and a chiral teradentate ligand {$N,N'$-ethylene-bis(N-methyl-(S)-alanine methylamide)}.\textsuperscript{2} Since the helical Co(II) complex has two stimuli responsive parts namely Co(II) center and amide groups, the achiral NO\textsubscript{3}– anion coordinates with the Co(II) center and interacts with the amide hydrogen to stabilize the $\Delta$ form of the Co(II) complex more effectively than the corresponding $\Lambda$ form. Based on this helicity inversion phenomenon around the metal center, the helical direction of achiral peptide chains in related peptide-ligand was successfully controlled upon NO\textsubscript{3}– anion stimulus.\textsuperscript{3} The terminal amide groups modified with ortho-methoxy substituted aromatics further respond to acid and base to switch a helical pitch of the complex.\textsuperscript{4} Here, we successfully demonstrate that the cobalt center further works as a redox responsive center to switch the lability of the complex between dynamic state and static state.\textsuperscript{5} The formed inert Co(III) complex having contracted-$\Lambda$ structure was able to be reduced to the labile Co(II) complex having contracted-$\Lambda$ structure. This was immediately converted to an extended-$\Lambda$ form in the presence of external H\textsuperscript{+} stimulus, the helicity of which was further inverted to $\Delta$ form by coexistence of NO\textsubscript{3}– anion. The details of this stimuli responsive system in helical cobalt complexes will be described.

Keywords: helicity, supramolecular chemistry, coordination chemistry, molecular memory, external stimulus

References

Fabrication of Plasmonic Array of Metallic Nanocylinders and Its Optical Properties

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Abstract

In periodic arrays of metal nanocylinders with the periodicity comparable to the optical wavelengths, both surface plasmon polaritons (SPPs) and light diffraction can be excited simultaneously. The diffracted light propagating on the plane excites SPPs in phase, giving the net response that is stronger than the simple sum of each SPP. This hybrid mode thus excited is called collective plasmonic mode. The distinctive difference of the hybrid modes from an isolated SPP is the field distribution. While an SPP is a localized mode bound on the metallic surface, these modes accompany the electric field that extends to the neighboring nanoparticles because of strong radiative coupling. From the viewpoint of efficient use of light, the plasmonic array is a good platform for light management: in such systems, the light energy is efficiently trapped in the plane of the array and/or the dielectric layer and can be utilized as energy for further reactions.

In this presentation, we will review our recent works on the fabrication of plasmonic arrays and exploration of their optical properties. We use various metals such as aluminum, titanium nitride and indium tin oxide, and the working frequency of the arrays ranges from near infrared to ultraviolet. We demonstrate the directionally-intensified photoluminescence from the light-emitting layer deposited on a plasmonic array.

Keywords: Surface plasmon polariton, plasmonic array, photoluminescence enhancement

References

Humidity-responsive switching of gas inclusion by using cooperative opening and closing of heterogeneous nano-cavities in a crystalline peptide Ni(II)-macrocyle

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Abstract

Controlling molecular bindings through cooperative structural changes by chemical stimuli is one of the significant features of environmental responsive functions in biological systems, such as catalysis and molecular transfer. Mimicking such cooperativity is also desired in artificial systems for developing sensitive and selective environmental responsive functions, especially, for gaseous stimuli due to their importance as environmental and/or biological factors.

In this study, we report ON/OFF switching of CO\textsubscript{2} gas inclusion by recognizing water molecules (i.e. humidity) in a peptide Ni(II)-macrocyle,\textsuperscript{1} which possesses heterogeneous crystalline cavities and undertakes reversible structural transformation between an “open form” and a “closed form” by water uptake into one of the cavities.\textsuperscript{2,3} Comparison of gas adsorption behavior of the crystalline peptide Ni(II)-macrocyle with and without water vapor, combined with gas-composition analysis by using gas chromatography, clarified that the hydrated sample (open form) adsorbs CO\textsubscript{2} gas up to 34 g mol\textsuperscript{-1} while the dehydrated sample (closed form) adsorbs a negligible amount of CO\textsubscript{2} gas. The investigation of water-content dependence of CO\textsubscript{2} adsorption and its structural studies (by X-ray and infrared spectroscopies) show that the switching of gas inclusion occurred abruptly over a narrow range of water-vapor pressure and was caused by the cooperative opening of vacant space due to the structural transformation by water uptake. In addition, we also clarified that included H\textsubscript{2}O and CO\textsubscript{2} in the crystalline cavities stabilized each other due to their cooperative inclusion.

Keywords: switch of guest inclusion, peptides, heterogeneous nano-cavities, cooperative effects

References
Transition-Metal Complexes with Silyl(2,2'-Bipyridine) Pincer Ligands: Synthesis and Catalysis for Functionalization of C–H/C–D Bonds

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Abstract

Design and synthesis of transition-metal catalysts promoting functionalization of inert C–H bonds under mild conditions is still an attractive target in organometallic chemistry. In this regard, some pincer ligands with a silyl coordinating moiety have recently been developed as supporting ligands for such catalysts. Strong σ-donating property of the silyl coordinating moiety makes a metal center electron rich and facilitates the oxidative addition of inert bonds such as C–H. This time, we developed new silyl(2,2'-bipyridine) pincer ligands (L^{SNN}), and demonstrated that iridium and ruthenium complexes bearing L^{SNN} catalyzed transformation reactions of arenes and alkenes via C–H or C–D bond activation.

Reaction of a ligand precursor, hydrosilane L^{SNN}(H), with metal complex precursors, i.e. [IrCl(cod)]_2 and Ru(H)Cl(PPh_3)_3, gave silyl pincer complexes 1 and 2, respectively, via ligand exchange and Si–H oxidative addition. In the presence of 1 mol% of 16-electron Ir complex 1 as a catalyst, arenes reacted with bis(pinacolato)diboron leading to C–H borylation under mild conditions (40 °C) in high yields (> 90%). On the other hand, alkenyl hydrogens of monosubstituted alkenes were deuterated at 60 °C in the presence of 10 mol% of 18-electron Ru complex 2 as a catalyst via arene C–D bond activation.

Keywords: silyl ligand, pincer ligand, iridium, ruthenium, C–H activation

References

Dinitrogen Activation by an Iron Complex of 1,1’-Bis(arylamido)vanadocene

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Abstract

Considerable attention has been paid to an activation of dinitrogen carried out by iron complexes. While a number of dinitrogen complexes of iron have been thus far prepared, only a few research groups have reported significant N-N bond weakening (N-N > 1.16 Å) in iron dinitrogen complexes by using bulky, electron-rich ligands with N or P donors. To add a new dimension to such studies, we began to explore iron complexes with a metalloligand including a metallocene skeleton, which would slightly stabilize the reduced species of iron through a metal-metal interaction. We report that a vanadocene bis-amide ligand has been found to afford formation of a dianionic three-coordinate iron dinitrogen complex, where the N-N bond length lies in the longest category in the reported values.

We synthesized a novel iron complex having 1,1’-bis(arylamido)vanadocene, characterized by X-ray crystallography. The molecular structure of the complex showed the Fe-V distance of 2.6369(7) Å, indicative of the bonding interaction between two metals. Reduction of the complex under dinitrogen atmosphere resulted in the formation of an iron dinitrogen complex, exhibiting an extremely long N-N bond length in N\textsubscript{2} moiety. The success of reduction reaction of the iron amide complex without decomposition would suggest that the vanadium center plays an important role in stabilization of the reduced iron center. The adaptability of the coordination environment in Fe-V derived from the metalloligand makes them promising candidates as functional models for biological N\textsubscript{2} fixation in a VFe protein.

Keywords: dinitrogen activation, heterobimetallic complex, metal-metal bond
Surface modification of nano-carbon materials by metal complexes or metal-organic network films

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Abstract

Nano-carbon materials such as carbon nanotubes, reduced graphene oxide (rGO), and graphene have unique properties such as high charge-carrier mobility, high thermal stability, specific surface area, and high conductivity, which have attracted much attention because of their potential applications in modified electrode, carbon catalyst, molecular device, and storage devices.\textsuperscript{1} However, the poor processability and low solubility of nano-carbon materials and nano-carbon based-composites have become serious obstacles for its efficient use and applications. It is still important to develop modification methods of nano-carbon materials.

We fabricated the surface modified nano-carbon materials by Ru complexes having pyrene anchors and the metal-organic network films via $\pi-\pi$ interaction and coordination bond, aiming at functionalization of nano-carbon materials such as graphene oxide and carbon nanotube.\textsuperscript{2,3} These nano-carbon based composites were characterized by microscopic observations and evaluated their optical and electrochemical properties by spectroscopic techniques.

Keywords: nano-carbon material, metal complex, metal-organic network film, surface modification

References

PTRF-XAFS study of single metal dispersion on an oxide single crystal surface by premodification with a functional organic molecule

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Abstract

Precise size control of metal species on an oxide surface, especially in the range of <1 nm, is now highly important to develop the next-generation catalysts, sensors, and electronic devices. However, this is not easy since metal atoms are easily aggregated to form large particles on an oxide surface. This is due to the small stabilization energy and/or the small activation energy for the metal diffusion. If one can obtain a monatomic metal species on an oxide surface, it can be a building block for synthesis of the metal cluster and helps us to control the cluster size in one-atom precision. Our group has developed the “premodified surface method” to obtain a highly dispersed metal species on an oxide single crystal surface (Figure 1). In the premodified surface method, the oxide surface is precovered with a functional organic molecule possessing a substituent atom which can strongly coordinate to a metal atom before metal deposition. We have determined the precise 3D structures of such metal species by polarization-dependent total reflection fluorescence (PTRF) XAFS technique.1-5

In this study, various metals such as Cu, Au, Ni and Pt were vacuum-deposited on a TiO2(110) surface premodified with o-mercaptobenzoic acid (o-MBA) and their 3D structures were determined by the PTRF-XAFS technique. We have found that Cu, Au and Ni were atomically dispersed by bond formation with sulfur of o-MBA and oxygen in the TiO2 lattice, but Pt was aggregated to form clusters. We will discuss the factors that govern single metal dispersion based on the energy difference between sulfur–metal–oxygen and metal–metal bond formations.1

Keywords: PTRF-XAFS, TiO2 single crystal surface, single metal dispersion

Figure 1 "Premodified surface method" for obtaining highly dispersed metal species on an oxide single crystal surface.

References
Syntheses of heterometallic clusters based on cubane type cores supported by macrocyclic triazacyclononane complexes

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Abstract

Heteromultinuclear clusters or mixed valence clusters are of interest in various scientific fields such as magnetism, photochemistry, catalyst, and enzyme. Especially, nitrogenase bearing a role of making ammonia from N\textsubscript{2} gas has molybdenum-iron heterometallic cluster structure containing cubane cores. Therefore, precise control of the structure of heterometallic cluster based on cuban core is promising way to obtain excellent biomimetic species\cite{1}. Molybdate anion of [MoO\textsubscript{4}]\textsuperscript{2-} forms tetrahedral geometry as a mononuclear complex in basic condition, whereas isopolymolybdate is generated by addition of acid to the aqueous solution. It is expected that various kinds of isopolymolybdates containing cubane type structure units exist in this system. However, the previous research for the isopolymolybdates are restricted to three kinds of major species of octamolybdate, heptamolybdate, and Lindqvist. Although these three isopolymolybdates contain cubane type units as a substructure, just cubane type species bearing Mo(VI) and bridging oxygen ligand has not been previously reported.

We have synthesized molybdate cubane type cluster capped by Co(tacn) (tacn = 1,4,7-triazacyclononane) and another tetrahedral molybdate units (cluster 3, see Graphical abstract). Furthermore, when the molar ratio of [Co(tacn)(H\textsubscript{2}O)]\textsuperscript{3+} and MoO\textsubscript{4}\textsuperscript{2-} as starting materials were systematically changed, another two molybdenum-cobalt heteromultinuclear clusters containing cubane like substructures were isolated. The solution structures can be characterized using NMR technique, because these species have only diamagnetic metal centers of Mo(VI) and Co(III). It is noteworthy that \textsuperscript{59}Co NMR spectra of cluster 3 show large solvent dependence between water and nitromethane in terms of full width half maximum (FWHM). As a consequence, we estimated that the solvent dependence is caused by deprotonation equilibrium from the cluster core. In this conference, we would like to introduce that in detail.

Keywords: heteromultinuclear, cubane-type cluster, structural transformation, \textsuperscript{59}Co NMR measurement, deprotonation equilibrium

References

Elemental Allotropes in Interactive Porous Coordination Networks

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Abstract

Chemistry of labile elemental allotropes are still veiled especially for their structures because of their extreme lability, even chemistry of elements has developed for long time. To visualize such labile species by X-ray, we have investigated the utilization of porous coordination network which have interactive pore sites. An interactive pore sites in the network can trap such labile species because the interactive sites stabilize the labile species.

Here we report the trapping of labile elemental allotropes such as small sulfur, white phosphorus, bromine utilizing interactive pore site of porous coordination networks and the structure determination by X-ray diffraction to unveil new chemistry of elements. First we succeeded in isolating bent-S$_3$ into an interactive network, [(ZnI$_2$)$_3$(TPT)$_2$]$_n$ (TPT = 2,4,6-tripyridyl-1,3,5-triazine) and determined the structure by ab initio X-ray powder diffraction analysis. Furthermore, when small sulfur was trapped kinetically into the single crystals of porous coordination network, [(CuI)$_2$(TPPM)]$_n$ (TPPM = tetra-4-(4-pyridyl)phenylmethane), we observed molecular transformation from S$_2$ to bent-S$_3$ via cyclo-S$_3^{2+}$ on the interactive iodide site. This is the first direct observation of small sulfur transformation. In the case of Br$_2$, Br$_2$ react with the network [(ZnI$_2$)$_3$(TPT)$_2$]$_n$ to produce new iso-structural porous coordination network [(ZnBr$_2$)$_3$(TPT)$_2$]$_n$, indicating network transformation by labile guest species. Furthermore, we succeeded in trapping P$_4$ in [(ZnI$_2$)$_3$(TPT)$_2$]$_n$, indicating the usage of safe P$_4$ reagents. This study unveils the new chemistry of elements.

Keywords: Elemental allotropes, X-ray diffraction, porous coordination networks, sulfur, phosphorus

References

Photoluminescence Switching of Rhenium(V) Complexes with Nitrido by Mechanochemical Reactions and Exposure of Water

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Abstract

Mechanochemical reactions giving a solid product from a solid substance and a solid reactant under solvent-free conditions are attractive because of treatment without harmful organic solvents. Reactions of solid compounds in a minimal amount of water that afford a solid compound in high yield are also useful methods. In the present study, significant luminescence intensity switching by mechanochemical reactions and exposure of water was conducted using five- and six-coordinate tetracyanidonitridorhenium(V) complexes.

The complexes, (PPh₄)₂[ReN(CN)₄]L (L = imidazole (Him) (1) and 1-methylimidazole (Mim) (4)) and (PPh₄)₂[ReN(CN)₄]Mim·Mim (5) showed intense luminescence (Φₑ ≈ 0.65 – 0.75) in the solid state at 296 K. Luminescence of (PPh₄)₂[ReN(CN)₄]Him·Him (2) was very weak (Φₑ < 0.01) in the solid state at 296 K. The mechanochemical reaction of 1 with 1 equiv. of Him in the solid state produced 2. The complex 2 was also obtained by the reaction of (PPh₄)₂[ReN(CN)₄] (3) with 2 equiv. of Him in the solid state. The compound 1 could be reproduced by placing solid 2 in water. The compound 3 was produced under vacuum at 185°C from 1 and 2 for several days, respectively. Both 4 and 5 showed intense luminescence with similar intensities. The weak photoemission of 2 may be due to quenching by the vibronic relaxation of the N–H···N hydrogen bond between the coordinate and free Him molecules.

Keywords: luminescence, mechanochemical reaction, solvent-free reaction, rhenium, nirido
Rare-earth Metallacyclopentadienes: Synthesis, Structure and Reactivity

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Abstract

Metallacyclopentadienes are considered as reactive intermediates in the stoichiometric and catalytic transformations of organic molecules, and have received considerable attention in organometallic chemistry, coordination chemistry and synthetic organic chemistry over the past six decades because of their unique metallacyclic structure [1,2]. Although metallacyclopentadienes of s-, p-, d-block and actinide elements have been well developed [1,2], no example of rare-earth metallacyclopentadiene has been reported.

We successfully synthesized the first series of rare-earth metallacyclopentadienes by reaction of dilithium reagents with mono/double Cp supported rare-earth metal chlorides [3]. They show high reactivity towards various small molecules, such as white phosphorous, carbodiimide, CO₂, aldehyde, imine, isocyanate, isocyanide. Especially, the reaction of mono Cp*-supported lutetacyclopentadiene with N,N'-diphenylcarbodiimide is highly dependent on the ratio of reactant and the solvent. We investigated this system carefully by both experimental and calculated methods. The mechanism is well elucidated, and the different products can be attributed to the effect of LiCl moiety coordinate to Lu.

Keywords: rare-earth metals, metallacyclopentadienes, insertion reaction, white phosphorous, carbodiimide

References

Size-dependent Polymorphism in Aluminum Carbide Cluster Anions AlₙC₂⁻

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Abstract

Aluminum carbide cluster anions AlₙC₂⁻ (n = 5–13) were observed as the most dominant products of gas phase reactions of Alₙ⁻, which is generated by laser vaporization method, with organic molecules, such as methanol, ethanol, pentane, acetonitrile or acetone. Density functional theory calculations predicted two possible isomeric structures for AlₙC₂⁻: one is isomers with two separated carbon atoms (type D), which is similar structure with the bulk aluminum carbide, and the other is novel isomers with acetylide-like C₂ unit. The latter isomers are further categorized into three types depending on the location of the C₂ unit: the C₂ unit is encapsulated within the Al cage (type I), contained in the surface of Al clusters (type S), and attached on the surface of Al clusters (type O). Size dependent behavior of the adiabatic electron affinities of AlₙC₂ determined by photoelectron spectroscopy was explained in terms of polymorphism as a function of size (n): type I for n = 5–8, type D for n = 9–11, type D or O for n = 12, and type O for n = 13. The tendency that the position of the C₂ unit was shifted from inside to outside with increase in n was ascribed to the balance between the stabilizations gained by forming the Al–C bonds and the Al–Al bonds. The smaller AlₙC₂⁻ clusters (n = 5–8) prefer to surround the acetylide-like C₂ unit with the Al atoms so as to maximize the number of the Al–C bonds, while larger ones (n = 12 and 13) prefer to attach the C₂ unit onto the surface of the Al clusters so as to maximize the number of the Al–Al bonds.

Keywords: photoelectron spectroscopy, mass spectrometry, DFT calculation, acetylide

Graphical abstract
Interface engineering of transition metal oxides as a new route for exploring functional properties

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Abstract

Metal-oxygen bonds in transition-metal oxides are responsible for a variety of functional properties. Artificial oxide heterostructures with chemically abrupt interfaces have provided a good platform for engineering novel bonding geometries that could lead to emergent phenomena not seen in bulk oxides. Here we show that the Ru-O bonds (or oxygen co-ordination environments) of a perovskite, SrRuO$_3$, can be controlled by heterostructuring SrRuO$_3$ with a thin (0–4 monolayers thick) Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ layer grown on a GdScO$_3$ substrate [1,2]. We found that a Ru-O-Ti bond angle characterizing the SrRuO$_3$/Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ interface structure can be engineered by layer-by-layer control of the Ca$_{0.5}$Sr$_{0.5}$TiO$_3$ layer thickness, and that the engineered Ru-O-Ti bond angle not only stabilizes a Ru-O-Ru bond angle never seen in bulk SrRuO$_3$ but also tunes the magnetic anisotropy in the entire SrRuO$_3$ layer. The results indicate that interface engineering of the metal-oxygen bonds is a good way to control additional degrees of freedom in functional oxide heterostructures. In this talk, I will also show that anomalous behavior in Hall effects, probably due to Topological Hall effect, can be seen in SrRuO$_3$ with the interfacially engineered Ru-O-Ru bonds. Furthermore, the anomalous Hall effect of SrRuO$_3$ can be electrically modulated [4].

Keywords: oxide heterostructures, metal-oxygen bonds, SrRuO$_3$, ABF-STE

References

Synthesis and Characterization of Pd-supported Fluoro-dodecavanadates

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Abstract

In Metal Organic Framework (MOF) chemistry, bidentate ligands are key factor to construct highly porous materials. To get best properties of MOF, we develop inorganic linker building unit for to substitute the organic ligand linker unit. The need of the new inorganic linker units is solved by making use of polyoxometalate functionalized with a metal.

To overcome the weak coordination ability of POM, halide anion is incorporated on a spherical polyoxovanadate (POV) because halide incorporation can reduce the surface charge and increases electronegativity. This in turn increases the coordination capability of POV.

In order to develop the intended inorganic linker, Pd is attached to the Fluoride incorporated dodecavanadate. The linker would not only be beneficial for framework (POMOF) material construction unit, but also would be beneficial for the purpose of oxidation catalysis.

Herein we report the synthesis of these types of POVs: \([n-\text{Bu}_4\text{N}]_4[V_{10}\text{O}_{26}F_2]\cdot\text{CH}_3\text{CN}\) (1), \([\text{VO(DMSO)}_5]_2[\{\text{Pd(DMSO)}_2\}_2V_{12}\text{O}_{32}(\text{F})_2].2\text{CH}_3\text{CN}\) (2), and \([n-\text{Bu}_4\text{N}]_4[\{\text{Pd(NO}_3)\text{(DMSO)}_2\}_2V_{10}\text{O}_{26}(\text{F})_2]·2\text{DMSO}\) (3). Complex 1 is prepared by reduction with hydrazine of \((n-\text{Bu}_4\text{N})_4[H\text{V}_{11}\text{O}_{29}F_2]\). Addition of Pd\textsuperscript{2+} to DMSO solution of 1 gave complex 2. Addition of nitrate salt of Pd\textsuperscript{2+} to DMSO solution of \([V_{10}\text{O}_{26}]^{4+}\) and F\textsuperscript{-} ion gave complex 3.

The successfully synthesized three complexes have spherical shapes anions containing two anions F\textsuperscript{-}. Anion 1 is mixed valence \([V_{10}^{V\textsuperscript{\text{V}}}_{10}\text{O}_{26}F_2]^{\text{V-V}}\) which shows electrochemical behavior potential for electron sponge application. The reaction of precursor complex 1 with Pd\textsuperscript{2+} and DMSO afforded complex 2 which is a first mixed valence Pd supported fluorododecavanadate linker. Spherical compound 2 anion consists of ten VO\textsubscript{5} units and two VO\textsubscript{4} units. Two palladiums with two DMSO ligands at both sides attached on the main cage. Cation \([\text{VO(DMSO)}_5]^{\text{V}}\) comes from the partial decomposition of complex 1 during the reaction. By the oxidation of decavanadate \(n-\text{Bu}_4\text{N}]_4[V_{10}\text{O}_{26}]\) in the presence of F\textsuperscript{-} and Pd(NO\textsubscript{3})\textsubscript{2} in DMSO, a palladium-supported fluoride-incorporated dodecavanadate 3 was synthesized. Even if sharing similar main cage shapes with 2, complex 3 is a fully oxidized form with nitrate and DMSO ligands attached to Pd.

Keywords: polyoxometalate, Palladium, dodecavanadate

References

Crystalline sponge method: X-ray structural analysis in the porous coordination network

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Abstract

X-ray single crystallographic diffraction (SCD) analysis is one of the most powerful analytical methods for determining a molecular structure. SCD analysis requires a single crystal of the target compound usually prepared by a crystallization. But the crystallization process often results in failure when target compounds are flexible, scarce or unstable. Recently, we developed crystallization-free SCD analysis protocol, crystalline sponge method\(^1\), which utilized a porous coordination network as a crystalline matrix to orient the absorbed guest molecules in a periodic fashion.

A porous coordination network of [(ZnI\(_2\))\(_3\)(tpt)]\(_n\) (1; tpt = tri(4-pyridyl)-1,3,5-triazine) was utilized as a crystalline sponge. Soaking a piece of 1 into a cyclohexane solution containing 5 µg of guaiazulene gave a guest inclusion crystal of 1. SCD analysis of the crystal revealed guaiazulene structure along with the host framework of 1. Furthermore, we successfully analyzed the structures of chiral molecules, HPLC separated fractions, potentially explosive secondary ozonides by the crystalline sponge method.

Keywords: Crystalline sponge method, X-ray crystallographic analysis, host-guest chemistry

Fig. (a) Schematic illustration of crystalline sponge method protocol. (b) Network structure of the guest inclusion 1 (guest guaiazulene molecules are drawn as CPK model). (c) X-ray structures of molecules analyzed by the crystalline sponge method (thermal ellipsoids are drawn at a 50% probability level).

References

Synthesis and Chemical Characteristics of the Freebase Forms of Quadruply Fused Porphyrins

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Abstract

Porphyrin derivatives bearing fused aromatic moieties at the periphery have been revealed to show unique optical and magnetic properties on the basis of co-planarity between the porphyrin core and the fused aromatic moieties and the resultant expansion of \(\pi\)-conjugation circuits.\textsuperscript{1} Recently, we have reported an efficient synthetic procedure of the Zn\textsuperscript{II} complex of a quadruply ring-fused porphyrin (Zn\textsuperscript{II}QFP, 1), having four fused five-membered rings at the periphery.\textsuperscript{2} Here, we report synthesis of a freebase derivative of QFP (H\textsubscript{2}QFP, 1) and its characteristics.

The basicity of the imino-nitrogen atoms of the fused pyrroles in 1 was investigated by UV-Vis titration with trifluoroacetic acid (TFA) as an acid in CH\textsubscript{2}Cl\textsubscript{2} at 298 K. The first protonation of 1 proceeds similarly to that of tetraphenylporphyrin, whereas the second protonation is hard to occur unless a large excess amount of TFA is added. Therefore, it is clarified that compound 1 undergoes two-step protonation.\textsuperscript{3}

To explore the NH tautomerism of H\textsubscript{2}QFP, introduction of a substituent at the \(\beta\)-position of a non-fused pyrrole was made to break the structural symmetry,\textsuperscript{4} since compound 1 has a symmetric structure to make the two inner NH atoms identical in the \(^1\text{H}\) NMR spectrum and the NH tautomerism cannot be clarified. The \(^1\text{H}\) NMR signal of the inner NH protons in \(\beta\)-mesityl-substituted 2 was observed as a broad singlet in CDCl\textsubscript{3} at 298 K, which indicates that the exchange process of the two inner NH protons (\textit{i.e.} NH tautomerism) is too fast relative to the NMR timescale. In contrast, at 293 K, the signal of the inner NH protons was observed as a slightly split signal, reflecting the different magnetic circumstances of the two protons, since the exchange process was slow enough to the NMR timescale at this temperature. The variable temperature NMR studies of 2 and the line-shape analysis allowed us to determine the activation parameters for the NH tautomerism of 2 in CDCl\textsubscript{3} to be \(\Delta H^\ddagger = 95 \text{ kJ mol}^{-1}\) and \(\Delta S^\ddagger = 89 \text{ J mol}^{-1} \text{ K}^{-1}.\textsuperscript{4}

Keywords: porphyrin, protonation, NH tautomerism, ring-fusion, expanded \(\pi\)-conjugation

References

Metal complexes with bistability

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Abstract

Molecules may have flexible structures with easily controlled electronic states. When molecules have several stable electronic states and their structures are flexible upon state changes, such molecular systems can be promising candidates for molecular switching devises.

Spin crossover (SCO) and mixed valence (MV) complexes rest in two spin states and two valence states, respectively. Multi-component molecules, in which each component possesses several states due to spin conversion and electron transfer, are expected to show synergistic behaviors with stepped and/or selective state conversions. In this lecture, multi-component systems showing selective spin state conversion, photo-induced SCM, and lability controlled cluster syntheses will be presented.

Keywords: Metal complexes, Molecular Magnetism

Figure (a) Mixed valence Fe$^{II/III}$ SCO complex, (b) Cyanide bridged 1D and discrete complexes (c-1&2) showing selective spin state conversion, photo-induced SCM and clusters generated from different electronic states, respectively.

References
Excited-state dynamics and photophysical properties of blue-emissive dicyanoaurate oligomers

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Abstract

The photophysics and photochemistry of Au(I) complexes have attracted much interest in the fields of photoelectronic devices because of their tunable and bright luminescence. Dicyanoaurate ([Au(CN)₂⁻]) in the ground state forms a loosely-bound oligomers due to weak aurophilic attractive interaction (~0.1 eV). With ultraviolet irradiation of the oligomer, an electron in the dz²-dz² antibonding orbital is excited to the pz-pz bonding orbital between the Au atoms, strengthening the Au-Au bond (~1 eV) to generate the excited oligomers with tight Au-Au covalent bond(s). Ultrafast dynamics of the Au-Au bond formation were directly observed in the excited-state trimer and dimer by means of femtosecond absorption spectroscopy. The theoretical analysis of the transient absorption for the excited trimer revealed the abrupt contraction of the Au-Au bond upon electronic excitation was followed by slower structural change (2 ps) from a loosely-bent to the rigid linear structure. The excited oligomers show emission from violet to yellow depending on the size of oligomers. While aqueous solutions of K[Au(CN)₂⁻] are weakly emissive (Q.E.<0.01), the emission intensity was found to increase considerably (Q.E.=0.4) in the presence of tetraethylammonium chloride (Et₄NCl). The enhancement of the emission is ascribed to suppression of deactivation process of large excited oligomers due to hydrophobic interactions between Et₄N⁺ and CN ligands. The hydrophobic interaction of [Au(CN)₂⁻] with Et₄N⁺ provided a highly emissive crystals of (Et₄N)[Au(CN)₂⁻] with one dimensional Au chains. While the crystalline sample exhibited broad emission due to the formation of tetramer and larger oligomers at high temperatures, intense sharp emission at 400 nm from the excited trimer was observed with Q.E.~1 at low temperatures. Zero-field splitting measurements and theoretical calculations revealed the emission of the excited trimer is phosphorescence induced by spin-orbit coupling of a Au-6p electron.

Keywords: Aurophilic interaction, Dicyanoaurate, Phosphorescence, Excited-state dynamics

References

Single Molecule Conductance Studies of Organometallic Molecular Wires with Ruthenium Acetylide Units

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Abstract

The quest for highly conducting molecules at the single-molecule level in the metal electrode-molecule-metal electrode (MMM) junctions is essential to achieve molecular devices. In general, conductance of common π-conjugated organic molecules is considerably low compared to metallic wires due to following two reasons; (1) the large energy gap between the Fermi level of the electrodes (usually gold electrodes are used) and the conducting frontier orbitals of the molecules, and (2) large contact resistance occurs between the terminal anchor groups and the electrodes. In this context, we recently reported that introducing organometallic ruthenium center could improve single molecule conductance of dipyridylbutadiyne despite the long molecular lengths, as a result of the energy-level alignment between Fermi level and the frontier orbital energies of the molecules (Figure 1).[1,2] Herein we report organometallic polyyne molecular wires with highly conducting properties accomplished by the small contact resistance.[3]

Single molecule conductance study was performed using STM-break junction technique and the molecular conductance of 1-3 was determined. It is notable that the conductance of the organometallic polyyne molecular wires 1-3 is significantly higher than those of common organic polyyne molecular wires with the similar molecular lengths. In this presentation, theoretical analysis on the basis of density functional theory (DFT) and Non-equilibrium Green Function (NEGF) will also be discussed.

Keywords: molecular wire, ruthenium acetylide, single-molecule conductance, STM-break junction.

Graphical abstract

Previous study

![Graphical abstract of previous study](image1)

This study

![Graphical abstract of this study](image2)


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Photochemical Hydrogen Evolution Assisted by Nonprecious Metal Complexes Bearing Redox-active Ligands

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Abstract

Molecular hydrogen is one of candidates as clean energy carrier.\textsuperscript{1} Because of the difficulty in the storage and transportation of hydrogen, the development of hydrogen-storage/-evolution materials is strongly desired. Among a several materials, organic compounds, known as organic hydrides, are fascinating candidate. Recently, quinoline/1,2,3,4-tetrahydroquinoline system was reported as efficient hydrogen-storage/-evolution material that can evolve hydrogen at relatively low temperatures (ca. 110-140 °C), under the presence of Ir-catalyst.\textsuperscript{2} However, even in the excellent example, the operating temperature in the hydrogen-evolution reaction (HER) is still high. Therefore, the creation of a HER operable at moderate temperature with use of nonprecious-metal catalysts is an important issue.

Recently, we reported interesting and important reactions of transition metal complexes with redox-active ligands.\textsuperscript{3} For example, Fe(II) complex with o-phenylenediamine (opda), [Fe\textsuperscript{II}(opda)\textsubscript{3}](ClO\textsubscript{4})\textsubscript{2}, was reported to show the photochemical HER at room temperature.\textsuperscript{4} In this reaction, the protons and electrons in opda ligand were found to be the source of photochemically evolved hydrogen. These results indicate the possibility for creation of novel hydrogen storage materials operable under room temperature based on the nonprecious metal-based complexes with redox-active ligands.

Here, we report the photochemical reaction of Fe(II) complex with redox-active ligand bearing heteroleptic coordination sites \textit{via} one amino and the deprotonated hydroxyl group, o-aminophenolato (apH\textsuperscript{−}). By the photoreaction of the complex in MeOH, the light-driven MeOH dehydrogenation under room temperature could be observed, and the detailed investigation on the elucidation of reaction mechanism, including photochemical hydrogen radical generation, will be presented.\textsuperscript{5}

Keywords: Redox-active Ligand, Nonprecious metal complex, Photochemical hydrogen evolution,

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References

Cold Crystallisation of Alkyl Substituted Nickel(II) Complexes Capable of Storing Heat Energy

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Abstract
Cold crystallization is a phenomenon of crystallisation upon heating process accompanied with the release of heat energy. Before this heating process, the compound is once heated to isotropic liquid phase. This is an endothermic phase transition, where the compound stores heat energy. Then the compound is cooled down, but the heat energy is not released in the cooling process. Of course, the process is highly dependent on the cooling rate, but the rate can be slow as 5°C/min. In the cooling process, the supercooled liquid state appears at first, and often 2nd order phase transition to glass state may be followed. Since the heat energy that is taken in at the heating process upon melting is kept inside the supercooled state, this compound can be regarded as heat storing material. Poly ethylene telephthalate (PET) is well known to exhibit such a property, and the phenomenon is thought as characteristic for polymeric compounds.

We have found and reported compound that exhibit thermochromism upon cold crystallisation with the alkylated pigment[1]. We will report on the alkylated nickel(II) complexes that is found to exhibit cold crystallization in the course of investigation. An example of DSC data is shown in the Figure given below. A tiny 1st order phase transition is observed prior to the cold crystallization.

Keywords: Cold Crystallisation, Nickel Complex, Heat Energy Storage, Phase Transition, Super Cooling

References
Function Integrated Space Based on Liposome and Metal Complexes

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Abstract

Rational and hierarchical integration of various functional components, such as cofactors and enzymes, is achieved using biomembrane and protein assemblies in nature, leading to coupling of different chemical reactions. Artificially creating such multifunctional reaction systems is one of the most considerable topics in current chemistry. Although various chemical reactors consisting of polymers and proteins have been studied, it is still a challenging issue to construct reaction systems in which different chemical reactions occur simultaneously. We focus on liposome, which is an artificially-prepared spherical vesicle composed of a lipid bilayer of phospholipids, as a chemical reaction space. It is expected that different functional molecules co-exist in or on one liposome hierarchically, because a liposome provides four different regions, namely - hydrophilic inner water phase, hydrophobic lipid bilayer, and inner and outer surfaces. To construct novel functional composites, we integrated metal complexes (e.g., catalyst, photoreceptor, luminant, electron mediator, and molecular storage and separator) into the liposome space site-specifically.

In the presentation, we will introduce the functionalization of liposome surface with lipophilic metal complexes such as the coordination polymer\(^1\), the water oxidation catalyst\(^2\), the photoinduced release of nitric oxide\(^3\), the enhancement FRET efficiency using lipid domain\(^4\) and the ion-channel driven direct synthesis of coordination polymers in the inner aqueous phase\(^5,6\).

Keywords: liposome, lipid bilayer, metal complex, coordination polymer

References

Polyelectrolyte and Polyampholyte Microgels. Swelling, Collapse and Interaction with Guest-Molecules

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Abstract

Internal structure of nano- and microgels resembles elements of macroscopic polymer network: linear chains (subchains) are covalently linked with each other into three-dimensional frame of the size in the range between tens of nanometers and few microns. The most remarkable property of the microgels is their ability to swell and collapse under variation of environmental conditions (temperature, pH, etc.). This property can efficiently be exploited in many applications, in particular, for uptake and release of guest molecules.\textsuperscript{1,2} It has been shown recently that the spherical microgels can serve as “soft”, penetrable and stimuli sensitive alternative of solid particles which can stabilize emulsions. Such emulsions have peculiar properties and can easily be destroyed under external stimuli leading to desorption of the microgel particles.\textsuperscript{3}

In the present paper, we report about new effects characteristic for the microgels, which (at the first glance) can be classified as counterintuitive. In particular, we demonstrate (i) inhomogeneous swelling of structurally homogeneous polyelectrolyte microgels revealing quasi-hollow central part and dense periphery,\textsuperscript{4,5} (ii) ability of polyampholyte core-shell microgels to serve as Coulomb trap, when charged shell of the microgel can serve as a potential barrier enforcing similarly charged nanoparticles (proteins) to “levitate” inside the core prohibiting their escape. Microgels adsorbed at water-oil interface reveal peculiar behavior comprising ability either to homogeneously mix two immiscible liquids (oil and water) inside the microgel or to weakly segregate them.\textsuperscript{6,7}

Keywords: microgels, electrostatic interactions, swelling and collapse, proteins

References


Acknowledgements. Financial support of the Russian Foundation for Basic Research is gratefully acknowledged.
Effect of Selective Localization of Salt and Filler on Thermal and Dielectric Properties of Poly(Ethylene Oxide)/Polyacrylate-Based Composite Polymer Electrolytes

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Abstract

The classic composite polymer electrolytes (CPEs) with lithium (Li) salt and nanofiller dissolved in poly(ethylene oxide) (PEO), display low conductivity $\sigma \sim 10^{-5}$ S cm$^{-1}$ which prohibit them from practical applications for rechargeable batteries. Blending of PEO (semicrystalline polymer) with polyacrylates (amorphous polymer) [e.g. poly(methyl methacrylate) (PMMA) [$T_g = 105^\circ C$], and poly(methyl acrylate) (PMA) ($T_g = 13^\circ C$)] results in miscible blends in molten state for all compositions. We focus on matrix-droplet microstructure of the blends with content of PEO in excess. Blends with addition of Li salt at relatively high mass fraction of salt (~$W_S > 0.10$) are still miscible in molten state. Upon cooling from the melt, crystallization of PEO takes place and hence phase separation of PEO crystalline phase and amorphous phase of multi-components (PEO, polyacrylate and salt) can be noticed. In these systems, there are PEO spherulites surrounded by amorphous phase of miscible PEO, polyacrylate and salt. The percolation path lies in the amorphous phase of the blends. In amorphous phase, PEO, PMMA and PMA possess oxygen in their respective chemical structures, which may be able to interact with the Li salt added. The conductivity of PEO-salt mixtures is slightly higher than that of the miscible systems of PEO/PMMA/salt but lower than PEO/PMA/Li. This may be due to reduced segmental motion cause by the increased $T_g$ of the blends in amorphous phase and hence a decrease in motion of ions in the amorphous phase of PEO. For PEO/PMA/Li when PEO in excess, the $T_g$ of the blends is still far below room temperature, hence the motion of ion at room temperature is not much affected. We observe also the percolation path lies in the amorphous PEO-rich phase of the blends. Hence, higher conductivity is noted for this system.

Addition of low mass fraction of nanofiller ($W_F < 0.05$) induces phase separation of miscible blends (in the melt) at $W_S = 0.12$. Again, we focus on the matrix-droplet microstructure of the CPEs. With judicious selection of materials at optimum compositions of blends and appreciable concentration of salt and nanofiller, preferential solubility of salt is at PEO phase for the percolation pathway and nanofiller is located at the interface of the parent polymers at high salt concentration. This is because the added nanofiller does not like polyacrylate phase and it loses in competing with Li salt to interact with PEO phase. For selected CPEs, enhancement of conductivity is noted as compared to PEO-salt mixtures. This may be due to the addition of nanofiller may counterbalance the negative effect of stiffer segmental motion of polymer chains (mainly PEO) when polymers interact with salt. If the polymer chains do not interact well with nanofiller, a very loose interfacial region around the nanofiller may exist. This region of lower polymer density and sufficiently high salt concentration may facilitate ion motion in interfacial region, which may lead to enhanced ionic conductivity.
Influence of ICP Etching on Hydrophobicity of Polymer Blend Surfaces

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Abstract

The concept of superhydrophobic or ultrahydrophobic surfaces inspired by the lotus leaf (Nelumbo) surface, gained a lot of significance in the past [1]. The specific surface roughness is essential for the superhydrophobicity and self-cleaning (lotus effect), but it also has great impact on type of fluid flow inside microchannels.

In this work a method for designing hydrophobicity of polymer blends by creating specific surface topography is described. Polymers used for polymer blend preparation are polylactide (PLA) and acrylonitrile butadiene styrene (ABS), two polymers which are most often used in fused deposition modelling - an additive manufacturing (3D printing) technology. Also, low-density polyethylene (PE-LD), and high-density polyethylene (PE-HD) were used. In order to increase hydrophobicity by changing the topography of two-phase polymer blend surface, blends are etched by using inductively coupled plasma (ICP) before the fluorocarbon-based coating treatment done in the second step [2]. During the surface treatment process of PLA/PE polymer blends, polylactide is etched significantly more than polyethylene and specific "island-like" surface morphology with 10° to 20° higher contact angle is created. ABS based polymer blends did not show this property.

This work has been supported by Croatian Science Foundation under the project entitled “Development of materials for 3D printing of microreactors” (UIP-2014-09-3154).

Keywords: hydrophobicity, polymer blend, ICP etching

References

Abstract

Hyaluronic acid (HA)-based hydrogel have gained considerable attention in recent studies as one of great attention in biomedical applications due to their unique potentials via combining the characteristics of a hydrogel system (e.g., hydrophilicity and extremely high water content). However, previous studies showed unmodified HA has a short life time and quickly degrade after administration as it limit its use in biomedical applications. In order to increase the lifetime of HA for long-term clinical applications, several strategies have been developed. Recent studies shows that incorporation of nanoparticles combined with suitable materials into a hydrogel matrix can overcome this problem. Gold nanoparticles (Au-NPs) have shown the great promise for development of drug delivery by various routes of administration and also made a great impact on clinical applications. The current challenge is to design hydrogels with good mechanical properties and at the same time a good syringeability. Development of HA based hydrogel nanocomposites by incorporating with suitable nanoparticles would be promise way to overcome the problems.

Nowadays, various seaweeds are widely used in life science due to their potential source of novel antioxidant. By considering this advantage properties of seaweed, Gracilaria Changgi (Gc) can also be used into hydrogel matrix to improve the overall properties of hydrogel nanocomposites. Thus, the goal of this present study is to prepare HA/Gc/Au-NPs hydrogel nanocomposites and to investigate the effect of Au-NPs and Gc seaweed on properties. 1-Ethyl-3-(3-dimethylaminopropyl) carbodiimide (EDC) was used as a cross linker for development of HA-based hydrogels with different ratios of HA/Gc (50/50, 60/40, 70/30, 80/20, 90/10). Hydrogel composites obtained from HA/Gc ratio of 80/20 and 90/10 showed the higher gel content compared to hydrogels of other compositions.

Keywords: hydrogels, Gracilaria Changgi, hyaluronic acid, EDC
Soft Nanocomposites with Tunable Matrix

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Abstract

New type of soft nanocomposites composed of transient network of entangled polymer-like wormlike surfactant micelles and inorganic particles was prepared. “Living” character of micellar chains imparts to the network significant advantages over similar polymeric systems, e.g. the ability to self-heal and to completely recover the properties after the mechanical degradation.

Within the nanocomposite, the particles demonstrate remarkable stability against aggregation and sedimentation, which can be due to their incorporation into the network of entangled WLMs by linking to energetically unfavorable micellar end-caps, which was evidenced by cryo-transmission electron microscopy. Particles enhance significantly the viscosity, the plateau modulus, and the relaxation time of the system acting as additional multifunctional physical cross-links in micellar network. The increase of rheological characteristics by added particles is more pronounced in nanocomposites with smaller content of low molecular salt KCl, when the WLMs are shorter in length and therefore contain larger amount of end-caps responsible for the interaction with the particles. At the same time, the addition of n-alkanes leads to the drop of viscosity by up to several orders of magnitude thus inducing the transition of a gel-like system to a fluid with low viscosity. SANS data evidence that this process is accompanied by the breaking of the cylindrical surfactant micelles with the formation of microemulsion droplets, which results in the disruption of the whole network. Thus, in the prepared nanocomposites, the particles strengthen the network, whereas the micellar component imparts a high responsiveness to hydrocarbons, which is important for various practical applications including oil recovery.

Keywords: viscoelastic surfactants, wormlike micelles, nanocomposites, polymer-like micelles

References


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Parking-Garage Structure in Densely Grafted Polymer Brushes

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Abstract

The dense tethering of \(AB\) copolymer on the solid substrate (polymer brush) is a perspective way to surface modification and generation of smart surfaces with tunable properties and definite response on external stimuli. Upon request the grafted \(AB\) copolymers could be assembled into different structures and then easily rearranged by change in temperature, pH, solvent quality etc. The scale and special symmetry of the morphologies depends on many factors, among which are the energy of \(A\) and \(B\) interaction with solvent and macromolecular architecture.

This study is devoted to the polymer brushes of macromolecules with amphiphilic \(A\)-graft-\(B\) monomer units. It was found that such brushes, depending on the solvent selectivity towards the backbone \(A\) or side \(B\) groups, could form the ultra-thin layers [1], having width about two-monomer size, the strands of few chains which are perpendicular to grafting surface [2], the lamellae with different domain spaces [3] and so-called parking garage structure [3]. The term "parking garage structure" recently introduced to describe such type of ordering in biological systems now finds application in other fields of science as well. In case under consideration, the parking garage structure joins together the lamellae with large (on the top of brushes) and small (close to grafted surface) domain spacing. The parallel ordering of lamellae and smooth connections between them justify comparison of such systems with parking garage.

Keywords: polymer brush, amphiphilic polymers, responsive surface, self-organization

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Macromolecular Helicity Control in Helical Polymer Brushes through Long-range Communication of Stereochemical Information

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Abstract

Dynamic helical polymers, such as polyisocyanates and polyacetylenes, are composed of interconvertible right- and left-handed helices, which are separated by a few helix reversals, and these polymers are known to show remarkable chiral amplification properties. For example, it is reported that the copolymerization of achiral monomers with a small amount of optically active monomers can produce optically active polymers with a greater excess of one single-handed helical conformation, which is called the "sergeants and soldiers effect".\textsuperscript{1} However, to the best of our knowledge, there have been no reports on the amplification of macromolecular helicity based on the sergeants and soldiers effect through long-range stereochemical communication.

We have designed and synthesized a series of helical poly(phenylacetylene)-based copolymer brushes bearing helical poly(phenyl isocyanate) pendants with and without an optically active group at their pendant termini (poly-(1\textsubscript{S}-co-2\textsubscript{L})) and demonstrated the first efficient and clear example of the sergeants and soldiers effect in dynamic helical polymers through long-range stereochemical communication.\textsuperscript{2,3} In addition, we found that a preferred-handed helix-sense was simultaneously biased in the dynamically racemic polyisocyanate pendants devoid of an optically active terminal group because of the induction of macromolecular helicity in the polyacetylene backbone.

Keywords: chiral amplification, helix, polymer brush, polyacetylene, polyisocyanate

References

Characterization of Elementary Processes of Alternating Radical Copolymerizations using Electron Spin Resonance (ESR) Spectroscopy

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Abstract

Mechanism of alternating radical co-polymerization of styrene with maleic anhydride has been investigated by electron spin resonance spectroscopic techniques. Time-resolved electron spin resonance (TR ESR) spectroscopy can exclusively observe the first radical addition reaction of a radical, generated from an initiator to a monomer (Scheme 1). Laser pulse generated spin polarized radicals relaxed to a thermally stable state with Boltzmann distribution and the relaxation process can be observed as ESR signals as shown in Figure 1.

In this research work, TR ESR spectroscopy has been applied to investigation of the initiation mechanism of an alternating copolymerization of styrene and maleic anhydride. There are at least two possibilities for the first radical addition to the monomer as shown in Scheme 1. Since TR ESR signal of styrene is totally different from that of maleic anhydride, we can distinguish clearly which is which. TR ESR can provide information what happens in the initial stage of the alternating copolymerization reaction. Overlapped signals of those styrene and maleic anhydride were observed indicating that P-centered radical added to the each monomer just like as in homo-polymerization even in a co-polymerization system. We can state that first radical addition of the P-centered radical to the monomers was done without any selectivity. The reactivity of the radical addition reaction of the each monomer seemed to be determined by the individual reactivity of the each monomer [1].

Steady-state ESR (SS ESR) spectra of the alternating co-polymerizations in the presence of RAFT (reversible addition fragmentation chain-transfer) agent provided information on the structure of propagating chain end.

Keywords: radical polymerization, alternating copolymerization, electron spin resonance, ESR/EPR

References

Structural Analyses of Sphere- and Cylinder-Forming Triblock Copolymer Thin Films Near the Free Surface

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Abstract

We investigated the structure near the free surface for three different triblock copolymers. Polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene (SEBS-8, $M_n = 6.7 \times 10^4$, $M_w/M_n = 1.04$, $\phi_{PS} = 0.084$) and polymethylmethacrylate-block-poly(n-butylacrylate)-block-polymethylmethacrylate (MAM, $M_w = 7.4 \times 10^4$, $M_w/M_n = 1.15$, $\phi_{PMMA} = 0.20$) specimens were spin-cast on a silicon wafer from toluene solution with polymer concentration of 10.0 wt% and 7.0 wt%; respectively, with 2000 rpm for 30 sec., at room temperature. The polystyrene-block-poly(ethylene-co-butylene)-block-polystyrene (SEBS-16, $M_n = 6.6 \times 10^4$, $M_w/M_n = 1.03$, $\phi_{PS} = 0.16$) specimen was prepared by casting the polymer solution from a mixture of n-heptane/methylene chloride (1:1) with 5.0 wt% polymer concentration in a petri dish. Then, the SEBS-8, SEBS-16, and MAM as-prepared specimens were thermally annealed at 140˚C, 210˚C, and 180˚C, respectively, under a nitrogen atmosphere. It was previously reported that the SEBS-8 specimen forms polystyrene (PS) spherical microdomains order in a body-centered cubic lattice (bcc) [1], while cylindrical microdomains were found to orient perpendicular to the film surface for the SEBS-16 specimen [2]. For the MAM specimen, it was revealed by small angle X-ray scattering (SAXS) that it forms spherical microdomains ordering in a bcc lattice. The surface structure of the three specimens was examined by the atomic force microscopy (AFM). Moreover, the grazing-incidence small angle X-ray scattering (GISAXS) was used to analyze the structure over a long range of the surface area. The X-ray photoelectron spectroscopy (XPS) was used to reveal the component selectively appearing on the outermost surface. It was found that a poly(ethylene-co-butylene) layer overlaying on the free surface of SEBS-8 and SEBS-16 specimens, while for the MAM specimen, a poly(n-butylacrylate) layer covers the outermost region of the surface. Actually, these results have a good agreement with the thermodynamic requirement that the component having lower surface free energy should cover the outermost layer of the free surface.

Keywords: block copolymers, surface topography, AFM, XPS, GISAXS.

References

Investigation of Electron Density Distribution Imaging by Maximum Entropy Method for Paracrystal Structure of Polyamide

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Abstract

Crystal structure of organic polymers is described as the so-called paracrystal structure which contains short and long-range lattice disordering. The number of Bragg’s reflections experimentally detectable for polymer crystals is small and their peak profiles are usually broad due to the paracrystal structure. Hosemann’s lattice distortion analysis with X-ray diffraction data can be applied for explaining the paracrystal structure quantitatively\textsuperscript{1}. However, as most Bragg’s reflections from polymer crystals are detected as weak overlapped peaks and it is difficult to evaluate the intensity of each \textit{hkl} reflection precisely, the details of the paracrystal structure hasn’t been clarified. On the other hand, maximum entropy method (MEM)\textsuperscript{2} has successfully been applied for visualization of the electron density distribution of crystal structures for organic small molecules, inorganic compounds, metal-organic frameworks and so on. Sasaki et al. have been carried out MEM analyses with powder X-ray diffraction data of Poly(3-hydroxybutyrate) crystal to discuss about the lattice disordering and intermolecular interaction. However, the intermolecular interaction including the hydrogen bonding hasn’t been visualized for polymers in the crystal state by MEM. The purpose of this study is to establish the experimental and analytical technique to visualize the electron density distribution for the paracrystal structure of polyamides by using X-ray diffraction data and MEM.

A sample used in this study is nylon 6. The $\text{I}_2$-type crystal structure of nylon 6 is monoclinic with the space group of $P2_1$.\textsuperscript{3} The hydrogen bonding is formed between the adjacent chains having antiparallel backbone packing in the unit cell. Solution-crystallized powder samples were prepared with a 0.05 wt% nylon 6 in HCOOH/EtOH (5 : 5 wt%). The crystallinity of the sample obtained after drying and annealing treatments was ca. 80%. Power X-ray diffraction profiles were measured at BL44B2 of SPring-8 (RIKEN, Hyogo, Japan) for the dried sample consisting of small single crystals and amorphous. As a result, sequent 636 reflections including overlapped ones were measured in 2 theta angles of 5.0 ~ 60.0 deg. After conducting various intensity corrections to the measured X-ray diffraction profile, peak separation was performed for it based on the relative intensity ratio of the \textit{hkl} reflections of the reported $\text{I}_2$-type crystal structure of nylon 6\textsuperscript{4}. Tentative results on crystal structure and MEM analyses will be explained in my poster presentation.

Keywords: electron density distribution mapping, nylon 6, maximum entropy method (MEM), crystal structure, synchrotron X-ray powder diffraction

References:

Noncovalently Immobilized Cationic Organocatalysts on Anionic Sulfated Chitin: Reusable Heterogeneous Supramolecular Catalysts

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Abstract

The development of polymer-immobilized organocatalysts have attracted growing attention because of the advantages such as ready separation of products and reusability of catalysts. The immobilization of organocatalysts has been commonly carried out by covalent attachment onto polymer supports, although the process involves multiple synthetic manipulations, which are time-consuming and costly. To avoid the drawback, novel immobilization methods using noncovalent ionic interactions were reported in 2008 by two groups.1,2 Taking advantage of the noncovalent immobilization strategy, in this study, we synthesized reusable heterogeneous supramolecular catalysts (poly-1•2 and poly-1•3), in which cationic organocatalysts such as flavin3 and imidazolidinone4 are noncovalently immobilized on a naturally occurring chitin-derived anionic polymeric support (poly-1) through noncovalent ionic interactions. The obtained poly-1•2 and poly-1•3 heterogeneously catalyzed the environment-friendly H2O2 oxidation and asymmetric Diels-Alder reaction, respectively. Their catalytic activity or enantioselectivity matched or was higher than that of the corresponding homogeneous monomeric organocatalysts. In addition, the catalysts were readily recovered by simple filtration and reused without loss of activity and selectivity.

Keywords: chitin, heterogeneous catalyst, flavin, imidazolidinone, organocatalyst

References
Enhanced Electroluminescence from Delayed-Fluorescence Emitters by Suppressing Nonradiative Decay

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Abstract

Organic light-emitting diodes (OLEDs) are now commercially available as displays in smartphones and TVs. OLEDs have also attracted considerable attention for use in flexible full-color flat-panel displays and next-generation solid-state lighting source. Recently, emissive materials that exhibit thermally activated delayed fluorescence (TADF) have been of great interest because they can convert all the excitons generated in OLEDs into light. The TADF efficiency strongly depends on the competition between radiative and nonradiative decays in an emitting molecule. Hence, achieving a fundamental understanding of the origin of radiative and nonradiative decays in organic molecules is essential for designing efficient TADF emitters.

Here, we report our recent progress in developing TADF emitters, focusing especially on molecular design of blue TADF emitters obtained by suppressing their non-radiative decay. Our strategy is based on a theoretical method that allows a visual understanding of radiative and nonradiative decays in organic molecules. From theoretical calculations, increasing spatial overlap between the highest occupied molecular orbital and lowest unoccupied molecular orbital leads to enhancing the radiative decay and consequently, increases the TADF efficiency.

Keywords: organic light-emitting diodes, thermally activated delayed fluorescence, non-radiative decay

References

Peptide ligands immobilization via single-step tyrosine oxidation for biologically active cardiovascular devices

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Abstract

Cardiovascular devices require the compatibility for not only blood but also the neointimal tissue. Since the most of synthetic biomaterials using as substrates of cardiovascular devices do not inherent any biological activities, immobilization of cell adhesive ligand peptides which were isolated from extracellular matrix proteins has been one of the powerful strategies for the design and functionalization of biomaterial substrates. For example, biomimetic surface with Arg-Gly-Asp-Ser peptide can provide cellular adhesiveness. However, the method for peptide immobilization was restricted, and the reactive groups should be introduced on substrates before the peptides immobilization. P. B. Messersmith reported the useful immobilization method of functional molecules including peptides with dopamine and 3,4-dihydroxyphenylalanine (DOPA) on a variety of materials\textsuperscript{1}. This method is imitative the adhesive protein secreted by marine mussel and utilizes the high reactivity of catechol group. A problem with this method is the difficulty in the synthesis of DOPA derivatives.

We successfully immobilized cell adhesive ligand peptides onto a variety of biomaterials using single-step oxidation of tyrosine (Tyr) residue to quinone using hydrogen peroxide and copper (II) chloride catalyst\textsuperscript{2, 3}, and we are working to apply this technique for preparing biologically active cardiovascular devices such as the re-endothelialization promoting vascular stent.

Keywords: peptide immobilization, biomaterials, tyrosine oxidation, cell adhesion, cardiovascular device

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Supramolecular Liquid-Crystalline Materials for Ion and Electron Transport and Stimuli-Responsive Emission

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Abstract

Liquid crystals combining molecular order and fluidity have versatile applications beyond displays. Supramolecular self-assembly of ionically and electronically active liquid-crystalline molecules can provide promising opportunities for efficient charge transport and modulation of emission. Here we show our recent approaches to the development of ionic liquid crystals that could potentially be used in batteries and water treatment and π-conjugated liquid crystals that exhibit electron transport and stimuli-responsive emission color change. Ionic columnar and bicontinuous cubic liquid crystals based on non-volatile ionic liquid electrolytes have been developed for proton and lithium ion transport. For example, we have found that the ionic conductivities of zwitterionic liquid-crystalline molecules complexed with acids and lithium salts are four orders of magnitude higher than those of zwitterionic molecules themselves. These results suggest that the zwitterionic moieties dissociate the acidic molecules and lithium salts and then form continuous one- and three-dimensional ion transport channels in the liquid-crystalline states. In addition, photopolymerizable ionic liquid crystals have been successfully applied to the fabrication of water treatment membranes. A new type of liquid-crystalline semiconductors and photoluminescent emitters that can respond to either mechanical stimulus or ionic stimulus has been developed for future sensor device applications. For example, a hydrogen-bonded guanine-oligothiophene conjugate forming an Im3m bicontinuous cubic phase exhibits ambipolar charge carrier transport (Fig. 1). The addition of potassium salt induces the structural change to the hexagonal columnar phase, accompanied by the emission color change from yellow to orange under the illumination of UV light. In addition, mechanical stimuli-responsive luminescent liquid crystals that show the reversible color changes at ambient temperature have been obtained for the oligothiophenes bearing branched alkyl chains.

Keywords: liquid crystal, ion transport, electron transport, photoluminescence

References

Molecular Computing by Tetranuclear Mixed-Valence Complexes: A Theoretical Study on Relationship between Molecular Structure and Device Operation of Molecular Quantum-Dot Cellular Automata

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Abstract

Quantum-dot cellular automata (QCA) is one of next-generation devices. QCA is expected to achieve a significant saving of energy and an increase in processing speed of computing because QCA which utilizes two degenerate states of QCA cell, "0" and "1", for operation is free from a current flow. For improvement in the operating temperature and size of the device, the idea of molecular QCA was proposed by C. S. Lent. Tetranuclear mixed-valence metal complexes are promising candidates for molecular QCA cell and has been investigated both experimentally and theoretically. However, capacity and behavior of molecular QCA is still not clear. Therefore, we have proposed a simple method for dynamic simulation of molecular QCA, taking dinuclear Ru complexes (Creutz-Taube complexes) as examples1. This method has been applied to the discussion on the kind of metal atoms and charge of complexes.

In this presentation, we will talk about our recent study about molecular QCA made of tetranuclear mixed-valence complexes such as Creutz-Taube square (square shape)2, biferrocenium dimer (rectangle shape)3, tetraferrocenyl boronate ester (parallelogram shape)3,4, and so on. These complexes consist of four dots so that are suitable for switching devices such as QCA. By quantum-chemical calculations, we have found that these complexes quickly respond to the switch of external input charges and the states of complex (0 or 1) are clearly explained from the distribution of molecular orbitals. Applicability of these complexes to molecular QCA logical device will be discussed from viewpoints of electronic and geometric structures of complexes.

Keywords: ferrocene, mixed-valence, molecular device, quantum dot, density functional theory

References

Self-Assembling Organic-Inorganic Hybrid Dendrimers with a Monodispersed Functional Nanoparticle-Core

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Abstract

Nanoparticle (NP)-based periodic structure formation has attracted a considerable attention in material science, because new synergistic functions could be derived from the periodic structure. Among organic soft materials, liquid-crystalline (LC) organic dendron is one of the most representatives to form spherical dendrimer-like structures by the self-assembling property. Such spherical assembly spontaneously forms a self-organized periodical structure. Thus, we focused our attention on introduction of such self-organization ability into inorganic NPs. As dendrons, we synthesized phenetyl ether-type dendrons with an amino-group at the apex. These dendrons themselves show thermotropic LC phases. The dendrons are attached as the outer corona, through amidation, to the carboxylic groups at the surface of the inner aliphatic corona encapsulating the NP. Purpose-designed CO₂H-modified monodisperse gold and CdS NPs were synthesized in the presence of 12-dodecanethiol (DT) and 16-mercaptohexadecanoic acid (MHA). The dendron-modified gold NP showed an LC hexagonal columnar phase at 130 °C and formed a simple cubic (SC) LC phase at 150 °C. The result indicated that the dendron-modified gold NPs can be regarded as organic-inorganic hybrid dendrimers with thermotropic LC behaviour. On the other hand, the dendron-modified CdS NPs also formed a thermotropic cubic LC phase with a novel, low-symmetry structure, space group $P2_13$ by annealing at 150 °C for 15 h. The cubic structure was retained at room temperature after cooling. In contrast, unannealed dendron-modified CdS NPs on glass substrate formed a disordered structure. In such a state, it showed strong photoluminescence (PL) when UV irradiated at 365 nm. However, PL was quenched when the dendron-modified CdS NPs formed the cubic phase after annealing at 150 °C followed by cooling. Such PL quenching behavior was totally reversible, and appears to be associated with the periodic structure of the dendron-modified CdS NPs (Figure 1). Such unusual PL behavior might be a powerful tool to develop future functional devices.

Keywords: Nanoparticle; Dendrimer; Self-Organization; Liquid Crystal; Quantum Dot

References

Organic long persistent luminescence

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Abstract

Based on a process called long persistent luminescence (LPL), glow-in-the-dark materials work by slowly releasing energy absorbed from ambient light. Used in watches and emergency signs, most commercial glow-in-the-dark materials are based on inorganic compounds and include rare metals. However, these materials are expensive, require high temperatures to manufacture, and scatter light when ground into powders for paints.\textsuperscript{1} Carbon-based organic materials—similar to those used in plastics and pigments—can overcome many of these disadvantages. They can be excellent emitters and are already widely used in organic light-emitting diodes (OLEDs). But achieving long-lived emission has been difficult, and the longest emission based on phosphorescence from organics at room temperature was only a few minutes.

In this research, we developed a novel LPL emitter consists of two simple organic molecules.\textsuperscript{2} By mixing an electron donating molecule and an accepting molecule, emission lasting for over an hour was demonstrated for the first time without the need for intense light sources or low temperatures. Absorption of light by an acceptor molecule gives the molecule extra energy that it can use to remove an electron from a donor molecule. The extra electron on the acceptor molecule can then hop to other acceptor molecules and move away from the positively charged donor molecule, resulting in separation of the charges. The separated charges gradually come back together—some slowly and some more quickly—and release their energy as light over the span of almost an hour, resulting in the glow-in-the-dark effect. The mixtures and processes are similar to what are found in organic solar cells and OLEDs. After building up separated charges like in a solar cell, the charges have nowhere to escape, so they eventually comeback together to emit light like an OLED. The key difference in the newly developed mixtures is that the charges can exist in a separated state for very long periods of times.

Keywords: persistent luminescence, excited state, charge transfer, organic semiconductor

References

Development of functional nanoparticles based on RAFT polymerization

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Abstract

Nanoparticles (NPs) have been paid numerous attentions for promising functional materials in various fields, such as electronics, medicine, cosmetics, and so on, because of the facile surface modification and high functionality. Considering the usage of NPs for electronics, the essential characteristics is the fine controllability of opto-electrical functionality, potentially enabling NPs to apply for various electronics. However, the facile and precise control of functionality in NPs is still a challenging issue. Herein, we developed the facile one-pot synthesis of various functional NPs by utilizing the self-assembly of amphiphilic block copolymers.1-5 Firstly, an amphiphilic block copolymer poly(PEGMA)-b-poly(DB3VT) was synthesized by RAFT polymerization. poly(PEGMA)-b-poly(DB3VT) formed a uniform core-shell micelle that consists of poly(PEGMA) shell and poly(DB3VT) core under the optimized THF/H2O mixed condition, and the selective Suzuki coupling reaction between a poly(DB3VT) block and diboronic monomer was carried out in the core simultaneously. By this one-pot reaction, uniform NPs with various functional core structure were successfully obtained. The size of NPs was tunable by adjusting the Suzuki coupling reaction condition. Furthermore, opto-electrical functionalities (i.e., functional core structure) could be controlled simply by selection of a diboronic monomer. Consequently, the precise and facile control of functionality in NPs was achieved by the one-pot method based on the self-assembly of amphiphilic block copolymers.

Keywords: RAFT polymerization, Suzuki coupling reaction, self-assembly, nanoparticle

References
Incorporating a TiO$_x$ Shell in Single-Walled Carbon Nanotube/Fullerodendron Coaxial Nanowires

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Abstract

Coaxial nanowires with a donor–acceptor heterojunction have shown great potential for applications in innovative photofunctional materials. Recent theoretical and experimental studies have indicated that coaxial nanowire structures could potentially improve the carrier collection and overall efficiency relative to bulk semiconductors of the same materials. We have reported the fabrication and efficient photo-induced electron-transfer processes of single-walled carbon nanotube SWCNT/fullerodendron supramolecular nanocomposites, wherein a coaxial nanowire structure provides a donor–acceptor heterojunction between the SWCNT-core and the C$_{60}$-based fullerodendrons. We have also shown that SWCNT/fullerodendron ($\Phi = 0.28$) and SWCNT/fullerodendron/SiO$_2$ ($\Phi = 0.31$) coaxial nanohybrid materials can be used as effective photosensitizers for the catalytic evolution of H$_2$ from water under irradiation with visible light ($\lambda = 450$ nm).

Moreover, we have reported the direct incorporation of a co-catalyst into the shell of SWCNT/fullerodendron supramolecular nano-composites. Upon chirality-selective photo-excitation using monochromatic light ($\lambda = 680$ nm), which is suitable for the $E_{22}$ absorption of (8,3) SWCNTs, we observed the first example for the evolution of H$_2$ ($\Phi = 0.015$) photosensitized by SWCNTs. However, further improvements of the quantum yield of the SWCNT photocatalyst are necessary in order to further develop this technology. These results prompt us to explore a new coaxial photosensitizer with a TiO$_x$ shell as an electron-extraction layer that covers a photofunctional SWCNTs/C$_{60}$ interface. Here we describe the fabrication of SWCNT/fullerodendron/TiO$_x$ coaxial nano-hybrids that can be used for the effective photo-catalytical evolution of H$_2$, which shows the highest AQYs ($\Phi = 0.47$) under irradiation with visible light ($\lambda = 450$ nm).

Keywords: Single-walled carbon nanotube, TiO$_x$, C$_{60}$, Photocatalytic H$_2$ evolution from water

References

Synthesis and gas permeability of poly(substituted acetylene)s and their mixed matrix membranes with metal chlorides

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Abstract

Poly(substituted acetylene)s exhibited relatively high gas permeability because their stiff main chain and the steric repulsion of bulky substituents leading to the sparse structure of the polymer membranes.1 In this study, we synthesized poly(diphenylacetylene) derivatives by metathesis polymerization and the gas permeability was investigated. The metathesis polymerization afforded poly(diphenylacetylene)s with high molecular weights. The membrane of poly(diphenylacetylene) showed high gas permeability, while the membrane of poly(diphenylacetylene) possessing methoxy groups showed lower gas permeability and higher selectivity.2 Polar groups such as methoxy groups strengthened the interaction of polymer chains, making the membrane dense. In addition, we prepared the mixed matrix membranes (MMMs) comprised of poly(diphenylacetylene)s and metal chlorides (TaCl5 etc.). MMMs consisting of various polymers with inorganic particles have been studied in order to improve the gas permeation performance.3 However, the addition of inorganic particles into polymer membranes causes the interface voids as non-selective defects if the aggregation of particles occurs during the preparation of MMAs. The MMMs prepared in the present study showed higher gas permeability than the original polymer membranes without the decrement of gas selectivity. Poly(substituted acetylene)s can interact with TaCl5 through π-electron of the back bone and thus the metal particles were uniformly dispersed in polymer matrix.

Keywords: metathesis polymerization, poly(substituted acetylene), separation membrane, gas permeability, mixed matrix membrane

References
Synthesis and Properties of a π-Stacked Antioxidant Polymer

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Abstract

Free radical species can initiate or undergo a wide variety of useful reactions including polymerization and chemical transformations leading to valuable chemicals while it also mediates unwanted reactions including degradation of materials and damage to substances in a living body. A way to suppress unwanted radical reaction is to use an antioxidant reagent which reacts and deactivates radical species. The scope of antioxidant encompasses natural polyphenols such as tea catechin and persimmon tannin and artificial phenols and aromatic amine derivatives.

We herein report the synthesis, structure and performance of poly(4-vinyl diphenylamine) [poly(VDPA)] as a novel antioxidant polymer bearing diphenylamine moiety in the side chain. In a model reaction with a free-radical oxidant, poly(VDPA) quenched it more efficiently compared with a monomeric unit model. Such an effect may arise from a π-stacked conformation through which radical introduced to poly(VDPA) chain from oxidant can be effectively delocalized. A polymer with appropriate design can thus undergo chemical reaction more efficiently than a corresponding small molecule in spite of the fact that polymers may generally appear disadvantageous from a view of steric hindrance and molecular mobility.

Keywords: antioxidant, polystyrene, radical, π-stacked conformation

References
Preferred Crystal Orientation of Melt-crystallized Biobased Polyesters in Thin Films on Si Substrates

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Abstract

Preferred crystal orientation is one of characteristic phenomena of crystalline polymer thin films with thicknesses below 1 \( \mu \)m. However, influential factors on crystal orientation have been still under discussion for the thin films in which polymer chains in the crystal and amorphous states coexist to form the hierarchical structure. In order to control mechanical/functional properties of polymer thin films, the hierarchical structure in the thin films should be controlled on the molecular and lamellar scales. In this study, crystal orientation of biobased poly(3-hydroxybutyrate-co-3-hydroxyhexanoate) (PHBH) thin films on Si substrates was precisely evaluated by grazing-incidence wide-angle X-ray diffraction (GIWAXD) measurements using synchrotron radiation. Also, thermodynamic effects on crystal orientation in nucleation in the PHBH/substrate interface were investigated for the films.

Samples used in this study were biobased poly(3-hydroxybutyrate) (P3HB) (SigmaAldrich Co., \( M_n=1.20\times10^5, M_w/M_n=4.50 \)) and PHBH having 3.2, 5.4, 5.8, 7.0 and 10.4 mol\% of uncrystallizable 3HH (Kaneka Corp., P3HB-3 (\( M_n=8.12\times10^5, M_w/M_n=3.22 \)), P3HB-5 (\( M_n=6.54\times10^5, M_w/M_n=3.31 \)), P3HB-6 (\( M_n=3.57\times10^5, M_w/M_n=2.86 \)), P3HB-7 (\( M_n=4.06\times10^5, M_w/M_n=3.32 \)) and P3HB-10 (\( M_n=4.13\times10^5, M_w/M_n=2.01 \)), respectively). Thin films with thicknesses of ca. 300 nm ~ 1 \( \mu \)m were prepared on Si substrates by a spin-coating method with 1.5 ~ 4.0 wt\% P3HB or PHBH in chloroform. The obtained films were isothermally crystallized at \( T_c = 295, 343, 363 \) and 383 K from the melt under a nitrogen atmosphere.

GIWAXD patterns measured for the films indicated that crystal orientation changed depending on the 3HH content in PHBHs. For PHBHs having the lower 3HH content, lamellae having the flat-on type, edge-on type and flat-on/edge-on biaxial-type orientation appeared depending on \( T_c \). On the other hand, for P3HBs having the higher 3HH content, the edge-on type lamellar orientation was dominant, which was independent of \( T_c \). The surface tension of the chain-folded surface and the lateral plane of a lamellar crystal were estimated from the reference data.\textsuperscript{2, 3} As a result, it was suggested that thermodynamic driving force near the substrate surface was of significance on lamellar orientation in P3HB thin films. However, another influential factor as well as thermodynamic driving force should be taken into consideration to explain preferred crystal orientation of PHBHs.

Keywords: Poly(3-hydroxybutyrate-co-3-hydroxyhexanoate), thin film, preferred lamellar orientation, surface tension, interface effect


Acknowledgment

This research was partly supported by CREST of JST, JSPS KAKENHI Grant Number 26410135 and the Cooperative Research Program of "Network Joint Research Center for Materials and Devices". The synchrotron radiation experiments were performed at BL45XU in SPring-8 with the approval of RIKEN (Proposal No. 20150076, 20160041, 20170094).
Characterization and Properties of Polymer Thin-Film Based on Poly(acrylic acid) and Lithium Perchlorate

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Abstract

The development of polymer electrolytes has attracted significant interest in recent decades because of their special and potentially useful features, including solvent-free, renewability, flexibility, eco-friendliness and low in weight. Novel polymer electrolytes based on poly(acrylic acid) and lithium perchlorate were prepared via solvent casting method. The characterization study provides with new findings on poly(acrylic acid)-lithium perchlorate based electrolytes, including preparation methods, electrical, electrochemical, structural, and thermal properties. Ionic conductivities of the polymer electrolytes was examined by electrochemical impedance spectroscopy. The best conductivity obtained at room temperature was found to be $2.4 \times 10^{-6}$ S cm$^{-1}$ for the polymer electrolyte with 10 wt.% of LiClO$_4$. Evaluation of electrochemical stability window was carried using linear sweep voltammetry. The results display a wide stability window of 10.5 V at ambient temperature. Higher amorphous region in the polymer electrolyte matrices was demonstrated with X-ray diffraction. The thermal stability of poly(acrylic acid)-based electrolytes was studied by thermogravimetric analysis. The information of the properties of this novel polymer electrolyte is important for the future design and assembly of new electrochemical devices.

Keywords: Polymer electrolytes, Poly(acrylic acid), Lithium perchlorate, Ionic conductivity, Electrochemical stability window

References

Additive manufacturing of polymeric microreactors for continuous flow synthesis

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Abstract

Continuous flow chemistry is making an inroad into manufacturing of fine chemicals and pharmaceuticals, owing to higher material and energy efficiency, simpler process control and increased safety compared to batch processing¹. Due to low manufacturing volumes of high-value products, milli- and micro-reactors are gaining more attention and are being considered for various applications. For the purpose of screening for potential applications and testing of different reactor dimensions and configurations, fast and cost effective prototyping is key to this process. Additive manufacturing based on polymeric materials, also known as 3D printing, is an ideal candidate for the purpose. The aim of this study was to examine the possibilities of two additive manufacturing technologies – fused filament fabrication and stereolithography, for manufacturing of functional microreactors with biodiesel synthesis as a case study.

Commercially available transparent filaments of a variety of polymers can be used for producing microreactors by fused filament fabrication. Chemical compatibility of filaments in contact with reactants and reaction products is an important property to be investigated before using the material, and polypropylene based filaments were selected as the most suitable material for biodiesel synthesis. Microreactors with quadratic cross-section of microchannels of different sizes were made and tested. Stereolithography has shown greater resolution, and was able to produce reactors with much smaller details compared to fused filament fabrication. The main limitation of stereolithography for microreactor prototyping was the inability to drain residual, uncured resin from the microchannel.

The microreactors with closed channel dimensions of 400 μm x 400 μm were successfully created by fused filament fabrication and tested for biodiesel production, maintaining structural integrity and transparency in reaction conditions.

Additive manufacturing has proven to be a useful tool for rapid prototyping of microreactors, where channel configuration and dimensions can easily be optimized for a particular application.

Keywords: microreactors, additive manufacturing, biodiesel synthesis

References


Acknowledgement

This work has been supported by Croatian Science Foundation under the project entitled “Development of materials for 3D printing of microreactors” (UIP-2014-09-3154).
Synthesis of Minor Flavonoids and Their Effects on Prostaglandin E\textsubscript{2} and Nitric Oxide Production in LPS/IFN-\gamma Stimulated Murine RAW 264.7 and Human U937 Cell

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Abstract

Secondary metabolites in plants such as flavonoids and their close analogues are a robust source of leads for drug discovery. In the present study, a total of seventy-six minor flavonoids have been successfully synthesized and characterized. Some of the compounds are novel, for example prenylated chalcone and prenylated aurone which have structural similarity to natural products such as broussochalcone A and artocarpuarone. The ability to procure sufficient quantity of molecules in natural product synthesis by simple and scalable routes was an important goal that has been achieved in this study. The optimization of prenylated chalcone was carried out via the [3, 3]-sigmatropic rearrangement followed by aldol condensation, while prenylated aurone was obtained in the subsequent step via the oxidative cyclization by mercury(II) acetate, Hg(OAc)\textsubscript{2}. Further experiments revealed that prenylated chalcone decreased the prostaglandin E\textsubscript{2} (PGE\textsubscript{2}) and nitric oxide (NO) secretion levels in murine macrophage cell line, RAW 264.7 cells. To ensure that the efficacy of synthesized compound was not limited to murine, the experiment was repeated using the human U937 cells. Remarkably, the compound displayed a comparable IC\textsubscript{50} value with murine cell. In the subsequent experiment, the molecular docking simulation allowed us to gain a deeper understanding on the plausible binding interactions between the compounds with COX-2 and mPGES-1 which is the essential enzymes in regulating prostanoid biosynthesis to transform of arachidonic acid (AA) into PGE\textsubscript{2}.

**Keywords:** minor flavonoids, prostaglandin E\textsubscript{2}, COX-2 inhibitor, docking studies

References

Effect of Water Blanching of Biological and Physicochemical Properties of Sweet Potato Slice

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Abstract

In this study, effects of blanching temperature and treatment time on biological and physicochemical properties of sweet potato (IMPOMOEA BATATAS L.) were investigated. Sweet potato was cut into cylindrical shape (29 mm in diameter, 15 mm in length). First, peroxidase activity was tested to determine temperature and time of completing of blanching (80; 90; 94; 96; 98°C for heating time 3; 5; 7; 10 minutes and cooled down in ice-water for 5 minutes before testing). Second, effect of low temperature blanching (50; 55; 60; 65; 70°C for 20; 40; 60 minutes and cooled down in ice-water for 5 minutes before testing) on pectin methyl esterase (PME) activation was estimated. Then, effect of combination of low and high temperature blanching on quality of sweet potato slice such as: texture, moisture, total soluble solid (°brix), total color change of sweet potato slice were studied.

The result showed that activity of peroxidase rapidly inactivated about 95% at 96°C for 5 minutes. PME was optimum activity at treated temperature at 60°C for 40 min, but declined rapidly from 60 minutes. The firmness of sample reached a peak point after 60 minutes at 60°C. Pre-heating at 50-70°C with treated time (20, 40, 60 minutes) significantly increased firmness of sample after blanching at 96°C for 5 minutes as compared to control sample. The moisture content obtained at 60°C for 20 to 40 minutes that were lower than that of other treatments, the total soluble solid (°brix) increased significantly from pre-heating treatment samples at 60°C for 20 minutes, Changes in color of sample blanched at 60°C for all heating time was less than other treatment conditions. Hot water blanching affected the sample in decreasing bright (L\textsuperscript{*}), changing hue to yellowish (b\textsuperscript{*}), and (a\textsuperscript{*}) decreased change to gloomy.

The low temperature blanching has a greater affect on firmness, total soluble solid losses, and total color change retention.

Keywords: sweet potato, firmness, blanching, pectin methyl esterase, peroxidase
Organometallic Antitumor Compounds: A new generation of Ferrociphenols

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Abstract

Bioorganometallic chemistry is a field of research that encompasses organometallic compounds in biology and medicine. This field has become increasingly popular owing to the good therapeutic activity of several organometallic compounds. We have shown that some ferrocene derivatives are very active against cancer cells. For example, hydroxyferrocifen, resulting from replacement of a phenyl group of hydroxytamoxifen, 1, with a ferrocenyl moiety, and ferrociphenol 2, display a dramatic improvement in cytotoxicity toward MDA-MB-231 cells (IC\textsubscript{50} = 0.5 \mu M and 0.64 \mu M, respectively).\textsuperscript{1,2}

We have developed a new generation of ferrocifen derivatives with strong antiproliferative activity. In particular, the hydroxypropyl derivative 3b exhibited exceptional antiproliferative activity against the cancer cell lines HepG2 and MDA-MB-231 TNBC, with IC\textsubscript{50} values of 0.07 and 0.11 \mu M, respectively.\textsuperscript{3-6}

We here present the syntheses of these new compounds, and their active metabolites. We found that the oxidation of compounds yields two kinds of quinone methides that readily react with nucleophiles such as glutathione.

Keywords: Bioorganometallic chemistry, ferrocene, anticancer agents, ferrocifen, quinone methide,

References

Measure of Regression Model Accuracy for Quantitative Structure-Activity (Property) Relationship Considering Applicability Domains

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Abstract

Several supervised learning methods for regression are used in chemometrics and data analysis, such as quantitative structure-activity relationship (QSAR) and quantitative structure-property relationship (QSPR) models. In QSAR, descriptors or explanatory variables $X$ that quantify molecular structures are calculated for a set of compounds for which the activity or an objective variable $y$ is known, that is, supervised data. A statistical model $y=f(X)$ is then constructed between $X$ and $y$ using a data set. By using the obtained model, it is possible to estimate activity for novel and even virtual chemical structures.

The coefficient of determination and the root-mean-squared error (RMSE) evaluate regression models for test samples without considering the applicability domains (ADs)\textsuperscript{1} of the models. ADs are data domains where models exhibit sufficient predictive performance for training samples and thus for new samples. In this study, a new measure for evaluating the predictive performance of regression models that considers their ADs was proposed. The purpose is not selecting the best regression model among various competing models, but determining an appropriate model group corresponding to the AD of each model. The proposed measure is the area under coverage and RMSE curve for coverage less than $p\%$ ($p\%$-AUCR\textsuperscript{2}) (please see Figure 1). It is confirmed that some regression models have global predictive ability and others have local predictive ability, and $p\%$-AUCR is an appropriate indicator for selecting between local and global regression models depending on the coverage and considering the AD. Selecting a regression model for each sample or each chemical structure using $p\%$-AUCR can improve the prediction accuracy of data sets.

The proposed $p\%$-AUCR can be used to select an appropriate model for each given samples in prediction, and then, model interpretation will be required to the selected models for diverse compounds.

Keywords: regression, measure, applicability domain, predictive performance, QSPR, QSAR

![Figure 1. The idea of $p\%$-AUCR for a coverage and RMSE curve\textsuperscript{1}.](image)

References

Creation of High Activity Water-Splitting Photocatalyst using Au25 cluster Cocatalyst

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Abstract

Our aim in this work is to activate a photocatalytic material which could be used as a practical material using gold cluster cocatalyst. Therefore, in these studies, we used BaLa₄Ti₄O₁₅ as the photocatalytic material because it is one of the most advanced water-splitting photocatalytic materials. We synthesized glutathione (SG)-protected Au25(SG)₁₈, and these clusters were subsequently adsorbed onto the surface of a BaLa₄Ti₄O₁₅. Au25 was subsequently loaded onto the BaLa₄Ti₄O₁₅ by removing the ligands through calcination. Various characterizations confirmed that almost none of the Au25 aggregates on the BaLa₄Ti₄O₁₅ surface and that majority of these ligands are removed. However, photocatalytic activity of obtained Au25-loaded BaLa₄Ti₄O₁₅ (Au25-BaLa₄Ti₄O₁₅) did not change compared with that of Au nanoparticle loaded BaLa₄Ti₄O₁₅ (Au25- BaLa₄Ti₄O₁₅). We revealed that the reason of this phenomenon is due to promotion of oxygen reduction reaction by Au25 cocatalyst. To suppress this reaction, we coated Au25 cocatalyst with chromium oxides (CrₓOᵧ) which oxygen can not penetrate. Then, we could succeed in suppressing this reaction and creating water-splitting photocatalytic material with high activity (Figure 1). This indicates that the use of Au25 cocatalyst coated by CrₓOᵧ as cocatalyst is effective method to increase photocatalytic activity. In addition, it was also demonstrated that aggregation of Au25 cocatalyst after photocatalytic reaction is suppressed by this method.²

Keywords: gold cluster, photocatalyst, cocatalysts, water-splitting photocatalytic reaction

References
Triphosphasumanenes: Janus-Type $\pi$-Conjugated Molecules and Their Out-of-Plane Anisotropy

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Abstract

Anisotropy in $\pi$-conjugated molecules is an important concept related to a variety of intriguing physical phenomena such as non-linear optics, molecular recognition, and molecular alignment at interfaces. In-plane electronic anisotropy, which originates from facile functionalization at the periphery of $\pi$-frameworks, usually results in a dipole moment parallel to the $\pi$-surface. Conversely, few molecules possessing out-of-plane anisotropy have been reported because of the limited synthetic methods to functionalize the front/back side of the $\pi$-surfaces. In this work, we designed and synthesized triphosphasumanene trisulfide (1), which three anisotropic phosphine sulfide moieties were incorporated into a heterasumanene skeleton. The out-of-plane anisotropy in 1 resulted in a large dipole moment (12.0 D) and affected the molecular packing of 1 and the interface between 1 and an Au surface.

Keywords: Heterasumanenes, Janus-type molecules, Out-of-plane anisotropy, Phospholes, metal-organic interfaces

References

Engineering of Phosphorus Metabolic Pathway: A Safeguard Strategy for Greater Use of Genetically Modified Microorganisms

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Abstract

Owing to the rapid evolution of biotechnology, genetically modified microorganisms (GMMs) hold great promise for the use in various application fields such as therapeutics, environmental clean-up, and agriculture. However, the scientific community still needs to resolve a number of biosafety and biosecurity issues to obtain regulatory approvals and ensure public acceptance for the use of GMMs in the open environment. A possible way to prevent the uncontrolled proliferation of GMMs is through biocontainment, which commonly involves modifying the essential genes in order to make the growth and survival of microorganisms dependent on the exogenously supplied chemicals. Here, we developed a novel, simple and cost-effective biocontainment strategy based on re-engineering the phosphorus metabolism of bacteria. Our approach combines the deletion of endogenous phosphate (H\textsubscript{3}PO\textsubscript{4}, Pi) transporters with the expression of the genes for metabolizing reduced phosphorus compounds, yielding an \textit{Escherichia coli} strain strictly dependent on the availability of phosphite (H\textsubscript{3}PO\textsubscript{3}, Pt) which is an ecologically rare but inexpensive chemical. Considering the extremely high containment efficacy and the simplicity of required genetic modifications, this strategy can contribute to the development of a reliable and cost-effective biocontainment system that enables highly secure and practical applications of GMMs.

\textbf{Keywords:} biotechnology, genetically modified microorganism, phosphite, biological containment

References

Symmetry Projection Approach for Strongly Correlated System

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Abstract

The precise calculation of electronic state for strongly correlated system such as multinuclear-transition complexes requires a large computational resource because the dimension of the Hilbert space to be considered increases exponentially with respect to the number of atoms. Broken-symmetry unrestricted Hartree—Fock (BS-UHF) and Kohn—Sham (BS-UKS) have been used routinely for large molecules with strong correlation\textsuperscript{1}, because these methods account for vast amounts of nondynamic correlation at the mean-field computational costs. A symmetry-breaking lowers the total energy as increase in the degrees of variational freedom, but the ambiguous electronic structure of such a BS scheme often leads to qualitatively incorrect optimal geometric structures and molecular properties.

The proper symmetries of a BS wavefunction can be restored by the symmetry projection prescriptions. Projected Hartree—Fock (PHF) method\textsuperscript{2} restores the symmetry of BS electronic states at the mean-field computational cost, retaining the description of nondynamic correlation. Among the possible symmetry projections, the spin-projected unrestricted Hartree—Fock (SUHF), which restores spin-symmetry exactly from a single spin-unrestricted Slater determinant, is especially promising. The variational optimization of the projected determinant, viz., the VAP-SUHF scheme, has been adopted to overcome the ill behavior of spontaneous symmetry breaking originating from the transition between degenerate/non-degenerate electronic states. However, the VAP scheme sometimes fails to converge in the self-consistent field (SCF) procedure or to locate the most stable solution for large molecules with the direct inversion of iterative subspace (DIIS) procedure, because of the presence of small eigenvalues in the orbital Hessian, that often appear in SUHF. Recently, we developed a quadratically convergent SCF (QCSCF) scheme to achieve convergence quickly.

We describe the PHF theory and its application to the multinuclear systems\textsuperscript{3}, where the static correlation is abundant. We also show that the QCSCF for SUHF is helpful to achieve convergence for the strongly correlated system.

Keywords: Quantum Chemistry, Spin projection, Point Group, QCSCF, Strong Correlation

References

Design and Syntheses of Ion-Conducting Metal-Organic Frameworks

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Abstract

Proton conductivity in solids is of importance not only for useful applications such as fuel cells but also for better understanding of the nature of proton-transport phenomena. Recently, metal–organic frameworks (MOFs) have been emerged as a novel class of proton-materials because the ability to rationally design and chemically tune their architecture allows chemists to establish various methods to control the proton conductivity. We have proposed three types (types I–III) of concepts to give high proton conductivity to MOFs. In type I, proton carriers are introduced as counterions into the pores (e.g., H$_3$O$^+$). In type II, acidic groups are placed on the framework (e.g., –COOH). In type III, charge-neutral proton-conducting species are incorporated within the pores (e.g., H$_3$PO$_4$).

We have synthesized (NH$_4$)$_2$(adp)[Zn$_2$(ox)$_3$]·3H$_2$O (adp = adipic acid; ox = oxalate), having both type I and type III features; (NH$_4$)$_2$(adp)[Zn$_2$(ox)$_3$]·3H$_2$O shows high proton conductivity because of the existence of two-dimensional (2-D) hydrogen-bonding networks which act as a crystalline proton-conducting pathways. Intentional control of proton conductivity and the proton dynamics in this MOF has been also studied.

On another front, hydroxide-ion conductors have received a great deal of interest as electrolytes for alkaline fuel cells that can operate without precious metal catalysts such as Pt. We have also focused on creating novel hydroxide ion conductors using the MOFs. We proposed a new strategy to introduce hydroxide ions into MOFs, i.e., which is “hydroxide salt inclusion into alkaline-stable MOFs”. We succeeded in synthesizing a novel MOF including alkylammonium hydroxide salt by employing an alkaline-stable ZIF-8\textsuperscript{5} framework (NBu$_4$-ZIF-8-OH) (Figure 1).\textsuperscript{6,7} Ionic conductivity of NBu$_4$-ZIF-8-OH was found to be 2.3 × 10$^{-8}$ S cm$^{-1}$ at maximum, which is four orders of magnitude higher than that of blank ZIF-8. Considering that the framework structure of NBu$_4$-ZIF-8-OH is the same as that of ZIF-8, the enhancement in the ionic conductivity can be attributed to the included salt.

**Keywords: **Metal-Organic Framework, Ionic Conduction

References

Rule Extraction and prediction for Ignition Point using Decision Tree and Random Forest

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Abstract

Ignition point is the temperature at which a chemical compound begins to burn naturally. From the viewpoints of industry and safety, the ignition point is one of the important values. Computational approach for chemistry, “Chemoinformatics”, has already tried to predict ignition point and got fine result, but the relationships between ignition point and molecular structure are still not clear.

I report the results of rule extraction and prediction for the ignition point of simple chemical compounds including carbon, oxygen and hydrogen only using data mining technique such as decision tree and random forest. I used fundamental material values and the number of characteristic structures as descriptors. The learning data includes 264 kinds of chemical compounds and the test data includes other 30 kinds. I used “rpart” and “randomForest” packages of the “R”, one of the statistical programming languages, in order to use decision tree and random forest. As the result, I got five rules for ignition point and their importance ranking using decision tree. The rules are mainly known empirically, but the importance ranking of them was unknown. I also got prediction results, but the accuracy was inadequate. Using random forest, I got better prediction results.

Keywords: data mining, ignition point, organic compound, functional group, descriptor

References

Nucleophilic-Type Ring Transformation: A Powerful Synthetic Tool

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Abstract

The ring transformation has been widely used in organic synthesis. While Diels-Alder-type and degenerated-type ring transformations have been energetically studied, nucleophilic-type ring transformation has not been studied well, which prompted us to study this third type ring transformation.

Highly electron-deficient 1-methyl-3,5-dinitro-2-pyridone and 3-methyl-5-nitro-4-pyrimidinone serve as excellent substrates. Reactions of these substrates with enolates of 1,3-dicarbonyl compounds afforded difunctionalized nitrophenols and 4-pyridones, respectively. In these cases, dinitropyridone serves as a synthetic equivalent of unstable nitromalonaldehyde, and nitropyrimidinone serves as that of activated diformylamine.

When dinitropyridone was treated with simple ketones in the presence of ammonium acetate as a nitrogen source, three-component ring transformation proceeded to afford 4-nitropyridines and nitroanilines. In addition, diazabicyclic compounds were also obtained. On the other hand, three-component ring transformation of nitropyrimidinone furnished 4,5-disubstituted pyrimidines and 3,5-difunctionalized 4-aminopyridines. Furthermore, a novel type ring transformation was also found, which leading to 5,6-disubstituted 3-nitro-2-pyridones. In this reaction, nitropyrimidinone serves as a synthetic equivalent of \( \alpha \)-nitroformylacetic acid.

As mentioned above, nucleophilic-type ring transformation facilitates the synthesis of polyfunctionalized aza-heterocyclic compounds that are not easily available by alternative methods.\textsuperscript{1} Hence, this method will be a powerful synthetic tool for organic chemists.

Keywords: Ring transformation; Aza-heterocyclic compounds; Dinitropyridone; Nitropyrimidinone

References

Psychological Well-being of Students in context of Education and Career

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Abstract

This study addresses students’ proactive attitudes in context of education and career. For the purpose of this study, the psychological well-being of adolescents is defined as having the “…ability to cope with life’s challenges, to accept others and most of all, to have a positive attitude towards oneself” (Malaysian Mental Health Association, 2008-2011, p.5). In this study, psychological well-being is indicated by proactive attitudes. It is recognized that students with proactive attitudes hold beliefs about their abilities to initiate activities such as, setting attainable goals for education and career. In addition, students’ proactive attitudes support their psychological well-being that enhances attainment of education and career goals in a changing environment. This study measured students’ proactive attitudes so as to provide insight to facilitate students’ attainment of education and career goals. In this study, a purposive sample (n = 100) comprising lower secondary school students was drawn from a Malaysian Chinese Independent (private) school situated in Johore, Malaysia. Using the survey research method, this study administered Prof. Schwarzer’s Proactive Attitude Scale. Results show that the students’ proactive attitudes as having the mean of 2.91 (maximum of 4; SD = .517). Underlying these results are uncertainties related to spending time identifying long-range goals (mean = 2.51; SD = .859) and unsure of being in charge to make things happen (mean = 2.43; SD = 1.037). However, these students expressed proactive attitudes as shown in having responsibility for their own life (mean = 3.40; SD = .791) and having the ability to choose their own actions (mean = 3.09; SD = .897). In general, these students indicated moderate proactive attitudes. These findings and their implications on attainment of psychological well-being are discussed in context of education and career.

Keywords: Proactive attitudes, psychological well-being, career

Acknowledgement

Note: This study is a part of the on-going Learning Enhancement Project among students of Chinese Independent Schools funded by HELP Department of Psychology and HELP University, Kuala Lumpur. The authors gratefully acknowledged the private secondary school administrators, counsellors, teachers and students for their assistance in data collection.
Recent Advances in Materials Simulations and Informatics

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Abstract

Since the US government launched “Material Genome Initiative” in 2011, Materials Informatics (MI) has attracted enormous attention all over the world. Utilizing big data (database) combined with first-principles/\textit{ab initio} simulations, high throughput virtual screening approaches based on machine learning efficiently explore (known) material databases for desirable materials whose properties had been unknown (neither computed nor experimentally observed). Although one of the most attractive issues in MI is computational exploration of novel materials (unknown compounds and structures) with desirable properties, the virtual screening cannot intrinsically create such materials \textit{in silico}. Computational materials design is an inverse problem of property prediction for a given structure. This problem is known to be quite hard to be solved because on-demand materials would be hidden in the huge material space including more than 10\textsuperscript{60} compounds, though we only know 10\textsuperscript{8} compounds at most therein.

To tackle this problem, we have recently proposed a new computational approach based on a good combination of Bayesian statistics, big data, and first-principles simulations [1]. The Bayesian approach efficiently creates/proposes new compounds and samples candidate compounds with preset properties according to a posterior distribution consisting of likelihood (regression/machine learning) multiplied by a prior distribution (Bayes’ law). Although this stochastic approach is very useful to explore new materials, from the viewpoint of reliability statistics/machine learning itself is not good at predicting properties for the new materials located outside the existing data, \textit{i.e.}, extrapolation in which simulations have a definite advantage over statistics/machine learning alone. In this sense, advances in simulations are also important to enhance the reliability of MI and to extend its applicability. In this talk, I will present not only our recent MI projects, but also our recent achievements in first-principles simulations [2-7] towards MI.

Keywords: Materials simulations, Quantum Monte Carlo, Density Functional Theory, Materials Informatics, Bayesian Statistics

References

Synthesis of Nanosheet Photocatalysts and Their Applications

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Abstract

Photocatalytic oxidation and reduction reactions occur on the material surfaces by the photo-generated hole and electron, respectively. So, it is important point to synthesize the materials with a large reaction area. Among the various photocatalysts, oxide and hydroxide nanosheets are unique two-dimensional crystallites with high aspect ratios and flat surfaces, and it has a lot of attention because of wide band gap and high energies of excited charge carriers. Moreover, almost all framework of MOx and M(OH)x are present very close to the surface. This is advantage for photocatalytic reaction because the distance between the photo-generated site and the reaction site is short. Recently, we had successfully prepared the photocatalytic glass for vehicles and synthesized the photocatalytic water splitting and CO2 reduction materials by using a nanosheet structure. In this presentation, I would like to introduce the photocatalytic materials using nanosheet structures.

Glasses with self-cleaning performance were prepared by coating Nb2O5 nanosheets. The glasses showed good optical transparency and hardness by heating at more than 450°C because the flake shape has advantages in realizing of low turbidity, excellent adhesion and high hardness. The resulting coating glasses exhibited photoinduced hydrophilicity under UV irradiation but low photocatalytic oxidation activity. Photocatalytic glass for vehicles had been successfully prepared by using nanosheets. Then, we have synthesized (Rh, Ru) doped Nb2O5 nanosheets, and evaluated water splitting activity. (Rh, Ru) co-doped Nb2O5 (Nb2.975Ru0.010Rh0.015O8) nanosheet (220 µmol/h) exhibited drastically higher hydrogen evolution than non-doped Nb2O5 (0.67 µmol/h). Additionally, (Rh, Ru) co-doped Zn2Cr layered double hydroxide (LDH) exhibited higher performance for the photocatalytic conversion of CO2 to CO under UV irradiation, comparing to non-doped LDH. The amount of CO evolved for (Ru, Rh)-doped Nb2O5 and Zn2Cr LDH are present very close to the surface, it plays a role in the catalytic reaction in the same way as co-catalyst loading. These results are obtained by using the characteristics of nanosheet structures, and it can be expected that photocatalytic materials with nanosheets have future growth potential. Finally, I would like to introduce about a mosquito catcher using photocatalyst.

Keywords: Photocatalysis, Nanosheet structure, Self-cleaning, Mosquito catcher

Acknowledgement

This work was financially supported by “a Grant-in-Aid for Young Scientists (A; 25708037)” and “a Grant-in-Aid for Challenging Exploratory Research (15K14118)” from Japan Society for the Promotion of Science (JSPS), and Joint Usage/Joint Research Center at Tokyo University of Science.

References

Laser Ionization Time-of-Flight Mass Spectrometry for the Analysis of Emulsions

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Abstract

An emulsion is a mixture of two or more immiscible liquids in which one is dispersed as droplets. The condition of an emulsion is easily changed, e.g., creaming, flocculation, and coalescence. Emulsions are used in a wide range of applications, such as food and cosmetics, and, therefore, it is important to evaluate the stability of emulsions.

Laser ionization time-of-flight mass spectrometry (LI-TOFMS) is a selective analytical means for the measurement of aromatic hydrocarbons. This method LI-TOFMS is mainly applied to the measurement of gaseous samples. We recently reported a technique for the introduction of a solution into TOFMS.\textsuperscript{1} Using this technique, an online monitoring of emulsion samples was demonstrated.\textsuperscript{2-4} By using LI-TOFMS, we continuously obtained a series of mass spectra, and then constructed a time profile of the peak area of a constituent. We reported the possibility that this method could be used for evaluating creaming of the emulsion. Moreover, we demonstrated the possibility of a quantitative analysis of an oil component in an emulsion via LI-TOFMS.\textsuperscript{5} Furthermore, we applied this method to the direct measurement of analytes in a multiple emulsion.\textsuperscript{6} LI-TOFMS has several advantages such as selectivity and robustness. Therefore, this method can be suitable for the evaluation of the stability of emulsions that have been inherently high concentration of each constituent.

Keywords: LI-TOFMS, emulsion, creaming, multiple emulsion

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Remediation of 2,4,6-trichlorophenol Contaminated Wastewater Using TiO2 Photocatalysis: Parametric & Kinetic Studies

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Abstract

Photocatalysis using TiO2 was employed in the treatment of 2,4,6-trichlorophenol. The effect of different parameters including different wavelengths, initial concentrations, TiO2 dosages and initial pH on the degradation efficiency of 2,4,6-TCP were investigated. The degradation efficiency of 2,4,6-TCP was found to increase in proportional to the increased of the TiO2 dosage and initial pH of the solution. While this efficiency decreased accordingly with the increase of initial concentration and irradiation wavelength. UV-C exhibited the highest degradation rate (88.12 %) compared to UV-B, UV-A and solar. The highest experimented photocatalyst dosage (0.08 mg/mL), achieved the best degradation effect (97.09%). Alkaline solution condition, pH 10.0, gave the best degradation rate, followed by pH 7.0 and acidic condition, pH 4.0. Degradation of 2,4,6-TCP using TiO2 achieved remarkable reduction in COD. The photo degradation of 2,4,6-TCP followed the first order reaction kinetic and was successfully carried out.

Keywords: 2,4,6-TCP, TiO2, photocatalysis

References

Adsorption behavior of organoarsenic compounds in soils

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Abstract

Anthropogenic originated organoarsenic compounds such as diphenylarsinic acid (DPAA) are a water pollution source as well as naturally occurring inorganic ones. For example, DPAA polluted well water caused serious health problems in Kamisu, Japan. However, their adsorption mechanisms in soils is still unknown. The adsorption property of chemical compounds influences its migration process in natural environments such as soil-water system. Thus, it is important to understand the adsorption behaviors of the arsenic compounds to predict the future fate of the compounds in environment. Fe- and Al-(oxyhydr)oxides have been known as good sorbents of inorganic arsenic compounds. Recently, we reported adsorption structures of phenyl-organoarsenic compounds on ferrihydrite obtained by X-ray absorption fine structure (XAFS) analysis and quantum chemical calculations.1

In this study, we report adsorption behaviors of methyl- and phenyl-organoarsenic compounds in soils based on the adsorption experiments for synthesized minerals and several soils, and analyses by ICP-MS and As K-edge XAFS measurements. We will discuss the host phase of these arsenic compounds in soils and the factors to determine the affinity of arsenic compounds to the sorbents in the soils.

Keywords: organoarsenic, XAFS, adsorption, Fe/Al-(oxyhydr)oxides, soil

References

Orientation dependent FRET as a tool to analyze DNA structures

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Abstract

Förster resonance energy transfer (FRET) is a physical phenomenon in which excited energy of a donor fluorophore is transferred to an acceptor. FRET is widely utilized for studying the structure and interactions of biomacromolecules such as proteins and nucleic acids, since FRET efficiency strongly depends on both distance and orientation between a donor and an acceptor. However, most of previous FRET studies utilized only distance dependence of FRET due to the difficulty in precise control of dye orientation.

We have developed novel FRET system by incorporating a donor and an acceptor into DNA through D-threoninol scaffold.\textsuperscript{1} The “FRET plot”, which shows dependence of FRET efficiency against the number of base-pairs between fluorophores, demonstrated distinct orientation dependence reflecting structural parameters of DNA duplex. In other words, it is possible to obtain structural information of double-helical structures in solution by measuring FRET efficiencies (Fig. 1). Hence, the FRET system can be used for structural analyses of various kinds of nucleic acid structures.

We here analyzed DNA duplexes containing nick or gap structure by using our orientation-dependent FRET system. Structural differences of nicked and gapped DNA duplexes were successfully analyzed.\textsuperscript{2} Since structural information of double helical structures in solution can be easily obtained with this method, we are now applying this method to the investigation of various kinds of DNA structures.

Keywords: DNA, FRET, pyrene, perylene

References

The Invisible Emerging Pollutants

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Abstract

About 71\% of the earth’s surface is covered with water. However, most of the water about 97\% is salt water, while of the remaining fresh water, 2\% is frozen in glaciers. So, in reality only 1\% fresh water can be utilized by humans. The flowing fresh water is used for agriculture (87\%), industry (10 \%) while domestic usage is only 3\%. In the world that is ever expanding in terms of population, the demand for clean and safe water is increasing. Rapid pace of development coupled with the effects of climate change has changed the scenario of water supply and management in many parts of the world. The current supply of fresh water in Malaysia as feeders to water treatment plants is under threat from a host of pollutants. Frequently, treatment plants have to shut down due to high ammoniacal nitrogen content, high manganese and high iron. Apart from these well known pollutants there is also a new type of pollutants known as emerging pollutants. Emerging pollutants can be defined as “entering into or being generated in the environment in appreciable amounts” with a “modicum of persistence” and “exhibit deleterious effects on organisms”. Generally, two big groups of chemicals fall within the definition of emerging pollutants namely pharmaceuticals and personal care products. Some of these pharmaceuticals and personal care products are also endocrine disruptors, which are capable of disrupting chemical signaling mechanisms controlling cellular development. The primary mode of entry into the rivers is through sewage which carries the excreta of humans, and from agricultural runoff containing livestock manure. Pharmaceuticals in particular which are not be fully utilised by humans or animals thus, will be excreted through the urine or faeces. Flushing of unused medicine is of minor importance. The study on the occurrence and distribution of pharmaceuticals in aquatic environment in Malaysia is still limited. However, research done by our team indicated the presence of some pharmaceuticals such as acetaminophen, caffeine, prazosin, carbamazepine, nifedipine and simvastatin in surface water and some in sewage treatment plant effluent. The way forward is to analyse for these emerging pollutants in our rivers. As we are geared to a high-income nation status by 2020, we must also incorporate latest techniques utilizing ozonation in our sewerage and water treatment plants to remove these potentially harmful pollutants. Finally, the irony of this phenomenon us that in this modern world that we live in, drug therapy has become a way of life to improve health. However, these drugs are re-entering our eco-system through our waters causing potentially adverse effects.

Keywords: Emerging pollutants, water quality, pharmaceuticals, treatment, sewage
Classification of Bird’s Nest by State Using Isotope Ratio Mass Spectrometry

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Abstract

The feasibility of using isotopic ratio mass spectroscopy (IRMS) to classify the Edible bird’s nest (EBN) according to its geographical origin was investigated. The Malaysian EBN is bird nest made from the saliva of swiftlet species. Here, the study aimed to determine the carbon, nitrogen, hydrogen and oxygen isotope ratios of EBN obtained from different parts of Malaysia and develop a suitable statistical model to classify the EBN by states. A total of 164 raw EBN samples from Johor, Kelantan, Perak, Terengganu, Sarawak, Labuan, Sabah and Penang were analysed using IRMS. The data were processed using multivariate analysis, namely cluster, principal component and discriminant analyses, enabling classification according to states (geographical origin) with satisfactory accuracy. The study demonstrated that the methodology has good potential in identifying the geographical origin for EBN cultivated at different locations. However, the model still needs to be further validated using more data as this was only a preliminary investigation based on limited number of samples and analyses.

Keywords: Bird Nest, IRMS, Geographical Origin, Multivariate Analysis
Electrochemical Detection of Antioxidants BHA, BHT and TBHQ in food samples using Graphite Nanocomposite Green Electrochemical Sensors

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Abstract

Butylated hydroxyanisole (BHA), butylated hydroxytoluene (BHT) and tert-butylhydroquinone (TBHQ) are antioxidant additives used in food. Consumption of these compounds at high concentration of above 3000 µg g⁻¹ in food could possibly promote cancer proliferation in cell. Thus, monitoring of these compounds in food is important. In this present study, an electrochemical method using a gold-nanoparticles graphite electrode has been proposed. It has been demonstrated that with surface modification on the graphite electrode, the 3 antioxidant compounds were successfully separated by a linear sweep voltammetry (LSV) method; and subsequently used in the quantitative analysis of various food products including oil, fat and emulsion based matrices. The analysis results were compared to the chromatography method, and a linear correlation coefficient of above 0.99 was obtained. The electrochemical characterization using the cyclic voltammetry was also performed and the order of antioxidant effectiveness was TBHQ > BHA > BHT.

Keywords: Butylated hydroxyanisole, butylated hydroxytoluene, tert-butylhydroquinone, gold nanoparticles, graphite, voltammetry, synthetic antioxidant, food analysis
Assessing arsenic health issues in the Mekong River basin of Cambodia

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Abstract

In the present study, we examine the adverse health effects of arsenic contamination in the Mekong River basin of Cambodia. We applied both field survey and laboratory analysis in different exposure scenarios in the Mekong River basin in order to investigate arsenic exposure of Cambodian residents. Environmental, ecological and biological samples collected from Kratie, Kampong Cham, Prey Veng and Kandal provinces were analysed for exposure levels and daily intake of inorganic arsenic was calculated. Analytical results indicated that groundwater arsenic in Kandal, Prey Veng and Kratie provinces were greater than the regulation limits of the World Health Organization and Cambodian drinking water quality standard. Health risk assessment using USEPA model revealed that 98.7 % of respondents from the Kandal province study area were at risk of non-cancer effect and an average cancer risk was found to be 5 in 1000 exposure. The calculations also indicated that 13.5% of respondents in the Kratie province study area were at risk of non-cancer and 33.7% were threatened by cancer, whereas none of residents in the Kampong Cham province study area is at risk of non-carcinogenic effect. On-site physical examination (following WHO diagnostic guideline) of arsenic related signs and symptoms of the exposed populations showed that some residents in Kandal and Prey Veng have developed skin lesions such as pigmentation, keratosis and melanosis; and some had developed serious stage of skin cancer. Our data also provides evidences that arsenic in groundwater have been transferred into the food chains through irrigation of groundwater in the agricultural farms. It seems like arsenic contamination in groundwater continue to be a public health concern in the Mekong River basin of Cambodia. Mitigation actions should take arsenic in agricultural produces into account to ensure protection and prevention of the potential adverse health effects of Cambodian people.

Keywords: Arsenic; groundwater; rice; foods; Cambodia

Acknowledgement

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Seasonal variation of metals (Cd, Cu, Fe, Pb and Zn) in surface water of tropical riverine system, Cambodia

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Abstract

We study the metal pollutants (Cd, Cu, Fe, Pb and Zn) in surface water of tropical riverine system (Mekong and Tonle Sap River, Cambodia). Contamination relates mainly to domestic pollution draining from adjacent urban areas, the large amount of chemical fertilizers, the dense channel network, human waste, organic matter, and industrial activities.

Then the study was further explored three test comparisons for metal uptake, relating to effect of seasons, river types, and localities along the river system. The surface water samples were collected from eight provinces (Tonle Sap River: Siem Reap, Pursat, Kompong Chhnang and Phnom Penh, and Mekong River: Steung Treng, Kratie, Kompong Cham and Kandal) during March-May 2017. In total 219 samples were investigated the metal levels (Cd, Cu, Fe, Pb and Zn) by using Flame Atomic Absorption Spectrometry (FAAS).

The metal level is significantly varied among metals and locations. The major heavily pollution impacted locality along Tonle Sap River was Pursat (with exception Fe). Fe was found the greatest and was varied with the distance from upper part to the downstream. The mean concentration of Cu, Fe, Pb and Zn was (0.0085-0.0191, 0.6246-3.2324, 0.2051-0.3967, 0.0154-0.0286, ppm), respectively and was lower than that of irrigated permitted standard level by (FAO, 2016). Comparing with the permitted standard level by Cambodia guideline indicated that the level of Cd, Pb in surface water of Tonle Sap lake is not safe for human consumption.

The mean concentration of Cd in surface water of Mekong River, was greatly exceed (> 4-15 times) the standard permitted level for irrigated water (FAO/WHO) and drinking water (Cambodia). The range of average concentration Cu, Fe, Pb and Zn was (0.0127-0.0324, 0.1429-0.1811, 0.0932-0.2585, 0.0046-0.0226; ppm, respectively) were lower than standard values and was within the range values in world wide’s river. The greatest contamination of Cd, Pb, and Zn occurred at Kandal province.

Keywords: Mekong River, Tonle Sap River, metals, surface water

References

Electrochemical remediation of prazosin using Graphite-PVC composite as anode

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Abstract

Prazosin (PRZ) is used as anti-disease drug due to its biological activity in human body. The frequent detection of pharmaceuticals in water samples requires alternative technology for the removal of these pollutants. In this study, the effect of sodium chloride (NaCl) and applied voltage was investigated during electrochemical degradation process. The results revealed that increasing NaCl and applied voltage could promote the generation of hypochlorite $\text{OCl}^-$ and thus enhance the degradation for PRZ. At 0.05 g NaCl, the removal is less impactful on the degradation process for PRZ, with a removal of 77\% after 60 min of treatment. For the complete disappearance of PRZ, 0.2 g NaCl was added for this purpose. PRZ was completely removed after 40 min at 8V. However, at 3V, its removal was only 55\% after 60 min. Furthermore, identification of chlorinated by-products was conducted using an accurate instrument LC-ToF/MS. This study is the first report on the electrochemical degradation for PRZ, and two chlorinated by-products TP-N1 ($C_{13}H_9Cl_3N_5O_3$, 3.8 ppm), and TP-N2 ($C_{10}H_6Cl_4N_2O_2$, 1.7 ppm) were identified using LC-ToF/MS. In the light of the results, electrochemical process is proven to be effective in the removal of PRZ, and their by-products within 160 min using graphite-PVC as anode.

Keywords: Prazosin, electrochemical, degradation, pollutants, chlorinated by-products
MGeND: A new Integrated Database of Clinical and Genomic Information developed in Japan

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Abstract

Recent advances in powerful technologies such as next-generation sequencing have provided an abundance of genomic information. Even in the clinical practice, genomic information of patients are generated and accumulated continuously. Genetic information, such as genotypes or genetic mutations, has a deep connection with disease onset and progress. For instance, cancer is a disease caused by a genetic mutation. Depending on what kind of mutation is occurring in cancer cells, it is possible to discriminate the type of cancer, and select an appropriate anticancer drug. One of the most important projects in clinical field is accumulating relation of genomic information and clinical patient information that is clinical significance, in an organized form in various disease area from many medical institutions. Some databases that store genetic information with clinical significance, such as Clinvar developed by NIH in United States, have already been released. Also in Japan, disease area specialized database such as Database of Pathogenic Variants (DPV) specialized for intractable diseases are being developed. However, there are no database that reflect the characteristics of the Japanese and do not specialize in the disease area. In this study, we developed a disease-related genomic information database, Medical Genomics Japan Database (MGeND), reflecting the characteristics of the Japanese population by collecting genomic and clinical information from 11 of clinical groups located in Japan. Initially we collect data from 5 disease area, namely “cancer”, “rare disease”, “infectious disease”, “dementia”, and “hearing-loss”. The development of MGeND realizes data-sharing of genomic and clinical information among clinical groups crossing disease area. The accumulation and share of genetic information with clinical significance will realize a more sophisticated precision medicine.

Keywords: Genomic information, Clinical information, disease-related genomic information database

References

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