3rd Dalton Transactions
International Symposium
Bioinorganic Chemistry

14 – 16 November 2011

Osaka University & I^{2}CNER, Kyushu University, Japan

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Welcome from Dr Jamie Humphrey, Editor of *Dalton Transactions*

Dear Colleagues

Welcome to the Third *Dalton Transactions* International Symposium. We are very pleased to be holding this exciting event this year in Japan, a country whose scientists have supported *Dalton Transactions* for many years. The purpose of these events is to bring together scientists in a stimulating and friendly environment that will foster collaborations between the researchers and the universities involved in the meetings and I hope that you will be able to make the most of this opportunity for interaction.

I would like to thank the hosts of the two meetings, Professor Shinobu Itoh at Osaka University and Professor Seiji Ogo at the I^{2}CNER of Kyushu University. Their help and support will ensure the success of this meeting.

Dalton Transactions, with a high impact factor of 3.6, is the Royal Society of Chemistry's journal that covers inorganic, bioinorganic and organometallic chemistry. The journal has a very long and successful history, which has seen the journal evolve and grow to be the popular and high impact journal that it is today. This growth in impact and number of published articles is largely thanks to the authors and referees who support the journal every day! I do hope that we will have the opportunity to publish some of your work in the journal, and if you would like to be a reviewer for the journal, please do let me know.

Dalton Transactions is represented in Japan by the Regional Associate Editor for Japan, Professor Shinobu Itoh, Osaka University. Professor Itoh has been central in helping this Symposium become a reality, following a discussion I had with him earlier this year.

Did you know that the Royal Society of Chemistry recently opened an office in Japan? Dr Hirofumi Seike is the RSC's representative in Japan, and is based in Tokyo. He is very happy to answer any questions you might have about the RSC. In July 2010, The RSC signed an International Cooperation Agreement with the Chemical Society of Japan (CSJ), which should lead to more collaborations between these two chemistry societies.

I hope that you enjoy the Symposium, thank you once again to our hosts and please take the opportunity to interact with each other! I look forward to meeting you.

Dr Jamie Humphrey
Editor
Dalton Transactions

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3rd *Dalton Transactions* International Symposium Programme Schedule

Icho Kaikan, Suita Campus, Osaka University, Osaka, Japan

14th November 2011

Time	Event
	Chair: Testuro Murahashi, Osaka University
09.30 – 09.45	Jamie Humphrey, *Royal Society of Chemistry* **Opening Remarks**
09.45 – 10.30	Shinobu Itoh, *Osaka University* **Reactivity of Mononuclear Copper Active-Oxygen Complexes**
10.30 – 10.45	**Tea and Coffee**
	Chair: Toshikazu Hirao, Osaka University
10.45 – 11.30	Chris Orvig, *University of British Columbia* **Medicinal Inorganic Chemistry**
11.30 – 12.15	Shun Hirota, *Nara Institute of Science and Technology* **Structural Changes of Metalloproteins and Metal-Peptide Complexes**
12.15 – 13.45	**Lunch**
	Chair: Hideki Sugimoto, Osaka University
13.45 – 14.30	Erwin Reisner, *University of Cambridge* **Solar Fuels through Bio-Inspired Chemistry**
14.30 – 15.15	Takashi Hayashi, *Osaka University* **Construction of Supramolecular Hemoprotein Self-Assembly Systems**
15.15 –15.30	**Tea and Coffee**
	Chair: Shinobu Itoh, Osaka University
15.30 – 16.15	Nils Metzler-Nolte, *Ruhr University* **Bioorganometallic Chemistry: Synthetic Strategies and Biomedical Applications for Metal-Peptide Bioconjugates**
16.15 – 17.00	Kazuya Kikuchi, *Osaka University* **Design, Synthesis and Biological Application of In Vivo Imaging Probes with Tunable Chemical Switches**
17.00 – 17.15	Jamie Humphrey, *Royal Society of Chemistry* **Closing Remarks**

3rd *Dalton Transactions* International Symposium Programme Schedule

Inamori Hall, 1[2]CNER /Kyushu University, Fukuoka, Japan*

16th November 2011

Time	Event
	Chair: Richard Tuenge, Kyushu University
09.30 – 09.45	Jamie Humphrey, *Royal Society of Chemistry* **Opening Remarks**
09.45 – 10.30	Seiji Ogo, *Kyushu University* **Energy from Hydrogen**
10.30 – 10.45	**Tea and Coffee**
	Chair: Takahiro Matsumoto, Kyushu University
10.45 – 11.30	Chris Orvig, *University of British Columbia* **Medicinal Inorganic Chemistry**
11.30 – 12.15	Yoshi Hisaeda, *Kyushu University* **Bioinspired Catalysts with Vitamin B_{12} Enzyme Functions**
12.15 – 13.45	**Lunch**
	Chair: Kiyoshi Isobe, Kyushu University
13.45 – 14.30	Erwin Reisner, *University of Cambridge* **Solar Fuels through Bio-Inspired Chemistry**
14.30 – 15.15	Yoshinori Naruta, *Kyushu University* **Oxygen Activation with Bio-Inspired Molecular Catalysts**
15.15 –15.30	**Tea and Coffee**
	Chair: Hidetaka Nakai, Kyushu University
15.30 – 16.15	Nils Metzler-Nolte, *Ruhr University* **Bioorganometallic Chemistry:** **Synthetic Strategies and Biomedical Applications for Metal-Peptide Bioconjugates**
16.15 – 17.00	Tsutomu Katsuki, *Kyushu University* **Oxygen Atom Transfer and Dehydrogenation Reactions using Molecular Oxygen as Oxidant**
17.00 – 17.15	Jamie Humphrey, *Royal Society of Chemistry* **Closing Remarks**
*Co-sponsored by I[2]CNER of Kyushu University.	

Speaker Biographies

Takashi Hayashi
Osaka University, Japan

Takashi Hayashi received his doctor degree from Kyoto University under the supervision of Professor Y. Itoh and became an assistant professor at Department of Synthetic Chemistry, Kyoto University in 1990, working with Professor H. Ogoshi. In addition, he worked with Professor C.-H. Wong, at the Scripps Research Institute from 1995 to 1996 as a visiting scientist. He moved to Faculty of Engineering, Kyushu University as an associate professor in 1997 and worked with Professor Y. Hisaeda, and concurrently became a PRESTO researcher supported by Japan Science and Technology Agency from 2000 to 2003. He was promoted to be a full Professor at Graduate School of Engineering, Osaka University in 2005. At the same time, he became a visiting professor of Institute of Molecular Science for two years. Furthermore, he was an invited professor of University of Strasbourg in 2010. He received Progress Award in Synthetic Organic Chemistry, Japan, and 1st JPP Young Investigator Award in Porphyrin Chemistry in 2000. Furthermore, he received the Chemical Society of Japan Award for Creative Work in 2009.

His current research interests lie in the area of bioinorganic chemistry, emphasizing directions to the modification of hemoproteins and nonheme proteins to obtain functionalized proteins and biomaterials.

Shun Hirota
Nara Institute of Science and Technology, Japan

Shun Hirota graduated from the Department of Hydrocarbon Chemistry, Faculty of Engineering, Kyoto University in 1990 and obtained his Master of Engineering degree from Kyoto University in 1992. He received his Ph.D. degree in 1995 from the Graduate University for Advanced Studies under the supervision of Professor Teizo Kitagawa at the Institute for Molecular Science in Okazaki. He was a JSPS Research Fellow between 1994-1996 and joined Professor Luigi G. Marzilli's research group at the Chemistry Department, Emory University, Atlanta, Georgia, USA in 1995-1996. He joined the Department of Chemistry, Graduate School of Science, Nagoya University as an assistant professor in 1996, and became an associate professor at Kyoto Pharmaceutical University in 2002. He was also a JST PRESTO researcher between 2004-2008. He was invited as a full professor to Nara Institute of Science and Technology in April 2007. His research interests include structure-function relationship and reaction mechanisms of metalloproteins.

Yoshio Hisaeda
Kyushu University, Japan

Yoshio Hisaeda was born in 1956 in Ehime Prefecture, Japan. He completed his undergraduate study and graduate study for his Master's degree at Kyushu University in 1979 and 1981, respectively. He subsequently became Research Associate and received his Ph.D. degree in 1986 under the supervision of Professor Yukito Murakami at Kyushu University. He was appointed Associate Professor in the Department of Organic Synthesis (now Department of Applied Chemistry), Faculty of Engineering at Kyushu University in 1988 and promoted to Professor in 1995. He spent a year (1993-1994) with Professor Jonathan L. Sessler at the University of Texas at Austin as a Visiting Professor. His research interests are concerned with bioinorganic and bioinspired chemistry as well as electroorganic chemistry based on coordination chemistry and organic synthesis.

Shinobu Itoh
Osaka University, Japan

Shinobu Itoh focuses his current research on chemical modelling and application of novel active sites in biological systems. He was formerly an assistant professor at Osaka University, where he worked on the chemistry of coenzyme PQQ and cofactor TTQ as well as model compounds of galactose oxidase. In 1994, he was promoted to Associate Professor at Osaka University, where he collaborated with Professor Shunichi Fukuzumi in copper/dioxygen chemistry research. In 1999, he moved to Osaka City University as a full professor and started biological studies of dinuclear copper proteins, such as hemocyanin and tyrosinase. He returned to Osaka University in 2008 and further expanded his research interests to the design of artificial non-heme metalloenzymes using genetic engineering.

Tsutomu Katsuki
Kyushu University, Japan

Tsutomu Katsuki was born in Saga, Japan, in 1946. He received a doctoral degree in 1976 from Kyushu University under the supervision of Professor M. Yamaguchi. He was a research associate at Kyushu University in 1971-1987. For two years from 1979, he was a post-doctoral fellow with Professor K. B. Sharpless at Stanford University and Massachusetts Institute of Technology, at which time he and Professor Sharpless published their paper on the asymmetric epoxidation of allylic alcohols. He was a full Professor at Kyushu University in 1988-2010. He is a University Professor at Institute for Advanced Study since 2010 and a Professor at International Institute for Carbon-Neutral Energy Research at the Kyushu University since 2011. His work has been recognized by the Inoue Science Award (1997), the Synthetic Organic Chemistry Award, Japan (1999), the Molecular Chirality Award, Japan (2001), the Chemical Society of Japan Award (2004), Ryoji Noyori Prize (2005) and the Commendation for Science and Technology by the Minister of Education, Culture, Sports, Science and Technology, Prizes for Science and Technology (2009)

His current research interests are focused on asymmetric catalysis of organo-transition-metal complexes.

Kazuya Kikuchi
Osaka University, Japan

Kazuya Kikuchi received his first degree in 1988 from the The University of Tokyo, Pharmaceutical Sciences, where he remained to complete a MS and Ph.D., which he received in 1994. He then moved to the University of California, San Diego for a one year post-doctorate position, and from there he moved to spend a further year in California at the Scripps Research Institute. In 1997 he moved back to the University of Tokyo to be an Assistant Professor at the Graduate School of Pharmaceutical Sciences and in 2000 he became an Associate Professor there. He moved west to Osaka in 2005 he take a position as Professor at the Graduate School of Engineering, Osaka University. Since 2008 he has also been Professor at the Immunology Frontier Research Center (IFReC) at Osaka University, where his research has a focus on developing chemical imaging techniques.

Nils Metzler-Nolte
Ruhr University Bochum, Germany

Nils Metzler-Nolte obtained his Ph.D. from LMU Munich (Germany) in 1994. After a postdoc with Prof. M. L. H. Green at the University of Oxford (U.K.) he started his independent research on bioorganometallic chemistry at the Max-Planck-Institut für Strahlenchemie (nowadays MPI for Bioinorganic Chemistry) in Mülheim, Germany. He was appointed Associate Professor at the University of Heidelberg (Germany) in 2000 and Full Professor at Ruhr-University Bochum (Germany) in 2006. He is Speaker of the DFG-funded Research Unit "Biological Function of Organometallic Compounds". He was a council member of the COST Action D39 "Metallo-drug Design and Action" and serves currently as counsellor for the Society of Bioinorganic Chemistry. Prof. Metzler-Nolte has published more than 130 original research articles, reviews and book chapters, and has co-authored and co-edited three books. He is a member of the international advisory boards of several journals. With research interests in medicinal inorganic chemistry, functional metal bio-conjugates and biosensors, the Metzler-Nolte group is running a full program from inorganic and biomolecular synthesis and characterization to cell biology. Prof. Metzler-Nolte is Speaker of the Ruhr University Bochum Research School and since 2010, he is also Vice-President for Early Career Researchers and International Affairs at Ruhr-University Bochum.

Yoshinori Naruta
Kyushu University, Japan

Yoshinori Naruta was born in Kyoto, 1948. He got his BEng, Kyoto University on 1972 and received his DSc from same University in 1981. He started his academic carrier as a assistant professor, Kyoto University on 1976. From 1983 to 1984, he engaged Japan-US Cooperative Program as a researcher with Prof. Jim Collman at Stanford University. Then, he worked as a associate professor at Kyoto University and Institute for Molecular Science. Then, he was appointed to a full professor of Kyushu University, Institute for Fundamental Research of Organic Chemistry (now reorganized to IMCE) in 1994. He has been appointed to a distinguished professor since 2009. He was also appointed to a PI of International Institute for Carbon-Neutral Energy Research at the Kyushu University since 2011. He is a member of Science Council of Japan since 2000. He has received awards, Young Researcher's Award, Chemical Society of Japan, Inoue Science Award.

His research interests are the study on photochemical/electrochemical water splitting and oxygen reduction with rationally designed molecular catalysts and the elucidation of their reaction mechanism.

Seiji Ogo
Kyushu University, Japan

Seiji Ogo received his Ph.D. from the Graduate University for Advanced Studies in 1996. After working in the Institute for Molecular Science (IMS) at Okazaki (1996–2001), Nagoya University (2001–2002), and Osaka University (2002–2005), in 2005 he joined Kyushu University as a full professor. He is currently a leader of the CREST (Core Research for Evolutional Science and Technology) project of the Japan Science and Technology Agency (JST). His research interests are in the activation of H_2, N_2, CO_2, O_2, and H_2O in water. He received the Japan Society for the Promotion of Science (JSPS) Prizes in 2008. He is an Advisory Board of *Dalton Transactions*, an international journal of inorganic chemistry.

Chris Orvig
University of British Columbia, Canada

Chris Orvig was born and raised in Montréal. He received his Hons. B.Sc. in chemistry from McGill University in 1976 and subsequently completed his doctorate (as a Natural Sciences and Engineering Research Council - NSERC – of Canada scholar) in technetium chemistry at M.I.T. with Prof. Alan Davison, FRS. After an NSERC postdoctoral fellowship with Prof. Kenneth N. Raymond at the University of California, Berkeley (1981-83) and one year with the late Prof. Colin J. L. Lock at McMaster University, he joined the Department of Chemistry at the University of British Columbia in 1984, where he is now Professor of Chemistry and Pharmaceutical Sciences, and Director of the Medicinal Inorganic Chemistry Group. His scientific interests are firmly based in the areas of medicinal inorganic chemistry and coordination chemistry – he has been involved over the years with radiopharmaceutical chemistry, metal ion decorporation, and metal ion neurotoxicology, as well as chemotherapeutic metal complexes and ligands. Orvig chairs the editorial board of *Dalton Transactions*, has received various research and teaching awards, has published more than 200 research papers, and is a co-inventor on many issued patents; he is also a Fellow of the Royal Society of Canada and a certified ski instructor.

Erwin Reisner
University of Cambridge, UK

Erwin Reisner received his formal degrees from the University of Vienna, Austria (Diploma, 2002; Ph.D., 2005; Habilitation, 2010). He worked as an Erwin Schrödinger postdoctoral fellow at the Massachusetts Institute of Technology (Cambridge, MA, USA) in the group of Stephen J. Lippard (2005-2007) and subsequently took up a post as a Research Assistant with Fraser A. Armstrong FRS at the University of Oxford, UK (2008-2009), where he was also active as a College Lecturer (St. John's) in Inorganic Chemistry. After one year as an EPSRC Career Acceleration fellow at The University of Manchester, UK, he joined the University of Cambridge in October 2010 as a University Lecturer and became a fellow of St. John's College in 2011. He works at the inorganic and biological chemistry interface with a focus on solar fuel research and the exploitation of redox enzymes and their synthetic models for the conversion of abundant raw materials (in particular water and carbon dioxide) into alternative energy carriers (hydrogen and carbon-feedstocks).

Abstracts

Construction of Supramolecular Hemoprotein Self-Assembly Systems

Takashi Hayashi

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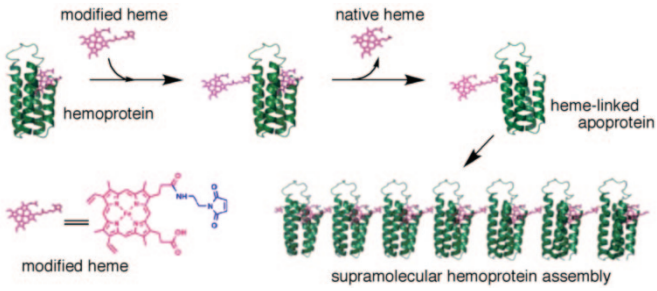
Biological self-assembly systems are one of the most attractive nanomaterials, which quite often consist of supramolecular biopolymers defined as thermally equilibrated polymeric architectures. The supramolecular structure has been formed by spontaneous connections of the monomer components through non-covalent intermolecular interaction. They are ubiquitous and fulfill their biological functions via well-organized conjugations in nature. Those beautiful and functionalized structures have been very attractive not only for biologists but also our chemists.
Over the last two decades, several groups have prepared a variety of self-assembly systems using organic and/or inorganic frameworks to mimic the biological supramolecular systems. Recently, we have also extended this basic principle of the supramolecular polymer chemistry to the supramolecular protein engineering using hemoproteins.



Almost all of hemoproteins have a non-covalently linked protoheme IX as a prosthetic group. The heme affinity for the heme pocket is generally very large with the binding constant of ca. 1010–1015 M–1. To construct a self-assembled hemoprotein polymer, our group focused on the interprotein heme–heme pocket interaction using a small hemoprotein, cytochrome b562, as an electron transfer protein, or myoglobin as an oxygen storage protein. Our strategy to prepare the hemoprotein self-assembly system is described as shown in the graphical image.[1] The apoprotein bearing an external heme moiety linked onto the protein surface is a unit (monomer) of the supramolecular self-assembly. The polymeric species were determined by size exclusion chromatography and UV-vis spectroscopic techniques. From those investigations, it is found that the size of the polymers is clearly controlled by thermodynamic condition. Moreover, the characteristic protein fibers with the length of 300–1000 nm were observed by AFM (atomic force microscopy) image on the graphite substrate. Furthermore, we have recently constructed the 2D and 3D polymeric protein composites based on the heme–heme pocket interactions.[2,3] In addition, it is found that the attractive conjugates between a gold surface and the hemoprotein assembly are available.[4,5] The methodology should be widely applicable to a creation of new nanobiomaterials based on a functional hemoprotein.

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Structural Changes of Metalloproteins and Metal-Peptide Complexes

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We have been investigating and regulating the structural changes of metalloproteins and metal-peptide complexes. For example, copper(II) ion-bound CysGly dipeptides were linked with an azobenzene derivative, and the azobenzene linked molecule was photoisomerized between the trans and cis forms. The two copper(II) ion centers were positioned close to each other in the cis form, whereas they were far away from each other in the trans form. The copper complex in the cis form exhibited DNA cleavage activity, whereas the activity in the trans form was negligible. Cytochrome *c* (cyt *c*) is a stable heme protein which functions in a monomeric state as an electron donor for cytochrome *c* oxidase. It is also released to the cytosol at the early stage of apoptosis. For nearly half a century, it has been known that cyt *c* forms polymers, but the polymerization mechanism remains unknown. We found that cyt *c* forms polymers by successive domain swapping, where the C-terminal helix is displaced from its original position in the monomer and Met-heme coordination is perturbed significantly. In the crystal structures of dimeric and trimeric cyt *c*, the C-terminal helices are replaced by the corresponding domain of other cyt *c* molecules and Met80 is dissociated from the heme. For dimeric, trimeric, and tetrameric cyt *c*, the ΔH of the oligomer dissociation to monomers was estimated to be about -20 kcal/mol per protomer unit, where Met-heme coordination appears to contribute largely to ΔH.

Bioinspired Catalysts with Vitamin B_{12} Enzyme Functions

Yoshio Hisaeda

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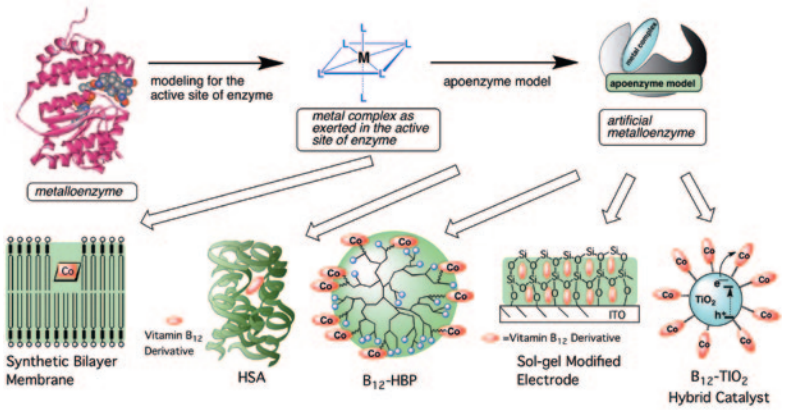
We have been dealing with a hydrophobic vitamin B_{12}, heptamethyl cobyrinate perchlorate, which has ester groups in place of the peripheral amide moieties of the naturally occurring vitamin B_{12}. In order to construct a good catalytic system, we prepared various nanomaterials with vitamin B_{12} activities. For example, vitamin B_{12}-hyperbranched polymers (B_{12}-HBP), human serum albumin (HSA) containing vitamin B_{12} derivatives, vitamin B_{12}-titanium dioxide hybrid catalyst (B_{12}-TiO_2), vitamin B_{12}-Ru complex combined catalyst, and so on. These bioinspired materials can apply to the catalytic reactions for degradation of organic halides and molecular transformations. These bioinspired catalysts are very interesting from the viewpoint of green chemistry.

Dehalorespiration is an anaerobic metabolism by microbes in which the dehalogenation of organic halides is coupled to energy conservation. Certain microbes utilize an electron transport chain which contain a vitamin B_{12} derivative as a cofactor of the involved enzymes. This metabolism attracts great interest due to its relevance to remediation technologies for reductively degrading halogenated pollutants, in which a sustainable process is also required.



We herein design a new bioinspired system composed of a vitamin B_{12} derivative and Rose Bengal (or Rhodamine B) with a noble metal-free process. This bioinspired system works under irradiation with visible light, and can be applied to the degradation of organic halide pollutants, 1,1-bis(4-chlorophenyl)-2,2,2-trichloroethane (DDT). The turnover numbers based on B_{12} and Rose Bengal are 100 and 1000, respectively. This system can apply to various molecular transformations.

Reactivity of Mononuclear Copper Active-Oxygen Complexes

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There have been significant advances in understanding the dioxygen-activation mechanism by mononuclear copper monooxygenases such as peptidylglycine α-hydroxylating monooxygenase (PHM) and dopamine β-monooxygenase (DβM). Recent structural and spectroscopic studies on a series of biomimetic model compounds have also provided new and valuable insights into the key reactive intermediates involved in the dioxygen processing at the mononuclear copper reaction centres in biological systems. In this talk, our recent studies on the reactivity of mononuclear copper(II)-superoxo and a copper(II)-alkylperoxo complexes are introduced.

Mononuclear copper(II)-superoxo complexes $\mathbf{1^X}$ having triplet (S = 1) ground states were obtained by the reaction of O_2 and a series of copper(I) complexes supported by tridentate ligands L^X [1-(2-p-X-phenethyl)-5-(2-pyridin-2-ylethyl)-1,5-diazacyclooctane; X = OCH_3, CH_3, H, Cl, NO_2] in various solvents. The superoxo complexes exhibit a structure (tetrahedral geometry with an end-on (η1)-bound $O_2^{\bullet-}$) and reactivity (aliphatic hydroxylation) similar to those of PHM and DβM.[1]

$\mathbf{L^XCu^{II}\text{-}OO^{-\bullet}}$ $\mathbf{1^X}$ $\qquad$ $\mathbf{LCu^{II}\text{-}OOR}$ $\mathbf{2}$

A detailed reactivity study has also been carried out on a new mononuclear alkylperoxo copper(II) complex **2**, which is generated by the reaction of copper(II) complex supported by the bis(pyridylmethyl)amine tridentate ligands and cumene hydroperoxide (CmOOH) in CH_3CN. The cumylperoxo copper(II) complex thus obtained has been found to undergo homolytic cleavage of the O-O bond and induce C-H bond activation of external substrates, providing important insights into the catalytic mechanism of the copper monooxygenases.[2, 3]

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Oxygen Atom Transfer and Dehydrogenation Reactions using Molecular Oxygen as Oxidant

Tsutomu Katsuki

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Oxygen atom transfer and dehydrogenative oxidation reactions are important tools for chemical transformation in organic synthesis. Biological oxidation reactions use molecular oxygen as the oxidant and they are stereoselective and ecologically benign. However, the reactions need sophisticated proton and electron transfer systems for activating molecular oxygen. It is still a challenge to develop stereoselective aerobic oxidation reactions, which do not need such proton and electron transfer systems. We have been exploring asymmetric catalysis of aerobic oxidation by ruthenium and iron complexes. In this paper, we will discuss our recent works [[1] and [2]].

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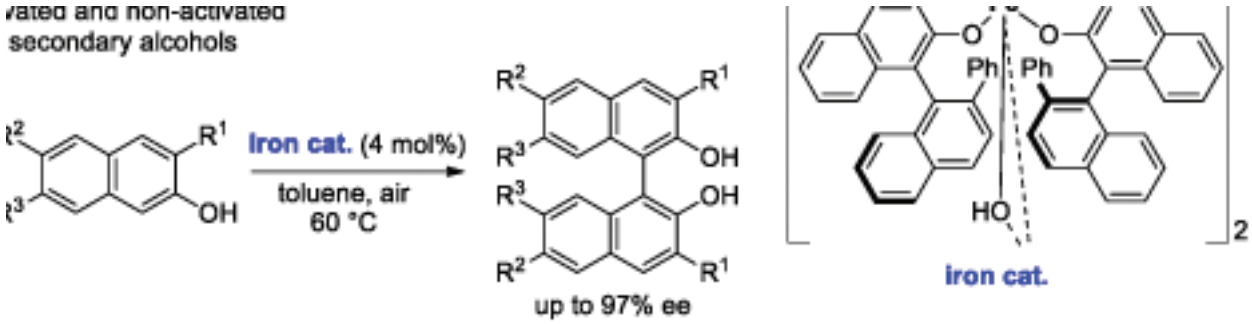

Design, Synthesis and Biological Application of In Vivo Imaging Probes with Tunable Chemical Switches

Kazuya Kikuchi

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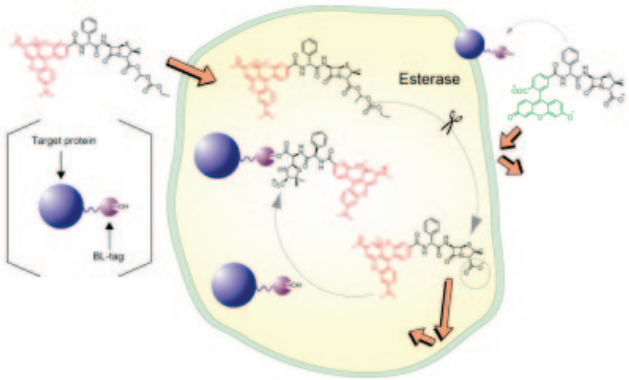
One of the great challenges in the post-genome era is to clarify the biological significance of intracellular molecules directly in living cells. If we can visualize a molecule in action, it is possible to acquire biological information, which is unavailable if we deal with cell homogenates. One possible approach is to design and synthesize chemical probes that can convert biological information to chemical output.

Protein fluorescent labelling provides an attractive approach to study the localization and function of proteins in living cells. Recently, a specific pair of a protein tag and its ligand has been utilized to visualize a protein of interest (POI). In this method, a POI is fused with a protein tag and the tag is labelled with the ligand connected to a fluorescent molecule. The advantage of this protein labelling system is that a variety of fluorescent molecules are potentially available as labelling reagents, and that the protein tag is conditionally labelled with its fluorescent ligand. However, in the existing labelling systems, there are some problems with the size of a protein tag, the specificity of the labelling or fluorogenicity of labelling reagents. Protein tags for labelling proteins of interest (POIs) with small molecule based probes have become important technique as practical alternatives to the fluorescent proteins (FPs) for live cell imaging. We have designed a protein labelling system that allows fluorophores to be linked to POI. The protein tag (BL-tag) is a mutant class A β-lactamase (TEM-1) modified to be covalently bound to the designed specific labelling probes and the labelling probes is consisted with a β-lactam ring (ampicillin, cephalosporin) attached to various fluorophores. A fluorogenetic labelling system can be designed using the unique property of cephalosporin, which release leaving group by subsequent reaction after opening the lactam ring. For further sophisticated application, multicolour imaging was done by adopting the colourful fluorophores.



Bioorganometallic Chemistry: Synthetic Strategies and Biomedical Applications for Metal-Peptide Bioconjugates

Prof. Dr. Nils Metzler-Nolte

Ruhr-University Bochum, Bochum, Germany
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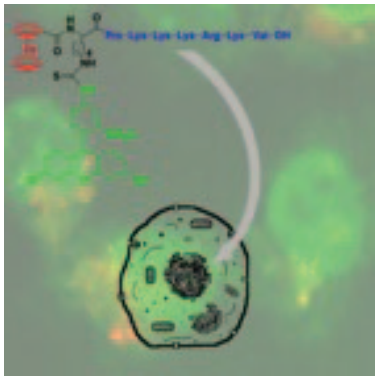
Our group uses the unique spectroscopic and chemical properties of organometallic complexes for the detection and modification of bioactive peptides as well as metal-peptide conjugates for biomedical applications. The experimental challenge is to identify air and water stable organometallic compounds with the desired properties, and to devise methods for the mild, biocompatible synthesis of bioconjugates with these metal complexes.



This lecture presents the solid phase synthesis of metal-peptide conjugates.[1, 2, 3] I will show how several different classes of metal complexes can be successfully used in solid phase synthesis techniques and subsequently for biomedical applications. Compounds used in our group include, inter alia, metallocenes, third-generation tris(pyrazolyl) borate (Tp') complexes, metal carbonyls, and metal complexes of functionalized N-heterocyclic carbenes and alkynes. The peptides were derived from sequences known for enhanced and / or cell-type specific uptake (e.g. TAT peptides or octreotate), or for intra-cellular delivery (such as nuclear or mitochondrial localization).[3, 4] I will also show how we make use of such metal-peptide conjugates for applications in chemical biology and to monitor drug uptake and control intra-cellular delivery. Overall, these metal-peptide conjugates provide new opportunities for targeted drugs and the study of mechanisms of action for metal-based drug candidates. [5]

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Oxygen Activation with Bio-Inspired Molecular Catalysts

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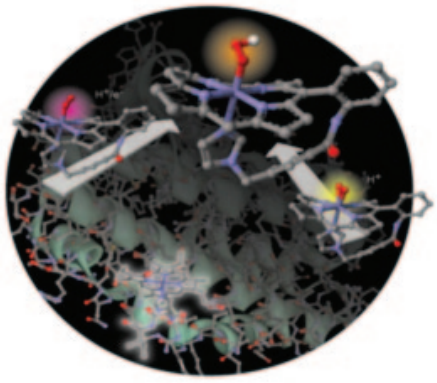

Oxygen activation is an essential reaction from aerobes to industry. Since reductive activation of dioxygen molecule tends to take various pathways to resultant formation of active oxygen species. Most of heme-containing enzymes, however, take selective formation of the corresponding iron hydroperoxy complexes (compound 0) as intermediates, which are thermally unstable. The O^2 activation mechanism and their behaviour on iron porphyrins are elucidated with use of new enzyme–inspired model complexes, which revealed the detail of the properties and reactivity of the intermediates [1,2].

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Energy from Hydrogen

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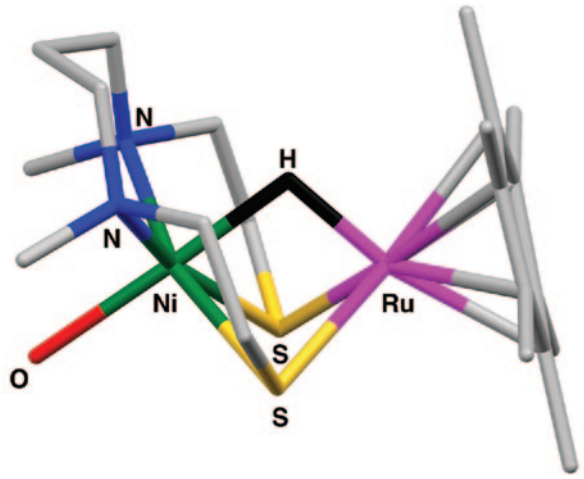
The growing need for hydrogen-based fuel cells has driven research into [NiFe]hydrogenase ([NiFe] H_2ase) — a natural enzyme that catalyses the extraction of electrons from H_2 in water under ambient conditions. Unfortunately, the exact mechanism by which [NiFe]H_2ase achieves this feat has remained a matter of some controversy until now, with many mechanisms being inconsistent with experimental data. Recently, however, we have been able to construct a robust [NiFe]H_2ase mimic based around a NiRu assembly, "Ogo catalyst", that replicates key aspects of H_2ase. This lecture begins with an overview of the research from many groups that preceded this discovery, followed by a detailed analysis of the key points that set our unique functional model apart — that is to say a proton-like "hydride" species, a surprisingly low-valent $Ni^{I}Ru^{I}$ complex and the key insight that two molecules of H_2 are required for electron extraction.



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Medicinal Inorganic Chemistry

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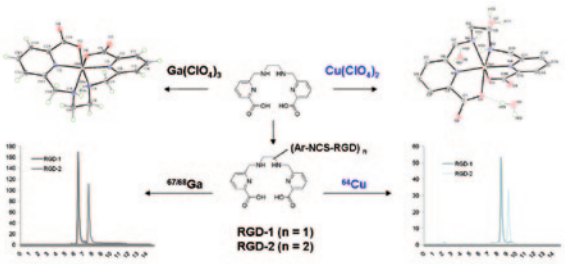

The role of metal complexes as therapeutic and diagnostic agents is burgeoning due to interest from many academic and industrial concerns; the design of ligands and their respective metal complexes plays a critical role in the success of such potential agents. Principles in the design of ligands and coordination compounds as drugs will be discussed in detail with examples from work in the speaker's research laboratories presented to illustrate these principles. These examples come from new radiopharmaceutical conjugates for diagnosis and therapy, ligands for the movement of endogenous metal ions, and vanadium compounds as insulin-enhancing agents.

Solar Fuels through Bio-Inspired Chemistry

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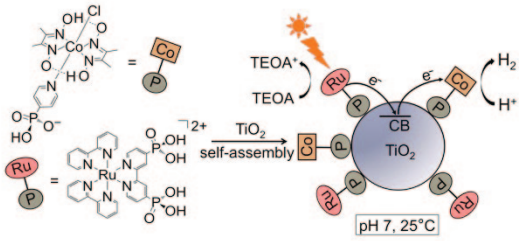

Natural photosynthesis serves as an inspiration for the development of sustainable fuel producing systems, which harvest and use electromagnetic energy to drive energetically uphill redox catalysis.[1] Dye-sensitization of the semiconductor TiO_2 allows for visible light absorption and charge separation,[2] and the resulting conduction band (CB) electrons can in principle be used to generate electricity in a solar cell or for solar fuel production. However, fuel generation also requires the presence of a suitable catalyst: ruthenium-dye sensitized TiO_2 nanoparticles can be modified with enzymes for proton reduction to H_2,[3,4] and the reduction of CO_2 to CO.[5] Remarkably, even a relatively simple and robust molecular cobalt complex containing diglyoxime ligands on dye-sensitized TiO_2 can generate H_2 gas upon irradiation from pH neutral buffered solution (Figure 1).[6] Solar fuel producing hybrid systems and prospects for replacing enzymes with synthetic catalysts will be discussed.

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