

**Organizing Chair:**

**Prof. B. Moon Kim (Seoul National University)**

**Prof. Kyo Han Ahn (POSTECH)**

**Organizing Committees:**

**Prof. Seonghoon Lee (Seoul National University)**

**Prof. Yan Lee (Seoul National University)**

**Prof. Moon Jeong Park (POSTECH)**

## CAMPUS Asia Program

### A Cooperative Asian Education Gateway for a Sustainable Society:

Expanding the Frontiers in Science and Technology of Chemistry and Materials  
(POSTECH-Seoul National University-Tohoku University Joint Symposium)

(Jan. 21<sup>st</sup> – 24<sup>th</sup>, 2013)

Jan. 21<sup>st</sup> (Mokam Hall, Seoul National University)

10:00-10:10     **Welcoming Address**  
Prof. Seokmin Shin (Chair, Department of Chemistry, SNU)

**SNU Session I**     Chair - Prof. Heon Kang

10:10-10:35     Prof. Akihiro Morita (Tohoku University)  
“Computational Analysis of Surface Nonlinear Spectroscopy and Liquid Interfaces”

10:35-11:00     Prof. Seonghoon Lee (Seoul National University)  
“The Excitons and Photons in an Artificial Atom and Its Assembly”

11:00-11:25     Prof. Masahiro Yamashita (Tohoku University)  
“Quantum Molecular Spintronics Based on Multiple-Decker Phthalocyaninato Lanthanide(III) Single-Molecule Magnets”

11:25-11:50     Prof. Yan Lee (Seoul National University)  
“Circulatory Osmotic Desalination Based on LCST Materials”

11:50-12:50     **Lunch**

**SNU Session II**     Chair - Prof. Seonghoon Lee

12:50-13:15     Prof. Hidetoshi Tokuyama (Tohoku University)  
“Total Synthesis of *N*-Heterocyclic Natural Products”

13:15-13:40     Prof. B. Moon Kim (Seoul National University)  
“Chiral Diamine Chemistry: Application to Efficient Synthesis of Chiral Piperazine Derivatives”

**Student Session**      Chair - Prof. Yan Lee

- 13:40-13:50      Takako Imamura (Tohoku University)  
"Water Orientational Structures at Aqueous Electrolyte Solution Surfaces"
- 13:50-14:00      Yeonju Seo (Seoul National University)  
"The Fast Growth of Ordered Anodic TiO<sub>2</sub> Nanotube Array by the Control of Electrolyte Composition"
- 14:00-14:10      Kazuaki Oniwa (Tohoku University)  
"Biphenyl End-Capped Furan-Incorporated Oligomers for Organic Light-Emitting FET"
- 14:10-14:20      Jiyeon Ham (Seoul National University)  
"Biocompatible Surface Coating of Silicone Bioimplants Using a Biomembrane-Mimic Polymer"
- 14:20-14:30      Takafumi Ishii (Tohoku University)  
"Preparation of Graphene Field-Effect Transistors by a Selective-Area Growth Method"
- 14:30-14:40      Joo Young Chung (Seoul National University)  
"Shape-Dependent Catalytic Activities of Pd Nanoparticles in Hydrogenation"
- 14:40-14:50      Taichi Shimizu (Tohoku University)  
"Preparation of Mesoporous Silica Supported Catalysts for Selective Hydrogenation Using Supercritical CO<sub>2</sub>"
- 14:50-15:00      **Closing Remarks**  
Prof. Akihiro Morita (Tohoku University)
- 15:00-15:30      **Lab Tour**

Jan. 23<sup>rd</sup> (Chemistry Bldg, POSTECH)

10:00-10:10    **Welcoming Address**  
Prof. Taihyun Chang  
(Chair Provost & Executive Vice President, POSTECH)

**POSTECH Session I**      Chair - Prof. Moon Jeong Park

10:10-10:35    Prof. Nagao Kobayashi (Tohoku University)  
“Synthesis, Applications, and Practical Use of Functional Metallophthalocyanines”

10:35-11:00    Prof. In Su Lee (POSTECH)  
“Fabrication of Hollow Nanoparticles with Functionalized Interior Surface for the Nanoreactor Application”

11:00-11:25    Prof. Ilya Gridnev (Tohoku University)  
“Mechanism of Enantioselection in Asymmetric Catalytic Reactions”

11:25-11:50    Prof. Young Ho Rhee (POSTECH)  
“Developing New Diversity-Generating Synthetic Strategies Based on Metal Catalysis”

11:50-13:30    **Lunch**

**POSTECH Session II**      Chair - Prof. In Su Lee

13:30-13:55    Prof. Nurbosyn U. Zhanpeisov (Tohoku University)  
“Cluster Approach for New Material Design: A Theoretical DFT Study”

13:55-14:20    Prof. Young Min Rhee (POSTECH)  
“All-Aom Semi-Classical Nonadabatic Simulations of Excitation Energy Transfer Process In Photosynthetic Fenna-Matthews-Olson Complex”

14:20-14:50    **Group Photo & Coffee Break**

**Student Session**      Chair - Prof. Young Ho Rhee

- 14:50-15:00      Hyun Woo Kim (POSTECH)  
"Simulating Coherent Energy Transfer in Photosynthetic Systems with All-atom Model"
- 15:00-15:10      Xiaolei Wang (Tohoku University)  
"Synthesis of New Nitroxyl Radical Spin Probes for In Vivo Electron Paramagnetic Resonance Imaging"
- 15:10-15:20      Hyunsoo Moon (POSTECH)  
"Significant Substituent Effects on the Photophysical Properties of Boron Complexes of 2-(Benzothiazol-2-yl)phenols"
- 15:20-15:30      Yuichiro Inagawa (Tohoku University)  
"Novel Silylene Copper Complexes having Dialkylsilylene Ligands"
- 15:30-15:40      Jae Woo Park (POSTECH)  
"Theoretical Investigation on the Photodynamics of Wild-type Green Fluorescent Protein: Interpolated Mechanics-Molecular Mechanics Simulation Combined with Simple Surface Hopping Scheme"
- 15:40-15:50      Naoki Kawano (Tohoku University)  
"Scintillation and Luminescence Properties of Self-Organized Organic-Inorganic Quantum Well Structure"
- 15:50-16:00      **Closing Remarks**  
Prof. Kyo Han Ahn (POSTECH)
- 16:00-17:30      **Lab Tour**

[S1-1]

## Computational Analysis of Surface Nonlinear Spectroscopy and Liquid Interfaces

Akihiro Morita

*Department of Chemistry, Graduate School of Science, Tohoku University, Sendai 980-8578, Japan*

Surface nonlinear spectroscopy based on the second order optical processes, such as second harmonic generation (SHG) or sum frequency generation (SFG), is widely used as surface characterization technique. In particular visible-infrared SFG spectroscopy can selectively detect vibrational spectra of molecules at interfaces, and thereby reveal microscopic details of surface species and their orientational structure. Though the spectroscopy offers sensitive information on the surface at a molecular scale, reliable interpretation of the observed spectra is often a challenging issue. Therefore we have proposed and developed theory and computational methods of vibrational SFG spectroscopy in combination of ab initio molecular modeling and molecular dynamics (MD) simulation [1]. The development in the theoretical aspect allows for close collaboration by SFG spectroscopy and MD simulation toward further understanding of wet interfaces.

In the present talk, I briefly summarize our recent efforts on elucidating water [2] and ice surfaces [3]. It has been a long standing problem to understand the hydrogen bonding network of water in the vicinity of the surface. Since the vibrational SFG spectra of water sensitively reflect local hydrogen bonding environment, the analysis of the SFG spectroscopy is quite useful for these purposes. Our recent MD analysis elucidated the spectroscopic features of the water and ice surfaces, respectively, in relation to the hydrogen bonding structure.

### References

- (1) A. Morita and T. Ishiyama, *Phys. Chem. Chem. Phys.* **2008**, *10*, 5801.
- (2) S. Nihonyanagi, T. Ishiyama, T. Lee, S. Yamaguchi, M. Bonn, A. Morita and T. Tahara, *J. Am. Chem. Soc.* **2011**, *133*, 16875.
- (3) T. Ishiyama and A. Morita, *J. Chem. Phys. Lett.* **2012**, *3*, 3001.

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Akihiro Morita is a Professor of Graduate School of Science, Tohoku University. He received his Ph. D in chemistry from Kyoto University under the direction of Prof. Shigeki Kato. He was a research associate in Kyoto University from 1992 to 2003. He was also a research associate at the University of Colorado from 1999 to 2000, working with Prof. Casey Hynes. He moved to the Institute for Molecular Science as an associate professor in 2004, and to Tohoku University as a professor in 2007. His research interests center on electronic structure and molecular dynamics in solutions and at liquid interfaces, including theory of sum frequency generation spectroscopy, mass transfer dynamics at liquid interfaces, and free energy calculations by QM/MM methods. Awards: Morino Science Foundation (2006) “Theoretical Study on Structure and Dynamics in Solutions and Solution Interfaces,” The CSJ Award for Creative Work (2012) “Development of Theory on Sum Frequency Generation Spectroscopy and Application to Liquid Interfaces.”

### Representative Publications:

- 1) K. Shiratori and A. Morita, Theory of Quadrupole Contributions from Interface and Bulk in Second-Order Optical Processes (award article), *Bull. Chem. Soc. Jpn.* **2012**, 85, 1061.
- 2) A. Morita and T. Ishiyama, Recent Progress in Theoretical Analysis of Vibrational Sum Frequency Generation Spectroscopy (perspectives), *Phys. Chem. Chem. Phys.* **2008**, 10, 5801.
- 3) B. C. Garrett, G. K. Schenter, A. Morita, Molecular Simulation of the Transport of Molecules across the Liquid/Vapor Interface of Water, *Chem. Rev.* **2006**, 106, 1355.

[S1-2]

## The Excitons and Photons in an Artificial Atom and Its Assembly

Seonghoon Lee

*School of Chemistry, Seoul National University, Seoul, Korea 151-747*

The control and motion of electrons and atoms at a nanoscale have been investigated in relation to the generation of new functional advanced material and to the understanding of life, biological system, and self-organized systems. The new properties or phenomena occurring at a nanoscale can be controlled or explained in terms of excitons (in artificial atoms), polarons (organic electronic molecules), and photons (optoelectronic nanomaterials).

In this talk, I will present the new kinds of chemical building elements called nanoscale artificial atoms. Excitons play a major role in determining various properties such as quantum confinement and nonlinear effects, of artificial atoms. Utilizing reactivity differences in precursors, we can produce artificial atoms in a large scale by a single-step synthetic method. Auger recombination processes, chemical/ photostability, photoluminescence quantum yield, and multiple exciton generation from high-energy photons were studied with these artificial atoms. The systematic analysis of the exciton-recombination zone within all-quantum dot (QD) multilayer films prepared by a layer-by-layer assembly method was made in order to realize various optoelectronic applications.

With regard to the practical applications, we produced various practical printable electronic devices such as very thin and large-area Red/Green/Blue/White quantum dot light emitting devices (QLEDs), next generation solid-state white lighting devices, and flexible large color composites.

### References

- (1) Multicolored Light-Emitting Diodes Based on All-Quantum-Dot Multilayer Films Using Layer-by-Layer Assembly Method, *Nano Letters*, **2010**, 10(7), 2368-2373, (Highlighted in *MRS Bulletin*, Aug, **2010**, 35, p566).
- (2) Highly Efficient Green Light-Emitting Diodes Based on CdSe@ZnS Quantum Dots with Chemical Composition Gradient. *Advanced Materials* **2009**, 21, 1690-1694. (Highlighted in *Nature Journal*).
- (3) Bright and Efficient Full-Color Colloidal Quantum Dot Light-Emitting Diodes Using an Inverted Device Structure, *Nano Letters*, **2012**, 12(5), 2362-2366. (Also reported and highlighted in **C&E News** in April 10, 2012 and in **British Web, PHYSORG.com** in April 20, 2012.)



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### Education:

- 1984 B. Sc., Seoul National University, Seoul, Korea
- 1986 M. Sc., Seoul National University, Seoul, Korea
- 1993 Ph.D., Harvard University, Cambridge, MA. U.S.A.

### Career:

- 1997 Research Fellow, Univ. of California, Santa Barbara, U.S.A.
- 2003 Associate Prof., GIST, Gwangju, Korea
- 2007~2009, Chairman, Program of Nano Science & Technology, SNU
- 2009~present. Professor, Nano Science & Technology, Graduate School of Convergence Science & Technology, SNU
- 2003-present, Professor, Chemistry, Seoul National University (SNU), Seoul, Korea.

### Honor:

- 2001 Science Advancement & Innovation Award by Korean Government

### Research interests:

He has researched structures and dynamics of atoms, molecules, weakly bound clusters of molecules such as van der Waals dimers, strongly bound clusters of metal or carbon atoms in terms of molecular beam high resolution spectroscopic methods, focusing on the search for the generalized analytical binary interaction potential. Met-Cars, a new class of chemical species published in *Science* was world-wide recognized. Now, as continued efforts to understand how materials properties develop as their dimension, size, and shape vary, he has been investigating low dimensional materials such as semiconductor quantum dots and metal nanoparticles (0-D), carbon nanotubes and nanowires (1-D), and thin films (2-D). He also realizes the electrical and optical devices with low dimensional materials such as CNT-FED, plastic solar cell, OLEDs, LD, white LEDs, solid state lighting. He studies electrical properties and transport phenomena of single species such as single molecule, single live neuron, a nanofiber, and their arrays using 4-Probe, SPM, CAFM, AFM-CLSM measurements for future molecular electronics or printable electronic applications.

### Representative Publications:

- 1) Bright and Efficient Full-Color Colloidal Quantum Dot Light-Emitting Diodes Using an Inverted Device Structure. *Nano Letters*, **2012**, 12(5), 2362-2366. Also reported in **C&E News in april 10, 2012** and in **British PHYSORG.com** in april 20, 2012.
- 2) InP@ZnSeS, Core@Composition Gradient Shell Quantum Dots with Enhanced Stability. *Chemistry of Materials*, **2011**, 23, 4459-4463.
- 3) Multicolored Light-Emitting Diodes Based on All-Quantum-Dot Multilayer Films Using Layer-by-Layer Assembly Method, *Nano Letters*, **2010**, 10(7), 2368-2373, (**Highlighted in MRS Bulletin**, Aug, **2010**, 35, p566).
- 4) Detection of TrkB Receptors Distributed in Cultured Hippocampal Neurons through Bioconjugation between Highly Luminescent (Quantum Dot-Neutravidin) and (Biotinylated Anti-TrkB Antibody) on Neurons by Combined Atomic Force Microscope and Confocal Laser Scanning Microscope. *Bioconjugate chemistry* **2010**, 21, 597-603.
- 5) Highly Efficient Green Light-Emitting Diodes Based on CdSe@ZnS Quantum Dots with Chemical Composition Gradient. *Advanced Materials* **2009**, 21, 1690-1694. (**Highlighted in Nature Journal**).
- 6) Solution-Based Direct Growth of Organic Crystals on an Active Channel Region for Printable Bottom-Contact OTFT, *Angew. Chem. Int. Ed.* **48**, 3096 (**2009**).
- 7) Organic Single-Nanofiber Transistors from Organogels. *Chemical Communications* **2009**, 310.

[S1-3]

## Quantum Molecular Spintronics Based on Multiple-Decker Phthalocyaninato Lanthanide(III) Single-Molecule Magnets

Masahiro Yamashita

*Department of Chemistry, Tohoku University, Sendai 980-8578, Japan*

Spintronics is a key technology in 21<sup>st</sup> century based on the freedoms of the charge, spin, as well as orbital of the electron. The MRAM systems (magnetic random access memory) by using GMR, CMR or TMR have several advantages such as no volatility of information, the high operation speed of nanoseconds, the high information memory storage density, and the low consuming electric power. Usually in these systems, the bulk magnets composed of the transition metal ions or conventional magnets are used, while in our study we will use Single-Molecule Quantum Magnets (SMMs), which are composed of multi-nuclear metal complexes and nano-size magnets. Moreover, SMMs show the slow magnetic relaxations with the double-well potential defined as  $|D|S^2$  and the quantum tunneling. Although the bulk magnets are used in conventional spintronics with the largest spin quantum number of 5/2 for example, we can create the artificial spin quantum numbers of 10, 20, 30, etc. in SMMs. Then, we can realize the new quantum molecular spintronics by using SMMs. According to such a strategy, we have synthesized the conducting SMM such as  $[\text{Pc}_2\text{Tb}]\text{Cl}_{0.6}$ , whose blocking temperature is 47K. The hysteresis is observed below 10K. This SMM shows the negative magnetoresistance below 8 K. As for the second strategy, we have a plane of the input/output of one memory into/from double-decker Tb(III) SMM ( $\text{Pc}_2\text{Tb}$ ) by using the spin polarized STM (Scanning Tunneling Microscopy). In this research, we have observed Kondo Effect at 4.8 K by using STS (Scanning Tunneling Spectroscopy) for the first time. We have succeeded in controlling the appearance and disappearance of Kondo Peak by the electron injection using STS, reversibly. This is considered as the first single-molecule memory device.<sup>1)</sup> As for the third strategy, we have made the FET (Field Effect Transistor) devices of SMMs. The  $\text{Pc}_2\text{Dy}$  device shows the ambipolar (n- and p-type) behavior, while the  $\text{Pc}_2\text{Tb}$  device shows the p-type behavior. Such a difference is explained by the energy levels of the lanthanide ions.<sup>2)</sup> As for the fourth strategy, we have made doping of Cs atoms onto  $\text{Pc}_2\text{Y}$ , where Kondo peaks have not observed by coupling of radical of Pc and s electron of Cs atom to make a single pair, while other  $\text{Pc}_2\text{Y}$  shows Kondo peak due to their radicals. Finally, we have succeeded to write the letters of T and U, which are the initials of Tohoku University, as shown in Figure.<sup>3-4)</sup>

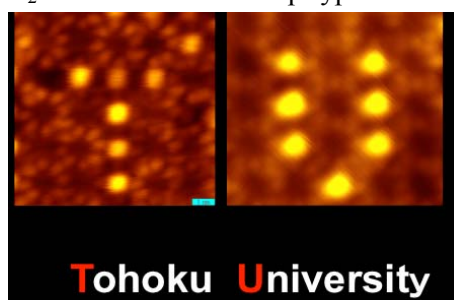


Fig. Initials of Tohoku University

### References

- (1) T. Komeda, M. Yamashita, et al., **Nature Commun.**, 2, 217 (2011).
- (2) K. Katoh, M. Yamashita, et al., **J. Am. Chem. Soc.**, 131, 9967 (2009).
- (3) Z. Wei-Xiong, M. Yamashita, et al., **J. Am. Chem. Soc.**, 134, 6908 (2012).
- (4) R. Robles, N. Lorente, T. Komeda, M. Yamashita, et al., **Nano Lett.**, in press(2012).

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1982 Kyushu University (PhD)  
1983 Assistant Professor of Kyushu University  
1987 Associate Professor of Nagoya University  
1998 Professor of Nagoya University  
1999 Professor of Tokyo Metropolitan University  
2004- Professor of Tohoku University  
2007- Concurrent Professor of Nanjing University (China), Zhenjiang University (China), and Cagliari University (Italy)

## Awards & Distinctions:

2002 Award of Inoue Scientific Foundation  
2005 The Chemical Society of Japan Award for Creative Work for 2005  
2009- Associate Member of Science Council of Japan

## Research Interests:

1. Quantum Molecular Spintronics Based on Single-Molecule Magnets
2. Nano-Wire Metal Complexes with Strong Electron Correlations

## Representative Publications:

- 1) Gigantic Optical Nonlinearity in One-Dimensional Mott-Hubbard Insulators, H. Kishida, H. Matsuzaki, H. Okamoto, T. Manabe, M. Yamashita, Y. Taguchi, and Y. Tokura, *Nature*, 405, 929-932 (2000).
- 2) Observation and Electric Current Control of a Local Spin in a Single-Molecule Magnet, T. Komeda, H. Isshiki, Y. F. Zhang, N. Lorente, K. Katoh, Y. Yoshida, M. Yamashita, and B. K. Breedlove, *Nature Commun.*, 2, 217-223 (2011).
- 3) New approach of constructing single-chain magnet: Canted antiferromagnetic manganese chains isolated by H-bonds of nucleobase moieties, Z. Wei-Xiong, T. Shiga, H. Miyasaka, and M. Yamashita, *J. Am. Chem. Soc.*, 134, 6908-6912 (2012).
- 4) Kondo resonance Observation of a Stable radical Molecule of 1,3,5-Triphenyl-6-Oxoverdazyl (TOV) Adsorbed on Au(111), T. Komeda, H. Isshiki, J. Liu, T. Morita, K. Katoh, and M. Yamashita, *J. Am. Chem. Soc.*, accepted (2012).
- 5) Spin Doping of Individual Molecules by Using Single-Atom Manipulation, R. Robles, N. Lorente, H. Isshiki, J. Liu, K. Katoh, M. Yamashita, and T. Komeda, *Nano. Lett.*, 12, 3609-3612 (2012).

[S1-4]

## **Circulatory Osmotic Desalination Based on LCST Materials**

Yan Lee

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Abrupt change of the effective concentration and osmotic pressure of lower critical solution temperature (LCST) mixtures allows us to design a continuous desalination method driven by mild temperature gradient. Water molecules could be drawn from a high-salt solution to the LCST mixture through a semipermeable membrane at a temperature lower than the phase transition temperature, at which the effective osmotic pressure of the LCST mixture was higher than the high-salt solution. After transfer of water to the high T unit where the LCST mixture was phase-separated, the upper water-rich phase could release the drawn water into a much diluted solution by spontaneous osmosis due to the significant decrease of the effective concentration. The lower LCST solute-rich phase could be recovered into the low T unit via the circulation process. The molar mass, phase transition temperature, and aqueous solubility of the LCST solute could be tuneable for the circulatory osmotic desalination system in which drawing, transfer, release of water, and the separation and recovery of the solutes could proceed simultaneously. Development of a practical desalination system to draw water molecules directly from seawater and to produce low-salt water with high purity by mild temperature gradient possibly induced by sunlight or waste heat could be attainable by a careful design of the molecular structure and combination of the circulatory desalination systems based on low- and high-molar-mass LCST draw solutes.

### **References**

- (1) Elimelech M, Philip WA. Desalination: energy, technology and the environment. *Science* 2011; 333: 712-17.
- (2) Kim H, Lee S, Noh M, Lee SH, Mok Y, Jin G, Seo J, Lee Y. Thermosensitivity control of polyethylenimine by simple acylation. *Polymer* 2011; 52: 1367-74.
- (3) Noh M, Mok Y, Lee S, Kim H, Lee SH, Jin G, Seo J, Koo H, Park TH, Lee Y. Novel lower critical solution temperature phase transition materials effectively control osmosis by mild temperature changes. *Chem Commun* 2012; 48: 3845-47.)

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2001 Ms. Sc., Seoul National University, Seoul, Korea  
2005 Dr. Sc., Seoul National University, Seoul, Korea  
2005 Postdoc, the University of Tokyo, Tokyo, Japan  
2008 Project Assist. Prof., the University of Tokyo, Tokyo, Japan  
2009 Assist. Prof., Seoul National University, Seoul, Korea

### Research interests:

Development of biocompatible functional materials responding to signals such as temperature, pH, ionic concentration, and reduction potentials

### Representative Publications:

- 1) "Novel lower critical solution temperature phase transition materials effectively control osmosis by mild temperature change" (2012) *Chem. Commun.* 48, 3845-3847
- 2) "Efficient delivery of bioactive antibodies into the cytoplasm of living cells by charge-conversional polyion complex micelles" (2010) *Angew. Chem. Int. Ed.* 49, 2552-2555.
- 3) "Charge-conversional PIC micelles – an efficient protein delivery nanocarrier into cytoplasm" (2009) *Angew. Chem. Int. Ed.* 48, 5309-5312.
- 4) "Charge-conversional ternary polyplex with endosome disruption moiety: a technique for efficient and safe gene delivery" (2008) *Angew. Chem. Int. Ed.* 47, 5163-5166.

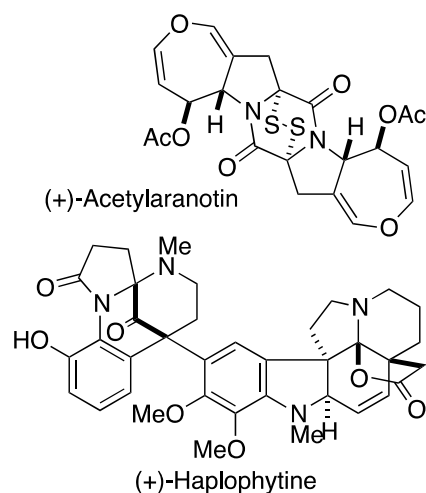
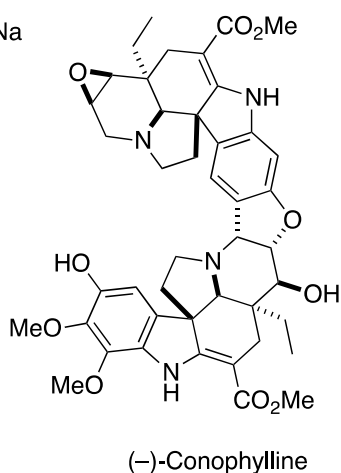
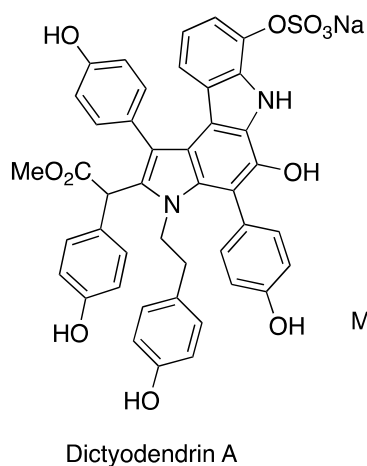
[S2-1]

## Total Synthesis of *N*-Heterocyclic Natural Products

Hidetoshi Tokuyama

*Graduate School of Pharmaceutical Sciences, Tohoku University, Aoba 6-3, Aramaki, Aoba-ku, Sendai 980-8578, Japan*

Since *N*-containing heterocyclic rings are the common structural motifs in biologically important natural products and functional molecules, development of new synthetic methodologies for formation of *N*-heterocycles have been one of the major research topics in the field of synthetic organic chemistry. In this talk, development of new synthetic methodologies and their application to total synthesis of complex alkaloids will be discussed. For formation of the per-substituted indole structure in dictyodendrin A, we have devised a one-pot benzyne-mediated cyclization- functionalization strategy, which led to completion of total syntheses of dictyodendrin A-E. In our total synthesis of a dimeric indole alkaloid, (+)-haplophytine, we have established an oxidative skeletal rearrangement for construction of the characteristic left-hand segment containing aminal and bridged ketone. The dihydrofuran moiety between monomer units in (–)-conophylline was formed by a region- and stereoselective Polonovsky-type reaction. An efficient protocol including diastereoselective vinylogous Rubottom oxidation and regioselective Baeyer-Villiger oxidation was developed for construction of the monomer unit of a dithiodiketopiperazine alkaloid acetylaranotin. The reactions and strategies developed in these synthetic studies would be useful for construction of a broad range of heterocyclic compounds such as drug candidates and other functional molecules.



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Hidetoshi Tokuyama was born in Yokohama in 1967. He received his Ph.D. in 1994 from Tokyo Institute of Technology under the direction of Professor Ei-ichi Nakamura. He spent one year (1994-1995) at the Department of Chemistry, University of Pennsylvania as a postdoctoral fellow with Professor Amos B. Smith, III. He joined the group of Professor Tohru Fukuyama at the Graduate School of Pharmaceutical Sciences, the University of Tokyo in 1995 and was appointed Associate Professor in 2003. In 2006, he moved to Tohoku University, where he is currently Professor of Pharmaceutical Sciences. His research interests are centered on development of synthetic methodologies and total synthesis of natural products.

Awards: The Pharmaceutical Society Japan Award for Young Scientist (2003); Banyu Young Chemist Award (2006); Young Scientist's Prize: The Commendation for Science and Technology by MEXT, Japan (2007); Asian Core Program Lectureship Award (2006, 2009); Nagase Foundation Award (2011).

### Representative Publications:

- 1) Total Synthesis of (–)-Acetylaranotin, H. Fujiwara, T. Kurogi, S. Okaya, K. Okano, H. Tokuyama, *Angew. Chem. Int. Ed.*, **51**, 13062-13065 (2012).
- 2) Total Synthesis of (–)-Conophylline and (–)-Conophyllidine, Y. Han-ya, H. Tokuyama, T. Fukuyama, *Angew. Chem. Int. Ed.*, **50**, 4884-4887 (2011).
- 3) Total Synthesis of Dictyodendrin A and B, K. Okano, H. Fujiwara, T. Noji, T. Fukuyama, H. Tokuyama, *Angew. Chem. Int. Ed.*, **49**, 5925-5929 (2010).
- 4) Total Synthesis of (+)-Haplophytine, H. Ueda, H. Satoh, K. Matsumoto, K. Sugimoto, T. Fukuyama, H. Tokuyama, *Angew. Chem. Int. Ed.*, **48**, 7600 (2009).

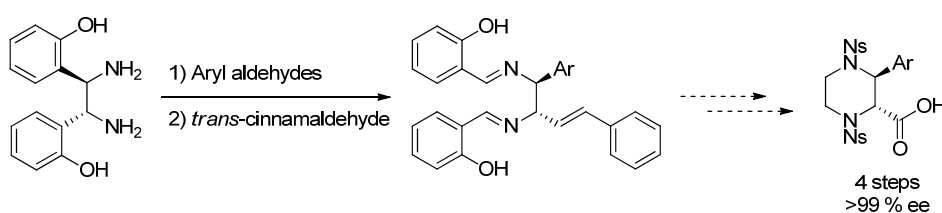
[S2-2]

## Chiral Diamine Chemistry: Application to Efficient Synthesis of Chiral Piperazine Derivatives

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Chiral vicinal diamines have been utilized for the development of chiral ligands for effective chiral catalysts and also as important intermediates for physiologically active substances. Development of efficient synthetic methods of the chiral vicinal diamines, therefore, has received much attention. Recently a new synthetic method incorporating diaza-Cope rearrangement as a key step has been developed and a variety of chiral vicinal diamines can now be synthesized.<sup>1</sup> Piperazine-2-carboxylic acid is as an amino acid surrogate and therefore has been utilized in many physiologically active compounds. Although many synthetic methods have been developed for 2-, 3-, or 2,3-disubstituted piperazines, chiral piperazine derivatives are still hard to obtain in an enantiomerically pure form. From our stereospecific synthesis of chiral vicinal diamines through the rearrangement of diimines prepared from 1 eq 1,2-bis(2-hydroxyphenyl)-1,2-diaminoethane (HPEN) and 1 eq each of two aldehydes, we have developed a new method for the synthesis of chiral piperazine derivatives. The chiral nonsymmetrical 2,3-disubstituted vicinal diamines prepared by diaza-Cope rearrangement (DCR) could serve as suitable intermediates for the preparation of chiral nonsymmetrical 2,3-substituted piperazines. Herein, we report on the development of an efficient route for enantiopure *trans*-3-arylpiperazine-2-carboxylic acid derivatives starting from optically pure HPEN via DCR using various aryl aldehydes and *trans*-cinnamaldehyde. Piperazine ring formation using the previously reported diphenylvinyl sulfonium triflate<sup>2</sup> followed by oxidation using ruthenium(III) chloride monohydrate in presence of sodium periodate provided the desired enantiopure *trans*-3-arylpiperazine-2-carboxylic acid derivatives.<sup>3</sup>



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2005 The Best Teacher of the Year Award, College of Natural Sciences, SNU  
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2010-2012 Review Board of Organic Chemistry, National Research Foundation, Korea  
2012- Chief Review Board of Chemistry, National Research Foundation, Korea

### Research Interests:

1. Synthetic Organic Chemistry, Asymmetric Synthesis and Heterogeneous Catalysis
2. Medicinal Chemistry on Anti-cancer, Anti-HCV and CRHR-1 Antagonist Development

### Representative Publications:

- 1) A short synthesis of enantiopure trans-3-arylpiperazine-2-carboxylic acid derivatives via diaza-Cope rearrangement (DCR), S. H. Kwon, S. M. Lee, S. M. Byun, J. Chin, B. M. Kim, *Org. Lett.* **14**, 3664-3667 (2012).
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[P1-1]

## Synthesis, Applications, and Practical Use of Functional Metallophthalocyanines

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Harmful organic molecules, bacteria, and viruses can be changed to other harmless compounds by oxidation reactions. Although oxidation reactions are quite often harmful for living organisms such as animals and plants, these are effectively catalyzed by several iron porphyrins, called heme proteins (peroxidase, oxygenase, catalase), in our body. If we can mimic the functions of these heme enzymes using easily-accessible artificial compounds, it may be possible to convert harmful organic molecules, viruses, and bacteria to harmless substances. As candidates for these artificial enzymes, we have prepared iron and cobalt phthalocyanines containing four or eight carboxyl groups in the periphery, i.e. Fe- or CoPc(COOH)<sub>4</sub> and Fe- or CoPc(COOH)<sub>8</sub>, and examined their catalytic activity for the oxidation of various compounds, including thiol, ammonia, mercaptan, aldehyde, hydrogen peroxide, hydrogen sulfide, amine, and halogenated phenols. The investigated organic compounds with bad odours were converted or decomposed to less odorous or less harmful compounds by these artificial catalysts via peroxidase-like, oxygenase-like, or catalase-like reactions, indicating that these compounds are potentially useable as deodorants. Setting the activity of activated charcoal at unity, the activity for the decomposition of gaseous substances with foul odours, such as triethylamine, ammonia, skatole, formaldehyde, methyl-mercaptan, and hydrogen sulphide, by FePc(COOH)<sub>8</sub>-adsorbed fibers was *ca.* 20, 20, 130, 80, 100 and 100, respectively. Thus, these iron and cobalt phthalocyanines have been applied in wallpapers and bedding, in addition to ventilation systems of bullet trains, and for underwear. It was also confirmed that many bacteria, such as *E. Coli*, *S. Aureus* (MRSA-41 and -165), and *C. Albicans*, can be killed effectively by the action of FePc(COOH)<sub>8</sub> in the presence of oxygen.

In addition, poly-halogenated organic compounds, such as trichlorophenol, can be easily decomposed within a few minutes, with the result that pilot plants to decompose these compounds have been built in several industrial districts in Japan. Viruses of human influenza and bird flu were killed by more than 99.999% within 10 min when FePc(COOH)<sub>8</sub> was bound to facemasks, so that 20000 masks were sent to Mexico when swine flu spread there a few years ago.

The use of several phthalocyanines containing zinc, silicon, magnesium, and aluminium as photosensitizers in photodynamic therapy (PDT) is also introduced, together with the mechanism of PDT. The author's aluminium-containing compound has been used in the hospitals of eastern Europe from 1994.

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The CSJ Award for Creative Work (2006)  
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### Research Fields:

Porphyrinoid chemistry; Phthalocyanine chemistry; CD and MCD Spectroscopy, Electrochemistry, Molecular orbital calculation

### Representative Publications:

- 1) Synthesis, Reactions, and Electronic Properties of 16-electron Octaisobutyltetraphenylporphyrin. Y. Yamamoto, Y. Hirata, A. Muranaka, M. Uchiyama, P. Chen, K. M. Kadish, and N. Kobayashi, *J. Am. Chem. Soc.* **132**, 12627-12638 (2010).
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- 3) Crystal Structures and Electronic Properties of Saddle-Distorted and Protonated Phthalocyanines. T. Honda, T. Kojima, N. Kobayashi, and S. Fukuzumi, *Angew. Chem. Int. Ed.* **50**, 2725-2728 (2011).
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[P1-2]

## **Fabrication of Hollow Nanoparticles with Functionalized Interior Surface for the Nanoreactor Application**

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An important research direction in nanoscience is to synthesize and fabricate colloidal hybrid-nanocrystals. Despite the recent development of synthetic methods, precise control of their phase, structure, and consequent properties is still a significant challenge. Most reported methods employ solution-based reactions to synthesize hybrid nanoparticles rather than solid-state reactions due to the high temperatures required in the latter process that causes coalescence and coarsening of the nanostructures. In this context, our research has been focused on developing a novel approach to manipulate hybrid nanoparticles based on an understanding of the solid-state reactions between nanoparticles. In this presentation, a novel method of synthesizing various hybrid-nanoparticles based on the solid-state reaction and transformation of the nanocrystals as confined within nano-sized silica sphere. I will also demonstrate the further transformation of silica nanosphere encapsulating hybrid-nanocrystals into the hollow nanospheres with functionalized interior cavity and their successful employment as a nanoreactor system for the high-concentration synthesis of metal nanocrystals with a potential as a catalyst in the fuel cell application. I will also present the fabrication of a novel nanoreactor framework consisting of a hollow silica shell with catalytically functionalized interior surface and their employment in the selective catalytic reactions.

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In Su Lee (born in Seoul, Korea in 1973) received his BS (1995) in chemistry from the Seoul National University. He obtained his PhD (2000) from the same institute under the supervision of Professor Young Keun Chung. After the work as a senior researcher at LG chemical (2000-2003), the post-doctoral research with Jeffrey Long at UC Berkeley (2003-2005), and the research with Taeghawn Hyeon for Creative Research Initiative Center for Oxide Nanocrystalline Materials at Seoul National University (2005-2006), he worked at Department of Applied Chemistry as an assistant and associate professor (2006-2011). After this, he moved to Pohang University of Science and Technology (POSTECH) in September 2011 and joined the Department of Chemistry as an associate professor. His current research is focused on the synthesis and modification of hollow metal and metal oxide nanoparticles with interior cavity and finding of their applications in catalysis and biomedical field.

### Representative Publications:

- 1) "Reversible and Cyclical Transformation between Solid and Hollow Nanostructures in the Confined Reaction of Manganese Oxide and Silica within a Nano-sized Sphere" Ha, T. L.; Kim, J. G.; Kim, S. M.; Lee, I. S. *J. Am. Chem. Soc.* *in press* (2013).
- 2) "Fe<sub>3</sub>O<sub>4</sub>/MnO Hybrid Nanoparticles as a Dual Contrast Agent of Both T<sub>1</sub>- and T<sub>2</sub>- Weighted in-vivo Liver MRI" Lim, G. H.; Kim, S. M.; Lee, D. K.; Lee, W. J.; Lee J. H., Lee, I. S. *Biomaterials* **34**, 2069 (2013).
- 3) "Electroless Pt deposition on Mn<sub>3</sub>O<sub>4</sub> nanoparticle via the galvanic replacement process: Catalytic nanocomposite with enhanced performance for oxygen reduction." Kim, K. W.; Kim, S. M.; Choi, S.; Kim, J.; Lee, I. S. *ACS Nano*. **6**, 5122 (2012).
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- 5) "Unexplored thermal transformation behavior of two-dimensionally bound gadolinium hydroxide layers: Fabrication of oriented crystalline films of gadolinium oxychloride suitable for the multicolor luminescence with color tunability." Yoon, Y.-s.; Byeon, S.-H.; Lee, I. S. *Adv. Mater.* **22**, 3272 (2010).

[P1-3]

## Mechanism of Enantioselection in Asymmetric Catalytic Reactions

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Deep understanding of the mechanisms of catalytic reactions is required for the conscious catalysts design that would lead to the development of tunable multifunctional catalytic systems demonstrating the utmost catalytic performance. This understanding is especially crucial in the case of asymmetric catalytic reactions since the perception of the intrinsic mechanisms of enantioselection would result in the development of the catalytic systems closely resembling the natural enzymes capable of producing a single enantiomer of the optically active compound with perfect stereoselectivity. We have recently applied the combination of state-of-art computational techniques with advanced spectroscopic methods, in particular NMR spectroscopy for the mechanistic studies of catalytic asymmetric reactions. In this talk several examples of such studies will be summarized.

Extensive investigations of the Rh-catalyzed asymmetric hydrogenation using chiral di- or monophosphines resulted in the change of the mechanistic paradigm in this industrially important reaction.<sup>1,2</sup> It has been shown that stereoselection in the Rh-catalyzed asymmetric hydrogenation is taking place in the octahedral Rh(III) complexes, and the stereoselective stage is the secondary coordination of the prochiral double bond to the chiral Rh(III) atom.<sup>1</sup>

Chiral bifunctional Ru and Ir complexes are effective catalysts for the enantioselective C–C and C–N bond formation reactions. Combined NMR and DFT studies of several reactions of this type provided the understanding of the mechanism of enantioselection based on the transfer of chirality from the ligand to the metal center.<sup>3,4</sup>

Soai's autocatalytic alkylzinc alkylation is practically the only example of the chemical reaction that effectively amplifies chirality of its own catalyst. Revealing the exact chemical mechanism of its operation is important for the understanding of the origin of chiral life on the Earth. We have used large scale DFT computations combined with NMR experiments and kinetic simulations for the outline of the catalytic cycle of the Soai reaction.<sup>5</sup>

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- (5) I. D. Gridnev and A. Kh. Vorob'ev, *ACS Catalysis* **2012**, 2, 2137-2149.

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Ilya Gridnev is an Associate Professor of Graduate School of Science, Tohoku University. He received his Ph.D in 1989 from Moscow University. In 1990-1998 he was employed by Russian Academy of Science (Institute of Organic Chemistry and Institute of Organoelement Compounds). After two postdoctoral stays in Japan (JSPS Fellowship, Hokkaido University with Prof. A. Suzuki) and Germany (A. v. Humboldt Fellowship, Göttingen University with Prof. A. Meller) he got his Dr. Sci. Degree (“Habilitation”) from A. V. Nesmeyanov Institute of Organoelement Compounds, Moscow, Russia. In 1998-2007 he was employed as a Research Associate in University of Rennes, France, Chiba University, Japan, and Oxford University, UK. In 2003-2007 he was Associate Professor in Tohoku University (Sendai, Japan). From April 2007 to March 2012 he worked as Associate Professor in Tokyo Institute of Technology. From March 2012 he is employed by Tohoku University (Sendai, Japan) as Associate Professor. His research interests cover organometallic chemistry, reaction mechanisms, and NMR spectroscopy.

### Representative Publications:

- 1) T. Imamoto, K. Tamura, Z. Zhang, Y. Horiuchi, M. Sugiya, K. Yoshida, A. Yanagisawa, I. D. Gridnev, Rigid P-Chiral Phosphine Ligands with *tert*-Butylmethylphosphino Groups for Rhodium-Catalyzed Asymmetric Hydrogenation of Functionalized alkenes. *J. Am. Chem. Soc.* **2012**, *134*, 1754-1769.
- 2) I. D. Gridnev, M. Watanabe, H. Wang, T. Ikariya, Mechanism of Enantioselective C–C Bond Formation with Bifunctional Chiral Ru Catalysts: NMR and DFT Study. *J. Am. Chem. Soc.* **2010**, *132*, 16637-16650.
- 3) I. D. Gridnev, T. Imamoto, G. Hoge, M. Kouchi; Takahashi H. Asymmetric Hydrogenation Catalyzed by a Rhodium Complex of (R)-(tert-Butylmethylphosphino)(di-tert-butylphosphino) methane: Scope of Enantioselectivity and Mechanistic Study. *J. Am. Chem. Soc.* **130**, 2560-2572.

[P1-4]

## Developing New Diversity-Generating Synthetic Strategies Based on Metal Catalysis

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The diversity of natural products has attracted synthetic chemists over the past decades. Thus, developing new methodologies that can introduce molecular diversity with high chemical efficiency represents a primary goal in synthetic organic chemistry. Due to their high reactivity and chemoselectivity, organometal catalysts may play a unique role. In this presentation, our achievements in this area will be briefly introduced. First part of the talk will focus on developing structural diversity-generating strategies using Au-catalyzed reactions of 3-alkoxy-1,6-enynes.<sup>1,2</sup> The second part of talk will reveal our recent results on the synthesis of Pd-catalyzed synthesis of stereodefined *N,O*-acetals and their utilities as key elements in developing stereodiversity-generating<sup>3,4</sup> and substituent diversity-generating strategies.<sup>5</sup> Mechanistic aspects of the catalytic reactions as well as potential synthetic applications will be also discussed.

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- (5) *Angew. Chem. Int. Ed.* **2012**, *51*, 10851.



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### Representative Publications:

- 1) H. Kim and Y. H. Rhee, A Perspective on the Stereodefined N,O-acetals; Synthesis and Potential Applications, *Synlett* **2012**, 23, 2875 (Synfacts contribution invited by Editor-in-Chief Prof. Peter Volhardt).
- 2) H. Kim and Y. H. Rhee, Stereodefined N,O-acetals: Pd-catalyzed Synthesis from Homopropargylic Amines and Utility in the Flexible Synthesis of 2,6-Substituted Piperidines, *J. Am. Chem. Soc.* **2012**, 134, 4011.
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[P2-1]

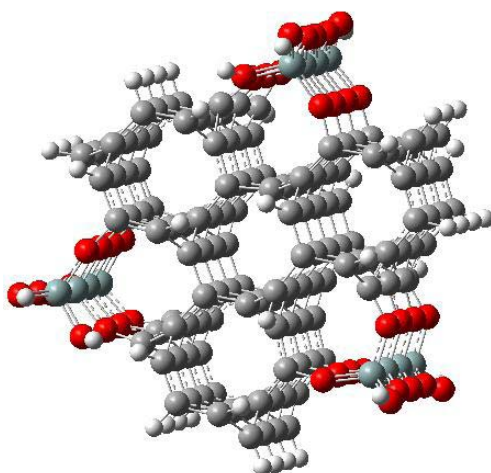
## Cluster Approach for New Material Design: A Theoretical DFT Study

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Over the years, we have applied the cluster approach for quantum chemical calculations on structures and chemical activity of representative transition metal and metal oxides as well as for other related issues. Particularly, we underlined the ultimate importance of proper modeling the structure and chemical activity of transition metal oxides as well as support structures to understand the mechanism of formation of precursor defect structures on TiO<sub>2</sub> (110) and number of surface catalytic reactions and transformations. It was also shown that the use of the finite size clusters in cluster calculations have well defined advantages in shedding light on tiny properties of various materials and reactions as well as could be even complimentary for other band structure or periodic slab calculations. Based on these results obtained, some discrepancies with the results of other theoretical investigations and studies in literature have been critically pointed out.

In line with the strategy in combining metal-organic frameworks (MOF) into extended IRMOF networks, a possible solution has been here proposed to stabilize and characterize new metallic carbon K4 crystal structures. A number of possibilities were considered which may include non-metal replacements of framework three-fold coordinated carbon atoms as well as some modifications involving either the selected C-H groups at each ends of the overall channel structure with a silica (or zeolite) or by the decoration of the whole carbon K4 structure by silicates (or zeolites) as shown in the Figure. This talk will discuss also the results of similar DFT cluster calculations obtained for modified IRMOF structures having ultrahigh surface areas.



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M. Sci. in Chemistry: Department of Inorganic Chemistry, Faculty of Chemistry, Kazakh State University, Alma-Ata, Kazakhstan (ex-USSR), 1979.

Thesis: *Radiation stimulated oxidation of phosphinates and phosphonates in aqueous solutions*

Ph.D. in Chemistry: Institute of Catalysis, Siberian Branch of the USSR Academy of Sciences, Novosibirsk, Russia (ex-USSR), 1987.

Thesis: *Quantum chemical study of solvation effects in heterogeneous catalytic reactions*

### **Publications:**

Author or co-author of more than 90 papers in International refereed journals as well as of more than 80 presentations in International Conferences.

### **Research Interests:**

Advanced theoretical quantum chemistry

Catalysis and chemisorption

Development of computational programs and softwares

Computational spectroscopy

[P2-2]

## All-Atom Semi-Classical Nonadiabatic Simulations of Excitation Energy Transfer Process In Photosynthetic Fenna-Matthews-Olson Complex

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Recent experimental and theoretical studies have revealed that the excitation energy transfer (EET) can exhibit coherent characteristics in various photosynthetic systems. However, how the noise-inducing protein helps to maintain the coherence has not been fully elucidated yet. Applying an all-atom nonadiabatic simulation technique will be extremely advantageous for the elucidation, as it can offer detailed views on protein-chromophore interactions. Here, we will present the results of our semiclassical Poisson bracket mapping equation simulations on EET of the Fenna-Matthews-Olson complex. We will show that the chromophore coupling maintained by the protein scaffold is the key factor for governing the coherence. The electrostatic modulations by the protein and the related site energy dispersion have only a limited effect. The role of thermal fluctuations in the chromophore couplings will be additionally inspected in view of EET pathway diversity. Limitations and future aspects of our approach will also be discussed as concluding remarks.

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### Representative Publications:

- 1) Park, J.W.; Rhee, Y.M. Interpolated Mechanics - Molecular Mechanics Study of Internal Rotation Dynamics of the Chromophore Unit in Blue Fluorescent Protein and Its Variants, *J. Phys. Chem. B* **2012**, *116*, 11137.
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