

2nd Campus Asia Symposium on Frontiers of Chemistry and Materials

March 11 - 13, 2013, Nanjing, China



Nagoya University

Pohang University of Science and Technology



Seoul National University

Tohoku University



Shanghai Jiao Tong University

Nanjing University



誠樸雄偉
勵學敦行

**2nd Campus Asia Symposium on
Frontiers of Chemistry and Materials**

Program & Abstracts

March 11-13, 2013

Nanjing, China

**School of Chemistry and Chemical Engineering
Nanjing University**

Preface

The first CAMPUS ASIA Symposium was successfully held in Nagoya last year. This year's symposium will be held in Nanjing University on March 11 to 13. On behalf of the organizing committee of this symposium, we would like to extend our warmest welcome to all the participants from home and abroad. The symposium is a continuous effort by scientists in this region to afford a channel for the exchange of innovative ideas and provide a platform for presentation and discussion of new research findings in the frontiers of chemistry and materials.

Nanjing University has been entrusted to host this 2nd Campus Asia Symposium on Frontiers of Chemistry and Materials. We feel very honored to have the Japanese and Korean delegation as well as colleagues from Shanghai Jiao Tong university as invite lecturers. The content of the abstract book comprises 33 presentations and 38 posters covering materials science, inorganic and organic chemistry, biochemistry, catalyst design and other interested topics in the frontiers of chemistry and materials.

There is a well-known saying in China, that is, "How happy we are, to meet friends from afar!" We are quite confident that highly effective discussions among the participants will lead to the great success of this symposium. We sincerely hope you will take this opportunity to take a glance over the fascinated sights in Nanjing and enjoy a colorful life in your leisure time.

Prof. Zijian Guo

Dean of School of Chemistry and Chemical Engineering
Nanjing University

Monday, March 11, 2013

18:00-20:00

Reception (Xiyuan Hotel)

Tuesday, March 12, 2013 (Second floor, Feiyimin Building)

Chairman: **Prof. Xinghua Xia**

8:30-9:10

Opening Ceremony

Prof. Yi Pan (Vice President of NJU)
Prof. Zijian Guo (Dean)
Group Photo

Chairman: **Zijian Guo** (Nanjing Univ.)

9:10-9:30

Metal-organic frameworks from highly symmetric and multidentate ligands: new methodology, structures, properties, perspectives

Jun-Feng Bai (Nanjing Univ.)

9:30-9:50

The Excitons in Colloidal Quantum Dots and Flexible, Portable QLEDs

Seonghoon Lee
(Seoul National Univ.)

9:50-10:10

Functional Materials Derived from Porous Hosts

Jiesheng Chen
(Shanghai Jiao Tong Univ.)

10:10-10:30

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

Masahiro Yamashita
(Tohoku Univ.)

10:30-10:40

Coffee Break

Chairman: **Seonghoon Lee** (Seoul National Univ.)

10:40-11:00

Photoresponsive Polymer Thin Films Possessing Mesoscopic Architectures

Takahiro Seki (Nagoya Univ.)

11:00-11:20

Luminescent Carbon Nanodots: A New Era in Graphitic Carbon Nanomaterials

Shi-Woo Rhee
(POSTECH)

11:20-11:40

Synthesis and Properties of Superazaporphyrins and Chiral and/or Low-Symmetry Subphthalocyanines

Nagao Kobayashi
(Tohoku Univ.)

11:40-12:00

Radical Chemistry with Weakly Coordinating Anions

Xinping Wang
(Nanjing Univ.)

12:00-13:00	Lunch	
13:00-15:00	Poster Exhibition (First floor, Feiyimin Building)	
Chairman: Masahiro Yamashita (Tohoku Univ.)		
15:00-15:20	Chiral mesoporous materials and their optical activity	Shun-Ai Che (Shanghai Jiao Tong Univ.)
15:20-15:40	Azobenzene-Containing Palladium Complexes and Their Self-Assembly	Mina Han (Nagoya Univ.)
15:40-16:00	Cluster Approach to Catalysis and New Materials Design	Nurbosyn U. Zhanpeisov (Tohoku Univ.)
16:00-16:20	Computer Simulations of Equilibrium and Kinetics Adsorptions of Carbon Dioxide on Zeolitic Imidazolate Frameworks	Fenglei Cao (Shanghai Jiao Tong Univ.)
16:20-16:30	Coffee Break	
Chairman: Shun-Ai Che (Shanghai Jiao Tong Univ.)		
16:30-16:50	Evaporation and Condensation Mechanisms through Monolayer Films	Akihiro Morita (Tohoku Univ.)
16:50-17:10	Advanced carbon-based nanotubes/nanocages for energy conversion and storage: synthesis, performance and mechanism	Zheng Hu (Nanjing Univ.)
17:10-17:30	Osmotic Control by Temperature-Sensitive Materials for Water Desalination	Yan Lee (Seoul National Univ.)
17:30-17:50	Insight into the Silica Mesoporous Crystals with Cage-type Structures	Lu Han (Shanghai Jiao Tong Univ.)
18:00	Dinner	
Wednesday, March 13, 2013 (Second floor, Feiyimin Building)		
Chairman: Zhen Liu (Nanjing Univ.)		
9:00-9:20	Molecular Recognition and Sensing: Challenges and Opportunities	Kyo Han Ahn (POSTECH)

9:20-9:40	Arsenic Analysis by Carrier-Mediated Counter-Transport Single Drop Microextraction/Capillary Electrophoresis	Doo Soo Chung (Seoul National Univ.)
9:40-10:00	An artificial Signal Transduction System Consisting of Electron Transfer Proteins	Hiroshi Nakajima (Nagoya Univ.)
10:00-10:20	Lesson from Nature: Mussel Adhesive Biomaterials	Hyung Joon Cha (POSTECH)
10:20-10:30	Coffee Break	
Chairman: Kyo Han Ahn (POSTECH)		
10:30-10:50	Insights on Peptide Self-Assembly and Protein Aggregation	Seokmin Shin (Seoul National Univ.)
10:50-11:10	Solid-phase Total Synthesis of Biologically Active Cyclodepsipeptide Natural Products	Takayuki Doi (Tohoku Univ.)
11:10-11:30	Chemosensors for Redox-responsible Biomolecules	Jong-In Hong (Seoul National Univ.)
11:30-11:50	Photolithographic Boronate Affinity Molecular Imprinting: a General and Facile Approach for Glycoprotein Imprinting	Zhen Liu (Nanjing Univ.)
12:00-13:00	Lunch	
13:00-15:00	Meeting of Campus Asia Committee	
Chairman: Susumu Saito (Nagoya Univ.)		
15:00-15:20	Development of Novel Heterocycles as Potent CRHR-1 Antagonists and Cdk Inhibitors	Byeong Moon Kim (Seoul National Univ.)
15:20-15:40	Ru-catalyzed Transformation of Alkyl Azides into <i>N</i> -unsubstituted Imines	Jaiwook park (POSTECH)
15:40-16:00	Chemo- and Enantioselective Hydrogenation of Functionalized Carbonyl Group and Their Applications in the Synthesis of Pharmaceutical Molecules	Zhaoguo Zhang (Shanghai Jiao Tong Univ.)
16:00-16:20	Enantioselective Synthesis of Heterocycles by Using Organocatalytic Intramolecular Aza-Michael Additions	Shouyun Yu (Nanjing Univ.)
16:20-16:30	Coffee Break	

Chairman: Yong Zhang (Shanghai Jiao Tong Univ.)		
16:30-16:50	From Supramolecular Polymers to Dynamic Catenanes by Orthogonal Self-Assembly	Leyong Wang (Nanjing Univ.)
16:50-17:10	Unraveling The Mechanism of Enantioselection in Rh-Catalyzed Asymmetric Hydrogenation	Ilya D. Gridnev (Tohoku Univ.)
17:10-17:30	Catalytic Hydrogenation of Unactivated Amides	Susumu Saito (Nagoya Univ.)
17:30-17:50	Hierarchical Supramolecular Arrays of Metal Complexes	Kentaro Tanaka (Nagoya Univ.)
17:50-18:10	Fluorescent Imaging of Biorelated Inorganic Species	Weijiang He (Nanjing Univ.)
18:10	Closing Remarks/Dinner	

Accommodation: Xiyuan Hotel and Anzhong Building (20# JinYin Street at Shanghai Road, Nanjing)

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Metal-organic frameworks from highly symmetric and multidentate ligands: new methodology, structures, properties, perspectives

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Keywords: Metal-organic frameworks; gases storage and separation, biomimic, functional groups

Abstract: These two decades have witnessed the rapid development of metal-organic frameworks (MOFs) due to their fantastic structures and various potential applications, such as strategic gases storage and separation, catalysis and chemical sensor. Exploring highly symmetrical multi-topic ligands to construct MOFs is of higher interests. In order to enrich and expand this interesting research area, we are devoted in new methodology, structures, properties, perspectives of MOFs. Herein, we present several interesting MOFs (Fig. 1a and 1b), their formation processes and their new properties. (Fig. 1c)

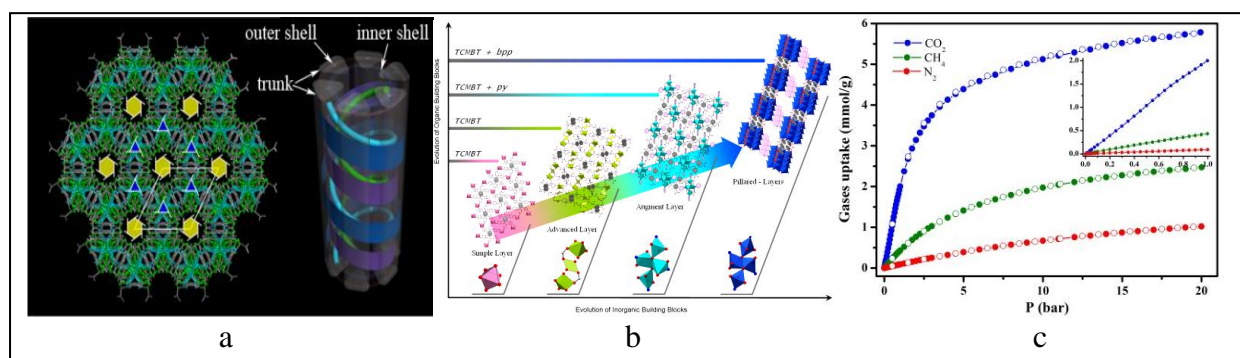


Fig. 1 (a) An unprecedented 3D architecture with multiwalled tubular channels and interweaving of single-helical and novel unequal double-helical chains. (b, c) A water stable MOF constructed through evolution approach shows good CO₂ adsorption and selectivity.

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- [4] Bai JF, Virovets AV, Scheer M. Synthesis of inorganic fullerene-like molecules [J]. Science 2003; 300: 781.

Short resume:

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Education:

1991 B. Sc., Northwest Normal University, Lanzhou, China
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Research interests:

Designing and constructing of metal-organic frameworks as new energy storage and gas separation materials, nanotechnology and crystal engineering.

Selected publications:

1. “Fine-Tuning Pore Size by Shifting Coordination Sites of Ligands and Surface Polarization of Metal-Organic Frameworks to Sharply Enhance the Selectivity for CO₂”, L.-T. Du, Z.-Y. Lu, K.-Y. Zheng, J.-Y. Wang, X. Zheng, Y. Pan, X.-Z. You and J.-F. Bai*, *J. Am.Chem.Soc.*,2013, 135, 562–565.
2. “High and selective CO₂ capture of two mesoporous acylamide-functionalized rht-type metal-organic frameworks”, B.-S. Zheng, Z. Yang, J.-F. Bai*, Y.-Z. Li, S.-H. Li*, *Chem. Commun.*, 2012, 48, 7025–7027.
3. “Highly selective CO₂ capture of an agw-type metal–organic framework with inserted amides: experimental and theoretical studies”, J.-G. Duan, Z. Yang, J.-F. Bai*, B.-S. Zheng, Y.-Z. Li, S.-H. Li*, *Chem. Commun.*, 2012, 48, 3058-3060.
4. “Water Stable Metal–Organic Framework Evolutionally Formed from a Flexible Multidentate Ligand with Acylamide Groups for Selective CO₂ Adsorption”, Z.-Y. Lu, H. Xing, R. Sun, J.-F. Bai*, B.-S Zheng, Y.-Z Li, *Cryst. Growth Des.* 2012, 12, 1081.
5. “Enhanced CO₂ Binding Affinity of a High-Uptake rht-Type Metal–Organic Framework Decorated with Acylamide Groups”, B.-S. Zheng, J.-F Bai*, J.-G. Duan, L. Wojtas and M. J. Zaworotko*, *J. Am.Chem.Soc.*,2011, 133, 748–751.
6. “Temperature controlled reversible change of the coordination modes of the highly symmetrical multitopic ligand to construct coordination assemblies: Experimental and theoretical studies”, B. Zheng, H. Dong, J.-F. Bai*, Y.-Z. Li, S.-H. Li*, M. Scheer*, *J. Am. Chem. Soc.*,2008, 130,7778-7779.
7. “Unprecedented interweaving of single-helical and unequal double-helical chains into chiral metal-organic open frameworks with multiwalled tubular structures”, S.-N. Wang, H. Xing, Y.-Z. Li, J.-F. Bai*, M. Scheer*, Y. Pan* and X.-Z. You, *Chem. Commun.*, 2007, 2293-2295.
8. “Synthesis of InorganicFullerene-Like Molecules”, J. Bai, A.V. Virovets, M. Scheer*, *Science*, 2003, 300, 781-783.

The Excitons in Colloidal Quantum Dots and Flexible, Portable QLEDs

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Keywords: Quantum dot, Exciton, Electroluminescence, Semiconductor, Display

The control and motion of electrons and atoms at a nanoscale have been investigated in relation to the creation of new functional advanced material and to the understanding of life, biological system(ubiquitous natural nanostructures), 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). I will present the new kinds of chemical building elements called nanoscale artificial atoms-semiconducting quantum dots. Excitons play a major role in such nanostructures. Various Quantum confinement, high QY, and nonlinear effects of artificial atoms can be explained in term of excitons at the nanoscale. Utilizing reactivity differences in precursors, we can produce artificial atoms in a large scale by a single-step synthetic method. The systematic analysis of the exciton in various nanostructures were done.

With a layer-by-layer assembly method, we have realized various useful optoelectronic devices. I'll present highly bright, low-voltage driven colloidal quantum dot based R/G/B/white light-emitting devices (white-QLEDs). White-QLEDs exhibiting luminance of 500 ~ 5,000 cd m⁻² at applied bias below 6 V and external quantum efficiency of 1% have been successfully realized. And practicable traffic signals, display back-lights, and white illumination sources are exemplified.

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- [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).
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- [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.)
- [4] 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**).

Short resume:

Full name: Seonghoon Lee

Education:

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1993 Ph.D., Harvard University, Cambridge, MA. U.S.A.



Professional 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.

Awards/ 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.

Selected Recent 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.

Functional Materials Derived from Porous Hosts

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Keywords: zeolites, porous hosts, functional materials, CO₂ decomposition, S₃ anionic radicals, water sensors, photocatalysis, methane coupling dehydrogenation, electron transfer

Zeolites and related porous materials have been widely used in the traditional fields of adsorption, separation and catalysis. However, these materials have recently attracted enormous attention as hosts for fabrication of host-guest functional materials as well. Through vapor reaction of metallic zinc with protonated zeolites, we have prepared univalent zinc-containing host-guest composites with various zeolite structures as the hosts. The univalent zinc species are attached on the pore walls of the zeolites, balancing the negative charges of the latter [1]. It is found that electrons may be transferred from the univalent zinc to elements with larger electronegativities to form anionic radicals such as S₃⁻ which functions as a supersensitive water sensor [2]. The univalent zinc located in ZSM-5 catalyzes methane conversion to ethane and hydrogen with high selectivity [3], whereas the Zn⁺-containing zeolite Y facilitates [4] the decomposition of CO₂ to C and O₂ under mild conditions. Electrons may also be transferred from zeolite frameworks to organic molecules, rendering the former paramagnetic [5].

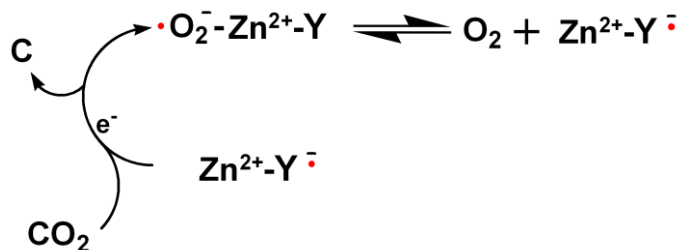


Fig. 1. Schematic representation for the decomposition of CO₂ to C and O₂ in Zn⁺-zeolite Y.

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Education:

- 1983 B. Sc., Zhongshan University, Guangzhou, China
1986 Ms. Sc., Zhongshan University, Guangzhou, China
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Professional career:

- 1990 Postdoc, Royal Institution of Great Britain, London, UK
1994 Prof., Jilin University, Changchun, China
2008 Prof., Shanghai Jiao Tong University, Shanghai, China



Research interests:

Solid state chemistry; inorganic synthesis; functional porous materials; catalysis; electrode materials for lithium-ion batteries; photoelectric conversions; sensors.

Selected publications:

1. L. Li, G. D. Li, C. Yan, X. Y. Mu, X. L. Pan, X. X. Zou, K. X. Wang, J. S. Chen*, Synergistic Effect on Photoactivation of Methane C-H Bond over Ga³⁺-Modified ETS-10, *Angew. Chem. Int. Ed.*, 2012, 51: 4702-4706.
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3. L. Li, G. D. Li, C. Yan, X. Y. Mu, X. L. Pan, X. X. Zou, K. X. Wang, J. S. Chen*, Efficient Sunlight-Driven Dehydrogenative Coupling of Methane to Ethane over a Zn⁺-Modified Zeolite, *Angew. Chem. Int. Ed.*, 2011, 50: 8299-8303.
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Quantum Molecular Spintronics Based on Multiple-Decker Phthalocyaninato Lanthanide(III) Single-Molecule Magnets

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Keywords: Quantum Molecular Spintronics, Single-Molecule Magnets, STM, STS

Spintronics is a key technology in 21st 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 (Pc_2Tb) 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.¹⁾ As for the third strategy, we have made the FET (Field Effect Transistor) devices of SMMs. The Pc_2Dy device shows the ambipolar (n- and p-type) behavior, while the Pc_2Tb device shows the p-type behavior. Such a difference is explained by the energy levels of the lanthanide ions.²⁾ As for the fourth strategy, we have made doping of Cs atoms onto Pc_2Y , 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 Pc_2Y 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.³⁻⁴

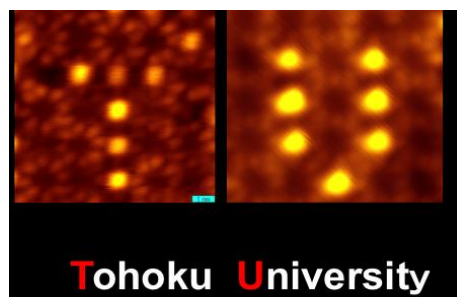


Fig. Initials of Tohoku University

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1998 Professor of Nagoya University

1999 Professor of Tokyo Metropolitan University

2002-2004 Visiting Professor of Institute for Molecular Science

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

Selected Publications

[1] Gigantic Optical Nonlinearity in One-Dimensional Mott-Hubbard Insulators, H. Kishida, H. Matsuzaki,

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Photoresponsive Polymer Thin Films Possessing Mesoscopic Architectures

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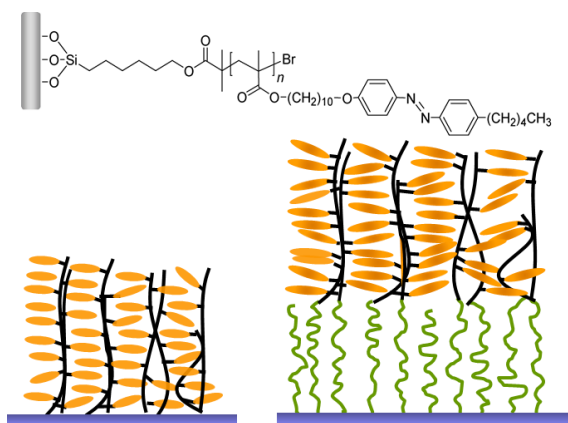
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Keywords: Polymer Thin Films, Liquid Crystals, Block copolymers, Surface Grafting, Azobenzene

Summary. Liquid crystalline (LC) photochromic polymers typically possessing an azobenzene (Az) unit exhibits strong motional cooperativity, leading to a highly oriented directional alignment and highly sensitive mass migrations. This paper introduces our recent approaches to control mesostructures in thin films of photoresponsive Az-containing LC polymers. We expect that these new smart system will find new applications in thin film technologies for dynamic functions.

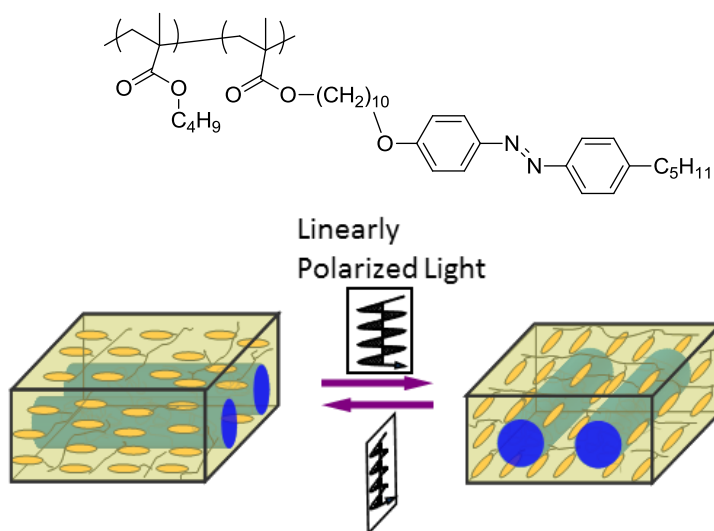
In-plane alignment in Surface-Grafting Architecture

In ordinary spincoated films of side chain LC polymers, the mesogens are oriented normal to the substrate surface. When one end of polymer chains is anchored on the substrate, they orient parallel to it. Such surface grafted LC Az chain is beneficial in the light of efficient light absorption and in-plane photoalignment. Highly ordered in-plane orientation is attained in this geometry [1]. We recently introduced a flexible amorphous polymer chain underneath the LC Az polymer in the surface-grafted framework. The flexible amorphous chain facilitates efficient in-plane photoorientation and reorientation, and thus works as a lubricant layer in the grafted chain film [2].



Microphase separation alignment of block copolymers by light

Surface photoalignment technology of LC materials started in 1988 [3], and now, this method has been introduced to large production processes of LC display devices. The photoalignment strategy can be further applied to induce and alter the alignment of microphase separation structures (MPSs) of block copolymer thin films [4,5]. The cooperative structuring in the liquid crystalline state leads to a highly ordered photoalignment. We recently achieved real-time observations of the dynamic photo(re)orientation behavior of MPS in a thin film, which is performed by the synchrotron orbital radiation. A low T_g block of poly(butyl methacrylate) allowed this direct evaluation of the reorientation behavior. A strong synergy effect in the hierarchical structuring has been revealed [6]. The orientation of MPS structure could be readily reoriented many times.



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1986 Researcher, Research Institute for Polymers and Textiles, AIST
1993 Senior Researcher, National Institute of Materials and Chemical Research
1995 Associate Professor Chemical Resources Laboratory, Tokyo Institute of Technology
2002 Professor, Graduate School of Engineering, Nagoya University, Nagoya

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2002 Wiley Polymer Science Award from The Society of Polymer Science, Japan
2005 Award for the Outstanding Paper in the Journal of Japanese Liquid Crystal Society
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Research interests:

Surface-mediated photocontrols of materials orientation and packing states
Photomechanical effects and mass migrations of photoresponsive polymers
Precise assembly of polymers at interfaces and their thermophysical properties



Selected publications:

- 1) Y. Hayata, S. Nagano, Y. Takeoka, T. Seki, Photoinduced Volume Transition in Liquid Crystalline Polymer Gels Swollen by a Nematic Solvent, *ACS Macro Letters*, **1(11)**, 1357-1361 (2012).
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Luminescent Carbon Nanodots: A New Era in Graphitic Carbon Nanomaterials

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Nanocrystals are referred to as ultrasmall crystals of metals, semiconductors, and organic materials in which size typically ranges from 2 to 20 nm.¹ Their optical and electrical properties can be readily tuned purely by varying the size, which opens new prospects for optoelectronic devices in the future. Formation of zero-dimensional nanocrystals is thus a substantial topic of current interest. So far, colloidal synthesis offers the excellent control of size and shape of nanocrystals, especially for metals and semiconductors, which conforms the La Mer model. This model implies that monodisperse nanocrystals can be prepared via solution-based reaction involving several consecutive steps: initial nucleation, growth of the nuclei, termination of the reaction, and isolation of formed nanocrystals reaching the desired size. For narrow size distribution, the nucleation event is temporally separated from the growth stage and the nucleation rate is neither too slow nor too fast with respect to the growth rate.²

Carbon nanodots (CNDs) offer strong potential for promising candidates to replace traditional semiconductor quantum dots due to cost reduction, low toxicity, biocompatibility, and reasonable photoluminescence.^{3,4} Typically, CNDs are composed of nanometer-sized sp^2 hybridized graphitic cores and carbonyl surface moieties. Since discovered by Xu et al. while purifying carbon nanotubes from arc-discharge soot, CNDs have been derived via various routes such as laser ablation, electrochemical oxidation, thermal oxidation, silica-supported, microwave, and hot injection methods.^{3,4} These methods have distinctive virtues such as low cost (abundant) molecular precursors, low temperature, and sustainability; however, most of them require strong acids, hydrothermal conditions (high pressure), or special equipment. In contrast to inorganic nanocrystals, formation of CNDs kinetically deviates from the La Mer model due to the irreversibility of carbonization. Since the dissolution of a nanocrystal to monomers (the reverse reaction) plays a critical role in focusing of the size distribution, CNDs have rather broad size distribution than inorganic nanocrystals.⁴ Furthermore, their slower nucleation rate than the growth rate at common carbonization temperature spurs the formation of bulk crystals or chunks to deteriorate the photoluminescence quality and the product yield. In this regard, exhaustive size selection procedures (e. g. liquid chromatography) are usually exploited to obtain the desired size, which imposes limitations on practical application of CNDs. Thus, a different approach should be taken to form uniformly sized CNDs irrespective of the La Mer model.

Herein, we review recent advances in the formation of CNDs and speculate on their future. Although a full understanding of the physical and optical properties has yet to emerge, CNDs are indeed interesting carbon nanomaterials due to their potential to serve as nontoxic alternatives to inorganic nanocrystals. Given their low cost, scalability, excellent chemical stability, biocompatibility, and bright luminescence, many applications in energy conversion, bioimaging, drug delivery, sensors, diagnostics, and lighting devices are envisioned in this field. As an exemplary, we introduce nitrogen-rich CNDs prepared by facile emulsion-templated carbonization excluding any unpractical size selection procedure.⁵ To realize their potential, we fabricate large-scale (20 × 20 cm) freestanding luminescent films of the CNDs based on a poly(methyl methacrylate) matrix. These films are low cost, fully flexible, thermally stable, eco-friendly, and mechanically robust. To realize

their potential, we demonstrate white LEDs consisting of the films as color-converting phosphors and InGaN blue LEDs as illuminators. The white LEDs produce warm-white light with no temporal degradation in the emission spectrum under practical operation conditions. Thus, we believe that these CND-based luminescent films could offer strong potential for future large-scale flexible solid-state lighting systems.

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Research interests:

Synthesis and application of luminescent carbon nanomaterials; electrocatalytic carbon materials for electrode applications; hybrid materials for electronic and photovoltaic devices

Selected publications:

1. W. Kwon, S.-W. Rhee, Chem. Commun. Vol. 48, (2012) 48, p. 5256.
2. W. Kwon, S. Do, S.-W. Rhee, RSC Adv. Vol. 2, (2012), p. 11223.
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5. W. Kwon, S. Do, D. C. Won, S.-W. Rhee, ACS Appl. Mater. Inter. (2013) DOI: 10.1021/am3023898.

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Synthesis and Properties of Superazaporphyrins and Chiral and/or Low-Symmetry Subphthalocyanines

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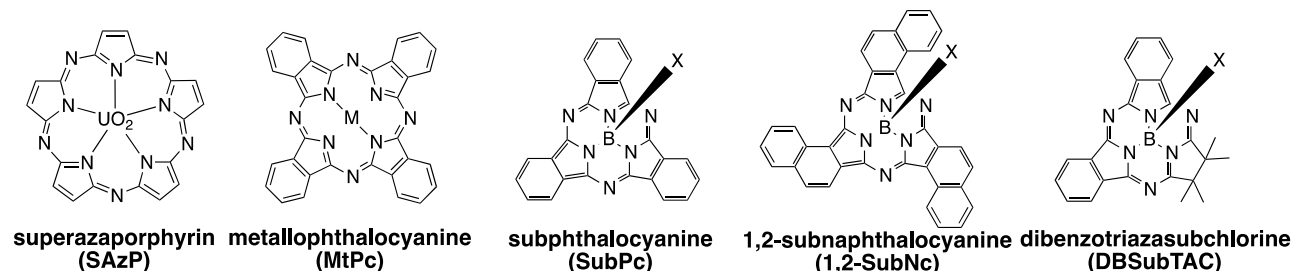
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Keywords: phthalocyanine, electronic absorption, magnetic circular dichroism, circular dichroism, molecular orbital calculation, azaporphyrin, chlorin, enantiomer, subphthalocyanine, X-ray

Summary. Pentapyrrolic azamacrocycles containing UO_2 as the central core (i.e. superazaporphyrins, SAzPs) have been synthesized from the pentacyclization reaction of a 3,4-bis(phenyl)pyrroline-2,5-diimine derivative using $UO_2(OAc)_2$ as a template, and their spectroscopic and electrochemical properties examined.[1] Their pi structure is not flat, but severely distorted in the solid state, and they show Q bands at around 870-890 nm. They are stable since both the LUMOs and HOMOs are stabilized compared to normal phthalocyanines (Pcs) and naphthalocyanines (Ncs). Magnetic circular dichroism (MCD) spectra showed that the first excited state is degenerate.

A subNc consisting of 1,2-naphthalene units was synthesized from 1,2-dicyanonaphthalene using BCl_3 as a template, and its C_1 and C_3 diastereomers and enantiomers were separated.[2] The chirality of this molecule, including the CD sign and intensities, was discussed with reference to enantiomerically-pure molecules whose absolute structures had been elucidated by single-crystal X-ray diffraction analysis. Viewing from the axial ligand side of boron (B), the compounds with a clockwise arrangement of benzene rings exhibited a negative CD band in the Q band region, while, inversely, those with an anti-clockwise arrangement showed positive CD bands.

A reduced pyrrole-ring-containing subPc (i.e. dibenzotriazasubchlorin) showed a significantly split Q band at 632 and 464 nm (splitting $E = ca. 5730\text{ cm}^{-1}$), while even the Soret band split at 308 and 269 nm (splitting $E = ca. 4700\text{ cm}^{-1}$) due to the lowering of the molecular symmetry.[3] The MCD spectrum showed $-/+/-/+$ pattern corresponding to the absorption peaks at 632, 464, 308, and 269 nm, respectively, indicating that the difference between the HOMO and HOMO-1 is larger than that between the LUMO and LUMO+1,[4] which was indeed reproduced by molecular orbital calculations.



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Awards/other information:

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2006 The JCS Award for Creative Work, Tokyo, Japan
2010 The Science and Technology Prize, MEXT, Japan



Research interests:

Synthesis and understanding of spectroscopic properties of novel physicochemically intriguing porphyrinoids and phthalocyaninoids (Pcs), particularly using various spectroscopies such as CD, MCD, electronic absorption, EPR, NMR, X-ray and electrochemistry. Application of Pcs in society.

Selected publications: About 360 original papers (of which *JACS* + *Angew Chem.* = more than 50), Review, Book Chapter, & Book = 58). Selected Publications in 2010-2012.

1. A Discrete Quadruple-Decker Phthalocyanine, T. Fukuda, T. Biyajima, and N. Kobayashi, *J. Am. Chem. Soc.* **132**, 6278-6279 (2010).
2. Synthesis, Reactions, and Electronic Properties of 16 π -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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7. Rationally Designed Phthalocyanines Having Their Main Absorption Band beyond 1000 nm. N. Kobayashi, T. Furuyama, and K. Sato, *J. Am. Chem. Soc.* **133**, 19642-19645 (2011).
8. Low Symmetry Phthalocyanines and Their Analogues. J. Mack, N. Kobayashi, *Chem. Rev.* **111**, 281- 321 (2011).
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11. Superazaporphyrins: *Meso*-Pentaazapentaphyrins and One of Their Low-Symmetry Derivatives. T. Furuyama, Y. Ogura, K. Yoza, and N. Kobayashi, *Angew. Chem. Int. Ed.* **51**, 11110-11114 (2012).
12. Circular Dichroism and Magnetic Circular Dichroism for Organic Chemists (*textbook*). N. Kobayashi, A. Muranaka, and J. Mack, Royal Society of Chemistry (2012)

Radical Chemistry with Weakly Coordinating Anions

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Keywords: radical, cation, weakly coordinating anion, mechanism, molecular electronics

Research in our group focuses on inorganic and organic chemistry, with particular interest in the field of radical chemistry. We hope to gain fundamental insight into the nature of bonding and reactivity of radicals that can contribute to interdisciplinary solutions for challenges in science. Radical cations are intermediates in many organic reactions and have potential applications to molecular electronics. They are generally short-lived species, but can be made persistently stable and isolated by using weakly coordinating anions. By using anions SbF_6^- and $\text{Al}(\text{OC}(\text{CF}_3)_3)_4^-$, we recently have successfully stabilized and isolated radical cations of anilines, dialkoxyanthracenes, phenyldiamines, and thiophenes.

Aniline radical cations ($\text{ArNR}_2^{+\cdot}$, R = H or alkyl) are highly reactive and often exist as short-lived intermediates occurring in dimerization, cationic polymerization, azo compound formation, benzidine rearrangement, proton transfer reactions, and various nucleophilic substitutions. With SbF_6^- , an aniline radical cation TBA $^{+\cdot}$ (TBA = 2, 4, 6-tri-*t*-BuC₆H₂NH₂) were successfully stabilized both in the solution and solid state, and its structure was determined by X-ray crystallography. The cation exists as two isomers interchanging with temperature and features an exceptionally long C-N bond beyond theoretical prediction. The reversible isomerization is unprecedented for a simple phenyl ring system and implies that the valence electrons of the radical cation can be controlled by temperature. The work provided the first example of an aniline radical cation in the solid state, which may be used as a stable intermediate for model studies.

C-C bond formation and cleavage are basic events in organic chemistry. The oxidative σ -dimerization of conjugated aromatic systems involving C-C coupling plays an essential role in organic syntheses, e.g. oxidative oligo- and polymerization, where σ -dimeric dication is suggested as a key intermediate. In the previously reported oxidative dimerizations, radical cations have not been directly observed and well confirmed due to their short lifetime. With salt $\text{AgAl}(\text{OC}(\text{CF}_3)_3)_4$, however, 9, 10-Dialkoxyanthracenes were oxidized to radical cations and stabilized in solution, which dimerize upon crystallization and come back to radical cations upon dissolution (Figure 1). The identity and stability of radical cations have been unequivocally confirmed by EPR and UV-vis spectroscopy. This work has provided conclusive evidence for reversible σ -dimerizations of persistent organic radical cations. Study of such reversible process may have an impact on exploring mechanism of oxidative oligo- and polymerization of aromatic systems.

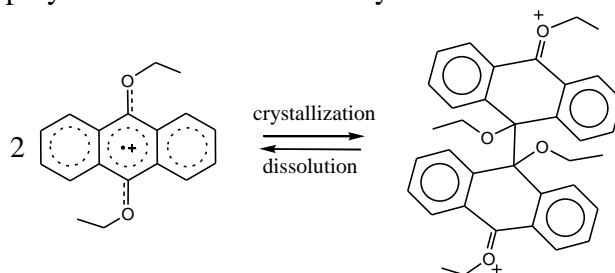


Figure 1

π -Conjugated polymers or oligomers have attracted considerable attention because of their potential applications to molecular electronics. Because of intrinsic instability as well as difficulty of crystallization, examples of π -stacked oxidized conjugated oligomers are rare. Upon one-electron

oxidation, radical cations of 4, 4'-terphenyldiamine and thiophene/phenylene co-oligomers have been isolated as stable crystals. The former shows face-to-face π -stacks and provides the first example of structurally characterized π -stacked oxidized *p*-phenylene oligomers, while the latter exhibits unique meso-helical stacking (Figure 2). These results imply π -stacks and π -interactions are important for conduction and might also play an important role in the conduction of π -conjugated polymers, in addition to the traditional model that conduction results from bipolaron (or polaron) migration along polymer chains. Moreover, the unusual helical structure of thiophene oligomer radical cation invokes the question what is the real interaction between oxidized polymers: face-to-face overlapping or others?

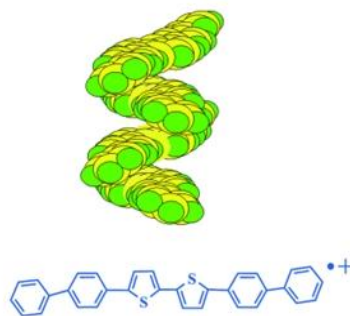


Figure 2

In summary, our recent work has demonstrated that weakly coordinating anions are effective tools for stabilizing and solubilizing some radical cation salts, where regular anions such as PCl_6^- and SO_3CF_3^- failed. More intriguing radical cations are thus expected to be accessible by using weakly coordinating anions. Isolation of such novel radical species together with their structural determination may have an impact on the fields of organic mechanism and molecular electronics.

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Focusing on main group, inorganic and organic chemistry, with particular interest in the field of radical chemistry; to gain fundamental insight into the nature of bonding and reactivity of radicals that can contribute to interdisciplinary solutions for challenges in science.

Selected publications:

1. X. Chen, X. Wang, Z. Zhou, Y. Li, Y. Sui, J. Ma, X. Wang, and P. P. Power, *Angew. Chem. Int. Ed.* 2013, 52, 589.
2. X. Chen, X. Wang, Y. Sui, Y. Li, J. Ma, J. Zuo, and X. Wang, *Angew. Chem. Int. Ed.* 2012, 51, 11878.
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Chiral mesoporous materials and their optical activity

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Keywords: chirality, optical activity, mesoporous materials, self-assembly, metal nanoparticles, metal oxide

Summary. Chiral mesoporous inorganic materials with ordered mesostructure and single helical pore were synthesized by cooperative self-assembly of chiral templates and inorganic precursors¹⁻⁶. (i) The chiral mesoporous silica (CMS) synthesized with amino acid derived amphiphiles exhibits a novel chiral mesostructure with hexagonally ordered chiral channels twisted from the two-dimensional hexagonal $p6mm$ ¹⁻². Chiroptical properties of CMS material have been achieved by dispersing achiral Ag isotropic spheric nanoparticles (AgNPs) and anisotropic nanowires (AgNWs) into CMS. Three types chirality: helical hexagonal surface, helical pore orientation, and helical arrangement of aminopropyl groups, all impart plasmonic circular dichroism (PCD). The helical pore orientation was considered to be predominantly responsible for the PCD response owing to the high efficiency of nanoscale chirality³. The multi-helix with a helical channel orientation and helical arrays of opposite handedness in CMS played a predominant effects on the transversal and longitudinal chirality of the AgNWs, respectively. This behavior differs from both isotropic nanoparticle and single helix-induced CD responses⁴. (ii) The synthesis of impeller-like helical DNA-silica complexes was achieved by co-structure agent route, and the handedness of helical architectures was reversed by the change of quaternary ammonium:DNA molar ratio, temperature and pH⁵. These materials also induce optical activity of inorganics. (iii) Contrast to organic helical materials, inorganic materials with optical activity resulting from electronic transitions are rare. The synthesis of chiral TiO₂ fibres with single pore was achieved via transcription of helical structure of amino acid-derived amphiphile fibres through fine coordination bonding interactions between the carboxylic groups and TiO₂ source. The amorphous and crystal TiO₂ double helical fibres exhibited optical response to circularly polarised light at their absorption bands, which was attributed to the semiconductor TiO₂-based electronic transitions from the valence band to the conduction band under a dissymmetric electric field⁶.

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Research interests:

Development of new type mesostructural materials by mimicking biosystems and their applications in catalyst, nanomedicine and biological engineering.

Selected publications:

1. S. Che*, Z. Liu, T. Ohsuna, K. Sakamoto, O. Terasaki and T. Tatsumi, Synthesis and Characterization of Mesoporous Silica with Chiral structure, *Nature* 2004, 429, 281-284.
2. S. Che*, A. E. Garcia-Bennett, T. Yokoi, K. Sakamoto, H. Kunieda, O. Terasaki and T. Tatsumi, Mesoporous Silica of Novel Structures with Periodic Modulations Synthesized by Anionic Surfactant Templating Route, *Nature Materials*, 2003, 2, 801-805.
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Azobenzene-Containing Palladium Complexes and Their Self-Assembly

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Summary. An appropriate combination of photoisomerizable azobenzene molecules with transition metal complexes would make it possible to elicit their intrinsic photochemical, electrochemical, and magnetic properties, originating from the d-electrons. We recently designed stable mononuclear palladium(II) complexes, with ortho-alkylated azobenzene ligands, capable of reversible photoswitching originating from a reversible change in their molecular structure. The formation of two-dimensional (2D) sheets with different size, ranging from nanometer-scale to micrometer-scale, could be achieved by the assembly of azobenzene-based palladium complexes.

Photoswitchable azobenzene-containing palladium complexes

Mononuclear palladium(II) complexes were successfully synthesized by a ligand-exchange reaction between the corresponding azobenzene and dichlorobis(benzonitrile)-palladium(II) [1,2]. An X-ray crystallographic study indicated that the metal center in the complex has a trans square-planar structure, with two azobenzene ligands coordinated to a palladium ion in a monodentate manner. $\text{PdCl}_2(\text{Azo})_2$ (Fig. 1) exhibited (i) good solubility and (ii) improved stability in common organic solvents [3]. Alternating ultraviolet and visible light irradiation of the complex gave rise to reversible conformational changes between the trans and cis forms, confirmed by absorption and NMR spectroscopic measurements.

Anisotropic two-dimensional (2D) sheets

For developing a new class of photochemically and electrochemically responsive materials, the creation of freestanding, 2D nano- and microstructures from transition metal complexes is desirable [4,5]. To prepare nano- and microstructured aggregates, we added water dropwise into $\text{PdCl}_2\text{Azo}_2$ THF solution under gentle stirring. With increasing water content, THF/water mixed solutions became orange milky and turbid. The size of parallelogram-shaped structures, ranging from nanometer-scale to micrometer-scale, can be adjusted by simply changing the initial complex concentration [6].

Unidirectional (in-plane) molecular orientation of metal complexes through π - π stacking interaction and uniform intermolecular distance is responsible for strong birefringence and dichroism of microsheets (Fig. 2). Such anisotropic planar sheets consisting of photoresponsive metal complexes might be interesting materials for applications in molecular electronics and photonics.

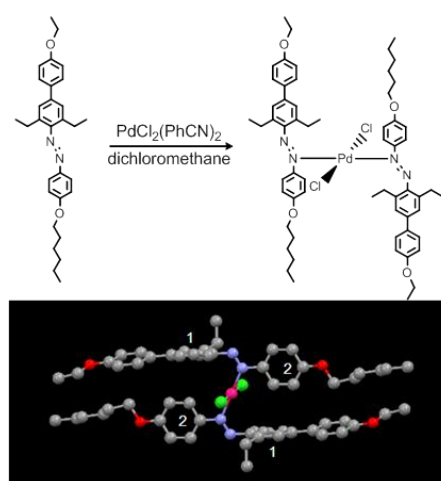


Fig. 1 Synthesis and X-ray crystal structure of $\text{PdCl}_2(\text{Azo})_2$.

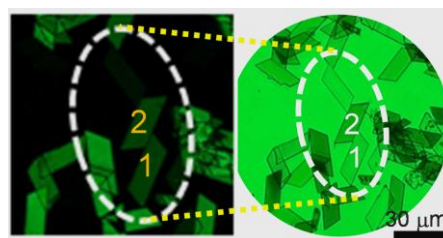


Fig. 2 POM and OM images of microsheets.

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Nano/Microstructures generated by self-assembly of photofunctional materials
Light-responsive surfaces
Fluorescent nano/micro-aggregates
Conversion of light energy into mechanical energy

Selected publications:

1. Y. Okui and M. Han, "Rational design of light-directed dynamic spheres", *Chem. Commun.*, **48**, 11763-11765 (2012).
2. H. W. Kim, M. Han, H. Shin, S. Lim, Y. Oh, K. Tamada, M. Hara, Y. Kim, M. Kawai and Y. Kuk, "Control of Rotating Molecular Rotor by Selection of Anchoring Sites", *Phys. Rev. Lett.*, **106**, 146101-1–146101-4 (2011). (Selected as a cover figure paper)
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Cluster Approach to Catalysis and New Materials Design

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Keywords: Cluster approach, DFT, transition metal oxides, rutile TiO₂, selective oxidation, new carbon K4, chemisorption, B3LYP

Summary. This paper discusses the results of ab initio and DFT studies of different substrates interactions and transformations on representative catalysts' surfaces when applying a well-known cluster approach. Attention is paid on ultimate importance of proper modeling of structure and chemical activity of transition metal and metal oxide catalysts taking properly into account their stoichiometry, electro-neutrality and boundary terminations. This approach has been then applied to mimic a finite-size carbon K4 structure created by cutting a piece from a large crystalline structure. Our DFT calculations indicate possible ways to create, stabilize, and characterize this new carbon K4 structure with its decagonal rings and very high symmetry.

Over the years, we have been exploiting the cluster approach. We have shown an ultimate importance of proper modeling of active site structure for proper description of chemical activity of transition metal and metal oxide catalysts. For example, the formation of oxygen vacancy site on rutile TiO₂ (110) and its interaction with molecular oxygen were considered [1]. It was shown that the experimental temperature programmed desorption (TPD) observations on triply exceeding concentration of O₂ per vacancy site at low temperature saturation coverage can be well explained without making an ill-assumption on the formation of the tetraoxygen fragment at the vacancy site [2], if one properly address the mechanism of formation of precursor defect sites (the nature of active sites) on rutile TiO₂ (110). Next we have shown that not only the active site structures but also support structures should be properly modeled for reliable description of the mechanism of selective oxidation of methanol into formaldehyde over vanadia supported on silica and titania catalysts [3]. An improper use of cluster models mimicking an intrinsic support structure [4,5] may result in the failure to explain the experimental findings on selective oxidation of methanol into formaldehyde over these modified oxide catalysts. Finally, we have critically pointed out also the importance of proper consideration of magnetic (spin) states of the selected cluster models when one describes an attractive bonding interaction not only for bromine at well-defined Pt (111) but also for all the three adsorption modes of NO on the same Pt (111) surface [6]. These results obtained gave some insight in understanding the target phenomena as well as offer some recipe on molecular modeling related other systems when one uses cluster approach [7].

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 including non-metal replacements and some decorations of the whole carbon K4 structure by silicates (or zeolites). 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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Computational Quantum Chemistry, Chemisorption and Catalysis, Photocatalysis, Theoretical Spectroscopy, DNA base-pair interactions

Selected publications:

1. N.U. Zhanpeisov, G.M. Zhidomirov and H. Fukumura. Interaction of a single water molecule with a single graphite layer: An integrated ONIOM study.
J. Phys. Chem. C 113 (2009) 6118-6123.
2. N.U. Zhanpeisov and H. Fukumura. Oxygen vacancy formation on rutile TiO₂(110) and its interaction with molecular oxygen: A theoretical density functional theory study.
J. Phys. Chem. C 111 (2007) 16941-16945.
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Computer Simulations of Equilibrium and Kinetics Adsorptions of Carbon Dioxide on Zeolitic Imidazolate Frameworks

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An alternative method for reducing CO₂ emissions is the development of carbon capture and storage (CCS) technologies [1,2]. This approach requires novel low-cost materials that can efficiently adsorb CO₂ gas. A new class of materials called zeolitic imidazolate frameworks (ZIFs), a subclass of metal-organic frameworks (MOFs) has recently been proposed as potential CCS materials. It has been demonstrated that ZIFs exhibit high CO₂ sorption capacity with high selectivity of CO₂ over CH₄, O₂, H₂ and CO.[3,4]

Computational simulations have been applied in studying the CO₂ adsorption mechanisms of several ZIFs using force field (FF)-based methods.[5-8] However, contrasting arguments regarding the accuracy of FF methods have been reported. However, contrasting arguments regarding the accuracy of FF methods have been reported. The simulation method is another major factor to be considered when simulated data are compared with experimental data.

By developing a FF describing the interactions between ZIF frameworks and CO₂ molecules based on the high-level CCSD(T)/CBS energy data and by rigorously validating FFs for CO₂-CO₂ interactions using VLE coexistence curve predictions, we were able to evaluate the simulation protocols independently from experimental isotherm data. It is found that with accurate force fields, the predicted isotherms for CO₂ on ZIFs are still significantly overestimated, which is similar to other predictions [17-19]. The NEMD simulations show that adsorption and desorption in the small channels are significantly slower than those in large channels. The calculated PMF energy barrier is relatively low (10 kJ/mol) for loading a CO₂ molecule to an HRP cage, but significantly high (25 kJ/mol to 30 kJ/mol) for removing the molecule from the same cage type. Based on these results along with an analysis of structures and energies, it is concluded that the small channels in ZIFs are determined to be blocked because of adsorbed molecules in HPR cages, as suggested by Babarao et al. [19] Excluding the small channels results in excellent agreement with experimental isotherms.

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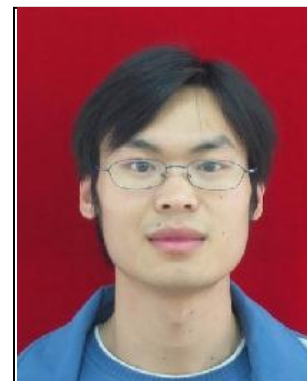
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Research interests:

Understanding of the interfacial behavior of water/surfactant/air and water/surfactant/oil systems; Predicting gas adsorption isotherms on metal oxides, zeolites and MOFs materials; developing coarse grain force field.

Selected publications:

- 1) **Fenglei Cao**, Wei Ren, Yu-Meng Ji and Cunyuan Zhao*. "The structural and electronic properties of amine-functionalized boron nitride nanotubes via ammonia plasmas: a density functional theory study", *Nanotechnology*, **2009**, *20*, 145703-7.
- 2) **Fenglei Cao**, Wei Ren, Xianyan Xu, Yue-Meng Ji and Cunyuan Zhao*. "Boron nitride nanotubes functionalized by a series of carbenes", *Phys. Chem. Chem. Phys.*, **2009**, *11*, 6256-6262.
- 3) **Fenglei Cao**, X Xu, Wei Ren and Cunyuan Z*. "Theoretical Study of O₂ Molecular Adsorption and Dissociation on Silicon Carbide Nanotubes", *J. Phys. Chem. C*, **2010**, *114*, 970–976.
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Evaporation and Condensation Mechanisms through Monolayer Films

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Keywords: Mass accommodation, Langmuir monolayer, molecular dynamics, Langevin dynamics.

It is well known that monolayer films drastically hinder evaporation and condensation rates at liquid-vapor interface, and the rate is sensitive to conditions of monolayers. For example, Langmuir monolayers of long-chain alcohols ($n=16-20$) reduce the evaporation by several orders of magnitude. The restricted evaporation by the Langmuir monolayers invoked application to keep water from open water storage in arid areas. In the atmospheric chemistry, organic layers on aqueous aerosols have great impact on the mass transfer rate and reactivity. The present study elucidates the fundamental mechanisms of mass transfer through monolayers by a combination of molecular dynamics and Langevin dynamics simulations.

Accurate understanding of the phenomenological mass transfer kinetics is a challenging issue, though its importance. This is because the phenomenological mass transfer rate is governed by a number of kinetic elements, including gas-phase diffusion, permeation through monolayer films, liquid-phase diffusion, solubility, etc. Among these kinetic elements, the mass transfer rate at the interface is defined with the mass accommodation coefficient α ,

$$\alpha = \frac{(\text{number of absorbed molecules})}{(\text{number of impinging molecules})}, \quad (1)$$

which is the microscopic probability of accommodation for impinging molecules, ranging from 0 to 1. The behavior of α is a key issue to understand the phenomenological mass transfer rate, though it is often challenging to observe it experimentally. Therefore, molecular dynamics simulation could help understanding the value of α and its microscopic mechanism.

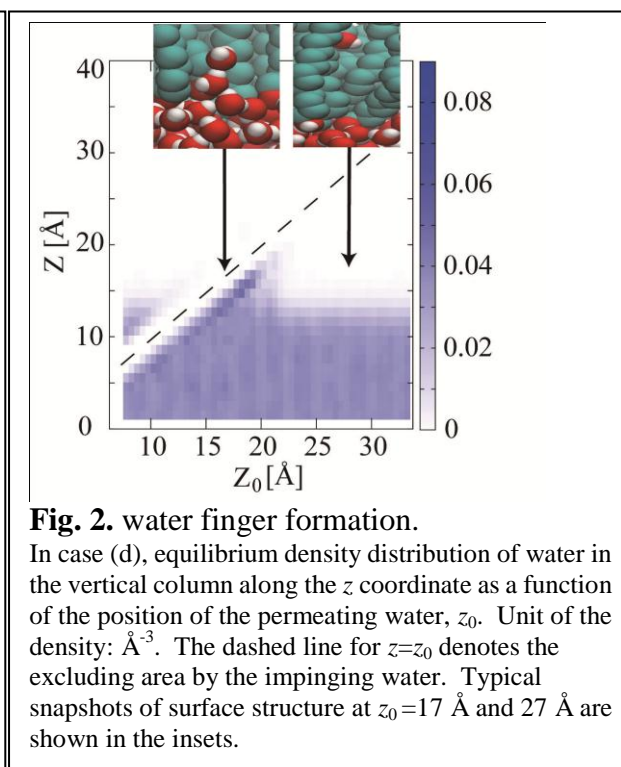
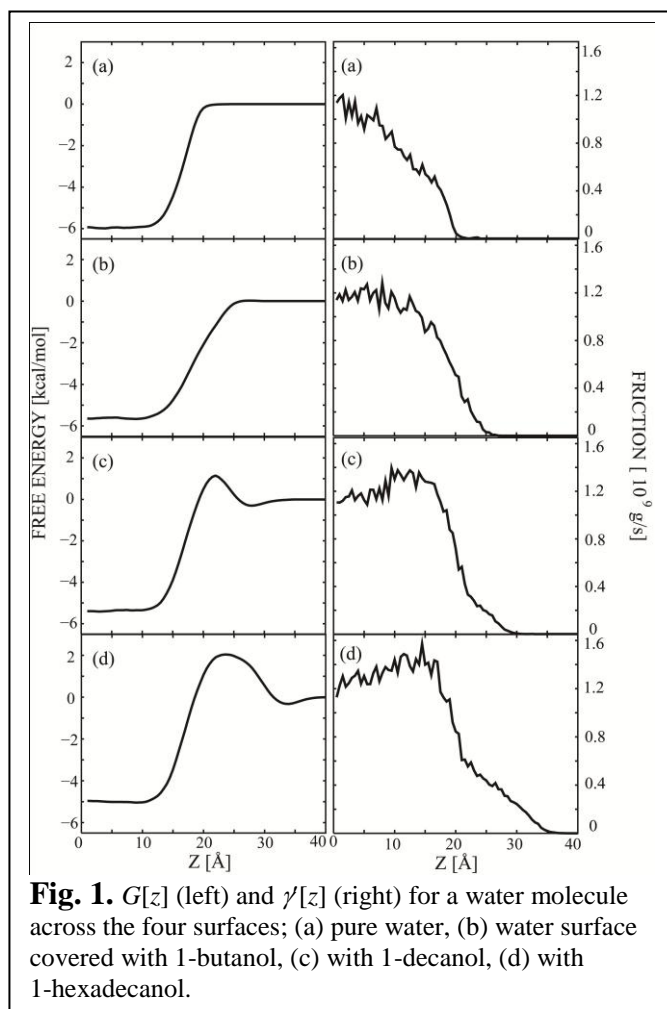
In the present study, we employed the Langevin dynamics simulation to investigate α instead of the straightforward molecular dynamics simulation, because the latter is not suitable to pursue rare events of accommodation ($\alpha \ll 1$) during long-time permeation dynamics through the monolayer films. The Langevin dynamics is described by the following Langevin equation,

$$m\ddot{z}(t) = -\frac{\partial G[z(t)]}{\partial z} - \gamma[z]\dot{z}(t) + R_z(z, t) \quad (2)$$

where z is the normal coordinate of the impinging molecule, $G[z]$ is the free energy curve for the imping molecule, $\gamma[z]$ is the friction, and $R_z(z, t)$ is the stochastic random force. In this system the friction $\gamma[z]$ should remarkably vary from gas region to the liquid region. The free energy curve $G[z]$ and the friction $\gamma[z]$ are calculated by molecular dynamics simulation, and the results are shown in Figure 1. As the alkyl chains of the film increase ((a) $n=0$, (b) 4, (c) 10, (d) 16), the free energy barrier emerges at $z \sim 23$ Å. We found that the permeation dynamics and solvation structure qualitatively changes at the barrier top. The barrier height and the accommodation coefficient are largely governed by the transition of the surface structure, associated to the “water finger” formation.

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Selected publications:

1. A. Morita and T. Ishiyama, *Phys. Chem. Chem. Phys.*, 10, 5801 (2008).
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Advanced carbon-based nanotubes/nanocages for energy conversion and storage: synthesis, performance and mechanism

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Keywords:

Energy conversion and storage; Carbon-based nanostructures; Mechanism; Structural regulation

Summary. Fuel cells, supercapacitors and lithium-ion batteries are the typical energy conversion and storage devices of great significance in which carbon-based nanostructures could play irreplaceable role. The functionalized carbon-based nanotubes/nanocages (CNTs/CNCs) could be applied to fuel cells to lower Pt loading by highly dispersing and immobilizing Pt-based nanoparticles, or to totally get rid of Pt with the metal-free electrocatalytic ability themselves. The abundant nanostructures and morphologies, tunable compositions, high surface area, good conductivity, small volume expansion, as well as the low cost and environmental benignity make the CNTs/CNCs have great potential as electrode materials of supercapacitors and lithium-ion batteries. In this talk I will give a brief introduction to the progressive advancements in our group about the synthesis, performance and mechanism of the CNTs/CNCs for this kind of energy conversion and storage. Special attention will be paid to the materials design by doping the CNTs/CNCs with electron-rich N, electron-deficient B, and the both to elucidate the correlation of the performance with the doping microstructures, which is a general interesting issue in developing the advanced carbon-based energy materials.

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Research interests:

Physical chemistry and materials chemistry addressing the growth mechanism, controllable synthesis, energy-oriented properties and applications of a range of nanoscale materials such as carbon-based nanotubes/nanocages and group III nitrides.

Selected publications:

1. Y. Zhao, L. J. Yang, S. Chen, X. Z. Wang, Y. W. Ma, Q. Wu, Y. F. Jiang, W. J. Qian, and Z. Hu*, "Can boron and nitrogen codoping improve oxygen reduction reaction activity of carbon nanotubes?" *J. Am. Chem. Soc.* **135** (2013)1201
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New Ether-functionalized Ionic Liquids as Electrolyte for Lithium Battery

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Ionic liquids (ILs) are molten salts with melting points at or below room temperature, which are composed of organic cations and various anions. Over the past decade, ILs have attracted growing interests as safe electrolytes for lithium battery, due to their negligible vapor pressure, non-flammability, good thermal and electrochemical stability, and high conductivity.

Currently, functionalized IL is a very noticeable topic in the field of IL research. Introducing different functional groups into IL cations, the physicochemical and electrochemical properties of ILs can be observably tuned, and providing more choices for applications of ILs. In comparison to other functional groups, ether group can reduce the viscosities and melting points of ILs without the obvious degradation of electrochemical stability.

During the past three years, our group has synthesized several kinds of ether-functionalized ILs, such as pyrazolium ILs with one ether group, pyrrolidinium and piperidinium ILs with two ether groups, guanidinium and trialkylimidazolium ILs with one or two ether groups, and quaternary ammonium ILs with three or four ether groups.[1-8] The structures of these ILs are shown in Figure 1. The introduction of ether group into IL cation can obviously affect IL physicochemical properties comparing to the counterpart IL without ether group. And we have found a lot of ether-functionalized ILs with low-melting point, low viscosity and wide electrochemical window. Meanwhile, some of these ILs with low viscosity have been applied as electrolytes for lithium battery without any additives and showed good performances.

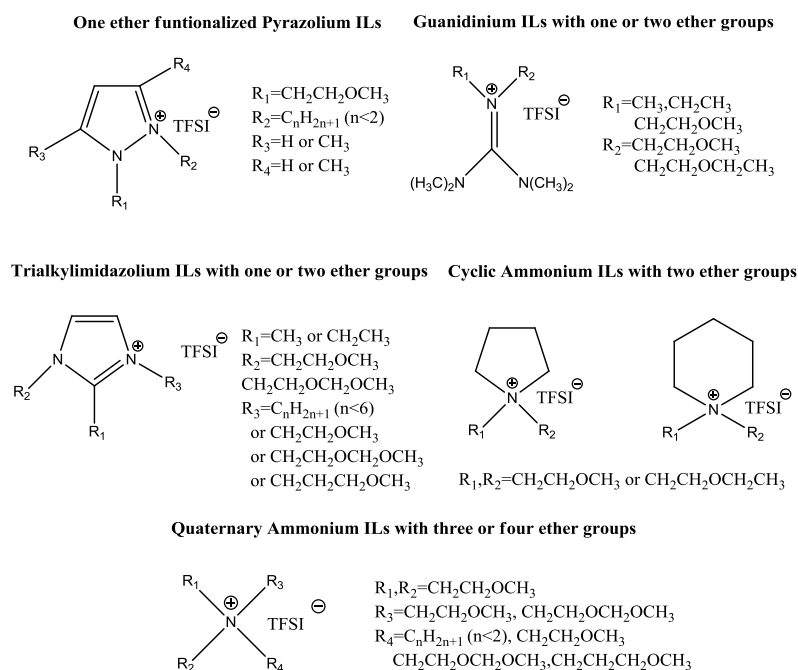


Fig. 1 Structures of ether-functionalized ILs

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Selected publications:

1. Li Yang, Zhengxi Zhang, Bingjia Yao, et al, Hydrogen Permeance and Surface States of Pd-Ag/Ceramic Composite Membranes, AIChE Journal, 52(8), 2783-2791, 2006
2. Li Yang, Bingjia Yao, et al. Study on the production of CH₄ in the hydrogen purification with palladium - silver/ceramic composite membranes, Industrial & Engineering Chemistry Research, 49, 4377-4382, 2010
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Osmotic Control by Temperature-Sensitive Materials for Water Desalination

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Keywords: Desalination, LCST, Osmosis, Water purification

Summary.

Recently, forward osmosis (FO) process is being highlighted as an eco-friendly desalination method with low-energy cost [1]. We have developed a simple, reversible, and effective method for controlling forward osmosis by mild temperature change, based on temperature-sensitive materials with lower critical solution temperature (LCST) transition [2].

Since our temperature-sensitive materials exhibit a phase separation from water over a certain temperature, the effective concentration of the solution is sharply decreased. We expected that the direction of osmosis can be changed along with the abrupt change of the effective concentration. *n*Bu-TAEA, one of our temperature-sensitive materials, can draw fresh water from a seawater equivalent at temperatures less than the phase separation temperature, and the osmotic flow was reversed into a physiological saline at higher temperatures. The effective osmotic drawing of water at low temperatures and the abrupt reversal of the osmotic flow at high temperatures by the temperature-sensitive materials could thus have a considerable impact on more efficient and practical desalination and water purification [3].

Furthermore, we have proposed a prototype desalination system by circulating LCST mixtures between low and high temperature (low T and high T) units. 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 [4].

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

Selected 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.

Insight into the Silica Mesoporous Crystals with Cage-type Structures

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Keywords: electron microscopy · crystallography · mesoporous silica · surfactant · self-assembly

Silica mesoporous crystals (SMCs), which can be considered as novel “cavity crystals”, were discovered in the early 1990s. SMCs can be formed upon surfactant micelles as templates for the self-assembly and subsequent condensation of inorganic precursors. The packing of the organic surfactant and the charge density matching between the surfactant and the inorganic precursor are essential for the formation of an ordered mesostructure.

Generally, the surfactant micelle types can be described by a surfactant packing parameter, $g = V/a_0l$, where V is the surfactant chain volume, a_0 is the effective hydrophobic/hydrophilic interfacial area, and l is chain length. With decreasing of g parameter, mesostructures can be formed in an order of bilayer, bi-/tri-continuous, cylindrical and cage-type structures, corresponding to g values 1, 2/3, 1/2 and 1/3, respectively.

The cage-type mesostructures are formed by regular/disordered packing of spherical/ellipsoidal micelles. There are several typical cage-type structures observed in SMCs, such as $Im-3m$ (SBA-16), $Fm-3m$ (FDU-11, SBA-12 and FDU-12), $P6_3/mmc$ (SBA-2 and SBA-12), $Pm-3n$ (SBA-1 and SBA-6), $Fd-3m$ (FDU-2 and AMS-8), $P4_2/mnm$ (AMS-9), $Pmmm$ (FDU-13), $P4/mmm$ (FDU-11), etc. They can be classified into two types based on the results of three dimensional (3D) reconstruction by the electron crystallography method. One has a single type of spherical cage such as $Im-3m$, $Fm-3m$, and $P6_3/mmc$ structures. The other has several types of spherical cages, typically two, such as $Pm-3n$ and $Fd-3m$ structures. The $P4_2/mnm$ structure is also considered as a cage-type structure with three types of cages. All these structures are made up of spherical micelles of block copolymer, cationic surfactant, or anionic surfactant in the mixture with silica oligomer.

$Fm-3m$ SMC has a cubic close-packed (ccp) arrangement. In general, the ccp structure is well-known as the structure having the highest packing density of perfect spheres of ~ 0.74 . The structural analogue, the hexagonal close-packed (hcp) structure with space group $P6_3/mmc$, also has the same packing density and easily makes an intergrowth with the ccp structure. The ccp structure can be described as ABC stacking of hexagonal close-packed layers along $\langle 111 \rangle_{\text{cub}}$ direction, and the hcp structure is also described as AB stacking of the layers along $[001]_{\text{hex}}$ axis.

Unlike the ccp/hcp structure, the structure of SMCs with $Pm-3n$, $Fd-3m$ and $P4_2/mnm$ symmetry can be described either by a packing of bi-/trimodal spherical cages, which are interconnected by small windows, or by a partition of space through a polyhedron with a tetrahedrally close-packed (tcp) structure, in which the micelle is not considered to be a perfect sphere but is soft and changeable in its shape like foam. Four polyhedra, 5^{12} , $5^{12}6^2$, $5^{12}6^3$, and $5^{12}6^4$ (Figure 1), are useful to construct the tcp structures proposed by Frank and Kasper.

By using Gemini type cationic surfactant as template and the negatively charged organosilane as co-structure directing agent (CSDA), various packing of cage-type SMCs have been obtained. It has been found that the mesostructure can be precisely tuned by the chemical composition, surfactant concentration, the types of CSDA, the pH of the reaction mixture and reaction temperature. Herein, the synthesis of the cage-type structure and the crystallographic study of the structural relationship, intergrowth and the defects observed in these SMCs will be presented in detail.

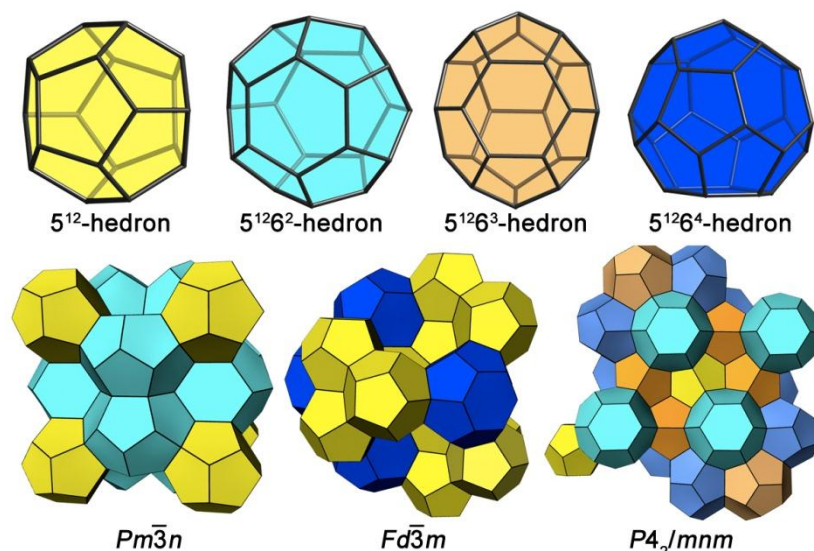


Figure 1. Schematic drawings of four types of polyhedra and the structural description of the top mesostructures with a polyhedra packing model.

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Selected publications:

- (1) Han, L.; Che, S.* *Chem. Soc. Rev.* **2013**, DOI: 10.1039/c2cs35297d.
 (2) Cao, Y.; Xie, J.; Liu, B.; Han, L.;* Che, S.* *Chem. Commun.* **2013**, DOI: 10.1039/c2cc37470f.
 (3) Liu, S.†; Han, L.†; Duan, Y.†; Asahina, S.; Terasaki, O.; Cao, Y.; Ben Liu; Ma, L.; Zhang, J.; Che, S.* *Nat. Commun.* **2012**, *3*, 1215 (†equal contribution).
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 (5) Liu, B.†; Han, L.†; Che, S.* *Angew. Chem. Int. Ed.* **2012**, *51*, 923 (†equal contribution).
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Molecular Recognition and Sensing: Challenges and Opportunities

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Introduction and objective

The molecular recognition and sensing of analytes of biochemical, clinical and environmental significance with high selectivity and sensitivity has attracted continuing research interest for their potential applications to biochemical studies, disease diagnosis, and monitoring of hazardous substances. For these purposes, fluorescent probes have received great attention for their high sensitivity and operational simplicity. A great number of molecular probes have been developed through a combination of a fluorescent dye and a recognition unit that selectively interacts with the target analyte by H-bonding, cation- π , hydrophobic interactions, and so on. Such a supramolecular approach is valuable and essential; however, sometimes it is challenging to achieve a high level of selectivity toward certain target species and also to realize turn-on type fluorescent response for the analytes that act as quenchers.

Methods

To address the low selectivity and sensitivity issues met with the conventional supramolecular sensing approach, we have been exploring two different types of sensing systems: 1) the reaction-based sensing system and 2) the “integrated” sensing system. Although the reaction-based approach was introduced a decade ago,¹ its full potential remained unexplored until a recent resurgence in the development of fluorescent probes for heavy metal species. To realize analyte specificity as well as turn-on type fluorescence response for anion species, we initiated the reaction-based approach to sense anions such as cyanide and carboxylates. To realize high analyte selectivity, we have also been exploring the integrated sensing systems where a number of single or multiple recognition groups are integrated onto nanoparticles or solid platforms through the self-assembly process.

Results

We have developed the first turn-on sensing system for the anions such as cyanide and carboxylates based on the reaction based approach. This reaction based approach has also been successfully applied to sense cationic species that cause quenching in the conventional supramolecular approach. We have thus developed the first reaction based sensing system for silver ions and nanoparticles, in addition to novel turn-on type fluorescence probes for methylmercury, mercury, gold, palladium species.²⁻⁹ We have also found that integrated recognition systems can provide a binding pocket or dimple on the surface, which provide unusual analyte selectivity in addition to very high sensitivity toward phosphate containing molecules (ATP, PPI) compared to the corresponding single receptor based systems.

Conclusion

We have demonstrated that the reaction based approach to sense anionic species can lead to turn-on fluorescence response in contrast to the conventional supramolecular based approach that leads to fluorescence quenching in general. We also have demonstrated that the integrated sensing systems can provide very high sensitivity as well as unusual selectivity compared to the corresponding “non-integrated” single receptor based approach.

Keywords: fluorescence, molecular probes, metal species, anions

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Arsenic Analysis by Carrier-Mediated Counter-Transport Single Drop Microextraction/Capillary Electrophoresis

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Keywords: Capillary electrophoresis (CE); Single drop microextraction (SDME); Carrier; Aliquat 336; Arsenic.

Summary. In single drop microextraction (SDME), a drop of an acceptor phase covered with an organic layer is hung at the inlet tip of a separation capillary. By adjusting the pH, analytes in the neutral form in an aqueous donor phase are first extracted into the organic layer, and then backextracted into the acceptor phase. However, the hydrophilic nature of the arsenic compounds, hampering the first extraction into the organic layer, lowers or even eradicates the efficiency of the SDME process. This problem can be solved by using $\text{CH}_3(\text{C}_8\text{H}_{17})_3\text{N}^+\text{Cl}^-$ (Aliquat 336) as a carrier in the organic layer. Aliquat 336 enhances the transport of the arsenic compounds across the organic layer by forming hydrophobic complexes. The arsenic enrichment process is driven by the concentration gradient of hydroxide or chloride ion in conjunction with arsenic extraction from the donor phase to the acceptor phase of a high concentration of hydroxide or chloride. The gradient of hydroxide concentration yielded high enrichment factors for arsenic compounds, including As(III), which was not extracted well with the gradient of chloride only. After extraction, the enriched arsenic compounds are separated by capillary electrophoresis (CE). The SDME and CE processes were performed in an in-line mode with a commercial CE instrument. Using an acceptor phase at a pH of 13, the enrichment factors obtained for a sample in unbuffered water with 15-min extraction were 390, 340, 1100, and 1300 for As(III), dimethylarsinic acid (DMA), monomethylarsonic acid (MMA), and As(V), respectively. The limits of detection ($S/N = 3$) with absorbance detection at 200 nm were 0.2, 0.7, 0.1, and 0.2 μM for As(III), DMA, MMA, and As(V), respectively. In order to take care of the donor matrix effects, standard additions were used for the analysis of tap water.

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Education:

- 1981 B. Sc. in Chemistry, Seoul National University, Seoul, Korea
- 1983 Ms. Sc. in Chemistry, Seoul National University, Seoul, Korea
- 1986 A. M. in Physics, Harvard University, Cambridge, MA, USA
- 1991 Ph. D. in Chemical Physics, Harvard University, Cambridge, MA, USA
- 1994 Postdoc, Massachusetts Institute of Technology & Harvard Medical School
- 1995 Postdoc, Iowa State University, Ames, IA, USA

Professional career:

- 1995 Assist. Prof., Seoul National University, Seoul, Korea
- 2005 Prof., Seoul National University, Seoul, Korea

Research interests:

We are working on a variety of topics ranging from the realization of molecule optics to bioanalytical chemistry.

Analogous to photon optics that is the control of light by the use of optical devices such as a lens, and ion optics that it is the control of ions by the use of electricity, a new field of science, "molecule optics" has emerged. Molecule optics is the control of molecular external degrees of freedom by "optical force" exerted on molecules by photons, which is a result of the momentum conservation.



Recently, we have demonstrated a "molecule lens" using the nonresonant dipole forces of a focused nanosecond IR laser pulse. This is the first experimental realization of molecule optics. Then, another component of molecule optics, "molecule prism", has been developed and used to spatially separate a benzene and nitric oxide mixture.

To make capillary electrophoresis be truly high performance, we are focusing on the enhancement of the sensitivity and reliability of capillary electrophoresis. Various preconcentration schemes such as transient isotachopheresis and single drop microextraction have been successfully applied to capillary electrophoresis of bioanalytical samples.

Selected publications:

[1] Bum Suk Zhao, Hoisung Chung, Keunchang Cho, Sung Hyup Lee, Sungu Hwang, Jongwan Yu, Y. H Ahn, J. Y. Sohn, D. S. Kim, Wee Kyung Kang, and Doo Soo Chung. Molecular Lens of the Nonresonant Dipole Force. *Phys. Rev. Lett.* 2000; 85: 2705.

[2] Bum Suk Zhao, Sung Hyup Lee, Hoi Sung Chung, Sungu Hwang, Wee Kyung Kang, Bretislav Friedrich, and Doo Soo Chung. Separation of a Benzene and Nitric Oxide Mixture by a Molecule Prism. *J. Chem. Phys.* 2003; 119: 8905.

[3] Kihwan Choi, Yongsung Kim, and Doo Soo Chung. Liquid-Phase Microextraction as an On-Line Preconcentration Method in Capillary Electrophoresis. *Anal. Chem.* 2004; 76: 855.

[4] Kihwan Choi, Su Ju Kim, Yoo Gon Jin, Yong Oh Jang, Jin-Soo Kim, and Doo Soo Chung. Single Drop Microextraction Using Commercial Capillary Electrophoresis Instruments. *Anal. Chem.* 2009; 81: 225.

An artificial Signal Transduction System Consisting of Electron Transfer Proteins

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Keywords: Signal transduction, Azurin, Cytochrome *c*, PNIPAM, Bioelectrochemistry

Hybrid molecules consisting of bio and artificial molecules have been considered to be a promising material bearing novel functions. One of the target functions of such molecules is some catalytic activity that are hardly achieved by original molecules alone. Our studies on protein engineering including protein mutagenesis [1, 2] conjugation of proteins with organometallics or organic compounds [3] are on the line of the target. Rapid progress in studies of artificial catalysts, however, have reduced the advantage of such hybridizations, which prompts us to explore novel functions more specific for the hybrid molecules. In this talk, I describe a hybrid molecule aiming signal transduction function inspired by a natural sensor protein[4]. In the present hybrid biomolecule, a structural change of an environment responsive molecule upon sensing is monitored as a change in an electron transfer rate between the proteins, azurin and cytochrome *c*; an environmental stimulus is transduced to electronic signals.

Figure 1 shows the outline of the present study. A temperature responsive polymer (poly-isopropyl acrylamide, PNIPAM) whose terminal is modified with imidazole is introduced to the Cu ion in an azurin variant as an external ligand. A temperature dependent morphological alteration of PNIPAM on azurin is transduced to a change in the electron transfer rate with cytochrome *c*, a redox partner of azurin. Results of the electro-

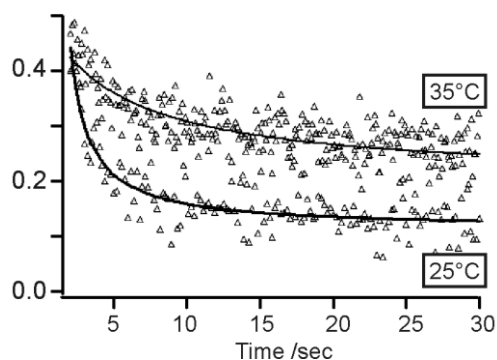


Fig. 2. Temperature dependent change in the electron transfer rate between PNIPAM-azurin and cytochrome *c*.

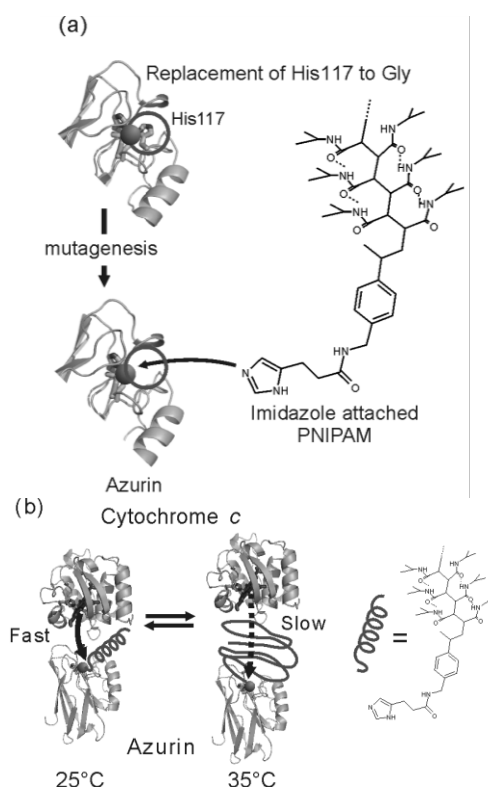


Fig. 1. (a) Introduction of PNIPAM to copper ion in azurin. The terminal imidazole group in PNIPAM serves as a ligand of an azurin variant (H117G) in which His117 is replaced to Gly. (b) The outline of the azurin- cytochrome *c* signal transduction system. PNIPAM shows a morphological change across a certain temperature (32 °C in the present case), which alters the specific azurin-cytochrome *c* association, resulting in change of the electron transfer rate between the proteins.

transfer experiments

are shown in Figure 2. Across the temperature of the morphological change in PNIPAM, significant change in the electron transfer rate is observed. The slower rate at higher temperature (35 °C) could be accounted for aggregation of PNIPAM over the surface of the active site of azurin, which disturbs the smooth inter-proteins interaction, resulting in the slower electron transfer.

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- [3] Tokita, Y., Yamada, S., Luo, W., Goto, Y., Ford, N., Nakajima, H., Watanabe, Y., *Angew. Chem. Int. Ed.* 2011, **50**, 11663-11666.
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Education:

- 1991 B. Sc., Osaka University, Osaka, Japan
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- 1996 Dr. Sc., The Graduate University for Advanced Studies, Aichi, Japan

Professional career:

- 1996 Assist. Prof., Japan Advanced Institute for Science and Technology, Ishikawa, Japan
- 2003 Assist. Prof., Institute for Molecular Science, Aichi, Japan
- 2003 Associate Prof., Nagoya University, Aichi, Japan

Awards/other information:

- 1994-96 JSPS Research Fellowship for Young Scientist

Research interests:

Chemical and biological transformation of thermally tolerant proteins; Elucidation of molecular mechanisms of signal transduction in natural sensor proteins; Design of artificial sensor proteins inspired by signal transducing mechanism of natural sensor proteins.

Selected publications:

1. Tokita, Y., Yamada, S., Luo, W., Goto, Y., Ford, N., Nakajima, H., Watanabe, Y., "Protein Photoconductors and Photodiodes" *Angew. Chem. Int. Ed.* 2011, **50**, 11663-11666.
2. Nakajima, H., Takatani, N., Yoshimitsu, K., Itoh, M., Aono, S., Takahashi, Y., Watanabe, Y., "The role of Fe-S cluster in the sensory domain of nitrogenase transcriptional activator VnfA *Azotobacter vinelandii*.", *FEBS J.* 2010, **277**, 817-832.
3. Tokita Y, Shimura J, Nakajima H, Goto Y, Watanabe Y, Mechanism of Intermolecular electron Transfer in the Photoexcited Zn-Substituted Cytochrome c: Theoretical and Experimental Perspective., *J. Am. Chem. Soc.* 2008, **130**, 5302-5310.
4. Satake Y., Abe S., Okazaki S., Ban N., Hikage T., Ueno T., Nakajima H., Suzuki A., Yamane T., Nishiyama H., and Watanabe Y., Incorporation of a phebox rhodium complex into apo-myoglobin affords a stable organometallic protein showing unprecedented arrangement of the complex in the cavity., *Organometallics* 2007, **26**, 4904-4908.
5. Ichikawa Y, Nakajima H, Watanabe Y, Characterization of peroxide bound heme species generated in reaction of thermally tolerant cytochrome *c*₅₅₂ with hydrogen peroxide., *ChemBioChem* 2006, **7**, 1582-1589.



Lesson from Nature: Mussel Adhesive Biomaterials

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Keywords: Mussel adhesive proteins, Biomaterials

Marine-fouling invertebrates (e.g., mussel, barnacle, sandcastle worm, hydroid, and sea star) form a strong attachment to the marine substratum against mechanical stresses arising from the tide, buoyancy, and drag using their special physical and chemical underwater adhesives. There are many unveiled lessons to learn from these organisms, and indeed, underwater adhesives from these marine organisms have been investigated as a source of potential underwater adhesives because of their fascinating properties. Therefore, an understanding of how adhesives are produced by marine organisms will inspire new paradigms for the design and engineering of adhesives for medical use.

Production capability and superior properties are very important for practical applications of mussel adhesive proteins. The natural proteins were initially extracted to study their biochemical properties; however, limited productivity hampered investigation of bulk-scale adhesive properties and biomedical and industrial applications. Thus far, extracts of mussel adhesive proteins containing primarily fp-1 and fp-2 are used commercially as a cell and tissue adhesive (Cell-TakTM, BD Biosciences). Recombinant protein approaches using cDNAs or synthetic constructs of mussel adhesive protein have been used to obtain practical amounts of the proteins in various bacterial, yeast, insect, plant, and mammalian cell expression systems.

Synthetic constructs of mussel adhesive proteins based on hybrid and fusion strategies have been successful in producing the proteins and provide the ability to apply the adhesive biomaterials to various application fields. In particular, research and applications have been initially concentrated on biomaterials for tissue engineering and biomedical engineering use due to the economic implications and functional performance.

At least 100 mg of adhesive protein is required to conduct small scale and conventional bulk tests, including tensile strength analysis for obtaining mechanical properties as adhesive biomaterials. Thus, few reports are available that measure the bulk adhesive strength of mussel adhesive proteins due to their very limited abundance. Thus far, the shear strength has only been reported for mussel foot extract (composed primarily of fp-1 and fp-2; on porcine skin, ~0.33 MPa under dry conditions and ~1 MPa under humid conditions), 10 repeats of fp-1 decapeptide (~0.3 MPa compressive shear strength on aluminum), tyrosinase-modified recombinant fp-5 (~1.11 MPa on aluminum adherents), tyrosinase-modified recombinant fp-151 (0.42~1.98 MPa on aluminum) and tyrosinase-modified recombinant fp-131 (1.87 MPa on aluminum). However, recombinant mussel adhesive proteins are expected to be used chiefly for practical applications due to their productivity and biocompatibility.

Ultimately, we expect that mussel adhesive proteins can be used as bioadhesives for binding items together in dry and wet environments, given their bulk-scale adhesive properties and biocompatibility. Moreover, mussel adhesive proteins will be utilized in various biomedical and industrial fields in the near future, given their diverse adhesive properties even in wet conditions, environmentally friendly properties and high biocompatibility and high productivity and economical cost. Recent results have shown the high potential of adhesive biomaterials as cell and tissue adhesives and extracellular matrix and scaffold-coating materials for tissue engineering, immobilizing agents for biochip preparation, gene and drug delivery carriers and skin and bone adhesives.

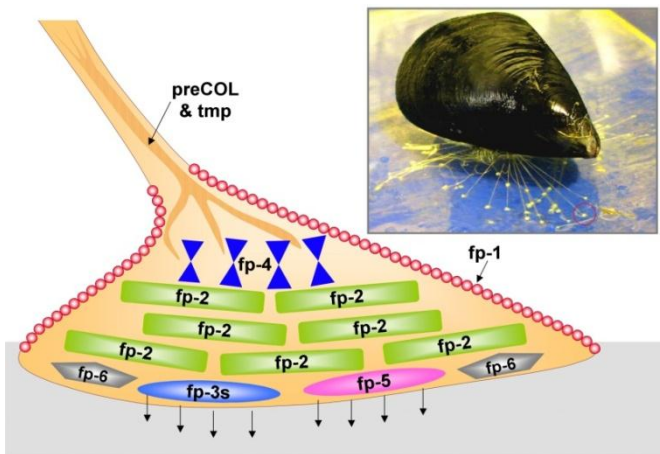


Figure 1. Byssal plaque proteins of *Mytilus*. A mussel (*Mytilus galloprovincialis*, inset) is shown attached to a sheet of mica. One of its plaques (red circle) is enlarged as a schematic drawing to illustrate the approximate distribution of proteins.

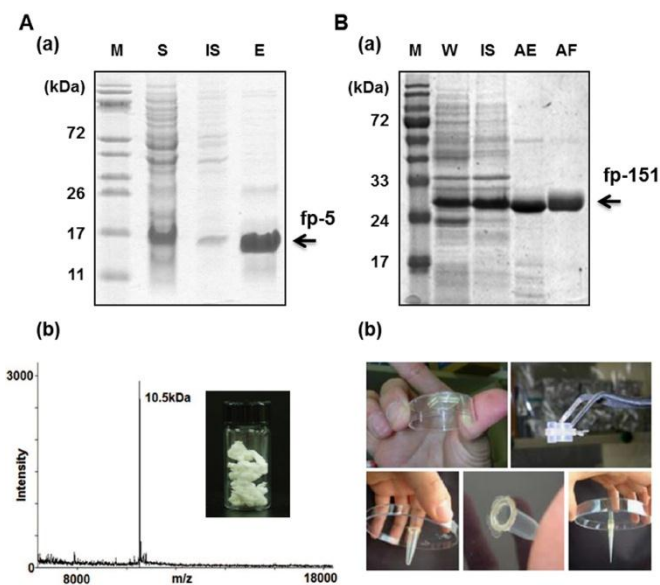


Figure 2. Bulk-scale production of recombinant mussel adhesive proteins. A. recombinant fp-5. (a) Tricine SDS-PAGE analysis for expression and purification of recombinant fp-5. Lanes: M, protein molecular weight marker; S, soluble fraction of cell lysate; IS, insoluble fraction of cell lysate; E, purified recombinant fp-5. (b) MALDI-TOF MS analysis and lyophilized power of purified fp-5. B. recombinant fp-151. (a) SDS-PAGE analysis for expression and purification of fp-151. Lanes: M, protein molecular weight marker; W, whole cell sample; IS, insoluble fraction of cell lysate; AE, fraction extracted with 25% (v/v) acetic acid; AF, eluted fraction using affinity chromatography. (b) Adhesion of laboratory plastic consumables using recombinant fp-151.

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Name of attendant: Hyung Joon Cha

Education:

Ph.D., Seoul National University, 1995

M.S., Seoul National University, 1992

B.S., Seoul National University, 1990



Professional career: (staff only)

- 2009.3. ~ Present : Professor, Department of Chemical Engineering, POSTECH

- 2009.3. ~ Present : Adjunct Professor, School of Environmental Science and Engineering, POSTECH

- 2004.3. ~ 2009.2 : Associate Professor, Department of Chemical Engineering, POSTECH

- 2004.3. ~ 2006.2. : Associate Professor, Division of Molecular and Life Sciences, POSTECH

Awards/other information: (if any)

12/2008 - Nomination on National R&D 100 Best Researches in 2007, Ministry of Education, Science, and Technology

10/2008 - Beom-Suk Award, Korean Institute of Chemical Engineering

5/2008 - Invention Day Award, Minister of Knowledge Economy Department

11/2007 - Samil Cultural Award, Samil Culture Foundation

Research interests:

- Marine Molecular Biotechnology : Marine bioadhesive, Marine silk protein

- Cell Molecular Biotechnology : Glycosylation pathway engineering, Antimicrobial peptide

- Nano Molecular Biotechnology : DNA chip, Carbohydrate chip, Biomolecule interaction

- Energy Molecular Biotechnology : Biohydrogen (E. coli / microalgae)

Selected publications:

Insights on Peptide Self-Assembly and Protein Aggregation

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Keywords: peptide self-assembly; bionanostructure; nanoring; protein aggregation; A β peptide; α -synuclein; Molecular Dynamics simulation.

Summary: Interests in artificial bionanostructures, including peptide-based self-assembled nanostructures have been very intense. Recently, a rational approach to construct β -barrel protein mimics from the self-assembly of peptide-based building blocks has been demonstrated. We performed MD simulations on the proposed nanoring structures formed by the self-assembly of β -sheet forming peptides. The stability of the nanoring structure with respect to the size is investigated and several factors contributing to the stability are examined. We have also performed MD simulations on the various β -barrel like peptides with the selective W to F mutations. It was found that nanorings with different sizes can be obtained by introducing such mutations. Insights on the basic driving force for the formation of such peptide-based nanostructures are expected to be useful in designing new functional bionanostructures. Understanding the mechanism of aggregation of misfolded proteins is very important to elucidate possible causes for various neurodegenerative disorders. Systematic replica exchange molecular dynamics (REMD) simulations have been performed on the formation of the oligomers of A β peptide and peptides from α -synuclein. The mechanism of aggregation and growth of these peptides is examined from detailed analysis of such simulations. We also performed MD simulations on two popular structural models of the A β fibrils for the wild type, F(19,20)I and F(19,20)L mutants. Our results suggested that different topologies suggested by the two structural models are favored in the different stages of aggregation: the early onset of the nuclei and the elongation process.

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Name of attendant:

Education:

1985 B. Sc., Seoul National University, Seoul, Korea
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1992 Ph. D., University of Chicago, Chicago, USA

Professional career:



1994 Postdoc, UCSB, Santa Barbara, USA
1995 Assist. Prof., Seoul National University, Seoul, Korea
1999 Assoc. Prof., Seoul National University, Seoul, Korea
2005 Prof., Seoul National University, Seoul, Korea

Awards/other information:

1987 McCormic Fellowship, University of Chicago, Chicago, USA
2003 Young Investigator Award in Physical Chemistry, Korean Chemical Society, Seoul, Korea

Research interests:

Chemical reactions in condensed matter; self-assembly at surfaces/interfaces; development of quantum control scheme; computational studies on nano structures; understanding protein misfolding and aggregation.

Selected publications:

1. "Tuning of the Band Structures of Zigzag Graphene Nanoribbons by an Electric Field and Adsorption of Pyridine and BF₃: A DFT Study", H. Park, J. Y. Lee and S. Shin, *J. Phys. Chem. C*, **2012**, *116*, 20054.
2. "Relativistic potential energy surfaces of initial oxidations of Si(100) by atomic oxygen : The importance of surface dimer triplet state", T.-R. Kim, S. Shin and C. H. Choi, *J. Chem. Phys.*, **2012**, *136*, 214704.
3. "Simulation Studies on the Stabilities of Aggregates Formed by Fibril-Forming Segments of α -Synuclein", J. Yoon, S. Jang, K. Lee and S. Shin, *J. Biomol. Struct. Dyn.*, **2009**, *27*, 259.
4. "Computational Study on the Structural Diversity of Amyloid β -Peptide (A β 10-35) Oligomers", S. Jang and S. Shin, *J. Phys. Chem. B*, **2008**, *112*, 3479.
5. "Selective photodissociation in diatomic molecules by dynamical Stark-shift control", H. Choi, W.-J. Son, S. Shin, B. Y. Chang, and I. R. Sola, *J. Chem. Phys.*, **2008**, *128*, 104315.

Solid-phase Total Synthesis of Biologically Active Cyclodepsipeptide Natural Products

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Keywords: total synthesis, natural products, cyclodepsipeptide, solid-phase synthesis.

Abstract

Cyclodepsipeptide natural products include optically active hydroxy acids as well as various unnatural amino acids and exhibit a variety of biological activity depending on the peptide sequence, chirality, and selection of the hydroxy acids [1,2]. Structure-activity relationships of a synthetic library of natural products could give us significant information of not only biologically important moieties but also intact positions in the biologically active small molecules. On the basis of the former information, more potent compounds and/or peptide mimetics can be designed. The latter information can also be important for making a molecular probe that is used for exploration of a target molecule. Methods for the combinatorial synthesis of natural product analogues using solid-phase [3] and biological evaluation of the analogues will be discussed.

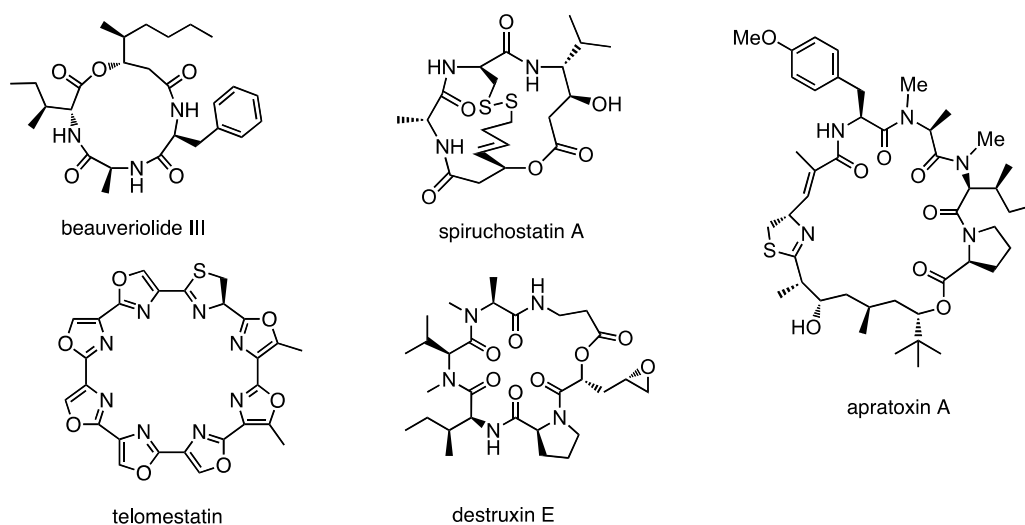


Figure 1. Solid-phase total synthesis of cyclodepsipeptide natural products

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Education:

- 1986 B. Eng., Tokyotech, Tokyo, Japan
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Professional career: (staff only)

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1993 Assist. Prof., Tokyotech, Tokyo, Japan
2001 Assoc.Prof., Tokyotech, Tokyo, Japan
2008 Prof., Tohoku University, Sendai, Japan

Awards/other information: (if any)

- 2001 Incentive Award in Synthetic Organic Chemistry, Japan
2013 Award for Divisional Promotion, The Pharmaceutical Society of Japan

Research interests:

Total synthesis of biologically active natural products and their analogues, Cyclodepsipeptides, Design and synthesis of peptidomimetics, Inhibitors of protein-protein interaction, Synthesis of molecular probes and analysis of target-protein complexes.

Selected publications:

- [1] M. Yoshida, K. Saito, Y. Fujino, and T. Doi, A Concise Synthesis of 3-Aroylflavones via Lewis Base 9-Azajulolidine-catalyzed Tandem Acyl Transfer-Cyclization: *Chem. Commun.*, **48**, 11796 (2012).
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Chemosensors for Redox-responsible Biomolecules

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Keywords: fluorescent sensor; electrochemiluminescent sensor; redox; biomolecules; phosphate

Abstract: Recently, fluorescent chemosensors have been intensively developed to detect specific biomolecules and monitor biological events. In particular, many chemosensors based on bis(Zn^{2+} -dipicolylamine) (dipicolylamine = DPA) complex have been synthesized to detect phosphate-containing biomolecules because this complex strongly binds to phosphate or diphosphate groups in water. There are many other kinds of phosphate-containing biomolecules that may play critical roles in a living system. However, selective detection methods for those biologically important phosphobiomolecules have not yet been established. Therefore, there is a real need to develop selective chemosensors, not only for the detection of phosphate-containing biomolecules, but also for biological applications and disease diagnosis. Herein we report our recent efforts towards the development of selective fluorescent sensors especially for redox-related biomolecules (FMN, FAD, NAD^+ , NADP^+ , etc.), using Zn^{2+} -DPA as a binding site. Electrochemiluminescent and fluorescent sensors for other biologically and clinically important analytes will also be presented.

References

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- [3] I.S. Shin, S.W. Bae, H. Kim and J.-I. Hong: *Anal. Chem.* 2010; 82: 8259-8265.
- [4] H.W. Rhee, C.R. Lee, S.H. Cho, M.R. Song, M. Cashel, H.E. Choy, Y.J. Seok and J.-I. Hong: *J. Am. Chem. Soc.* 2008; 130: 784-785.
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Professional career:

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1997 Associate Prof., Seoul National University, Seoul, Korea
2003 Prof., Seoul National University, Seoul, Korea

Awards/other information:

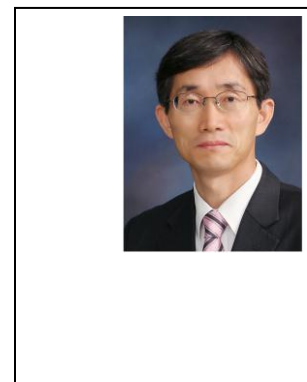
2006 KCS Organic Division Shim Sang Chul Award, Korean Chemical Society
2010 Excellent Research Award, College of Natural Sciences, Seoul National University
2010 Sigma Aldrich Award, Korean Chemical Society

Research interests:

Bioorganic Chemistry and Materials Chemistry: Chemosensors for Biologically Important Molecules, Electrochemiluminescent Sensors, Organic Materials for Optoelectronics (OSCs, OLEDs and OTFTs)

Selected publications:

1. J.-K. Bin, N.-S. Cho, J.-I. Hong, New Host Material for High-Performance Blue Phosphorescent Organic Electroluminescent Devices, *Adv. Mater.* **2012**, *24*, 2911-2915.
2. I.-S. Shin, S. W. Bae, H. Kim, J.-I. Hong, Electrogenerated Chemiluminescent Anion Sensing: Selective Recognition and Sensing of Pyrophosphate, *Anal. Chem.* **2010**, *82*, 8259-8265.
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Photolithographic Boronate Affinity Molecular Imprinting: a General and Facile Approach for Glycoprotein Imprinting

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Keywords: antibody mimics; boronate affinity; glycoproteins; molecular imprinting; UV-initiated polymerization

Abstract: Molecular imprinting of proteins is of great importance but remains a challenge. Particularly, universal and rapid methodologies are limited. Here we report a general and facile approach, photolithographic boronate affinity molecular imprinting, for the imprinting of glycoproteins. The approach relied on boronic acid-based UV-initiated polymerization, in which a boronic acid played essential roles. MIP thin-layer arrays were produced using a photolithographic fabrication route. The generality of the approach was demonstrated with the successful imprinting of five distinct glycoproteins. The approach showed fast speed and the potential for easy mass production. The prepared MIP arrays exhibited several highly attractive features that are beyond normal expectation, particularly superb tolerance for interference and the applicability to a wide range of sample pH. The feasibility for real-world applications was demonstrated with the analysis of trace glycoproteins in human serum.

Molecularly imprinted polymers (MIPs)[1], as economical and stable mimics of antibodies and enzymes, have found important applications such as chemical separation and catalysis. The imprinting of proteins is challenging, due to conformational changes during polymerization and slow mass transfer in the polymers [2]. Although several strategies, such as surface imprinting [3], epitope imprinting [4], and Pickering emulsion [5], have been proposed to solve these issues, the imprinting of proteins still remains a challenge.

Glycoproteins, which occupy more than 50% of the total proteins in mammalian systems, play key roles in many biological processes, such as molecular recognition, inter- and intra-cellular signaling, and immune response. Besides, many glycoproteins are disease biomarkers and therapeutic targets. Therefore, the imprinting of glycoproteins is of great importance and in high demand. A variety of approaches have been proposed to imprint glycoproteins [1c-1e,6], however, a universal and simple approach for glycoprotein imprinting has not been reported yet.

Boronic acids can covalently interact with cis-diol-containing molecules such as sugars to form stable cyclic esters in an alkaline aqueous solution while the boronate esters dissociate when the environmental pH is switched to acidic [7]. This reversible binding has made boronic acids excellent affinity for creating functionalized materials [8]. As such easy on/off chemistry favors the imprinting and removal of glycoprotein templates, boronic acids can be promising functional monomers for establishing a general approach for glycoprotein imprinting. However, such a possibility has never been well explored. Mosbach et al. [6a] first reported covalent imprinting of glycoproteins, in which transferrin was successfully imprinted with boronate-silane; however, attempts to imprint other glycoproteins with the same approach had not been successful due to problems such as protein precipitation. Although boronic acids have been demonstrated as important functional monomers for

the covalent imprinting of small molecules [9], most attempts [6c,6d,10] on boronic acid-based protein imprinting used *m*-aminophenylboronic acid as a polymerizable reagent, in which benefits from boronate affinity interactions for imprinting have not been demonstrated.

Here we report a general and facile approach, photolitho-graphic boronate affinity molecular imprinting, for the imprinting of glycoproteins. The key of the approach was boronic acid-based UV-initiated polymerization, in which a boronic acid, as the sole functional monomer, was found to play essential roles. MIP thin-layer arrays were produced using a photolithographic fabrication procedure [11]. The generality of the approach was demonstrated with the successful imprinting of five distinct glycoproteins. The approach showed fast speed (total processing time less than 3 h) and the potential for easy mass production. More interestingly, the prepared MIP arrays exhibited several highly favorable features that are beyond normal expectation, particularly superb tolerance for interference and the applicability to a wide range of sample pH. The feasibility for real-world applications was demonstrated with an MIP array-based enzyme-linked immunosorbent assay (ELISA) of trace α -fetoprotein (AFP) in human serum.

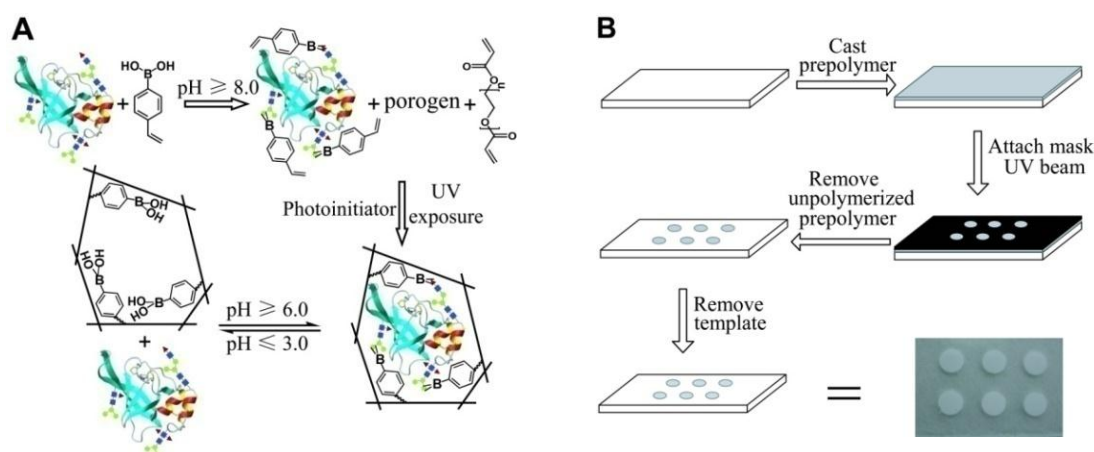


Fig. 1 The principle (A) and the procedure (B) of photolithographic boronate affinity molecular imprinting.

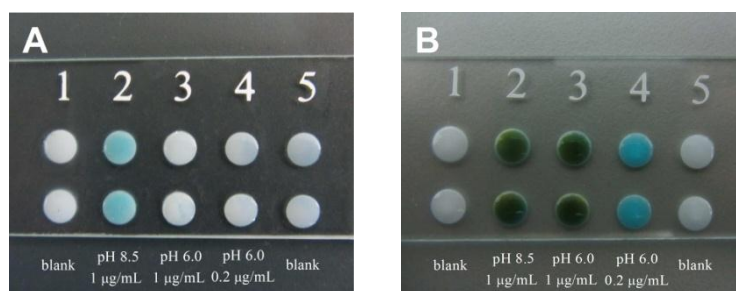


Fig. 2 Comparison of the affinity of NIP (A) and HRP-imprinted MIP towards the template at different pHs. The HRP extracted was stained with 3,3',5',5'-tetramethylbenzidine dihydrochloride (TMB) (a denser color indicates that more template molecules were extracted).

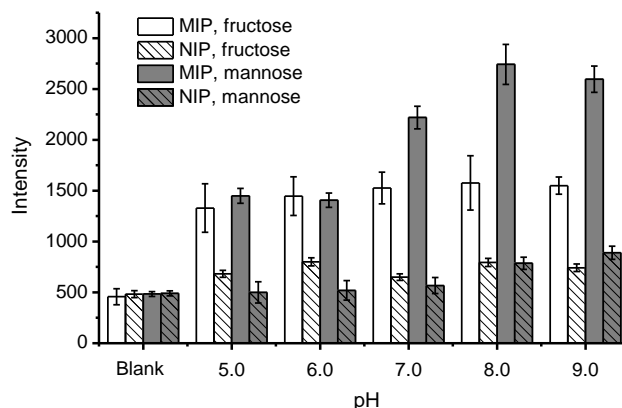


Fig. 3 Comparison of the affinity of MIP and NIP towards the template HRP in the presence of competing sugar at different sample pHs. Chemiluminescence detection; Sample, 10 ng/mL HRP, 10 mg/mL fructose in 100 mM phosphate buffer at different pHs.

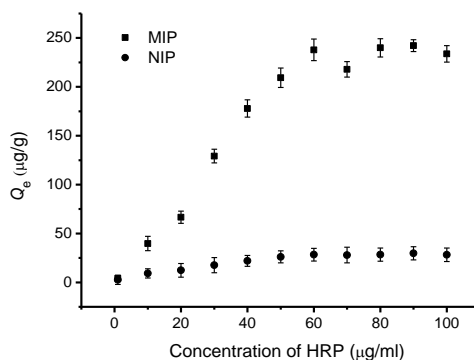


Fig. 4 Binding isotherms of an HRP-imprinted array and a NIP array.

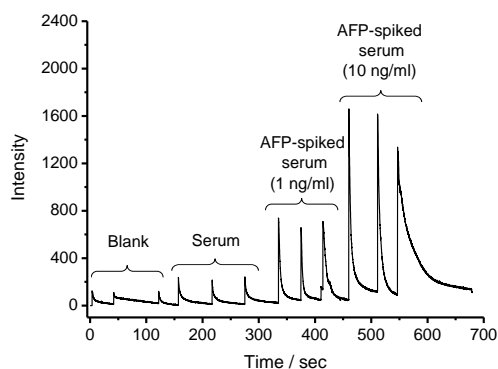


Fig. 5 MIP array-based immunochemiluminescence assay of human serum samples spiked with different concentrations of AFP.

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Research interests:

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Selected publications:

1. *Angewandte Chemie International Edition*, 2009, 48, 6704-6707.
2. *Chemical Communications*, 2011, 47, 2255 - 2257.
3. *Chemical Communications*, 2011, 47, 5067 - 5069.
4. *Chemical Science*, 2012, 3, 1467-1471.
5. *Chemical Communications*, 2012, 48, 4115–4117.
6. *Analytical Chemistry*, 2013, in press (DOI: 10.1021/ac3033917).

Development of Novel Heterocycles as Potent CRHR-1 Antagonists and Cdk Inhibitors

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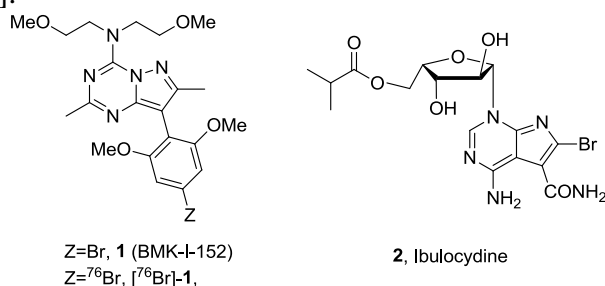
Keywords: Hepatocellular carcinoma, cyclin-dependent kinase, apoptosis, CRHR-1, antagonist.

Summary. This paper describes a series of pyrazolotriazine structures exhibiting potent CRHR-1 antagonistic activities and nucleoside analogs that exhibit potential anti-cancer activities.

Development of CRHR-1 Antagonists

Corticotropin releasing hormone (or factor, CRH or CRF) coordinates endocrine, autonomic, behavioral, and immune response to stress. Therefore, CRH receptors have become one of the most important therapeutic targets for major diseases such as depression, anxiety, and irritable bowel syndrome (IBS) [1].

Potent nonpeptide CRH receptor-1 (CRHR1) antagonists have been designed and synthesized for the purpose of understanding and eventually controlling the CRH-related diseases. The design and synthesis of new antagonists have been pursued based upon pyrazolotriazine core structure. Labeling BMK-I-152, an efficient antagonist to CRHR-1, with proper isotopes would allow us to noninvasively investigate the receptor distribution, population, and drug-receptor interaction [2]. With in vitro autoradiography saturation and competition studies, compound [^{76}Br]-1 was shown to have subnanomolar affinity for the CRHR1 and regional distribution in rat and monkey brain. The in vivo studies with rats and mice indicated [^{76}Br]-1 can penetrate the BBB remaining primarily unmetabolized [^{76}Br]-1 [3].



Development of Cdk Inhibitors

Hepatocellular carcinoma (HCC) is one of the most common and serious cancers world-wide. Chronic infection with hepatitis B or hepatitis C virus increases the risk of developing HCC. Usually HCC cells are characterized by high levels of cyclin-dependent kinase (Cdks) activity. Up-regulation of Cdks may result from inactivation of Cdk inhibitory proteins, or from abnormal activation of Cyclins. Treatment of HCC is difficult, as HCCs express multidrug resistance transporters and become highly insensitive to current chemotherapeutic agents. Therefore, Cdk inhibitors may be suitable candidates for HCC therapy. BMK-Y101, the parent compound of Ibulocydine, inhibits cell growth of HCC cells and its prodrug Ibulocydine strongly inhibits cell growth of HCC cells more effectively than BMK-Y101 and existing Cdk inhibitors, olomoucine and roscovitine do [4]. Synthesis of BMK-Y101 involves interesting chemoselectivity in the formation of glycosidic bonds.

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 1994 Research Fellow, Merck Research Laboratories, Inc. USA
 1995 Assist. Prof. Seoul National University, Korea
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 2003 Adjunct Investigator, NIDDK, National Institute of Diabetes, Digestive and Kidney Diseases, NIH, USA
 2005- Professor, Seoul National University, Korea
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 2005 Best Teacher of the Year Award, College of Natural Sciences, Seoul National University
 2009 Asian Core Program Lectureship Award, ICCEOCA (Taiwan)
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 2012 Excellence in Education Award, Seoul National University
 2012 Asian Core Program Lectureship Awards, ICCEOCA (China & Japan)

Research interests:

Heterogeneous catalysis using nanoparticles and mesoporous materials; synthesis of physiologically active molecules; asymmetric synthesis using chiral diamines; development of efficient chemotherapeutic agents against cancer, hepatitis C infection and CNS diseases.

Selected publications:

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Ru-catalyzed Transformation of Alkyl Azides into *N*-unsubstituted Imines

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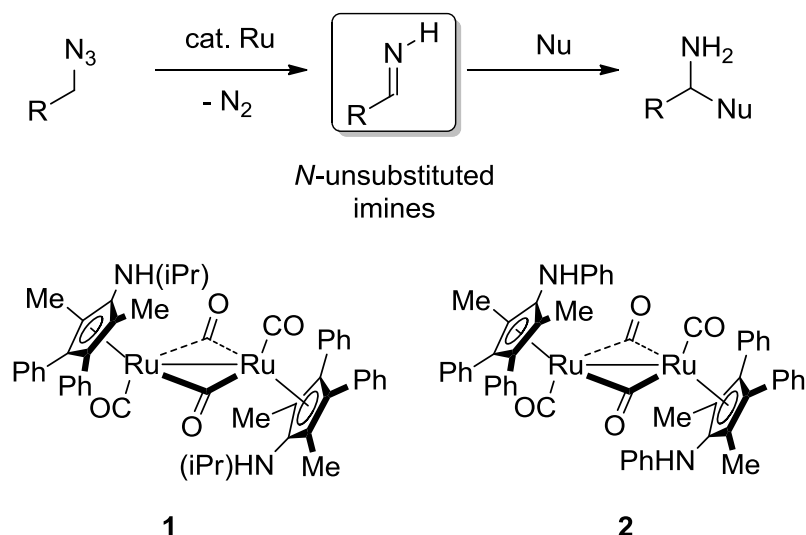
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Introduction and Objective

Imines have been recognized as pivotal intermediates in organic synthesis, particularly for the preparation of nitrogen-containing bioactive natural products and derivatives. Compared with the carbonyl groups, imines are more difficult to handle due to their chemically labile nature. Because of this problem, the transformation into the amine products usually employs imines possessing a substituent on the nitrogen (*N*-substituted imines). However, this protocol raises a fundamental question from a synthetic viewpoint because the substituent should be removed to access the amine products. In this regard, the use of *N*-unsubstituted imines would be ideal in that the elimination step is not necessary.

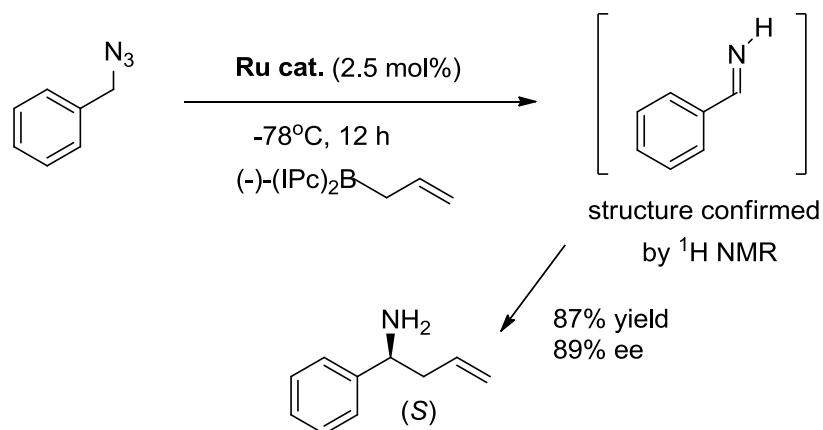
Methods

From a conceptual viewpoint, *N*-unsubstituted imines can be potentially accessed from easily available alkyl azide precursors with the removal of N₂ and subsequent migration of hydrogen. This method is particularly attractive because the reaction can proceed under very mild conditions. In fact, stoichiometric formation of metal-imine complex based upon this concept has already been reported. However, attempts using photolytic or metal-catalyzed conditions could not deliver the free *N*-unsubstituted imines, presumably due to the instability and the high reactivity of the imines. Recently, we reported a simple synthesis of an isolable bridged diruthenium complex **1** and its utility under photolytic conditions for the racemization of secondary alcohols¹ and the chemoselective hydrosilylation of aldehydes.² We wish to present that *N*-unsubstituted imines can be efficiently generated using **1** and structurally related Ru complex **2**.³ Remarkably, the mild conditions used in this transformation even allowed the observation of *cis/trans* isomers of *N*-unsubstituted imines on the basis of the NMR spectroscopy taken at room temperature. Moreover, this new protocol enabled various chemoselective transformations of *N*-unsubstituted imines.



Results

We developed a new synthetic method for the *N*-unsubstituted imines. The chemoselective nature of the reaction is highlighted by the observation of the *cis/trans* isomers of various *N*-unsubstituted imines. The synthetic utility of this method was demonstrated by the one-pot imine formation-asymmetric allylation of benzyl azide and the highly efficient synthesis of *N*-substituted imines.



Conclusion

We developed a novel Ru catalyst system which enabled generation of various *N*-unsubstituted imines under mild conditions. As demonstrated by the observation of geometrical isomers of the enolizable *N*-unsubstituted imines, chemoselective preparation of structurally well-defined *N*-unsubstituted imines was of crucial importance.

Keywords: imines, ruthenium, photolysis, allylation, azides

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Chemo- and Enantioselective Hydrogenation of Functionalized Carbonyl Group and Their Applications in the Synthesis of Pharmaceutical Molecules

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Keywords: Chemoselective, Enantioselective, Carbonyl, Asymmetric Hydrogenation.

Asymmetric hydrogenation of carbonyls has become a routine method for building up chiral alcohol centers in organic synthesis. The more polyfunctionalized a ketone is, the more versatile the hydrogenation product will be. For example, *syn*-3,5-dihydroxyhept-6-enoic acid is a key substructure in side chains for Statins. Epothilone and its congeners contain a common C₁-C₆ block derived from an enantiopure 3-hydroxyl glutaric acid structure. However, poly-functionalized ketones are relatively intractable substrates. The primary difficulty lies in the emulative coordination of multiple directing groups with the catalyst. When two carbonyl directing groups C(O)X and C(O)Y are present in one molecule, the configurations of the resultant alcohol are usually antipodal in cases when one overrides in the emulation. More often than not, both directing groups would comparably participate in the chelating. Chemo- and enantioselective hydrogenation of such substrates is challenging.

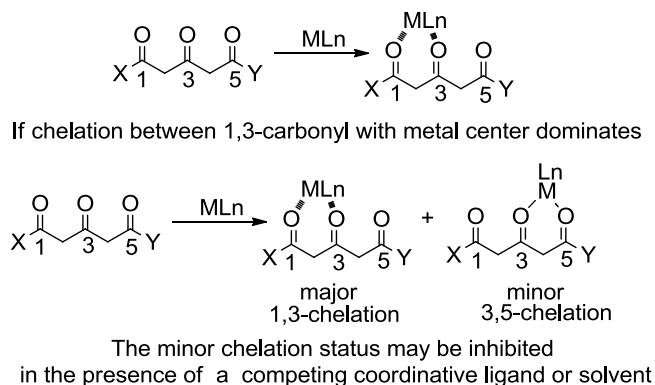


Fig. 1 Coordination models of poly-functionalized ketones with transition metal

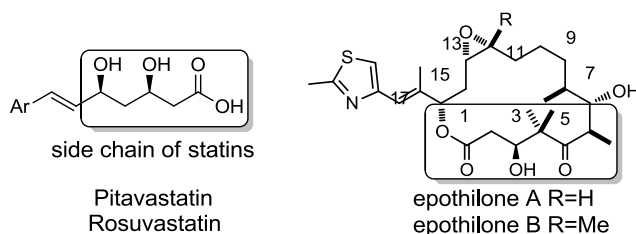


Fig. 2 Synthesis of pharmaceutical molecules with chemo- and enantioselective hydrogenation

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Transition-metal catalyzed reactions, homogeneous catalysis including asymmetric synthesis, and the synthesis of pharmaceutical intermediates and small functional molecules.

Selected publications:

1. Tao, X.; Li, W.; Li, X.; Xie, X.; Zhang, Z. *Org. Lett.* **2013**, 15, 72-75.
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Enantioselective Synthesis of Heterocycles by Using Organocatalytic Intramolecular Aza-Michael Additions

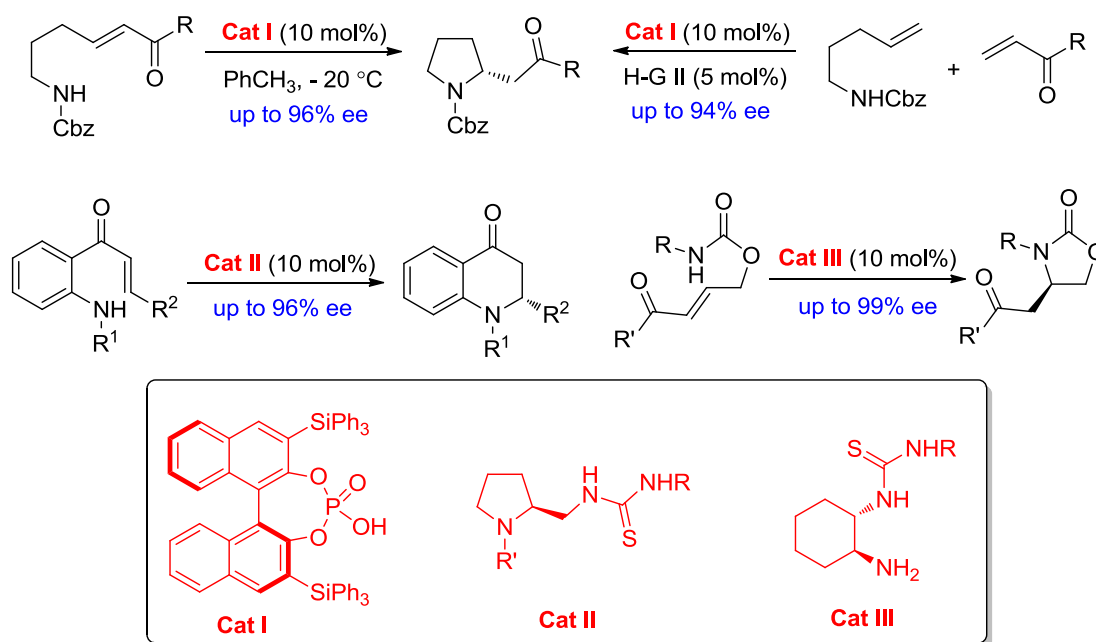
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Summary. The Michael addition represents one of the most important methods for the formation of carbon–carbon bonds in organic synthesis.^[1] Aza-Michael addition has been intensely investigated as a powerful carbon-nitrogen bond formation reaction in the preparation of amines and nitrogen heterocyclic compounds.^[2] Due to the strong Lewis basicity of nitrogen, organometallic catalytic aza-Michael addition remains a challenging task. This inherent problem could be addressed by organocatalysis. Here we presented enantioselective synthesis of several heterocycles by using organocatalytic intramolecular aza-Michael additions. Total synthesis of alkaloids by using the same strategy was also described.^[3]



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Total synthesis of biologically active natural products; Asymmetric catalysis.

Selected publications:

1. H. Liu, C. Zeng, J. Guo, M. Zhang and S. Yu*, Enantioselective Synthesis of 2-Substituted Pyrrolidines *via* Domino Cross Metathesis/Intramolecular aza-Michael Addition. *RSC Adv.*, **2013**, *3*, 1666.
2. H. Jiang, C. Huang, J. Guo, C. Zeng, Y. Zhang* and S. Yu*, Direct C-H Functionalization of Enamides and Enecarbamates by Using Visible-Light Photoredox Catalysis. *Chem Eur. J.*, **2012**, *18*, 15158.
3. C. Zeng, H. Liu, M. Zhang, J. Guo, S. Jiang and S. Yu*, Enantioselective Synthesis of Cryptopleurine and Boehmeriasin A *via* Organocatalytic Intramolecular Aza-Michael Addition. *Synlett*, **2012**, *23*, 2251.
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From Supramolecular Polymers to Dynamic Catenanes by Orthogonal Self-Assembly

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During the past few decades, the self-assembly of catenanes have received considerable attention owing to their unique topologically nontrivial structures and potential applications in molecular machines. Up to know, the synthesis of catenanes employing noncovalent binding interactions within the macrocycles are relatively less common. The use of dynamic noncovalent bonded macrocycle in the assembly of interlocked molecules was pioneered by Fujita[1] and Sauvage[2]. However, the reported [2]catenanes and rotaxanes, containing non-covalent bonded macrocycles were mainly focused on dynamic metal–ligand coordination.

The formation of supramolecular polymers [3] based on two kinds of non-covalent interactions was reported in our group. Moreover, we made research of Electron rich dioxynaphthalene (DNP) group bridged bifunctional ureidopyrimidinone (UPy) derivatives, which could form small cyclic monomers, oligomers or linear supramolecular polymers at certain concentration in solution, to achieve a highly controllable ring-chain equilibrium self-assembling supramolecular system. (Fig 1 left) Monomer **L1a** with the shortest length of oligoEO chain is present as an exclusive type of intramolecularly hydrogen-bonded assembly, namely the cyclic monomers, over a broad concentration range (1.6 - 500 mM) in solution. Single crystal structure of the cyclic monomer **L1b**, which is an analogue of **L1a**, was thoroughly studied. However, **L2** and **L3** could perform selective cyclization over the entire concentration range in solution after threading into the tetracationic cyclobis(paraquat-*p*-phenylene) cyclophane (CBPQT⁴⁺) driven by host-guest interaction, which provides another supramolecular strategy to control ring-chain equilibrium. Considering of the view from supramolecular topological molecules, we prepared for the first time a novel type of reversible [2]catenanes in which one of the two macrocycles was bonded by the quadruple hydrogen bonding interactions. Further exploration of the supramolecular polymers based on ureido-pyrimidinone motif and its application as smart materials are in progress in our lab. (Fig 1 right) [4-5]

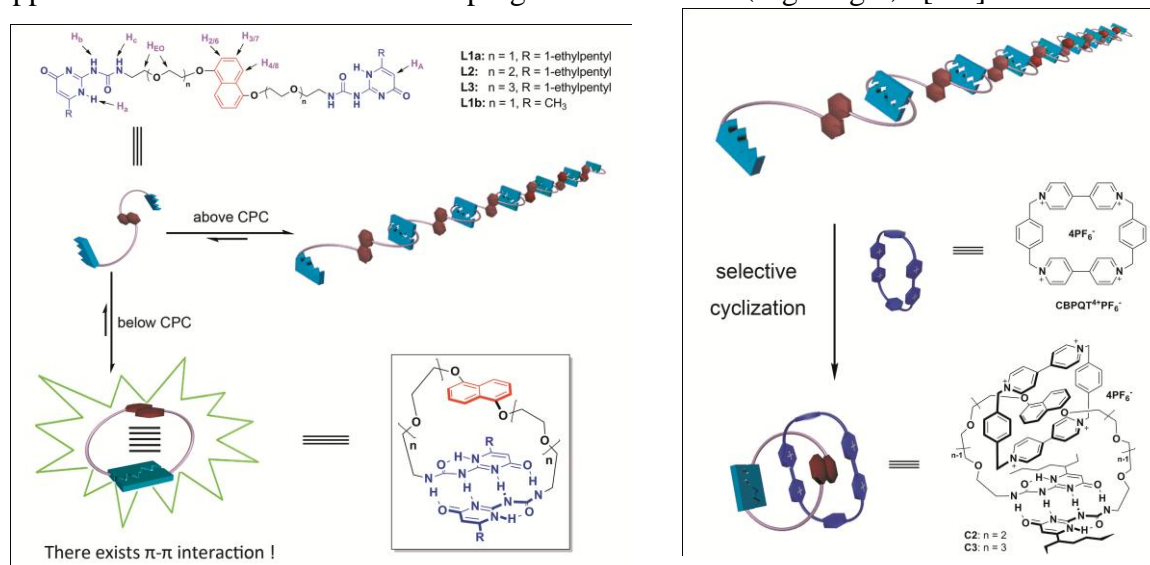


Figure 1. Representations of the ring-chain equilibrium of DNP bridged bifunctional UPy derivatives (Left) and Representation of the selective cyclization of **L2** or **L3** after threading into CBPQT⁴⁺(right)

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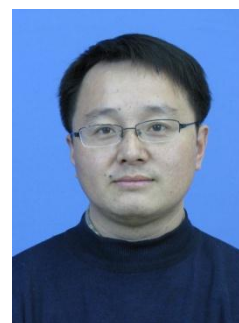
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Unraveling The Mechanism of Enantioselection in Rh-Catalyzed Asymmetric Hydrogenation

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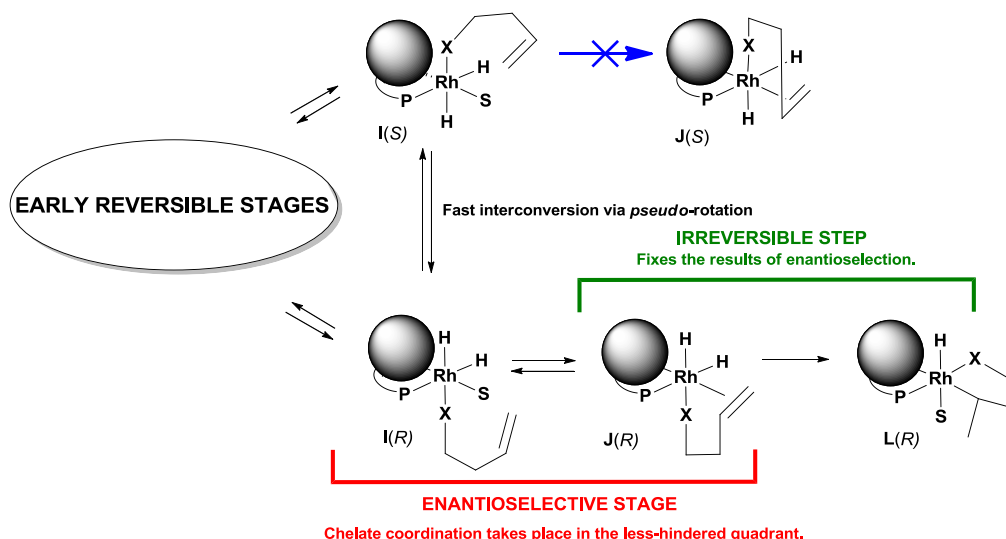
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Keywords: asymmetric catalysis, asymmetric hydrogenation, Rh complexes, DFT calculations..

Summary. The talk summarizes the research of the mechanism of the Rh-catalyzed asymmetric hydrogenation. Detection of solvate dihydrides, their low-temperature reactions with the prochiral substrates, sense of enantioselection, structure of the intercepted intermediates and detailed DFT computations of the multiple reaction pathways allowed to outline the mechanism of enantioselection that is taking place in the Rh(III) octahedral complexes.

The mechanism of enantioselectivity in the Rh-catalyzed asymmetric hydrogenation based on the difference in reactivities of the square planar catalyst-substrate complexes has remained in the mainstream thinking for over three decades.^[1] However, recent findings give ample reasons to reconsider the stereodiscriminating step in the Rh-catalyzed asymmetric hydrogenation. We were first to characterize solvate dihydrides of the Rh-diphosphine complexes^[2] that gave opportunity to study their low temperature reactions with prochiral substrates of asymmetric hydrogenation.^[3-5] Since all these reactions gave quantitatively the corresponding hydrogenation products with the ee's of the same sign and order as the catalytic reactions, we concluded that the early stages of the catalytic cycle are reversible, whereas the sense and order of the enantioselection is determined on the stage of the formation of the chelate cycle in the octahedral Rh(III) dihydride intermediate (Fig. 1).^[6,7] This stage is immediately followed by the very fast migratory insertion step that fixes the results of the reversible enantioselection.

Chelate coordination is kinetically hindered and does not occur.



Chelate coordination takes place in the less-hindered quadrant.

Figure 1. Stereoselection in Rh-catalyzed asymmetric hydrogenation takes place on the stage of association of the double bond in the non-chelating dihydride complexes.

Importantly, the stereodifferentiating step within this mechanism of enantioselection is neither the rate-limiting one, nor irreversible. Considering this conclusion carefully, one can realize that such a situation is actually beneficial for the successful stereoselection. The rapid pre-equilibrium between I(R) and I(S) that takes place immediately prior to the fast and irreversible migratory insertion step, makes possible a “trial and error” method of enantioselection, since there are numerous sideways leading back to

$I(R)$ (and ultimately to $J(R)$), which can be surpassed while trying to climb the high barrier for the association of the double bond forming $J(S)$ (Fig. 2). This mechanism resembles the three-step mechanism of protein/substrate interactions in the photosynthetic redox chain, which involves the initial formation of a multitude of pre-oriented complexes, their isomerization to the fully bound complex and the immediate reaction of the latter after the proper conformation is achieved. The conclusions of these studies would affect the approach to the catalyst design as well as general views on the principles of enantioselection.

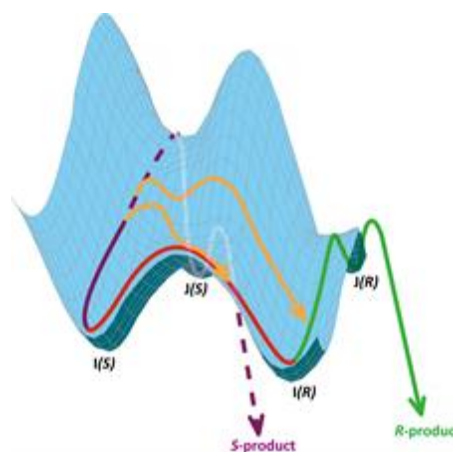


Figure 2. Trial-and-Error“ mechanism of enantioselection

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Understanding of the intrinsic reaction pathways of asymmetric catalytic transformations; NMR spectroscopy; computational chemistry.



Catalytic Hydrogenation of Unactivated Amides

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Summary. A general method for catalytic hydrogenation of unactivated amides was achieved. During catalyst induction period, a novel structural change was observed involving full hydrogenation of the interior unsaturated bonds of the pyridines of the Ru-containing catalyst precursor. Based on this observation, the mechanism of amide hydrogenation may involve two-step pathway, wherein the Ru catalyst having an H–Ru–N–H functionality is generated in the first step, followed by the amide carbonyl group interacting with the outer, rather than the inner, sphere of the Ru catalyst.

Amides are abundant functional groups which can be found, for example, in the repeating units of polypeptide macromolecules and artificial polymeric materials (e.g., poly(acrylamide), nylons, Kevlar), and their respective monomers (e.g., α,β -unsaturated carboxamides, ϵ -caprolactam), which can be produced on an enormous scale via existing industrial processes. Were it possible to develop catalytic transformations of amide resources without the salt-containing wastes formed in stoichiometric amounts with respect to the amide, such chemical processes would provide a shortcut or alternative route to presently known and/or unknown materials or chemicals. However, activation of unactivated amides is frequently hampered by high thermodynamic stability and kinetic inertness due to the low electrophilicity of the amide carbonyl carbon. In particular, the catalytic hydrogenation of unactivated amides has rarely been accomplished using existing homogeneous catalysis methods. Recently, Cole-Hamilton,[1] Ikariya,[2] Milstein[3] and Bergens[4] reported ruthenium (Ru) complexes, which effectively hydrogenate a range of strongly or moderately activated amides, including *N*-phenyl-, *N*-acyl-, α -alkoxy amides and morpholino ketones. As part of our research on the catalytic transformation of amides,[5] herein is presented a more general method for the hydrogenation of unactivated amides (Fig. 1), using a new Ru complex **1a**,[5a,d,e] which is shelf-stable and can be stored under air. For example, treatment of a toluene solution of *N*-benzylbenzamide (**3a**) with catalytic **1a** and sterically bulky base **2a** gave benzyl alcohol (**4a**) and benzylamine (**5a**), both in 92% yields.

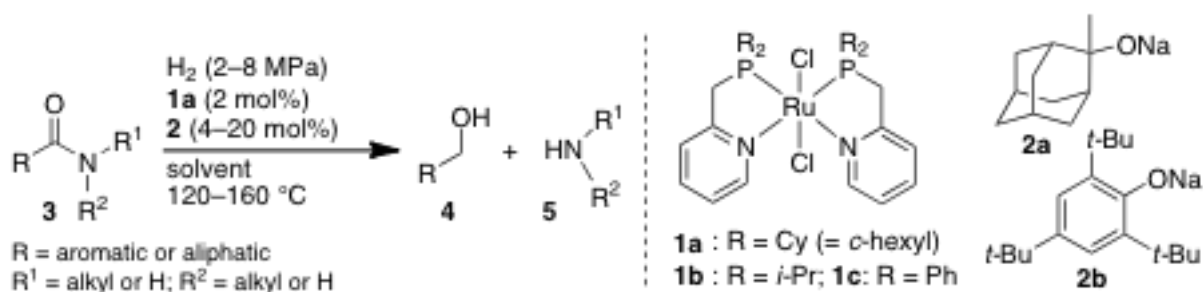


Figure 1. General scheme for the hydrogenation of unactivated amides.

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Selected publications:

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- Oishi, S.; Yoshimoto, J.; Saito, S. "Importance of Open Structure of Non-metal Based Catalyst in Hydrogen Bond-promoted Methanolysis of Activated Amide: Structure Dynamics between Monomer and Dimer Enabling Recombination of Covalent, Dative, and Hydrogen Bonds" *J. Am. Chem. Soc.* **2009**, *131*, 8748–8749. (*Org. Chem. Highlights* 2009, <http://www.organic-chemistry.org/Highlights/2009/26October.shtm>)
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Hierarchical Supramolecular Arrays of Metal Complexes

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Summary. Electronic communication between molecules is sensitive to their relative spatial arrangements. Recently, we have reported a mechanically linked co-facially stacked dimer of metallo-porphyrin and metallo-phthalocyanine via four-fold rotaxane formation and its switchable spin-spin communication induced by external stimuli [1]. To form the heterogeneous dimer, we chose mechanically interlocked supramolecular systems, rotaxanes, in which two or more molecular components are inseparable but their interactions are flexibly convertible. Herein, we report mechanically linked cofacially stacked discrete oligomers of metalloporphyrin and metallophthalocyanine units generated via rotaxane formation and their switchable spin-spin communications induced by external stimuli.

Supramolecular Programmable Metal Arrays. A four-fold rotaxane **3** was prepared from a phthalocyanine with four peripheral crown ethers **1** and a porphyrin with four alkyl ammonium chains **2** via pseudo-rotaxane formation and locking reaction. In a dinuclear Cu^{2+} complex of the four-fold rotaxane, the Cu^{2+} -porphyrin and the Cu^{2+} -phthalocyanine were cofacially stacked on one another to afford spin-spin communication. Spin states of the dinuclear complex were reversibly switchable between the protonated (doublet) and deprotonated (singlet) forms. The number of assembled phthalocyanines on the porphyrin template can be programmed by the number of ammonium moieties on the each peripheral alkyl chain, yielding one-dimensional stacked phthalocyanine arrays. The switching ability of the intermolecular communication could possibly extend from the spin-spin interaction to electron and energy transfer, catalytic reaction on metal centers, and so on.



Fig. 1 Four-fold rotaxane consisted of porphyrin and phthalocyanine

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2. Interactive control between nanoscale (molecular) properties and meso- or macroscopic phenomena of materials.
3. Chemical nano-spaces in soft materials.
4. Bio-inspired supramolecular chemistry: Programmable arraying of metal complexes toward nano-materials and physiological control.
5. Molecular devices consisting of precisely programmed molecular components.

Selected publications:

1. "Switchable Intermolecular Communication in a Four-Fold Rotaxane", Y. Yamada, M. Okamoto, K. Furukawa, T. Kato, and K. Tanaka, *Angew. Chem. Int. Ed.* **2012**, *51*, 709 (Highlighted in *Nature Chemistry*).
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Fluorescent Imaging of Biorelated Inorganic Species

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Keywords: Fluorescent sensor, molecular imaging, biorelated inorganic species, heavy metal.

Biorelated inorganic species play essential roles in living system via regulating or affecting the activity of biomacromolecules such as proteins, nucleic acids, and enzymes. Besides the well-known species such as Na^+ , K^+ , Ca^{2+} , Mg^{2+} , the transition metal cations such as $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Cu}^{2+}/\text{Cu}^+$, Zn^{2+} , the neutral inorganic species such as H_2S , NO , CO , and ROS, the anionic species such as phosphates, Cl^- , are now attracting much more attention, since their significance is being recognized currently [1]. Besides the endogenous inorganic species, the exogenous inorganic species such as the theronostic agents (Pt(II) complexes, Gd(III) complexes, and $\text{As}(\text{OH})_3$) and toxic heavy metal cations (Hg^{2+} , Cd^{2+} , and CN^-), are always in the list of scientists for their essence related to human health [2]. To clarify the variable roles of all these inorganic species in physiological processes, the techniques able to offer the temporal spatial information of their homeostasis are especially demanded. As most inorganic species were involved in the very quick processes, fluorescence imaging stands up from other molecular imaging techniques for their ability to track specifically the target of interest almost instantly in situ. Both the fluorescent sensors and the imaging technique are of great importance for this method, and our study on the development of fluorescent sensors focuses on the in vivo imaging of small animal mode and in vitro imaging for specific organelles especially using the ratiometric sensors, and inorganic species we are interested in are neurotransmitters, Zn^{2+} and H_2S , redox species $\text{Fe}^{3+}/\text{Fe}^{2+}$, $\text{Cu}^{2+}/\text{Cu}^+$ and heavy metal cations such as Hg^{2+} and Cd^{2+} .

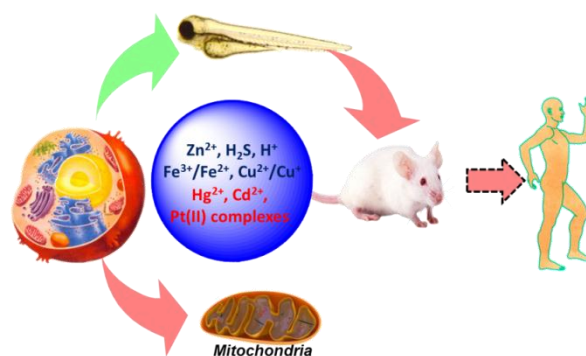


Figure 1 A schematic diagram showing the targets of our sensors: the biorelated inorganic species in organelles, cells, zebra fish larva and naked mouse.

Visible light excitable fluorescent probe for zinc cation has been developed to realize the intracellular zinc imaging, and the in vivo zinc imaging has been realized respectively in zebra fish larva and naked mouse, especially optical imaging for Zn^{2+} has been carried out in a ratiometric mode. On the other hand, a mitochondria-targetable ratiometric fluorescent sensor has been developed based on the strategy of modifying the donor of ICT fluorophore as zinc ionophore. The false impression given by the imaging with "turn-on" type zinc probe that the hydrogen peroxide can't stimulate the release of mitochondrial Zn^{2+} was corrected via zinc imaging with this new sensor. For the neurotransmitter H_2S , a new mitochondria-targetable ratiometric fluorescent sensor was constructed as the most rapid organic probe for hydrogen sulfide so far, and the rapid tracking of the mitochondrial hydrogen sulfide enhancement in 80 s was realized with this sensor. Finally, two sensitive sensors for Cd^{2+} and Hg^{2+} were designated based on the different sensing mechanisms, and

their detection limits are distinctly lower the allowable level in drinking water established by WHO or EPA. Moreover, the fluorescence imaging of Cd²⁺ and Hg²⁺ in living cells and zebra fish larva was realized.

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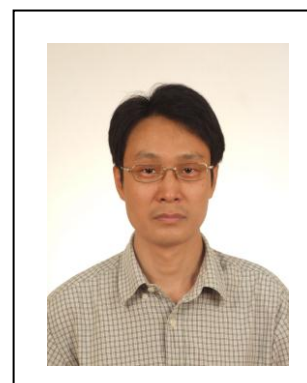
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Fluorescent sensing and imaging of bioinorganic species, fluorescent investigation of artificial metalloenzymes, and photoactivable theronostic agents.



Selected publications:

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2. Yuncong Chen, Chengcheng Zhu, Zhenghao Yang, Junjie Chen, Yafeng He, Yang Jiao, Weijiang He,* Lin Qiu, Jiajie Cen, and Zijian Guo*. A ratiometric fluorescent probe for rapid detection of hydrogen sulfide in mitochondria, *Angew. Chem. Int. Ed.* 2013, 52, 1688 -1691.
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Controlling the Translocation Velocity of a Single DNA Molecule through Nanopore Channels

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Keywords: Translocation control; DNA; Nanopore channel; Electrophoresis.

Introduction. Recently, nanometer-sized nanopores can serve as a single molecule sensor to detect DNA base sequences at a single DNA molecule level. Reduction of the velocity of a single DNA molecule through nanopore channels is highly demanded to minimize reading errors at nanopore sequencing process. Reduction of the translocation velocity was performed by adjusting solution temperature, salt concentration, viscosity and electrical voltage [1]. In this research, we used nanopore channel to measure the velocity of a DNA molecule. We studied the relation between the length of the nanochannel and DNA velocity through the nanochannels by changing the electric voltage and the channel design.

Experiment. We measured the translocation velocity of DNA in the nanopore channel. The Solutions of double-stranded T4 DNA (165.5 kbp, 5 ng/ μ l) was fluorescently stained with the intercalating dye YOYO-1 at a base pair-to-dye ratio of 5:1 in a 5 X TE buffer solutions. Inverted microscope is used to observe the electrophoresis situation of DNA at different applied voltage such as 3, 7, 10 V respectively. Then we repeated the experiment 200 times for the different base pair sequence Lambda DNA (48.5 kbp), 10 kbp DNA and 7 kbp DNA under similar experimental condition.

Conclusion. In this work, we could successfully reduce the translocation velocity of DNA by gradually decreasing the applied electric field. In the future, we are focusing on measuring the change in DNA translocation velocity by controlling the rapidly formed electric field gradient in nanopore area by suitable design of nanopore channel.

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Selective Sensing of ATP with Polydiacetylene Liposomes

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Keywords: liposomes, microreactors, nucleotides, sensors, zinc

The efficient detection of phosphate-containing molecules has attracted steady interest owing to their biological significance. Several notable fluorescent sensing systems have been developed so far; however, most of them are small-molecule based ones and thus operate in the homogenous state. Furthermore, most of these sensing systems suffer from interference by competing analytes. Therefore, it remains a challenging issue to develop a highly selective sensing system for a given analyte. In contrast to the homogeneous sensing systems, heterogeneous sensing systems are much less explored, although they have a potential to be applied to chip-based assays.

Polymer based optical sensors present several important advantages, such as signal amplification, enhanced binding efficiency and easy fabrication onto devices, etc.¹ Among them, polydiacetylene (PDA) based liposomes are recognized as a particularly interesting sensing platform. PDA liposomes are well known for their environment-sensitive absorption and emission behaviors. They show color change from blue-to red as well as fluorescence change in response to various stimuli such as heat, organic solvents, mechanical stress, and analyte-receptor interactions. In addition, PDA vesicles can be readily immobilized onto solid substrates.

In recent years, we have shown for the first time that we can realize very high sensitivity as well as unusual analyte selectivity through mixed liposome systems in which more than two liposome components are combined.² For example, a Zn^{II}(cyclen)-functionalized PDA liposome microarray chip system can selectively detect ATP over ADP or PPI with a very high sensitivity down to 1 pM level. I wish to present our liposome based sensing approach to selectively sense a target phosphate-containing molecule.

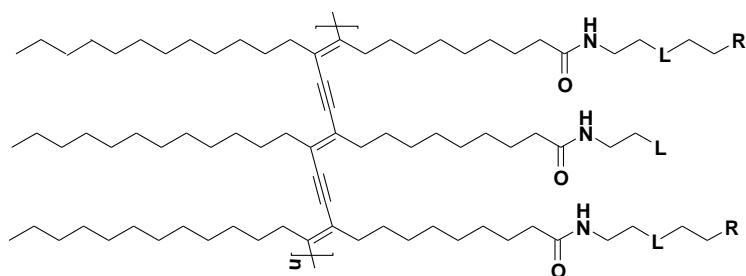


Figure 1. A polymerized liposome sensing system for nucleotides (L = linker, R = recognition group).

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Development of a novel draw solute with thermosensitivity for the application to forward osmosis (FO)

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Keywords: LCST (Lower Critical Solution Temperature) transition, FO (Forward Osmosis),

Distillation and reverse osmosis (RO) for desalination have been used to obtain fresh water from seater until now. But those methods for desalination have to consume a lot of energy. Therefore, another method which could save consumption of energy for desalination is required. Meanwhile, it is reported that forward osmosis (FO) method could be more energy-efficient for desalination. [1]

In our lab, we developed a novel FO solute with LCST(Lower Critical Solution Temperature) transition which is simply synthesized by simple acylation between tris(2-aminoethyl)amine (TAEA) and n-butyric anhydride. The solution with the newly synthesized draw solute in water is highly soluble enough to have osmotic pressure which can draw fresh water from seawater (0.60M NaCl equivalent) below a certain temperature (LCST) [Table 1]. Above the LCST, the draw solute is separated from water and therefore the effective concentration of solution is lowered enough to release the drawn water into physiological saline (0.15M NaCl equivalent) [Table 2]. Because phase transition temperature of this solution occurs around 20-30 °C, FO method by using this solution could be a very promising method with lower-energy cost. It will be shown that osmotic flow is controlled between seawater and physiological saline by mild temperature change [Figure 1] [2].

[Table 1]. Osmotic flux : *n*Bu-TAEA solution to NaCl solution below phase transition temperature.

<i>n</i> Bu-TAEA[M]	0.50			1.0			2.0			2.2			
NaCl [M]	0.050	0.10	0.15	0.10	0.20	0.30	0.20	0.40	0.60	0	0.20	0.40	0.60
Flux [LMH]	0.91	0.62	0.25	1.1	0.46	0.074	0.82	0.17	0	4.4	1.4	0.39	0.16

[Table 2]. Osmotic flux : NaCl solution to *n*Bu-TAEA solution above phase transition temperature.

<i>n</i> Bu-TAEA[M]	0.80			1.2			1.6		
NaCl [M]	0.15	0.25	0.35	0.15	0.35	0.50	0.15	.035	0.60
Flux [LMH]	0.16	0.30	0.27	0.11	0.30	0.47	0.13	0.27	0.80

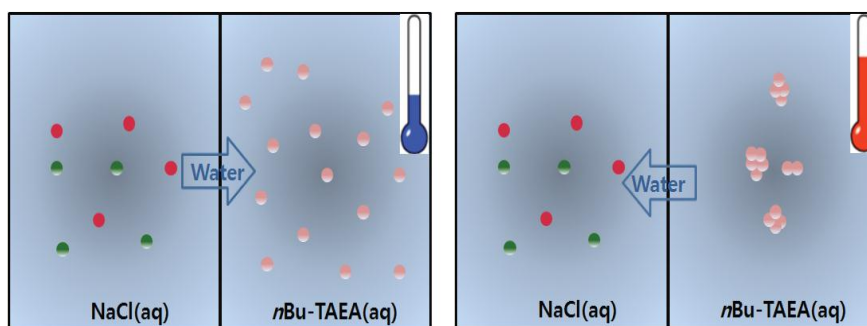


Fig. 1. Osmotic flow is controlled by mild temperature changes

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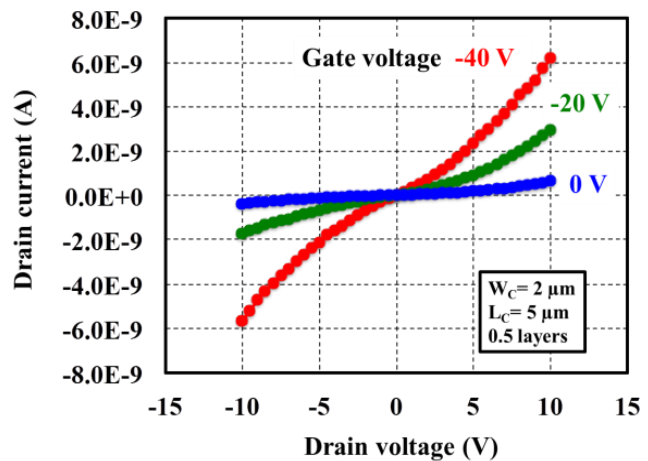
Preparation of graphene field-effect transistors by a selective-area growth method

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Keywords: graphene, carbon thin film, FET, field effect transistor

Graphene is a single atomic layer of carbon atoms that form a honeycomb structure, and thus, it is a kind of ultimate thin layer. Thanks to its high carrier mobility, graphene is one of the most promising materials to open a new era of electrical and optical integrated circuits[1,2]. In order to fabricate electrical and optical devices using graphene, it is necessary to develop a method that allows a direct and selective graphene growth on a sub-nm-order flat insulating layer. Since the current big Si-based electronics industry has accumulated enormous amounts of knowledge and know-how, it is desirable and practical to use a Si wafer as a substrate for such a graphene growth.

We recently reported a selective-area growth method for graphene on a fine-patterned Al_2O_3 layer, which is sputter-deposited on a SiO_2/Si substrate [3]. In the present work, using this selective-area growth method, we successfully fabricated graphene FET which has a high on/off ratio more than 20 when the average number of graphene layer is 0.5 (Fig. 1). Moreover, the electrical characteristic of the graphene is changed to the metallic behavior from semiconducting by increasing the number of carbon honeycomb layers of the graphene.



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Fine-Tuning Pore Size by Shifting Coordination Sites of Ligands and Surface Polarization of Metal-Organic Frameworks to Sharply Enhance the Selectivity for CO₂

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Keywords: metal-organic frameworks; pore size tuning; surface polarization; carbon dioxide selectivity.

Metal-organic frameworks are of high interest as new candidates for CO₂ storage and separation. Traditional strategies for enhancing MOFs' affinity with CO₂, such as pore decoration, always lead to the decline of surface area and porosity^[1,2]. Herein, based on the (3,6)-connected MOF {Cu(L1) 2H₂O · 1.5DMF}_∞ (L1 = 5-(pyridin-4-yl) isophthalic acid) (SYSU), we synthesized two iso-structural {Cu(L2) DMF}_∞ (L2 = 5-(pyridin-3-yl) isophthalic acid) (NJU-Bai7) and {Cu(L3) DMF H₂O}_∞ (L3 = 5-(pyrimidin-5-yl) isophthalic acid) (NJU-Bai8) by an unprecedented strategy of shifting the coordination sites of ligands to fine-tune pore size and polarizing the inner surface with uncoordinated nitrogen atoms (Fig. 1), respectively, with almost no changes in surface area or porosity (Fig. 2a). Compared with those of the prototype SYSU, both the adsorption enthalpy and selectivity of CO₂ for NJU-Bai7 and NJU-Bai8 have been greatly enhanced (Fig. 2b and 2c), which makes NJU-Bai7 and NJU-Bai8 good candidates for postcombustion CO₂ capture.

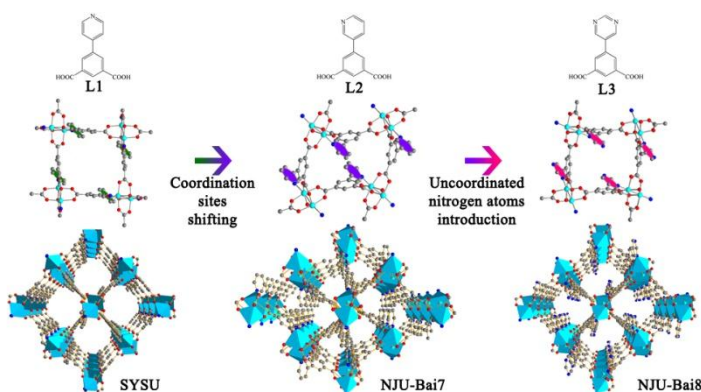


Figure 1. The synthesis scheme of NJU-Bai7 and NJU-Bai8

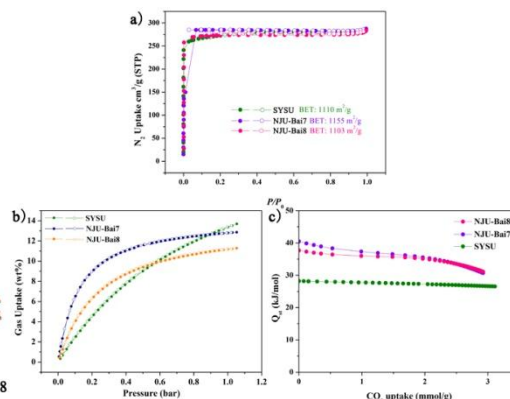


Figure 2. Adsorption isotherms (a: N₂ at 77 K; b: CO₂ at 298 K) and CO₂ adsorption enthalpies (c) for SYSU, NJU-Bai7 and NJU-Bai8.

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Controlled Preparation of Hierarchical Porous MoO₂ Nanotubes through One-step Carbothermal Reduction Method for Lithium Ion Batteries

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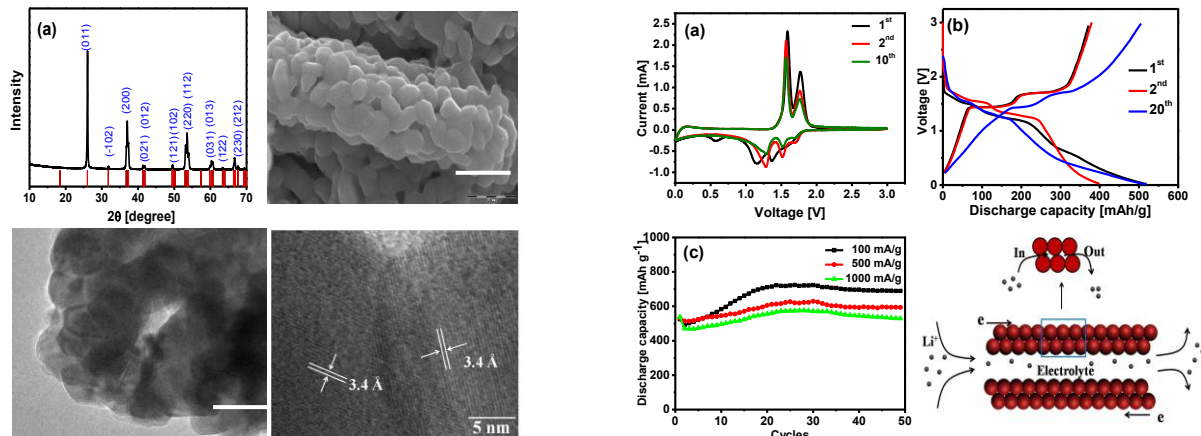
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Keywords: hierarchical porous • nanotube • molybdenum dioxide • lithium ion batteries • carbothermal reduction.

Molybdenum dioxide is an attractive host material for lithium storage because of its rich chemistry associated with multiple valent states, low electrical resistivity, high electrochemical activity toward lithium, and its affordable cost.^[1] However, the lithiation of bulk MoO₂ is limited to an addition-type reaction with only one-electron reduction ($x\text{Li} + \text{MoO}_2 = \text{Li}_x\text{MoO}_2$, $0 \leq x \leq 0.98$) at room temperature because of the sluggish kinetics.^[2] The introduction of a hierarchical porous structure is an efficient way to improve the performance of MoO₂ because of the decreased diffusion length of lithium ions and sufficient contact surface between electrode and electrolyte.^[3]

Herein, we successfully prepared hierarchical porous MoO₂ nanotubes through a one-step carbothermal reduction method. The hierarchical porous structure which can be regarded as the assembly of MoO₂ nanoparticles is beneficial for lithium ion and electron transportation. When used as an anode material, it not only exhibits a charge/discharge capacity but also a super cycling performance and rate capability. This one-step carbothermal reduction method can be easily used for the mass production of hierarchical porous materials.



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Preparation and Swelling of Ionic ABA Triblock Copolymer Gels

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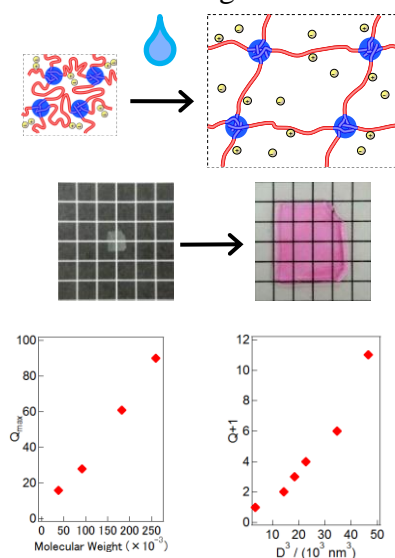
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Keywords: Block copolymer gel, Nanophase-separated structure, Swelling.

Introduction Ionic polymer gels are known as three-dimensional cross-linked polymer networks at the molecular level. Because of inhomogeneous network structures, precise control of swelling of conventional ionic polymer gels can be attained just empirically. In this study, we report preparation of ionic polymer gels with comparatively homogeneous polymer networks at the molecular level by using nanophase separation of ABA triblock copolymers bearing ionic B blocks, where bridge-type B blocks behave as strands between A block microdomains (Fig.1a). The degree of swelling of the gels was also investigated.

Experiments Four triblock copolymers of polystyrene-*b*-poly(4-vinylpyridine)-*b*-polystyrene (SPS) ($M_n = 22\text{k}, 53\text{k}, 104\text{k}, 145\text{k}$) with ϕ_S of ~ 0.25 were synthesized by RAFT polymerization. P blocks were quaternized by reacting with bromoethane, which provided ionic triblock copolymers (i-SPS) with ionization rates of $\sim 90\%$ ($M_n = 38\text{k}, 91\text{k}, 182\text{k}, 259\text{k}$). Sample films of i-SPS were prepared by solvent-casting from THF/MeOH (1/1, v/v) solutions of i-SPS and solvent-annealing with the same solvent. These films were swollen by addition of water, leading to hydrogel formation. Nanostructures of ionic triblock polymer gels were investigated by small angle X-ray scattering (SAXS).

Results and Discussion Solvent-cast films of i-SPS were immersed into a large amount of deionized water, which provided ionic polymer gels (Fig.1b). Maximum degree of swelling $Q_{\max} (= (w_{\max} - w_0)/w_0)$, where w_{\max} and w_0 represent weight of a wet gel at maximum and that of a dry film, respectively) was found to increase with increase in the molecular weight of i-SPS (Fig.1c). Domain spacing, D , of nanophase separated structures determined by SAXS also increased monotonically with increase in the addition of water. Normalized weight ($Q+1 = w/w_0$) is an indicator of macroscopic degree of expansion, while the cube of the domain spacing, D^3 , can be regarded as the volume at the microscale level. Proportionality was seen between $Q+1$ and D^3 in Fig.1d, suggesting that ionic block copolymer gels represent affine deformation when gels were formed by addition of water.



Development of fluorescent probes for gold species

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Keywords: gold ions, fluorescence detection, reaction based fluorescence probes

Fluorescence detection of biologically or environmentally important metal ions has been widely studied due to their simple operation and high sensitivity and selectivity. Many researchers have been developed numerous fluorescence molecular probes for various metal ions. Among those metal ions, recently gold ions have been started to attract as prospectively important target metal ions. Although gold complexes have been used as rheumatoid arthritis drugs,^[1] they were considered to be “catalytically dead”^[2] for a long time. Since 1985 gold complexes, however, grow to be used as heterogeneous catalysts and now this area has become a highly active research field. Gold species show strong affinity toward unsaturated carbon-carbon bonds, in particular, carbon-carbon triple bonds. Based on this property of gold ions (I/III), several reaction-based fluorescence probes have been developed in recent years. We reported a rhodamine *N*-propargyl lactam based fluorescence probe for gold ions.^[3] The probe shows a large fluorescence enhancement upon reaction with gold species; however, the reaction gave undesired side products including nonfluorescent products.^[4] Therefore, we investigated a new approach that could alleviate the side reactions observed in the original system. Our idea is to separate the reactive moiety from the fluorescence dye to preclude the undesired reaction that gives fluorescence. As a proof-of-concept model, we have devised (2-ethynyl)benzoate as the reactive moiety. One of the fluorescein benzoates showed a turn-on type fluorescence change upon interaction with gold species as the gold species promoted hydrolysis of the ester moiety (Figure 1).^[5] This new sensing scheme is promising for the development of efficient gold probes. The probe, however, showed sensitivity toward esterase in cells. I wish to present our efforts in the development of gold probes that are applicable to study biological effects of gold species.

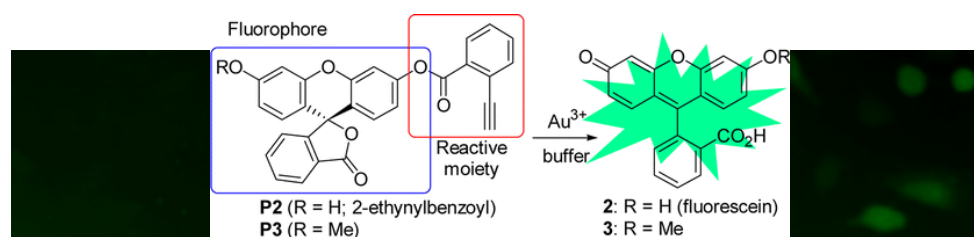


Figure 1. Schematic representation of a novel reaction-based sensing scheme for gold species.

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pH-Sensitive CaP Nanoparticles Coated with a Phosphate-Based Block Copolymer for Efficient Gene Delivery

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Key Words: Block copolymer, Calcium phosphate, Gene delivery, Nanoparticles, pH-sensitivity

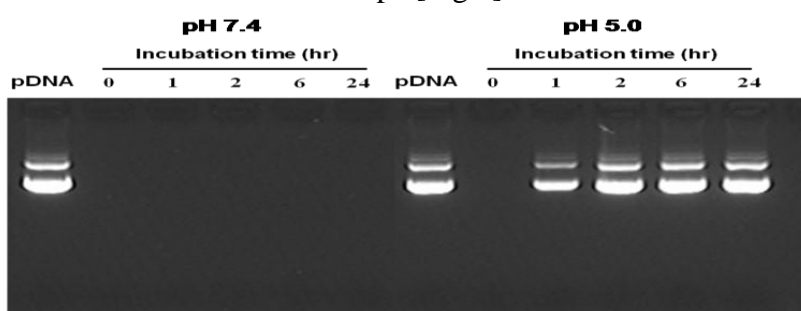
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A phosphate-based block polymer, PEG-*b*-PMOEP (poly(ethylene glycol)-*b*-(2-methacryloyloxyethyl phosphate)), with a narrow molecular weight distribution (PD = 1.06) was synthesized by atomic transfer radical polymerization (ATRP) [Table 1], and have constructed calcium phosphate nanoparticles (CaPNs) coated with the block copolymer as an efficient and safe intracellular gene delivery carrier.

[Table 1]. Measurement of molecular weights of polymers

	M_{n1}^a	M_{n2}^b	M_w^b	PD [M_w/M_n] ^b
PEG-Br initiator	5.15×10^3	4.95×10^3	5.10×10^3	1.03
PEG- <i>b</i> -PMOEP	1.56×10^4	1.72×10^4	1.82×10^4	1.06

The phosphate-mimic PMOEP block could be incorporated into the calcium phosphate (CaP) core to entrap pDNA, with the PEG block forming a shell to prevent uncontrolled growth of CaP precipitates and aggregates in physiological fluids. The CaPNs showed high colloidal stability at pH 7.4, but released entrapped pDNA at an endosomal pH of 5.0 through a pH-dependent protonation of phosphate moieties for efficient endosomal escape [Fig 1].



[Fig 1] pH-sensitive release of pDNA from PEG-*b*-PMOEP/CaP nanoparticles on pH 7.4 and pH 5.0

The PEG-*b*-PMOEP/CaP/pDNA nanoparticles, which were formed simply by mixing, exhibited great potential as gene delivery carriers for future gene therapy applications due to their high transfection efficiency, low toxicity, and good stability under physiological conditions.

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Measurements and Prediction of VOCs Adsorption Behavior in Supercritical Carbon Dioxide

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Keywords: Adsorption, Activated carbon, Supercritical fluid

Supercritical carbon dioxide (scCO₂) has been widely used in the fields of extraction[1], reactions[2] and cleaning[3] because its properties can be dramatically varied with temperature or pressure at mild conditions (T_c : 304.1 K). Recycle of the solvent is essential in terms of preventing emissions and reducing running cost for industrial use of scCO₂. We have focused on adsorption due to its separation capability of dilute solutes with energetical advantages. For optimizing this operation, measurement and prediction of VOCs (Volatile organic compounds) adsorption behavior in scCO₂ has been studied in this research from both experimental and predictive viewpoints.

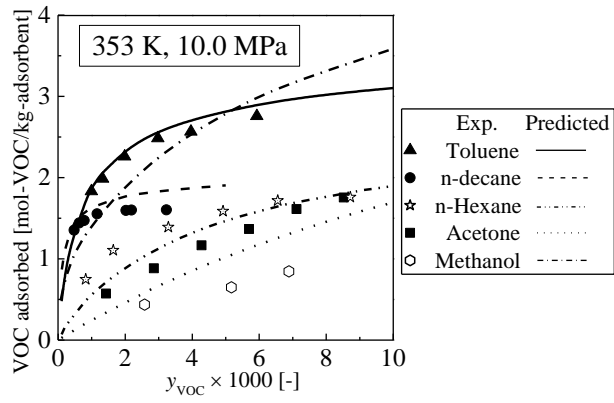
Breakthrough curves of five VOCs (Acetone, n-Hexane, Toluene, n-Decane, Methanol) on activated carbon were measured by a fixed bed method. The amount of adsorbed VOC was evaluated from the breakthrough curve in the pressure range of 4.2-15.0 MPa at 313-353 K. The Dubinin-Astakhov equation [4] and the ideal adsorbed solutions theory (IAST) [5] were applied to predict the adsorption equilibrium by using pure component adsorption data.

Fig. 1 shows measurement results of adsorption equilibrium in scCO₂ [6, 7]. The behavior of the adsorption isotherms strongly depended on the species of VOCs. This is probably due to the difference of interactions between VOCs - activated carbon and/or VOCs-CO₂.

Fig. 1 and Table 1 indicate the prediction results of VOC adsorption equilibria in scCO₂. The predictive model provided a good estimation of experimental values in the cases of non-polar substance and at lower pressure conditions. On the other hand, relatively large deviations occurred in the cases of polar substances like methanol and also at higher pressure conditions, which could be caused by large non-ideality in the adsorbed phase.

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Systems	Pressure[MPa]	ARD [%]
Toluene - CO ₂	4.2	9.5
	15.0	24.6
n-Hexane - CO ₂	4.2	7.6
	15.0	42.8
Decane - CO ₂	10.0	9.1
	15.0	16.9
Acetone - CO ₂	4.2	11.2
	15.0	48.7
Methanol - CO ₂	4.2	25.6
	15.0	60.6

Boronate affinity monolithic capillary-based rapid selection of high-specificity glycoprotein-binding DNA aptamers

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Keywords: aptamers, boronate monolithic column, SELEX, glycoprotein

Aptamers are oligonucleic acids or peptides that can specifically bind a target molecule. Aptamers are usually selected from a large random oligonucleic acid pool by systematic evolution of ligands by exponential enrichment (SELEX). The key step in SELEX is to isolate target-binding aptamers from the random pool. Widely used isolation methods include affinity chromatography, ultrafiltration, magnetic beads, capillary electrophoresis (CE) and surface plasmon resonance (SPR). All the widely used methods are associated with some apparent drawbacks, such as labor intensive, time consuming, strong non-specific binding towards targets and oligonucleotides. Therefore, novel methods that can effectively overcome these drawbacks are still much needed.

Glycoproteins exist widely in organisms and play important roles in molecular recognition, inter- and intracellular signaling, immune response and sperm–egg interaction. In recent years, our laboratory has developed a variety of boronate affinity functionalized materials, such as magnetic nanoparticles [1] and monolithic capillaries [2], for the specific recognition of glycoproteins. In this study, we developed a boronate affinity monolithic capillary-based SELEX approach for rapid selection of high-specificity glycoprotein-binding DNA aptamers.

The principle of the approach is shown in Fig. 1. Horseradish peroxidase (HRP), a typical glycoprotein was employed as target. HRP was captured by boronate affinity monolithic column under neutral condition, then the monolithic column was used to select ssDNA that could be captured by HRP, while the unbound ssDNA was discarded. HRP-ssDNA complexes were evaluated by CE and amplified by PCR. The amplified species were sent for a new round of selection, and the process was repeated again and again until the binding affinity met the requirement or did not decrease any more.

After six cycles of selection within 2 days, HRP-binding aptamers with a binding constant of 11 nM were obtained. For such a task, conventional affinity SELEX methods usually need 8–12 cycles or 2–4 weeks. The approach also exhibited other significant advantages over conventional SELEX methods, including high specificity towards the target molecules and minute reagent consumption. This method could be developed into a universal method to select aptamers to bind glycoproteins.

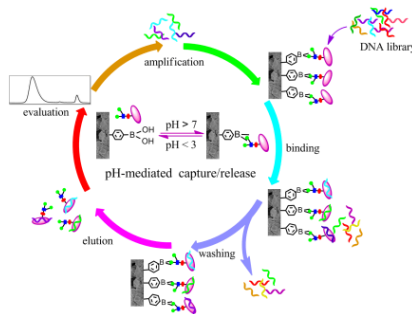


Figure 1. Schematic of boronate affinity monolithic capillary-based SELEX approach

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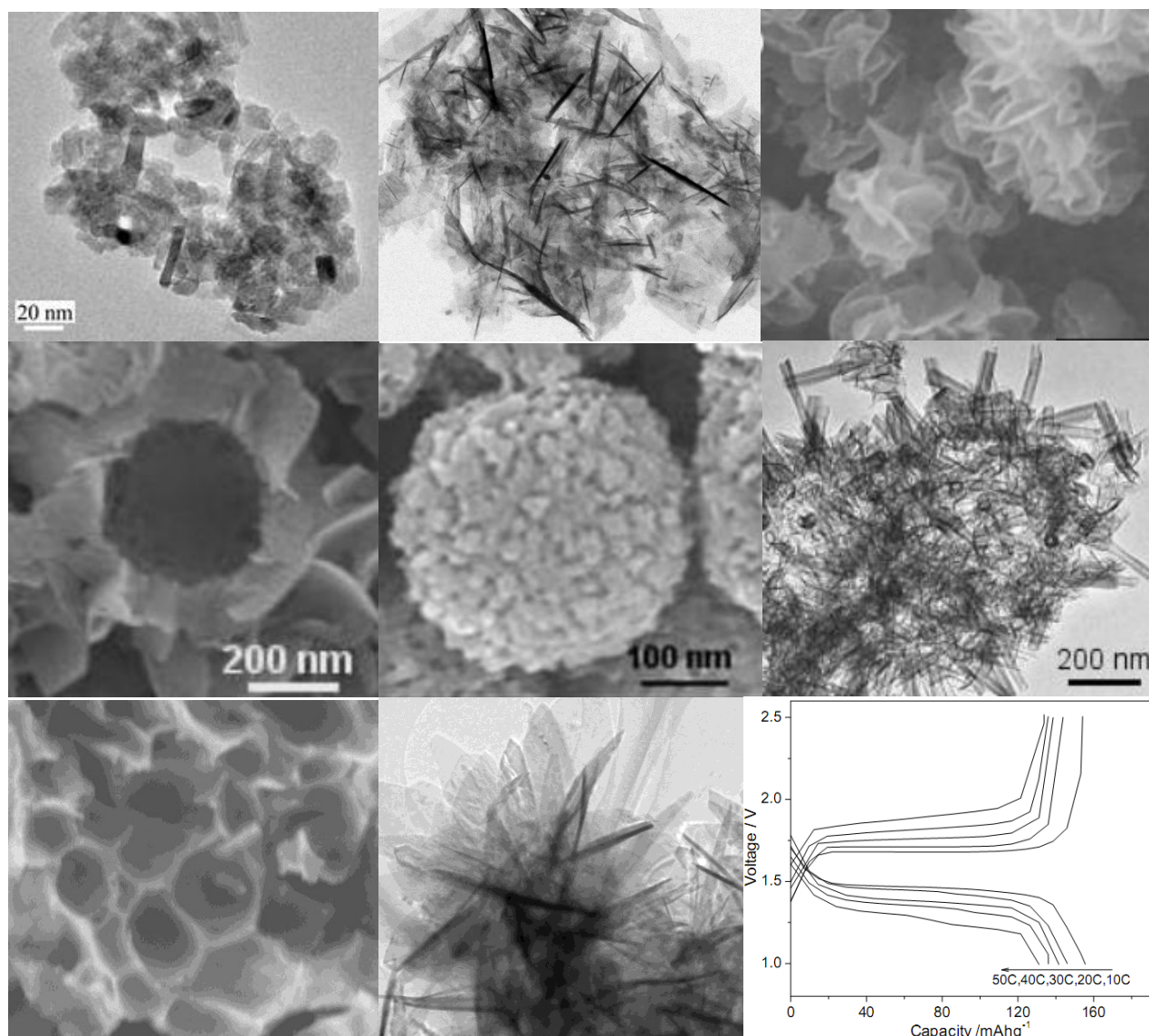
Li₄Ti₅O₁₂ Anode Materials Prepared by Hydrothermal Reactions for High-rate Lithium Ion Batteries

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Keywords: Li₄Ti₅O₁₂; hydrothermal; anode; Lithium ion batteries; high rate

Using hydrothermal methods and subsequent calcinations, Li₄Ti₅O₁₂ anode materials are prepared. Various morphologies are obtained, namely nanoparticles [1], nanosheets, flower-like Li₄Ti₅O₁₂ consisting of nanosheets [2], hollow microspheres assembled by nanosheets [3], mesoporous microspheres [4], hollow microspheres assembled by nanotubes [5], mesoporous nest-like Li₄Ti₅O₁₂ [6], and sawtooth-like nanosheets [7]. Excellent high-rate performances are obtained. For example, 131 mAh/g is acquired at 50 C (8750 mA/g, merely 1 min for discharge or charge) [3].



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Precise Synthesis and Characterization of Tadpole-shaped Polymers

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Keywords: tadpole-shaped polymer, ring polymer, SEC-MALS, HPLC

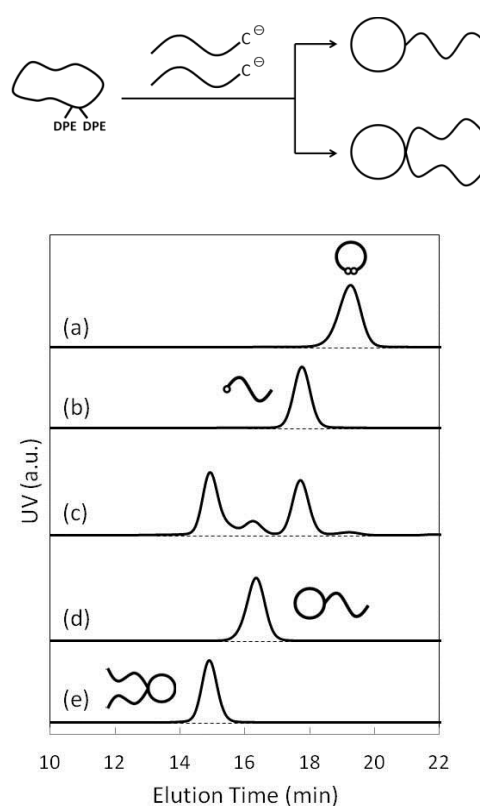
Introduction

Ring polymers are of great interest in investigation of topological effects on their physical properties such as solution or viscoelastic properties. Recently it has been found out that the pure rings do not reveal apparent rubbery plateau, and they relax faster than linear chains. Moreover, surprisingly it was also found out that a drastic appearance of rubbery plateau was observed when merely a small amount of linear polymer was added [1]. Taking these interesting experimental facts into account, it is considered that a polymer possessing both ring and linear chain in one molecule, which can be called “tadpole-shaped polymer”, might be a quite intriguing model polymer from viscoelastic aspects.

In this study, we prepared tadpole-shaped polystyrenes by a coupling reaction among a highly purified ring polystyrene having two functional groups with living linear polystyrenes. The samples were purified by multistep HPLC fractionation procedures. The prepared tadpole-shaped samples with high purity were carefully characterized by SEC-MALS and HPLC analyses.

Results and Discussion

Telechelic polystyrene with diphenylethylene (DPE) type double bonds on both ends ($M_w=57.6k$, $M_w/M_n=1.04$) was anionically synthesized. It was cyclized in THF at dilute condition, followed by introducing DPE-type double bonds. Since cyclization product contained unreacted telechelic polymer and various kinds of polycondensation products, HPLC fractionation was conducted. Thus, the ring polystyrene with DPE functional groups with high purity over 99% was obtained (R-PS, $M_w=57.2k$, $M_w/M_n=1.02$, Figure 1a). Tadpole-shaped polystyrenes were prepared by coupling reaction between the ring polystyrene and living linear polystyrene (L-PS, $M_w=66.0k$, $M_w/M_n=1.02$, Figure 1b) as shown in Scheme 1. Crude coupling product was confirmed to include unreacted linear tail polymer and tadpole-shaped polymer having one linear tail (single-tail, St-PS) and two linear tails (twin-tail, Tt-PS) as shown in Figure 1c. St-PS ($M_w=123k$, $M_w/M_n=1.01$, Figure 1d) and Tt-PS ($M_w=188k$, $M_w/M_n=1.01$, Figure 1e) were successfully obtained by multistep HPLC fractionations. Furthermore it was clarified that the two tadpole polymers reveal ultrahigh purity over 99% by rigorous HPLC analyses [2].



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Recyclable Metal Nanoparticle Catalysts Entrapped in AlO(OH) for Selective Transformation of Silanes into Silanols

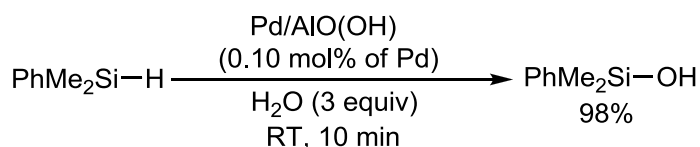
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Silanols are compounds having Si-OH groups and have received great attention in the synthesis of silicon-based polymeric materials as well as in organic synthesis. Particularly, in organic synthesis, silanols are employed as nucleophilic partners in transition-metal catalyzed carbon-carbon cross-coupling reactions, organocatalysts for activating carbonyl compounds, intramolecular guiding groups for C-H bond activation reactions, isosteres of pheromones, and inhibitors of enzymes.

Although there are various methods for preparing silanols, the catalytic oxidation of organosilanes with water and/or molecular oxygen, which produce H₂ and/or H₂O as the by-products, would be clearly preferable over conventional methods which require toxic reagents and produce harmful wastes. Among the known catalytic methods, recent examples employing metal nanoparticle catalysts are noticeable in efficiency and reusability. However, there are still needs to improve substrate scope, reaction conditions and catalyst efficiency.

Recently, we developed highly selective and efficient transformation of organosilanes into silanols was achieved using readily available heterogeneous metal nanoparticle catalysts on an aluminum oxyhydroxide support [M/AlO(OH), M = Pd, Au, Rh, Ru, and Cu]. The transformation was performed under ambient conditions with water. Among the catalysts investigated, the palladium catalyst showed the highest activity. Furthermore, the turnover number (TON=99,000) and turnover frequency (TOF=20,000 h⁻¹) are the highest among those reported so far. The palladium catalyst was effective for a wide range of silanes, and the catalyst could be reused at least ten times without any loss in activity.



Studies toward the Total Synthesis of Poitediene

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Keywords: macrocyclization, zinc iodide, natural products, total synthesis

We present here a novel approach to the enantioselective total synthesis of poitediene, a metabolite of red algae possessing the unique “in-out” bridges cyclic structure [1]. We expect that its highly strained 12-membered macrocyclic ether is constructed from a hetero atom-stabilized carbocation intermediate. The oxolane core was built from epoxy alcohol by zinc-catalyzed etherification, which was a newly founded condition in our group. Described in this poster are the details of our synthetic route that provides efficient access to the highly functionalized 2,12- dioxabicyclo[9.2.1]tetradecane system.

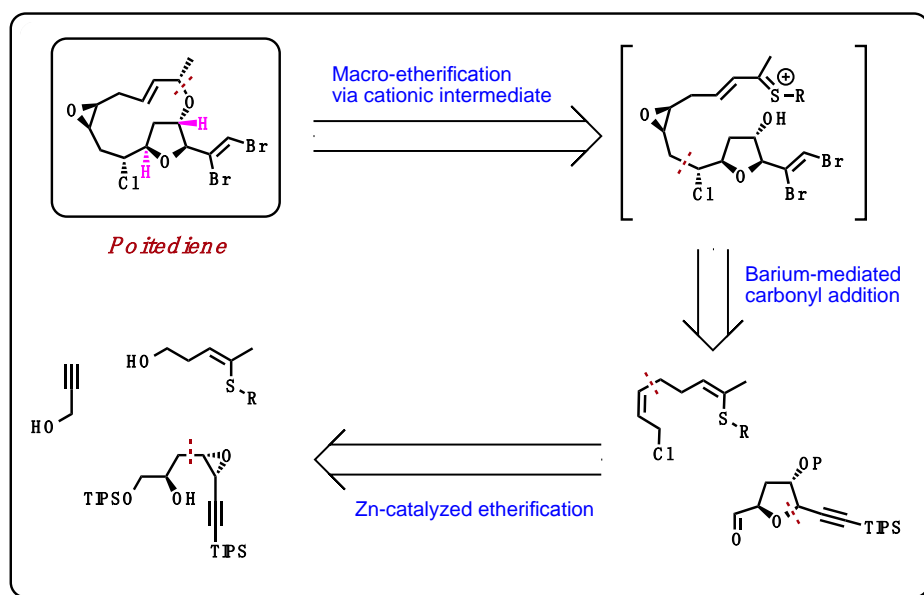


Fig. 1 Retrosynthetic Analysis

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Computational analysis of water orientations at surfaces of various aqueous electrolyte solutions

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Keywords: molecular orientation, aqueous surface, electric double layer, Sum frequency generation spectroscopy, Molecular Dynamics simulation

Water molecules in bulk region have random orientation, while at surface they tend to slightly direct their hydrogen atoms into water interior. This spontaneous orientational polarization can be detected by Sum frequency generation (SFG) spectrum. SFG is intrinsically surface sensitive, and provides vibrational spectra.^[1] There is often ambiguity to correlate SFG signals to surface molecular structure, which emphasizes the need for reliable theoretical support for the analysis of the spectra. Therefore, we have developed theories to compute the SFG spectra in combination with ab initio molecular modelling and molecular dynamics (MD) simulation. Using this method, we have elucidated surface molecular structures of aqueous solutions containing surface active ions, such as iodide (I⁻) and hydronium (H₃O⁺).

In the present study, our focus is on surface non-active ionic species, such as NaOH, NaF, and Na₂SO₄. They were repelled from the surface according to prior MD simulations. However, these three solutions have shown remarkably different SFG spectra (Fig. 1). The present MD analysis confirmed that all the ionic species do reside in inner layer of water surface, though their experimental SFG spectra are well reproduced. The difference in their surface structures is observed in the subsurface region, where slight charge separation occurs in the Na₂SO₄ and NaOH solutions. The perturbation in the SFG spectra is attributed to the water orientation not at the topmost layer but in a fairly deep region of the surface.

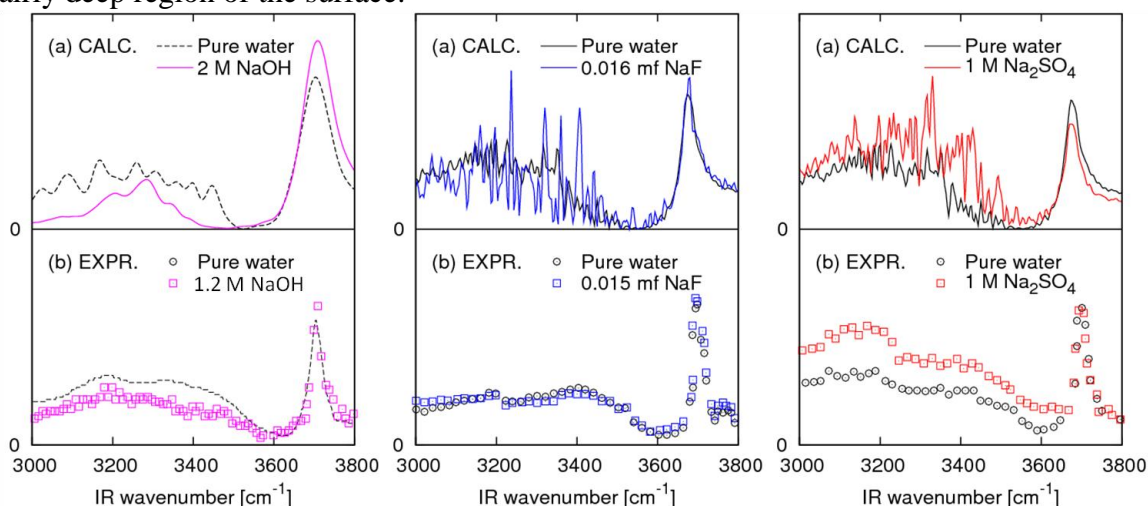


Fig. 1 SFG spectra of various aqueous electrolyte solutions. Top: calculation. Bottom: experiment.

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Enantioselective synthesis of 2-substituted pyrrolidines via domino cross metathesis/intramolecular aza-Michael addition

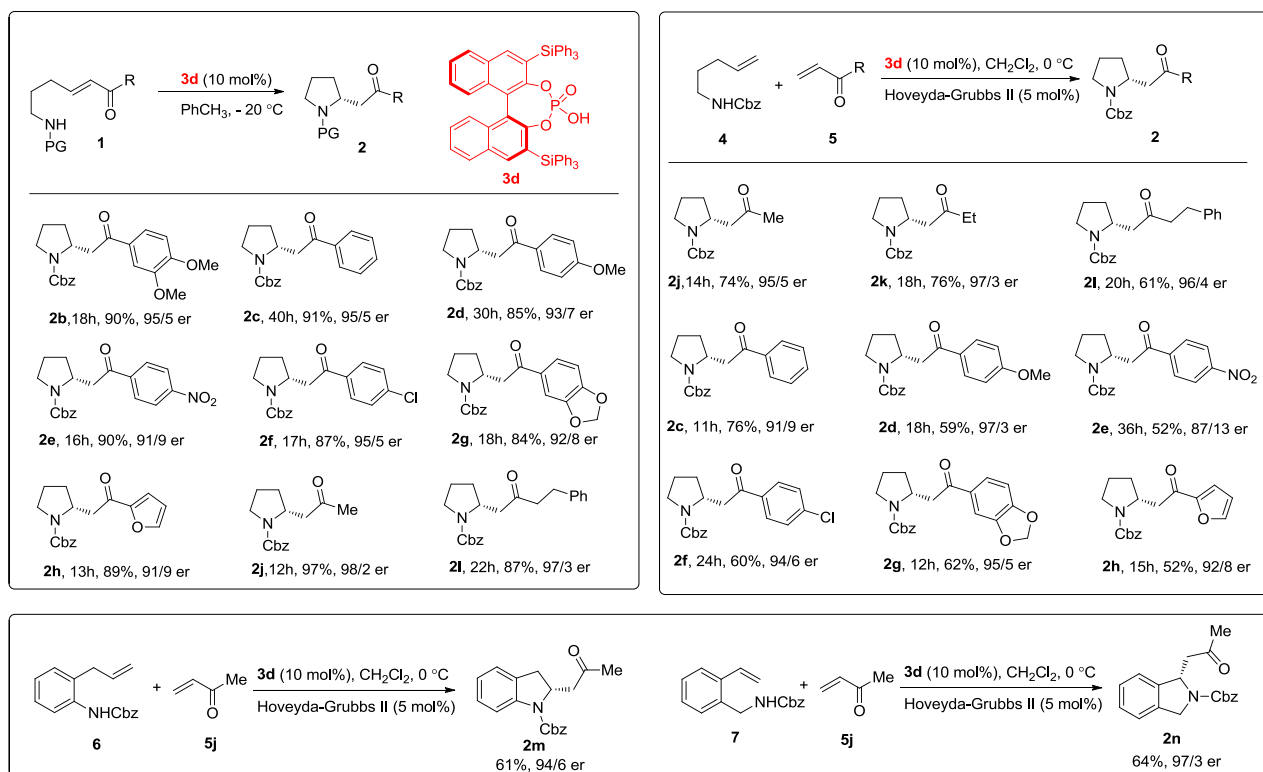
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Keywords: aza-Michael addition, domino cross metathesis, chiral Brønsted acid

High enantioselective intramolecular aza-Michael addition of enalcabamates catalyzed by TMS-prolinol derivative was elaborated by Fustero^[1] and Carter^[1] independently. Recently, we are engaging in synthesis of the phenanthroindolizidine and phenanthroquinolizidine alkaloids^[4] via organocatalytic intramolecular aza-Michael addition. Several phenanthroquinolizidine alkaloids have been synthesized by us using modified Fan^[2] and Fustero's methodology. However, we failed to synthesize phenanthroindolizidine alkaloids using the similar strategy. Intramolecular aza-Michael addition catalyzed by TFA salt of quinine derived primary amine could give the desired product in good yield but almost in racemic form. So we had to find a more efficient catalyst for this transformation. During the previous investigations, we found TFA itself could catalyze this reaction, which suggested that chiral Brønsted acids^[3] may be the solution to this problem. The best result could be achieved (93% yield and 94/6 er) when the reaction was catalyzed by (S)-phosphoric acid **3d** in toluene at $-20\text{ }^{\circ}\text{C}$.



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Living Cationic Polymerization and Copolymerization of Plant-Derived β -Methylstyrene Derivatives

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Keywords: Anethole derivatives, Elastomer, Living cationic polymerization, β -Methylstyrene, Renewable monomers, Copolymerization

Introduction

Several β -methylstyrene derivatives are available from renewable resources like natural plant oil. However, due to their low polymerizability, there are few reports on the controlled polymerization of β -methylstyrenes. Recently, we have reported the living cationic (co)polymerizations of plant-derived β -methylstyrenes, such as *trans*-anethole (Ane) and isoeugenol with ROH/BF₃·OEt₂.^[1,2]

Results and Discussion

In this work, we investigated the cationic homopolymerization and copolymerization of various plant-derived β -methylstyrenes such as Ane, and isosafrole (ISa) with an R–Cl/SnCl₄/*n*-Bu₄NCl initiating system, with which living polymerization of styrene derivatives has already been reported.^[3] Especially, in conjunction with the HCl adduct of Ane (**1**) as the R–Cl, the polymerization of Ane proceeded in a living fashion to give the homopolymers with controlled molecular weight, whereas the other plant-derived β -methylstyrenes only resulted in oligomers. In contrast, all these β -methylstyrenes afforded living copolymers with petrochemical-derived *p*-methoxystyrene (pMOS) using the R–Cl/SnCl₄/*n*-Bu₄NCl system. More specifically for Ane and pMOS, not only the living copolymerization of Ane and pMOS completed within 10 minutes with a quantitative consumption of pMOS, but the subsequent living polymerization of Ane proceeded to afford the block copolymer [poly(pMOS-*r*-Ane)-*b*-poly(Ane)] with relatively narrow molecular distributions ($M_w/M_n = 1.1 - 1.3$) (Figure 1).

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Supramolecular velcro for reversible underwater adhesion

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Keywords: cucurbiturils, underwater adhesion, host-guest systems, multivalency, supramolecular chemistry

Underwater adhesion is a challenging task for most synthetic adhesives. Efforts to overcome this challenge have largely focused on modifying natural molecules produced by marine organisms. In particular, the adhesive 3,4-dihydroxy-L-phenylalanine (DOPA) residue found in proteins secreted by mussels has been a popular inspiration for several synthetic underwater adhesives.^[1] Although such biomimetic approaches can be powerful, synthetic materials that are able to achieve similar function via orthogonal mechanisms can be valuable alternatives. For examples, most DOPA based adhesives require curing agents that irreversibly crosslink the residues to the surfaces.^[2] Efforts to achieve reversibility have largely been limited to the microscopic level.^[3] Therefore, we showed an orthogonal strategy for achieving strong and reversible underwater adhesion based on a synthetic ultrahigh-affinity host-guest binding pair^[4] of cucurbit[7]uril (CB[7]) and aminomethylferrocene (Fc).^[5] The CB[7] “loops” and Fc “hooks” form a supramolecular “velcro” which adheres in water without need of any curing agents (Figure 1). Our “velcro” exhibits excellent holding power and lap shear adhesion strength which can be tuned by controlling the density of Fc “hooks”. Remarkably, our strategy offers both mechanical reversibility and chemical switchability at the macroscopic level - a trait seldom observed in natural underwater adhesives.

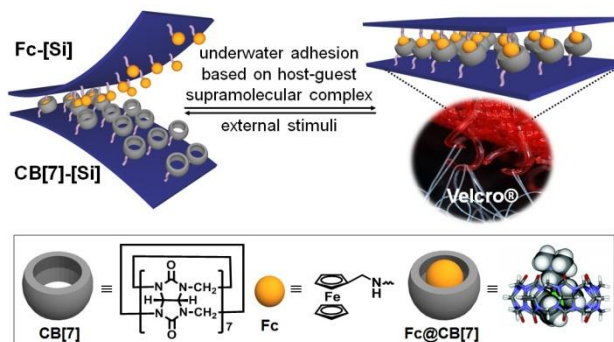


Figure 1. Supramolecular “velcro” strategy for underwater adhesion based on CB[7] and Fc modified surfaces.

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Short Synthesis of Enantiopure *trans*-3-Arylpiperazine-2-carboxylic Acid Derivatives

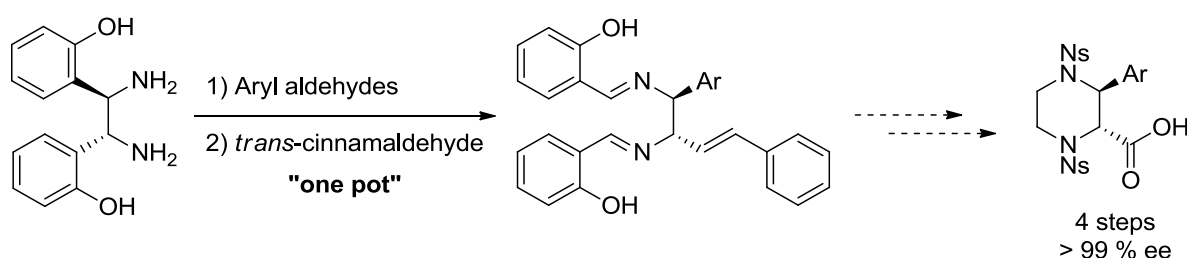
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Keywords: chiral piperazines, diaza-Cope rearrangement, chiral diamines

Piperazine-2-carboxylic acid can be regarded as an artificial amino acid and therefore has been utilized in many peptidomimetic structures for therapeutically important and biologically active compounds. We have recently developed a stereospecific synthesis of symmetric chiral vicinal diamines through the rearrangement of chiral diimines prepared from the reaction of (*R,R*)/(*S,S*)-1,2-bis(2-hydroxyphenyl)-1,2-diaminoethane (HPEN) and 2 equiv of aldehydes [1,2]. The rearrangement reaction was nicely extended to a stereospecific "one pot" route to α -substituted syn- α,β -diamino esters [3]. We envisioned that the chiral nonsymmetrical 1,2-disubstituted vicinal diamine synthesized by diaza-Cope rearrangement (DCR) could serve as suitable intermediates for the preparation of chiral nonsymmetrical 2,3-substituted piperazines. Herein, an efficient synthetic method was developed for the construction of enantiomerically pure *trans*-3-arylpiperazine-2-carboxylic acid derivatives using DCR as a key step starting from (*R,R*)-HPEN [4]. A complete transfer of stereochemical integrity was observed for the transformation. Piperazine ring formation from the chiral 1,2-ethylenediamine derivatives using diphenylvinylsulfonium triflate followed by oxidation of the double bond using ruthenium(III) chloride monohydrate in the presence of sodium periodate provided the desired enantiopure *trans*-3-arylpiperazine-2-carboxylic acids. Use of the chiral 3-arylpiperazine-2-carboxylic acids as an artificial amino acid analogue in the construction of physiologically active compounds is in progress and will be reported in due course.



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Novel Copper Complexes having Dialkylsilylene Ligands

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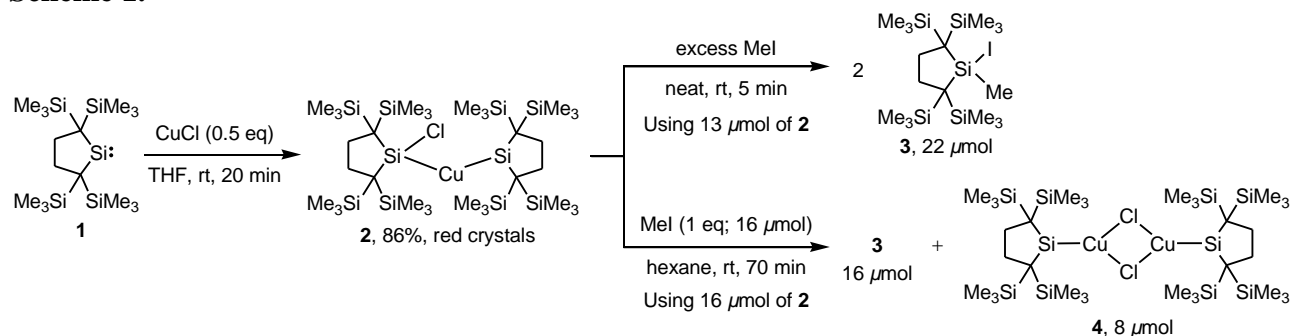
Keywords: Silylene, Copper Complex

Silylene copper complexes have been proposed as important intermediates of the Rochow's direct process that is a well-known industrial method for preparing organochlorosilanes [1]. However, no diorganosilylene copper complex has been reported until now [2]. Recently we have found that the isolable dialkylsilylene **1** works as a ligand of group-10 metal complexes [3]. Herein we report the synthesis, structures and reactions of dialkylsilylene copper complexes.

Reaction of silylene **1** with a half equivalent of copper(I) chloride gave chlorosilyl(silylene)copper complex **2** in 86% yield as air-sensitive red crystals (Scheme 1). Molecular structure of **2** was determined by X-ray crystallographic analysis. In complex **2**, chlorosilyl substituent and silylene ligand coordinate to the central copper atom in a slightly bent manner with a Si–Cu–Si angle of 168.34(2)°. The Silylene–Cu bond length [2.2670(6) Å] is shorter than the Silyl–Cu bond length [2.3104(6) Å].

It should be interesting to investigate the reaction of **2** with haloalkanes because in the Rochow's direct process, silylene copper complexes are proposed to react with haloalkane to give halogen-carbon insertion products of silylene. Complex **2** (13 μmol) reacted with excess of methyl iodide to give iodomethylsilane **3** (22 μmol). This result indicates that the two silicon ligands react with methyl iodide as silylene ligands. On the other hand, complex **2** (16 μmol) reacted with one equivalent of methyl iodide to give dimeric silylene copper chloride complex **4** (8 μmol) together with iodomethylsilane **3** (16 μmol). Formation of **4** suggests the chlorine atom migration from silicon atom to copper atom. From these results, it seems reasonable to assume that the reaction of **2** with methyl iodide proceeds via the chlorine atom migration process.

Scheme 1.



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Phosphine Oxide Functional Group Based Three-Station Molecular Shuttle

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Phosphine oxide is a good hydrogen bond acceptor. A series of rotaxanes based on hydrogen bonding between phosphine oxide and benzylic amide had been reported by Leigh.[1] Urea plays a key role in the recognition of halide anions and Y-shaped carboxylate anions. It possesses unique switchable properties for designing molecular switches.[2-3] Herein we will present a switchable three-station rotaxane based molecular shuttle with the phosphine oxide, dibenzylammonium, and urea functional groups, where the macrocycle can be easily switched between three different binding sites along the rotaxane thread by addition of acid/base or anions resulting in three stable states.[4] (Fig. 1) The introduction of phosphine oxide as a potential recognition binding unit for rotaxane-based molecular shuttles would provide a new class of molecular shuttles.

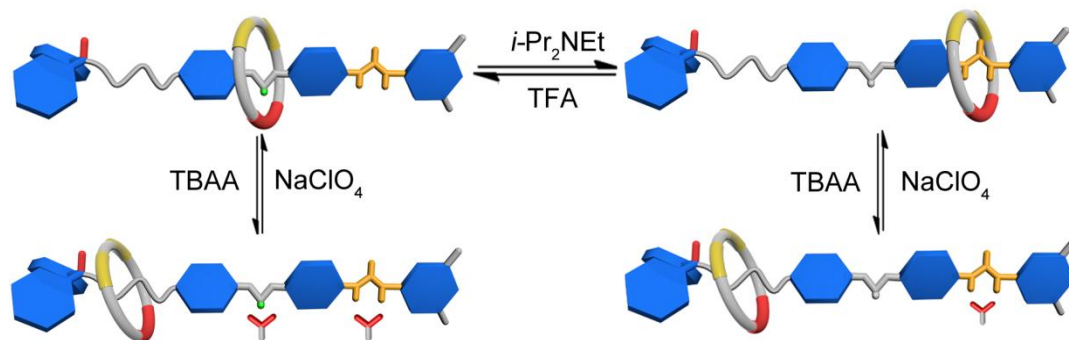


Fig. 1 The shuttling process of the macrocycle along the rotaxane thread.

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Hydration of Terminal Alkynes Catalyzed by Water-Soluble Cobalt Porphyrin Complexes

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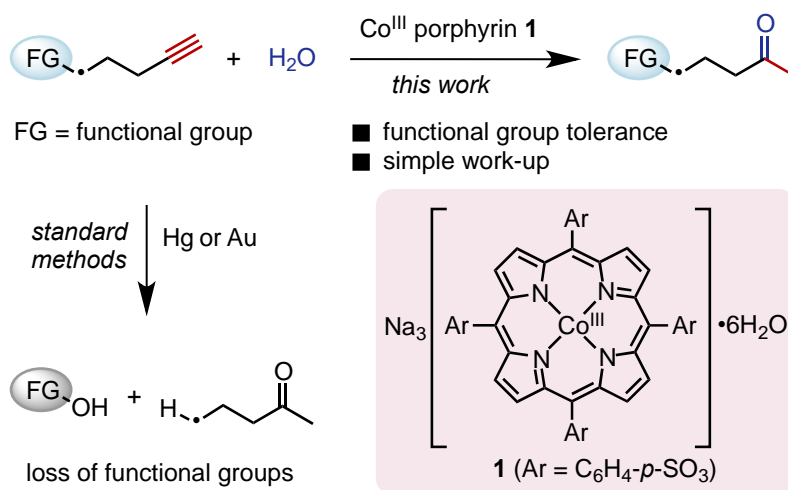
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Keywords: Hydration, Terminal Alkynes, Cobalt, Catalysis,

Markovnikov-type hydration of terminal alkynes represents a powerful method for the synthesis of methyl ketones using water as a reagent, based mainly on mercury and gold catalysts.¹ However, hydration of terminal alkynes bearing acid-sensitive functional groups still remains a challenge in selective organic synthesis, as the functional groups are not well-tolerated under the typical hydration conditions.

To address this issue, we have developed a method for the hydration of terminal alkynes in the presence of the water-soluble cobalt(III) porphyrin complex **1**.² The alkyne hydration proceeded in a good to excellent yield with 0.1 to 2 mol % cobalt catalyst **1** and was compatible with the presence of acid/base- or redox-sensitive functional groups such as alkyl silyl ethers; allyl ethers; trityl ethers; benzyl ethers; carboxylic esters; boronic esters; carboxamides; nitriles; and acetal groups. Some of the alkyne substrates tested here are otherwise difficult to hydrate. The alkyne hydration can be performed on a gram scale, and the catalyst can be recovered by aqueous workup.



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Reinforced multi-functionalized nanofibrous scaffolds based on mussel adhesive proteins

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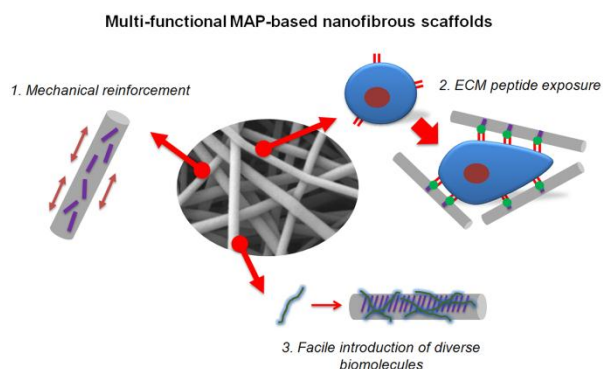
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Keywords: Mussel adhesive proteins, Electrospun nanofibers, Surface functionalization, Tissue engineering

Nanofiber technology is the promising one that can create the extracellular matrix (ECM)-like porous structure. Synthetic polymers have been used for fabrication of electrospun nanofibers. However, poor bioactivity is the limitation for the use of tissue engineering application. Previously, we suggested that our recombinant mussel adhesive protein (MAP) which have a great cell adhesion ability and biocompatibility can be the potential biomaterials for tissue engineering.

In this study, we propose to use MAP as a natural biomaterial that serves as a blending partner for the preparation of sticky nanofibrous scaffolds which provides a facile, efficient, and multifunctionalizing platform for generating novel nanofibrous scaffolds (Scheme 1).



Scheme 1. Schematic representation of multi-functional MAP-based nanofibrous scaffolds.

Nanofibrous scaffolds based on MAPs with various kinds of biodegradable polymer partners were fabricated via a simple electrospinning process. Using PCL as a model blending partner, we identified that incorporation of MAP via the blending strategy strengthened the rigidity of the composite nanofibers and rendered nanofiber

surfaces more hydrophilic, which indicated that MAPs were successfully exposed on the surface of the composite nanofibers.

In our *in vitro* cell culture experiments, pre-osteoblast cell adhesion and proliferation were enhanced on the PCL/MAP nanofibers compared to sole PCL nanofibers.

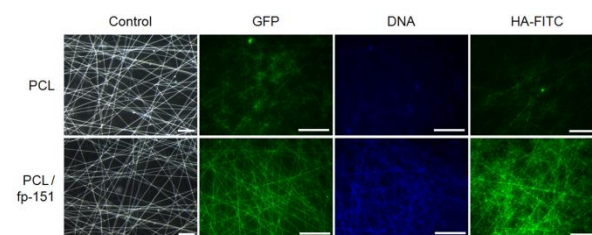


Figure 1. Fluorescence images of GFP, DNA, and HA-coated PCL and PCL/MAP nanofibers. The scale bar is 100 μ m.

Also, we investigated the role of PCL/MAP nanofibers as coating platforms against many types of biomolecules by simple coating experiments without any chemical treatment (Figure 1).

In conclusion, this novel, multiple biofunctional coating nanofiber platform based on MAPs could be a promising tool for successful tissue engineering applications.

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Change in optical properties induced by resonance between Wannier and Frenkel excitons

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Under resonance, hybrid excitons have been predicted to be formed between Wannier and Frenkel excitons.[1] However, such resonant coupling has not been observed yet. In this research, the Wannier exciton energy level was controlled by varying the composition of the inorganic layer in layered perovskite-type compounds. Hence, we could investigate the luminescence properties of compounds in which the Wannier and Frenkel exciton energy levels are in near resonance.

PbX_2 and $\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3\text{X}$ ($\text{X} = \text{Br}, \text{I}$), or $\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3\text{X}$ ($\text{X} = \text{Cl}, \text{Br}$) were dissolved in *N,N*-dimethylformamide (DMF) in a stoichiometric ratio and stirred for 0.5 h. Powders of $(\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3)_2\text{PbBr}_x\text{I}_{4-x}$ ($x = 0-4$) and $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_x\text{Br}_{4-x}$ ($x = 0-4$) were obtained by evaporating the solvent. Thin films were obtained by spin-coating the DMF solution of these powders. The absorption and luminescence spectra were then measured.

Fig. 1 and Fig. 2 show the luminescence spectra of $(\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3)_2\text{PbBr}_x\text{I}_{4-x}$ and $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_x\text{Br}_{4-x}$ ($x = 0-4$) films at 10 K. Excitonic luminescence from the inorganic layer was observed when the x values of both the films were 0.[2][3] On the other hand, phosphorescence from the organic layer was observed when the x values of both the films were 4. Wannier exciton energies in the inorganic layer shifted toward higher energies when I (Br) was replaced with Br (Cl). The phosphorescence was the result of energy transfer from the inorganic to the organic layer.[3] These results indicate that triplet excited states in the naphthylmethyl and benzyl moieties lie within the variable range of Wannier exciton energy levels.

Based on the change in luminescence properties, we fabricated the films in which the Wannier exciton and triplet excited levels in the organic layer are in near resonance. A unique quenching in the vibrational peaks at 520–566 nm was observed in $(\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3)_2\text{PbBr}_x\text{I}_{4-x}$ films with x values of 1.87 and 1.75. The decrease in the luminescence relative intensity at vibrational peaks was also observed in $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_x\text{Br}_{4-x}$ films with x values of 3.75. These unique peaks did not correspond to the sum of the peaks of the Wannier and Frenkel excitons. This mismatch suggests that resonance between Wannier and Frenkel excitons was induced.

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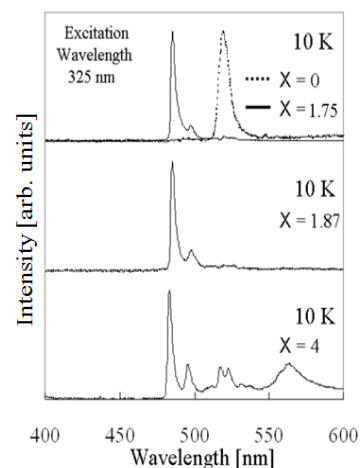


Fig.1 Luminescence spectra of $(\text{C}_{10}\text{H}_7\text{CH}_2\text{NH}_3)_2\text{PbBr}_x\text{I}_{4-x}$ spin-coated films at 10 K

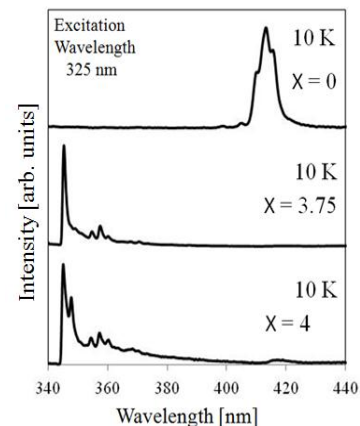


Fig.2 Luminescence spectra of $(\text{C}_6\text{H}_5\text{CH}_2\text{NH}_3)_2\text{PbCl}_x\text{Br}_{4-x}$ spin-coated films at 10 K

Reversible σ -Dimerizations of Persistent Organic Radical Cations

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C-C bond formation and cleavage are basic events in organic chemistry. The oxidative σ -dimerization of conjugated aromatic systems involving C-C coupling plays an essential role in organic syntheses, e.g. oxidative oligo- and polymerization, where σ -dimeric dication is suggested as a key intermediate [1]. In the previously reported oxidative dimerizations, radical cations have not been directly observed and well confirmed due to their short lifetime [2]. With salt $\text{AgAl}(\text{OC}(\text{CF}_3)_3)_4$, however, 9,10-Dialkoxyanthracenes were oxidized to radical cations and stabilized in solution, which dimerize upon crystallization and come back to radical cations upon dissolution (Fig.1) [3]. The identity and stability of radical cations have been unequivocally confirmed by EPR and UV-vis spectroscopy. This work has provided conclusive evidence for reversible σ -dimerizations of persistent organic radical cations. Study of such reversible process may have an impact on exploring mechanism of oxidative oligo- and polymerization of aromatic systems.

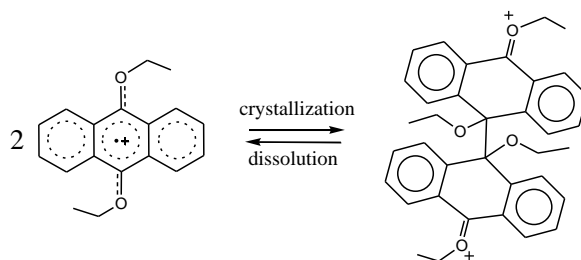


Figure 1

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Nanostructured Redox-active Polymers for Biosensor and Biofuel Energy

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There are growing needs to develop future energy source and concomitantly, extensive efforts have been paid to a variety of systems such as fuel cells and batteries. Biofuel energies are considered one of the most effective and promising future energy sources for bio-micro system. Since biofuel energy consumes biomass, i.e., glucose, their renewable nature has been highlighted. However, limitations in the operation of common biofuel cells are arising from their low power densities because of inefficient fuel transportation and low electron transport rate. One of widely studied methodology to enhance the power density is the use of electron mediator, which can help electron transport from biofuel binding site (enzyme) to electrode surface. Various materials possessing the ability of electron mediation have been reported which include nano-carbons, redox polymers, cofactor relay, and metal nanoparticles. In present study, we have described new approach, that of integration of enzymes and nanostructured redox-active polymers. Polyferrocenylsilane (PFS) containing block copolymers have been employed as an electron mediator, which can help the electron transportation from enzyme to electrode surface. The electrode is assembled Tri-layer system, porous carbon, enzyme, and nanostructured redox-active polymers. The stability of fabricated electrodes was improved by chemical cross-linking of redox polymers without the loss of electron mediating properties. We demonstrated that the electron transfer rate between redox polymer and enzyme is sensitive function of the morphology of redox polymers.

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Freestanding Luminescent Films of Nitrogen-rich Carbon Nanodots towards Large-scale Phosphor-based White Light-emitting Devices

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Keywords: carbon nanodots, photoluminescence, phosphor, luminescent films, light-emitting

Carbon nanodots (CNDs) are emerging as a new type of luminescent materials, which offers strong potential for cost reduction and biocompatibility vis-à-vis inorganic nanocrystals.¹ These luminescent carbon nanomaterials have quasi-spherical graphitic nano-cores (typically below 5 nm) and oxygenic surface functional groups. Among a variety of synthetic routes to CNDs reported thus far, the emulsion-templated method can afford highly luminescent and fairly monodisperse CNDs via carbonization of readily-available carbon sources (glucose, citric acid, polymers, etc.).²⁻⁵ This method is promising because any unpractical size-selection procedure, special equipment, and high-temperature heating can be excluded.

Considering that there are increasing demands for light-emitting devices (LEDs) as a potential replacement for traditional light sources, CNDs could offer prospects for phosphor technology due to their strong visible light emission, less toxicity, and high thermal stability. Recently, several research groups have therefore attempted to use CNDs as an active material in LEDs.⁶⁻⁸ As an exemplary, Chen and coworkers reported phosphor-based LEDs with CNDs derived from photonic crystals. They successfully render three different colors, but the obtained CNDs showed limited absorption in the long-UV region. Thus, InGaN blue LEDs, mostly used base LEDs, cannot be much effective for this system. Furthermore, the aggregation of solid-state CNDs typically leads to serious luminescence quenching, which would significantly limit the performance of CND-based LEDs.⁹

In this work, we derive nitrogen-rich CNDs from polyacrylamide (PAA) via one-step emulsion-templated carbonization without any unpractical size selection procedure. By varying the molecular weight (MW) of polyacrylamide, we control the size of the CNDs and study the effect of the size on their optical property. The obtained CNDs produce bright visible light under UV illumination, which is very suitable for phosphor applications. To realize their potential, we demonstrate the fabrication of large-area freestanding films of the CNDs based on a poly(methyl methacrylate) (PMMA) matrix. Since the CNDs are “dispersed” in the polymer matrix, we find no significant reduction in the luminescence due to any type of quenching. The as-obtained films also have physical advantages such as full-flexibility, air-stability, mechanical strength, and harmlessness. Thus, this study would suggest a promising way to exploit the luminescence from solid-state CNDs and offer strong potential for future CND-based solid-state lighting systems.

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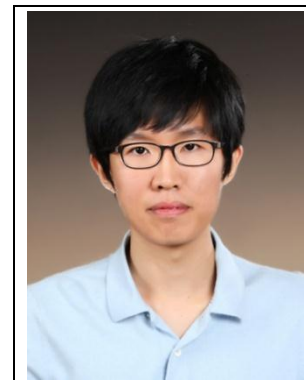
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Research interests:

Synthesis and application of luminescent carbon nanomaterials; electrocatalytic carbon materials for electrode applications; hybrid materials for electronic and photovoltaic devices

Selected publications:

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Synthesis of Spin Probe For In Vivo Electron Paramagnetic Resonance Imaging of Cerebral Nicotinic Receptor

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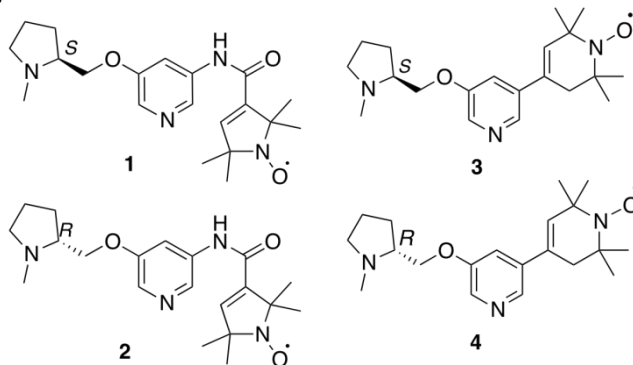
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Keywords: spin probe, nitroxyl radical, synthesis

Neuronal nicotinic acetylcholine receptors (nAChRs) are widely distributed in the human brain. Several lines of evidence suggest that two major subtypes ($\alpha 4\beta 2$ and $\alpha 7$) of nAChRs play an important role in the pathophysiology of Alzheimer's disease. Melwyn *et al* reported 3-pyridyl-ether compounds that generally possess subnanomolar affinity for brain nAChRs.[1] A novel EPR imaging technique,



which enables the visualization of the spatial distributions of two nitroxyl radicals simultaneously in vivo has been recently reported.[2] Therefore, we aim to develop novel spin probe pairs that can be used to study the difference of localization in mouse brain with the simultaneous EPR imaging. A pairs of probes were designed to possess affinity for nAChRs receptor and with nitroxyl radicals also. The result suggested that the first-generation spin probes (Fig. 1) were blood-brain-barrier impermeable so that they could not be used in EPR imaging of brain. To overcome this problem, the second-generation nAChRs ligand-nitroxyl-probes (Fig. 2) were synthesized. The results of mouse brain in vivo EPR imaging showed that compounds 3 and 4 were BBB permeable. However, whether they could be used as promising probes for in vivo EPR imaging, we need to make further investigations.

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A Reversible Plasmonic Probe Sensitive for pH in Micro/nano-spaces Based on i-motif-modulated Morpholino-AuNPs Assembly

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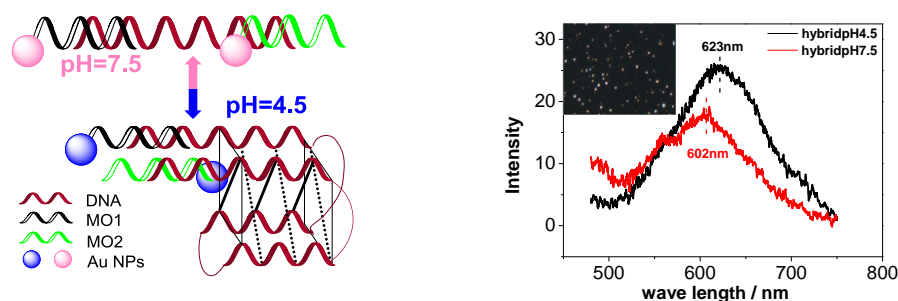
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Keywords: i-Motif DNA, morpholino, pH-sensitive, gold nanoparticle assembly, micro/nano-spaces

Exploring local pH in micro/nano scale is fundamental for understanding microprocesses including corrosion of metal[1] and metabolism of cell.[2] Regular fluorescence pH probe[3] and potentiometric electrode[4] either show low signal intensity or lack of special resolution when being applied in micro/nano environment.

Gold nanoparticles (AuNPs) have attracted much attention because of their unique surface plasmonic properties and relatively good biocompatibility. By measuring the optical signal of AuNPs at different aggregation state, chemical information such as biorecognition reaction can be extracted.[5] Recently, Nam[6] demonstrated a “smart” gold nanoparticle decorated with pH-sensitive molecule which aggregated in mild acidic intracellular environments and facilitated the photothermal cancer therapy. Single AuNP is of more interests because it can act as a nanoprobe for converting chemical information from microenvironment into optical signal. Since the spectrum of single AuNP is intensive and stable, it becomes a promising candidate for pH detection at micro/nano-scale level.

In the present work, we developed a nanoscale reversible pH probe based on the plasmonic coupling effect of i-motif modulated gold nanoparticle (AuNP) assembly. The pH probe shows reversible and high sensitive response to pH variation between 4.5 and 7.5. Introduction of morpholino[7] (MO), a neutral analog of DNA, into the assembly endow the pH probe with high stability even under low salt concentration. The intense optical signal of AuNP enables local pH being read out not only in micro/nanofluidic channel but also on a single i-motif-MO-AuNP assembly. Recording of the strong plasmonic resonance scattering spectrum of AuNP, provides a promising method for extracting chemical information in nanospace of biological systems.



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Synthesis of Hydrophilic poly-*L*-lysine/Graphene hybrid through Multiple Non-Covalent Interactions for hemoglobin immobilization and H₂O₂ sensing

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Keywords: Poly-*L*-lysine, graphene, hybrid, non-covalent interaction, hemoglobin, biosensor

Surface modification has been proved to be one of the effective strategies for enhancing the properties of graphene sheets. When non-covalent modification method is appropriately designed, novel opportunities for better performance of graphene nanosheets can be expected since this strategy can tailor the properties of graphene while its natural structure will be retained. We introduces a simple route to prepare highly biocompatible, stable and conductive graphene hybrid modified by poly-*L*-lysine (PLL) using the non-covalent strategy. Results show that PLL adopts random conformation with the nonpolar parts exposing to outside since its side chains are positively charged under neutral conditions. This conformation allows the strong adhesion of PLL to graphene surface via the hydrophobic interaction between butyl chains of PLL and graphene surface, cation- π interaction of protonated amine groups on PLL with the π electrons in graphene, and electrostatic interaction between the protonated amine groups on PLL and the negatively charged carboxyl groups remaining on graphene. All these interactions make the resultant PLL-G hybrid stable and dispersible in aqueous solutions. The resultant hybrid is then used to construct high performance biosensor. As demonstration, hemoglobin (Hb) carrying negative charges can be easily immobilized on the hybrid via electrostatic interactions with positively charged lysineside chains of PLL modified on graphene surface, forming Hb@PLL-G bionanocomposite. The immobilized protein retains its native 3D-structure and exhibits reversible direct electrochemistry. The Hb@PLL-G based enzymatic electrochemical biosensor shows excellent catalytic activity toward its substrate hydrogen peroxide. It electrochemical response shows linear dependence of hydrogen peroxide concentration in a range between 10 μ M-80 μ M with a detection limit of 0.1 μ M. The apparent Michaelis–Menten constant is calculated as 0.0753 mM, demonstrating the significant catalytic ability of the protein. The present strategy can be extended to modify other carbon materials and the resultant nanocomposites are promising for the construction of biosensors, bioelectronics and biofuel cells.

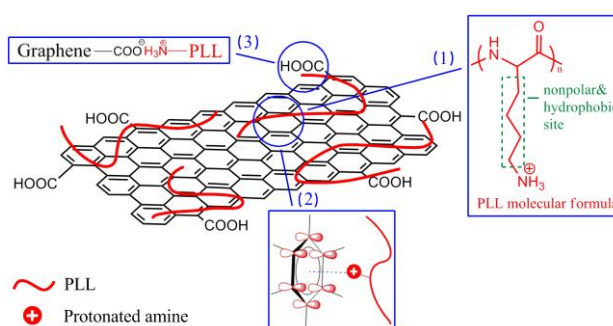


Figure 1. Schematic representation of the mechanisms that PLL interacts with hydrazine hydrate reduced graphene.

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Electron Transition-Based Optical Activity (ETOA) of Achiral Metal Oxides Derived from Chiral Mesoporous Silica

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Keywords: chirality, optical activity, electronic transition, inorganic materials, metal oxides.

Abstract.

Electronic transition-based optical activity (ETOA) is ubiquitous in organic materials. However, chiral inorganic materials exhibiting optical activity at their characteristic absorption bands attributed to electronic transitions are rare [1]. Here, we report the synthesis and optical activity of several metal oxide nanoparticles introduced into the helical pores of chiral mesoporous silica supports. Chiral mesoporous silica ribbon (CMR) was used as helical supports [2]. The optical activity of various complexes was unambiguously detected by solid-state diffuse-reflectance circular dichroism (DRCD). Coloured metal oxides (e.g., Co_3O_4 , CuO , Fe_2O_3) and colourless metal oxides (e.g., PbO , CdO , ZrO_2) loaded in the antipodal CMRs exhibited distinct opposite signals in the CD spectra at the long UV-visible region and only a single Cotton effect at the near ultraviolet region, respectively. All signals of the DRCD spectra were corresponding to the absorption bands of metal oxides, which were attributed to electronic transitions from the ground state to excited states under an asymmetric electric field.

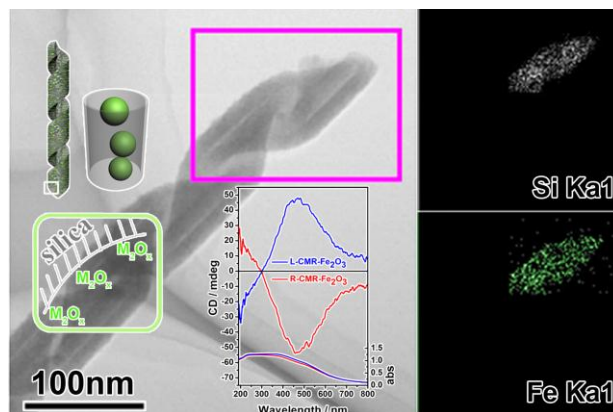


Figure 1. Schematic illustration of inorganic materials with ETOA.

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Formation of Enantiomeric Impeller-Like Helical Architectures by DNA Self-Assembly and Silica Mineralization

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Keywords: chiral liquid crystal phase, DNA self-assembly, mineralization, helicity

Abstract

Understanding the formation of biologically relevant materials is essential for revealing the structural components of life and assists the development of new functional materials that mimic the state-of-the-art morphologies and structures observed in nature. Here, we developed an *in vitro* mineral model system. This system, which was composed of a biomolecule template (DNA), a chiral inducing agent (Mg^{2+}), a co-structure directing agent (*N*-trimethoxysilylpropyl-*N,N,N*-trimethylammonium chloride, TMAPS) and a silica source (tetraethoxy-silane, TEOS), self-assembled into impeller-like helical DNA-silica complexes (IHDSCs). Enantiomeric IHDSCs were formed by tuning temperature, pH value and quaternary ammonium:DNA molar ratio due to the enantiomeric DNA layer-by-layer chiral packing. The pitch length of the IHDSCs was significantly decreased with increasing Mg^{2+} or TMAPS. Both the handedness and the pitch length of the DNA packing were determined through the competitive interaction between DNA-TMAPS and DNA- Mg^{2+} .

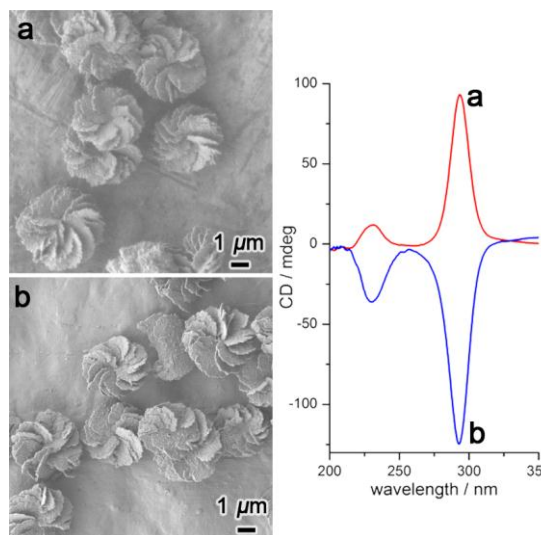


Figure 1. SEM images and corresponding CD patterns of enantiomeric IHDSCs. The right-handed IHDSCs (*ee* = -80%) and the left-handed IHDSCs (*ee* = 50%) were synthesized at 25 °C (a) and 0 °C (b), respectively.

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Solution pH Modulated Rectification of Ionic Current in Highly Ordered Nanochannels Array Patterned with Chemical Functional Groups at Designed Positions

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Keywords: nanofluidics, ion transport, rectification, porous alumina, protonation/deprotonation

A new ionic current rectification device responsive to a broad range of pH stimuli has been established using highly ordered nanochannels of porous anodic alumina membrane with abrupt surface charge discontinuity. The asymmetric surface charge distribution is achieved by patterning the nanochannels with surface amine functional groups at designed positions using a two-step anodization process. Due to the protonation/deprotonation of the patterned amine and the remaining intrinsic hydroxyl groups upon solution pH variation, the nanochannels array-based device is able to regulate ion transport selectivity and ionic current rectification properties. The rectification ratio of the device is mainly determined by the nanochannel size, and the rectification ratio is less sensitive to the patterned length of the amine groups when the nanochannels size is defined. Thus, the isoelectric point of nanochannels can be easily estimated to be the pH value with unite rectification ratio. The present ionic device is promising for biosensing, molecular transport and separation, and drug delivery in confined environments.

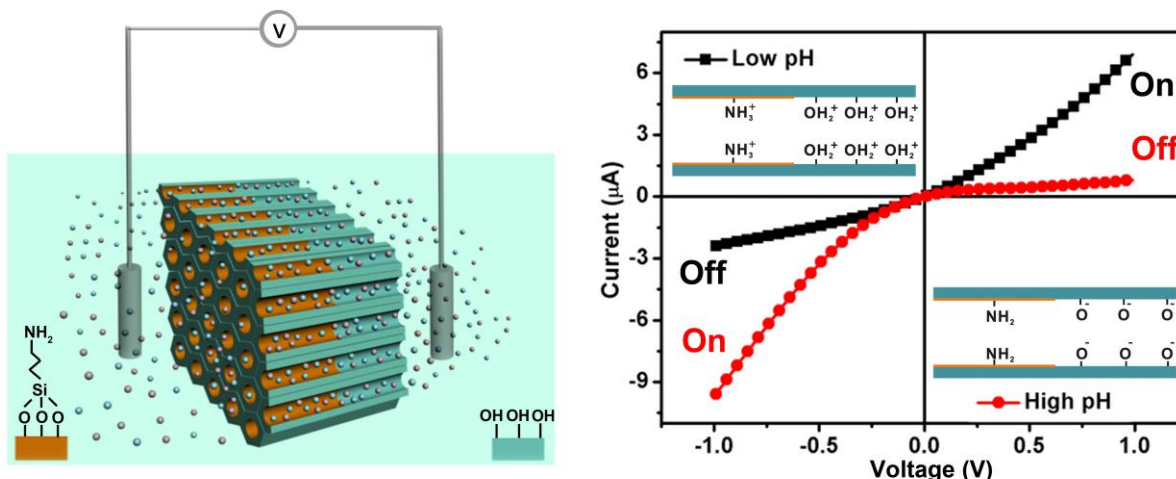


Figure 1 Schematic illustration of rectification characterization for PAA membrane patterned with 3-aminopropyltrimethoxy-silane (APTMS).

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Synthesis and Characterization of Multi-helical DNA-Silica Fibers

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Keywords: DNA assembly, biomineralization, helical fibers

The chiral morphology of DNA assembling induced by amino molecules has shown certain significations in the study of assembly behavior of helical macromolecules, and has ability to promote the understanding of the packing structure of DNA molecules on nucleosome in bioresearch [1, 2]. Herein, multi-helical DNA-silica fibers (MHDSFs) and non-helical DNA-silica fibers (NHDSFs) were synthesised by the self-assembly of DNA molecules with cationic organosilane and silica source. By electron microscopy images and circular dichroism spectra, three-level helical structures in the silica fibers have been revealed, *i.e.* the DNA double-helix, the secondary left-handed DNA packing and the tertiary right-handed twisting. These findings may be useful in conjecturing the role of alkaline proteins in DNA packing *in vivo*.

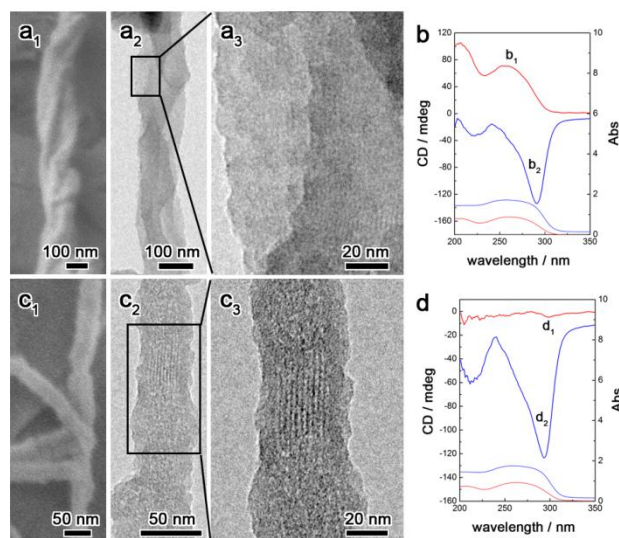


Fig. 1 (a) SEM (a₁) and HRTEM images (a₂, a₃) of the MHDSFs synthesised with APS/DNA molar ratios of 6; (b) The DRCD and UV/Vis spectra of MHDSFs under dry (b₁) and wet (b₂) states; (c) SEM (c₁) and HRTEM images (c₂, c₃) of the NHDSFs synthesised with APS/DNA molar ratios of 3; (d) The DRCD and UV/Vis spectra of NHDSFs under dry (d₁) and wet (d₂) states.

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Synthesis of rhodium nanoparticles in mesoporous silica using supercritical carbon dioxide

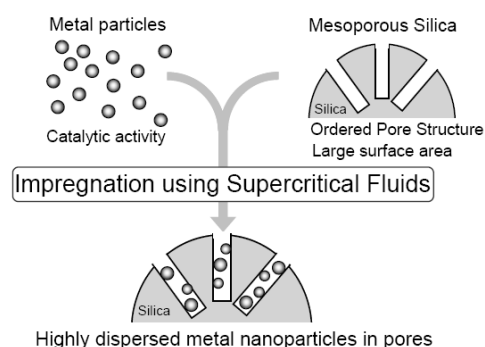
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Keywords: Supercritical carbon dioxide, catalyst preparation, mesoporous silica

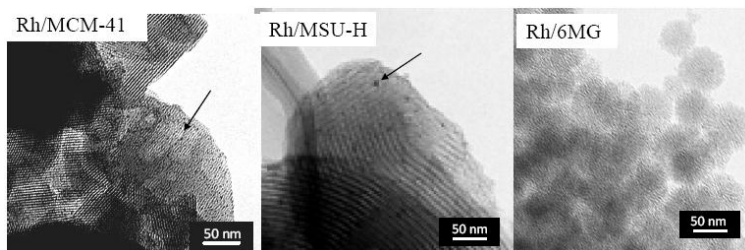
The mesoporous silica containing metal nanoparticles is considered as one of hybrid functional materials for highly active and selective catalysts. Recently, we have reported that supercritical CO₂ can allow metal precursors to penetrate into mesopores due to its high diffusivity and low surface tension¹), leading to good dispersion of precipitated particles compared with the liquid solvents. It was also demonstrated that the obtained materials could exhibit specific features as catalysts through on hydrogenation reaction catalyzed by rhodium catalysts. In this work, we examined the effects of calcination conditions on morphology and distribution of rhodium particles in three types of mesoporous silica (Table 1).



Experimental conditions were temperatures from 333 K, pressures from 20 MPa and a contact time of 24 h. To convert the precursor to rhodium particles, the obtained samples were calcined in a muffle oven at 673 K for 3 h.

The rhodium loading in the mesoporous silica was determined to be 4 wt% by EDX. TEM images (Fig. 2) showed Rh/6MG achieved highest dispersion of rhodium which is difficult to observe by TEM. This is probably attributed to strong interaction between rhodium and 6MG surface. On the other hand, rhodium particles in Rh/MSU-H are larger than any other catalysts due to large pore size of MSU-H. In regard to catalytic activity, cinnamaldehyde hydrogenation reaction is being studied using the obtained catalysts.

	BET surface area [m ² /g]	Pore volume [cm ³ /g]	Average pore diameter [nm]
MCM-41	941	0.89	2.7
MSU-H	686	0.89	8.4
6MG	922	1.3	3.0



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Molecular Dynamics Study of Na⁺/NH₄⁺ Exchange Process in Faujasite Zeolite: Free Energy Calculations

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Keywords: faujasite zeolite, cation exchange, cation distribution, thermodynamic integration.

Zeolite Y, which is a synthetic faujasite (FAU) with silicon/aluminum ratio (Si/Al) greater than 1.5, has a wide range of industrial applications. Among these applications, the Na/NH₄ ion exchange is an important industrial process. The synthesized zeolite Y is usually in its sodium form (Na-Y). In order to make its hydrogen form (H-Y) which is used as catalyst, a common way is to use ammonium solution to exchange the Na⁺ by NH₄⁺, and then remove water and NH₃ by heating (deamination). However, the complete NH₄⁺ exchanged in Na-Y is difficult to achieve, excessive amount of ammonia are usually used, which causes serious environmental consequences.

The isotherms of NH₄⁺-exchange for Na⁺ in different zeolites have been measured experimentally^[1-4]. Although the ion exchange profiles are different from each other in experimental work because of the difference of synthesis method of zeolite, all results can be summarized as: zeolite Y exhibits a high selectivity for NH₄⁺ ion and the complete NH₄⁺ exchange of Na-Y cannot be achieved directly. However, the fully understand of this results is still lack at atomistic level.

In this work, we perform the free energy calculations to predict the equilibrium constant of the NH₄⁺ exchange with of Na⁺ in Y type zeolite and further predicted the cation exchange isotherms using thermodynamic integration (TI) method. Because the force field is critical, we first carried out quantum mechanics (QM) calculations and developed force field based on the QM data to correctly describe the interactions and structures between zeolite framework and cations. Then we carried out hybrid MC and MD simulations to predict the equilibrium various amount of different cations in the zeolite. Finally we perform TI calculations at different distributions to obtain the equilibrium constants. From the equilibrium constants, we obtained the exchange isotherms and compared with known experimental data.

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A highly selective ratiometric fluorescent probe for Cu²⁺ based on FRET and its application in living cells

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Keywords: fluorescent sensor, copper (II), fluorescence imaging

Copper is one of the most abundant transition metal in human body, and play essential roles in different biological process. Due to its noninvasiveness, high sensitivity, and the ability to offering temporal-spatial information in situ, fluorescent imaging is a powerful technique to clarify the physiological and pathological roles of Cu²⁺ in living system [1]. Ratiometric sensors are much more favorable than “turn-on” sensors for offering the quantitative information of its target, since the internal calibration between two different wavelengths for the apo- and bound sensor can eliminate the artifacts induced by the dynamic microenvironments [2]. A novel ratiometric Cu²⁺ sensor **CSBPA** was developed via coupling a coumarin fluorophore (donor fluorophore) with a sulfonlated benzoxadiazole fluorophore (SBD, acceptor fluorophore) based on a FRET mechanism. The emission spectrum of **CSBPA** was shifted from 555 nm to 460 nm in response to Cu²⁺, displaying the favorable ratiometric sensing ability for Cu²⁺. The specific Cu²⁺ sensing behavior over other metal cations is pH-independent, and can be ascribed to the decreased FRET efficiency from coumarin to SBD fluorophore. The successful intracellular Cu²⁺ imaging with **CSBPA** suggests its potential in imaging application, and this study gives a new example of FRET sensing using a small molecule.

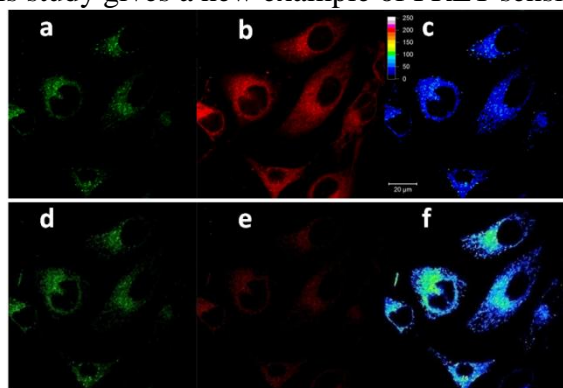


Fig. 1 Confocal fluorescence images of MCF-7 cells incubated with 10 μM **CSBPA** (15 min) in the absence (up row) and presence (bottom row) of 200 μM Cu²⁺. Fluorescence image of cells obtained from the green channel (430-480 nm, **a**) and the red channel (500-600 nm, **b**). (**c**) Pseudo-colour image of the fluorescence ratio of (**a**) and (**b**). Fluorescence image obtained from the green channel (**d**) and the red channel (**e**) for the cells in (**a**) treated further by incubation with 200 μM Cu²⁺ for 15 min. (**f**) Pseudo-colour image of the fluorescence ratio of (**d**) and (**e**). All images were obtained directly by confocal microscope (Zeiss LMS710) upon irradiation at 405 nm. Scale bar: 20 μm .

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