

**Joint Symposium of Peking University & Waseda University  
on Practical Nanochemistry**

Lecture Hall, Chemistry Building

Peking University, Beijing, China

March 19-22, 2006

Organized by 21COE Program “ Practical Nano-Chemistry”

at Waseda University from MEXT, Japan

and College of Chemistry, Peking University, China.

## Scientific Program

March 20, 2006 (Mon.) 8:30-12:30  
Lecture Hall, Chemistry Building  
Peking University, Beijing, China

8:30 Welcoming Remarks ( Prof. Z. F. Xi)

8:40 Opening Remarks (Prof. H. Nishide)

**Chairman: Prof. Z. C. Li**

8:40-9:10 Prof. H. Nishide (Waseda Univ.)

**Proton-Conducting New Polymers for Fuel Cells**

9:10-9:40 Prof. Y. Ma (Peking Univ.)

**Hydrogen-Bond Mediated Self-Assembly of Macromolecules**

9:40-10:10 Prof. S. Hosokawa (Waseda Univ.)

**Chemistry of Ketene *N,O*-Acetals and Enolates**

**Chairman: Prof. J. Huang**

10:10-10:40 Prof. I. Hirasawa (Waseda Univ.)

**Research Trends in Advanced Crystallization Engineering**

10:40-11:10 Prof. Y. Li (Peking Univ.)

**Creation of Inorganic Nanostructures Using AFM Dip-Pen Nanolithography**

**11:10-11:30 Coffee Break and Photograph Taking**

11:30-12:20

**Poster Presentation**

12:20-14:00 Lunch ( Fang Zheng Restaurant)

## Proton-Conducting New Polymers for Fuel Cells

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A water-free and membrane-forming hydrocarbon-based polymer with a high proton conductivity is the undeveloped key material for the polymer electrolyte fuel cell (PEFC). One of the approaches to the PEFC membrane has focused on a protonic acid-doped base polymer and a base-doped acid polymer, such as polybenzimidazole doped or complexed with phosphoric acid. Some of them showed a proton conductivity, as high as  $10^{-2}$ – $10^{-3}$  S cm $^{-1}$ , comparable with that of Nafion, but the doped acid was eluted out during the FC operation.

Mixing of the aqueous solutions of an acid polymer and a base polymer immediately produced a water-insoluble aggregate or a polymer complex of the acid polymer (polyanion) and the base polymer (polycation). However, the polymer complex is a fibrous material, which does not give a dense membrane and does not show a high proton conductivity. A molecular-level polymer complex is assembled by a layer-by-layer complexation technique. A cationic substrate is dipped in a polyanion (acid polymer) solution and rinsed, then dipped in a polycation (base polymer) solution and rinsed. By using a protonic acid polymer and a base polymer, greater than 1000 layered polymer complex membranes were prepared. For example, the polymer complex membrane of the simple combination of poly(styrene sulfonic acid) and poly(allylamine) was water insoluble and displayed an anisotropic but very high proton conductivity of  $10^{-3}$  S cm $^{-1}$ .

By extending such molecular designs, we have synthesized a series of acid-base polymers by copolymerizing protonic source (acid) monomers and proton acceptor (base) monomers. However, some of these copolymers were water-soluble or insoluble in all solvents, while the others showed only conductivities below  $10^{-4}$  S cm $^{-1}$ . Among them, the aromatic polyamide derived from 2,5-disulfamide acid-substituted-1,4-tetraphthalic acid and diaminodiphenylether produced a tough and thermostable membrane, which displayed the proton conductivity of  $10^{-2}$ – $10^{-3}$  S cm $^{-1}$  in the temperature range of 30–180 °C under dry conditions. The “sulfamide acid” R–CO–NH–SO $_3$ H is a novel protonic source which is characterized by the remarkably high proton dissociation capability in a water-free state due to its  $\pi$ -conjugated chemical structure. The polyamidesulfamide acid also behaved as a super acid in the dry membrane state to realize a high proton conductivity with a significantly low activation energy.

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## Hydrogen-Bond Mediated Self-Assembly of Macromolecules

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A series of heterocyclic molecular units containing complementary sets of donor-acceptor hydrogen bonding arrays (DDA-AAD and DAD-ADA) were designed to self-assemble into supramolecular aggregates. Depending on the position and the specific angles between hydrogen bonding motifs, these units were able to direct the formation of either cyclic or star-shaped macromolecular structures. To investigate the ability of these units in promoting the self-assembly of dendrimers, a series of first, second, and third generation Fréchet-type dendrons were synthesized with the core attached to the non-hydrogen bonding site of this moiety. Studies using  $^1\text{H}$  NMR, size exclusion chromatography and dynamic light scattering technique support the cooperative formation of cyclic hexamers in solution. The stability of these self-assembled dendrimers depends on the size of the tethered dendron and the solvent polarity. Organization of these self-assembled units into higher-level supramolecular architectures, such as discotic liquid crystalline phase, was also demonstrated.

## Chemistry of Ketene *N,O*-Acetals and Enolates

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Chemistry of chiral enolates has been developed during a few decades. Numerous enolates have been investigated and some of them have been studied in detail and applied to the natural product synthesis. However, there are few precedents to construct a tetra-substituted carbon and are also few to study ketene *N,O*-acetals. During research of such problems, we have developed some new chiral enolate chemistry. The enolates and ketene *N,O*-acetals in Figure 1 showed specific features. The enolates **1**, **2**, and the ketene *N,O*-acetal **3** afforded the products having a tetra-substituted carbon with high stereoselectivity, and ketene *N,O*-acetals **3** and **4** exhibited the remote stereinduction at the  $\gamma$ -position.<sup>1-5</sup>

These chemistry have been applied to the syntheses of compounds

Figure 1

shown in Figure 2.<sup>6-8</sup> The origin of the high stereoselectivity will also be discussed.

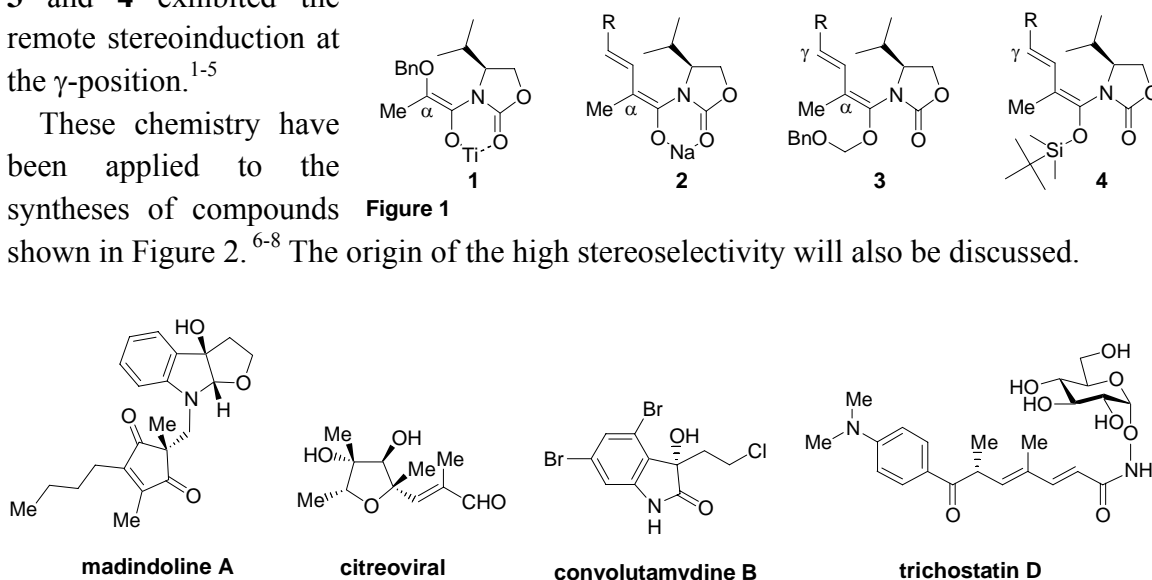


Figure 2

**Acknowledgments.** Financial support from the 21COE “Practical Nano-Chemistry” from MEXT, Japan is gratefully acknowledged.

- [1] Yoshihisa Murata, et al., *Tetrahedron Letters*, **43**, 8021-8023 (2002).
- [2] Tomoaki Abe, et. al., *Tetrahedron Letters*, **44**, 9303-9305 (2003).
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- [8] Tomoaki Nakamura, et. al., *Organic Letters*, **8**, 677-679 (2006).

## Research Trends in Advanced Crystallization Engineering

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We are striving to develop an environmental friendly crystalline product of a desired quality as a 21<sup>st</sup> century material for biotechnological and environmental use. To make crystals in a solution (known as crystallization), supersaturated condition is necessary to produce seeds of a crystal (crystal nuclei). These seeds are grown to cultivate large crystals. By controlling the number of seeds and their growth rate during this process, it is possible to control the size, shape and structure of the crystals. While crystals are inanimate, they appear like living organisms that are born as seeds and grow as if they are alive. We have organized projects below and also heat storage process development (storing heat utilizing the latent heat of crystallization).

**Environment and Recycling:** We are constructing processes that are capable of not only removing but also recovering substances that have adverse affects on the environment, including such nutrients as ammonium and phosphate and such industrial emissions as fluoride and metal ions, on the new concept of nm crystal agglomeration.

**Creation of Nano-Crystals:** Crystals in the nano-size ( $10^{-9}$  m) range have a large surface area per gram and exhibit functions that are not seen in larger crystals. We are trying to produce a crystal of this size in a highly supersaturated region. In order to produce functional crystals (such as those that emit blue or red fluorescence or those with a confined distribution of nano-size particles), we are attempting to produce nano-size crystals, focusing on crystallization with polyelectrolyte, controlling nucleation with the presence of heterogeneous crystals, and nucleation induced by ultrasonic waves.

### **Controlled Crystallization of Pharmaceuticals (API) and Organic Substances:**

Many crystalline products in pharmaceuticals are hydrophobic and, hence, cannot be dissolved or absorbed in the human body efficiently. Accordingly, it is important to obtain crystals having a desirable solubility and nano-size crystals. We are conducting research aimed at creating such crystals.

**Acknowledgments** Financial support from the 21COE “Practical Nano-Chemistry” from MEXT, Japan is gratefully acknowledged.

<http://www.waseda-appchem.jp/lab/hirasawa.html>

<http://www.sci.waseda.ac.jp/research/BELONG/E/01705.html>

## Creation of Inorganic Nanostructures Using AFM Dip-Pen Nanolithography

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Dip-Pen Nanolithography (DPN) utilizes the tiny water meniscus forming spontaneously in the tip-substrate system as the transport media to deposit materials from the tip to the substrate. This technique has been widely used in patterning organic and bio- molecules. However, it is not so suitable for patterning inorganic materials with the normal DPN. Here, a few novel DPN processes for preparing inorganic nanopatterns were developed.

A DPN process capable of depositing nanoscaled structures of semiconducting CdS materials was developed by careful control of the reaction speed between the precursors. The new development expanded the scope of the powerful DPN process and provided more insight in the deposition mechanism. Features ranging from several hundreds of nanometers to sub-50 nanometers were generated and characterized. The effects of the surface property of the substrate, the relative humidity, the translating rate, and the temperature were systematically investigated. X-ray photoelectron spectroscopy (XPS) was used to verify the chemical composition of the patterns. In principle, this simple and convenient method should be applicable to deposit various metal sulfides on suitable substrates.

A fast DPN process for directly patterning inorganic nano-clusters was proposed. With this method, one can deposit nanoclusters onto the specific area at the speed of tens of microns per second, which is as high as 10K times of the normal DPN process.

The DPN technique was also used to deposit nanomaterials onto the specified location at nano-meter-scaled precision.

## Poster Session:

- P-1. "Synthesis and Conductive Characteristics of Phenoxyl Radical-Substituted Polythiophenes" Manabu Tanaka (Waseda Univ.)
- P-2. "Radical Polymer and Its Application to a Non-Volatile Memory" Yasunori Yonekuta (Waseda Univ.)
- P-3. "Highly Efficient Red-Emitting Materials by Fluorescence Resonance Energy Transfer and Steric Effect" Xiao-Fei Duan (Peking Univ.)
- P-4. "Nanosized Gradient  $\pi$ -Conjugated Thienylethynylene Dendrimers for Light-Harvesting: Synthesis and Properties" Jin-Liang Wang (Peking Univ.)
- P-5. "Synthesis and Electronic State of Nitroxide Diradicals Bearing a Triarylamine Moiety" Kenichiro Koshika (Waseda Univ.)
- P-6. "Photoreactions of Triphenylamine (TPA) Derivatives with Chloroalkane Compounds, and the Self-assembly of TPA Derivative in Dodecane" Kai-Bo Li (Peking Univ.)
- P-7. "Total Synthesis of (+)-tubelactomicin A" Masashi Seki (Waseda Univ.)
- P-8. "The Synthesis Study of Micrandilactone A : Yandong Zhang (Peking Univ.)
- P-9. "Direct Growth of Carbon Nanotube Junctions by a Two-step Chemical Vapor Deposition" Zhong Jin (Peking Univ.)
- P-10. "Investigation of Primary Nucleation Phenomena -Crystallization of Aspirin in the Supercooled Solution Affected by Ultrasound" Etsuko Miyasaka (Waseda Univ.)