

CAMPUS ASIA PROGRAM

CAMPUS ASIA SENDAI SYMPOSIUM

BOOK OF ABSTRACTS



December 17 2012
Tohoku University Aobayama Campus
Aobayama Memorial Hall

Campus Asia Sendai Symposium

December 17, 2012

Tohoku University Aobayama Campus

Aobayama Memorial Hall

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- 9:10-9:50 Heon Kang, Seoul National University, Korea
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- 9:50-10:30 Akihiro Morita, Tohoku University
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- 10:40-11:20 Shunchao Gu, Shanghai Jiao Tong University
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- 11:20-12:00 Hiroshi Inomata, Tohoku University
New Particle Powder Formation from Aqueous Solutions Using High Density Carbon Dioxide
- 12:00-13:30 Lunch Break
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- 14:10-14:50 Ilya Gridnev, Tohoku University
Mechanism of Enantioselection in Asymmetric Catalytic Reactions
- 15:00-15:40 Byeang Hyeon Kim, POSTECH, Korea
Fluorescent Nucleic Acid Systems: Design and Construction
- 15:40-16:20 Takehiko Wada, Tohoku University
Novel Strategy for Cancer Cell Specific Oligonucleotide Therapeutics with Intracellular Environmental Condition Responsible Artificial Nucleic Acid: Peptide Ribonucleic Acids (PRNA)
- 16:30-17:10 Li-Min Zheng, Nanjing University
Modulation the Magnetic Behaviors of Metal Phosphonates
- 17:10-17:50 Masahiro Yamashita, Tohoku University
Quantum Molecular Spintronics Based on Multiple-Decker Phthalocyanato Lanthanide(III) Single-Molecule Magnets
- 17:50-18:00 Closing remarks
- 18:30~ Conference Dinner (Shikisai restaurant)

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Heon Kang leads a surface science research group at SNU. He received his BSc from Seoul National University (SNU) and a Ph.D. in Physical Chemistry from the California Institute of Technology for his study of gas-phase ion chemistry under the supervision of Prof. Jack Beauchamp. After working on low-energy ion–surface interactions as a postdoc with Prof. J. Wayne Rabalais at the University of Houston, he joined the chemistry faculty of POSTECH in 1987. In 2001 he moved to SNU, where he is currently the director of the Center for Space-Time Molecular Dynamics.

Proton vs. Hydroxide Transport in Ice

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Ice is a unique type of solid conductor containing hydronium (H_3O^+) and hydroxide (OH^-) ions as intrinsic charge carriers. These species exist as positive and negative ion defects, respectively, in the ice lattice where they are in proton transfer equilibrium with constituting water molecules. We have explored some open questions related to the charge transport mechanism in ice: what is the relative efficiency of charge transport by positive and negative ion defects? Do they move like “mirror images” in ice with only the proton transfer directions reversed, or via intrinsically different molecular mechanisms? To answer them, we have measured the transport distances of H_3O^+ and OH^- through an ice film by placing H_3O^+ (or OH^-) at the ice film surface and its counter base (or acid) in the ice interior. The ice films were prepared at low temperature (< 100 K) in ultrahigh vacuum conditions, and the acid-base reactions were monitored with IR spectroscopy and reactive ion scattering methods. The study showed that H_3O^+ travels a substantially longer distance than OH^- in the ice [1]. This difference is explained by the occurrence of an efficient proton-relay channel (Grotthuss mechanism) for H_3O^+ , which does not exist for OH^- . Other related subjects that may be discussed in the seminar include the partition behaviors of H_3O^+ and OH^- between the ice surface and interior [2], and the acidity of adsorbed water layer on a Ru(0001) surface [3].

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Water and Ice Surfaces studied by Combination of Nonlinear Spectroscopy and Molecular Dynamics Simulation

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

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

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Soap-free Synthesis of Monodisperse Polymer Particles

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Current research of soap-free emulsion polymerization, which is suitable for synthesis of polymer particles with high purity, is reported together with fundamental aspects concerning the mechanism of this polymerization.

Conventional methods of soap-free emulsion polymerization were only applicable to the synthesis of monodisperse submicron-sized polymer particles. According to the mechanism of particle formation in the polymerization, resultant particle size distributions are expected to be strongly dependent on particle coagulation that can be controlled by electrostatic interaction between particles. This basic concept for the particle formation has led to development of a new type of soap-free emulsion polymerization that employs an amphoteric initiator in combination with pH control. This method has enabled the production of highly monodisperse polystyrene particles up to 3 μ m in a single stage polymerization. Larger particles can be produced with a simple method of monomer addition to polymerization system after the formation of particles. The new soap-free emulsion polymerization is also applicable to the polymerization of methyl methacrylate.

Recent works have shown that soap-free polymerization methods are widely applied to the synthesis of monodisperse composite particles. The examples described are magnetite (Fe₃O₄)/polystyrene polymer latex, multilayered gold/silica/polystyrene core-shell particles.

Composite particles of magnetite (Fe₃O₄)/polystyrene polymer latex were synthesized in soap-free emulsion polymerization in the presence of magnetite particles that were modified with a silane-coupling reagent, methacryloxypropyltrimethoxysilane (MPTMS), or a silane-coupling reagent, methacryloxypropyldimethoxysilane (MPDMS). The polymerization was carried out with an initiator, potassium persulfate (KPS) at different pH of the reactant solution to control heterogeneous coagulation between polymer particles and magnetite particles. The morphology of the magnetic polymer particles depended on the silane-coupling reagent. Use of the tri-functional coupling reagent MPTMS produced particles having a disk-like or concave-like shape, whereas use of the di-functional coupling reagent MPDMS produced spherical particles that had a coefficient of variation of 4.4%. The colloidal dispersion stability of magnetic polymer particles was improved by the addition of an ionic monomer, sodium p-styrenesulfonate (NaSS) during the polymerization.

A new composite particle synthetic method which combined silicon alkoxide polymerization, surface modification reaction, heterogeneous polymerization reaction was proposed. This method is to prepare monodisperse mono-core composite particle which the center is gold/silica composite particle, and the outside is organic polymer. To begin with, the nano fine gold particle was made to be a nucleus, and it was encapsulated with silica by hydrolysis and condensation reaction of the silicon alkoxide. In continue, for gold/silica particle, surface treatment was carried out by the silane-coupling reagent with reactive vinyl group. In addition, the organic monomer was

added, and gold/silica particle was encapsulated with organic polymer by the polymerization reaction. In order to prevent the aggregation of the particles in the polymerization reaction, the reactive surfactant was also added. The present method was examined in the polymerizations of styrene using potassium persulfate (KPS) as initiator, methacryloxypropyltrimethoxysilane (MPTMS) as surface modification reagent, and p-sodium styrenesulfonate as surfactant in ethanol solution. By selecting adequate conditions of reaction such as initiator concentration, silane coupling agent and surfactant concentration, it was possible to get gold/silica/polystyrene monodisperse mono-core encapsulation particle by the convenient operation. The thickness of the polystyrene layer could be controlled by adjusting the quantity of the addition styrene monomer, while the monodispersity of the composite particle size distribution was maintained.

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He was a research associate in Tohoku University from 1984 to 1989, a lecture from 1989 to 1992, and an associate professor in Tohoku University from 1992 to 1997. He spent a year as a visiting research associate at Princeton University in 1995, working with Prof. Pablo Debenedetti. He was promoted to a professor of Tohoku University in 1997.

His research interests high pressure fluid properties including supercritical fluids, and thermodynamic modeling of fluids and supercritical fluid technology. On-going projects on supercritical fluid are cleaning process, high performance filter recycling, polymer processing, solvent free spray painting, natural plant extraction/separation, catalyst preparation, polymer chemical recycle, upgrading crude oil, wet oxidation of biomass, etc.

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New Particle Powder Formation from Aqueous Solutions Using High Density Carbon Dioxide

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A new drying process of nano-particles dispersed in aqueous solutions by using high density carbon dioxide was proposed to produce metal/metal oxide fine particles powder. This proposed method is composed of aqueous colloid formation by rapid mixing of high density carbon dioxide and sample aqueous solution, and successive expansion spraying by depressurizing the colloidal solution, in which CO₂ is used as both an aqueous colloid dispersing solvent and also a compressible fluid for spraying. Through this, it would be expected to control the particles aggregation. This idea was supported by previous reports on micromixer in hydrothermal reaction [1] and RESS process of supercritical CO₂ [2][3].

An experimental setup was built based on the proposed idea and verified with zirconia 8nm-particle aqueous solutions. The aqueous colloidal content was set to be more than 10wt% from an industrial viewpoint, which is extremely high in high density CO₂ phase compared with that from thermodynamic solubility of water into carbon dioxide. Therefore the aqueous colloids tend to aggregate shortly and to induce macroscopic phase separation. The proposed idea focuses on the time scale of such unstable colloids and aims to spray the colloids in CO₂ media via a nozzle within a very short time before starting colloid aggregation. In addition, the sprayed colloids could be broken down into small droplets and frozen due to Joule-Thomson expansion of high density CO₂ through the nozzle.

The experimental results revealed the validity of our idea and indicated that we can produce powders of nano-particles with controlling particle aggregation.

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Novel Chiral Ligands and Catalysts For Efficient Asymmetric Catalytic Reactions

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Recently, we are interested in the design of novel, efficient and high-usage chiral ligands and catalysts. Several kinds of chiral ligands and catalysts with novel design concepts were developed by us successfully (Figure 1). When these ligands and catalysts were used in several important asymmetric catalytic reactions, excellent results were obtained [1-5].

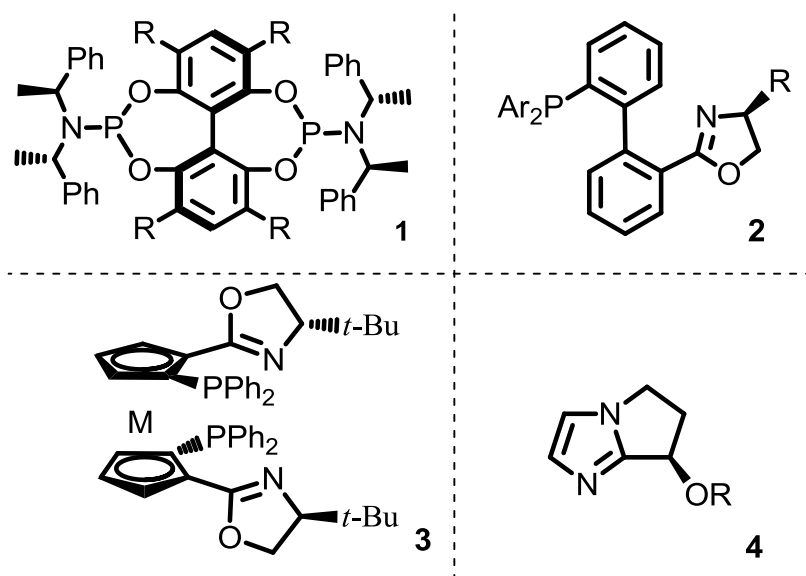


Figure 1. Excellent Chiral Ligands and Catalysts Developed by Zhang Group

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Mechanism of Enantioselection in Asymmetric Catalytic Reactions

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

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

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

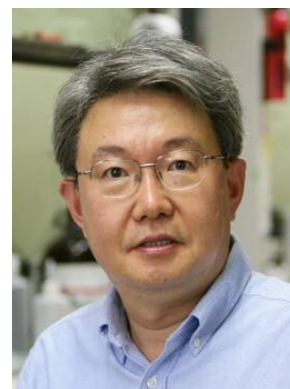
Soai's autocatalytic alkylzinc alkylation is practically the only example of the chemical reaction that effectively amplifies chirality of its own catalyst. Revealing the exact chemical mechanism of its operation is important for the understanding of the origin of chiral life on the Earth. We have used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

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Selected Publications

1. I. J. Lee and B. H. Kim, "Monitoring i-motif transitions through the exciplex emission of a fluorescent probe incorporating two PyA units", *Chem. Commun.*, **2012**, 48, 2074.
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Fluorescent Nucleic Acid Systems: Design and Construction

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Fluorescent nucleic acid systems are widely applied in various fields, from fundamental biological probes to nano-construction.^[1] Nucleic acids are used as a scaffold for arranging aromatic fluorophore assemblies, either by insertion into the DNA base pairs or by stacking via the duplex. Moreover, chemical modifications of nucleic acids are accessible by the modified DNA phosphoramidites or postsynthetic approach, and provide with new and interesting fluorescent nucleic acid systems. Fluorescent nucleic acid systems represent an extensive and exciting research area in chemistry as well as in biotechnology and photophysics. We synthesized and investigated new fluorescent nucleic acid systems for probing single nucleotide polymorphisms (SNPs),^[2] structural changes of DNA,^[3] ligand interaction with RNA bulge, and applying various optical devices.

We have developed the new type of molecular beacon, quencher-free molecular beacon (QF-MB), that exhibits several advantageous features, including a high level discrimination between the target and its single-mismatched congeners and an economical device set-up due to the absence of the quencher. We have also designed and synthesized the probing system for quadruplex structures of DNA, G-quadruplex and i-motif, and B-Z transition.

Strong π - π stacking interactions in nucleic acids can be used to generate novel secondary structures. We investigated the fluorescent phenomena and structures of pyrene modified oligodeoxyadenylate and oligodeoxyguanylate. The covalently linked pyrenes induced the formation of a self-assembled oligodeoxyadenylate duplex^[4] and divergent structures of oligodeoxyguanylate with unique fluorescence phenomena.^[5]

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Novel Strategy for Cancer Cell Specific Oligonucleotide Therapeutics with Intracellular Environmental Condition Responsible Artificial Nucleic Acid: Peptide Ribonucleic Acids (PRNA)

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We have recently proposed a new strategy and a practical tool for cancer cell specific gene therapeutic artificial nucleic acids, named Peptide Ribonucleic Acids (PRNAs) with active *on-off* control of miRNA function corresponding the cancer cell specific intracellular environmental condition. The PRNAs can be actively switching the target miRNA complexation behavior by a low oxygen concentration of the cancer cellular cytoplasm. This strategy utilizes a new category of artificial nucleic acid that carries a ribonucleoside unit tethered to a peptide backbone as a recognition and stimulus-sensitive module. In this artificial nucleic acid called peptide ribonucleic acid (PRNA), the 5'-amino-5'-deoxypyrimidine ribonucleoside unit, which is in the anti conformation in normal cellular cytoplasm condition in the presence of borate, but functions as a built-in switch to be triggered by a low oxygen concentration of the cancer cellular cytoplasm, is attached to the alpha-glutamine backbone as a pendant. Under normal cellular cytoplasm condition, the cis-2',3'-diol of ribose forms a cyclic borate ester with phenyl boric acid moiety of the PRNA to switch the nucleobase orientation from anti to syn through the change in sugar puckering to 2',3'-planar-O4'-exo synchronized with the hydrogen-bond formation between the 5'-amide proton of ribose and the 2-carbonyl oxygen of pyrimidine nucleobase. The results obtained in these studies are promising, validating that the original alpha-PRNAs with anti-oriented nucleobases form stable complexes with the target miRNA under low cytoplasm pH (pH = ca. 6.5) of a low oxygen concentration of the cancer cell, which are readily dissociated under normal cellular cytoplasm pH (pH = ca. 7.2). This means that the PRNA strategy can be used as a powerful tool for on-off switching the miRNA complexation behavior, which is potentially applicable to the cancer cell specific oligonucleotide-based gene therapeutics of the next generation.

Nevertheless, RNA specific cleavage activities of PRNA-RNA complex with RNase H might be moderate due to a lack of negative charge of the PRNA backbone and unnatural double helical structure of PRNA-RNA complex. RNase H activities of antisense molecules would be one of the most crucial factors for practical antisense, siRNA, and miRNA related drugs.² Thus, in this study, we have been design PRNA-DNA chimera, in which both PRNA and DNA domains work as recognition sites for the complementary DNA and/or RNAs to form stable complex, while DNA-RNA hybrids formed in the DNA domains of DNA-PRNA chimera should be substrates to the hydrolysis by RNase H and PRNA moieties work as recognition control/switching devices and as inhibitor for the hydrolysis of the chimera by nuclease.

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Modulation the Magnetic Behaviors of Metal Phosphonates

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Metal phosphonates are a class of important hybrid materials which integrate the organic and inorganic components in the same molecular composites. A significant feature of these materials is that they often display layered or pillared layered structures where the organic groups fill in the interlayer spaces. But low dimensional materials can also be obtained by introducing the templates or co-ligands. During the last two decades, an increasing attention has been paid to synthesis and characterization of new metal phosphonates, owing to their potential applications in such areas as exchange and sorption, catalysis, proton conductivity, and optics etc. Magnetic materials based on metal phosphonates have been much less explored because the phosphonate group can only mediate very weak magnetic interactions, which prevents the formation of magnetic materials with high ordering temperatures. Nevertheless, the phosphonate ligands with their geometries different from the popular carboxylate ligands can be valuable candidates for the construction of low dimensional magnetic materials. A number of phosphonate-based metal clusters or chains have been reported recently, which show new architectures and interesting magnetic properties such as single molecule magnet and single chain magnet behaviors. In this presentation, we shall focus on the metal phosphonates with tunable magnetic properties, through the design of particular phosphonate ligands and the size control of layered phosphonate material.

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Selected Publications

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Quantum Molecular Spintronics Based on Multiple-Decker

Phthalocyanato Lanthanide(III) Single-Molecule Magnets

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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⁾

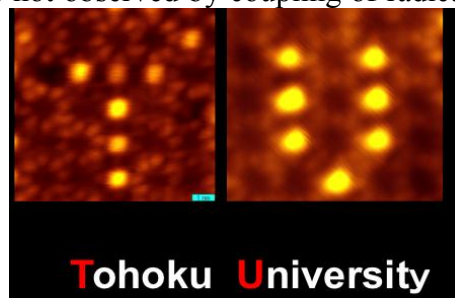


Fig. Initials of Tohoku University

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