

The 21st Nano Bio Info Chemistry Symposium

December 5-6, 2024

Overview:

The 21st Nano Bio Info Chemistry Symposium will be held at the Library Hall of Central Library, Hiroshima University, December 5th Thu - 6th Fri, 2024.

Organizers

- Chairperson
Katsuya INOUE (CResCent, WPI-SKCM2 , Hiroshima University)

- Co-Chairperson
Goulven COSQUER (CResCent, WPI-SKCM², Hiroshima University)
Satoru MURAMATSU (Hiroshima University)
Kyota YASUDA (WPI-SKCM², Hiroshima University)

Co-organizers

The Chugoku Shikoku Branch, The Chemical Society of Japan
The Chugoku Shikoku Branch, The Society of Synthetic Organic Chemistry, Japan
The Chugoku Shikoku Branch, The Japan Society for Analytical Chemistry
The Chugoku Shikoku Branch, The Spectroscopical Society of Japan
International Institute for Sustainability with Knotted Chiral Meta Matter

Contributions

Alumni Association of Department of Chemistry, Hiroshima University
The Chugoku Shikoku Branch, The Chemical Society of Japan

2024 December 5 th Thursday		
13:30	Opening Address	
	Chairman : Satoru MURAMATSU	
13:40	1A1a	Shunsuke TAKANO
		Thermomechanical Coupling Influenced by Intertwined Skyrmions
14:00	1A2b	Takayuki SHIGENAGA
		Harnessing Skyrmion Hall Effect by Thickness Gradients in Wedge-Shaped Samples of Cubic Helimagnets
14:15	1A3b	Yuki MATSUSHITA
		The properties of the field-stabilized bimerons in cubic helimagnets
14:30	1A4b	Kaito NAKAMURA
		Mechanism of skyrmionium stability
14:45	BREAK	
	Chairman : Katsuya INOUE	
15:00	1B1a	Ali HAIDER
		Textile-Like Structure of Skin: A Chiral Investigation of Skin Aging from Homochirality to Heterochirality
15:20	1B2IL	Hikaru YABUTA
		What asteroid Ryugu samples told us
16:10		

a: 20 min presentation including Q&A

b: 15 min presentation including Q&A

IL: 50 min presentation including Q&A

2024 December 6 th Friday		
	Chairman : Kyota YASUDA	
9:00	2A1b	Truc Minh Thanh GIANG
		Crystal Growth of Layered Chiral Inorganic Magnets Using Chemical Transport Method
9:15	2A2b	Yuma NAKAMURA
		Development of Photo-Degradable Supramolecular Graft Polymer Gels Formed by Molecular Recognition of Cavitand-Based Self-Assembled Capsule and Guest-Attached Polyester
9:30	2A3b	Keisuke YUKAWA
		Effect of thiolate ligand on core structures of cadmium-sulfide clusters studied by collision-induced dissociation mass spectrometry
9:45	2A4b	Toshiki SHIROUCHI
		Synthesis of a Pincer-type Bis(boryl) Ligand and Reaction with Pt(PtBu ₃) ₂
10:00	BREAK	
	Chairman : Goulven COSQUER	
10:15	2B1a	Chi-Chun CHEN
		SeqCP: A sequence-based algorithm for searching circularly permuted proteins
10:35	2B2IL	Makoto INOKUCHI
		Shear Stress Effect on Organic Crystals
11:25	Closing Remark	

a: 20 min presentation including Q&A

b: 15 min presentation including Q&A

IL: 50 min presentation including Q&A

Thermomechanical Coupling Influenced by Intertwined Skyrmions

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In turbines, the flow of water vapour drives the blades to rotate and produce electrical power. The chiral shape of the turbine blades functions to convert the translational flow into rotational motion. This conversion phenomenon also appears on smaller scales at the molecular level: chiral liquid-crystalline molecules exhibit collective precessions by the permeation of alcohol vapour;¹ and even the heat flow induces the rotation of the molecules.² The latter is called thermally driven rotation and is explained by two theories on the thermomechanical coupling, i.e. Leslie theory and Akopyan–Zel’dovich theory.³ While Leslie theory argues that the chirality of the molecule itself allows the generation of torques driven by the heat flow, Akopyan–Zel’dovich theory considers the twist deformation of the molecular alignment, which extends over 10^3 times larger than the molecules. The rotation direction is inverted when the twist sense is opposite, which is demonstrated for chiral spiral arrangement of a liquid crystal formed with achiral molecules.⁴

Thermally driven rotation is well-investigated for cholesteric phases belonging to the D_∞ point group, whose geometry includes the coexistence with the isotropic phase^{2,4} or heterogeneous emulsions.^{5,6} Here we focused on a cholesteric phase dispersed in glycerol, which does not mix with the liquid crystalline phase and imposes the planar anchoring at the interface. The cholesteric phase forms spherical droplets to minimise the interfacial free energy and self-organise a spiral arrangement around the radial axis, such that the longitudinal axis of the molecules lay parallel to the interface.⁷ Poincaré–Hopf theorem predicts the generation of topological defects with the total winding number equal to Euler characteristics of the two-dimensional sphere. The stable structure has a single topological defect with the winding number +2, composed of a pair of half-skyrmion cylinders intertwined with each other. We observed that the rotational behaviour of the cholesteric phase depends on the radius of the droplet, in particular, smaller droplets rotate in the opposite direction to larger droplets. This reversal possibly originates from the intertwining direction of the skyrmions. As is generally known that yarns become stable and tear resistant when intertwined in the opposite direction to the torsion direction of the fibres, for the cholesteric phase, the skyrmions intertwined in the opposite direction to the surroundings ensure the structural stability.⁷ Thus, the topological defect induces Akopyan–Zel’dovich thermomechanical torque in the opposite direction to the surroundings. Since the volumetric fraction of the defect increases as the radius of the droplet decreases, the rotation direction switches in a radius-dependent fashion.

1 Tabe, Y.; Yokoyama, H. *Nat. Mater.* **2003**, *2*, 806.

2 Oswald, P.; Dequidt, A. *Phys. Rev. Lett.* **2008**, *100*, 217802.

3 Akopyan, R. S.; Zel’dovich, B. Y. *Sov. Phys. JETP* **1984**, *60*, 953; Pleiner, H.; Brand, H. R. *Hydrodynamics and Electrohydrodynamics of Liquid Crystals*. In *Pattern Formation in Liquid Crystals*; Buka, A.; Kramer, L., Eds.; New York: Springer, 1996; pp 15–67.

4 Ignés-Mullol, J.; Poy, G.; Oswald, P. *Phys. Rev. Lett.* **2016**, *117*, 057801.

5 Yoshioka, J.; Araoka, F. *Nat. Commun.* **2018**, *9*, 432.

6 Takano, S.; Bono, S.; Tabe, Y. *J. Phys. Soc. Jpn.* **2023**, *92*, 024601.

7 Seč, D.; Porenta, T.; Ravnik, M.; Žumer, S. *Soft Matter* **2012**, *8*, 11982.

Harnessing Skyrmion Hall Effect by Thickness Gradients in Wedge-Shaped Samples of Cubic Helimagnets

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Magnetic skyrmions are particle-like topological excitations with complex non-coplanar spin structure [1]. Recently, they have been observed in conducting and insulating helimagnets [2] as well as in frustrated (centrosymmetric) materials [3] under an applied magnetic field. Small size, topological protection and the ease with which isolated skyrmions can be manipulated by electric currents generated much interest in using them as information carriers in nanoscale memory and logic devices [4]. In this study [5], we investigate the properties of skyrmions in wedge-shaped nanostructures, which have not been well studied, in comparison with those of skyrmions in thin films.

I. Static properties: “pitstop” phenomenon

Skyrmions in thin films are more stable than those in bulk, which is attributed to chiral magnetic twists that occur near the free surface of skyrmions in thin films [1, 6]. However, when the film thickness is very thin, the two surface twists overlap, reducing rather than enhancing the stability of skyrmions. The fact that the stability of skyrmions is thickness-dependent and that the overlap of surface twists produces an eigen-energy minimum of skyrmions suggests that there is the energy minimum in wedge-shape nanostructures.

In addition, the edge state in thin films also has significance for the stability of skyrmions. This edge-skyrmion interaction (repulsion) attempts to keep skyrmions in thin films in racetrack memory using skyrmions. This repulsion decreases with the distance of skyrmions from the edge and eventually becomes constant (Fig. 1. (a)). At thin edges in wedge-shaped nanostructures, there are complex magnetic states that differ from those in thin films, and the edges are repulsive to skyrmions as in thin films. Above a certain film thickness, the stability of skyrmions decreases, resulting in an energy barrier. As a result, there is a local energy minimum in wedge-shaped nanostructures below a certain angle (Fig. 1. (b)).

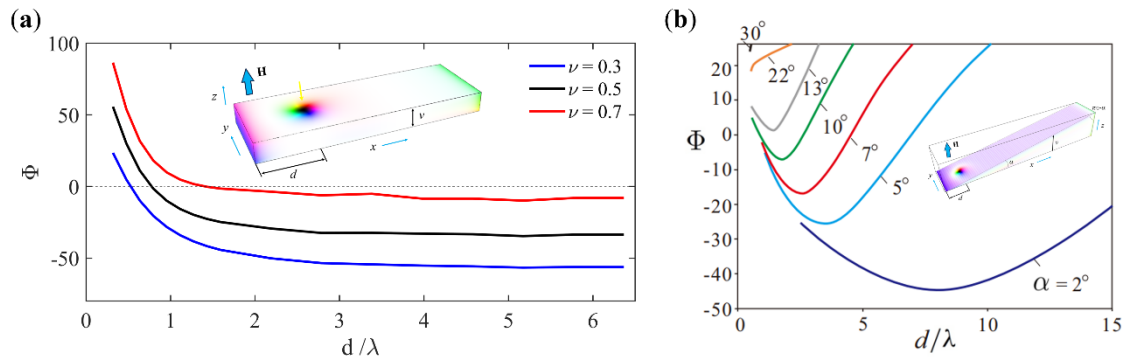


Figure 1. Edge-skyrmion interaction potentials in thin films with different thickness ν (a) and in wedge-shape nanostructures with different angle α (b).

II. Dynamic properties: trajectory splitting

The skyrmion Hall effect (SHE), in which the trajectory of moving skyrmions is curved due to lateral skyrmion deflections, is a hurdle in the practical application of racetrack memory based on skyrmions [7, 8] (Fig. 2. (a)). As one way to overcome this SHE, it is theoretically shown that the skyrmion Hall effect can be suppressed in wedge-shaped nanostructures of cubic helimagnets (Fig. 2. (b)). Under an applied electric current, ordinary isolated skyrmions with the topological charge 1 were found to move along the straight trajectories parallel to the wedge boundaries. Depending on the current density, such skyrmion tracks are located at different thicknesses uphill along the wedge. Numerical simulations show that such an equilibrium is achieved due to the balance between the Magnus force, which instigates skyrmion shift towards the wedge elevation, and the force, which restores the skyrmion position near the sharp wedge boundary due to the minimum of the edge–skyrmion interaction potential. Current-driven dynamics is found to be highly non-linear and to rest on the internal properties of isolated skyrmions in wedge geometries; both the skyrmion size and the helicity are modified in a non-trivial way with an increasing sample thickness. Our results are useful from both the fundamental point of view, since they systematize the internal properties of isolated skyrmions, and from the point of view of applications, since they point to the parameter region, where the skyrmion dynamics could be utilized.

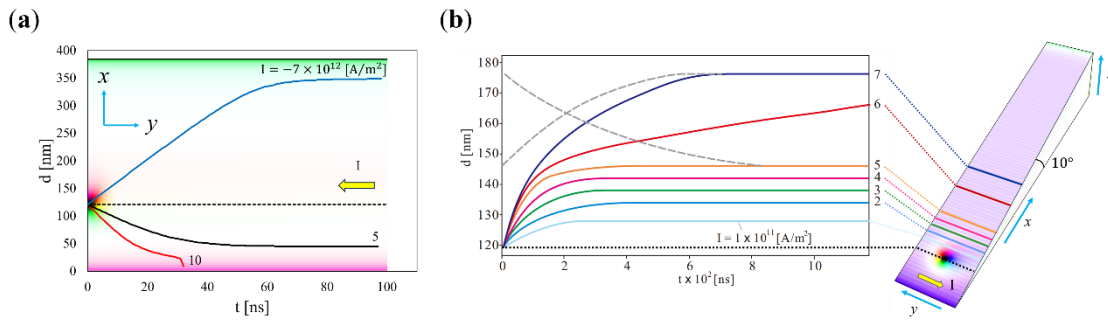


Figure 2. The trajectories of moving isolated skyrmions for different current values as the time-dependent curves in thin films (a) and in wedge-shape nanostructures (b).

References:

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- [5] T. Shigenaga, A. Leonov, *Nanomaterials*, **2023**, *13*, 2073.
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The properties of the field-stabilized bimerons in cubic helimagnets

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Magnetic skyrmions [1,2] are nanoscale topological spin textures, which behave as quasiparticles within the surrounding homogeneous state and have prospects of being used as information carriers in novel spintronic devices [3]. Magnetic skyrmions are stabilized by the Dzyaloshinskii-Moriya interaction in chiral magnets, which helps to overcome the limitations of the Derrick-Hobart theorem and specifies the internal skyrmion structure.

Magnetic bimerons are topological counterparts of axisymmetric skyrmions. Since they are embraced by the in-plane magnetization, they become non-axisymmetric and represent pairs of coupled merons with the same topological charge $|1/2|$, but the opposite vorticity and polarity [4].

The in-plane “vacuum” state surrounding bimerons can be created either by the easy-plane anisotropy [5,6] or by the in-plane magnetic field. In spite of the structural similarity, two types of bimerons possess essentially different properties.

In the present study, we focus on the second type of the field-stabilized bimerons (FSBM). We analyze their static and dynamic properties and contrast them with ordinary axisymmetric skyrmions to extend their functionality for spintronics.

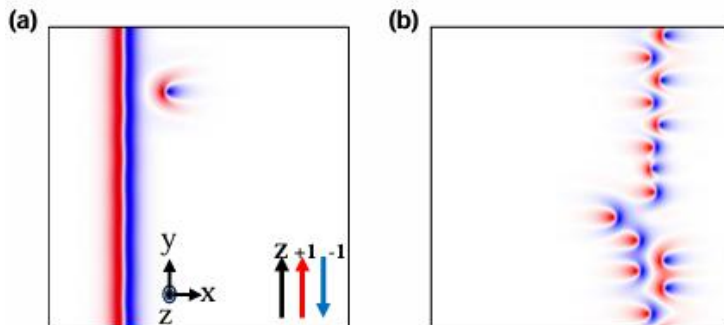


Figure 1. (a) Schematics of a current-driven bimeron approaching a 360° domain wall. (b) Transformation of a DW into congregation of bimerons with opposite polarities due to the interaction with an external himeron.

First of all, we study the inter-bimeron interaction potential which exhibits a number of local minima and enables bimeron cluster formation.

Current-driven dynamics of bimerons shows that only for selected directions of the spin-polarized current bimerons move intact whereas they are destroyed otherwise.

Interaction of bimerons with domain walls (Fig. 1) allows to consider domain walls from

different perspective as reservoirs of bimerons with opposite polarities. An approaching bimeron decouples the domain-wall bimerons and thus allows to multiply the bimeron number. To select bimerons with the same polarity, one can rotate an applied magnetic field out-of-plane and back. By this, “desirable” bimerons transform into skyrmions, whereas “undesirable” bimerons collapse.

References

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- [2] L. Bannenberg, *npj (Nature Partner Journal) Quantum Materials* **4**, 11 (2019).
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- [6] N. Mukai, Andrey O. Leonov, *Phys. Rev.* **106**, 224428 (2022)

Mechanism of skyrmionium stability

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The magnetic structure known as a skyrmion[1], which appears in chiral magnetic materials with broken space-inversion symmetry, is expected to be applied in magnetic storage media such as racetrack memory[2], due to its topological stability and small size. A related structure that has recently attracted attention is the skyrmionium[3], which contains skyrmions of opposite polarities within a single structure. Since the topological invariants of these skyrmions are opposite in sign, the total topological invariant of the skyrmionium is zero. This suggests that skyrmioniums may not possess topological protection. However, skyrmioniums have been experimentally observed[4], and it has been shown that they exhibit some form of energy barrier.

I . The reason of energy minima of skyrmionium

In this study, we used magnetic simulations to investigate the skyrmionium's behavior and discovered that by varying its radius, an energy minimum can be obtained. We focused on the balance between the internal and external skyrmions of a skyrmionium, and discovered that this balance leads to the emergence of an energy minimum. I then used a mathematical model to prove this. The radius of the skyrmionium at which the energy minimum occurs changes with uniaxial magnetic anisotropy and magnetic field. Therefore, I aim to identify the range of uniaxial magnetic anisotropy and magnetic field where the energy minimum of the skyrmionium occurs, and represent this in a phase diagram.

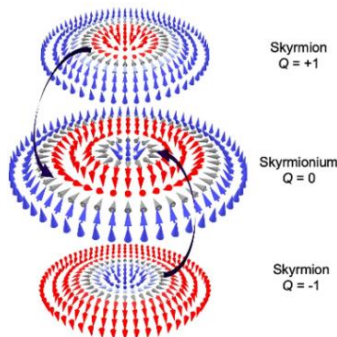


Figure 1. Magnetic structures of Skyrmionium and Skyrmion

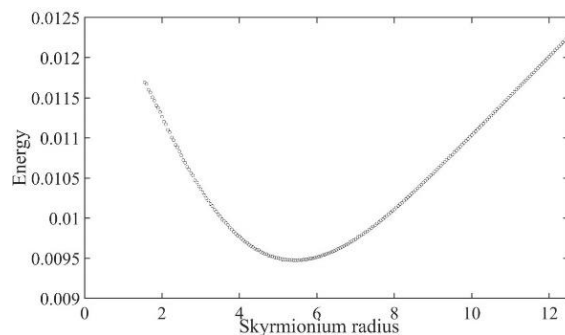


Figure 2. The plot of the radius and energy of the Skyrmionium

II. Skyrmionium lattice

We have discovered a lattice structure formed by skyrmionium. This structure is quasi-stable, similar to individual skyrmions, and consists of two types of lattices where the polarity of the central skyrmion is reversed. The skyrmionium exists in a spiral phase and has lower energy than the skyrmion lattice, which suggests that it may be more stable within this range. However, because the skyrmion lattice is quasi-stable, it tends to elongate in order to approach the spiral phase, leading to a loss of its original structure. To address this issue, we propose a solution by utilizing skyrmions instead.

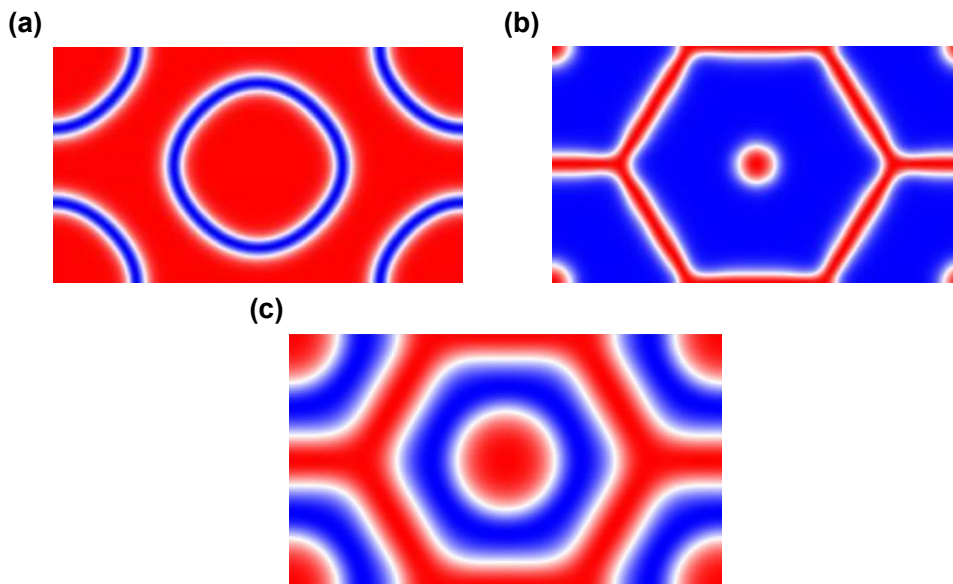


Figure 3. skyrmionium lattices in different magnetic field (a) $h=0.3$ (b) $h=-0.3$ (c) $h=0$

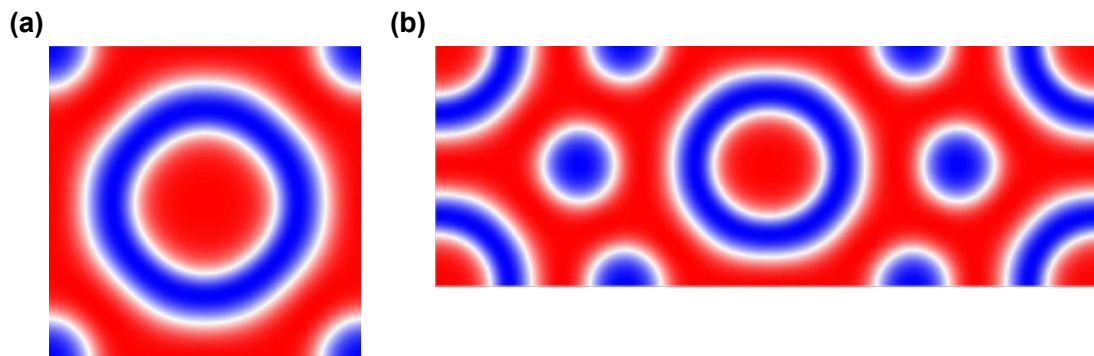


Figure 4. Skyrmionium-skyrmion mixed lattices (a) 1-skyrmion type (b) 2-skyrmion type

References:

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Textile-Like Structure of Skin: A Chiral Investigation of Skin Aging – From Homochirality to Heterochirality

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The aging process profoundly impacts the structural and functional properties of human skin, leading to visible changes such as wrinkles and reduced elasticity. At the molecular level, these changes are closely tied to alterations in collagen fiber organization and peptide chirality. Our research employs advanced spectroscopic techniques, including Quantum Cascade Laser Vibrational Circular Dichroism (QCL-VCD) and Vacuum Ultraviolet Circular Dichroism (VUV-CD), to investigate the intricate relationship between aging and the textile-like structure of skin. By analyzing skin samples from young, middle-aged, and elderly, we aim to decipher how homochirality transitions to heterochirality and how these shifts influence collagen fiber alignment and peptide secondary structures, such as alpha-helices and beta-sheets. Preliminary results reveal significant age-related modifications in both molecular chirality and fiber arrangement, giving a deeper understanding of the structural and biochemical transformations occurring in aging skin. Comparative analyses with model proteins, including keratin and elastin, serve as benchmarks to validate our findings and establish correlations between peptide chirality and the mechanical properties of skin. Prospects of this work involve advancing from mesoscale observations to the molecular scale. By employing mathematical modeling and machine learning, we aim to map the molecular chirality of peptides and unravel the precise textile structure of collagen fibrils at a nanoscale. This multidisciplinary framework bridges spectroscopy, molecular modeling, and computational science to uncover the secrets of skin aging and foster novel solutions for regenerative medicine and material science applications.

What asteroid Ryugu samples told us

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Hayabusa2 is JAXA's asteroid sample return mission that targeted the carbonaceous (C-type) asteroid (162173) Ryugu. The mission aims to unveil the origin and evolution of organic compounds and water in the early Solar System as life's building blocks [1]. Following the arrival of the Hayabusa2 spacecraft at Ryugu on June 27, 2018, observations by onboard remote sensing instruments revealed that Ryugu is a top-shaped asteroid with a very low geometric albedo [2-4] and that its surface is probably partially dehydrated [5]. The Mobile Asteroid Surface Scout (MASCOT) lander observed two types of boulders on the surface of Ryugu: one type was dark and cauliflower-like with a similar morphology to primitive carbonaceous chondrites, and another type was bright and smooth [6]. The lander's radiometer revealed that Ryugu has low thermal conductivity and high porosity unlike any chondritic meteorites, while these thermal properties have similar values to comets [7]. Thanks to the formation of the artificial crater on Ryugu's surface by a small carry-on impactor [8], two successful touchdowns on February 22 and July 11, 2019 have enabled collections of samples from two distinct locations on the asteroid, providing an advantage for investigating the origin and evolution of the Solar System as well as the surface processes of the asteroid. After the sample return on December 6, 2020, the curatorial work on the Ryugu sample has been conducted at JAXA for the first 6 months [9]. With the significant guidance from the observations and curation, the initial sample analysis has a one-year mission from June 2021 to June 2022 to address the question of what kind of asteroid Ryugu is. In this talk I will review the results from the initial sample analysis of the Ryugu samples.

References:

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Crystal Growth of Layered Chiral Inorganic Magnets Using Chemical Transport Method

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Intercalated transition metal dichalcogenides (I-TMDCs) have emerged as promising candidates for exploring novel physical phenomena including non-trivial spin textures and topological magnetic phases, which are essential for spintronic and quantum information applications. Among these materials, the intercalation of the *3d* transition metals into the van der Waals gaps significantly influences a new paradigm of layered chiral materials, offering fascinating opportunities for exploring unconventional magnetic phenomena, particularly chiral solitons and the phase transition. The tunability of the magnetism in these systems is limited by their fixed relatively stoichiometric. The quantity of intercalant plays an important role in determining the magnetic transition temperature, with increasing intercalant concentration generally enhancing the magnetic interactions and thereby affecting the phase transition. This correlation arises from the modulation of electronic and structural parameters, which alter the magnetic exchange interactions within the I-TMDC matrix. Specifically, the intercalation modifies the spacing and symmetry of the layers, affecting the super-exchange pathways and anisotropy, crucial for magnetic ordering.

The motivation to integrate these insights into the development of I-TMDCs is driven by the potential to harness similar mechanisms to achieve enhanced magnetic and superconducting properties. By strategically intercalating specific elements that induce chiral magnetic states and leveraging spin-orbit coupling, it is possible to create I-TMDCs with tailored magnetic transition temperatures and robust long-range spin-triplet superconductivity. The growth process employs a systematic approach to intercalated transition metal species into a host van der Waals layer, leveraging the capability of the chemical vapor transport method to optimize chiral symmetry, intercalant concentration, and defect density. This approach not only aims to develop materials with superior magnetic characteristics but also seeks to expand the fundamental understanding of the interplay between intercalation, magnetism, and superconductivity in low-dimensional systems.

References

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- [2] G. W. Paterson, et al., *Phys. Rev. B*, **2019**, 99, 224429.
- [3] A. E. Hall, et al., *Phys. Rev. Mater.*, **2022**, 6, 024407.

Development of Photo-Degradable Supramolecular Graft Polymer Gels Formed by Molecular Recognition of Cavitand-Based Self-Assembled Capsule and Guest-Attached Polyester

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Photo-responsive polymers have attracted considerable research attention due to their potential in the development of drug delivery systems and smart windows. We have demonstrated that a cavitand-based self-assembled capsule encapsulates biphenyl guest molecules[1], which provides access to the supramolecular graft polymer poly-**H1**•poly-**G1**, which exhibits self-healing properties in the gel phase[2]. The metal coordination of bipyridine is known to be inhibited by protonation, which led us to consider that the addition of photoacid generator (PAG) to the polymer gel can allow the polymer gel to have the photodegradable nature. In this presentation, I will report on the photodegradability of poly-**H1**•poly-**G1** in the gel phase.

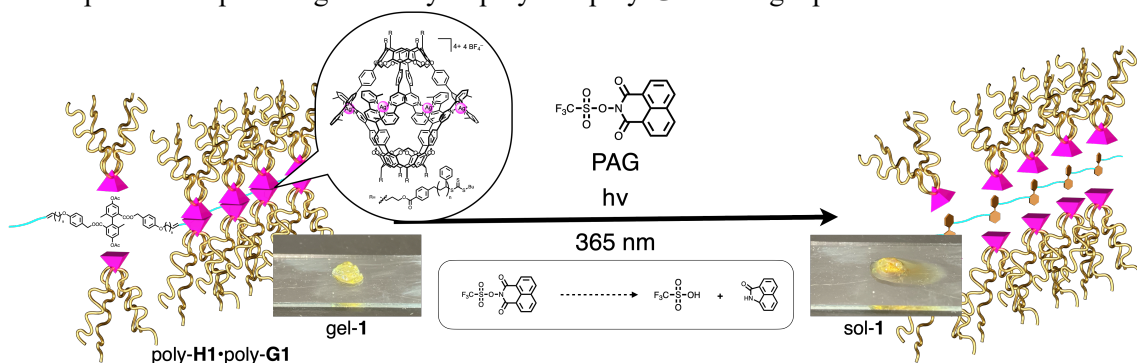


Figure 1. Strategy for the synthesis of photo-degradable polymer gels.

A mixture of poly-**H1**•poly-**G1** and PAG in 1,1,2,2-tetrachloroethane was stirred and then left for 1 hour, resulting in gel-1. Gel-1 collapsed when exposed to UV light at 365 nm (Figure 1). ¹H NMR spectra of a mixture of poly-**H1**•poly-**G1** and **PAG** before and after UV irradiation displayed discernible shifts of the resonance peaks of the bipyridine moiety; thereby, the light irradiation cleaved the dative bonds around the Ag ions. Further support for the de-metalation comes from the hydrodynamic radii of species in the solution of the mixture estimated by 2D DOSY NMR measurements. The hydrodynamic radius of the species in the polymer solution significantly decreased upon UV irradiation. These results suggest that the UV irradiation to poly-**H1**•poly-**G1** in the presence of PAG resulted in the disassembly of poly-**H1** and poly-**G1**, leading to the degradation of gel-1.

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Effect of thiolate ligand on core structures of cadmium-sulfide clusters studied by collision induced dissociation mass spectrometry

Keisuke Yukawa,¹ Satoru Muramatsu,¹ Ryo Takahata,²
Toshiharu Teranishi,² Yoshiya Inokuchi¹

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Collision-induced dissociation mass spectrometry (CID-MS) has recently gained growing interest as a powerful technique for investigating the structures and bonding characters of metal-cluster materials. For example, our recent studies on ligand-protected gold clusters have demonstrated that fission of the cluster core can be facilitated by significant structural change in the core induced by buffer-gas collisions [1]. To further extend the scope of CID-MS-based metal-cluster studies, we herein focused on a thiolate-protected cadmium-sulfur cluster, $[\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$ (Figure 1). Single-crystal X-ray diffraction analyses revealed a tetrahedral structure composed of symmetrically arranged six-membered $(\text{Cd-S})_3$ ring units [3]. We investigated how such characteristic core structures affect the dissociation patterns and energies of the clusters.

Electrospray ionization (ESI) mass spectrometry of $[\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}](\text{NMe}_4)_4$ dissolved in acetonitrile exhibited intense mass peaks of $[\text{Cd}_9\text{S}_4(\text{SPh})_{12}]^{2-}$ (**Cd9**) and $[\text{Cd}_9\text{S}_4(\text{SPh})_{11}]^{-}$ (**Cd9'**), plausibly due to facile dissociation of the target cluster $[\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$ during the desolvation process. While both **Cd9** and **Cd9'** consist of nine cadmium atoms, they possess the different number of SPh^- ligands. Strikingly, a comparison of the CID mass spectra of mass-selected **Cd9** and **Cd9'** revealed a significant difference in dissociation energy (ca.

0.25 eV), despite both producing the same dissociation product, $[\text{Cd}_8\text{S}_4(\text{SPh})_9]^-$ (Figure 2). The cause of this deviation, attributed to the difference of a single SPh^- ligand, was investigated by using quantum chemical calculations. The most stable structure of **Cd9** was calculated to adopt a three-fold symmetric pyramidal structure (C_{3v}), similar to that of $[\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$. In contrast, **Cd9'** had a lower-symmetry core structure (C_1), characterized by additional Cd-S bonds via forming several four-membered $(\text{Cd-S})_2$ units. The calculated dissociation energies of **Cd9** and **Cd9'** were 0.36 and 1.70 eV, respectively, qualitatively reproducing the above-described experimental difference. Thus, this study demonstrates that a single SPh^- ligand drastically affects the core structure and stability of cadmium-sulfur clusters.

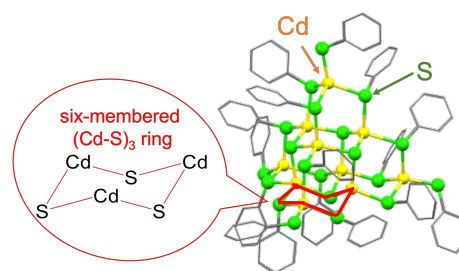


Fig. 1. Crystal structure of $[\text{Cd}_{10}\text{S}_4(\text{SPh})_{16}]^{4-}$. The Ph groups are represented by a wire frame. Inside the red box shows six-membered $(\text{Cd-S})_3$ ring unit.

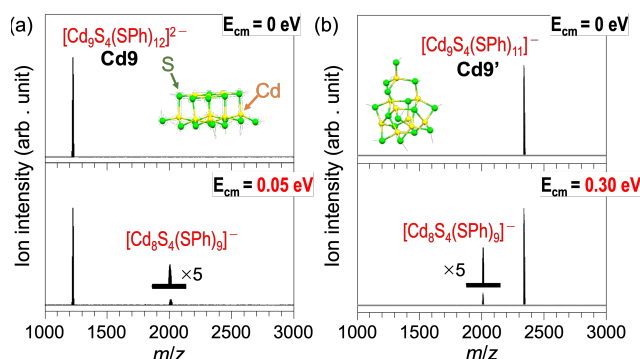


Fig. 2. CID mass spectra of (a) **Cd9** and (b) **Cd9'**. E_{cm} represents collision energy in the center-of-mass frame. Insets show DFT-optimized most stable structures while substituting the Ph groups to Me groups (wireframe).

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Synthesis of a Pincer-type Bis(boryl) Ligand and Reaction with $\text{Pt}(\text{PtBu}_3)_2$

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1. Introduction

Pincer ligands strongly coordinate to a metal center to form a stable complex, which are used as metal catalysts and luminescent materials. Pincer ligands can be categorized as neutral (L_3 -type), anionic (L_2X -type), and dianionic (LX_2 -type) systems. Among the three types of ligand systems, the LX_2 -type is the most difficult to prepare, since a neutral precursor has to be converted to dianionic form during the coordination process. While such ionization is relatively easy for electro-negative donating atoms such as O and N, examples in which donating elements are electro-positive boron are scarce. We targeted to synthesize bis(boryl) complexes (BNB pincer complexes) (**Figure 1**). By employing the boryl ligands, the polarity of the M-X bonds can be reversed from the case of the 14–16 elements (**Figure 2**). The high σ -donating ability of boryl ligand afford electron rich metals.

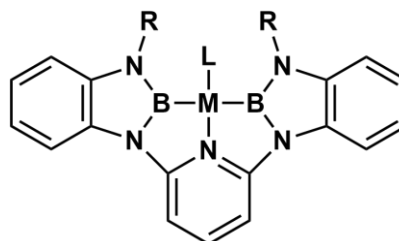
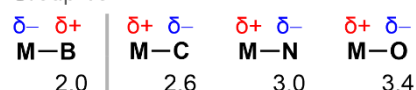


Figure 1 Target LX_2 -type pincer complex (BNB complex)

Reversed polarity on M-E bonds

Group 13



Decreasing electronegativity

← Increasing σ -donating ability

Figure 2 The polarities between the coordination atoms and metals

2. Result and Discussion

As neutral precursors of the BNB pincer ligands, we designed two types of ligands having B-Br and B-H bonds.

The compound **3b** was afforded by $\text{S}_{\text{N}}2$ reaction with **1** and iodomethane. Then, the compound **4b** was obtained by Backward Hartwig cross coupling. These compounds were purified by silica gel column chromatography.

The synthesis of compound **5b-Br** did not proceed in toluene and dichloromethane. Some reactions took place in tetrahydrofuran. But unfortunately, BBr_3 reacted with not **4b** but THF to form polymerized THF. On the other hand, BH_3 successfully reacted with **4b** based on the ^{11}B NMR of the reaction mixture. A crude product was allowed to react with $[\text{Ir}(\text{cod})\text{Cl}]_2$, $[\text{Rh}(\text{cod})\text{Cl}]_2$, and $[\text{Pt}(\text{PtBu}_3)_2]$. The ^{31}P NMR spectrum of the reaction mixture of the last platinum complex showed the ligand **5b** coordinate to a platinum center, although a coordination mode (mono- or tri-dentate) of the ligand is still unclear.

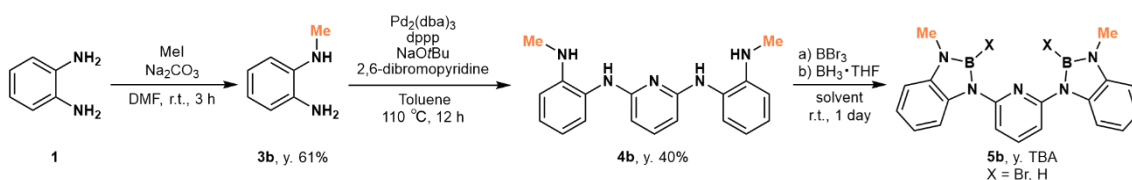


Figure 3 Synthetic route for **5b**

SeqCP: A sequence-based algorithm for searching circularly permuted proteins

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Circular permutation (CP) is a protein sequence rearrangement where the amino- and carboxyl-terminal regions of two proteins can connect in different ways. Despite the rearrangement, the functions and three-dimensional structures of circularly permuted proteins are usually conserved. Comparing CP structures allows for insights into protein folding, stability, function, and enzymatic activity, often in ways traditional mutagenesis cannot. However, most CP detection algorithms rely on structural information, limiting the identification of CP pairs in proteins without known structures. By conquering the limitations, SeqCP, a sequence-based CP detector was designed for circular permutant (CPM) identification.

SeqCP operates in four steps: (1) it aligns a normal and a duplicated query sequence against a target database to retrieve potential CPMs, (2) filters the list based on the CPM features, (3) calculates SeqCP scores for reliability evaluation, and (4) outputs the final list with additional information.

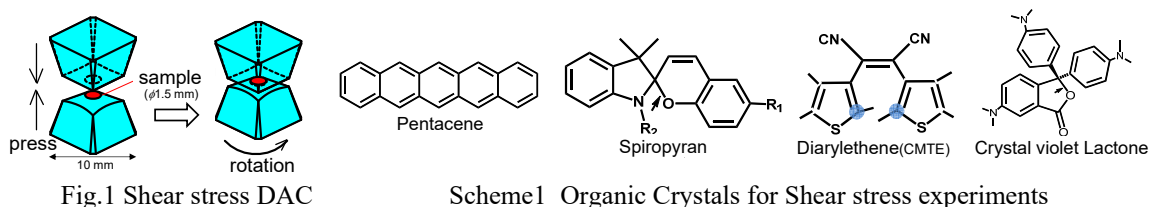
SeqCP has successfully identified numerous candidate CPMs, many of which can aid protein annotation, structural modeling, and CP evolution studies. SeqCP outperforms existing sequence-based methods and detects more CPMs than structure-based approaches. It also has the potential for integration into other algorithm pipelines. The SeqCP web server is accessible at: <http://pcnas.life.nthu.edu.tw/SeqCP/>.

Shear Stress Effect on Organic Crystals

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Recently, mechanochemistry is attracting attention, because mechanical stresses to solid materials can be utilized as external stimuli to induced interesting chemical phenomena such as phase transitions, colorations and chemical reactions. Mortars and ball mills are commonly used, but their stresses are rather complex to investigate “pure” stress effects and frictional heat is also generated. Among various stresses, normal stress and tangential stress, i.e. shear stress, are fundamental. While normal stress has been commonly used as hydrostatic pressure, shear stress has not been studied extensively. We have performed the in-situ observations of organic crystals under shear stress using a DAC-type sapphire anvil cell with a rotating mechanism (Fig. 1).



Pentacene thin film showed an irreversible color change from blue to yellow on applying shear stress [1]. This coloration suggested that the conjugated system was partly broken under shear stress accompanying chemical bond conversion from SP² to SP³. Therefore, we were interested in the compounds with chemical bonds that reversibly convert.

Spiropyrans and diarylethenes exhibit the photoisomerization between the open- and closed-ring isomers on irradiation of visible and UV light. When the shear stress was applied to crystalline nitro-spiropyran (R₁=NO₂, R₂=CH₃, Sch. 1), the color turned from yellow to green, and then changed to purple after releasing the stress. Green intermediate state is considered to be distorted open-ring isomer merocyanine form. This result indicates that shear stress induces solid-state isomerization. On the other hand, the isomerization of the diarylethene derivatives was not induced by only shear stress. For diarylethene CMTE crystal, however, the combination of shear stress and visible light around 500 nm could induce the photoisomerization from the open-ring isomer to the closed-ring isomer [2]. It is known that the crystalline state photochromism of CMTE was caused by UV light of wavelength shorter than 390 nm. Therefore, this result shows that shear stress could adjust the wavelength for the isomerization from UV to visible light region.

Crystal Violet Lactone (CVL) is an acid-base indicator that shows a color change from colorless to blue with the bond cleavage of the lactone ring in acidic solution. A white CVL crystal changed to dark green (λ_{\max} =650 nm) on applying shear stress and then turned to blue-green (λ_{\max} =630 nm) on releasing stress. The infrared spectrum indicated that shear stress induces ring-opening reactions in CVL crystals. The green state could be observed under hydrostatic pressure as well. However, the stable blue-green state after releasing stress was obtained only under shear stress, which is so strong to change the crystal morphology to amorphous state.

In this study, the shear stress effects on organic crystals are presented and the possibility of controlling chemical bonding by stress is discussed.

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[2] T. Inoue, M. Inokuchi, *Bull. Chem. Soc. Jpn.*, 2016, **89**, 671.