

The 20th Nano Bio Info Chemistry Symposium

December 8-9, 2023

Overview:

The 20th Nano Bio Info Chemistry Symposium will be held at the Reception Hall of the Hiroshima University Faculty Club, in Higashi-Hiroshima Campus of Hiroshima University, December 8-9, 2023.

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

2023 December 8th Friday

13:30	Opening Address	
Chairman: Satoru Muramatsu		
13:40	1A1a	Naoyuki Hisano
		Sequence-controlled supramolecular complex directed by the cooperative molecular recognition of tris(zinc porphyrin)
14:00	1A2b	Takayuki Shigenaga
		Harnessing Skyrmion Hall Effect by Thickness Gradients in Wedge-Shaped Samples of Cubic Helimagnets
14:15	1A3b	Ayumu Sakamoto
		Enhanced CO ₂ Reduction Activity on Organically Modified Cu ₂ O Nanostructures
14:30	1A4b	Keisuke Sugiura
		Development of single molecule magnets with a triangular spin structure and toroidal moment
14:45	Break	
Chairman: Peerapat Wangchingchai		
15:00	1B1a	Hiroki Matsubara
		Spontaneous Pickering emulsion demulsification induced by competitive adsorption of silica particle and cationic surfactant at the oil-water interface
15:20	1B2b	Kumiko Nanamori
		Magnetic properties of Ni ₆ Dy ₃ SMM induced by pH changes
15:35	1B3b	Kouta Tanabe
		Synthesis and Guest Binding Behavior of Macrocyclic Tetrakisporphyrin with Two Cavities.
15:50	1B4a	Yuma Takemoto
		Dielectric properties of wheel-shaped polyoxometalate as a function of inner cations
16:10	Break	
Chairman: Naoto Tsuchiya		
16:25	1C1a	Kentaro Harada
		Circularly Polarized Luminescence of an Achiral Biaryl Guest within a Chiral Resorcinarene-based Capsule
16:45	1C2b	Tomoki Kodama
		Synthesis of supramolecular complexes directed by the cooperative molecular recognition of multi-layered zinc porphyrin
17:00	1C3b	Tao Nianze
		On The Way of Accurate Prediction of Complex Chemical System via Generic Graph Neural Networks
17:15	1C4a	Yudai Ono
		Selective Solvent Adsorption in Molecular Crystal of Tris(phenylisoxazolyl)benzene

2023 December 9th Saturday		
Chairman: Kyota Yasuda		
9:30	2A1a	Natsuki Mukai
		Static and dynamic properties of bimerons in two-dimensional chiral magnets
9:50	2A2b	Temmaru Hirota
		Highly Oriented Polymer Film of Donor-Acceptor Type: Orientation Mechanism of SOFT Method Explored by in-situ Time-Resolved Spectroscopy
10:05	2A3a	Nguyen Dong Thanh Truc
		Revisiting the magnetic properties of Mn-formate framework chiral antiferromagnet: orientation dependance of $\text{NH}_4\text{Mn}(\text{HCOO})_3$ and $\text{CsMn}(\text{HCOO})_3$
10:25	2A4a	Masahiro Koyama
		Cryogenic gas-phase spectroscopy of $[(\text{CX}_2)_2]^+$ (X = O, S): Correlation of cluster conformations and charge resonance interaction
10:45	Break	
Chairman: Katsuya Inoue		
11:00	2IL	Ivan Smalyukh
		Knotted chiral meta matter
11:50	Closing Remark	

a: 20 min presentation including Q&A

b: 15 min presentation including Q&A

IL: 50 min presentation including Q&A

Sequence-controlled supramolecular complex directed by the cooperative molecular recognition of tris(zinc porphyrin)

Naoyuki Hisano,¹ Tomoki Kodama,^{1,2} Takeharu Haino^{1,2}

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² International Institute of Sustainability with Knotted Chiral Meta Matter (WPI-SKCM²), Hiroshima University

Our group developed a triple-layered trisporphyrin molecule possessing two cleft cavities, which encapsulated electron-deficient aromatic molecules in a negative cooperative fashion. In this study, we synthesized tris(zinc-porphyrin) **1**, which captured donor and acceptor guests **L1** and **G1** driven by dative bond and donor-acceptor interaction. Tris(zinc-porphyrin) **1** showed homotropic negative cooperativity in the guest binding of **G1** and **L1**. The homotropic negative cooperativity led to the selective formation of ternary host-guest complex. Upon the addition of **L2** into a solution of the ternary host-guest complex, a sequence-controlled multi-component host-guest complex (**L1**•**1**•**G1**)₂**L2** was constructed (Figure 1).

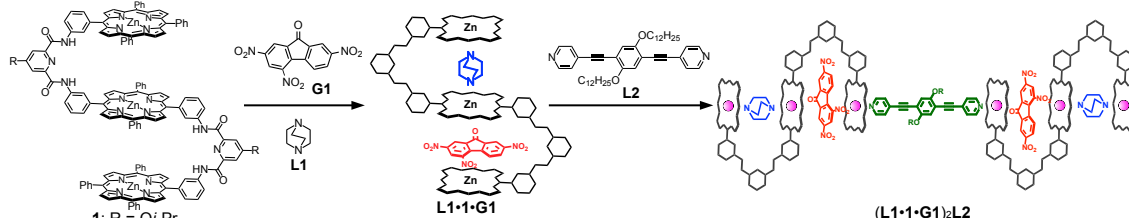


Figure 1. Molecular structures of trisporphyrin, ternary host-guest complex **L1**•**1**•**G1**, and multi-component host-guest complex (**L1**•**1**•**G1**)₂**L2**.

In the crystal structure of **1** with **G1** and **L1**, **G1** was accommodated within the cavity of **1**, whereas **L1** was located within the resting cavity. One of three porphyrin units still has the binding ability to the ditopic ligand **L1**. The excess of **L1** formed (**L1**•**1**•**G1**)₂**L1** (Figure 2a). The guest binding behavior in solution was studied using ¹H NMR spectroscopy. A 1:1:1 mixture of **1**, **G1**, and **L1** in chloroform-*d* showed the upfield-shifts of protons of **G1** and **L1**, indicating the formation of the ternary complex (Figure 2b). Upon adding 0.5 equivalent of **L2** into the solution of **L1**•**1**•**G1**, a new set of proton signals appeared, which was assigned to coordinated **L2**, and the protons of bound **G1** and **L1** remained (Figure 2c). These results indicated the formation of a multi-component host-guest complex (**L1**•**1**•**G1**)₂**L2**.

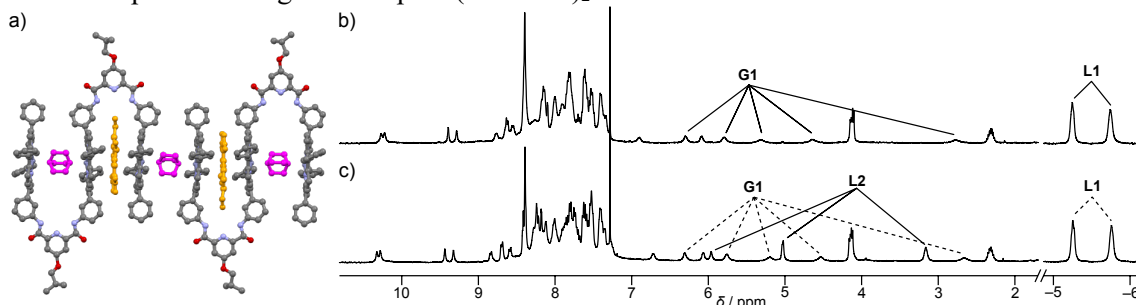


Figure 2. (a) Crystal structure of **1** with **G1** and **L1**. ¹H NMR spectra of (b) a 1:1:1 mixture of **1**, **G1**, and **L1**, (c) a 1:1:1:0.5 mixture of **1**, **G1**, **L1**, and **L2** in chloroform-*d*.

Reference

[1] Hisano, N.; Kodama, T.; Haino, T. *Chem. Eur. J.* **2023**, e202300107.

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 [6, 7]. 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)).

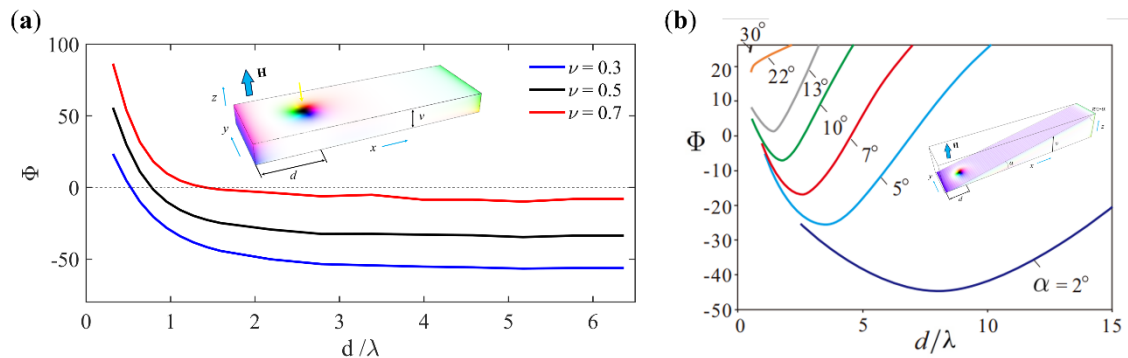


Figure 1. Edge-skyrmion interaction potentials in thin films with different thickness ν (a) and in wedge-shape nanostructures with different angle α (b).

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 [8, 9] (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.

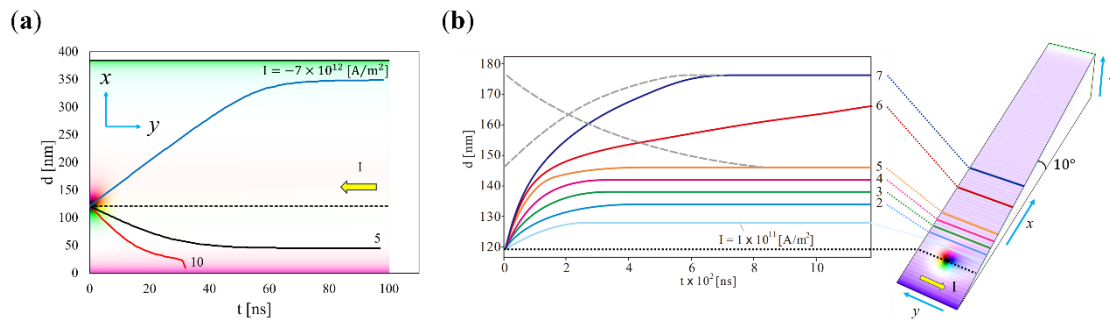


Figure 2. The trajectories of moving isolated skyrmions for different current values as the time-dependent curves in thin films (a) and in wedge-shape nanostructures (b).

References:

- [1] A. Leonov *et al.*, *Phys. Rev. Lett.* **117**, 087202 (2016).
- [2] L. Bannenberg, *npj (Nature Partner Journal) Quantum Materials* **4**, 11 (2019).
- [3] A. O. Leonov, M. Mostovoy, *Nat. Commun.* **6**, 8275 (2015).
- [4] A. Leonov *et al.*, *Appl. Phys. Lett.* **109**, 172404 (2016).
- [5] T. Shigenaga, A. Leonov, *Nanomaterials*, **13**, 2073 (2023).
- [6] F. Rybakov *et al.*, *Phys. Rev. B*, **87**, 094424 (2013).
- [7] A. Leonov *et al.*, *Phys. Rev. Lett.* **117**, 087202 (2016).
- [8] D. Toscano *et al.*, *J. Magn. Magn. Mater.* **504**, 166655 (2020).
- [9] B. Gobel *et al.*, *Phys. Rev. B*, **99**, 020405(R) (2019).

Enhanced CO₂ Reduction Activity on Organically Modified Cu₂O Nanostructures

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¹Graduate School of Advanced Science and Engineering, Hiroshima University

1. Purpose

Cu electrodes can reduce CO₂ to useful chemicals including hydrocarbons and alcohols through multi-electron process, while selectivity among them remains a challenge. We have developed a modification method of Cu electrodes with organic network polymers grown by CuAAC reaction. Those modifications improved CO₂ reduction selectivity¹⁻³, possibly due to selective mass transport of CO₂ against H₂O, in addition to direct intervention of molecular reduction process. In this study, we further elucidate the role of organic layer by focusing on two structural factors: the organic/Cu interface and the molecular components within the organic layer. We prepared Cu₂O electrodes with various shapes by electrodeposition, and modified them by introduction of molecular sites that can interact with CO₂ and protons.

2. Experiment

Cu₂O was grown into large crystals by electroreduction of Cu²⁺ on a Cu electrode (Block-type (BI)). Tuning electrodeposition conditions led to growth of Cu₂O with different morphologies. These electrodes were immersed in a solution containing ethynyl (Ph or Am) and azide substrates to form organic layer on the surface (Figure 1a).

3. Results and Discussion

While the surface structure of the unmodified Block-type electrode collapses upon CO₂ reduction, the structure of BI_Ph modified with Ph is maintained after CO₂ reduction (Figure 1b), from which the organic layer was still detected. Therefore, CO₂ reduction occurred at the Cu surface underneath the organic layer throughout the operation.

CO₂ reduction products of the Block-type electrode (Figure 1c) showed significant suppression of hydrogen evolution from the modified electrode. The introduction of a tertiary amine group into the layer further reduced hydrogen evolution and ethylene formation was increased. The surface hydrophobicity was BI_Am, BI_Ph > Block, suggesting that the exclusion of water molecules from Cu surface led to the suppression of hydrogen evolution. The selectivity of BI_Am suggests that proton mediation by the tertiary amine moiety is directly involved in the transformation of the CO₂ reduction intermediate.

- (1) Kume *et al.*, *ChemElectroChem*, **2020**, *12*, 2575. (2) Kume *et al.*, *Front. Chem.*, **2019**, *7*, 860. (3) Kume *et al.*, *Chem. Commun.*, **2022**, *58*, 8053.

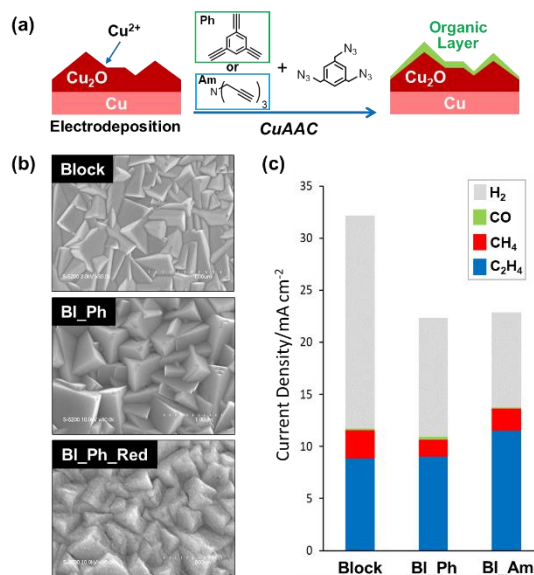


Figure 1 (a) Electrodeposition and modification of Cu₂O (b) SEM images of BI and BI_Ph electrodes before and after CO₂ reduction (c) Products in CO₂ electrolysis (-1.4 V vs. RHE, 0.1 M KHCO₃) of Block, BI_Ph and BI_Am

Development of single molecule magnets with a triangular spin structure and toroidal moment

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Single molecule magnets (SMM) are magnetic materials that exhibit slow magnetic relaxation after being magnetized below a blocking temperature (T_B),^[1] and frequency dependence of the magnetic susceptibility is observed. Recently, it has been suggested that the magnetic anisotropy axis of Dy^{3+} in triangular SMM can adopt a cyclic orientation and a toroidal moment arises from its magnetic structure (Fig.1)^[2]. Therefore, the magnetic anisotropy axis is closely related to the expression of the toroidal moment in SMM. The magnetic anisotropy axis orientation depends on the intramolecular charge environment and molecular structure. We aimed to elucidate the effects of modification of the magnetic anisotropy on the toroidal moment and magnetic properties of a SMM. In this study, we synthesized complexes of lanthanide ions with a triangular core structure and investigated their molecular structure and magnetic properties.

The structure of the Zn_3Ln_3 ($Ln=Dy^{3+}, Tb^{3+}$) hexanuclear complexes successfully isolated in this study were determined at 100 K (Fig.2). The crystal structure was refined in the $R3c$ space group and show a triangular core. In the Zn_3Dy_3 hexanuclear complex, the magnetic anisotropic axis of Dy^{3+} has a cyclic structure, suggesting the presence of toroidal moments. The measurement of the temperature-frequency dependence of the AC susceptibility in that complex shows a frequency dependence at low temperature and under magnetic field, indicating a SMM behavior.

[1] Sessoli, R., Gatteschi, D, *et al.*, *Nature*. **1993**, 365, 141. [2] J. Tang, *et al.*, *Angew. Chem. Int. Ed.* **2006**, 45, 1729.

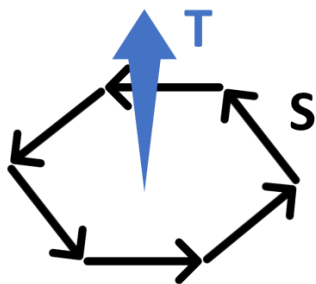


Fig.1: Schematic diagram of toroidal moment

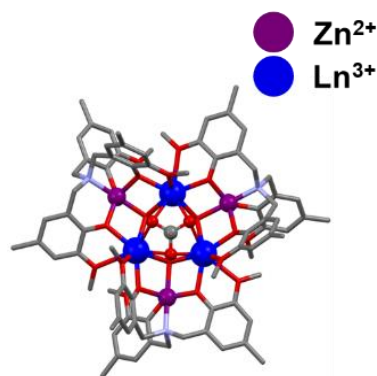


Fig.2. Crystal structure of Zn_3Ln_3 hexanuclear complex at 100 K.

Spontaneous Pickering emulsion demulsification induced by competitive adsorption of silica particle and cationic surfactant at the oil-water interface

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In recent years, nanoparticles adsorbed at the air-liquid and liquid-liquid interfaces have been attracting wide attention to develop a new function of nanoparticles such as liquid marbles and Pickering emulsions. Although nanoparticles in such systems coexist with various surface-active substances in practical applications, there are many unclear issues about the competitive adsorption and its effects on the physical properties of liquid marbles and Pickering emulsions. However, a precise understanding of the interfacial state including the competitive adsorption effects can clarify the limit of the additive concentration that can stably prepare multicomponent liquid marbles and Pickering emulsions, and also enable us to design microcapsules that release contained molecules by switching adsorbed components between nanoparticles and coexisting other surface-active molecules.

We have previously showed that the adsorbed film of a cationic surfactant (cetyltrimethylammonium chloride: CTAC) at the tetradecane (C14) - water interface undergoes a first-order surface transition from two-dimensional liquid to solid states upon cooling. In this study, we utilized this surface freezing transition to realize a spontaneous demulsification of Pickering emulsions stabilized by silica particles (Figure 1). In the temperature range above the surface freezing transition, the interfacial tension of silica laden oil-water interface was lower than CTAC adsorbed film, hence, stable Pickering emulsion was obtained by vortex mixing. However, the interfacial tension of CTAC adsorbed film decreased rapidly below the surface freezing temperature and became lower than the silica laden interface. The reversal of the interfacial tensions between silica laden and CTAC adsorbed films gave rise to Pickering emulsion demulsification by the desorption of silica particles from the oil-water interface.

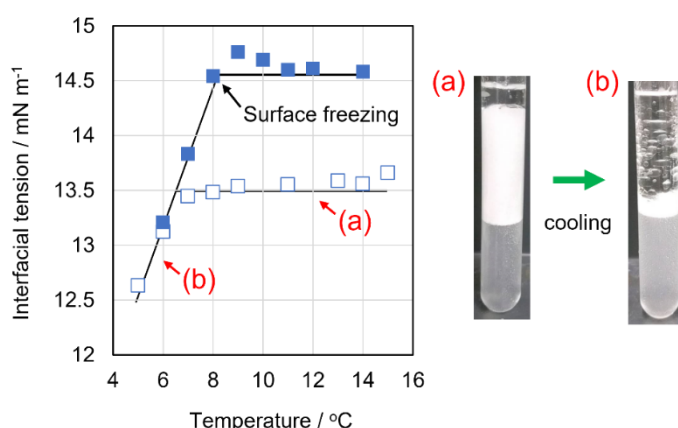


Figure 1: Interfacial tension measured in the absence (filled squares) and in the presence (open squares) of silica particles. (a) and (b) shows pictures of Pickering emulsions taken under the continuous cooling.

Magnetic properties of Ni₆Dy₃ SMM induced by pH changes

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Single molecule magnets (SMMs) are single molecule that exhibit magnetic hysteresis and slow relaxation of their magnetization processes. These properties are due to presence of a large magnetic moment and a uni-axial magnetic anisotropy. The aim of this study is to determine the effect of the pH on the magnetic properties of SMMs. Previous studies have shown dependence of the direction of the magnetic anisotropy axis on the polarization of a hydrogen bond.^[1] Therefore, we wanted to extend this study by switching magnetic properties by protons addition or subtraction.

In this study, we focused on SMM composed of six Ni²⁺ ions and three Dy³⁺ ions (Ni₆Dy₃).^[2] The core of the complex is composed of three metallocubane, sharing dysprosium ions, in a triangular configuration (Figure 1). Six ligands, arranged perpendicularly to the core plan, complete the molecule. The hydroxy group of this ligand is bound to the ions and provide numerous proton acceptor and donor. Therefore, we aim to control the magnetic behavior of the complex molecules by protonating/ deprotonating this binding site.

In the present report, we discuss the static and dynamic magnetic properties of the neutral Ni₆Dy₃ and deprotonated Ni₆Dy₃ complexes.

[1] G, Cosquer, *et al.*, *Eur. J. Inorg. Chem.*, **2014**, 1, 69-82.

[2] A. B. Canaj, *et al.*, *Inorg. Chem.*, **2015**, 54, 7089-7095.

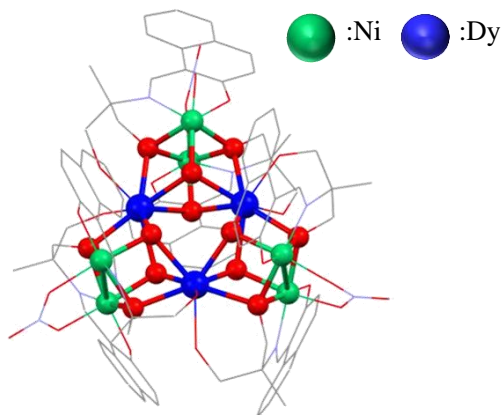


Figure 1: structure of the Ni₆Dy₃ core.

Synthesis and Guest Binding Behavior of Macrocylic Tetrakisporphyrin with Two Cavities.

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Our group has developed S-shaped tetrakisporphyrin possessing two cleft cavities connected with a butadiyne linker.^[1,2] The cleft cavities encapsulated electron-deficient aromatic molecules driven by donor-acceptor and π - π stacking interactions. In this study, we newly synthesized a novel macrocylic tetrakisporphyrin molecule **1** with rigid linkers. The macrocylic tetrakisporphyrin molecule showed positive cooperativity in the guest binding.

The guest binding behavior in the solution was investigated using ¹H NMR spectroscopy. When **1** was added to a solution of **G1**, the upfield-shifts of the aromatic protons of **G1** were observed (Figure 2a), indicating that **G1** was located within the cavities of tetrakisporphyrin, where the aromatic protons of **G1** experienced the strong shielding effect of the porphyrin rings. The detailed insight into guest binding behavior was studied using UV/vis spectroscopy. Upon the addition of **G1** to a solution of **1**, the Soret band at 419 nm decreased and a new absorption band emerged (Figure 2b). The Job plot revealed that the host-guest complex was formed in a ratio of 1:2 (Figure 2c). Non-linear fitting analysis provided to obtain the binding constants K_1 and K_2 for **G1**-**G5** (Table 1). The binding constants of **1** were one order of magnitude as large as those of non-macrocylic molecule **2**, which indicates that the macrocyclization of S-shaped tetrakisporphyrin led to the preorganization of the cleft cavities and enhanced the binding ability. The cooperativity parameters ($\alpha = 4K_2/K_1$) of **1** suggested strong positive cooperativity in the guest binding, while those of **2** showed non-cooperativity. Due to the conformational rigidity of the two cavities, the first guest binding causes the preorganization of the remaining binding cavity.

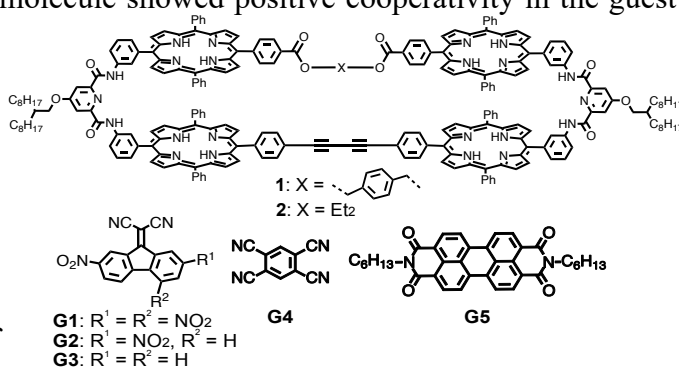


Figure 1. Molecular structures of **1**, **2**, and **G1**-**G5**.

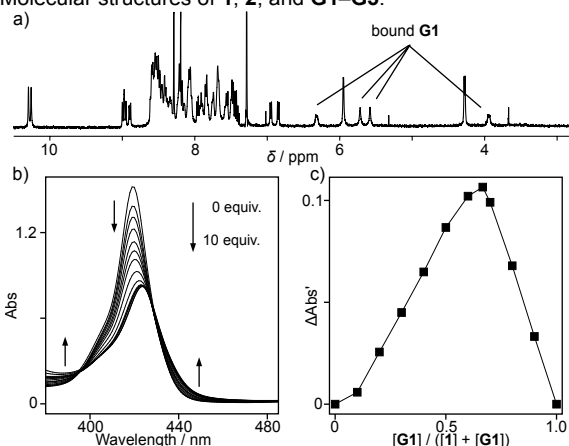


Figure 2. (a) ¹H NMR spectrum of a 1:2 mixture of **1** and **G1**. (b) UV/vis spectra and (c) Job plots of **1** with **G1**.

Table 1. Binding Constants of the Host-Guest Complexation.

Host	Guest	K_1 (10 ⁵ L mol ⁻¹)	K_2 (10 ⁵ L mol ⁻¹)	α (4K ₁ /K ₂)
1	G1	49(2)	41(2)	3.4
2	G1	3.71(2)	0.55(2)	0.60
1	G2	41(1)	21.8(7)	2.1
1	G3	0.501(2)	0.229(9)	1.8
1	G4	0.446(5)	0.52(1)	4.7
2	G4	0.0490(7)	0.0077(2)	0.63
1	G5	1.5(2)	0.7(1)	2.2
2	G5	0.32(3)	0.046(8)	0.58

Due to the conformational rigidity of the two cavities, the first guest binding causes the preorganization of the remaining binding cavity.

(1) N. Hisano, T. Hirao, K. Tanabe, T. Haino, *J. Porphyrins Phthalocyanines*. **2022**, 26, 683. (2) T. Haino, T. Fujii, A. Watanabe, U. Takayanagi, *Proc. Natl. Acad. Sci. USA*. **2009**, 106, 10477.

Dielectric properties of wheel-shaped polyoxometalate as a function of inner cations

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Ferroelectric behaviors are caused by long-range order of dipole-dipole interactions between molecules or atoms, and are therefore considered as bulk properties. However, we reported single-molecule electret (SME) which are single molecule that behaves like a ferroelectric material without intermolecular interactions.^[1] These behaviors were observed in donut-shaped inorganic molecule that is called Preyssler-type polyoxometalate (Fig.1). This molecule incorporates a terbium ion (Tb^{3+}) that has two stable sites in a cavity, so molecular polarization occurred depending on the position of Tb^{3+} ion. In dielectric measurements, ferroelectric materials show a peak at the phase transition temperature and a polarization vs. electric field (P - E) hysteresis in the ferroelectric phase *i.e.* below the transition temperature. However, from the temperature dependence of dielectric properties measurements, phase transition was not observed in SME. On the other hands, SME showed P - E hysteresis near room temperature so this molecule behave like ferroelectric materials without long-range order (Fig.2).

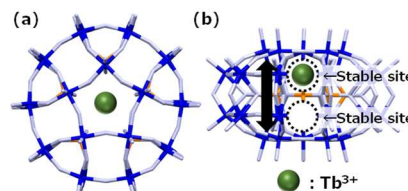


Fig.1. (a)Top and (b)side view of Preyssler-type POM.

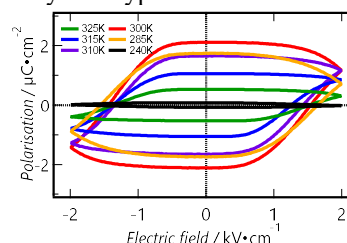


Fig.2. P - E loops of SME.

In my research, I focused on wheel-shape inorganic molecule $K^+ \subset W48$ that incorporates eight potassium ions (purple and pink sphere in Fig.3).^[2] As four of them delocalize between two stable sites in the cavity so this molecule, this compound will behave as a new SME. From the temperature dependence of the dielectric constant measurements, a first-order phase transition was not observed up to 450 K. On the other hands, this molecule showed P - E hysteresis from 300K to 450 K. For these reasons this molecule will behave as a high temperature SME. In addition, the inner cations can be exchanged to NH_4^+ ions, affecting the dielectric properties. In my presentation, I will introduce about ion exchanging synthesis and inner ions dependence of the dielectric properties.

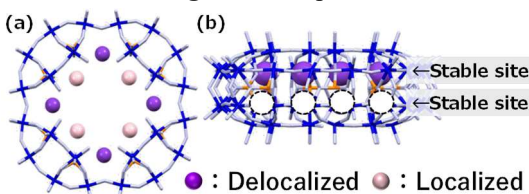


Fig.3. (a)Top and (b)side view of $K^+ \subset W48$.

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Circularly Polarized Luminescence of an Achiral Biaryl Guest within a Chiral Resorcinarene-based Capsule

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Our group has reported that two resorcinarene-based cavitands bearing four bipyridyl arms at the wide rim are self-assembled by metal coordination to give rise to D_4 symmetric supramolecular capsule **1** [1]. **1** allows dynamic interconversion between (*P*)- and (*M*)- helicity in the solution containing a small portion of acetonitrile. The enforced cavity of **1** can encapsulate several guest molecules possessing acetyl methyl substituent, which forms CH- π interaction to the electron-rich aromatic rings of resorcinarene scaffold. A chiral hydrogen bonding complex (AcOH)₂ · *L*(+)-**G1** was well fitted within the cavity of **1**, resulting in the mixture of the two diastereomer (AcOH)₂ · *L*(+)-**G1**⊂(*P*)-**1** and (AcOH)₂ · *L*(+)-**G1**⊂(*M*)-**1**. The ratio of the two diastereomers were biased through the helicity interconversion to give rise to (AcOH)₂ · *L*(+)-**G1**⊂(*P*)-**1** in 91%*de*. An enantiomerically enriched capsule (*P*)-**1** was prepared by the removal of the chiral template.

Achiral 4,4'-diacetoxybiphenyl guest **G2** was synthesized bearing two fluorescent benzothiadiazole units. CD spectra and DFT calculation of **G2**⊂(*P*)-**1** demonstrated that the dynamic axial chirality of **G2** within (*P*)-**1** was biased to (*S*)-helicity, producing circularly polarized luminescence from benzothiadiazole units in the NIR region [2].

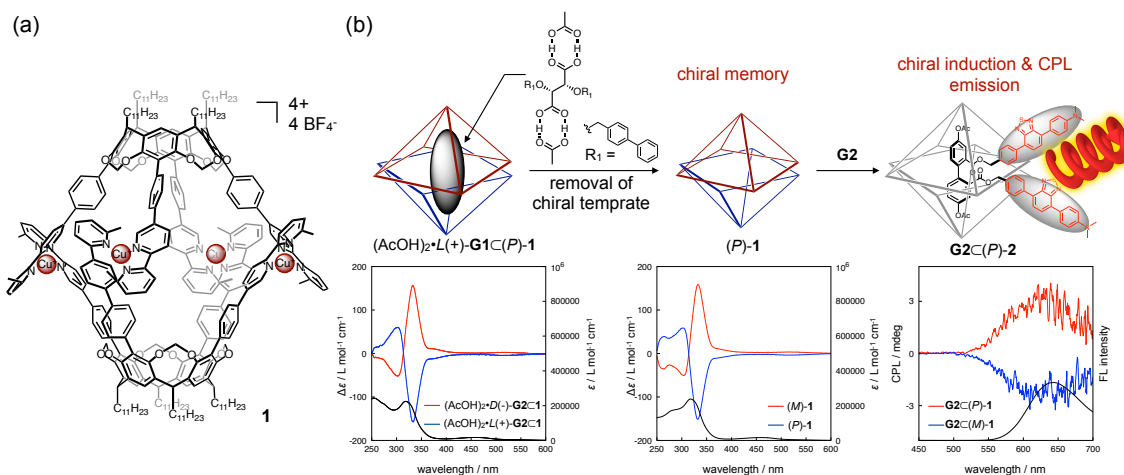


FIGURE 1. (a) Molecular structure of capsule **1**. (b) Preparation of enantiomerically enriched capsule **1**, which imposes the axial chirality on guest **G2** to produce CPL in the NIR region.

Keywords: Supramolecular Chemistry; Host-Guest Chemistry; Supramolecular Capsule; Molecular Recognition; Circularly Polarized Luminescence

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Synthesis of supramolecular complexes directed by the cooperative molecular recognition of multi-layered zinc porphyrin

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Our group developed a triple-layered trisporphyrin molecule possessing two cleft cavities, which encapsulated electron-deficient aromatic molecules in a negative cooperative fashion.^[1] In this study, we synthesized tris(zinc-porphyrin) **1** and pentakis(zinc-porphyrin) **2**, which captured donor and acceptor guests **L1** and **G1** driven by dative bond and donor-acceptor interaction. Tris(zinc-porphyrin) **1** showed homotropic negative cooperativity in the guest binding of **G1** and **L1**. The homotropic negative cooperativity led to the selective formation of ternary host-guest complex **G1·1·L1**.

The guest binding behavior of **1** in solution was studied using ¹H NMR spectroscopy. A 1:1:1 mixture of **1**, **G1**, and **L1** in chloroform-*d* showed the upfield-shifts of protons of **G1** and **L1**, indicating the formation of the ternary complex (Figure 2a-c). In the crystal structure of **1** with **G1** and **L1**, **G1** was accommodated within the cavity of **1**, whereas **L1** was within the resting cavity. One of three porphyrin units still has the binding ability to the ditopic ligand **L1**. The excess of **L1** formed (**L1·1·G1**)₂**L1** (Figure 2d). The crystal structure inspired us to develop multiple layered porphyrin clefts that sequentially encapsulate multiple guest molecules. Therefore, we developed multiple layered porphyrin cleft **2**. The guest binding behavior of **2** was investigated using UV/vis absorption spectroscopy. The host-guest ratios of **2** with **G1** and **L1** were determined to be 1:2 (Figure 2e,f). Upon the addition of **L1** to a solution of **2** with excess **G1**, the UV/vis spectra changed without guest exchange (Figure 2g,h). The spectrum was consistent with the solution after adding **G1** to the solution of **2** with excess **L1**. These results indicated that two molecules of **L1** and two molecules of **G1** were simultaneously encapsulated within **2**, forming thermodynamically stable complex **L1·G1·2·L1·G1**.

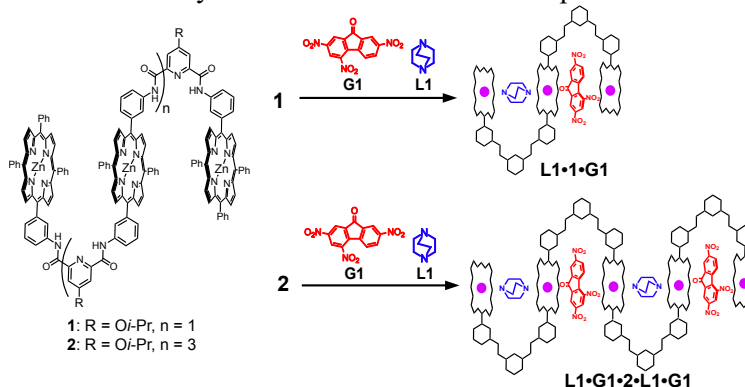


Figure 1. Molecular structures and guest binding behavior of **1** and **2**.

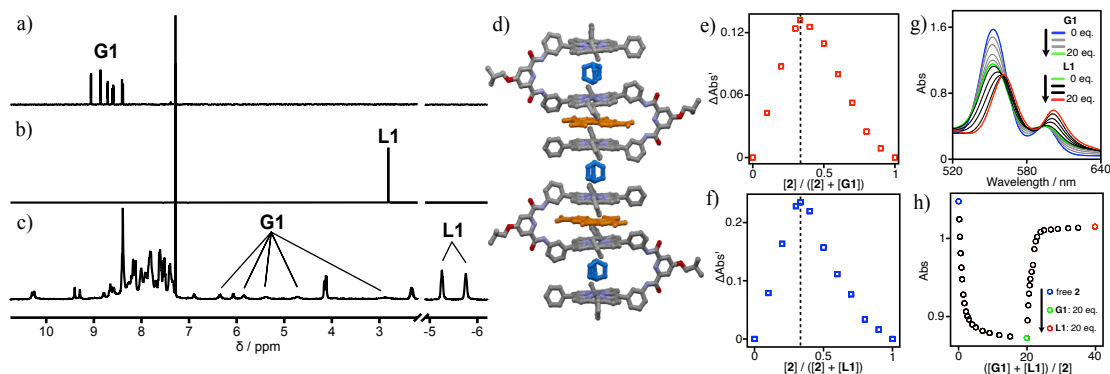


Figure 2. Partial ¹H NMR spectra of (b) **G1**, (c) **L1**, (d) 1:1:1 mixture of **1**, **G1**, and **L1** at 295 K in chloroform-*d*. (d) Crystal structure of **1** with **G1** and **L1**. Job plot **2** with (e) **G1**, (f) **L1**. (g) Changes in the UV/vis absorption of **2** (2.0×10^{-5} mol/L) upon the sequential addition of **G1** and **L1**. (h) Plots of Abs ($\lambda = 563$ nm) against $([\text{G1}] + [\text{L1}]) / [\text{2}]$.

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On The Way of Accurate Prediction of Complex Chemical System via Generic Graph Neural Networks

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We developed a novel asymmetric graph-to-SMILES autoencoder¹ that maps the 2-dimensional molecular graphs into latent space by the graph neural network (GNN) encoder and transforms the latent vectors in the latent space into the original SMILES representation by the transformer decoder. With our dedicatedly designed graph encoding method, our GNN encoder can handle not only single molecule input but a mixture system with temperature dependency, which cannot be input into a GNN in all pervious works because of the lack of adjacency information between each 2D molecular structures, that makes our model *generic* to all chemical systems that can be represented by one or a group of 2D graphs. By playing with the latent space, we enabled our model to work in a bidirectional style (see Figure 1):

1. We managed to extract the properties of systems in high accuracy from the latent space via a multilayer perceptron (MLP) readout network.

2. By a latent space diffusion process (inserting a diffusion model between encoder and decoder), we generated molecular structures utilising the desirable properties as a guidance.

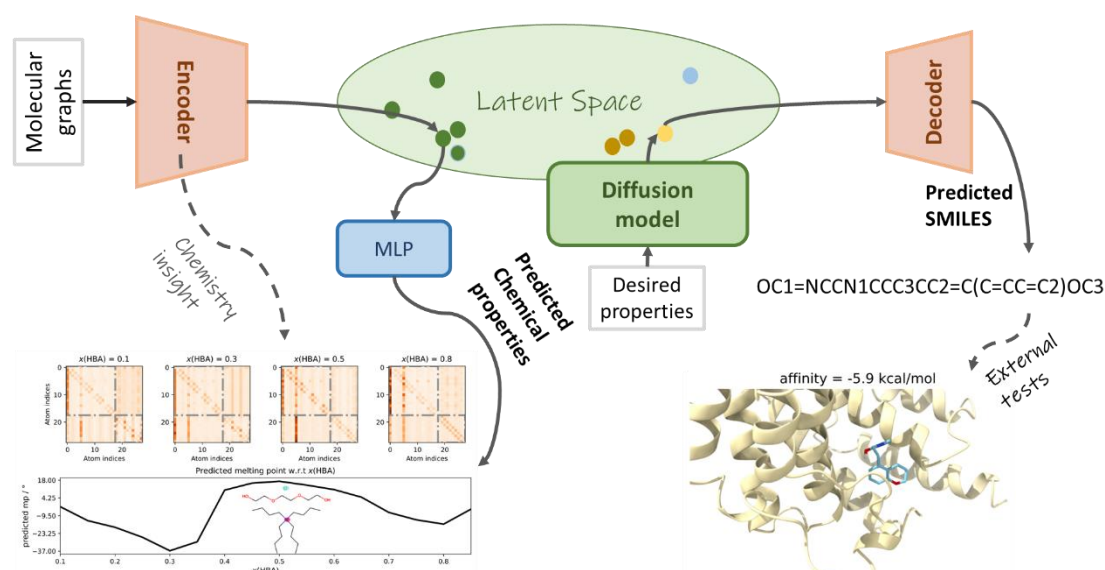
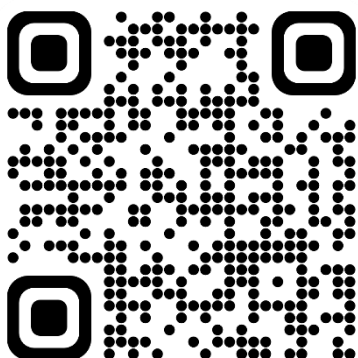


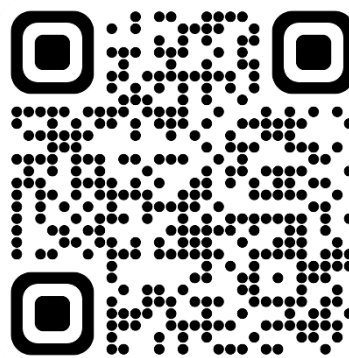
Figure 1. The working scheme of our model.

We further claimed that our proposed model was productive, robust, and transferable, rather than a toy that only play well with the existing datasets. In the experiments, we have found that our model outperformed the human, by whom the empirical formula was used, in prediction the $n - \pi^*$ and $\pi - \pi^*$ transition wavelength, no need to say that our model outperformed or was competitive to published state-of-the-art models (to August 2023) in several benchmarks (MoleculeNet², QM9³, PhotoSwitch⁴) of property prediction and classification tasks. We could not only predict a range of properties of deep eutectic solvents (DES), which are special mixtures whose melting point is lower than that of individual components, more accurate than previous

studies that used conventional machine learning method but generate novel DES pairs as well. Last but not least, we also found that the model understood chemistry: the property-related structures were highlighted inside the model; in the experiment of generating protein ligands, the model was capable of giving reasonable molecular structures that bound to both known and unseen binding sites of a protein, of which the quaternary structure did not present in the training data. The details will be presented in the day of conference.



Scan QR code to get access to the GitHub repository of our model AkAne (AsymmetriC AutoeNcodEr → ACANE → AkAne).



Feel free to try our web APP demo on Huggingface Spaces. Please note that the service might be very slow since the model is running on 2 CPU cores, and we have no money to pay for the better server.

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Selective Solvent Adsorption in Molecular Crystal of Tris(phenylisoxazolyl)benzene

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Porous organic crystals such as metal-organic frameworks (MOFs) and intrinsically porous molecular crystals (IPMs) have attracted the application of molecular adsorption and separation. Our group has reported that tris(phenylisoxazolyl)benzene derivatives were stacked in a columnar fashion to form supramolecular polymers through π - π stacking and dipole-dipole interactions.^[1] In this work, we newly synthesized tris(phenylisoxazolyl)benzene **1** modified side chains by methoxy groups to achieve high crystallinity (Figure 1a).

The single crystal $\text{CHCl}_3@1$ was obtained from a chloroform solution with a space group $C2/c$ (Figure 1b). In the crystalline state, molecules **1** formed a stacking structure and created a pore for encapsulation of chloroform molecules. A detailed analysis of the crystal **1** was carried out using single-crystal and powder X-ray diffraction analysis. When the crystal $\text{CHCl}_3@1$ was heated and evaporated, it changed to nonporous crystal **1 α** and **1 β** . The **1 α** and **1 β** powder was exposed to the vaporous *cis*- and *trans*-decalin, resulting remarkable *cis*-selective adsorption even in a *cis*:*trans* ratio of 4:96 (Figure 1c). Latent pores in nonporous **1 α** and **1 β** crystals remained dormant until exposed to complementary guest vapors, opening cavities to encapsulate decalin molecules.

Here, we introduce the details of crystal structure and adsorption behavior of **1**, including the mechanistic consideration of solvent adsorption.

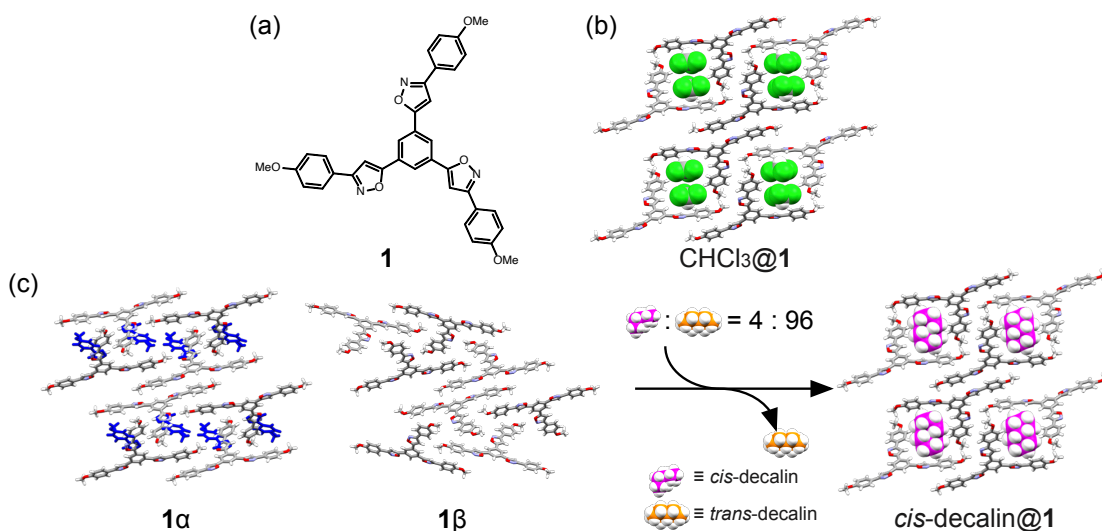


Figure 1. (a) Molecular structure of **1**. (b) Single-crystal structure of $\text{CHCl}_3@1$ generated from a CHCl_3 solution of **1**. (c) Schematic representation of selective adsorption of **1** against vaporous *cis*- and *trans*-decalin mixture.

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Static and dynamic properties of bimerons in two-dimensional chiral magnets

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I. Introduction: bimerons are non-axisymmetric analogues of skyrmions

Magnetic skyrmions [1,2] are topologically nontrivial spin textures with smooth rotation of the magnetization, which are commonly embedded into homogeneously magnetized “parental” states and are stabilized by a specific Dzyaloshinskii-Moriya interaction (DMI) [3]. In modern spintronics, skyrmions are considered as promising objects for the next-generation memory and logic devices: they are “topologically protected”, have nanometer size and can be manipulated by spin-polarized currents [4].

Magnetic bimerons are topological counterparts of axisymmetric skyrmions, which represent particle-like states of coupled merons with a half-integer topological charge $|Q|=1/2$. In two-dimensional chiral magnets with induced DMI and uniaxial anisotropy, two types of bimerons can be formed distinct by their internal structure and by a surrounding “vacuum” state.

II. Bimerons within the cycloidal state

On the one hand, bimerons are viewed as ruptures of a spiral state (Fig. 1 (c)) and play the role of topological quanta during the phase transition between the cycloid and the hexagonal skyrmion lattice (green and blue areas at the phase diagram, Fig. 1 (b)). At some critical field (deep within the blue area of the thermodynamically stable SkL), the energy of such a meron pair with equal topological charges $Q=1/2$ becomes negative with respect to the cycloidal background and thus initiates the avalanche phase transition with plentiful bimerons nucleated and gathered into the

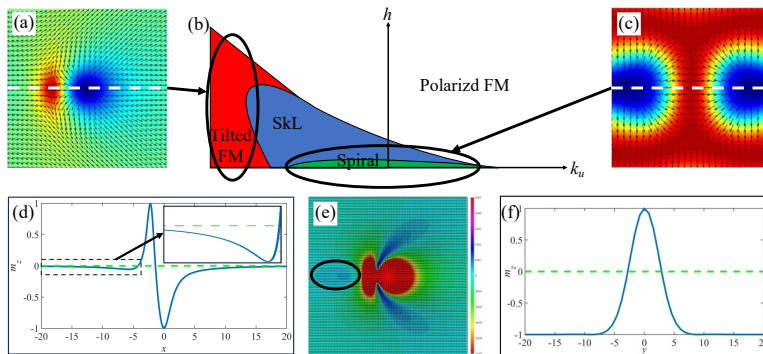


Fig. 1. Two varieties of bimerons with their “natural habitat” at the phase diagram of states (see text for details).

closely packed hexagonal order of skyrmions. Additionally, bimerons may set up a metastable hexagonal arrangement of elongated skyrmions, which “shadows” the original SkL [5]. According to the phase diagram (Fig. 1 (b)), the introduced bimeron variety exists for both signs of the uniaxial anisotropy and for

relatively moderate magnetic fields.

Interestingly, merons with the opposite topological charges $Q=+1/2$ and $Q=-1/2$ can also grapple and form a bimeron with the total topological charge $Q=0$. Such a bimeron is not subject to the skyrmion Hall effect and moves intact along the current in racetrack devices. Current-velocity characteristics in this case, however, demonstrate nonreciprocity with respect to the current

direction: for a positive value of the current, the merons are forced to slide past each other; for the negative value of the current, the pair of merons is ripped.

III. Bimerons within tilted ferromagnetic phases

On the other hand, non-axisymmetric bimerons (Fig. 1 (a)) can be shaped within the in-plane homogeneous state stabilized by the strong easy-plane anisotropy in the red area of the phase diagram (Fig. 1 (b)). The composite merons in this case are both charged with the same positive skyrmion number $Q=+1/2$ (or with the same negative charge $Q=-1/2$). However, one of them represents a circular meron with the magnetization in its center pointing down, whereas the other one represents an anti-meron, which deforms into a crescent with the magnetization pointing up (Fig. 1 (a)).

The physics of bimerons in this parameter region and the prospects of their use in spintronic devices rest on the attracting nature of the inter-bimeron potential. Remarkably, the magnetization pattern, which develops according to the DMI throughout the sample, exhibits a small “egg-shaped” area behind the anti-meron with the opposite rotation sense and thus with the positive energy density (Fig. 1 (d), (e)). We notice that for bimerons within the cycloids, the sense of the magnetization rotation remains the same (Fig. 1 (f)).

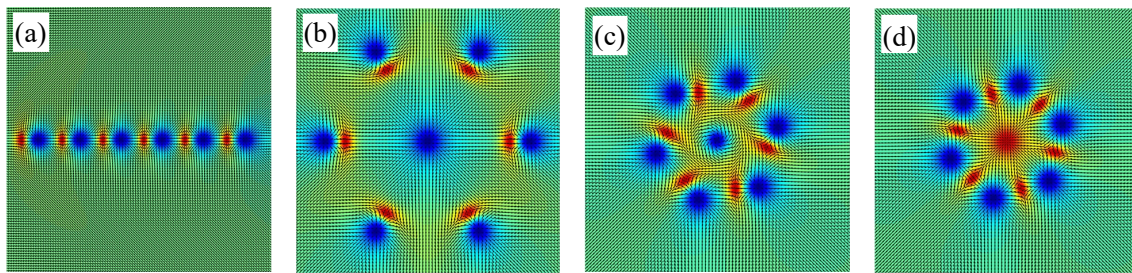


Fig. 2. Bimeron conglomerates: chains (a); rings with the outer bimerons pointing towards the center (b) and circling around the central meron with the negative (c) and positive (d) polarity.

As a consequence, one can speculate about the ordered networks from the bimerons as the building blocks. In the simplest case, bimerons align into chains to cover the regions with the wrong sense of rotation in neighboring bimerons. Since one such area at the end of a chain still remains, one would try to enclose a chain and thus form a ring-shaped bimeron cluster. In turn, two types of such bimeron rings are feasible: (i) in the first type (Fig. 2 (b)), the internal stability is based on the pairwise attraction of all bimerons forming the ring (outer bimerons) with the central meron (such a meron will inevitably be formed and thus contribute to the total topological charge); (ii) in the second type (Fig. 2 (c), (d)), the ring stability rests on the pairwise attraction between the outer bimerons, although they develop repulsion with the central meron.

In the present study, we investigate the stability of bimeron rings depending on the number of constituent solitons. Subsequently, we address transformations between aforementioned bimeron states. Eventually, we construct extended bimeron “polymers” covering the whole area of a sample.

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Highly Oriented Polymer Film of Donor-Acceptor Type: Orientation Mechanism of SOFT Method Explored by *in-situ* Time-Resolved Spectroscopy

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Conjugated polymers are organic conductive materials, and their orientations significantly improve optoelectronic properties. Recently, a new method to prepare a highly oriented film of conductive polymer, “Simple way of Orienting Films using Templating cellulose (SOFT)”, was developed in our laboratory [1]. This method has various advantages: i) high orientation factor (~0.9), ii) high reproducibility (~96%), iii) low surface roughness (~50 nm), and iv) robust orientation (i.e., no degradation after folding 100–500 times at angle of 320°). In our previous study, an oriented film of a conjugated polymer, PFO composed of a monomer F8 unit (Fig.1a), was prepared by the SOFT method, and its orientation mechanism was investigated by *in-situ* time-resolved spectroscopy [2]. However, the orientation mechanism of other conjugated polymers has not been understood so far. In particular, a donor-acceptor (D-A) type conjugated polymer has attracted much attention because of its low-band gap energy, strong interchain interaction, and high carrier mobility, all of which can improve efficient organic photovoltaics and field-effect transistors. Herein, we investigated the orientation and its dynamics of D-A type conjugated polymer using *in-situ* time-resolved spectroscopy. The D-A type polymer of F8BT (Fig. 1b) we chosen had the same unit (i.e., F8 donor unit) to the PFO, which was no D-A type conjugated polymer. Thus, detail orientation mechanisms with or without D-A unit could be understood by comparing with each result.

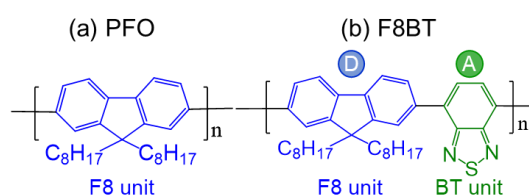


Fig. 1 Structure of monomer units of (a) poly(9,9-dioctylfluorene) (PFO) and (b) poly(9,9-dioctylfluorene-alt-benzo thiadiazole) (F8BT)

The orientation of an F8BT film during a SOFT procedure was tracked by *in-situ* time-resolved fluorescence and Raman spectroscopies. As a result, the F8BT film, prepared by the SOFT method, showed higher orientation than that of PFO. In addition, the PFO film was oriented during a heating process (30 - 200 °C), whereas the F8BT film exhibited significant orientation during both heating (30 - 200 °C) and cooling (200 - 40 °C) processes. These orientation differences between the F8BT and PFO films were attributed to an electrostatic interaction of the D-A unit of F8BT on a substrate, with a template effect driven by an uniaxially coated methylcellulose film. Details of the structural change and dynamics of the F8BT and PFO polymer chains before and after orientations will also be presented.

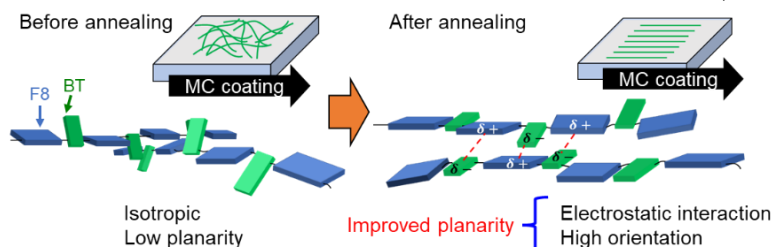


Fig. 2 Orientation mechanism of F8BT

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Revisiting the magnetic properties of Mn-formate framework chiral antiferromagnet: orientation dependance of $\text{NH}_4\text{Mn}(\text{HCOO})_3$ and $\text{CsMn}(\text{HCOO})_3$

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Perovskite refers to the type of crystal structure with a general formula ABX_3 , not only inorganic compounds but also hybrid organic-inorganic structure with the X-site can be polyatomic and/or organic ligands. The diversity of X ligands allows the formation of many different compounds with various degrees of freedom, along with a wide range of structure-related properties can be exhibited. Among the family of hybrid organic-inorganic compounds, metal-formate framework forms the largest group. Many $\text{AM}(\text{HCOO})_3$ analogues with various physical properties have been reported throughout the years, in which magnetism provides the focal interest. The formate bridging ligands prolong the distance of the neighboring metal sites, resulting in weak magnetic coupling and low critical temperature. It also allows the tilting of these metal sites into non-centrosymmetric disposition, as well as the emergence of Dzyaloshinskii-Moriya interaction and resulting in spin-canting phenomena that can escalate into peculiar magnetic structures.

A member of metal formate framework family, $\text{NH}_4\text{Mn}(\text{HCOO})_3$ had been reported to be a chiral antiferromagnet with evidence of chiral soliton (CS) phase by Ichiraku et al. in 2019.^[1] In a monoaxial chiral helimagnet, CS is the result from the competition between exchange and Dzyaloshinskii-Moriya interactions propagating along the crystallographic axis, which is called DM axis or helical axis. The spins align on the planes perpendicular to the helical axis into a long-range helix order. The application of magnetic fields regarding the field direction distorts the helix in different ways (Fig. 1). CS is realized in ferromagnet CrNb_3S_6 and had been intensively studied for its physical properties. CS in antiferromagnet, on the other hand, is still short in studies, especially in hybrid organic-inorganic frameworks such as $\text{NH}_4\text{Mn}(\text{HCOO})_3$. The compound crystallized in hexagonal chiral space group $P6_322$ and the experimental indication of CSL was observed in the magnetic c -measurement under the magnetic field perpendicular to the chiral axis of crystal structure - c -axis.

In order to provide more evidence of antiferromagnetic chiral soliton lattice as well as clarify the relationship between the crystal structure and magnetic structure in hybrid organic-inorganic perovskite, we revisit the magnetic properties of $\text{NH}_4\text{Mn}(\text{HCOO})_3$ in term of orientation dependance measurement. Meanwhile, we synthesized $\text{CsMn}(\text{HCOO})_3$, a compound that shares many similarities to $\text{NH}_4\text{Mn}(\text{HCOO})_3$ in crystal structure and studied its magnetic properties in comparison to $\text{NH}_4\text{Mn}(\text{HCOO})_3$.

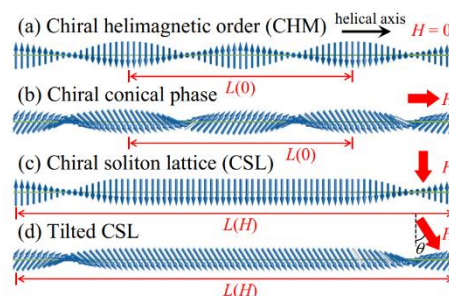


Figure 1. Magnetic phases formed in a monoaxial chiral magnetic crystal.^[2]

Cryogenic gas-phase spectroscopy of $[(CX_2)_2]^{+\bullet}$ ($X = O, S$): Correlation of cluster conformations and charge resonance interaction

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Charge-resonance (CR) interaction mainly contributes unique chemical bonds in radical cations of molecular clusters [1]. Although strength of CR interactions seems largely dependent on conformations of molecular clusters, it has been challenging to reveal these correlations because ion temperatures have not been fully regulated in conventional jet-spectroscopic studies on molecular cluster ions. In the present study, we focused on $[(CX_2)_2]^{+\bullet}$ ($X = O, S$) ions [2,3] isolated in a cryogenic (~ 5 K) ion trap [4], which “freezes” their conformations to allow access to the correlation with CR interactions.

Photodissociation (PD) spectra of $[(CX_2)_2]^{+\bullet}$ ($X = O, S$) in a quadrupole ion trap (QIT) at 410–1000 nm exhibited broad absorptions attributed to CR bands [5]. In particular for $[(CS_2)_2]^{+\bullet}$, significant blueshift (~ 3000 cm^{-1}) was observed upon cryogenic cooling from room temperature (295–300 K) to 5 K. Quantum chemical calculations by coupled-cluster singles and doubles (CCSD) method identified two conformers (**S'** and **F'**; Figure 1) of $[(CS_2)_2]^{+\bullet}$ with relative energy of only 200 cm^{-1} . We concluded that their relative populations largely depend on temperature (5 K or room temperature (295–300 K)) and that a difference in strength of their CR interactions resulted in the temperature-dependent band positions. This study highlights exceptional ability of our cryogenic QIT-based gas-phase spectroscopic technique for structural investigations of highly flexible molecular cluster ions.

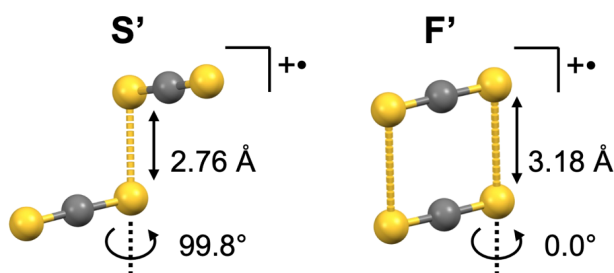


Figure 1. Calculated geometric structures of two conformers **S'** and **F'** of $[(CS_2)_2]^{+\bullet}$.

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Acknowledgement: We are grateful to Prof. F. Misaizu, Dr. K. Ohshimo, and Dr. Y. Ito (Tohoku Univ.) for their expert advice on quantum chemical calculations.

Knotted chiral meta matter

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Everything we see around us, ourselves included, is ordinary matter. Antimatter can exist too, but no macroscopic amounts of antimatter have ever been observed, albeit antiparticles are generated at accelerators and in processes like cosmic ray collisions. This talk will introduce the paradigm of “knotted chiral meta matter (KCM²)”, which will have its own analogs of fundamental particles/antiparticles and physical principles for designing new materials based on them; it will offer profoundly deep insights ranging from the inner workings of the World to the origins of life, as well as fundamental breakthroughs capable of enabling green technologies needed to sustain it. Aiming to create entirely new embodiments of everything, from fundamental (anti)particles to quasi-atoms and quasi-molecules to both liquid & solid crystals of knots and to materials with highly unusual properties, our WPI’s KCM² paradigm will deepen fundamental understanding of natural phenomena through creating their pre-designed analogs, as well as will solve the knotty Global problems of growing energy demand & climate change by designing matter with highly desirable material properties.

Einstein proved the existence of atoms while explaining Brownian motion & introducing the notion of so-called “colloidal atoms”. This later led to using colloids to gain insights into the behavior of atomic crystals and glasses, and recently to the large variety of optical, mechanical and other types of metamaterials made from pre-designed, artificial “quasi-atom” building blocks. However, the meta-matter-like behavior of known metamaterials made from such man-made building blocks is limited to only certain types of properties, like the refractive index or mechanical behavior. We work towards the creation of the “knotted chiral meta matter”, the KCM² paradigm that builds on particle-like quasi-atom properties of topological knot solitons, knotted vortices and knots in colloidal or (bio)polymer molecular strands. Our KCM² is anticipated to share and explain many properties of ordinary matter and antimatter, but also overcome their fundamental limitations. While knotted solitons can have chiral nature, the key role played by chirality is in enabling the energetic stability of such particle-like objects. Like in these examples, the World of KCM² that we design and create will help to overcome the perceived limits of the World around us. In implementing this vision, we take advantage of the recent developments in topology in both physical and momentum spaces, and in a large variety of order parameter spaces ranging from chiral liquid crystals to colloids, magnets, (bio)polymers, gels & other condensed matter & biological systems. The lecture will discuss how within the KCM² paradigm, we will gain insights into the nature of fundamental building blocks of (anti)matter & origins of life & will create foundations to address global problems of growing energy demand, climate change & human health vulnerability.