



広島大学 CResCent(キラル国際研究拠点) 第 10 回「キラル物性セミナー」
Prof. Prasanna S. Ghalsasi, Dr. Goulven Cosquer, Dr. Masaru Fujibayashi

日時：2019年7月11日(木) 14:00 ~ 17:20

開催場所：広島大学 理学研究科 B501

7月から、インド The Maharaja Sayajirao University of Baroda からサバティカルで半年こちらで研究される Prasanna S. Ghalsasi 教授、および7月1日付で固体物性の助教に就任された COSQUER Goulven 博士、4月より固体物性のポスドクとして研究されている、藤林将博士の合同セミナーを以下の要領で開催しますので、興味がある方はご参加ください。

【プログラム】

- 14:00-15:20 Prof. Dr. Prasanna S. GHALSASI (MSU Baroda)
“Designing Intermolecular Dialogues: Building Molecular Magnets to Stereo and Enantioselective C-C Oxidative Coupling”
- 15:20-15:30 Break Time
- 15:30-16:30 Dr. Goulven COSQUER (HU)
“Multi-functionality in single-molecule magnet”
- 16:30-17:20 Dr. Masaru FUJIBAYASHI (HU)
“Basket-Shaped Polyoxometalates Grafted with Organic Phosphonates”
有機ホスホン酸を修飾したバスケット型ポリオキソメタレート



Core to Core Program 「スピんキラリティを軸にした先端材料コンソーシアム」

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Designing Intermolecular *Dialogues*: Building Molecular Magnets to Stereo and Enantioselective C-C Oxidative Coupling

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Designing of molecular magnets is challenging task because molecules with unpaired electrons (spins) normally *die-merize* rather than sustaining paramagnetic nature in lattice or a domain with multiple dimensions. Therefore, practice of inserting good *magnetic exchangers* is normally observed in literature. My efforts in this direction are discussed by taking three distinct studies: (a) cyanide -with Prof. Katsuya Inoue- resulted in first chiral magnet;¹ (b) azide- designing of conglomerate to racemic structures;² and (c) chloride – reversible accommodation or sorption of HCl gas- a case of interconversion of complex to salt at solid-gas phase interface.³

Talk will also discuss our results on (1) how to introduce polarity (chirality) or ferroelectricity in simple organic salts?⁴, (2) application of back-bonding for observing Poisson like effect-elastic behaviour.⁵

Recently we explored role of $[Ag(NH_3)_2]^+$ for oxidative Carbon-Carbon coupling reaction-beta-naphthol to BINOL conversion. Although reaction follows familiar silver mirror test pattern, it poses many intriguing questions due to generating enantio-selectivity or selective cross coupling without addition of an *extra* reagent or change in catalysts structure! This is the first report where role of adhesion (not adsorption) is employed for driving oxidative coupling reaction⁶

1. Inoue, K.; Imai, H.; Ghalsasi, Prasanna; Kikuchi, K.; Ohba, M.; Okawa, H.; Yakhmi, J.V. A Chiral Molecule-Based Three-dimensional Ferrimagnet with High TC of 53K. *Angew. Chem. Int. Ed. Engl.* 2001, 40 (22), 4242-4245
2. Interplay of Chiral Auxiliary Ligand and Azide Bridging Ligand during the Coordination Network Formation with Copper(II). Hemant M. Mande, Prasanna S. Ghalsasi*, Navamoney, A.; *Cryst. Growth Des.* 2014, 14 (9), 4254-257
3. Accommodative Behavior of Nonporous Molecular crystal at Solid-Gas and Solid-Liquid Interface. Hemant M. Mande, Prasanna S. Ghalsasi* *Scientific Reports* 2015, 5, 14460-14468. (full waiver)
4. Designing Chiral, pro-Polar Structures for inducing Ferroelectricity: Molecular Analogue of KNO₃. Hemant M. Mande, Prasanna S. Ghalsasi* *Cryst. Growth Des.* 2016, 16 (1), 3–7.
5. Back-Bonding Signature with High Pressure: Raman Studies on Silver Nitroprusside. PP Ghalsasi, Prasanna S Ghalsasi*, DVS Muthu, *Inorganic Chemistry* 2017, 56 (16), 9669-9675.
6. (a) C-C oxidative coupling of phenols and its derivatives. Prasanna S. Ghalsasi and Khubhoo Bhanderi (Indian Patent) 201621005382; and (b) Molecular to Macroscopic surface for Asymmetric Syntheses P Ghalsasi and Khubhoo Bhanderi, C. Gonsalves (Indian Patent) 201712039245 CBR 20884.

Multi-functionality in single-molecule magnet

COSQUER Goulven

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A single-molecule Magnet (SMM) can be defined as a magnetically isolated molecule which can maintain its magnetization without external magnetic field. In the family of the SMM, the single-ion magnet (SIM) are characterized by the presence of a unique magnetic ion. In the case of lanthanide ions, crystal field, by affecting the ground state configuration, is the key point to observe SMM property. Here, I would like to introduce SMM with additional functionality. A double-decker complexes with annulene ligands functionalized with indolenine groups and Dy ion have been used to prepare pH sensitive SMM. A clear correlation among the degree of protonation of the complex, the opening of the hysteresis, and the slow magnetic relaxation time was observed. Hydrogen bond between the two ligands of the complex induced a modification of the crystal field.

Multi-functionality can be also a quantitative tool to analyse SMM behaviour. Mononuclear complexes of Yb^{III} ion where the coordination polyhedron is described as a distorted triangular dodecahedron prism (*D_{2d}* symmetry) can be used. The influence of this distortion on the magnetic and photo-physical properties is determined from static magnetic measurements and luminescence spectra. The Yb^{III} luminescence spectra shape is directly correlated to the energy splitting of the *M_J* states that stem from the ²F_{7/2} multiplet ground state. This energy splitting can be also determined from the fit of the static magnetic measurements. A perfectly matches between this two method allow to precisely characterize the SMM state.

Finally, a conducting single-molecule magnet, combining organic conductor and Co based SMM, was synthesized and structurally, physically and theoretically investigated. Charge transfer (CT) between the organic conductor and the SMM unit as well as intra-SMM CT from the Co ion to the ligand was observed. The strong interactions, combined with the CT, cause high electrical conductivity with an almost zero activation energy and a magneto-resistance effect. The role of the d- π interactions were determined to be an origin of these properties.

- 1) Liang, Z.; Damjanović, M.; Kamila, M.; Cosquer, G.; Breedlove, B. K.; Enders, M.; Yamashita, M. ; *Inorg. Chem.* **2017**, *56* (11), 6512–6521. DOI: [10.1021/acs.inorgchem.7b00626](https://doi.org/10.1021/acs.inorgchem.7b00626)
- 2) Cosquer, G.; Pointillart, F.; Jung, J.; Le Guennic, B.; Golhen, S.; Cador, O.; Guyot, Y.; Brenier, A.; Maury, O.; Ouahab, L. ; *Eur. J. Inorg. Chem.* **2014**, No. 1, 69–82. DOI: [10.1002/ejic.201301358](https://doi.org/10.1002/ejic.201301358)
- 3) Shen, Y.; Cosquer, G.; Izuogu, D.C.; Thom, A.J.W.; Ina, T.; Uruga, T.; Yoshida, T.; Breedlove, B.K.; Yamashita, M.; **Submitted**.

有機ホスホン酸を修飾したバスケット型ポリオキシメタレート Basket-Shaped Polyoxometalates Grafted with Organic Phosphonates

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Mo や W などの前期遷移金属イオンが酸素配位子を介して形成される分子性の金属酸化物群はポリオキシメタレート (POM) と総称され、多彩な分子形状を示す巨大無機分子である。POM は電子貯蔵能や酸化還元能を示す点で、有機無機複合材料における無機ホストとしても注目を浴びており、高い分子設計性を有している。我々は、これまで Mo₁₈ 核から成る金属骨格に 4 つの有機ホスホン酸を表面修飾したバスケット型 POM $[\text{Na}(\text{SO}_3)_2(\text{R-PO}_3)_4\text{Mo}^{\text{V}}_4\text{Mo}^{\text{VI}}_{14}\text{O}_{49}]^{5-}$ (R = Ph, Et, EtCl, *n*-Pr, *n*-Bu, *t*-Bu) について、有機部位の置換による分子機能性の開拓を狙ってきた^[1]。単結晶 X 線構造回折装置を用いた構造評価より、有機部位の違いにより、Mo-O 骨格の対称性が異なる 2 つの構造異性体が存在することを明らかにした (図 1)。特に、*n*-Bu 基を修飾した POM では、この二つの異性体間を相転移することを見出した。本研究では、各分子の結晶構造を中心に、構造相転移の機構などについて詳細を報告する。

図 1 には、構造異性体について、その分子構造をまとめた。単結晶を用いた X 線構造解析より、各分子骨格を比較したところ、C₂ 対称な Mo-O 骨格もしくは歪んだ Mo-O 骨格を持つ 2 種類の構造異性体が存在することが分かった。加えて Mo-O 骨格が歪みに伴い、分子内に包接されている Na⁺イオン (図中紫球) の位置に違いが確認された。結晶構造の比較より、これらの構造の相違は結晶中での充填度に依存しており、密な充填構造が保持されることで、Mo-O 骨格が歪む傾向が示唆された。加えて、*n*-Bu 基を修飾した POM では、温度変化による結晶格子の変化量が他の単結晶に比べて大きく、2 つの領域を行き来することが可能となったため、構造相転移を示すことを明らかにした。

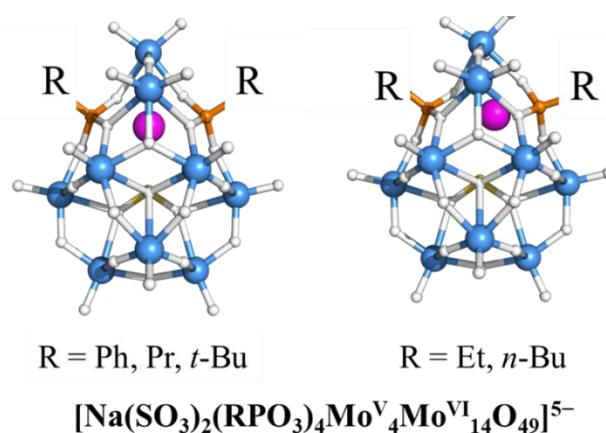


図 1. バスケット型 POM の構造異性

- [1] (a) R. Tsunashima, M. Fujibayashi *et al.*, *J. Am. Chem. Soc.*, **2015**, *137*, 6524-6530. (b) M. Fujiabyashi, *et al.*, *New J. Chem.*, **2016**, *40*, 8488. (c) M. Fujibayashi, *et al.*, *Bull. Chem. Soc. Jap.*, **2019**, *92*, 918-922.