様式 Form 7
（外国人招へい研究者）

Fellowship ID：BR230204

2024 年　05 月　24 日
YYYY/MM/DD

独立行政法人日本学術振興会理事長　殿

To: President, Japan Society for the Promotion of Science

研究活動報告書

Research Report

1．受入研究者/ Host researcher

受入研究機関・部局・職 Name of Host Institution, Department and Title	Hiroshima University, Faculty of Science, CResCent (WPI-SKCM2)
受入研究者氏名 Host Researcher's Name	Katsuya INOUE (Professor)

2．外国人招へい研究者/ Fellow

所属研究機関・部局・職 Name of Institution, Department and Title	Laboratoire des Multimatériaux et Interfaces (UMR 5615) Université Claude Bernard Lyon 1 – Villeurbanne - France
外国人招へい研究者氏名 Fellow's Name	Dominique Luneau (Professor)

3．採用期間/ Fellowship Period

2024 年　03 月　20　日　～　2024 年　05 月　03 日

4．研究課題/ Research Theme

Molecule-based magnetic material

5．研究活動報告/ Research Report

During my fellowship time I was hosted by Professor Katsuya INOUE at Hiroshima University and shared my time in between his group at the Faculty of Sciences and at the *WPI: International Institute for Sustainability with Knotted Chiral Meta Matter* (SKCM2 https://wpi-skcm2.hiroshima-u.ac.jp/). I use this time in research activities, drafting joint publications and deepening our collaborative network.

（注）採用期間終了後 3 ヶ月以内に提出
※　(Note) Submit the form within 3 months after the expiration of fellowship.
※　様式 1 に記載された情報を元に確認しますので、部局名等の名称含め、内容に誤りが無いか必ずご確認ください。

5.1）研究活動の概要・成果/ Summary of Research Results

Connected with researches on "establishing synthesis strategy of chiral magnet" at SKCM2 and CRESCENT (Chirality Research Center : https://kotai.hiroshima-u.ac.jp/chiral/en/) I investigated the crystal structures of a series of compounds made of the coordination of lanthanide ions (Gd, Tb, Dy) with nitronyl nitroxide NITImH (Figure 1a). These were synthesised in my group at Université Claude Bernard Lyon 1 and were designed with objective to get chiral single-molecule magnets as well as precursors of 2D and 3D lanthanide-radical frameworks. As anticipated, the single-crystal X-rays diffraction performed at Hiroshima University evidences the compounds crystallise in the non-enantiogenic $C222_1$ space group. Preliminary magnetic studies agree well with one lanthanide coordinated with three radical. However, as is often observe for chiral compounds single crystals have many defect that do not allow getting high quality crystal structures and this requires new synthesis and crystallisation. This will be pursued by Sabrina Grenda, doctoral student under my supervision next summer as a JSPS fellow of the summer program also in the group of Prof. Inoue at Hiroshima University.

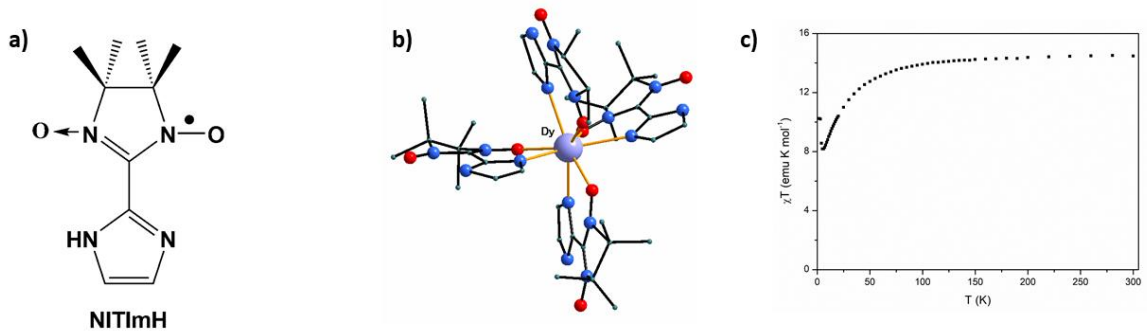


Figure 1: Crystal structure of dysprosium(III) complex (b) with nitronyl nitroxide NITImH (a) and temperature dependence of the product of magnetic susceptibility with temperature(c).

5.2）主な研究発表（雑誌論文、学会、集会、知的財産権等）/ Main Research Publications

I also used the time of my fellowship to discuss and wrote two publications.

Publication 1: ***Electron crystallography elucidation of the structure of two 2D metal-radical frameworks breakthroughs the investigation of molecule-based magnets with nanosized crystals*** Emre Yoruk, Constance Lecourt, Dominique Housset, Yuuta Izumi, Wai Li Ling, Stéphanie Kodjikian, Evgeny Tretyakov, Katsuya Inoue, Kseniya Maryunina, Cédric Desroches, Holger Klein, Dominique Luneau (*Submitted to the Journal of American Chemical Society*)

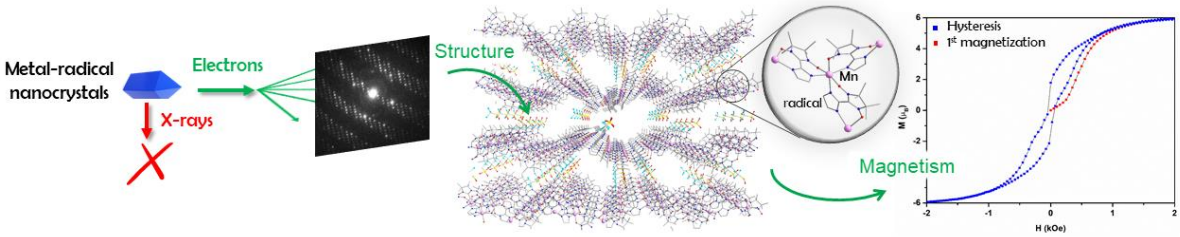


Figure 2. Electron crystallography of 2D metal-radical coordination frameworks with metamagnetic properties

This publication reports the synthesis, crystal structures and magnetic properties of two coordination polymers made of manganese(II) coordinated with nitronyl nitroxide radical NITImH (Figure 1a). Magnetic measurements show a ferrimagnetic behavior within the 2D metal-radical sheets due to alternating antiferromagnetically coupled spins ($S_{Mn^{2+}} = 5/2$ and $S_{radical} = 1/2$). Both compounds exhibit a long-range 3D ordering of weak ferromagnetic

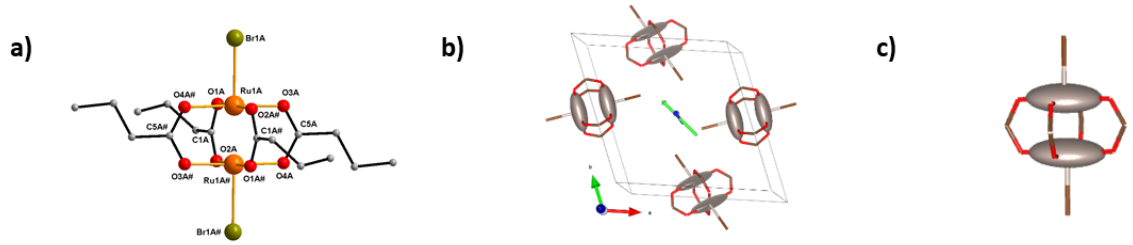
（注）採用期間終了後 3 ヶ月以内に提出
※　(Note) Submit the form within 3 months after the expiration of fellowship.
※　様式 1 に記載された情報を元に確認しますので、部局名等の名称含め、内容に誤りが無いか必ずご確認ください。

nature with Curie temperatures T_c = 45 K - 40 K. This is associated with spin canting and a field-induced metamagnetic transition from antiferromagnetic to ferromagnetic coupling of 2D metal-radical sheets is observed. In this work, we demonstrate how electron crystallography has been instrumental for the determination of the crystal structure and how this result could boost research in molecule-base magnets.

The work was **internationally collaborative** involving Université Claude Bernard Lyon 1 (France), Hiroshima University (Japan), Université Grenoble Alpes (France), Novosibirsk State University (Russia) and N. D. Zelinsky Institute of Organic Chemistry (Russia). I will also present this work during the 34th European Crystallographic Meeting (26-30 August 2024 Padova Italy).

Related to publication 1 gave a lecture on my work on April 4th 2024 titled "Memories in coordination chemistry of nitroxide radicals" (https://wpi-skcm2.hiroshima-u.ac.jp/seminars/dominique-luneau-university-claude-bernard-lyon-1memories-in-coordination-chemistry-of-nitroxide-radicals/).

Publication 2: ***Spin density distribution and local magnetic anisotropy in a Ru(II,III) paddle-wheel tetracarboxylate dimer*** Sabrina Grenda, Haruki Yairi, Torao Fujimoto, Oscar Fabelo, Iurii Kibalin, Nicolas Claiser, Rémi Maurice, Arsen Gukasov, Laura Canadillas-Delgado, José A. Rodriguez Velamazan Jean-François Jacquot, Ryoji Mitsuhashi, Masahiro Mikuriya, Makoto Handa and Dominique Luneau



The peculiar electronic structure of diruthenium tetracarboxylate compounds, combining a high spin state with a large ZFS has prompted their use as building blocks of molecule-based magnets. Along this, one-, two- and three-dimensional systems comprising diruthenium tetracarboxylate with paramagnetic axial linkers like nitroxide radicals or hexacyanidometalate ions have been reported by the group of Profs Handa (Shimane University) and Prof. Mikuriya (Kansai Gakuin University) and have high Curie temperature (Tc= 40-50K). To increase the performance of these molecule-based magnets, it is important to understand the magneto-structural relationships at the molecular level and this raises two main questions we address in this paper. One question is how the unpaired electrons are delocalized on the ligands, as it is related to how large magnetic interaction. A second question is how large is the molecular magnetic anisotropy and how are oriented are the principal. In this work, we revisit these questions combining experimental Polarized Neutron Diffraction (PND) and high-resolution X-ray diffraction and quantum calculation.

The work was **internationally collaborative** involving Université Claude Bernard Lyon 1 (France), Shimane University (Japan), Kanazawa University (Japan), Institut Laue Langevin (France), Institut Léon Brillouin (France), Université Rennes 1 (France) and CEA-Grenoble (France).

Related to publication 2, I also have discussions with Ryoji Mitsuhashi at Kanazawa University and Prof. Handa at Shimane University where I gave a lecture titled "Molecular magnetic anisotropy as seen by Polarized Neutron Diffraction" on April 24th 2024.

5.3）その他/ Remarks

All along my stay at Hiroshima University supported by the Bridge fellowship, I have had many discussions with Prof. Inoue and with many members of the *WPI: International Institute for Sustainability with Knotted Chiral Meta Matter* (**SKCM2** https://wpi-skcm2.hiroshima-u.ac.jp/) during formal and informal meetings. This has been very profitable to collaboration with Prof. Inoue. Especially this gives me a better vision of how I can actively contribute to researches activities within WPI: SKCM2 of which I am now an associated member of the WPI.

（注）採用期間終了後 3 ヶ月以内に提出
※ (Note) Submit the form within 3 months after the expiration of fellowship.
※ 様式 1 に記載された情報を元に確認しますので、部局名等の名称含め、内容に誤りが無いか必ずご確認ください。