

アカデミックプログラム [B講演] | 09. 錯体化学・有機金属化学：口頭B講演

📅 2025年3月29日(土) 9:00 ~ 11:20 📍 [B]A307(第2学舎 1号館 [3階] A307)

**[[B]A307-4am] 09. 錯体化学・有機金属化学**

座長：小林 厚志、森本 祐麻

## ◆ 英語

9:00 ~ 9:20

[[B]A307-4am-01]

Mn錯体を触媒として用いた低濃度CO<sub>2</sub>のCOへの選択的光触媒還元反応○鴨川 径<sup>1</sup>、石谷 治<sup>2</sup> (1. 東京科学大理、2. 広島大院先進理工)

## ◆ 英語

9:20 ~ 9:40

[[B]A307-4am-02]

*fac*-Tricarbonyl Bipyridine Re Complexes Catalyze Visible-light-driven Carboxylation of Phenyl Vinyl Sulfone with CO<sub>2</sub>○Phurinat Lorwongkamol<sup>1</sup>, Masaki Kitada<sup>2</sup>, Taito Watanabe<sup>1</sup>, Yutaka Saga<sup>1</sup>, Tetsuya Kambe<sup>1</sup>, Mio Kondo<sup>2</sup>, Shigeyuki Masaoka<sup>1</sup> (1. Osaka University, 2. Institute of Science Tokyo)

## ◆ 英語

9:40 ~ 10:00

[[B]A307-4am-03]

Water-Mediated Selectivity Modulation and Steric Regulation of Activity in Photochemical CO<sub>2</sub> Reduction Catalyzed by RhCp\*(bpy) Complexes○Dongseob Lee<sup>1</sup>, Kosei Yamauchi<sup>1</sup>, Ken Sakai<sup>1</sup> (1. Kyushu Univ.)

## ◆ 英語

10:00 ~ 10:20

[[B]A307-4am-04]

Dirhodium Complexes with a Redox Flexibility Supported by a Macrocyclic PDI<sub>2</sub> Ligand○Liping Yan<sup>1</sup>, Yuma Morimoto<sup>1</sup>, Makoto Yamashita<sup>1</sup> (1. Institute of Science Tokyo)

## ◆ 日本語

10:20 ~ 10:40

[[B]A307-4am-05]

混合原子価マンガン酸化物クラスターの光熱変換特性とポスト機能化

○福井 智也<sup>1,2</sup>、嘉藤 幹也<sup>1</sup>、福島 孝典<sup>1,2</sup> (1. 科学大化生研、2. 科学大ASMat)

## ◆ 英語

10:40 ~ 11:00

[[B]A307-4am-06]

五配位 Mn<sup>II</sup> 錯体が見せるマグネトルミネッセンス○樋川 岳真<sup>1</sup>、松岡 亮太<sup>1</sup>、水野 麻人<sup>1</sup>、木村 尚次郎<sup>2</sup>、草本 哲郎<sup>1,3,4</sup> (1. 阪大院基礎工、2. 東北大金研、3. JST創発、4. OTRI-Spin 阪大)

## ◆ 日本語

11:00 ~ 11:20

[[B]A307-4am-07]

## 巨大分極を示す無水強誘電イオン伝導体の開発

○木村 紗彩<sup>1</sup>、大谷 亮<sup>1</sup>、大場 正昭<sup>1</sup> (1. 九州大学大学院)

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# Efficient and Selective Photocatalytic Conversion of Low-Concentration CO<sub>2</sub> to CO using a Mn Complex Catalyst

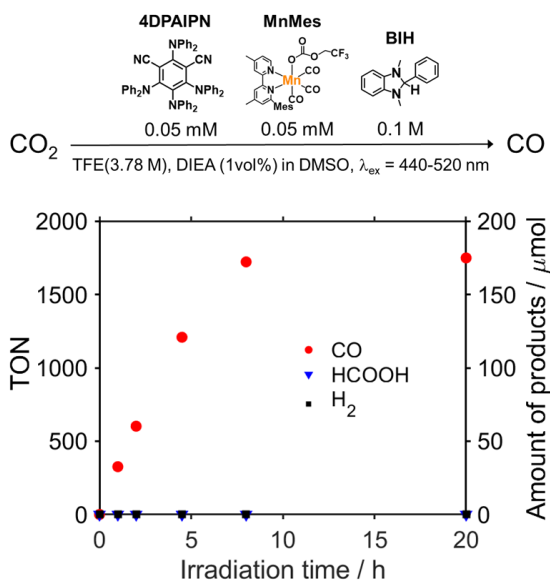
(<sup>1</sup>*School of Science, Institute of Science Tokyo*, <sup>2</sup>*Graduate School of Advanced Science and Engineering, Hiroshima University*) ○Kei Kamogawa,<sup>1</sup> Osamu Ishitani<sup>2</sup>

**Keywords:** Carbon dioxide reduction, Photocatalyst, Metal Complex

The development of efficient photocatalytic systems for CO<sub>2</sub> reduction using abundant metal complex catalysts has been actively pursued. Among these, *fac*-[Mn<sup>I</sup>(diimine)(CO)<sub>3</sub>L]<sup>n+</sup>-type complexes have emerged as promising candidates.<sup>1,2</sup> Nevertheless, the dimerization of the one-electron reduced Mn complexes, which leads to photodecomposition of the resulting Mn dimers due to their strong absorption in visible region, significantly limits the durability of the Mn-complex catalysts in photocatalytic CO<sub>2</sub> reduction reactions.

In this work, we designed a Mn(I) carbonate ester complex featuring a bulky mesityl group positioned near the central Mn (**MnMes** in Figure 1). In the presence of the organic photosensitizer **4DPAIPN** and the sacrificial electron donor BIH, **MnMes** selectively reduced CO<sub>2</sub> in a DMSO solution containing 2,2,2-trifluoroethanol (TFE) and *N,N*-diisopropylethylamine (DIEA). During the photocatalytic reaction, dimerization of **MnMes** was completely suppressed, enabling high turnover number (TON<sub>CO</sub> = 1750), selectivity (>99.9%) and turnover frequency (TOF<sub>CO</sub> = 6.03 min<sup>-1</sup>) for CO formation (Figure 1). Furthermore, even under Ar gas with low CO<sub>2</sub> concentrations, such as 10% and 1%, CO production maintained high selectivity and proceeded at relatively high reaction rates (TOF<sub>CO</sub> = 5.31 min<sup>-1</sup>, and 2.66 min<sup>-1</sup>, respectively). Under these conditions, the CO<sub>2</sub> in the reaction vessel was completely consumed by photocatalysis. These findings demonstrate that **MnMes** exhibits high catalytic activity even at extremely low CO<sub>2</sub> concentrations.

(1) H. Takeda, O. Ishitani, *et. al.*, *Chem. Commun.*, 2014, **50**, 1491. (2) H. Takeda, O. Ishitani, *et. al.*, *J. Am. Chem. Soc.*, 2018, **140**, 17241.



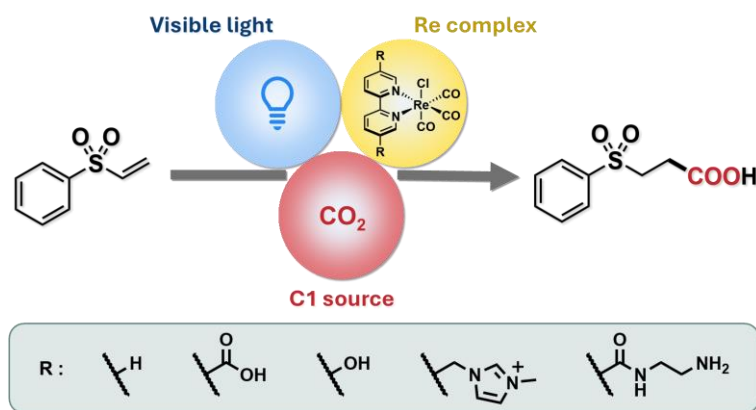
**Figure 1.** Photocatalytic formation of CO (red), H<sub>2</sub> (black), and formic acid (blue) as a function of irradiation time. A CO<sub>2</sub> saturated DMSO solution containing **4DPAIPN** (0.05 mM), **MnMes** (0.05 mM), **BIH** (0.1 M), TFE (3.78 M) and DIEA (1 vol%) was irradiated with a LED light (λ<sub>ex</sub> = 440-520 nm).

## *fac*-Tricarbonyl bipyridine Re complexes catalyze visible-light-driven carboxylation of phenyl vinyl sulfone with CO<sub>2</sub>

(<sup>1</sup>Graduate School of Engineering, Osaka University, <sup>2</sup>School of Science, Institute of Science Tokyo) ○Phurinat Lorwongkamol,<sup>1</sup> Masaki Kitada,<sup>2</sup> Taito Watanabe,<sup>1</sup> Yutaka Saga,<sup>1</sup> Tetsuya Kambe,<sup>1</sup> Mio Kondo,<sup>2</sup> Shigeyuki Masaoka<sup>1</sup>

**Keywords:** CO<sub>2</sub>; carboxylation; visible light; photocatalysis; Re complex

The direct carboxylation of organic molecules using CO<sub>2</sub> as an abundant and non-toxic C1 building block offers an appealing and atom-economic synthesis of carboxylic acids. However, this approach is highly energy-demanding due to the inherent stability of the CO<sub>2</sub> itself. Therefore, the development of effective catalysts has become of great interest.<sup>1</sup> Encouraged by our previous work,<sup>2</sup> we demonstrate in this work that *fac*-[Re(2,2'-bipyridine)(CO)<sub>3</sub>Cl], a well-known photocatalyst for the conversion of CO<sub>2</sub> to CO,<sup>3,4,5</sup> has catalytic potential for the visible-light-driven carboxylation of alkene with CO<sub>2</sub>. Our photocatalytic system successfully promoted the carboxylation of phenyl vinyl sulfone (PVS) to the corresponding carboxylic acid. We found that the photodimerization of PVS is the main competing reaction, and the product selectivity can be altered by changing the solvent. Additionally, we have developed a series of Re complexes using various derivatives of bipyridine ligands. The characterization and catalytic activity of these complexes will be presented.



1) Q. Liu, L. Wu, R. Jackstell, M. Beller, *Nat Commun.*, **2015**, 6, 5933. 2) M. Kitada, Z. L. Goo, K. Kosugi, Y. Saga, N. Yoshinari, M. Kondo, S. Masaoka, *Chem. Lett.*, **2023**, 52, 512. 3) J. Hawecker, J.-M. Lehn, R. Ziessel, *J. Chem. Soc., Chem. Commun.*, **1983**, 286, 536. 4) Y. Yamazaki, M. Miyaji, O. Ishitani, *J. Am. Chem. Soc.*, **2022**, 144, 6640. 5) K. Kamogawa, Y. Kato, Y. Tamaki, T. Noguchi, K. Nozaki, T. Nakagawa, O. Ishitani, *Chem. Sci.*, **2024**, 15, 2074.

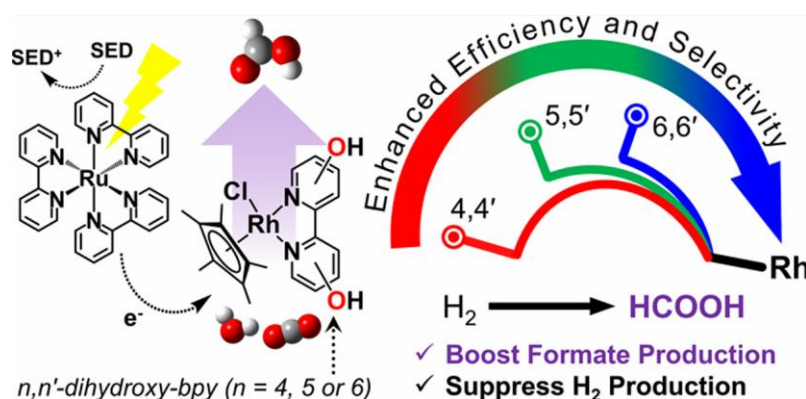
## Water-Mediated Selectivity Modulation and Steric Regulation of Activity in Photochemical CO<sub>2</sub> Reduction Catalyzed by RhCp\*(bpy) Complexes

(<sup>1</sup>Dept. Chem. Kyushu University) ○Dongseob Lee<sup>1</sup>, Kosei Yamauchi<sup>1</sup>, Ken Sakai<sup>1</sup>

**Keywords:** Photocatalysis, CO<sub>2</sub> reduction, Rhodium catalyst, formate selectivity, DFT studies

Photocatalytic reduction of CO<sub>2</sub> to formic acid (HCOOH) was investigated in either organic or aqueous/organic media by employing three water-soluble [Rh<sup>III</sup>Cp\*(LH<sub>2</sub>)Cl]<sup>+</sup> (LH<sub>2</sub> = *n,n'*-dihydroxy-2,2'-bipyridine; *n* = 4, 5, or 6) in the presence of [Ru(bpy)<sub>3</sub>]<sup>2+</sup>, BIH and TEOA. Through studying the electron-donating effects of two hydroxyl groups introduced into the bipyridyl ligand, we found that the substituent positions greatly affect both the catalytic efficiency and selectivity in CO<sub>2</sub> reduction.<sup>1</sup>

More importantly, the HCOOH selectivity shows a dramatic increase from 14 to 83% upon switching the solvent media from pure organic to an aqueous/organic mixture, where the H<sub>2</sub> selectivity shows a reverse phenomenon. The enhanced HCOOH selectivity and the drastic decrease in the H<sub>2</sub> yield are well rationalized by the fact that the catalytic CO<sub>2</sub> hydrogenation is not only driven photochemically via the attack of Rh<sup>III</sup>(H)Cp\*(LH<sub>2</sub><sup>−</sup>) on CO<sub>2</sub> but also partly bypassed by a dark H<sub>2</sub> addition reaction yielding [Rh<sup>III</sup>(H)Cp\*(L)]<sup>−</sup> from [Rh<sup>III</sup>Cp\*(L)Cl]<sup>+</sup>, which was also separately investigated under dark conditions. A combination of experimental and theoretical approaches was made to clarify the p*K*<sub>a</sub> values of catalyst intermediates together with the abundant species responsible for the major catalytic processes. Our DFT studies unveil that the exceptionally large structural strain given by the steric contacts between the 6,6'-dihydroxyl groups and the Cp\* moiety plays a significant role in bringing about an outstanding catalytic performance of the 6,6'-substituted derivative.



1) D. Lee, K. Yamauchi, K. Sakai, *J. Am. Chem. Soc.*, **2024**, *146*, 31597.

## Dirhodium Complexes with a Redox Flexibility Supported by a Macrocyclic PDI<sub>2</sub> Ligand

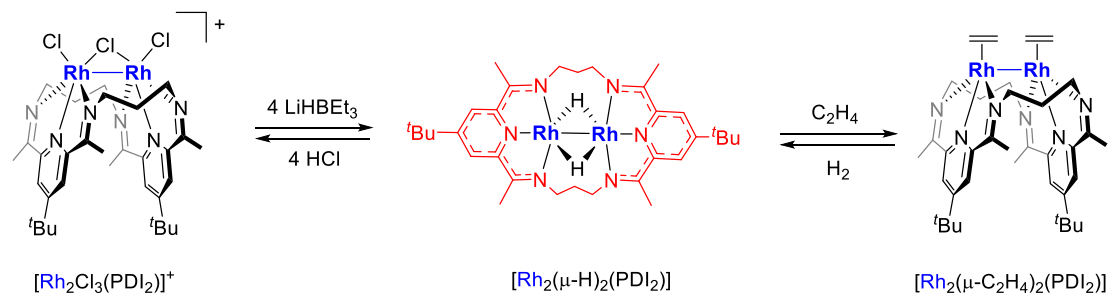
(School of Science, Institute of Science Tokyo) ○ Liping YAN, Yuma Morimoto, Makoto Yamashita

**Keywords:** Dirhodium Complexes, Macrocyclic Ligand, Hydride, Redox Active Ligand

Dinuclear metal complexes have attracted attention due to their catalytic capabilities, arising from the synergistic interplay between metal centers and their coordination environments. Typically, dirhodium(II) complexes have been extensively studied for their unique catalytic properties facilitated by the Rh–Rh core stabilized by rigid bridging ligands, e.g. acetate and naphthyridine. However, the influence of the distance and relative position of metal centers on redox properties and cooperativity in chemical reactions remains elusive, hindering the efficient design of dinuclear metal catalysts. Inspired by the catalytic efficiency of mononuclear metal complexes with pyridinediimine (PDI) ligands, known for their redox non-innocence and robustness, we herein report the synthesis and characterization of a novel dirhodium system supported by a macrocyclic ligand with two 2,6-pyridyldiimine moieties and propylene linkers (PDI<sub>2</sub>), and investigated their reactivity.

The macrocyclic ligand (PDI<sub>2</sub>) was used to synthesize a dinuclear Rh(II) complex [Rh<sup>II</sup><sub>2</sub>(μ-Cl)(PDI<sub>2</sub>)Cl<sub>2</sub>]<sup>+</sup> (**Scheme 1**) with 72% yield. Further treatment of the complex with four equimolar amounts of LiHBEt<sub>3</sub> in THF yielded a dirhodium dihydride complex [Rh<sub>2</sub>(μ-H)<sub>2</sub>(PDI<sub>2</sub>)], which is characterized by <sup>1</sup>H NMR with hydride signal (triplet 2H, –9.8 ppm) and single crystal X-ray diffraction analysis. Upon reduction, Rh–Rh distance elongated from 2.5804(6) Å to 2.8286(8) Å accompanied by a change in the ligand-folding structure, indicating a decrease in the Rh–Rh interaction. The dirhodium dihydride complex [Rh<sub>2</sub>(μ-H)<sub>2</sub>(PDI<sub>2</sub>)] could react with four equivalents of HCl to reversibly generate [Rh<sup>II</sup><sub>2</sub>(μ-Cl)(PDI<sub>2</sub>)Cl<sub>2</sub>]<sup>+</sup>. Notably, dinuclear Rh(0) complex [Rh<sub>2</sub>(H<sub>2</sub>C=CH<sub>2</sub>)<sub>2</sub>(PDI<sub>2</sub>)] was isolated and characterized after exposing [Rh<sub>2</sub>(μ-H)<sub>2</sub>(PDI<sub>2</sub>)] to ethylene. Exposure of [Rh<sub>2</sub>(H<sub>2</sub>C=CH<sub>2</sub>)<sub>2</sub>(PDI<sub>2</sub>)] to H<sub>2</sub> results in the reversible formation of [Rh<sub>2</sub>(μ-H)<sub>2</sub>(PDI<sub>2</sub>)]. The reduction state of the PDI ligand in these dinuclear Rh complexes was elucidated based on structural analyses and electronic absorption spectrum, then endorsed by DFT calculations. In this talk, we will discuss the drastic change in the oxidation state of the dirhodium complex supported by the high flexibility of the ligand.

**Scheme 1.** Synthetic scheme for the dinuclear Rh complexes



## 混合原子価マンガン酸化物クラスターの光熱変換特性とポスト機能化

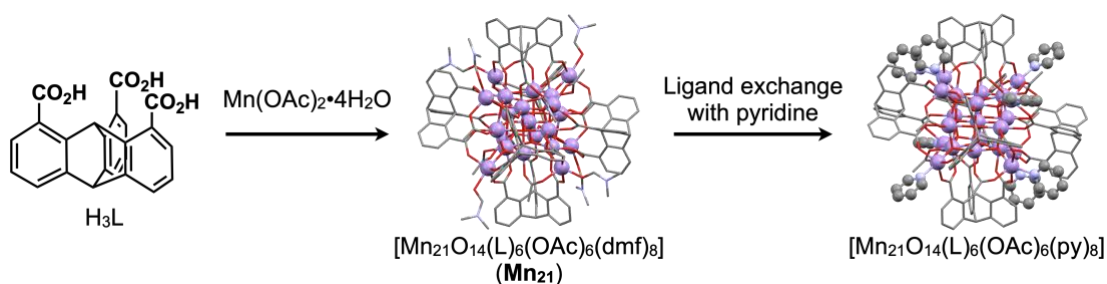
(科学大化生研<sup>1</sup>・科学大物質理工<sup>2</sup>・科学大 ASMat<sup>3</sup>) ○福井 智也<sup>1,2,3</sup>・嘉藤 幹也<sup>1,2</sup>・福島 孝典<sup>1,2,3</sup>

Post-modification of mixed-valence Mn-oxo clusters exhibiting efficient photothermal conversion (<sup>1</sup>*CLS, Science Tokyo*, <sup>2</sup>*Sch. Mater. Chem. Tech., Science Tokyo*, <sup>3</sup>*ASMat, Science Tokyo*) ○Tomoya Fukui,<sup>1,2,3</sup> Mikiya Kato,<sup>1,2</sup> Takanori Fukushima<sup>1,2,3</sup>

We have reported the selective construction of a decanuclear zinc-oxo cluster using the complexation of 1,8,13-tricarboxytriptycene with zinc acetate dihydrate.<sup>1)</sup> In the present work, we found that when 1,8,13-tricarboxytriptycene is reacted with manganese acetate tetrahydrate, a neutral henicosanuclear manganese oxo cluster (**Mn<sub>21</sub>**) is obtained, which exhibits efficient photothermal conversion comparable to single-walled carbon nanotubes. Furthermore, using a ligand exchange reaction, **Mn<sub>21</sub>** can be post-modified while retaining its photothermal conversion properties. Here we will report the synthesis, photothermal conversion properties, and post-modification of the manganese oxo clusters.

**Keywords :** Polynuclear complex; Multidentate ligand; Triptycene; Manganese oxide; Mixed-valence complex

最近、我々は 1,8,13-トリカルボキシトリプチセンと酢酸亜鉛の錯形成により、四面体状 10 核亜鉛酸化物クラスターが選択的に形成されることを報告した<sup>1)</sup>。今回、1,8,13-トリカルボキシトリプチセンと酢酸マンガンの錯形成により、優れた光熱変換特性を示す 21 核マンガン酸化物クラスターが得られることを見いだした。さらに、このマンガン酸化物クラスターにピリジル基を含む配位子を作用させると、位置選択的な配位子交換が進行し、光熱変換特性を損なうことなく様々な機能団でポスト機能化が可能であることを明らかにした。本発表では、マンガン酸化物クラスターのポスト機能化について議論する。



1) M. Kato, T. Fukui, H. Sato, Y. Shoji, T. Fukushima, *Inorg. Chem.* **2022**, *61*, 3649.

## Magnetoluminescence for a five-coordinated Mn<sup>II</sup> complex

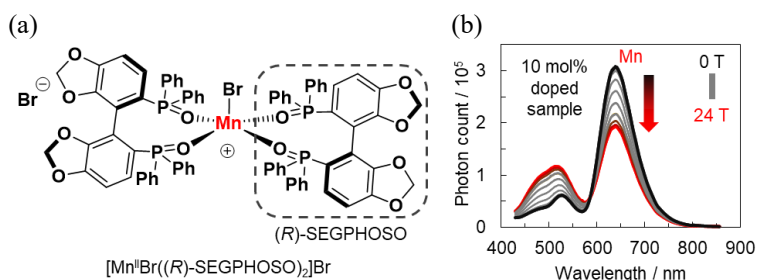
(<sup>1</sup>Grad. Sch. of Eng. Sci., Osaka Univ., <sup>2</sup>IMR, Tohoku Univ., <sup>3</sup>JST-FOREST, <sup>4</sup>OTRI-Spin, Osaka Univ.) ○Takema Hikawa<sup>1</sup>, Ryota Matsuoka<sup>1</sup>, Asato Mizuno<sup>1</sup>, Shojiro Kimura<sup>2</sup>, Tetsuro Kusamoto<sup>1,3,4</sup>

**Keywords:** Magnetic-field effect, Divalent manganese ion, Luminescence, Magnetism, Open-shell molecule

Magnetic field effects on luminescence (i.e., Magnetoluminescence, MagLum) are attractive photophysical phenomena, which have been mainly observed in molecular systems containing radical pairs or triplet pairs, and in assembled radicals. In the assembled radicals, the ground-state spin statistics (i.e., the Boltzmann distribution) is proposed to be the key to MagLum<sup>1)</sup>.

Recently, we investigated MagLum behavior of a high-spin Mn<sup>II</sup> complex with its spin multiplicity (spin-sextet ground state) larger than that of the reported MagLum-active molecular systems. Compared with the assembled radical systems, [Mn<sup>II</sup>(dppmO<sub>2</sub>)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub><sup>2)</sup> with an octahedral coordination geometry showed a different type of MagLum. However, its mechanism has not been fully elucidated. Herein, to gain more insight into the mechanism, we investigated MagLum of [Mn<sup>II</sup>Br((*R*)-SEGP<sub>2</sub>PHOSO)<sub>2</sub>]<sup>3)</sup> with a square pyramidal coordination geometry (Figure 1a).

We dispersed [Mn<sup>II</sup>Br((*R*)-SEGP<sub>2</sub>PHOSO)<sub>2</sub>]<sup>3)</sup>Br into solid (*R*)-SEGP<sub>2</sub>PHOSO at various concentrations and investigated the magnetic field dependence of their luminescence properties. The spectral changes of luminescence were observed under magnetic fields of up to 24 T (Figure 1b). The results suggest that the energy transfer processes are involved in the mechanism of MagLum for [Mn<sup>II</sup>Br((*R*)-SEGP<sub>2</sub>PHOSO)<sub>2</sub>]<sup>3)</sup>Br, as proposed similarly in that for [Mn<sup>II</sup>(dppmO<sub>2</sub>)<sub>3</sub>](BF<sub>4</sub>)<sub>2</sub>.



**Figure 1.** (a) Chemical structure of [Mn<sup>II</sup>Br(SEGP<sub>2</sub>PHOSO)<sub>2</sub>]<sup>3)</sup>Br. (b) Emission spectra of 10 mol% [Mn<sup>II</sup>Br(SEGP<sub>2</sub>PHOSO)<sub>2</sub>]<sup>3)</sup>Br dispersed in SEGP<sub>2</sub>PHOSO under magnetic fields of up to 24 T at 4.2 K ( $\lambda_{\text{ex}} = 340$  nm).

1) S. Kimura, S. Kimura, K. Kato, Y. Teki, H. Nishihara, and T. Kusamoto, *Chem. Sci.* **2021**, *12*, 2025-2029. 2) T. Mibu, R. Matsuoka, and T. Kusamoto, *CSJ Annual meeting* **2024**, F1233-3vn-03, Funabashi. 3) Z. Zhou, T. Jiang, Y. Yang, Y. Deng, M. Wang, Y. Ma, S. Liu, and Q. Zhao, *Adv. Opt. Mater.* **2024**, *12*, 2302185.



## 巨大分極を示す無水強誘電イオン伝導体の開発

(九州大学) ○木村紗彩・大谷亮・大場正昭

Large polarization of an anhydrous ferroelectric ion conductor (*Kyushu University*) ○Saaya Kimura, Ryo Ohtani, Masaaki Ohba

Polar crystals are functional materials that have non-centrosymmetric structures and exhibit various physical properties. We synthesized a new ferroelectric ion conductor  $(\text{NH}_2\text{Me}_2)_2[\text{ReN}(\text{CN})_4]$  consisting of a one-dimensional chain structure bridged by nitride. This compound undergoes a polar-nonpolar transition around 300 K. This structural transition caused noticeable changes of ion conduction behavior confirmed by impedance measurements under anhydrous conditions. Ferroelectric measurements at 303 K showed a large hysteresis with the polarization of  $1.0 \text{ mC/cm}^2$ , indicating that the polarization coupled with the ion conduction.

*Keywords : Polarity, Cyanide, Ion conductor, Ferroelectricity*

極性結晶は、空間反転対称性の破れた結晶構造を持ち強誘電性や特異な相転移挙動など様々な物性を示す機能性材料である。近年、極性構造中をイオン伝導する極性結晶の開発が進められている。本研究では、非対称な五配位ユニットである  $[\text{ReN}(\text{CN})_4]^{2-}$  に着目し、極性金属錯体  $(\text{NH}_2\text{Me}_2)_2[\text{ReN}(\text{CN})_4]$  (**DMARe**) を合成した。結晶構造解析から、ニトリド基を介した架橋した一次元鎖構造をもち、300 K 付近において極性—無極性相転移することが分かった。Ar 雰囲気下で密封した粉末ペレットでインピーダンス測定を行ったところ、イオン伝導を示すことが分かり、相転移前後で伝導性が変化することが明らかになった。さらに、同ペレットにおける強誘電測定の結果から、303 K で  $1.0 \text{ mC/cm}^2$  の非常に大きな分極値を示すことが分かった。

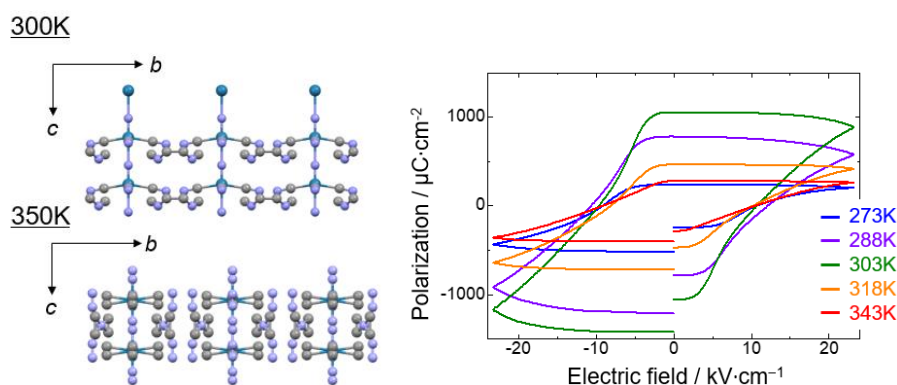


図 : **DMARe** の異なる温度における構造と強誘電測定の結果