



HOKKAIDO UNIVERSITY

Title	Studies on Construction and Crystal Size Control of Porous Coordination Polymers Composed of a Luminescent Ruthenium(II) Metalloligand
Author(s)	齋藤, 英里佳
Degree Grantor	北海道大学
Degree Name	博士(理学)
Dissertation Number	甲第12778号
Issue Date	2017-03-23
DOI	https://doi.org/10.14943/doctoral.k12778
Doc URL	https://hdl.handle.net/2115/65668
Type	doctoral thesis
File Information	Erika_Saitoh.pdf



Studies on Construction and Crystal Size Control of Porous Coordination Polymers Composed
of a Luminescent Ruthenium(II) Metalloligand

Ru(II)錯体を用いた多孔性配位高分子の構築と結晶サイズ制御に関する研究

Graduate School of Chemical Sciences and Engineering, Hokkaido University

Erika Saitoh

●Contents

Chapter 1

General Introduction

1-1 Metal-organic frameworks and Porous coordination polymers	-5-
1-2 Functionalization of MOF/PCP by metalloligand	-7-
1-3 Crystal downsizing of MOF/PCP crystals	-9-
1-4 Shape memory behavior	-10-
1-5 Luminescent Ru-complex	-11-
1-6 Purpose of the thesis	-12-
1-7 Outline of the thesis	-12-
1-8 References	-13-

Chapter 2

Construction of flexible coordination polymers composed of luminescent ruthenium(II) metalloligands

2-1 Introduction	-16-
2-2 Experimental	-17-
2-2-1 Materials and synthesis	-17-
2-2-2 Photo physical properties	-18-
2-2-3 Single-Crystal X-ray Structural Determination	-18-
2-2-4 Powder X-ray Diffraction	-18-
2-2-5 Adsorption Isotherms	-19-
2-2-6 Thermogravimetric Analysis	-19-
2-3 Results and Discussions	-20-
2-3-1 Crystal structures of [4Ru]-based PCPs	-20-
2-3-2 Vapor-induced structural transformations	-26-
2-3-3 Light absorption and emission properties	-36-
2-4 Conclusion	-38-
2-5 References	-39-

Chapter 3

Reduction in crystal size of flexible porous coordination polymers built from luminescent Ru(II)-metalloligands

3-1	Introduction	-41-
3-2	Experimental	-43-
3-2-1	Materials and synthesis	-43-
3-2-2	Scanning electron microscopy	-44-
3-2-3	Powder X-ray diffraction	-44-
3-2-4	Adsorption isotherms	-44-
3-2-5	UV-vis spectrophotometric measurement	-44-
3-3	Results and Discussions	-45-
3-3-1	Synthesis and assembled structure of <i>m</i> - Sr₂[4Ru]	-45-
3-3-2	Synthesis and assembled structure of <i>m</i> - Mg₂[4Ru]	-53-
3-3-3	Vapor adsorption behaviors	-60-
3-4	Conclusion	-69-
3-5	References	-70-

Chapter 4

General conclusion	-72-
--------------------	------

Acknowledgement	-74-
-----------------	------

Chapter 1
General introduction

1-1 Metal-organic frameworks and Porous coordination polymers

Metal-organic frameworks (MOFs) and porous coordination polymers (PCPs) have drawn considerable attention in recent decades because of their controllable porous frameworks,¹ interesting gas and vapor adsorption properties,² and catalytic activity,³ among other properties.⁴ Taking advantages of the structural designability, extensive studies have been done for developing the gas adsorption behaviors, because the pore size of the MOF/PCP system can be easily and finely modified by changing the bridging organic (and inorganic) linkers as shown in Figure 1-1.⁵

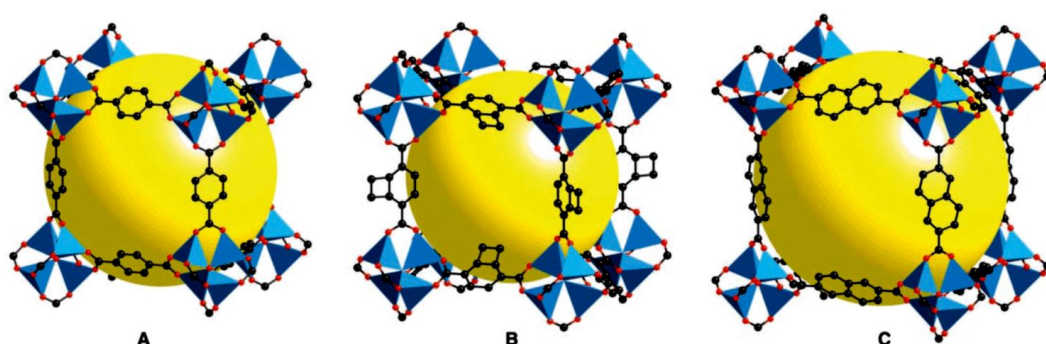


Figure 1-1. Control of the porous framework of MOF system by changing the bridging organic ligand from (A) terephthalate (MOF-5) to (C) 2,6-naphthalenedicarboxylate (IR-MOF-8).

Activated carbon and zeolite are well known porous materials and applied in many technical fields. The pore diameter of zeolite can be widely controlled from microporous to mesoporous region. Although the porous framework of zeolite is composed of inorganic Si-O and Al-O bonds to form rigid and stable pores for acid and bases, it is difficult to design the porous framework with lattice flexibility. In this context, PCP/MOF system are promising candidate as advanced porous materials with fine tunability of pore diameter and the lattice flexibility. In addition, the theoretical surface area of activated carbon and zeolite are 2400-2500 m²/g and 500 m²/g, respectively, whereas several MOF/PCP with the surface area exceeding them have been recently reported. Until now, various metal ions and organic bridging ligands have been utilized to achieve a larger surface area and/or diameter of the porous channels,⁶ to enhance the host-guest interaction,⁷ and to introduce a catalytic center in the porous frameworks.^{3,8} Some PCPs show structural transitions accompanied with guest adsorption/desorption,⁹ derived from the moderate

coordination bond strength of metal ions. The variable coordination environment of the metal ions is one of the most important characteristic features of PCPs compared to other porous materials. Therefore, interesting physical properties based on the designable porous framework of PCPs by the selection/modification of the metal ion and/or organic ligand are possible.

1-2 Functionalization of MOF / PCP by metalloligand

Compared to well-known porous materials like zeolites and activated carbons, porous coordination-network materials like PCPs and MOFs have several advantages in further functionalization.¹⁰⁻¹² In particular, functionalization based on metal complex ligands, so-called metalloligands, is one of the more promising methods to design multifunctional porous materials because the incorporation of functional molecules into the coordination network structure is easily achieved by the introduction of coordinating functional groups such as carboxylate.¹³⁻¹⁵ For example, Noro et al. reported a coordination polymer containing a functional Cu(II) metalloligand,¹⁶ and Kitaura et al. reported on PCPs with coordinatively unsaturated metal centers fabricated from metallo Schiff bases, with $[M(\text{salphdc})]^{2-}$ [$M = \text{Ni}^{2+}, \text{Cu}^{2+}$; $\text{H}_4\text{salphdc} = \text{N,N}'$ -phenylenebis (salicylideneimine)-dicarboxylic acid] as the metalloligand (Figure 1-2).¹⁷ Huang et al. also reported the MOFs; $\{[\text{Ln}_2(\text{ODA})_6\text{Cd}_3(\text{H}_2\text{O})_6] \cdot m\text{H}_2\text{O}\}_n$ ($\text{H}_2\text{ODA} = \text{oxydiacetic acid}$) composed of a lanthanide metalloligand as the lumiphore (Figure 1-3).¹⁸ In addition, Wang et al. recently reported a MOF catalyst composed of simple organic linkers with a metalloligand catalyst that has a similar molecular shape to the original organic linkers.¹⁹

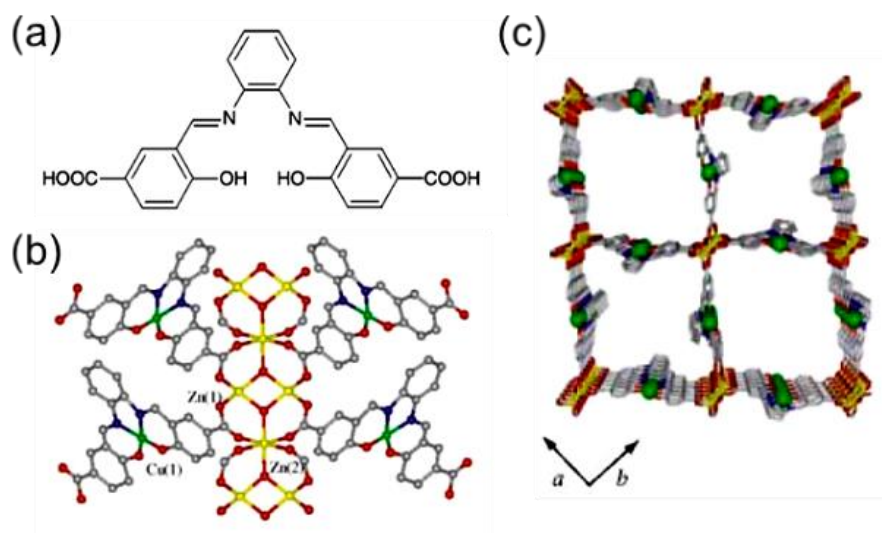


Figure 1-2. (a) Structure of $\text{H}_4\text{salphdc}$ used as metalloligand anatomy. (b) The building unit in the 3D porous coordination polymer. (c) The structure of 3D porous coordination polymer ($M = \text{Cu}^{2+}$)

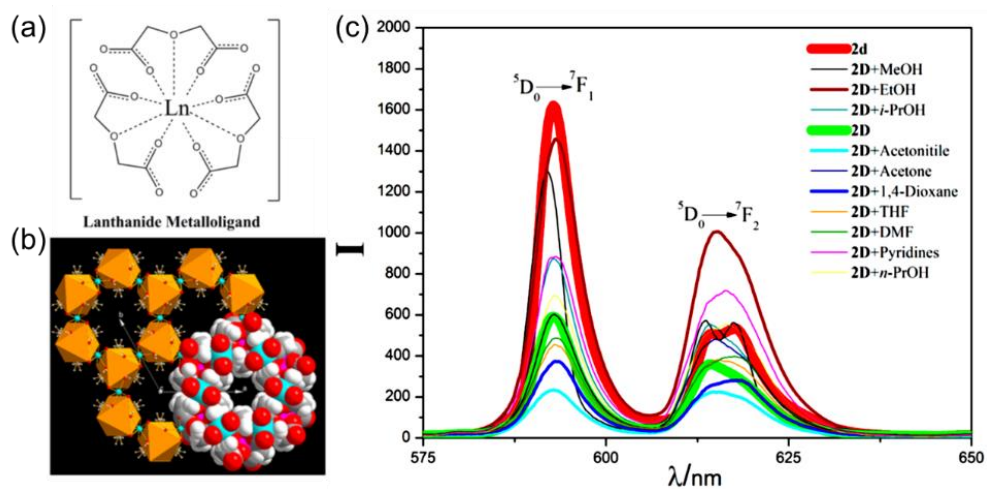


Figure 1-3. (a) Structure of lanthanide metalloligand. (b) The packing view of $\{[Ln_2(ODA)_6Cd_3(H_2O)_6] \cdot mH_2O\}_n$. (c) Guest-induced luminescent properties of the MOF excited at 397 nm.

1-3 Crystal downsizing of MOF/PCP crystals

From the viewpoint of the application of MOFs/PCPs to heterogeneous catalysis and drug delivery systems, the reduction in the size of these porous crystals (*crystal downsizing*) to the meso- or nanoscale is expected to improve the catalytic activity,²⁰ guest adsorption-desorption response, and dispersibility of the crystals in aqueous and organic solvents effectively. Several methods to reduce crystal size to the nanoscale have been reported so far.^{21–26} For instance, Furukawa et al. reported the coordination modulation method for crystal downsizing using the monocarboxylic modulator for control the nucleation rate of PCP by competitive the coordination interaction during the crystal formation process (Figure 1-4).²³ Qiu et al. reported the crystal downsizing method of MOF using ultrasonic to activate reactants locally by very large gradients of temperature, pressure, and the rapid motion of molecules.²⁵ Ni et al. reported using microwave-assisted solvothermal synthesis method to control the nucleation process in the solvothermal synthesis system.²⁶

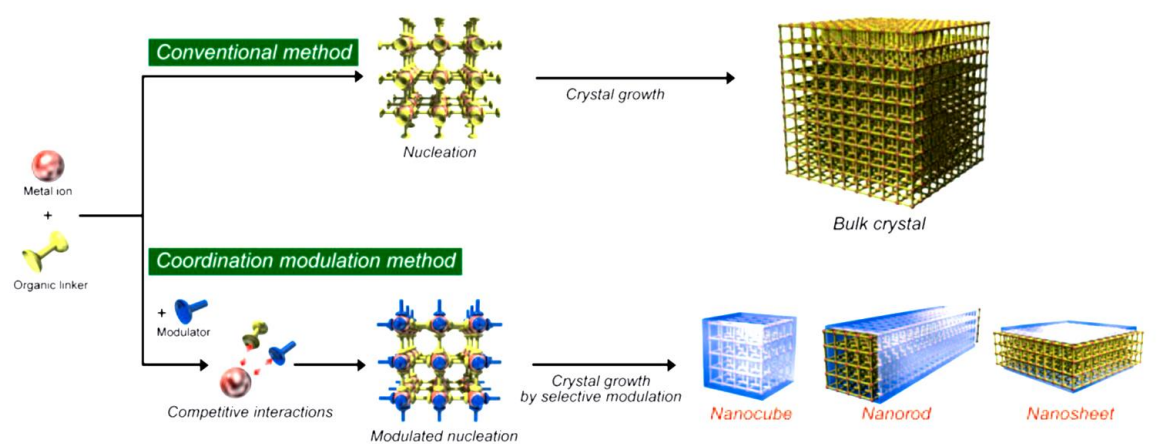


Figure 1-4. Coordination modulation method for controlling not only the size, but also the shape of PCP crystal.

1-4 Shape memory behavior

Some MOF/PCP have been reported to exhibit a characteristic guest-adsorption behavior, so called “Gate-opening phenomenon”. This phenomenon was firstly observed in the N₂ or Ar adsorption of Cu(II)-based PCP by Li et al in 2000. This is a unique behavior for MOF/PCP system with lattice flexibility that MOF/PCP suddenly adsorbs guest molecules at a certain the vapor relative pressure. This feature has been never observed in the other porous materials like zeolites and activated carbon materials.

One interesting finding concerning the downsizing effect on the guest adsorption behavior has been recently reported by Kitagawa and co-workers; that is, the porous structure of bulk crystals of pillared-layer-type PCP [Cu₂(bdc)₂(bpy)]_n (bdc = 1,4-benzenedicarboxylate; bpy = 4,4'-bipyridine) is closed by guest desorption, whereas the nano-sized (~50 nm) crystals of the same PCP maintain a porous structure without guest molecules in the pores (Figure 1-5).²⁷ The mechanism explaining the effect of crystal downsizing on the guest adsorption behavior of porous coordination compounds composed of Zn²⁺ or Cu²⁺ ion has been reported recently.^{28–30} In contrast, the effects of downsizing on porous coordination compounds composed of labile bridging metal ions (e.g., alkaline and alkaline-earth metal ions) have not been reported whereas the synthesis and application of nanocrystal of MOF composed Mg²⁺ ion has been reported.³¹

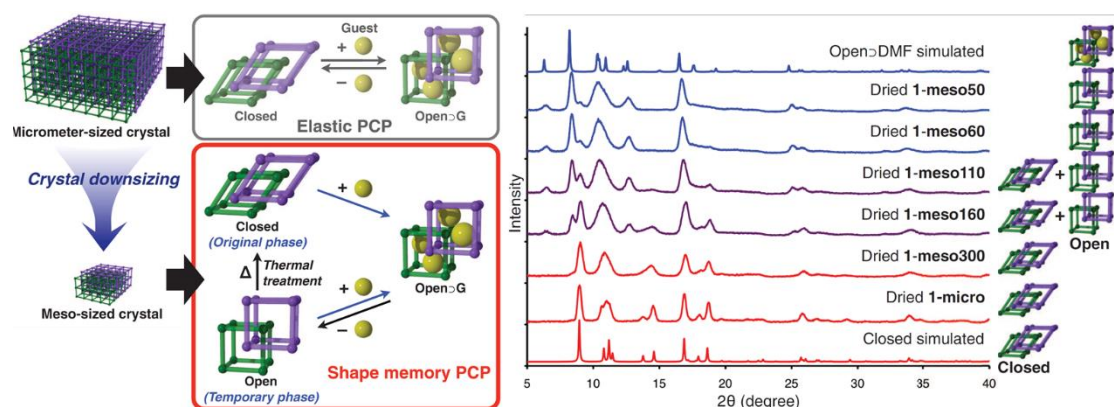


Figure 1-5. The conceptual diagram of the shape memory behavior and the crystal-size responsibility of the structural transition caused by the guest desorption

1-5 Luminescent Ru-complex

Polypyridine-ruthenium(II) complex has been studied as a luminescent complex molecule from long ago and shows luminescence derived from the $^3\text{MLCT}$ excited state. These ruthenium complexes have been extensively studied on their luminescent properties, and some of them are promising candidate for Visible light absorber for solar fuel production. Specifically, they are used as a photosensitizer for a photocatalytic hydrogen/oxygen generation reaction. However, most of the Ru(II) complexes reported so far are easily decomposed at photoexcited/one-electron-transferred states. In this context, incorporation of the luminescent Ru(II) complex to the porous framework of PCP/MOF crystals could be interesting method to improve the photo/electro-stability of Ru(II) complex, because the Ru(II) complex could be fixed in the coordination network structure. Several examples have recently been reported by Lin and coworkers; they demonstrated several interesting photocatalytic activities and energy-transfer dynamics in ruthenium(II) and osmium(II) metalloligand based MOFs (Figure 1-6).³² Generally, most photophysical phenomena are known to be sensitive to the environment of the functional molecule (e.g., solvent, temperature, and existence of a quencher). Thus, incorporating photofunctional molecules into flexible PCPs may be a promising method to develop new environmentally responsive materials with high sensitivity.

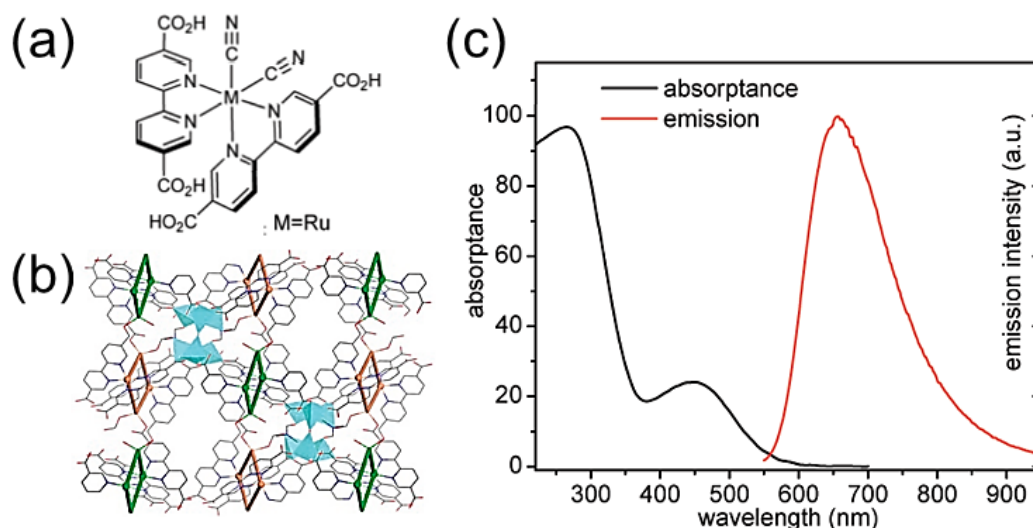


Figure 1-6. (a)Photoactive building block of MOF (b)The building unit in the 3D porous coordination polymer. (c)Absorbance and emission spectra of photoactive MOF. Absorbance values were calculated from transmission and diffuse reflectance measurements.

1-6 Purpose of this thesis

In this thesis, firstly, to design a photofunctional and flexible MOF/PCP system, two PCPs composed of Ru(II)-metalloligand with six carboxyl groups and redox-innocent Mg^{2+} or Sr^{2+} ions are synthesized. Since the Ru(II)-metalloligand has six carboxyl groups, the non-coordinated carboxylates are expected to interact with the guest molecules. Secondly, the scale down of these PCP crystals were examined to clarify the effect of crystal downsizing not only on the guest adsorption behavior but also on the light absorption and emission properties of Ru(II)-metalloligand.

1-7 Outline of this thesis

This thesis consists of 4 chapters as follows.

In chapter 1, the general background and the purpose of this thesis are described.

In chapter 2, the syntheses, crystal structures, vapor-adsorption behaviors and luminescent properties of newly synthesized luminescent PCPs, **$\text{Mg}_2[4\text{Ru}]$** and **$\text{Sr}_2[4\text{Ru}]$** that are composed of luminescent Ru(II) metalloligand, $[\text{Ru}(4,4'\text{-dcbpy})]^{4+}$ (**$[4\text{Ru}]$** ; 4,4'-dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) and Mg^{2+} or Sr^{2+} ion of the alkaline earth metals. These two PCPs showed the characteristic adsorption properties with gate-opening behavior to H_2O or MeOH vapor.

In chapter 3, crystal down-sizing of these two PCPs by coordination modulation are discussed. Obtained meso-scaled PCPs, *m*- **$\text{Sr}_2[4\text{Ru}]$** and *m*- **$\text{Mg}_2[4\text{Ru}]$** showed the similar photo-physical properties to that of the bulk crystals. In contrast, *m*- **$\text{Sr}_2[4\text{Ru}]$** showed quite different vapor adsorption behavior to that of bulk crystal, while the behavior of *m*- **$\text{Mg}_2[4\text{Ru}]$** was found to be similar to bulk crystal.

Finally, the author concludes this Ph.D. thesis by giving the general conclusions in chapter 4.

1-8 References

- 1) (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (c) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.
- 2) (a) Dinca, M.; Long, J. R. *Angew. Chem., Int. Ed.* **2008**, *47*, 6766. (b) Navarro, J. A. R.; Barea, E.; Salas, J. M.; Masciocchi, N.; Calli, S.; Sironi, A.; Ania, C. O.; Parra, J. B. *Inorg. Chem.* **2006**, *45*, 2397. (c) Mulfort, K. L.; Hupp, J. T. *Inorg. Chem.* **2008**, *47*, 7936.
- 3) (a) Seo, J. S.; Whang, D.; Lee, H.; Jun, S. I.; Oh, J.; Jeon, Y. J.; Kim, K. *Nature* **2000**, *404*, 982. (b) Dybtsev, D. N.; Nuzhdin, A. L.; Chun, H.; Bryliakov, K. P.; Talsi, E. P.; Fedin, V. P.; Kim, K. *Angew. Chem., Int. Ed.* **2006**, *45*, 916.
- 4) (a) Lee, C. Y.; Farha, O. K.; Hong, B. J.; Sarjeant, A. A.; Nguyen, S. T.; Hupp, J. T. *J. Am. Chem. Soc.* **2011**, *133*, 15858. (b) Cui, H.; Wang, Z.; Takahashi, K.; Okano, Y.; Kobayashi, H.; Kobayashi, A. *J. Am. Chem. Soc.* **2006**, *128*, 15074. (c) White, K. A.; Chengelis, D. A.; Gogick, K. A.; Stehman, J.; Rosi, N. L.; Petoud, S. *J. Am. Chem. Soc.* **2009**, *131*, 18069. (d) Zucchi, G.; Maury, O.; Thuéry, P.; Ephritikhine, M. *Inorg. Chem.* **2008**, *47*, 10398.
- 5) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keeffe, M.; Yaghi, M. *Science*, **2003**, *300*, 1127
- 6) (a) Noro, S.; Kitaura, R.; Kudo, M.; Kitagawa, S.; Ishii, T.; Matsuzaka, H.; Yamashita, M. *J. Am. Chem. Soc.* **2002**, *124*, 2568. (b) Rosi, N. L.; Kim, J.; Eddaoudi, M.; Chen, B.; O’Keeffe, M.; Yaghi, O. M. *J. Am. Chem. Soc.* **2005**, *127*, 1504. (c) Devic, T.; Serre, C.; Audebrand, N.; Marrot, J.; Férey, G. *J. Am. Chem. Soc.* **2005**, *127*, 12788. (d) Koh, K.; Wong-Foy, A. G.; Matzger, A. J. *J. Am. Chem. Soc.* **2009**, *131*, 4184. (e) Zhao, D.; Yuan, D.; Sun, D.; Zhou, H.-C. *J. Am. Chem. Soc.* **2009**, *131*, 9186.
- 7) (a) Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376. (b) Zhou, W.; Wu, H.; Yildirim, T. *J. Am. Chem. Soc.* **2008**, *130*, 15268. (c) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 806. (d) Lee, W. R.; Ryu, D. W.; Lee, J. W.; Yoon, J. H.; Koh, E. K.; Hong, C. S. *Inorg. Chem.* **2010**, *49*, 4723.
- 8) (a) Hasegawa, S.; Horike, S.; Matsuda, R.; Furukawa, S.; Mochizuki, K.; Kinoshita, Y.; Kitagawa, S. *J. Am. Chem. Soc.* **2007**, *129*, 2607. (b) Shultz, A. M.; Farha, O. K.; Hupp, J. T.; Nguyen, S. T. *J. Am. Chem. Soc.* **2009**, *131*, 4204.
- 9) (a) Halder, G. J.; Kepert, C. J.; Moubaraki, B.; Murray, K. S.; Cashion, J. D. *Science* **2002**, *298*, 1762. (b) Halder, G. J.; Kepert, C. J. *J. Am. Chem. Soc.* **2005**, *127*, 7891. (d) Horike, S.; Shimomura, S.; Kitagawa, S. *Nat. Chem.* **2009**, *1*, 695. (c) Fukushima, T.; Horike, S.; Inubushi, Y.; Nakagawa, K.; Kubota, Y.; Takata, M.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2010**, *49*, 4820.
- 10) Li, S.; Dharmarwardana, M.; Welch, R. P.; Ren, Y.; Thompson, S.; Smaldone, R. A.; Gassensmith, J. J. *Angew. Chem. Int. Ed.* **2016**, *55*, 1–7.

- 11) Evans, J. D.; Sumby, C. J.; Doonan, C. J. *Chem. Soc. Rev.* **2014**, *43*, 5933–5951.
- 12) Wang, Z.; Cohen, S. M. *J. Am. Chem. Soc.* **2007**, *129*, 12368–12369.
- 13) Marmier, M.; Wise, M. D.; Holstein, J.; Pattison, P.; Schenk, K.; Solari, E.; Scopelliti, R.; Severin, K. *Inorg. Chem.* **2016**, *55*, 4006–4015.
- 14) Kumar, G.; Gupta, R. *Chem. Soc. Rev.* **2013**, *42*, 9403–9453.
- 15) Das, M. C.; Xiang, S.; Zhang, Z.; Chen, B. *Angew. Chem. Int. Ed.* **2011**, *50*, 10510–10520.
- 16) Noro, S.; Kitagawa, S.; Yamashita, M.; Wada, T. *Cryst. Eng. Comm.* **2002**, *4*, 162–164.
- 17) Kitaura, R.; Onoyama, G.; Sakamoto, H.; Matsuda, R.; Noro, S.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2684.
- 18) Huang, X.-F.; Ma, J.-X.; Liu, W.-S. *Inorg. Chem.* **2014**, *53*, 5922–5930.
- 19) Wang, C.; Xie, Z.; deKrafft, K. E.; Lin, W. *J. Am. Chem. Soc.* **2011**, *133*, 13445–13454.
- 20) Zhang, S.; Li, L.; Zhao, S.; Sun, Z.; Hong, M.; Luo, J. *J. Mater. Chem. A* **2015**, *3*, 15764–15768.
- 21) Yue, Y.; Fulvio, P. F.; Dai, S. *Acc. Chem. Res.* **2015**, *48*, 3044–3052.
- 22) Furukawa, S.; Reboul, J.; Diring, S.; Sumida, K.; Kitagawa, S. *Chem. Soc. Rev.* **2014**, *43*, 5700–5734.
- 23) (a) Diring, S.; Furukawa, S.; Takashima, Y.; Tsuruoka, T.; Kitagawa, S. *Chem. Mater.* **2010**, *22*, 4531–4538. (b) Tsuruoka, T.; Furukawa, S.; Takashima, Y.; Yoshida, K.; Isoda, S.; Kitagawa, S. *Angew. Chem. Int. Ed.*, **2009**, *48*, 4739.
- 24) Tanaka, D.; Henke, A.; Albrecht, K.; Moeller, M.; Nakagawa, K.; Kitagawa, S.; Groll, J. *Nat. Chem.* **2010**, *2*, 401–416.
- 25) Qiu, L.-G.; Li, Z.-Q.; Wu, Y.; Wang, W.; Xu, T.; Jiang, X. *Chem. Commun.* **2008**, 3642–3644.
- 26) Ni, Z.; Masel, R. I. *J. Am. Chem. Soc.* **2006**, *128*, 12394–12395.
- 27) Sakata Y.; Furukawa S.; Kondo M.; Hirai K.; Horike N.; Takashima Y.; Uehara H.; Louvain N.; Meilikhov M.; Tsuruoka T.; Isoda S.; Kosaka W.; Sakata O.; Kitagawa S. *Science* **2013**, *339*, 193–196.
- 28) Linder-Patton, O. M.; Bloch, W. M.; Coghlan, C. J.; Sumida, K.; Kitagawa, S.; Furukawa, S.; Doonan, C. J.; Sumby, C. J. *Cryst. Eng. Comm.* **2016**, *18*, 4172–4179.
- 29) Tanaka, S.; Fujita, K.; Miyake, Y.; Miyamoto, M.; Hasegawa, Y.; Makino, T.; Perre, S. V.; Remi, J. C. S.; Assche, T. V.; Baron, G. V.; Denayer, J. F. M. *J. Phys. Chem. C* **2015**, *119*, 28430–28439.
- 30) Zhang, C.; Gee, J. A.; Sholl, D. S.; Lively, R. P. *J. Phys. Chem. C* **2014**, *118*, 20727–20733.
- 31) Bae, T.-H.; Long, J. R. *Energy Environ. Sci.* **2013**, *6*, 3565–3569.
- 32) (a) Kent, C. A.; Mehl, B. P.; Ma, L.; Papanikolas, J. M.; Meyer, T. J.; Lin, W. *J. Am. Chem. Soc.* **2010**, *132*, 12767. (b) Kent, C. A.; Liu, D.; Meyer, T. J.; Lin, W. *J. Am. Chem. Soc.* **2012**, *134*, 3991.

Chapter 2

**Flexible coordination polymers composed of luminescent ruthenium(II)
metalloligands**

2-1 Introduction

Kobayashi *et al.* recently reported on cobalt(III) metalloligand based PCPs, $\{\text{Ln}[\text{Co}(4,4'\text{-dcbpy})_3]\}$ ($\text{Ln} = \text{La}^{3+}, \text{Nd}^{3+}, \text{Gd}^{3+}$; $4,4'\text{-H}_2\text{dcbpy} = 4,4'\text{-dicarboxy-2,2'-bipyridine}$) and found that the porous frameworks are flexible enough to allow the transformation of their crystal structures when accompanied by guest adsorption/desorption (Figure 2-1).¹ In order to incorporate the other interesting functions of $[\text{M}(\text{bpy})_3]$ -type complex to the MOF/PCP system, a similar ruthenium(II) metalloligand bearing six carboxy groups in one molecule, $[\text{Ru}(4,4'\text{-dcbpy})_3]^{4-}$ (**[4Ru]**), was chosen as the photofunctional building block to introduce new photofunctions into such flexible PCP systems. Alkaline-earth metal ions were selected for coordination polymerization reactions because of their closed-shell d^0 electronic configurations that retain the emission properties of the ruthenium(II) metalloligands. In addition, the various coordination modes of larger metal ion such as Sr^{2+} may be able to contribute to the construction of flexible PCPs. In this chapter, the syntheses, crystal structures, luminescence properties, and vapor-induced reversible structural transitions of new luminescent PCPs formulated as $[\text{Mg}(\text{H}_2\text{O})_6]\{\text{[Mg}(\text{H}_2\text{O})_3]\text{[4Ru]}\} \cdot 4\text{H}_2\text{O}$ (**Mg₂[4Ru]**·13H₂O), $\{\text{[Sr}_4(\text{H}_2\text{O})_9]\text{[4Ru]}_2 \cdot 9\text{H}_2\text{O}\}$ (**Sr₂[4Ru]**·9H₂O)₂ are discussed in detail.

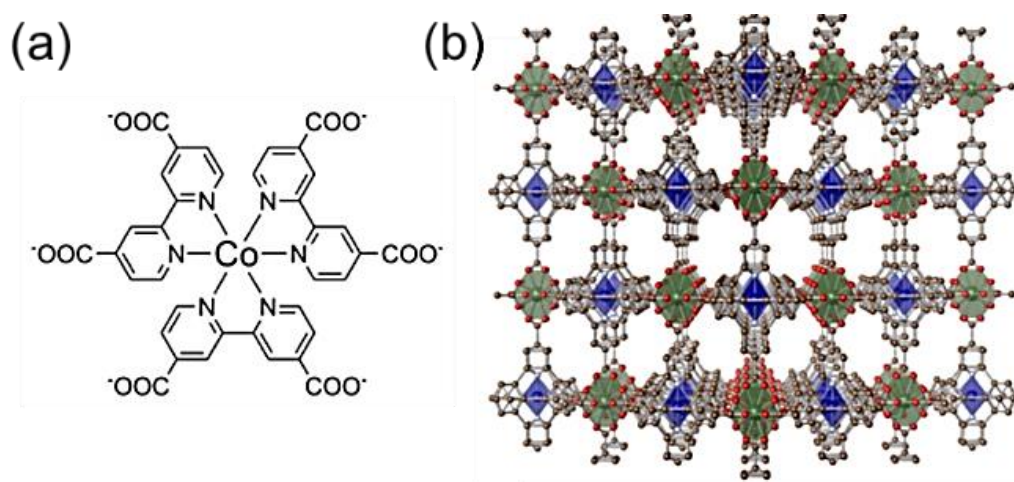


Figure 2-1. (a) Metalloligand of Co-MOF (b) Packing diagrams of Er-Co PCP viewed along the $a + b$ axis.

2-2 Experimental

2-2-1 Materials and Synthesis

All starting materials, $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, and $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ were used as received from commercial sources. Solvents were used without any further purification. Unless otherwise stated, all reactions were performed in air. Ruthenium(II) metalloligands, $[\text{Ru}(4,4'\text{-H}_2\text{dcbpy})(4,4'\text{-Hdc bpy})_2]$ (**[4Ru]**) was prepared according to published methods.^{2,3} Elemental analysis was performed at the analysis center of Hokkaido University.

Synthesis of $[\text{Mg}(\text{H}_2\text{O})_6] \{[\text{Mg}(\text{H}_2\text{O})_3][\text{4Ru}] \cdot 4\text{H}_2\text{O}\} (\text{Mg}_2[\text{4Ru}] \cdot 13\text{H}_2\text{O})$

[4Ru] (25 mg, 30 μmol) was dissolved in a mixed solution of triethanolamine (0.075 mL) and water (3 mL). To the resulting clear red solution, an EtOH solution (5 mL) of **Mg₂[4Ru]** $\cdot 13\text{H}_2\text{O}$ was slowly diffused in a straight glass tube at 323 K. Red crystal of **Mg₂[4Ru]** were obtained after 10 days. The crystals were collected by filtration, washed with a small amount of water, and then dried in air for 1 day to afford **Mg₂[4Ru]** $\cdot 13\text{H}_2\text{O}$ (28.4 mg) in 91 % yield based on **[4Ru]**. Anal. Calcd. for $\text{C}_{36}\text{H}_{18}\text{N}_6\text{O}_{12}\text{RuMg}_2 \cdot 13\text{H}_2\text{O}$: C, 38.94; H, 3.99; N, 7.57. Found: C, 38.84; H, 4.19; N, 7.51. IR (KBr, cm^{-1}): 3367 s, 1596 S, 1542 s, 1434 m, 1407 m, 1380 s, 1292 w, 1262 w, 1235 m, 1160 w, 1025 w, 908 w, 877 w, 780 m, 699 m, 459 w, 417 w.

Synthesis of $\{[\text{Sr}_4(\text{H}_2\text{O})_9][\text{4Ru}]_2 \cdot 9\text{H}_2\text{O}\} (([\text{Sr}_2[\text{4Ru}] \cdot 9\text{H}_2\text{O}])_2)$

[4Ru] (25 mg, 30 μmol) was dissolved in a mixed solution of triethanolamine (0.075 mL) and water (3 mL). To the resulting clear red solution was slowly diffused in a straight glass tube at 323 K an EtOH solution (5 mL) of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (26.3 mg, 100 μmol). Red single crystals of **Sr₂[4Ru]** $\cdot 9\text{H}_2\text{O}$ were obtained after 10 days. The crystals were collected by filtration, washed with a small amount of water, and then dried in air for 1 day to afford **Sr₂[4Ru]** $\cdot 9\text{H}_2\text{O}$ (28.7 mg) in 96 % yield based on **[4Ru]**. Anal. Calcd. for $\text{C}_{36}\text{H}_{18}\text{N}_6\text{O}_{12}\text{RuSr}_2 \cdot 9\text{H}_2\text{O}$: C, 37.11; H, 3.11; N, 7.21. Found: C, 37.10; H, 3.22; N, 7.49. IR (KBr, cm^{-1}): 3400 m, 2360 w, 2330 w, 1601 s, 1543 m, 1430 w, 1406 m, 1380 s, 1296 w, 1235 w, 1033 w, 915 w, 862 w, 788 m, 709 w, 671 w, 448 w.

2-2-2 Photo physical Properties

The UV–vis absorption spectrum of each complex was recorded on a Hitachi U-3000 spectrophotometer. The diffuse-reflectance spectrum of each complex was recorded on a Shimadzu UV-2400PC spectrophotometer. The obtained reflectance spectra were converted to absorption spectra using the Kubelka-Munk function $F(R_{\infty})$. Emission and excitation spectra were recorded under various conditions on a Jasco FP-6600 spectrofluorometer. The luminescence quantum efficiency was recorded on a Hamamatsu C9920-02 absolute photoluminescence quantum yield measurement system equipped with an integrating sphere apparatus and 150-W continuous-wave xenon light source.

2-2-3 Single-Crystal X-ray Structural Determination

Single-crystal X-ray diffraction measurements for $\text{Mg}_2[\text{4Ru}] \cdot 13\text{H}_2\text{O}$ and $([\text{Sr}_2[\text{4Ru}] \cdot 9\text{H}_2\text{O}])_2$ were carried out using a Rigaku Mercury CCD diffractometer at the NW2A beamline [$\lambda = 0.6890(1) \text{ \AA}$] of the Advanced Ring, Photon Factory, KEK, Japan. Each single crystal was mounted on a MicroMount with paraffin oil. A nitrogen-gas-flow temperature controller was used to cool the sample. The diffraction data were collected and processed using *CrystalClear*.⁴ The structure was solved by direct methods using *SIR2004*⁵ and refined by full-matrix least squares using *SHELXL-97*.⁶ The non-H atoms were refined anisotropically, while H atoms were refined using the riding model. All calculations were performed using the *Crystal Structure* crystallographic software package.⁷ Estimation of the void volume in each complex was calculated by *Platon SQUEEZE*,⁸ wherein the non-coordinated water molecules were excluded (but coordinated water molecules were included) in the calculation.

2-2-4 Powder X-ray Diffraction (PXRD)

PXRD measurements were carried out using a Rigaku SPD diffractometer at beamline BL-8B of the Photon Factory, KEK, Japan. The wavelength of the synchrotron X-ray was $0.9985(1) \text{ \AA}$. The relative humidity (RH) of the sample placed in an open glass capillary was controlled by using saturated salt solutions (LiCl , KCH_3COO , K_2CO_3 , NaCl , and KCl for RH = 11, 23, 43, 75, and 85 %, respectively)⁹ as the water-vapor source.

2-2-5 Adsorption Isotherms

The adsorption isotherms for water and methanol vapors at 298 K were performed using an automatic volumetric adsorption apparatus (BELSORP-MAX; BEL Japan, Inc.)

2-2-6 Thermogravimetric Analysis (TGA)

TGA and differential thermal analysis were performed using a Rigaku ThermoEvo TG8120 analyzer.

2-3 Results and Discussion

2-3-1 Crystal structures of [4Ru]-based PCPs

The crystallographic data of **M₂[4Ru]** from single-crystal X-ray structural determination are summarized in Table 2-1. Selected bond lengths around the **[4Ru]** metalloligand are listed in Table 2-2. The coordination environment of the M²⁺ ion and the data about the porosity of each **M₂[4Ru]** are summarized in Table 2-3.

Table 2-1. Crystal parameters and refinement data of **M₂[4Ru]**

	Mg₂[4Ru]	Sr₂[4Ru]
<i>T</i> / K	150(1)	150(1)
formula	C ₃₆ H ₁₈ Mg ₂ N ₆ O ₁₂ Ru•12H ₂ O	C ₃₆ H ₁₈ N ₆ O ₁₂ RuSr ₂ •9H ₂ O
fw	1068.24	1165.02
cryst syst	trigonal	monoclinic
space group	<i>R</i> 32	<i>P</i> 2 ₁ / <i>c</i>
<i>a</i> / Å	14.190(4)	24.750(5)
<i>b</i> / Å	14.190(4)	15.008(3)
<i>c</i> / Å	40.593(10)	25.792(6)
<i>α</i> / deg	90	90
<i>β</i> / deg	90	111.957
<i>γ</i> / deg	120	90
<i>V</i> / Å ³	7079(3)	8885(3)
<i>Z</i>	6	8
<i>D</i> _{calcd} / g·cm ⁻³	1.503	1.742
reflns collected	41073	140118
unique reflns	5000	28154
GOF	1.131	1.022
<i>R</i> _{int}	0.0435	0.0593
<i>R</i> [<i>I</i> > 2.00σ(<i>I</i>)]	0.0509	0.0767
<i>R</i> _w ^α	0.1661	0.2436
flack parameter	0.01(4)	-

$$^{\alpha}R_w = [\Sigma(w(F_o^2 - F_c^2)^2) / \Sigma(w(F_o^2)^2)]^{1/2}$$

Table 2-2. Selected bond distances of [4Ru] metalloligand

	Mg₂[4Ru]	Sr₂[4Ru]	
		Ru1	Ru2
Ru-N1	2.057(3)	2.058(3)	2.057(3)
Ru-N2	2.057(4)	2.056(4)	2.082(4)
Ru-N3	-	2.054(4)	2.056(5)
Ru-N4	-	2.065(5)	2.043(4)
Ru-N5	-	2.068(4)	2.062(4)
Ru-N6	-	2.059(3)	2.060(5)
C11-O1	1.244(5)	1.242(10)	1.250(6)
C11-O2	1.261(6)	1.235(12)	1.264(7)
C12-O3	1.250(4)	1.243(9)	1.227(11)
C12-O4	1.242(6)	1.254(8)	1.284(9)
C23-O5	-	1.247(5)	1.248(6)
C23-O6	-	1.278(6)	1.250(8)
C24-O7	-	1.249(8)	1.227(8)
C24-O8	-	1.278(6)	1.237(7)
C35-O9	-	1.256(5)	1.256(11)
C35-O10	-	1.261(6)	1.267(8)
C36-O11	-	1.243(8)	1.243(8)
C36-O12	-	1.263(7)	1.257(10)

Table 2-3. Coordination environment of M²⁺ ions and data of porous frameworks of M₂[4Ru]

	Mg₂[4Ru]		Sr₂[4Ru]			
	Mg1	Mg2	Sr1	Sr2	Sr3	Sr4
coordination no. of M ²⁺	6	6	9	7	7	8
no. of water molecules coordinated to M ²⁺	3	6	3	1	2	5
void fraction (%)	11.4		15.0			
void space in one unit cell ^a (Å ³)	809.0		1332.0			
pore size (Å ³)	4.2 × 3.7		4.0 × 4.0			

^aCalculated by *Platon SQUEEZE*.⁸ Noncoordinated water molecules are excluded from the calculations.

Figure 2-2(a) shows the coordination environment of the Mg^{2+} cation and the **[4Ru]** metalloligand of $\text{Mg}_2[\text{4Ru}] \cdot 13\text{H}_2\text{O}$. This complex crystallized in the trigonal $R\bar{3}2$ space group and one Ru^{II} cation, two Mg^{II} cations, and one 4,4'-dcbpy ligand were found to be crystallographically independent. Because the Ru1 atom was found to be on the 3-fold axis, three 4,4'-dcbpy ligands in one **[4Ru]** anion are equivalent to each other. The observed Ru–N bond lengths [2.057(3) and 2.057(4) Å] are almost similar to the starting metalloligand **[4Ru]** (2.046–2.068 Å),² indicating that the Ru cation remains in the divalent oxidation state. Interestingly, only one enantiomer, $\Delta\text{[Ru(4,4'-dcbpy)}_3\text{]}^{4-}$, was found in this crystal structure and flack parameter was 0.01(4), consistent with the acentric space group ($R\bar{3}2$). The observed C–O bond distances ranging between 1.244(5) and 1.261(6) Å suggest that all of the carboxy groups are deprotonated and three of the six are bonded to Mg^{II} cations in the monodentate mode, as shown in Figure 2-2(a). Two types of Mg^{II} cations with six coordinated octahedral structure were found. One type, located on the 3-fold axis, is bound by three carboxy groups and three water molecules (which occupied the *fac* positions) to form two-dimensional (2D) honeycomb-like coordination networks, $\{[\text{Mg}(\text{H}_2\text{O})_3][\text{4Ru}]\}_n^{2n-}$, in the *ab* plane, as shown in Figure 2-2(b). As a result, the uncoordinated carboxylates of **[4Ru]** are exposed on both surfaces of the 2D coordination sheet. The other six-coordinated octahedral structure of the Mg^{2+} cation is surrounded by six-coordinated water molecules and located between two 2D coordination sheets of $\{[\text{Mg}(\text{H}_2\text{O})_3][\text{4Ru}]\}_n^{2n-}$, as shown in Figure 2-2(c). A void space of $\sim 809 \text{ \AA}^3$ (11.4% void fraction), as calculated by Platon SQUEEZE,⁸ was found in the $[\text{Mg}(\text{H}_2\text{O})_6]^{2+}$ layer. Considering the results of elemental analysis and the water vapor adsorption isotherm (see Figure 2-5 shown below), this void space is probably occupied by more than four water molecules per **[4Ru]** metalloligand.

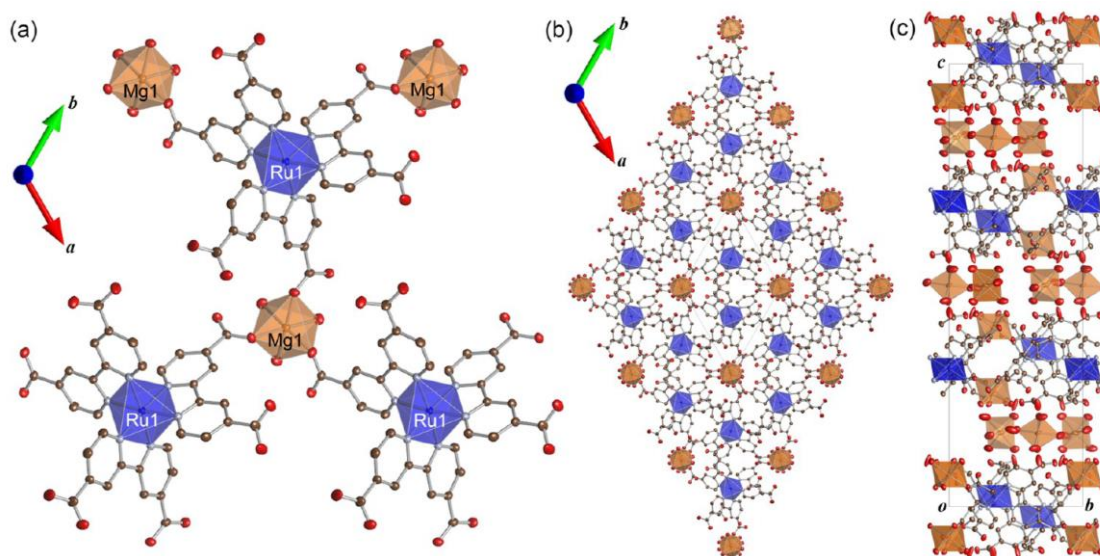


Figure 2-2. (a) Coordination structures of Mg²⁺ and Ru²⁺ cations, (b) 2D layer structure of {[Mg(H₂O)₃][4Ru]}²⁺ in the *ab* plane, and (c) stacking structure viewed along the *a* axis of Mg₂[4Ru]·13H₂O. The coordination spheres of Ru^{II} and Mg^{II} ions are shown as blue and orange octahedra, respectively. Brown, light blue, and red ellipsoids represent C, N, and O atoms, respectively. Noncoordinated water molecules and H atoms are omitted for clarity.

The different metal ion was used for the syntheses of [4Ru]-based PCPs to control not only the porous structure but also the structural flexibility. Figures 2-3 (a) and (b) show the coordination modes of two independent [4Ru] in (Sr₂[4Ru]·9H₂O)₂. This complex crystallized in the monoclinic *P*2₁/*c* space group, and two crystallographically independent [4Ru] metalloligands and four Sr²⁺ cations were found in the unit cell. Similar to Mg₂[4Ru]·13H₂O, the observed Ru–N bond distances [2.043(4)–2.082(4) Å] suggest that the oxidation state of the Ru centers remains in the divalent state. In contrast to the chiral crystal of Mg₂[4Ru]·13H₂O, (Sr₂[4Ru]·9H₂O)₂ formed a racemic crystal composed of the Λ and Δ isomers of [4Ru]. As shown in Figure 2-3(a), one [4Ru] metalloligand (labeled as Ru1) was bonded to nine Sr²⁺ cations. The observed C–O bond lengths for all of the carboxy groups were in the range of 1.235(9)–1.280(5) Å, suggesting that all of the carboxy groups of [4Ru] were deprotonated.² Three of the six carboxy groups were not only bonded in the bidentate mode but also bridged between two Sr²⁺ cations. Two of the remaining carboxy groups were bonded to Sr²⁺ cations in simple monodentate mode and one carboxy group was bonded to Sr²⁺ cation in the bidentate mode. In contrast, another crystallographically independent [4Ru] metalloligand (labeled as Ru2) was surrounded by only six Sr²⁺ cations, as shown in Figure 2-3(b). All C–O bond lengths [1.227(8)–1.284(9) Å] also

indicate that all six carboxy groups were in the deprotonated form. Interestingly, one of the six carboxy groups was not coordinated to any cations. Four of the carboxylate groups were coordinated in a simple monodentate fashion, and only one carboxy group was bonded in a bidentate fashion, in which one O atom was bridged between two Sr^{2+} cations. Parts c and d of Figure 2-3 show the coordination environments of four crystallographically independent Sr^{2+} cations. Sr1 and Sr2 were bridged by three O atoms of the carboxy groups from three different **[4Ru]** metalloligands, which were also coordinated to Sr1 in a bidentate fashion. Three water molecules were also bonded to Sr1, resulting in the nine coordinated polyhedral structure. In contrast, only one water molecule was bonded to Sr2, together with three monodentate carboxy groups of **[4Ru]**, to form a seven-coordinated structure. As a result, this dinuclear Sr core was coordinated by six **[4Ru]** metalloligands. The other two Sr^{2+} cations, Sr3 and Sr4, also formed a dinuclear core bridged by one water molecule and one O atom from the carboxy group of **[4Ru]**. This bridging carboxy group also coordinated to Sr4 in a bidentate fashion. In addition to the bridging water molecule, four water molecules and one monodentate carboxy group were bonded to Sr4 to form an eight-coordinated polyhedral structure. In contrast, only one terminal water molecule and two bidentate and one monodentate carboxy groups coordinated to Sr3 to form a seven-coordinated structure. Because of the coordination polymerization of the **[4Ru]** metalloligand by the Sr^{2+} cations, a three-dimensional (3D) coordination network structure was formed, as shown in Figure 2-3(e). Notably, small one-dimensional (1D) void spaces with ~ 4.0 Å diameter along the *b* axis were found at the center, corners of the *ac* plane, and midpoints of the *a* and *c* axes. Several noncoordinated crystal water molecules were found in these voids by X-ray analysis. The estimated void volume excluding noncoordinated crystal water molecules was 1332 Å^3 (15.0% void fraction) in the unit cell.

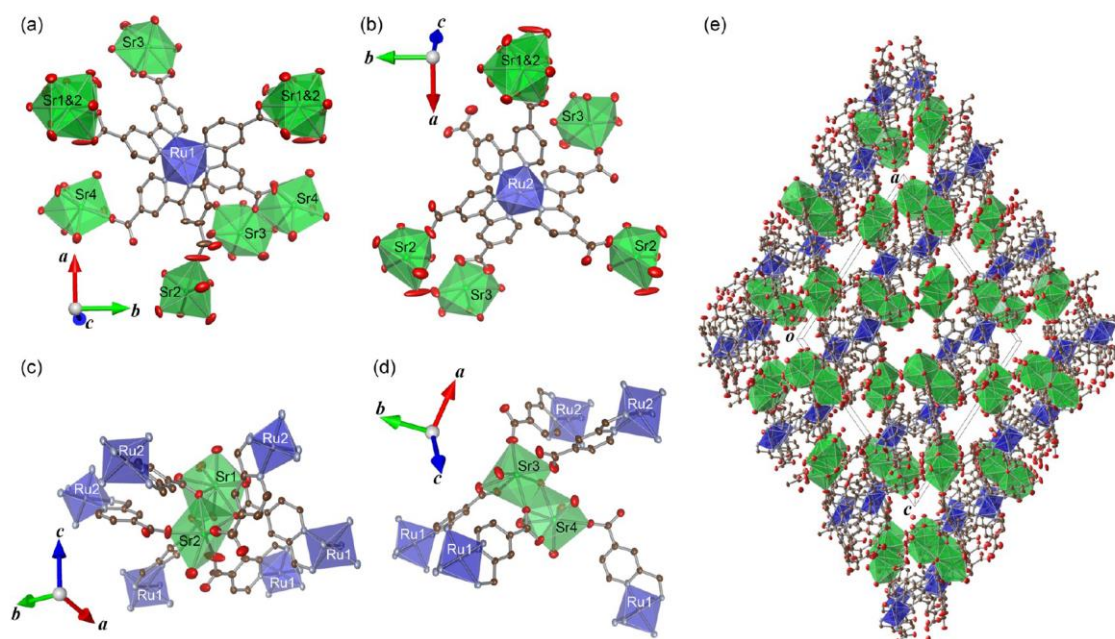


Figure 2-3. Coordination environments of (a and b) two crystallographically independent **[4Ru]** and (c and d) four Sr^{2+} cations. (e) Packing diagram of $(\text{Sr}_2[\mathbf{4Ru}] \cdot 9\text{H}_2\text{O})_2$ viewed along the b axis. The coordination spheres of the Ru^{II} and Sr^{II} ions are shown as blue and green octahedral, respectively. Brown, light-blue, and ellipsoids represent C, N, and O atoms, respectively. Noncoordinated water molecules and H atoms are omitted for clarity.

As discussed above, there are large differences in the crystal structures between $\text{Mg}_2[\mathbf{4Ru}] \cdot 13\text{H}_2\text{O}$ and $(\text{Sr}_2[\mathbf{4Ru}] \cdot 9\text{H}_2\text{O})_2$, even though both use the same metalloligand **[4Ru]**. This metalloligand forms a 2D coordination sheet structure by the reaction with the Mg^{2+} cation, while the reaction with the Sr^{2+} cation leads to the formation of a 3D network structure. These differences are probably due to the large differences in the hydration enthalpy and ionic radius between the two cations. In fact, the Mg^{2+} cations in $\text{Mg}_2[\mathbf{4Ru}] \cdot 13\text{H}_2\text{O}$ were coordinated by three or six water molecules, whereas the Sr^{2+} cations in $(\text{Sr}_2[\mathbf{4Ru}] \cdot 9\text{H}_2\text{O})_2$ are surrounded by at most three coordinated water molecules. It should be noted that both PCPs have large amounts of coordinated and noncoordinated water molecules accompanied by small void spaces with a void fraction of 11.4% for $\text{Mg}_2[\mathbf{4Ru}] \cdot 13\text{H}_2\text{O}$ and 15.0% for $(\text{Sr}_2[\mathbf{4Ru}] \cdot 9\text{H}_2\text{O})_2$. These void spaces and fractions suggest that both compounds can have vapor adsorption abilities.

2-3-2 Vapor-induced structural transformations

As discussed in the Introduction, interesting that reversible amorphous–crystalline phase transitions of the cobalt(III) metalloligand based PCPs, $\{Ln[Co(4,4'\text{-dcbpy})_3]\}$, were reported to be induced by vapor adsorption/desorption.¹⁰ Because we have used the ruthenium(II) metalloligands **[4Ru]**, which has almost the same molecular structure as that of $[Co(4,4'\text{-dcbpy})_3]^{3-}$, similar vapor-induced structural transformations are expected. In order to clarify the structural flexibility of the newly obtained PCPs **M₂[4Ru]**, PXRD patterns under several conditions were conducted. Figure 2-4 shows the changes in the PXRD patterns of **Mg₂[4Ru]** and **Sr₂[4Ru]**. The synthesized samples showed diffraction patterns very similar to the simulated PXRD pattern calculated from their crystal structures, indicating that their porous frameworks are stable enough to retain their structures in air. After drying at 423 K for 1 day, the patterns of both **M₂[4Ru]** changed remarkably, suggesting that the porous structures could not be retained without crystal water molecules. In TG analysis, about $\approx 21.6\%$ and 15.2% weight losses were observed by heating up to 423 K for **Mg₂[4Ru]** and **Sr₂[4Ru]**, respectively, which agreed with the calculated amounts of hydrated water molecules (21.1% and 14.0% for **Mg₂[4Ru]·13H₂O** and **Sr₂[4Ru]·9H₂O**, respectively). This result suggests that most of the crystal water molecules included in **M₂[4Ru]** were removed at 423 K (Figure 2-5). In fact, negligible weight losses were observed for the dried **M₂[4Ru]**, and temperature dependences of IR spectra of **Mg₂[4Ru]·13H₂O** and **Sr₂[4Ru]·9H₂O** clearly showed that the $\nu(\text{O-H})$ absorption band remarkably decreased above 423 K (Figure 2-6). After these dried samples were exposed to saturated water vapor, the observed patterns were almost identical with the simulated patterns, indicating that both **M₂[4Ru]** can reversibly adsorb/desorb water vapor, accompanied by structural transformation. Interestingly, the diffraction patterns of dried **Mg₂[4Ru]** and **Sr₂[4Ru]** also changed remarkably under exposure to methanol vapor, suggesting the possibility of methanol vapor adsorption. It should be noted that the pattern of **Sr₂[4Ru]** under exposure to methanol vapor is almost the same as that under water-vapor exposure, whereas the patterns of **Mg₂[4Ru]** under methanol and water vapor were different from each other. Thus, the methanol-adsorbed structure of **Sr₂[4Ru]** should almost be the same porous framework structure of $(\text{Sr}_2[4\text{Ru}] \cdot 9\text{H}_2\text{O})_2$, while the methanol- and water-adsorbed structures of **Mg₂[4Ru]** should be different. In order to clarify the vapor adsorption properties of

Mg₂[4Ru], water and methanol vapor adsorption isotherms were measured. Figure 2-7 shows the water vapor adsorption isotherms of **Mg₂[4Ru]** and **Sr₂[4Ru]** at 298 K. Before each measurement, the samples were dried at 373 K under vacuum to remove all hydrated water. As expected from the crystal structures with large hydration numbers, both PCPs can adsorb large amounts of water vapor, over 10 mol mol⁻¹ per **[4Ru]** unit. It should be noted that the adsorption profile of **Sr₂[4Ru]** was remarkably different from that of **Mg₂[4Ru]**. The water vapor adsorption of **Sr₂[4Ru]** proceeded in three steps: after two-step adsorption at low pressure (below $P / P_0 = 0.20$, ca. 5.8 mol mol⁻¹), the isotherm reached a wide plateau region, after which it showed a sudden increase above $P / P_0 = 0.75$. The saturation point was 10 mol mol⁻¹, which is very close to the hydration number of **Sr₂[4Ru]**. During the desorption process, the absorbed amount was almost constant above $P / P_0 = 0.32$, after which it sharply decreased to ~6 mol mol⁻¹, which is almost consistent with the number of coordinated water molecules in **Sr₂[4Ru]**. In contrast, the isotherm for **Mg₂[4Ru]** showed a two-step adsorption profile below $P / P_0 = 0.5$ via a small shoulder at $P / P_0 = 0.20$. The saturated amount was 16.0 mol mol⁻¹, which is larger than that of **Sr₂[4Ru]** and is close to the hydration number for **Mg₂[4Ru]** as estimated from elemental analysis. In the desorption process, the absorbed amount decreased sharply below $P / P_0 = 0.15$. These large hysteresis values for both **Sr₂[4Ru]** and **Mg₂[4Ru]** suggest that structural transition occurs during the vapor adsorption and desorption processes. In order to gain more information about the water-vapor-induced structural transition, the PXRD patterns of the RH dependences of **Sr₂[4Ru]** and **Mg₂[4Ru]** were measured. As shown in Figure 2-8, the PXRD pattern of **Mg₂[4Ru]** interestingly changed to almost the same pattern as the simulated pattern above RH = 23%, where the amount of water vapor adsorbed was about 8.6 mol mol⁻¹. Considering the fact that the number of water molecules coordinated to the Mg²⁺ cations in **Mg₂[4Ru]** was determined to be 9 mol per **[4Ru]** unit (Table 2-3), the driving force for regeneration of the porous 2D sheet structure should be the adsorption and coordination of water molecules to two different Mg²⁺ cations. The second adsorption of water vapor above $P / P_0 = 0.2$ corresponds to adsorption to the porous channels formed in the [Mg(H₂O)₆]²⁺ cationic layers. In contrast, the pattern of **Sr₂[4Ru]** was still unchanged at this low-RH region, where about 5 mol mol⁻¹ of water vapor was adsorbed. A pattern almost identical with the simulated pattern of **Sr₂[4Ru]** was observed above RH = 75%, which

corresponds to the third adsorption step observed in the water vapor adsorption isotherm. As discussed in the crystal structure section, the number of water molecules coordinated to Sr^{2+} cations per **[4Ru]** unit is estimated to be 5, suggesting that the two-step increases observed in the adsorption isotherm should correspond to the adsorption and coordination of water to the Sr^{2+} cations. However, in contrast to **Mg₂[4Ru]**, a larger amount of water adsorption is required to regenerate the porous framework. This difference may originate from the difference in the hydration enthalpy between Mg^{2+} and Sr^{2+} . The large difference of the relative pressure for the reconstruction of the porous structure was observed between **Sr₂[4Ru]** and **Mg₂[4Ru]**. The porous structure of **Sr₂[4Ru]** was reconstructed by adsorption the 8.5 molecules of water per **[4Ru]** (Figure 2-9), therefore the reconstruction of the porous structure need not the coordination the coordinated water but the adsorption crystal water. On the other hand, the porous structure of **Mg₂[4Ru]** was reconstructed by adsorption the 9 molecules of water per **[4Ru]** (Figure 2-10) which mean that the porous structure was reconstructed by the coordination of water molecules to both the Mg^{2+} cations within the 2-D coordination sheets and between the sheets. The porous structure of **Sr₂[4Ru]** recovered by adsorption of crystal water, on the other hand, the porous structure of **Mg₂[4Ru]** recovered by coordination of coordination water. Therefore, the difference of water molecules which recover the porous structure caused the difference relative pressure which reconstructs the porous structure between **Sr₂[4Ru]** and **Mg₂[4Ru]**.

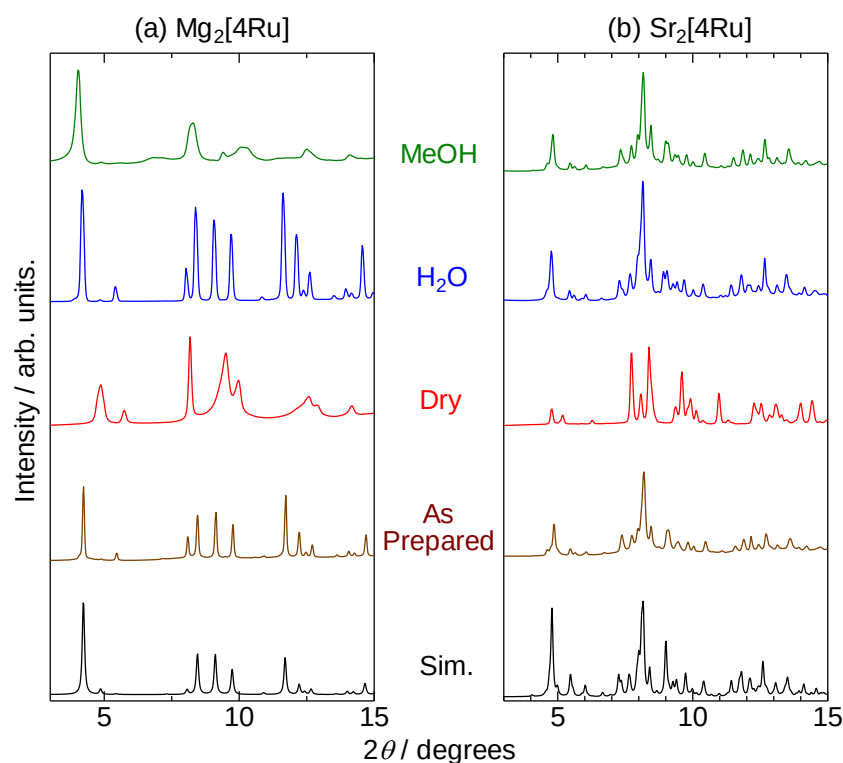


Figure 2-4. Changes of the PXRD patterns [$\lambda = 0.9985(1) \text{ \AA}$] of (a) $\text{Mg}_2[4\text{Ru}]$ and (b) $\text{Sr}_2[4\text{Ru}]$ under exposure to dried air, H_2O , and MeOH vapor at room temperature. The bottom two are the patterns of as-prepared samples and simulated patterns calculated from corresponding crystal structures.

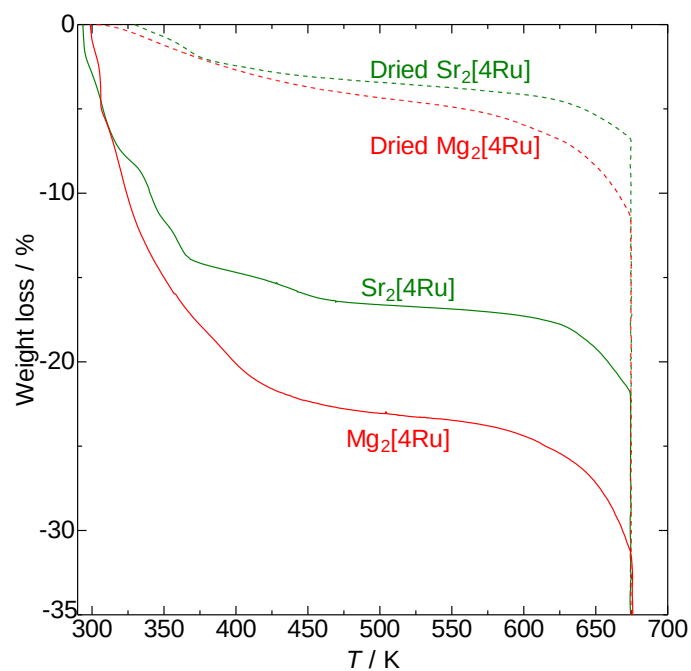


Figure 2-5. TG curves of the $\text{Mg}_2[4\text{Ru}] \cdot 13\text{H}_2\text{O}$ and $\text{Sr}_2[4\text{Ru}] \cdot 9\text{H}_2\text{O}$ under Ar flow (300 ml/min) before (solid lines) and after drying at 423 K for 15 hours (dotted lines). Small weight losses ($< 5.0\%$) for both the dried samples are due to the water adsorbed in the sample preparation process before TG measurements.

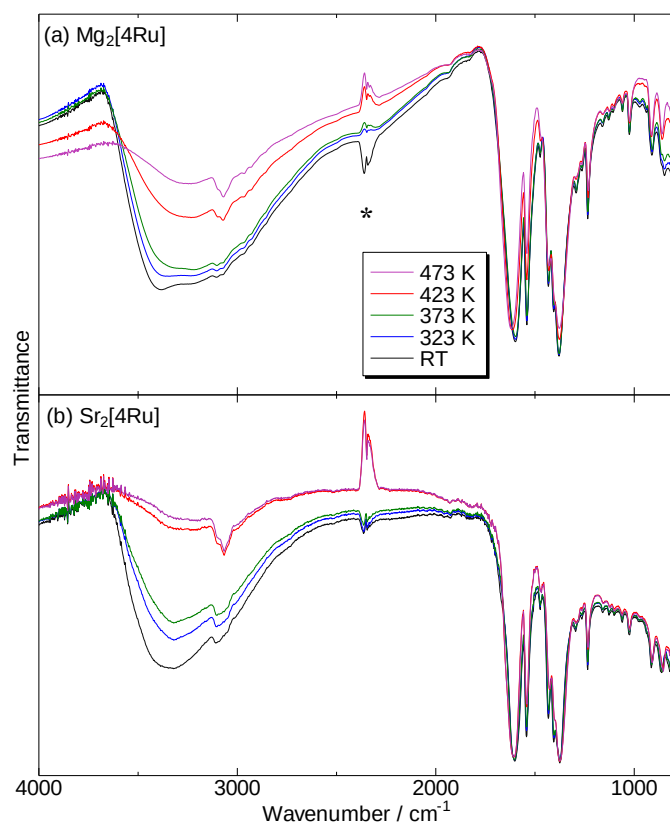


Figure 2-6. Temperature dependences of IR spectra of (a) $\text{Mg}_2[4\text{Ru}]$ and (b) $\text{Sr}_2[4\text{Ru}]$. The marked sharp peak at 2360 cm^{-1} is attributed to the vibration of CO_2 in the air.

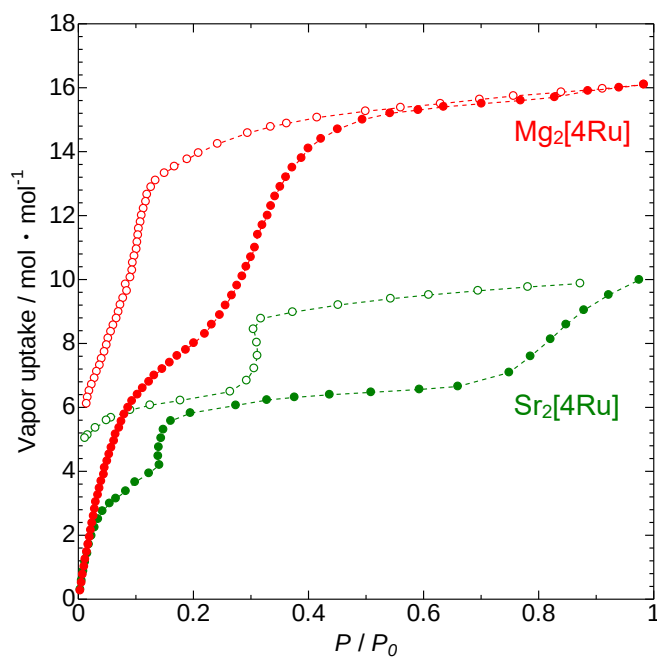


Figure 2-7. Water vapor adsorption isotherms of $\text{Mg}_2[4\text{Ru}]$ (red squares) and $\text{Sr}_2[4\text{Ru}]$ (green circles) at 298 K. Closed and open symbols show adsorption and desorption processes, respectively.

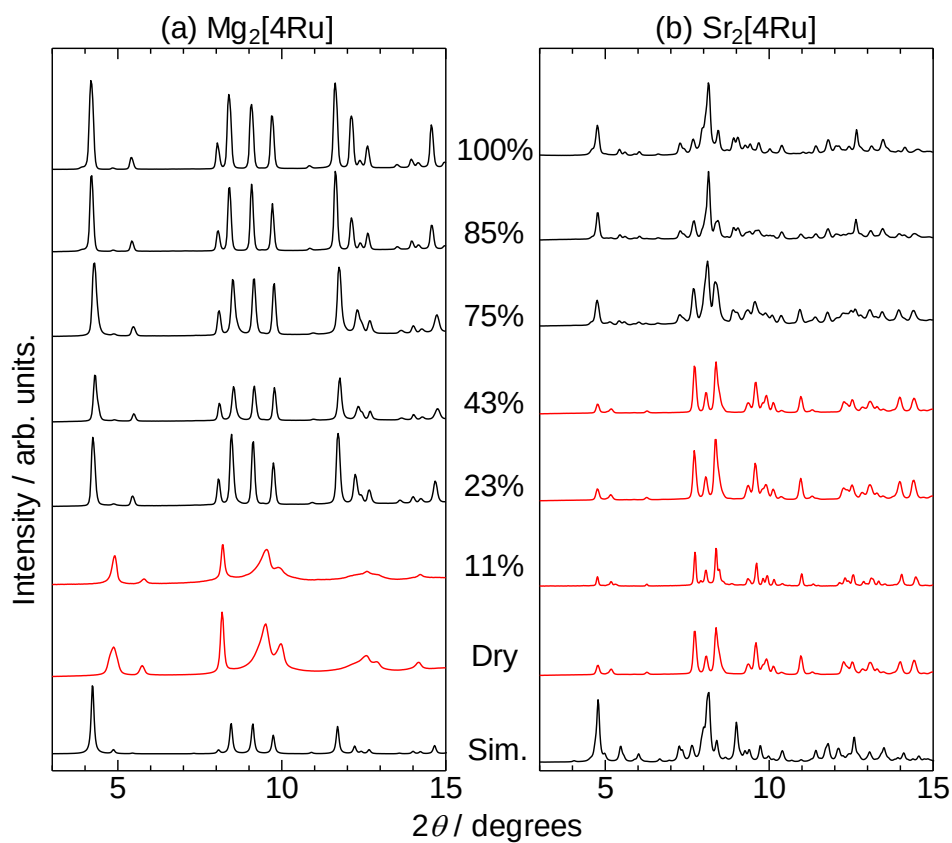


Figure 2-8. PXRD patterns [$\lambda = 0.9985(1) \text{ \AA}$] of the RH dependence of (a) **Mg₂[4Ru]** and (b) **Sr₂[4Ru]** at room temperature. Bottom patterns are simulated patterns calculated from corresponding crystal structures.

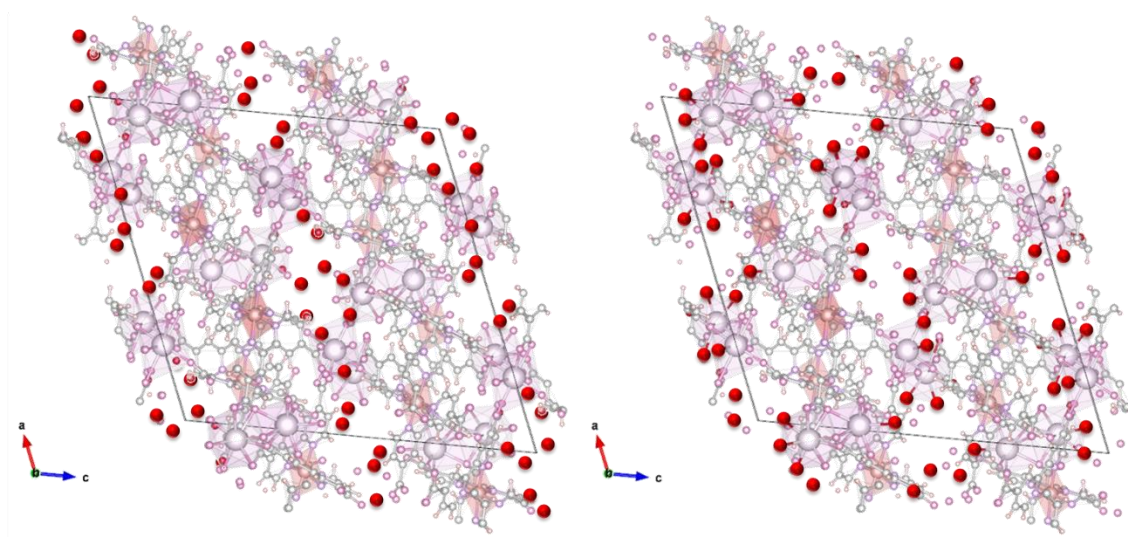


Figure 2-9. The crystal water molecules (left) and coordinated water molecules (right) of **Sr₂[4Ru]**. The red balls are showed the oxygen derived water

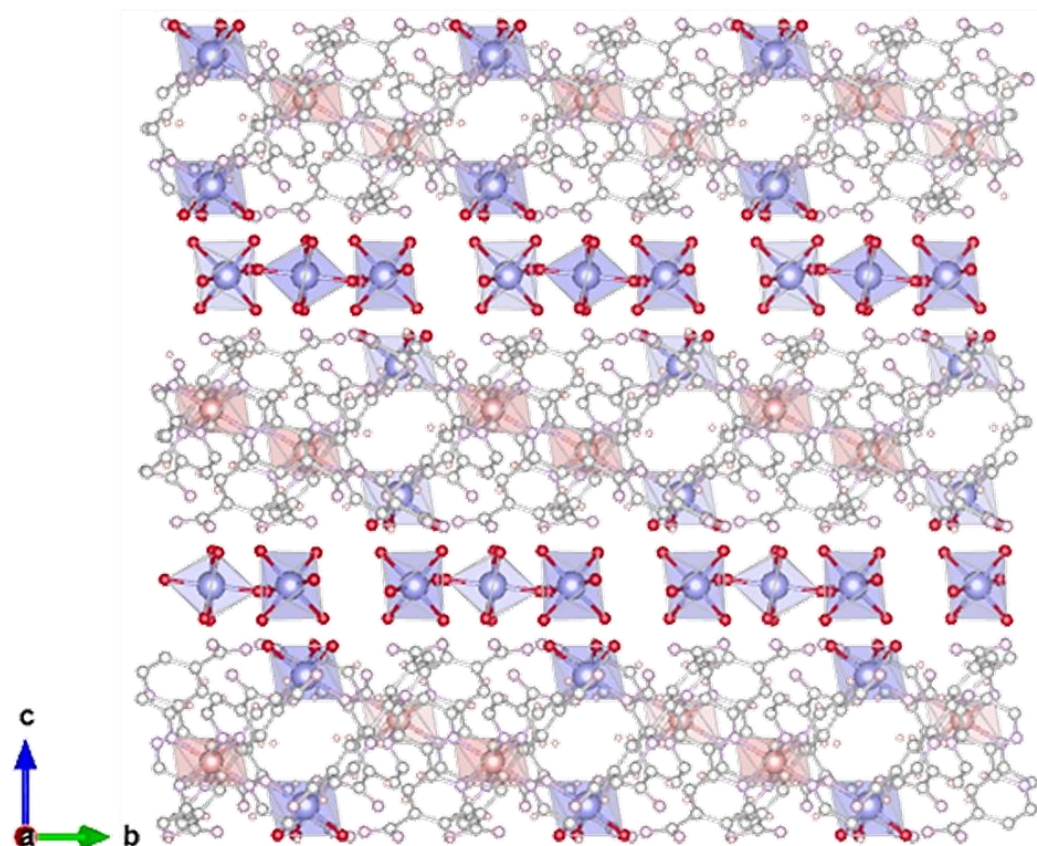


Figure 2-10. The coordinated water molecules of **Mg₂[4Ru]**. The red balls are showed the oxygen derived water

Figure 2-11 shows the methanol vapor adsorption isotherms of **Mg₂[4Ru]** and **Sr₂[4Ru]** at 298 K. As expected from the changes in the PXRD patterns (Figure 2-4), these two PCPs can adsorb methanol vapor. In contrast to the large difference between the saturated water vapor adsorption amounts of **Mg₂[4Ru]** and **Sr₂[4Ru]**, the adsorbed methanol amounts at $P / P_0 = 0.73$ are almost the same: 4.7 and 4.5 mol mol⁻¹ per [4Ru] unit for **Mg₂[4Ru]** and **Sr₂[4Ru]**, respectively. As mentioned above, the structure of the methanol-adsorbed **Sr₂[4Ru]** was almost the same as that of fully hydrated (**Sr₂[4Ru]**·9H₂O)₂, whereas the methanol- and water-adsorbed phases of **Mg₂[4Ru]** showed different framework structures (Figure 2-2). Considering the difference between the molecular volumes of methanol and water, the guest-accessible volume of the **Sr₂[4Ru]** complex will be fully occupied by the adsorbed methanol molecules, resulting in the formation of almost the same structure as that of the fully hydrated (**Sr₂[4Ru]**·9H₂O)₂. In contrast, the saturated amount of methanol vapor adsorption of **Mg₂[4Ru]** is quite smaller than the amount of water vapor

adsorption, suggesting that the volume occupied by the adsorbed methanol is not sufficient to fully occupy the guest accessible space in $\text{Mg}_2[4\text{Ru}]\cdot 16\text{H}_2\text{O}$. As a result, the methanol-adsorbed structure of $\text{Mg}_2[4\text{Ru}]$ will be different from the structure of $\text{Mg}_2[4\text{Ru}]\cdot 16\text{H}_2\text{O}$.

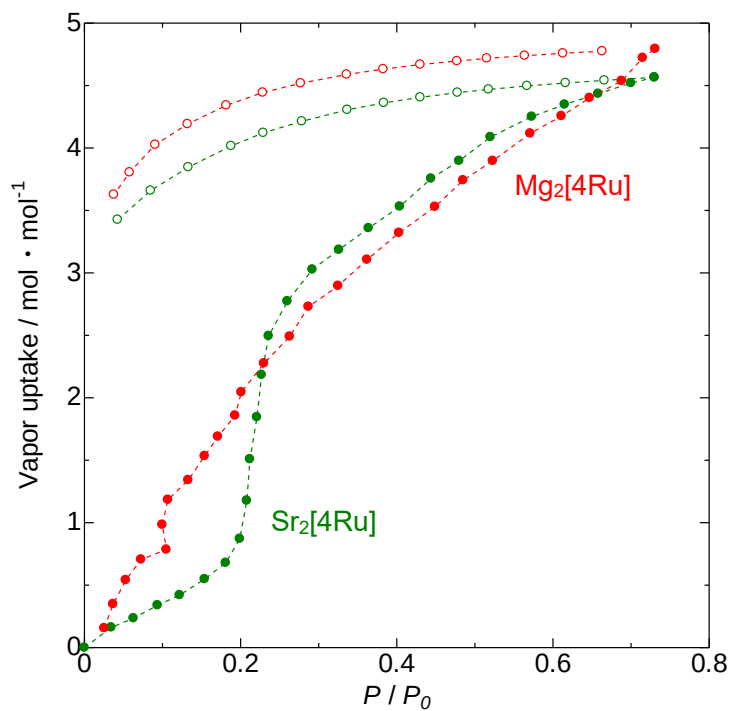


Figure 2-11. Methanol vapor adsorption isotherms of $\text{Mg}_2[4\text{Ru}]$ (red squares) and $\text{Sr}_2[4\text{Ru}]$ (green circles) at 298 K. Closed and open symbols show adsorption and desorption processes, respectively.

Before each vapor adsorption measurement, these PCPs were dried at 373 K for 1 day to remove all hydrated water in order to form the anhydrous state of the PCPs. In the anhydrous state, the coordination sites of the M^{2+} cation could either be occupied by the carboxy groups of the **[4Ru]** metalloligand or remain in a coordinatively unsaturated state. Considering the fact that these unsaturated sites can act as the guest adsorption sites,^{11,12} methanol vapor is probably adsorbed and coordinated to the M^{2+} centers. In the case of water vapor adsorption, the first guest adsorption site should also be the same coordinatively unsaturated sites. However, the additional vapor adsorption occurs because of the smaller molecular volume and high hydrogen-bonding ability of water vapor compared to methanol. The isotherm of **Sr₂[4Ru]** showed a sharp increase at $P/P_0 = 0.20$, whereas the adsorption amount of **Mg₂[4Ru]** monotonically increased from the low-pressure region. This difference can be related to structural dimensionality. In contrast to the 2D coordination sheet structure of **Mg₂[4Ru]·13H₂O**, (**Sr₂[4Ru]·9H₂O**)₂ has a more rigid 3D coordination network structure, supported by the bridging carboxylates, implying that the structural flexibility of **Sr₂[4Ru]** is lower than that of **Mg₂[4Ru]**. In addition, the 2D-layered structure of **Mg₂[4Ru]·13H₂O** may enable the complex to retain the guest-accessible layers formed from the Mg^{2+} cations, even in the anhydrous form. Moreover, these two PCPs were found to hardly adsorb CO₂ gas (less than 0.1 mol mol⁻¹; see Figure 2-12), implying that their porous channels in the dried states would have a highly hydrophilic nature and/or a smaller pore diameter than the molecular size of CO₂.

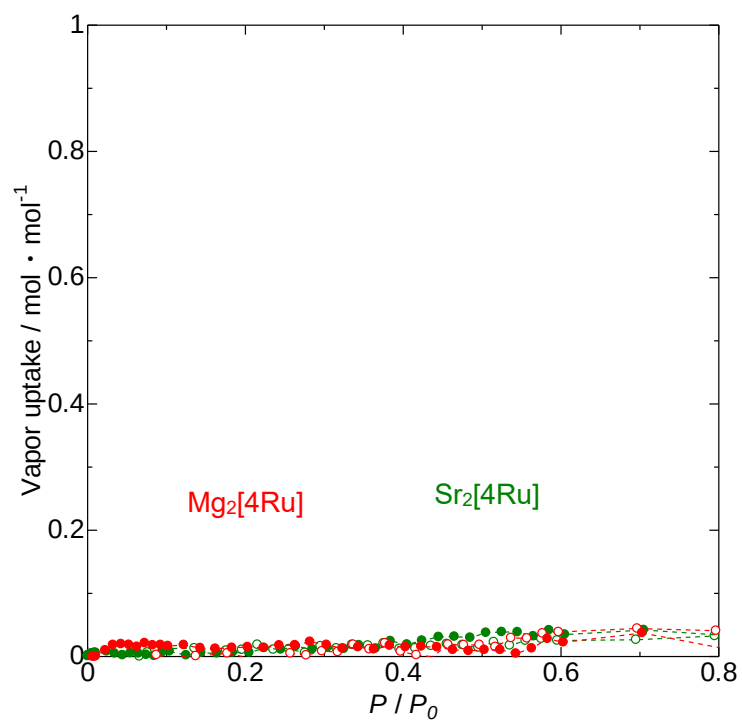


Figure 2-12. CO₂ adsorption isotherms of **Mg₂[4Ru]** (red) and **Sr₂[4Ru]** (green) at 194 K. Closed and open symbols show adsorption and desorption process, respectively.

2-3-3 Light absorption and emission properties

As mentioned in the Introduction, ruthenium(II) polypyridine complexes show interesting absorption and emission properties derived from metal-to-ligand charge-transfer (MLCT) transitions.¹³ To investigate the effect of coordination polymerization on the light absorption and emission properties of the metalloligands **[4Ru]**, UV diffuse-reflectance and luminescence spectra in the solid state were measured. The results were compared with those of the metalloligands in a basic aqueous solution and are shown in Figure 2-13. The observed energies of the absorption edge and emission maxima are summarized in Table 2-4. The ruthenium(II) metalloligands **[4Ru]** showed absorption bands at 467 nm and emission bands at 633 nm. These absorption and emission bands are assigned as the singlet and triplet MLCT transitions; our results are consistent with the previous report by Kalyanasundaram et al.¹³ All of the obtained **M₂[4Ru]** PCPs showed a very broad absorption band below 600 nm and a emission band at ~680 nm. The emission lifetime for (**Sr₂[4Ru]·9H₂O**)₂ (256 ns) is in the same time scale as that of **[4Ru]** in aqueous solutions (700 ns), suggesting that these absorption and emission bands are assignable to the ¹MLCT absorption and ³MLCT emission of each **[4Ru]** moiety. Observed red shift of adsorption and emission maximum of **M₂[4Ru]** was caused by stabilization of the excitation state from the stabilization of π^* orbital of bipyridine ligand. The slightly shorter emission lifetime of (**Sr₂[4Ru]·9H₂O**)₂ than that of **[4Ru]** in the aqueous solution would be due to the heavy-atom effect of the Sr²⁺ ion. The change in the luminescence quantum yield (Φ_{em}) of **M₂[4Ru]** before and after removal of the crystal water was also checked. The yield of dried **Sr₂[4Ru]** was estimated to be 1.6% at room temperature and slightly increased to 2.4% by the adsorption of water vapor. In contrast, the yield of dried **Mg₂[4Ru]** was found to be 3.7% and slightly decreased to 2.7% by the adsorption of water vapor. These luminescence quantum yields are smaller than that of **[4Ru]** in aqueous solution ($\Phi_{em} = 6.03\%$),¹⁴ suggesting that the photo-excited state generated in the **M₂[4Ru]** solid state tends to be deactivated more rapidly than that in the solution state. The different behavior between **Mg₂[4Ru]** and **Sr₂[4Ru]** would be due to the difference in the amounts of adsorbed water molecules in these PCPs.

Table 2-4. Absorption and emission spectral data of **M₂[4Ru]** at room temperature

complex	λ_{abs} (nm)	λ_{em} (nm)
[4Ru] (aq.)	436, 467	633 ^b
Mg₂[4Ru]·13H₂O	600 ^a	681 ^c
(Sr₂[4Ru]·9H₂O)₂	595 ^a	683 ^c

^a Wavelength of half-absorption at 500 nm.

^b $\lambda_{\text{ex}} = 500$ nm. ^c $\lambda_{\text{ex}} = 500$ nm.

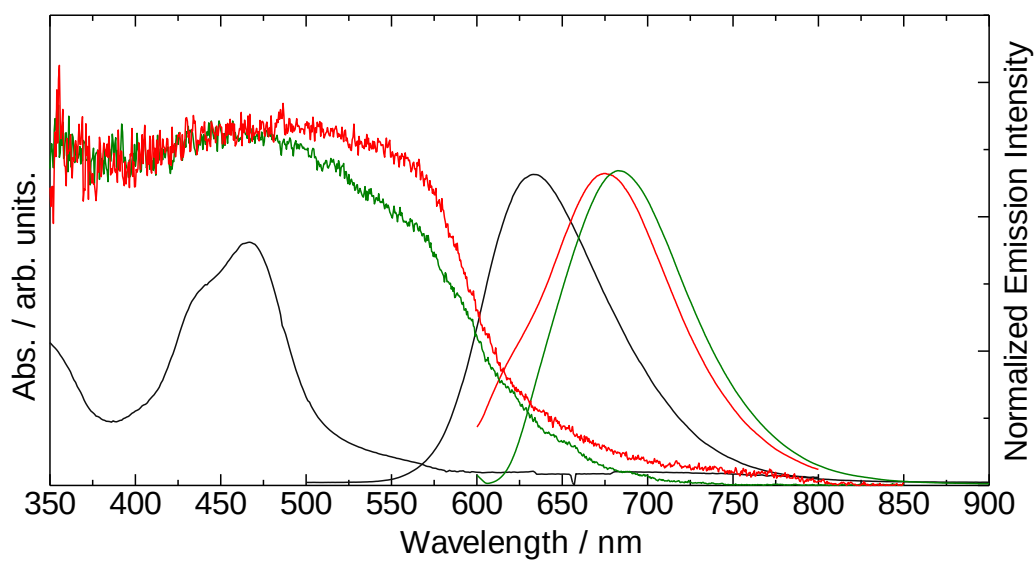


Figure 2-13. UV diffuse-reflectance and luminescence spectra of (a) **Mg₂[4Ru]·13H₂O** (red line) and **Sr₂[4Ru]·9H₂O** (green) from the solid state at room temperature. Spectra of metalloligands **[4Ru]** in basic aqueous solutions are shown in black.

2-4 Conclusion

Two novel luminescent PCPs composed of ruthenium(II) metalloligands, $[\text{Ru}(4,4'\text{-dc bpy})_3]^{4-}$ (**[4Ru]**) and divalent metal ions $\text{Mg}_2[\text{4Ru}] \cdot 13\text{H}_2\text{O}$ and $(\text{Sr}_2[\text{4Ru}] \cdot 9\text{H}_2\text{O})_2$ have been successfully synthesized. Obtained PCPs, **Mg₂[4Ru]** and **Sr₂[4Ru]** had 2D-sheet structure and 3D-lattice structure, respectively. Their crystal structures are determined by single-crystal X-ray diffraction. **M₂[4Ru]** PCPs showing reversible structural transitions accompanied by water or methanol vapor adsorption/desorption. The absorption and emission properties of the **[4Ru]** metalloligand in **M₂[4Ru]** are characterized by the same singlet and triplet MLCT transitions as those of **[4Ru]** in aqueous solution. By using photoactive metalloligand, the constructing the PCPs which have the luminescence properties from **[4Ru]** and the different structure dimension was succeeded.

2-5 References

- 1) Kobayashi, A.; Suzuki, Y.; Ohba, T.; Noro, S.; Chang, H.-C. Kato, M. *Inorg. Chem.* **2011**, *50*, 2061.
- 2) Eskelinen, E.; Luukkanen, S.; Haukka, M.; Ahlgrén, M.; Pakkanen, T. A. *J. Chem. Soc., Dalton Trans.* **2000**, 2745.
- 3) Matthews, C. J.; Elsegood, M. R. J.; Bernardinelli, G.; Clegge, W.; Williams, A. F. *Dalton Trans.* **2004**, 492.
- 4) *CrystalClear*; Molecular Structure Corp.: Orem, UT, 2001.
- 5) *SIR2004*: Burla, M. C.; Caliandro, R.; Camalli, M.; Carrozzini, B.; Cascarano, G. L.; De Caro, L.; Giacovazzo, C.; Polidori, G.; Spagana, R. *J. Appl. Crystallogr.* **2005**, *38*, 381.
- 6) *SHLEX97*: Sheldrick, G. M. *Acta Crystallogr., Sect. A* **2008**, *64*, 112.
- 7) *CrystalStructure 4.0; Crystal Structure Analysis Package*; Rigaku Corp.: Tokyo, Japan, 2000.
- 8) Platon SQUEEZE: Spek, A. L. *J. Appl. Crystallogr.* **2003**, *36*, 7.
- 9) Rockland, L. B. *Anal. Chem.* **1960**, *32*, 1375.
- 10) (a) Kitagawa, S.; Kitaura, R.; Noro, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2334. (b) Li, H.; Eddaoudi, M.; O’Keeffe, M.; Yaghi, O. M. *Nature* **1999**, *402*, 276. (c) Rosi, N. L.; Eckert, J.; Eddaoudi, M.; Vodak, D. T.; Kim, J.; O’Keeffe, M.; Yaghi, O. M. *Science* **2003**, *300*, 1127.
- 11) (a) Dinca, M.; Long, J. R. *J. Am. Chem. Soc.* **2005**, *127*, 9376. (b) Zhou, W.; Wu, H.; Yildirim, T. *J. Am. Chem. Soc.* **2008**, *130*, 15268. (c) Kaye, S. S.; Long, J. R. *J. Am. Chem. Soc.* **2008**, *130*, 806. (d) Lee, W. R.; Ryu, D. W.; Lee, J. W.; Yoon, J. H.; Koh, E. K.; Hong, C. S. *Inorg. Chem.* **2010**, *49*, 4723.
- 12) Kitaura, R.; Onoyama, G.; Sakamoto, H.; Matsuda, R.; Noro, S.; Kitagawa, S. *Angew. Chem., Int. Ed.* **2004**, *43*, 2684.
- 13) (a) Kalyanasundaram, K. *Photochemistry of Polypyridine and Porphyrin Complexes*; Academic Press: London, **1992**. (b) Juris, A.; Balzani, V.; Barigelletti, F.; Campagna, S.; Belser, P.; Zelewsky, A. V. *Coord. Chem. Rev.* **1988**, *84*, 85. (c) Nazeeruddin, Md. K.; Kalyanasundaram, K. *Inorg. Chem.* **1989**, *28*, 4251.
- 14) Suzuki, K.; Kobayashi, A.; Kaneko, S.; Takehira, K.; Yoshihara, T.; Ishida, H.; Shiina, Y.; Oishi, S.; Tobita, S. *Phys. Chem. Chem. Phys.* **2009**, *11*, 9850.

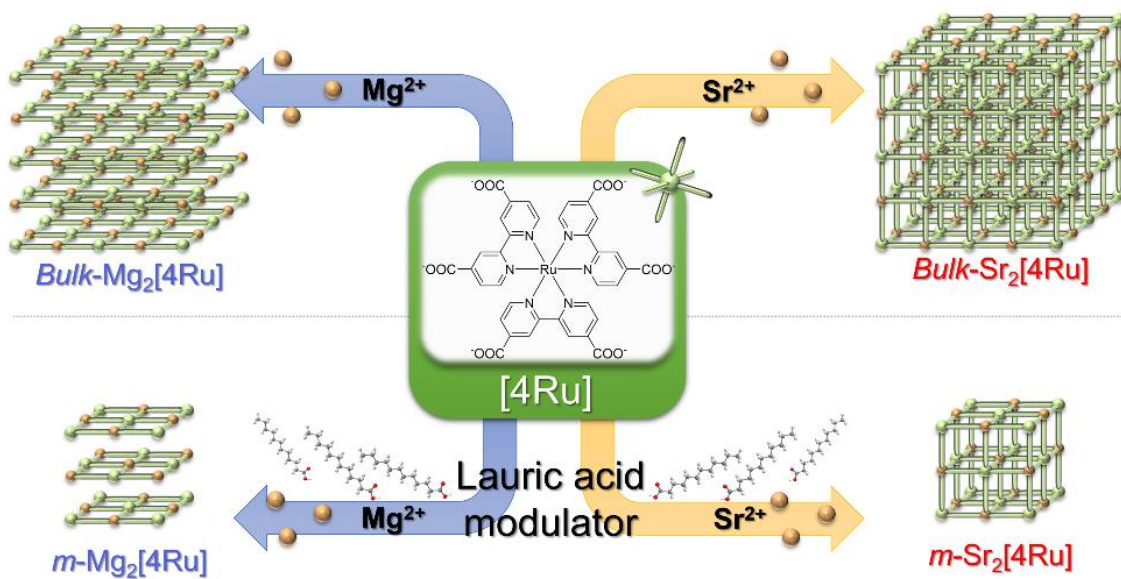
Chapter 3

Reduction in crystal size of flexible porous coordination polymers built from luminescent Ru(II)-metalloligands

3-1 Introduction

As discussed in Chapter 2, we recently synthesized two different MOFs composed of the $[\text{Ru}(\text{dcbpy})_3]^{4+}$ (**[4Ru]**:H₂dcbpy = 4,4'-dicarboxy-2,2'-bipyridine) metalloligand with divalent cations $[\text{Mg}(\text{H}_2\text{O})_6]\{[\text{Mg}(\text{H}_2\text{O})_3][\text{4Ru}]\} \cdot 4\text{H}_2\text{O}$ (**Mg₂[4Ru]**·13H₂O), $\{[\text{Sr}_4(\text{H}_2\text{O})_9][\text{4Ru}]_2 \cdot 9\text{H}_2\text{O}\}$ (**Sr₂[4Ru]**·9H₂O)₂, and demonstrated that these MOFs have different coordination network structures (e.g., three-dimensional (3-D) lattice and two-dimensional (2-D) sheet structures for **Sr₂[4Ru]** and **Mg₂[4Ru]**, respectively). Furthermore, both MOFs show *Gate-opening*-type adsorption behavior on exposure to H₂O and MeOH vapors.¹

In this chapter, I have focused on the effect of crystal downsizing on the guest adsorption properties of two different PCPs, **Sr₂[4Ru]** and **Mg₂[4Ru]**, that have different 3-D and 2-D coordination network structures composed of labile alkaline-earth metal ions (Scheme 3-1). The crystal sizes of both PCPs were successfully reduced to the mesoscale (about 500 nm width and 10 nm thickness for **Sr₂[4Ru]**, and about 1 μm width and 30 nm thickness for **Mg₂[4Ru]**) using the coordination modulation method of Furukawa *et al.*² It was found that meso-sized 3-D lattice-type PCP *m*-**Sr₂[4Ru]** showed completely different water adsorption behavior to that of the bulk crystals, whereas the meso-sized 2-D sheet-type PCP *m*-**Mg₂[4Ru]** showed a very similar adsorption behavior to that of the bulk crystals. This finding suggests that the dimensionality of coordination network structure is one of the important factors influencing the crystal downsizing effect on the guest adsorption behavior of MOFs/PCPs.



Scheme 3-1. Crystal downsizing of luminescent PCPs, $\text{Mg}_2[4\text{Ru}]$ and $\text{Sr}_2[4\text{Ru}]$ based on coordination modulation method. Lauric acid was used as the modulator.

3-2 Experimental

3-2-1 Materials and synthesis

All starting materials $\text{RuCl}_3 \cdot 3\text{H}_2\text{O}$, $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$, $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$, and 4-methylpyridine were purchased and used as received. Solvents were used without any further purification. Unless otherwise stated, all reactions were performed in air. The ruthenium(II) metalloligand $[\text{Ru}(\text{4,4'}\text{-H}_2\text{dcbpy})_2(\text{4,4'}\text{-dcbpy})]$ and the bulk crystals of **Sr₂[4Ru]** and **Mg₂[4Ru]** were prepared according to published methods.¹ Elemental analysis was performed at the analysis center of Hokkaido University.

Synthesis of *meso*-sized **Sr₂[4Ru]** crystals (*m*-**Sr₂[4Ru]**)

$[\text{Ru}(\text{4,4'}\text{-H}_2\text{dcbpy})_2(\text{4,4'}\text{-dcbpy})]$ (8.4 mg, 0.010 mmol) and lauric acid (20.0 mg, 0.100 mmol), which was used as the coordination modulator, were dissolved in a mixed solution of triethanolamine (0.25 mL) and H_2O (10 mL). To the resultant clear red solution, an ethanolic solution (40 mL) of $\text{SrCl}_2 \cdot 6\text{H}_2\text{O}$ (8.8 mg, 0.033 mmol) was added at a rate of 1 mL/min with continuous stirring. After additional stirring for 10 min, we obtained a red solution, and this was stored at $-10\text{ }^\circ\text{C}$ overnight. From this solution, fine orange crystals were obtained and collected by centrifugation (5000 rpm), washed with EtOH three times, and air dried. Yield: 9.6 mg (0.0081 mmol), 81% based on $[\text{Ru}(\text{4,4'}\text{-H}_2\text{dcbpy})_3]$. Anal. (%) Calcd for $\text{C}_{36}\text{H}_{18}\text{N}_6\text{O}_{12}\text{RuSr}_2 \cdot 11\text{H}_2\text{O}$: C, 36.00; H, 3.36; N, 7.00. Found: C, 36.12; H, 3.29; N, 7.10. IR (KBr, cm^{-1}): 3401 m, 1598 s, 1543 m, 1431 w, 1405 m, 1379 s, 1298 w, 1235 w, 1027 w, 914 w, 861 w, 784 m, 707 w, 668 w, 445 w.

Synthesis of *meso*-sized **Mg₂[4Ru]** crystals (*m*-**Mg₂[4Ru]**)

$[\text{Ru}(\text{4,4'}\text{-H}_2\text{dcbpy})_2(\text{4,4'}\text{-dcbpy})]$ (8.4 mg, 0.010 mmol) and lauric acid (20.0 mg, 0.100 mmol), which was used as the coordination modulator, were dissolved in a mixed solution of triethanolamine (0.25 mL) and H_2O (10 mL). To the resultant clear red solution, an ethanolic solution (10 mL) of $\text{Mg}(\text{CH}_3\text{COO})_2 \cdot 4\text{H}_2\text{O}$ (7.1 mg, 0.033 mmol) was added at a rate of 1 mL/min, followed by an additional portion of EtOH (30 mL), which was used as a poor solvent. After additional stirring for 10 min, the obtained solution was stored at $-10\text{ }^\circ\text{C}$ overnight. From this solution, fine orange crystals were obtained. The crystals were collected by centrifugation (5000 rpm) and washed with EtOH three times and air dried. Yield: 7.4 mg (0.0067 mmol), 67% based

on [Ru(4,4'-Hdc bpy)₃]. Anal. (%) Calcd for C₃₆H₁₈N₆O₁₂RuMg₂·13H₂O: C, 38.94; H, 3.99; N, 7.57. Found: C, 38.66; H, 3.71; N, 7.44. IR (KBr, cm⁻¹): 3381 s, 1601 s, 1542 s, 1433 m, 1405 m, 1380 s, 1293 w, 1266 w, 1236 m, 1160 w, 1128 w, 915 w, 781 m, 724 w, 700 m, 458 w, 419 w.

3-2-2 Scanning electron microscopy

Scanning electron microscopy (SEM) images were obtained on a JEOL Ltd. JSM-6360LA. SEM images were operated at 15 kV, 11 mm of WD.

3-2-3 Powder X-ray diffraction

Powder X-ray diffraction (PXRD) measurements were carried out using a Bruker D8 Advance diffractometer equipped with a graphite monochromator, using Cu-K α radiation, and a one-dimensional LinxEye detector. Some PXRD measurements were carried out using a Rigaku SPD diffractometer at beamline BL-8B of the Photon Factory, KEK, Japan. The synchrotron X-ray wavelength was 1.5455 Å, and all values of 2 θ were converted to the equivalent wavelength of Cu-K α radiation. The sample was placed in a glass capillary of diameter 0.5 mm, and the relative humidity inside of each capillary was controlled by a published method.³

3-2-4 Adsorption isotherms

The adsorption isotherms for water and methanol vapors at 298 K were collected using an automatic volumetric adsorption apparatus (BELSORP-MAX; MicrotracBEL, Inc.)

3-2-5 UV-vis spectrophotometric measurement

Thermogravimetric analysis (TGA) and differential thermal analysis (DTA) were performed using a Rigaku ThermoEvo TG8120 analyzer.

3-3 Results and Discussions

3-3-1 Synthesis and assembled structure of *m*-Sr₂[4Ru]

Figure 3-1 shows SEM images of two samples of *m*-Sr₂[4Ru] obtained by the coordination polymerization reaction in the absence and presence of 10 equiv. lauric acid, which was used as the coordination modulator. Both samples formed unique flower-like aggregates, but the aggregates were significantly different in size; those obtained from reaction without lauric acid were estimated to be about 1 μm in diameter and 300 nm in thickness, as shown in the inset of Figure 3-1(a), whereas those formed in the presence of the lauric acid modulator were two times larger (about 2 μm in diameter and 1 μm in thickness), as shown in the inset of Figure 3-1(b). In both cases, the aggregates were composed of a large number of nano-sized platelet-like crystals. From the SEM images, the sizes of nanocrystallites were estimated to be roughly 300 nm in length and 50 nm in thickness for both samples, in contrast the crystal size of the bulk sample was estimated to be roughly 1-200 μm in length and 1.5-20 μm in thickness (Figure 3-2). The dependence of the particle size of the flower-like aggregate on the amount of lauric acid modulator is shown in Figure 3-1(c). The size of the aggregates clearly increased with increasing quantity of lauric acid modulator, from 0 to 20 equiv., and the maximum size of the aggregates increased to 2.6 μm in diameter and 1.5 μm in thickness (see Figure 3-3). In contrast, the sizes of the nanocrystals in the aggregates were not affected by the amount of modulator. These largely different results suggest that the lauric acid modulator plays a key role in the aggregation of nano-sized crystals.

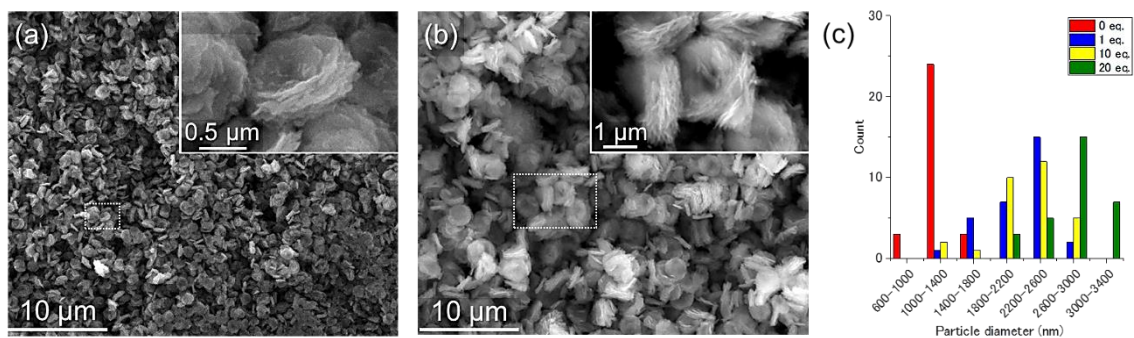


Figure 3-1. SEM images of $m\text{-Sr}_2[4\text{Ru}]$ samples prepared by (a) without lauric acid and (b) with 10 equiv. lauric acid. (c) Diameter distribution of the flower-like aggregates of $m\text{-Sr}_2[4\text{Ru}]$ prepared with various amounts of the lauric acid modulator.

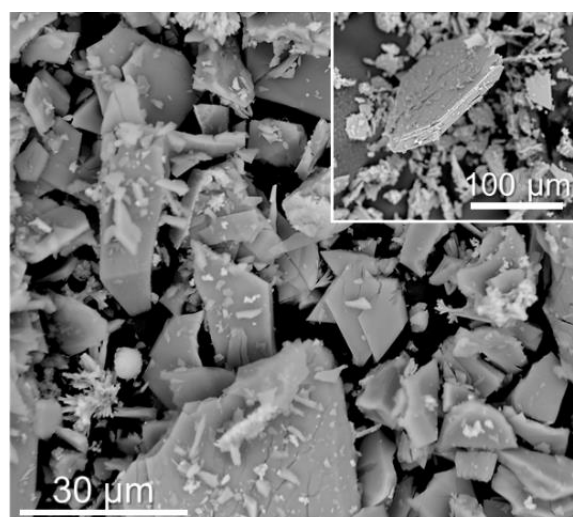


Figure 3-2. SEM images of $\text{Bulk-Sr}_2[4\text{Ru}]$ samples.

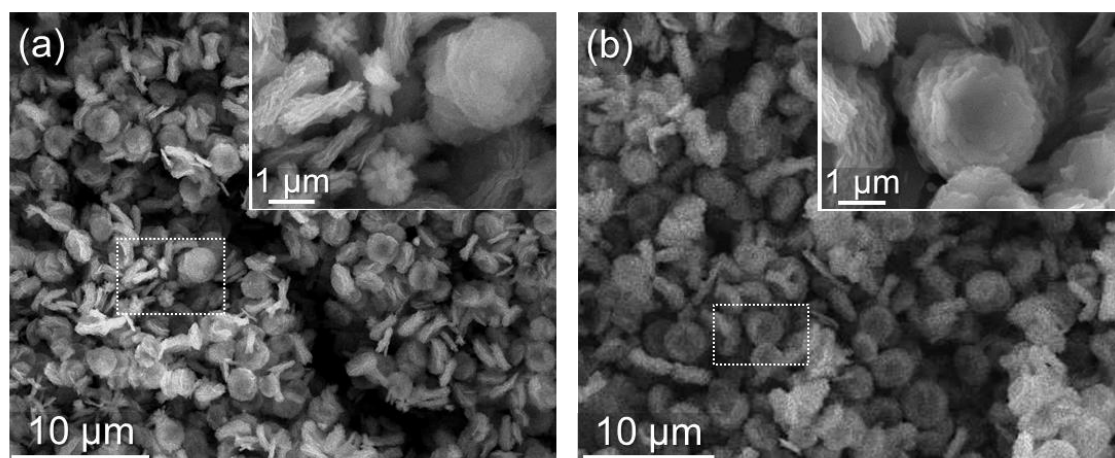


Figure 3-3. SEM images of $m\text{-Sr}_2[4\text{Ru}]$ samples synthesized in the presence of (a) 1 eq. and, (b) 20 eq. lauric acid.

Because the diameters of the flower-like aggregates strongly depend on the amount of lauric acid, we also examined the dependence of the concentration of bridging Sr^{2+} ions (see Figure 3-4). Similar flower-like aggregates with diameters of 2.5 μm were obtained in the presence of the twice the quantity of Sr^{2+} ions. However, when the Sr^{2+} concentration was increased to four times the original amount, flower-like aggregates were not observed, and only microcrystals with lengths less than 1.5 μm were formed (note that the amounts of lauric acid, 10 equiv. were constant in these reactions). This clear difference observed at higher Sr^{2+} concentrations could be caused by the decrease in the concentration of free laurate due to its coordination to Sr^{2+} ions, leading to covering of the nanocrystalline $m\text{-Sr}_2[4\text{Ru}]$ by Sr^{2+} ions. As a result, the positive charge of the surface of $m\text{-Sr}_2[4\text{Ru}]$ nanocrystals would suppress the formation of the flower-like aggregates by electrostatic repulsion. In other words, the hydrophobic interaction between the laurate-covered nanocrystals of $\text{Sr}_2[4\text{Ru}]$ could be important for the formation of flower-like aggregates. We also synthesized $m\text{-Sr}_2[4\text{Ru}]$ by changing the temperature for the crystal growth from $-10\text{ }^\circ\text{C}$ to room temperature, but only negligible change in the size of flower-like aggregate was observed in SEM image (see Figure 3-5).

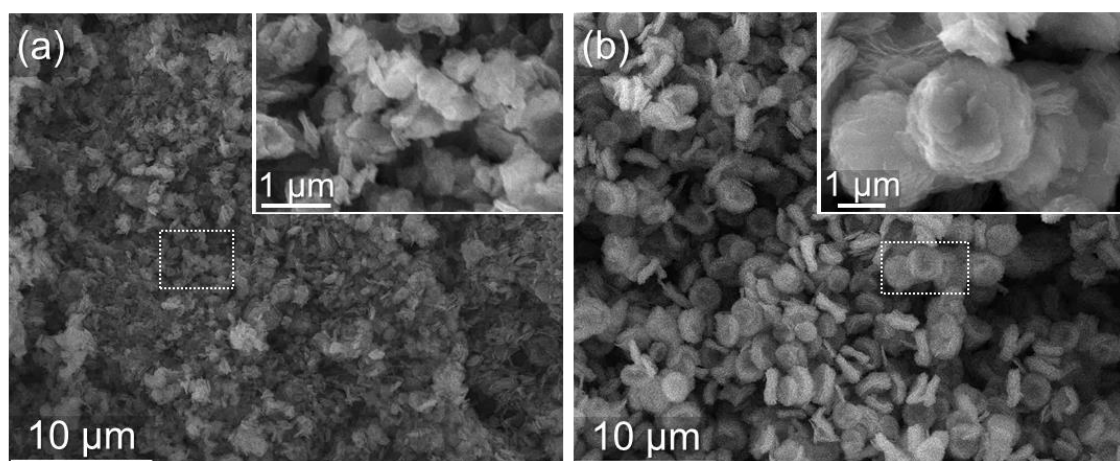


Figure 3-4. SEM images of $m\text{-Sr}_2[4\text{Ru}]$ samples synthesized in the presence of (a) four times larger concentration, and (b) twice larger concentration of Sr^{2+} .

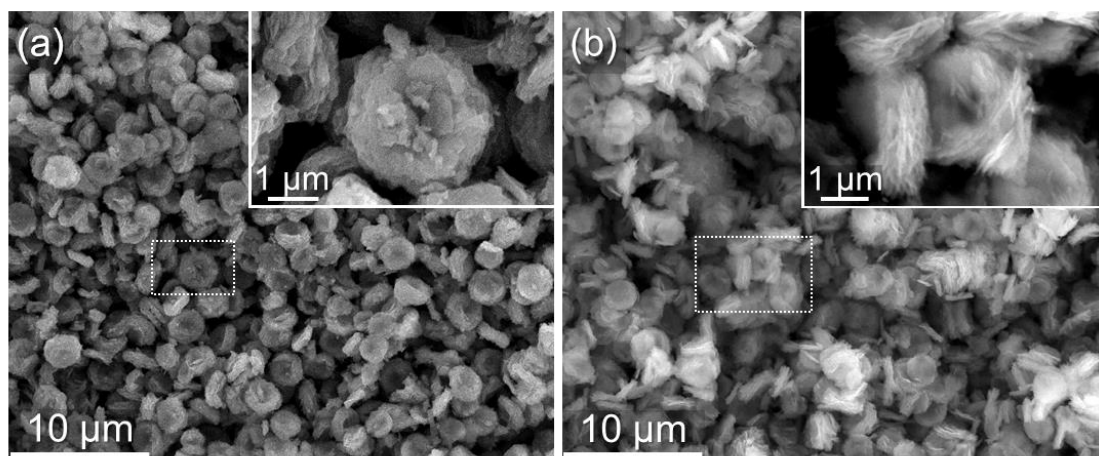


Figure 3-5. SEM images of $m\text{-Sr}_2[4\text{Ru}]$ samples synthesized at (a) R.T. and, (b) -10 $^{\circ}\text{C}$. The image shown in (b) is the same image of Figure 1(b).

To investigate the crystal structure of the flower-like aggregates of *m*-Sr₂[4Ru], powder X-ray diffraction patterns were measured. As shown in Figure 3-6, all observed peaks for the *m*-Sr₂[4Ru] obtained by the reaction in the presence of 10 equiv. of lauric acid were broad, but the pattern itself was qualitatively similar to the simulated pattern of *Bulk*-Sr₂[4Ru] with a full-width at half-maximum (FWHM) of 0.5°. The crystal size estimated from this broaden PXRD pattern by using Scherrer equation is about 30 nm, being consistent to the size of nanocrystal estimated by SEM image. The elemental analysis of *m*-Sr₂[4Ru] agreed quantitatively with the calculated value of Sr₂[4Ru] with eleven hydrated water molecules as well as that of the bulk sample (see Experimental section). These results suggest that downsizing of Sr₂[4Ru] crystals to the submicron size was successfully achieved by using the coordination modulation method. In the elemental analysis, the C content in *m*-Sr₂[4Ru] was almost identical to that of the *Bulk*-Sr₂[4Ru], implying that no laurate was coordinated to the crystal surface in *m*-Sr₂[4Ru]. This is also supported by the result that no characteristic peak of the modulator was observed in IR spectrum of *m*-Sr₂[4Ru] (see Figure 3-7). This may be due to the labile nature of Sr²⁺ ions, resulting in easy removal of laurate from the crystal surfaces on washing with EtOH. The broadening of the peaks in the PXRD-pattern of *m*-Sr₂[4Ru] may result from lower crystallinity originating from the shorter crystallization time required by the coordination modulation method (within 1 day) compared to that of the *Bulk*-Sr₂[4Ru] crystals (about 1 week). PXRD patterns of *m*-Sr₂[4Ru] samples synthesized using different quantities of the lauric acid modulator (see Figure 3-8) were qualitatively similar, except for the sample obtained using 20 equiv. of lauric acid. The PXRD pattern of this sample was significantly different, containing many sharp peaks in addition to the broad peaks originated from *m*-Sr₂[4Ru]. These sharp peaks may arise from crystalline byproducts formed from laurate and Sr²⁺. Also the excitation and emission spectra of three different *m*-Sr₂[4Ru] obtained in the absence or presence of 1 or 10 equiv. of lauric acid were measured and found that the emission and excitation maxima are close to those of the bulk sample but shifted to shorter wavelengths (see Figure 3-9), suggesting that this may be an effect of crystal downsizing; that is, the environment of [4Ru] metalloligand on the crystal surface is different to that inside the bulk crystal. In addition, negligible difference was observed for the spectra of three *m*-Sr₂[4Ru] with the different size of flower-like aggregates, suggesting that the spectral shifts compared to

the *Bulk-Sr₂[4Ru]* is not due to the formation of the aggregates, but due to the crystal downsizing to the mesoscopic region.

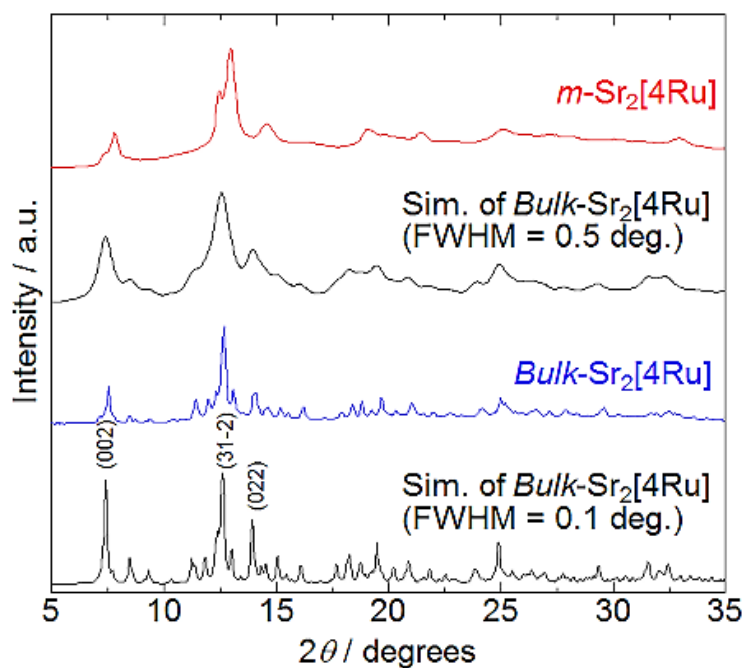


Figure 3-6. PXRD pattern of *m-Sr₂[4Ru]* (red) and *Bulk-Sr₂[4Ru]* (blue). The two black lines show simulations based on the crystal structure of *Bulk-Sr₂[4Ru]* with FWHMs of 0.1 and 0.5°. The integers in parentheses indicate the *hkl* indexes of main diffraction peaks.

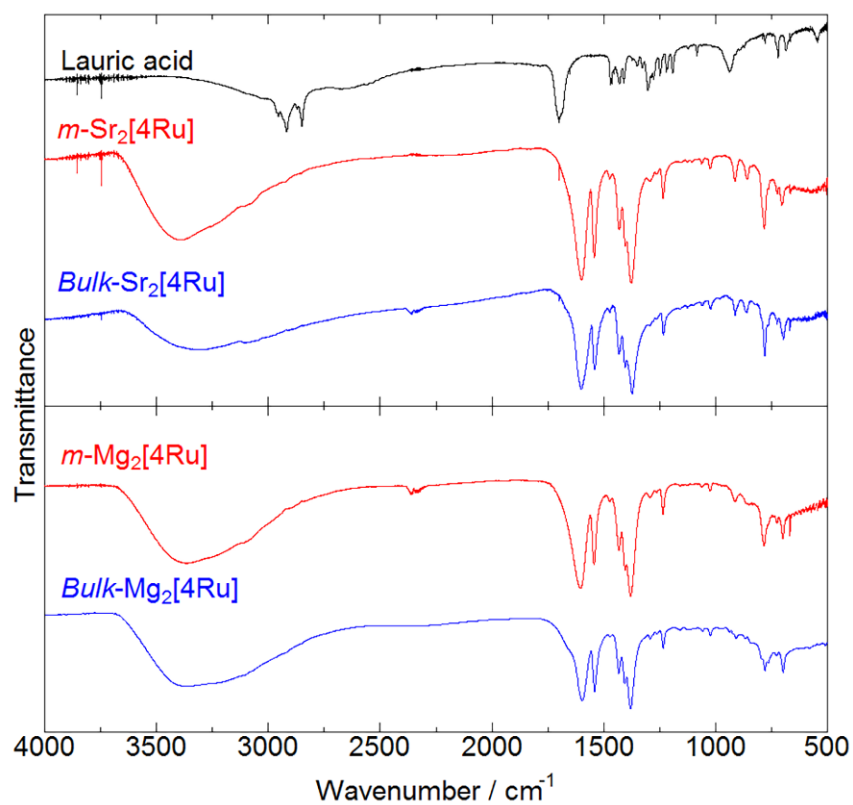


Figure 3-7. IR spectra of bulk- and meso-sized **M₂[4Ru]** (M= Sr²⁺ and Mg²⁺) compared with that of lauric acid.

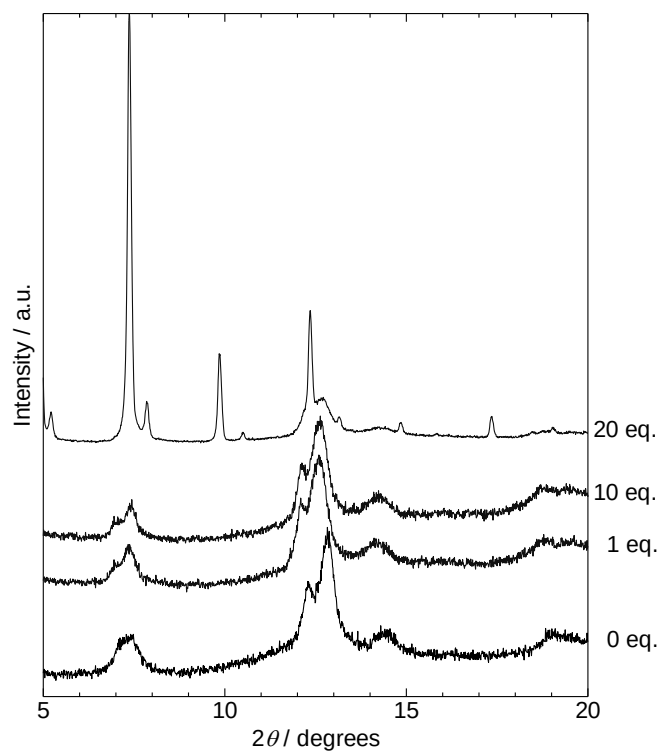


Figure 3-8. PXRD patterns of *m*-Sr₂[4Ru] synthesized with various equivalences of lauric acid.

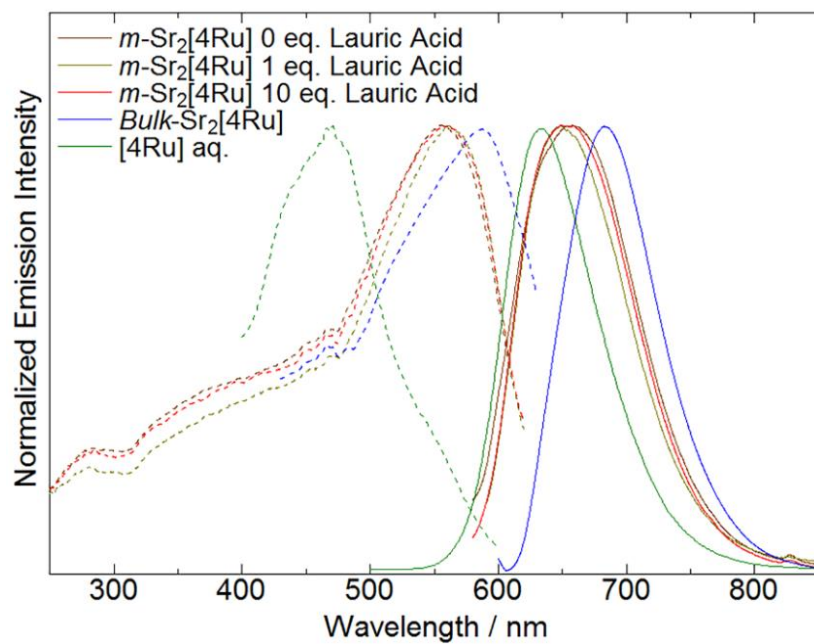


Figure 3-9. Emission (solid lines) and excitation (broken lines) spectra of *m*-Sr₂[4Ru] obtained in the presence of 0 eq. (brown), 1 eq. (yellow), or 10 eq. (red) of lauric acid modulator and Bulk-Sr₂[4Ru] (blue) in the solid state at room temperature compared with the spectra of metalloligand [4Ru] (green) in basic aqueous solution ($\lambda_{\text{ex}} = 558$ nm, *m*-Sr₂[4Ru]; $\lambda_{\text{ex}} = 594$ nm, Bulk-Sr₂[4Ru]; $\lambda_{\text{ex}} = 576$ nm, [4Ru] aq.).

3-3-2 Synthesis and assembled structure of *m*-Mg₂[4Ru]

The crystal downsizing of Sr₂[4Ru] by the coordination modulation method afforded interesting submicron to micron sized flower-like aggregates, as mentioned above. This observation motivated us to investigate the crystal downsizing of the other coordination polymers with different bridging metal ions because the comparison between these two CPs may provide information regarding the formation of the flower-like aggregates of *m*-Sr₂[4Ru]. Therefore, Mg₂[4Ru], which has a 2-D coordination sheet structure unlike the 3-D coordination lattice framework of Sr₂[4Ru], was chosen to further test the effects of downsizing. SEM images of the samples of *m*-Mg₂[4Ru] synthesized both in the absence and presence of 10 equiv. of lauric acid against [4Ru] are shown in Figure 3-10.

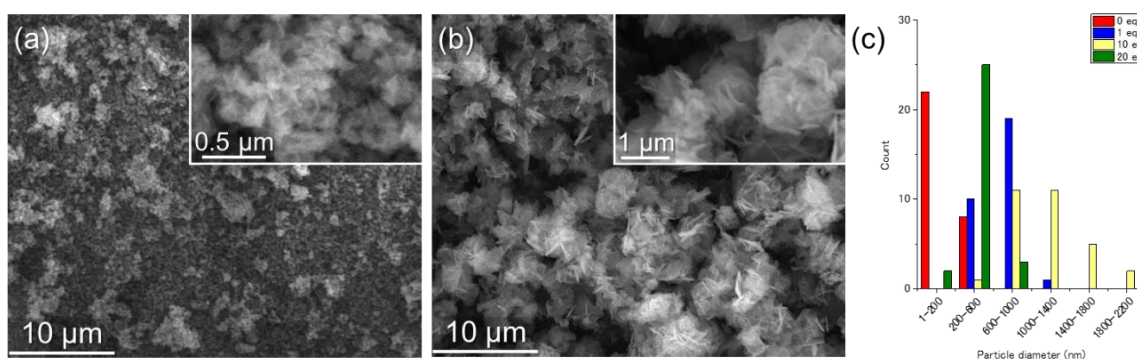


Figure 3-10. SEM images of *m*-Mg₂[4Ru] samples prepared (a) without lauric acid and (b) with 10 equiv. lauric acid. (c) Diameter distribution of the aggregates of *m*-Mg₂[4Ru] prepared with various amounts of the lauric acid modulator.

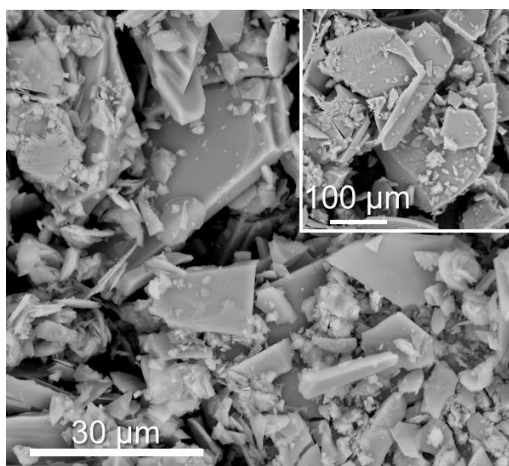


Figure 3-11. SEM images of Bulk-Mg₂[4Ru] samples.

Tiny platelet crystals, 150 nm wide and 30 nm thick, were observed for the sample synthesized with no lauric acid (Fig. 3-10(a)), whereas the size of bulk-sample was estimated to be roughly 1-100 μm in length and 0.5-10 μm in thickness (Figure 3-11). In contrast, larger platelet crystals, 1 μm wide and about 100 nm thick, were observed for the sample synthesized with 10 equiv. of the lauric acid modulator. The micron-sized crystals of *m*-**Mg₂[4Ru]** aggregated, but no flower-like aggregates were observed. The dependence of the size distribution of the platelet microcrystal with the amount of lauric acid modulator is shown in Figure 3-10(c). As in the case of *m*-**Sr₂[4Ru]**, a similar trend was observed for *m*-**Mg₂[4Ru]**; that is, the size of the crystals increased with increasing concentration of lauric acid modulator. This trend is consistent with results reported to date concerning the synthesis of nano-sized PCPs by the coordination modulation method. However, an exception to this trend was observed for the sample synthesized with 20 equiv. of lauric acid. The average crystal size was smaller, about 500 nm in width and 50 nm in thickness (See Figure 3-12). This might be caused by the generation of micelles at high concentrations of lauric acid in the presence of Mg^{2+} ions. We measured PXRD patterns of *m*-**Mg₂[4Ru]** to clarify whether the micron-sized platelet crystals of *m*-**Mg₂[4Ru]** maintained the structure of *Bulk*-**Mg₂[4Ru]**. As shown in Figure 3-13, the peaks in the diffraction pattern of *m*-**Mg₂[4Ru]** synthesized with 10 equiv. of lauric acid are significantly broader than those observed in the diffraction pattern of *Bulk*-**Mg₂[4Ru]**; however, the observed and simulated PXRD patterns agree qualitatively with that of *Bulk*-**Mg₂[4Ru]**, indicating that the crystal structure of *m*-**Mg₂[4Ru]** was that of *Bulk*-**Mg₂[4Ru]**. The crystal size from the broaden PXRD pattern was also estimated to be 12 nm, being comparable to the thickness of platelet nanocrystal estimated by the SEM image of *m*-**Mg₂[4Ru]**. In addition, the results of the elemental analysis suggest that *m*-**Mg₂[4Ru]** contained 13 water molecules for each **[4Ru]**, which is consistent with the hydration number of *Bulk*-**Mg₂[4Ru]**. PXRD measurements also revealed that the crystal structures of *m*-**Mg₂[4Ru]** synthesized in the absence and presence of 1 and 20 equiv. of lauric acid modulator also have same structure as that of *Bulk*-**Mg₂[4Ru]** (see Figure 3-14). As with the case of *m*-**Sr₂[4Ru]**, the lauric acid modulator may coordinate to the *m*-**Mg₂[4Ru]** crystal surface, but this would be easily removed by washing with EtOH (see Figure 3-7). *m*-**Mg₂[4Ru]** also yielded similar excitation and emission spectra to that of the *Bulk*-**Mg₂[4Ru]**, but the emission maximum shifted to shorter

wavelengths, comparable to those of **[4Ru]** in aqueous solution (Figure 3-15), implying a different environment of **[4Ru]** at the crystal surface.

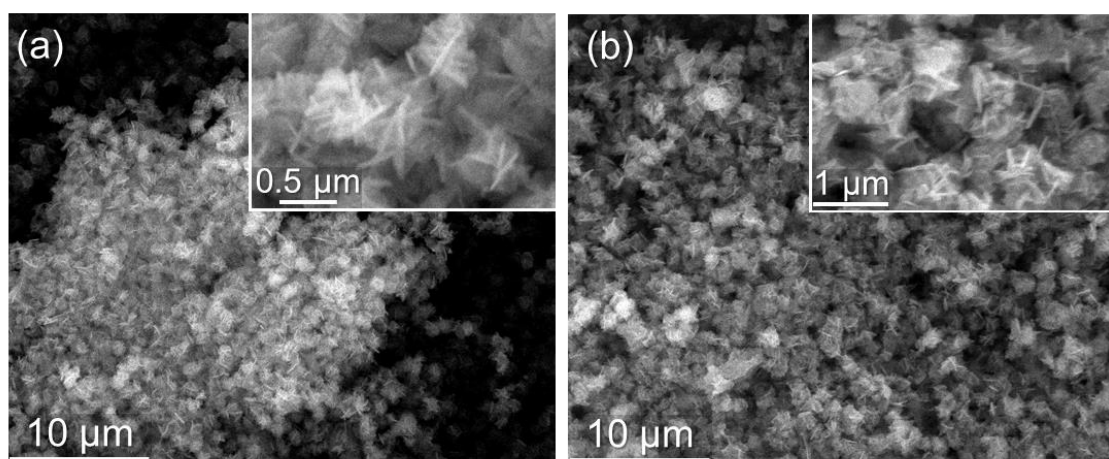


Figure 3-12. SEM images of $m\text{-Mg}_2[4\text{Ru}]$ synthesized in the presence of (a) 1 eq. and, (b) 20 eq. lauric acid.

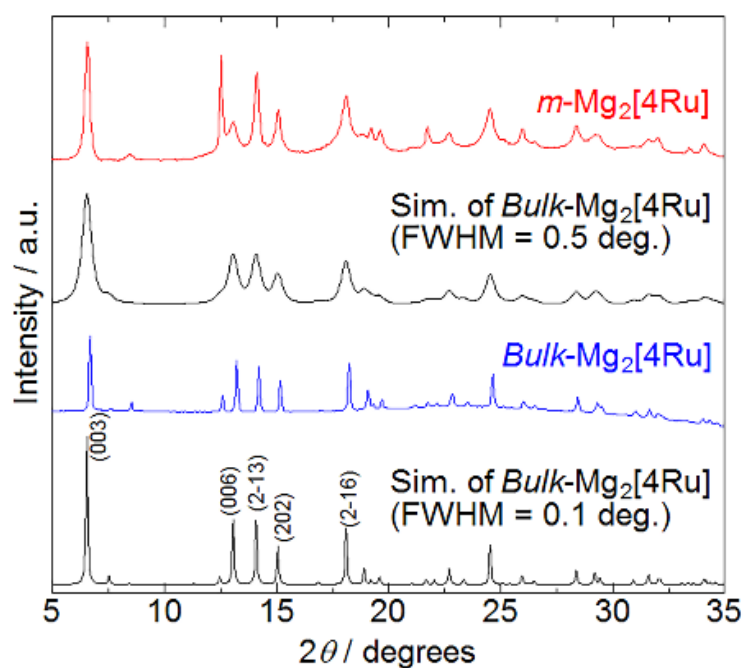


Figure 3-13. PXRD patterns of $m\text{-Mg}_2[4\text{Ru}]$ (red) and $\text{Bulk-Mg}_2[4\text{Ru}]$ (blue). The two black lines are simulations based on the crystal structure of $\text{Mg}_2[4\text{Ru}]$ with FWHMs of 0.1 and 0.5°. The integers in parentheses indicate the hkl indexes of main diffraction peaks.

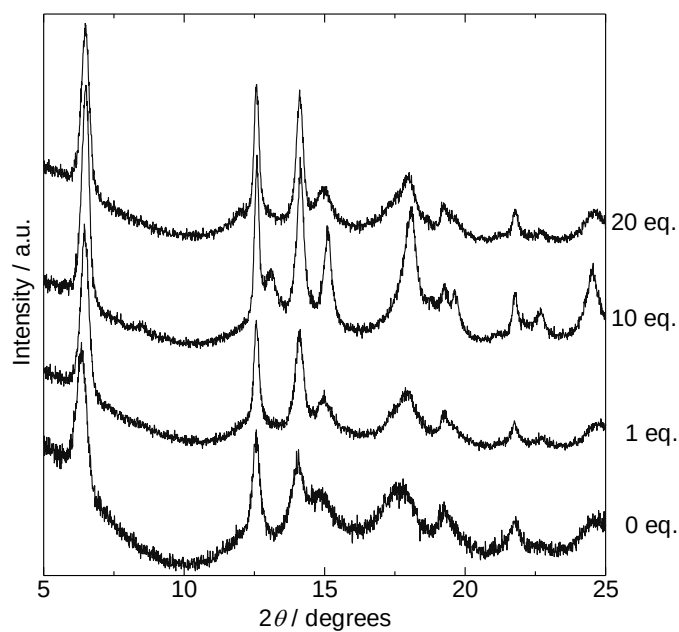


Figure 3-14. PXRD patterns of *m*-**Mg₂[4Ru]** synthesized in the presence of various equivalences of lauric acid modulator compared with the pattern.

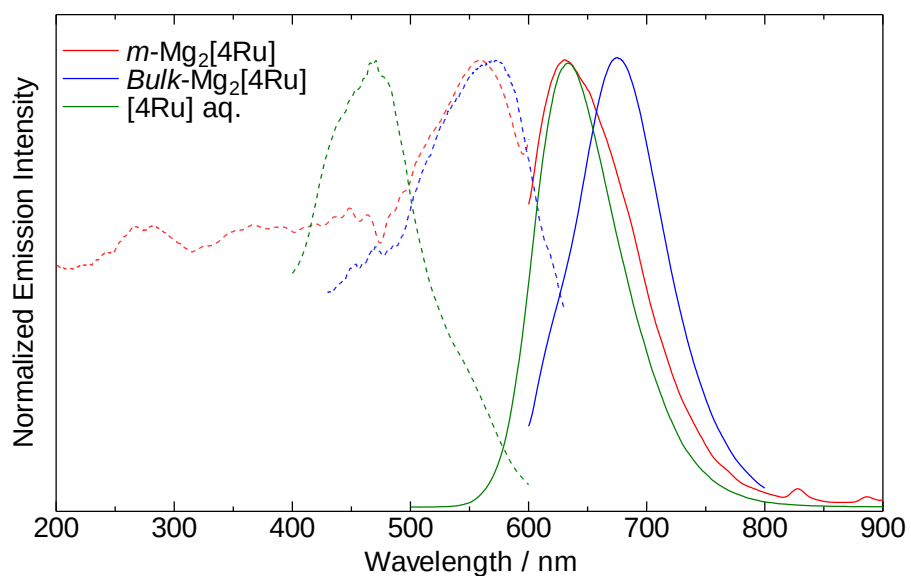


Figure 3-15. Emission and excitation spectra of *m*-**Mg₂[4Ru]** and *Bulk*-**Mg₂[4Ru]** in the solid state at room temperature compared with the spectra of metalloligand **[4Ru]** in basic aqueous solution ($\lambda_{\text{ex}} = 559$ nm, 10 eq.; $\lambda_{\text{ex}} = 576$ nm, *Bulk*-**Mg₂[4Ru]**; $\lambda_{\text{ex}} = 576$ nm, **[4Ru]** aq.).

Emission spectra of $m\text{-M}_2[4\text{Ru}]$ were analyzed by the spectral fitting based on the spectra of $[4\text{Ru}]$ and $\text{Bulk-M}_2[4\text{Ru}]$ (Figures 3-16, 17). Observed spectrum of $m\text{-Sr}_2[4\text{Ru}]$ was well agreed to the sum of the spectra of $[4\text{Ru}]$ to $\text{Bulk-Sr}_2[4\text{Ru}]$ with the intensity ratio to be 1.75 to 1. On the other hand, the ratio of $[4\text{Ru}]$ to $\text{Bulk-Mg}_2[4\text{Ru}]$ for the spectrum of $m\text{-Mg}_2[4\text{Ru}]$ was significantly changed to be 3.30 to 1. Considering the difference of coordination mode of $[4\text{Ru}]$ between in aqueous solution and in the solid state, the intensity ratios suggest the electronic state of $[4\text{Ru}]$ located at the surface of the meso-sized crystals. In other words, the $[4\text{Ru}]$ metalloligands at the surface would bonded to smaller number of M^{2+} cations (Scheme 3-2), resulting in the spectral shifts to shorter wavelength compared to that of the bulk crystals. Larger shift of $m\text{-Mg}_2[4\text{Ru}]$ than that of $m\text{-Sr}_2[4\text{Ru}]$ implies that the $[4\text{Ru}]$ metalloligand on the surface of $m\text{-Mg}_2[4\text{Ru}]$ might not coordinate to the Mg^{2+} cation at all, but be bound on the crystal surface electrostatically.

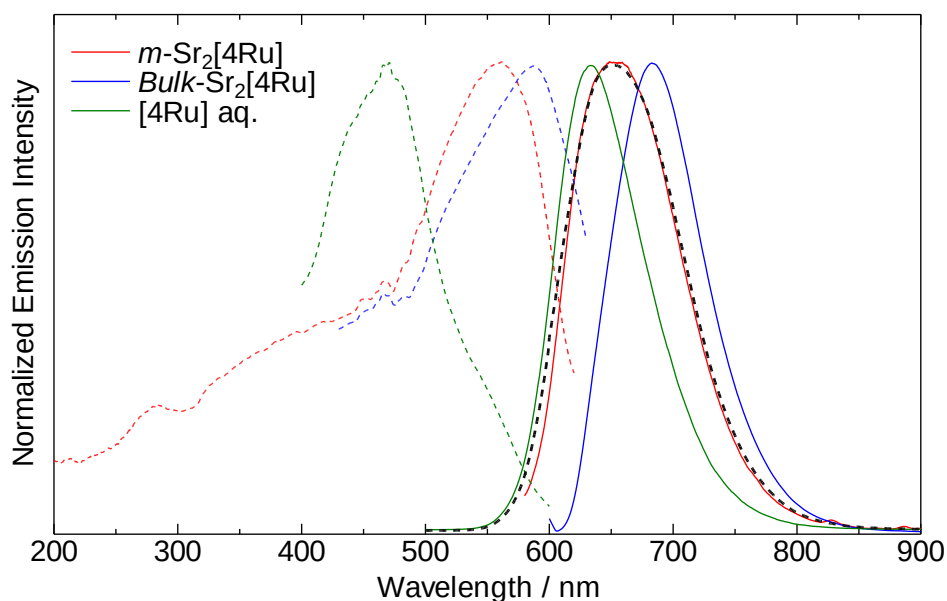


Figure 3-16. Emission (solid lines) and excitation (broken lines) spectra of $m\text{-Sr}_2[4\text{Ru}]$ obtained in the presence of 0 eq. (brown), 1 eq. (yellow), or 10 eq. (red) of lauric acid modulator and $\text{Bulk-Sr}_2[4\text{Ru}]$ (blue) in the solid state at room temperature compared with the spectra of metalloligand $[4\text{Ru}]$ (green) in basic aqueous solution ($\lambda_{\text{ex}} = 558$ nm, $m\text{-Sr}_2[4\text{Ru}]$; $\lambda_{\text{ex}} = 594$ nm, $\text{Bulk-Sr}_2[4\text{Ru}]$; $\lambda_{\text{ex}} = 576$ nm, $[4\text{Ru}]$ aq.).

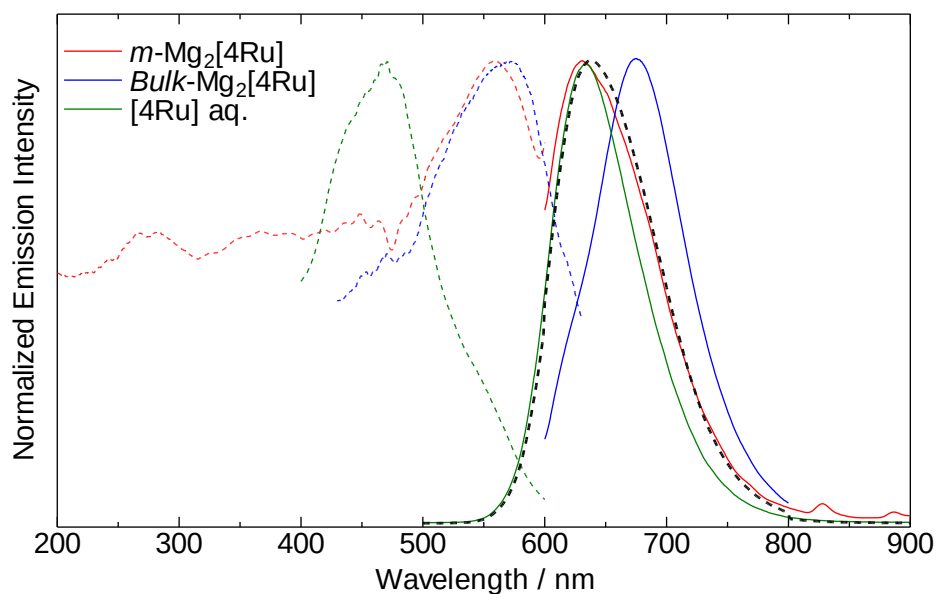
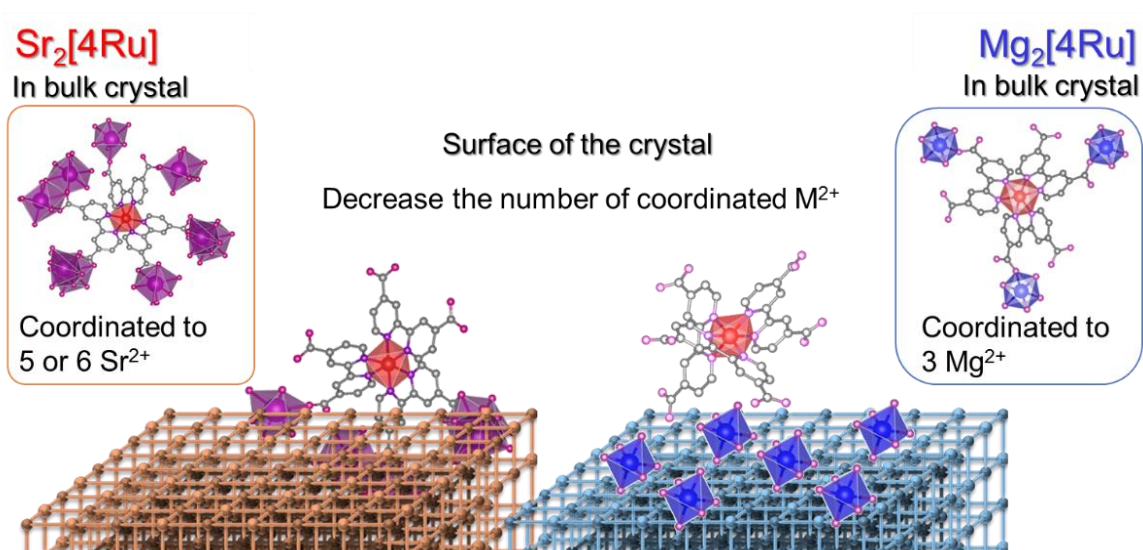


Figure 3-17. Emission and excitation spectra of *m*-**Mg₂[4Ru]** and *Bulk*-**Mg₂[4Ru]** in the solid state at room temperature compared with the spectra of metalloligand **[4Ru]** in basic aqueous solution ($\lambda_{\text{ex}} = 559$ nm, 10 eq.; $\lambda_{\text{ex}} = 576$ nm, *Bulk*-**Mg₂[4Ru]**; $\lambda_{\text{ex}} = 576$ nm, **[4Ru]** aq.).



Scheme 3-2. Schematic images of the surface conditions of *m*-**M₂[4Ru]** crystal.

3-3-3 Vapor adsorption behaviors

To clarify the effect of crystal downsizing on the vapor adsorption behaviors of the crystals, the water vapor adsorption isotherms of *m*-**Sr₂[4Ru]** and *m*-**Mg₂[4Ru]** were measured. The samples used in these measurements were synthesized in the presence of 10 equiv. of the lauric acid modulator, as described in the sections of 3-3-1 and 3-3-2. The measured samples were heated at 100 °C for 30 h in vacuo before measurement to remove all adsorbed water molecules. As discussed in Chapter 2, *Bulk*-**Sr₂[4Ru]** was found to have a three-step adsorption process and a two-step desorption process with a large hysteresis originating from a water-vapor-induced structural transformation, as shown in Figure 3-18(a). Interestingly, this characteristic *Gate-opening* behavior of *Bulk*-**Sr₂[4Ru]** was not observed for *m*-**Sr₂[4Ru]** synthesized by the coordination modulation method. Instead, simple, type I adsorption isotherms characteristic of microporous materials were observed for *m*-**Sr₂[4Ru]**. This remarkable difference suggests that the porous structure of **Sr₂[4Ru]** is stabilized by crystal downsizing to the submicron region. Similar difference between *Bulk*-**Sr₂[4Ru]** and *m*-**Sr₂[4Ru]** was also observed in their methanol vapor adsorption isotherms (see Figure 3-19). In contrast, the saturation amounts of water vapor for both *m*-**Sr₂[4Ru]** and *Bulk*-**Sr₂[4Ru]** are identical, eleven water molecules per **[4Ru]**, suggesting that the difference in porosity of both samples is negligible.

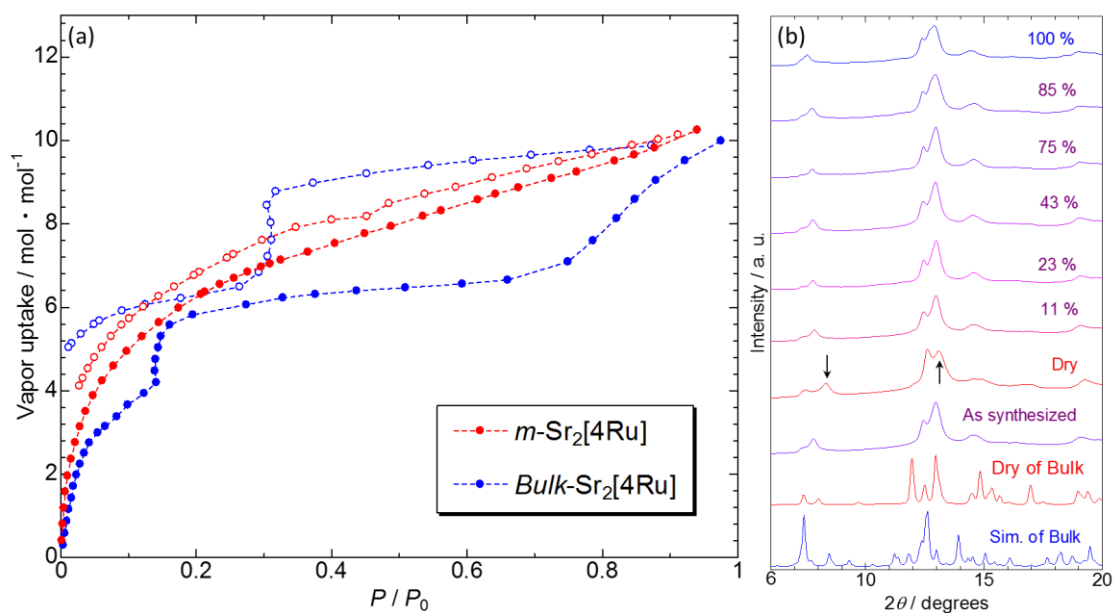


Figure 3-18. (a) Water vapor adsorption isotherms of $m\text{-Sr}_2[4\text{Ru}]$ (red) and $\text{Bulk-Sr}_2[4\text{Ru}]$ (blue) at 298 K. Closed and open symbols represent the adsorption and desorption processes, respectively. (b) PXRD pattern of $m\text{-Sr}_2[4\text{Ru}]$ at various relative humidities.

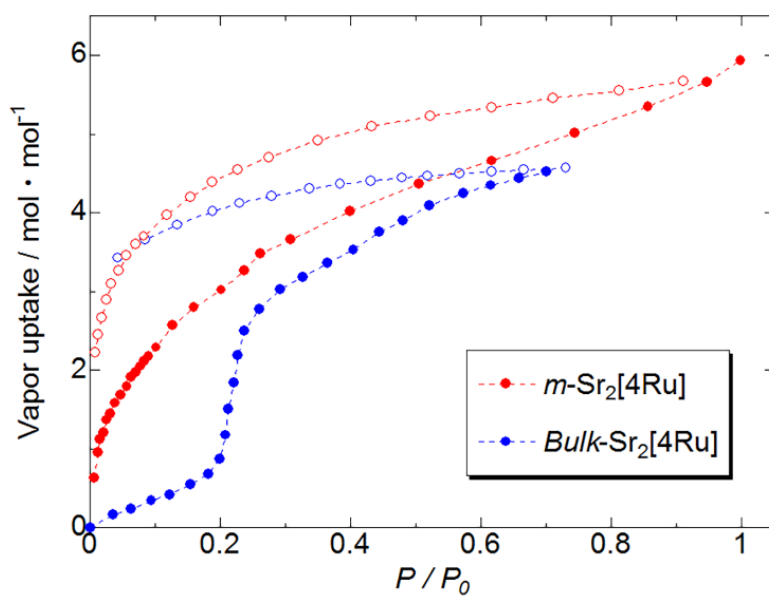


Figure 3-19. MeOH vapor adsorption isotherms of $m\text{-Sr}_2[4\text{Ru}]$ (red) and $\text{Bulk-Sr}_2[4\text{Ru}]$ (blue) at 298 K. Closed and open symbols show adsorption and desorption process, respectively.

To clarify the structural transformation in the water adsorption process of *m*-**Sr₂[4Ru]**, PXRD patterns of *m*-**Sr₂[4Ru]** at various relative humidities (RH) were measured. As shown in Figure 3-18 (b) and Chapter 2, the PXRD pattern of *Bulk*-**Sr₂[4Ru]** was drastically altered on drying followed by the re-adsorption of water vapor (Figure 2-6); this change originates from the collapse and reconstruction of the porous structure (see Figure 3-20). In contrast, such a drastic change was not observed for *m*-**Sr₂[4Ru]**; the dried *m*-**Sr₂[4Ru]** showing similar pattern to that of the as-synthesized one except for the new peak appeared at 8° and the shape change of diffraction peaks at around 13° (indicated by arrows in Figure 3-14(b)). The new peak at 8° gradually shifted to the lower angle with increasing RH. At higher RH (above 23%), the observed PXRD patterns were almost identical to that of the as-synthesized *m*-**Sr₂[4Ru]**. This result contrasts with that of *Bulk*-**Sr₂[4Ru]** where a drastic change in the PXRD pattern was observed at around 75% RH, corresponding to the reconstruction of the porous structure of **Sr₂[4Ru]**. Considering that the amounts of water at the saturation point determined from the adsorption of water vapor of both *Bulk*- and *m*-**Sr₂[4Ru]** agreed well, the adsorption of water vapor of the meso-sized *m*-**Sr₂[4Ru]** could not be due to the large structural transformations required to open the gate but, instead, to physisorption in the already open microporous channels of **Sr₂[4Ru]**, resulting in only small structural modifications. On the other hand, the emission intensity of *m*-**Sr₂[4Ru]** decreased by removal of adsorbed water (see Figure 3-21) as *bulk*-**Sr₂[4Ru]** (section of 2-3-3), implying that the small structural modification of the porous framework would give an effect on the deactivation process from the ³MLCT emissive state.

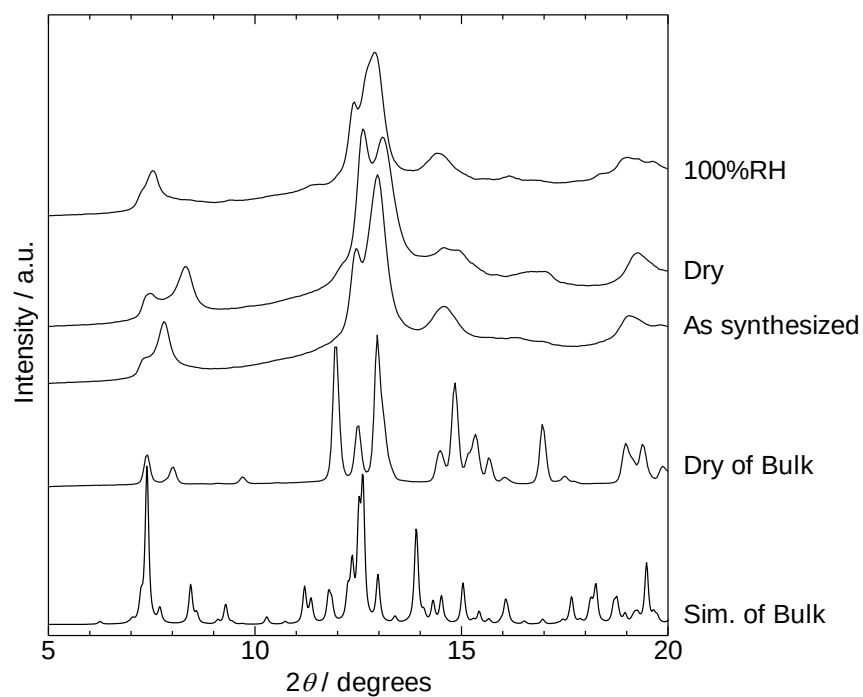


Figure 3-20. PXRD patterns of *m*-Sr₂[4Ru] in various conditions compared with the patterns of *Bulk*-Sr₂[4Ru].

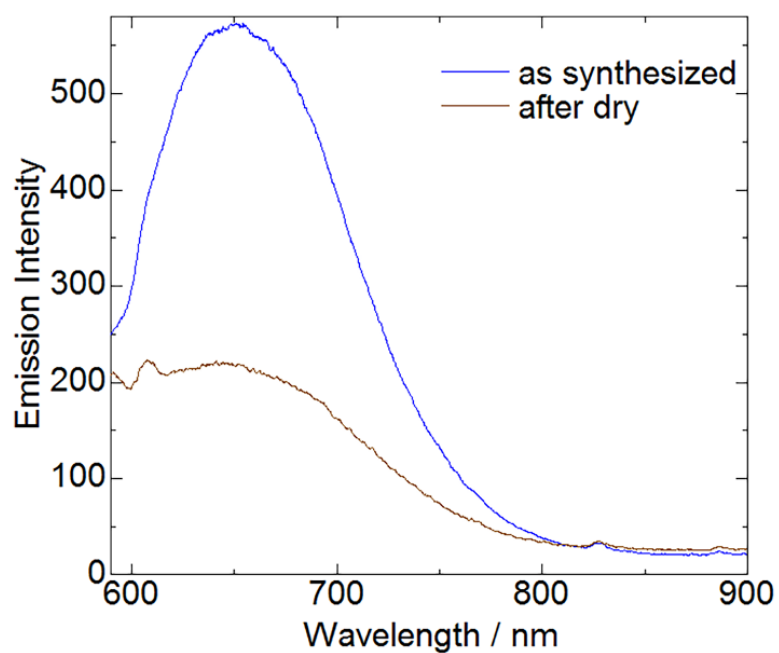


Figure 3-21. Change of emission spectrum of *m*-Sr₂[4Ru] by drying at 100°C. Blue and brown lines show the spectra taken before and after drying, respectively. $\lambda_{\text{ex}} = 558$ nm.

Also the effect of crystal downsizing on the water vapor adsorption behavior of **Mg₂[4Ru]** was examined (Figure 3-22(a)), because the dimensionality of coordination framework of **Mg₂[4Ru]** (2-D sheet structure) is completely different to that of **Sr₂[4Ru]** (3-D lattice structure). As reported in Chapter 2, *Bulk-Mg₂[4Ru]* shows a two-step adsorption and desorption processes in the isotherm with the large hysteresis originated from the vapor-adsorption-driven reconstruction of the porous structure like *Gate-opening* behavior (Figure 2-7). The *m-Mg₂[4Ru]* synthesized with 10 equiv. of laurate modulator has a very similar water vapor adsorption isotherm to that of the *Bulk-Mg₂[4Ru]*; the first step adsorption process, up to 7.5 mol/mol was observed below a relative pressure (P / P_0) of 0.2, as with the bulk sample. Notably, for *m-Mg₂[4Ru]*, the vapor uptake in the second adsorption step (above $P / P_0 = 0.2$) increased more moderately than that of *Bulk-Mg₂[4Ru]* with increasing relative humidity. Furthermore, the large hysteresis in the second step was significantly smaller for *m-Mg₂[4Ru]* than for *Bulk-Mg₂[4Ru]*. On the other hand, the saturated amount of adsorbed water vapor for *m-Mg₂[4Ru]* was found to be 17 molecules per [4Ru] unit, which is consistent with the value for *Bulk-Mg₂[4Ru]*. This result is further evidence indicating that *m-Mg₂[4Ru]* has a porous structure similar to that of the bulk sample.

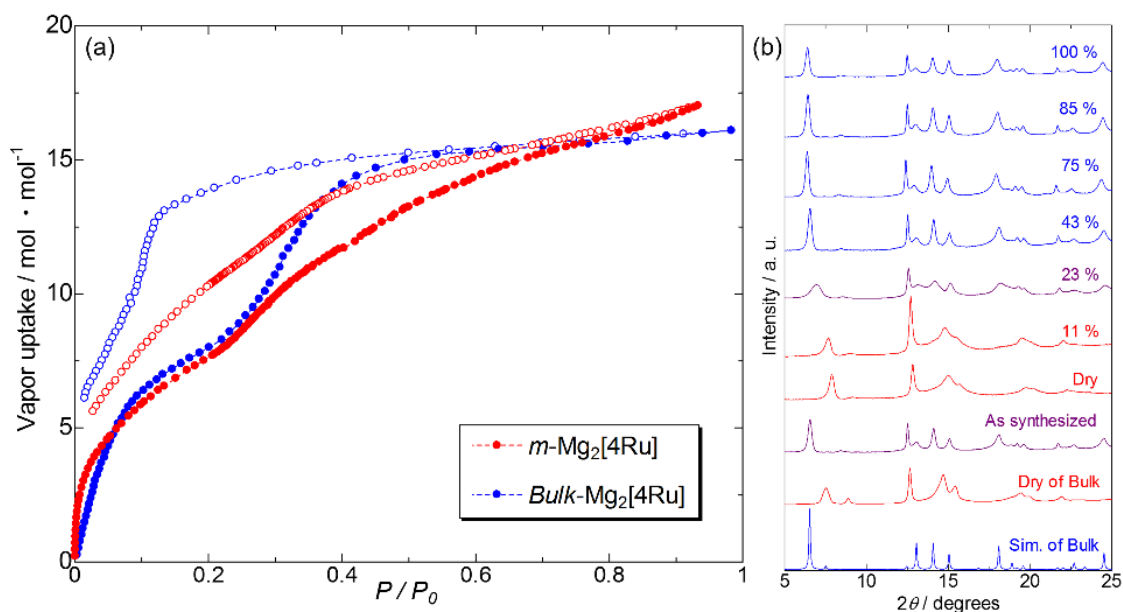


Figure 3-22. (a) Water vapor adsorption isotherms of *m-Mg₂[4Ru]* (red) and *Bulk-Mg₂[4Ru]* (blue) at 298 K. Closed and open symbols represent the adsorption and desorption processes, respectively. (b) PXRD pattern of *m-Mg₂[4Ru]* at various humidities.

The relative humidity dependence of the PXRD pattern of *m*-**Mg₂[4Ru]** was also determined to monitor the structural changes on water vapor adsorption. As discussed in the PXRD pattern of *Bulk*-**Mg₂[4Ru]** changes significantly on desorption and re-adsorption of water vapor, in which the (003) reflection observed at 6.52°, corresponding to the distance between the 2-D coordination sheets, shifted to higher angle side during desorption and shifted back to the original position during the re-adsorption process (see Figure 3-23). The observed PXRD pattern of *m*-**Mg₂[4Ru]** after drying was broader than that of the dried *Bulk*-**Mg₂[4Ru]**, but these patterns were qualitatively similar. Notably, the *m*-**Mg₂[4Ru]** peak observed at low angle (7.89°) was located at a higher angle than that of the *Bulk* **Mg₂[4Ru]** (7.54°). This peak can be assigned to the (003) reflection; therefore, the 2-D coordination sheets of **Mg₂[4Ru]** may be more tightly packed in the downsized *m*-**Mg₂[4Ru]** than in the *Bulk*-**Mg₂[4Ru]**. During the water vapor adsorption process, the *Bulk*-**Mg₂[4Ru]** showed a clear structural transition from the dried non-porous phase to the water adsorbed porous phase between 11 and 23% RH. Similarly, the observed PXRD pattern of *m*-**Mg₂[4Ru]** at 23% RH was broader than patterns at higher RH, although, judging by the two characteristic peaks at around 15°, the pattern can be assigned to the water adsorbed phase. The position of the (003) peak gradually shifted to lower angle with increasing RH, indicating that the distance between the 2-D coordination sheets increased, probably due to the adsorption of water vapor between the sheets. This hypothesis is supported by the fact that the position of (003) peak was almost constant above 75% RH, where the fully hydrated phase was already formed. These PXRD results clearly indicate that the effect of crystal downsizing on the vapor adsorption property is significantly smaller in **Mg₂[4Ru]** than **Sr₂[4Ru]**.

N₂ gas adsorption isotherms of *m*-**Sr₂[4Ru]** and *m*-**Mg₂[4Ru]** were also measured to estimate the surface area based on BET analysis, but these complexes were found to hardly adsorb N₂ gas at 77 K (see Figure 3-24), probably due to the polar nature derived from the M²⁺ cation with highly charged **[4Ru]⁴⁻** anions of the porous frameworks as well as the case of the bulk crystals.

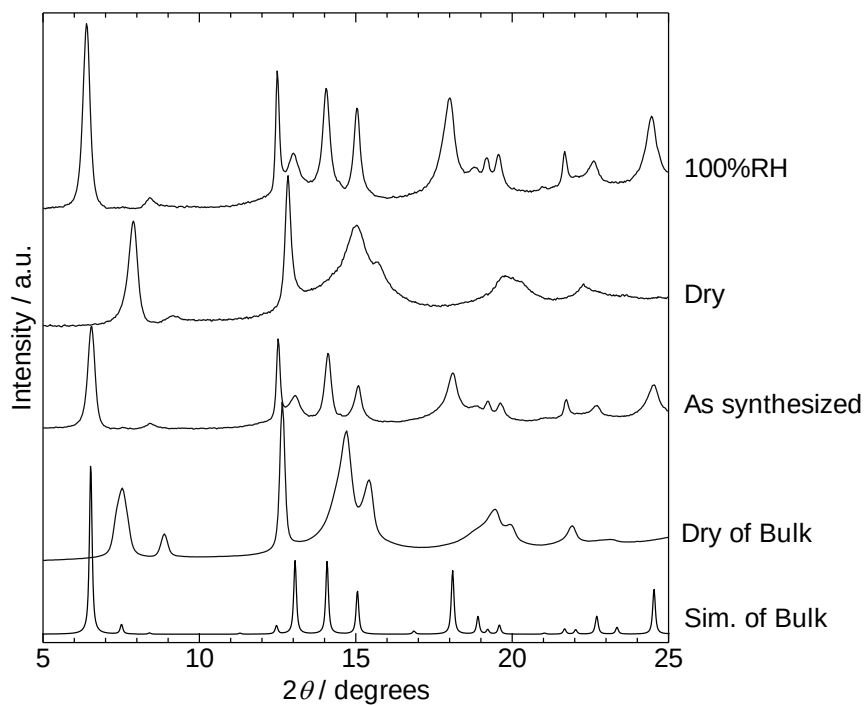


Figure 3-23. PXRD patterns of *m*-**Mg₂[4Ru]** in various conditions compared with the patterns of *Bulk*-**Mg₂[4Ru]**.

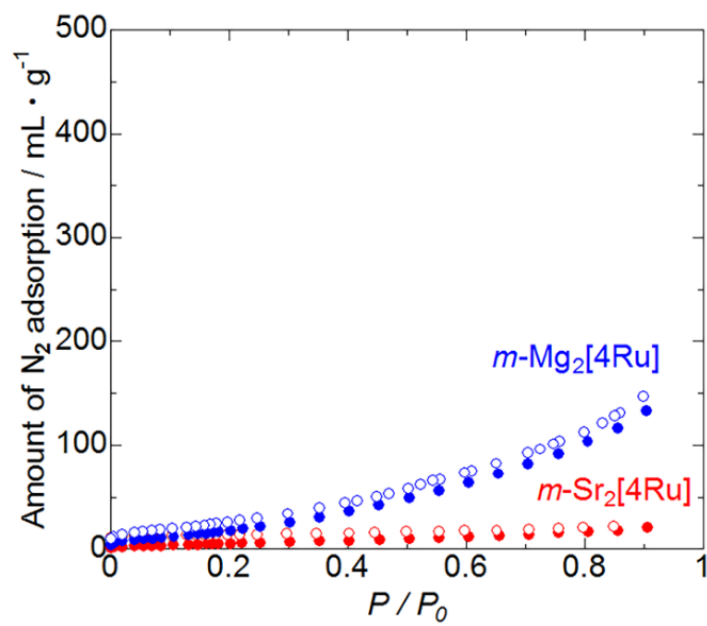
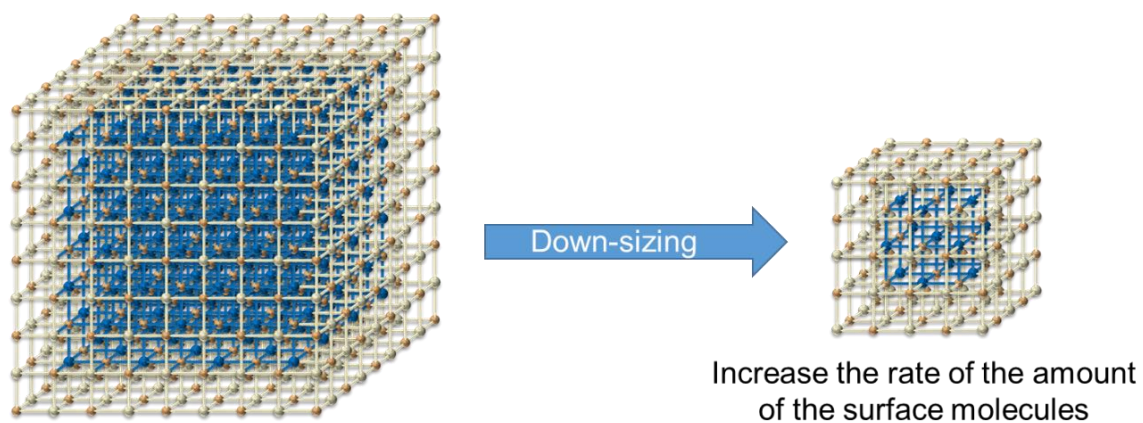


Figure 3-24. Nitrogen adsorption isotherms of *m*-**Mg₂[4Ru]** (blue) and *Bulk*-**Mg₂[4Ru]** (red) at 77 K. Closed and open symbols represent the adsorption and desorption processes, respectively.

These contrasting results may arise because of differences between the dimensionality of the coordination network structure of **M₂[4Ru]**. For example, Tanaka *et al.* reported that the structural flexibility of ZIF-8 is regulated by the size of crystal, and the flexibility of smaller crystal is more rigid than that of larger crystals, suppressing structural transformations.⁴ In the crystals discussed here, the size of crystals of *m*-**M₂[4Ru]** are comparable (widths of several hundred nanometers and thicknesses of tens of nanometers); however, no coordination bonds were formed between the 2-D coordination sheets of **Mg₂[4Ru]** (see Figure 2-1(c)) in contrast with the 3-D coordination structure of **Sr₂[4Ru]** (Figure 2-2(e)), which affects the flexibility of the coordination network structure. Thus, the removal of water from the as-synthesized *m*-**Sr₂[4Ru]** did not induce complete structural collapse of the porous structure because of the enhanced rigidity of the framework induced by the reduction of crystal size to the mesoscale, resulting in maintenance of an open porous structure. In contrast, structural transformations occur easily in *m*-**Mg₂[4Ru]** on removal of water owing to the lack of coordination bonds between the sheets. As a result, large differences in water adsorption behavior were observed for *m*-**Sr₂[4Ru]**, whereas similar isotherms between bulk and *m*-**Mg₂[4Ru]** were observed.

The vapor-adsorption behaviors of *Bulk*-**M₂[4Ru]** observed in this work are essentially originated from the porosity and framework flexibility of bulk crystals because of the negligible molecular ratio at the surface to the inside of crystal. On the other hand, the ratio of *meso*-sized **M₂[4Ru]** should increase and give an effect on the vapor adsorption behavior. The coordination structure at the crystal surface should be different from the inside of crystal because of their terminational position of the crystal (Scheme 3-4). This surface structure is one of the plausible origins of the different vapor-adsorption behaviors between *m*-**M₂[4Ru]** and *Bulk*-**M₂[4Ru]**.



Scheme 3-4. Schematic images of the crystal down-sizing. Metal ions and linkers located at the surface of the crystals are highlighted by pale orange color.

3-4 Conclusion

In this chapter, the reduction of the crystallite size of two MOFs, **Sr₂[4Ru]** and **Mg₂[4Ru]** was discussed in detail. These MOFs have coordination networks of different dimensionalities, and their sizes were controlled using the well-known coordination modulation method. *m*-**Sr₂[4Ru]**, which has a 3-D coordination network structure, formed interesting flower-like aggregates with 2 μm average diameter and 1 μm thickness; these aggregates are composed of nanoplate crystals with widths of 700 nm and thicknesses of 50 nm. The downsized crystals of *m*-**Mg₂[4Ru]** were obtained as micron-sized platelet crystals with widths of 1 μm and thicknesses of 100 nm; however, flower-like aggregates, like those observed for *m*-**Sr₂[4Ru]**, were not observed. Based on the clear differences between *m*-**Sr₂[4Ru]** and *Bulk*-**Sr₂[4Ru]** concerning water vapor adsorption isotherms and the changes in the PXRD patterns at different humidities, the porous structure of *Bulk*-**Sr₂[4Ru]** collapses under dry conditions, whereas *m*-**Sr₂[4Ru]** retains porosity in the absence of hydrating water molecules. This result suggests that the stability of the porous structure of **Sr₂[4Ru]** is enhanced by the reduction in crystal size to the mesoscale. In contrast, *m*-**Mg₂[4Ru]**, obtained by the same coordination modulation method, was found to have similar crystal sizes to those of *m*-**Sr₂[4Ru]**, but the water vapor adsorption isotherm of *m*-**Mg₂[4Ru]** was very similar to that of the bulk sample. Thus, these results suggest that the effect of crystal downsizing on vapor adsorption is more apparent in MOFs with 3-D coordination networks than in those with 2-D coordination sheet structures.

3-5 References

- 1) Kobayashi, A.; Ohba, T.; Saitoh, E.; Suzuki, Y.; Noro, S.; Chang, H.; Kato, M. *Inorg. Chem.* **2014**, 53, 2910–2921.
- 2) Diring, S.; Furukawa, S.; Takashima, Y.; Tsuruoka, T.; Kitagawa, S. *Chem. Mater.* **2010**, 22, 4531–4538.
- 3) Goderis, H. L.; Fouwe, B. L.; Cauwenbergh, S. M. V.; Tobback, P. P. *Anal. Chem.* **1986**, 58, 1561–1563.
- 4) Tanaka, S.; Fujita, K.; Miyake, Y.; Miyamoto, M.; Hasegawa, Y.; Makino, T.; Perre, S. V.; Remi, J. C. S.; Assche, T. V.; Baron, G. V.; Denayer, J. F. M. *J. Phys. Chem. C* **2015**, 119, 28430–28439.

Chapter 4
General Conclusion

In this thesis, the background and purpose of this thesis are described in chapter 1.

In chapter 2, the syntheses, crystal structures, guest adsorption behaviors and luminescent properties of two PCPs composed of luminescent Ru(II)-metalloligand and Mg^{2+} or Sr^{2+} ion are described. The PCP with Mg^{2+} ion, **Mg₂[4Ru]** has a 2D-sheet coordination-network structure, while 3D-lattice structure was formed in the PCP with Sr^{2+} ion, **Sr₂[4Ru]**. These PCPs exhibited interesting vapor-adsorption property with the gate-opening behavior, suggesting that the lattice flexibility of these PCPs is soft enough to change the network structure in the guest adsorption/desorption processes (Figure 4-1).

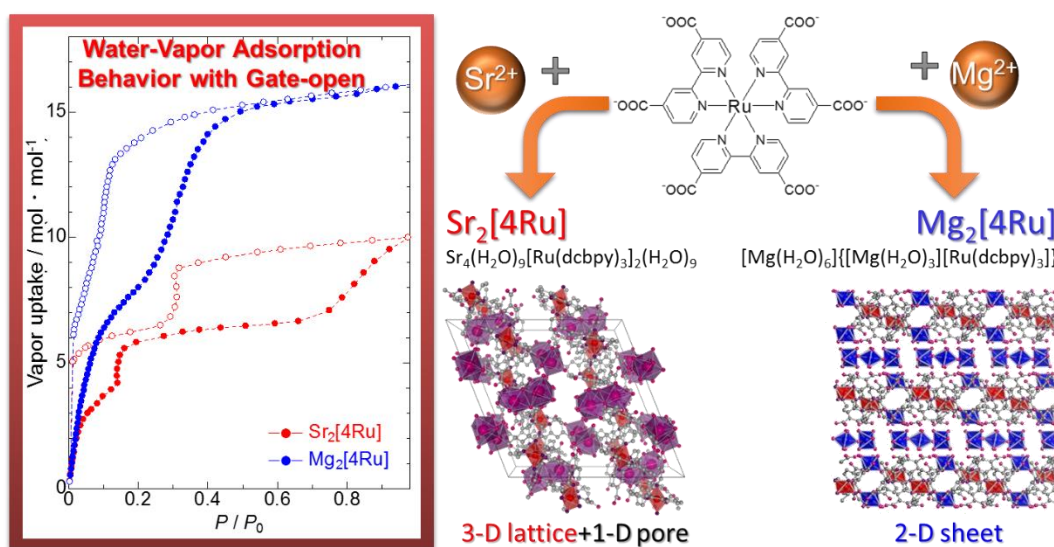


Figure 4-1. The structures and the H₂O vapor adsorption isotherm of **Mg₂[4Ru]** and **Sr₂[4Ru]**.

In chapter 3, the down-sizing of the PCP crystals obtained in chapter 2 (**Mg₂[4Ru]** and **Sr₂[4Ru]**) was examined by using the coordination modulation method. The crystal down-sizing to ~1 μm scale were achieved (**m-Mg₂[4Ru]** and **m-Sr₂[4Ru]**) and did not affect on the crystal structure. In particular, **m-Sr₂[4Ru]** formed unique flower-like aggregates. The water-vapor adsorption property of **Sr₂[4Ru]** was drastically changed by crystal down-sizing to mesoscopic region, whereas almost similar adsorption behavior was observed for **Mg₂[4Ru]**, probably due to the difference in dimensionality of the coordination network structure. (Figure 4-2).

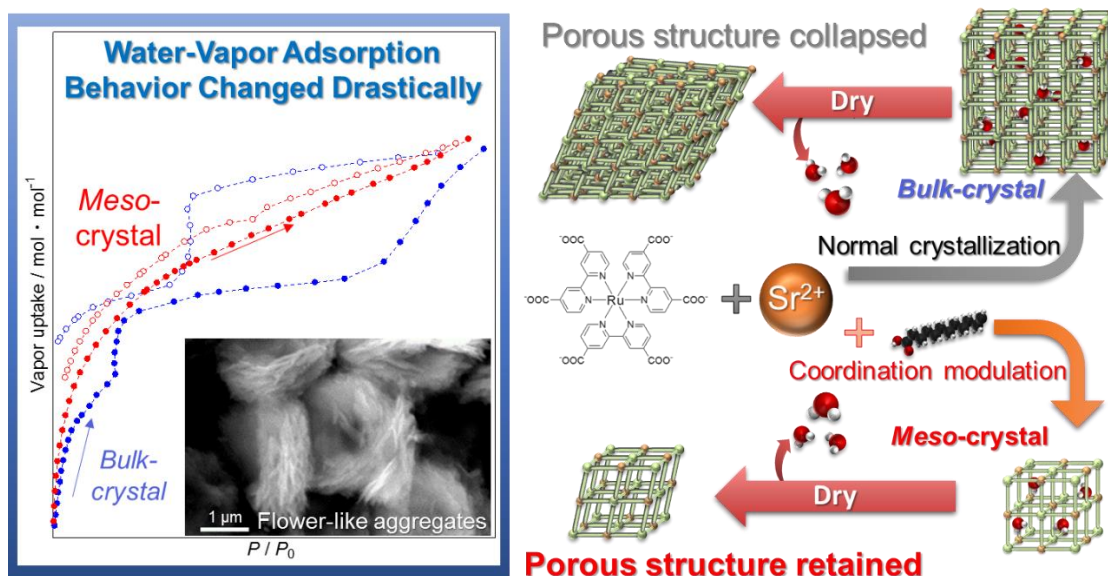


Figure 4-2. The conceptual diagram of the adsorption behavior and the H₂O vapor adsorption isotherm of Sr₂[4Ru].

In this thesis, the constructing the PCP using Ru(II)-metalloligand and the crystal down-sizing were examined in detail. The similar light absorption and emission property of the Ru(II) - metalloligand to the molecular Ru(II) complex were observed in these two PCPs. In addition, interesting guest adsorption properties with the gate-opening behavior was successfully designed by using labile M²⁺ ions as the bridging metal ion. Further, this characteristic guest adsorption behavior was certainly modified by the crystal down-sizing in the system with 3D-lattice-type PCP, while the effect of crystal down-sizing on the guest adsorption behavior of 2-D-sheet-type PCP was not obvious than that of 3D-lattice-type system.

Acknowledgement

This study on this thesis has been carried out under the direction of Professor Kato during April 2012-March 2017 at the Graduate School of Chemical Sciences and Engineering, Hokkaido University.

I owe my deepest gratitude to Professor Masako Kato for her earnest guidance and proper suggestions. I would like to express my gratitude to Professor Ho-Chol Chang (present address, Chuo University), and Dr. Atsushi Kobayashi, Dr. W. M. C. Sameera and Dr. Masaki Yoshida for invaluable suggestion and discussions. I am deeply grateful to Professor Tamotsu Inabe, Professor Kazuki Sada and Professor Toshihiro Shimada for reviewing this thesis. I would like to offer my special thanks to Professor Reiji Kumai and Mr. Yasuhiro Niwa for synchrotron radiation measurement at KEK.

I am thankful to Ms. Mayu Shimizu, Ms. Mariko Tsukada, and Yuriko Zeff for their kind secretarial works. I would like thank to Dr. Takeshi Matsumoto, Dr. Tadashi Ohba, Dr. Hiroki Ohara for helpful advice. I am indebted to Mr. Tomohiro Ogawa and Mr. Yasuhiro Shigeta. Special thanks also to all members of the group of Professor Kato for their friendship during the time in the laboratory.

I am much indebted for their financial supports of TOBE MAKI Scholarship Foundation.

Finally, I would like to express special thanks to my family and friends for supports and encouragement.

Erika Saitoh

Graduate School of Chemical Sciences and Engineering, Hokkaido University