

Title	Crystal Engineering of Porous Lanthanide Coordination Polymers with Multicarboxylate Ligands
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Osaka University

Abstract of Thesis

Name (Supaphorn Thammakan)

Title

Crystal Engineering of Porous Lanthanide Coordination Polymers with Multicarboxylate Ligands
(多座カルボキシレート配位子をもつ多孔性希土類配位高分子の結晶工学)

Abstract of Thesis

Interest in porous lanthanide coordination polymers (LnCPs) originated from their tunable structures and unique properties. However, crystal engineering of LnCPs is challenging due to the large possibility of the coordination number and geometry of lanthanide ions (Ln^{III}). The commonly used ligands in the design of LnCPs are multicarboxylate ligands, which have been modified by adding various functional groups. Nevertheless, creating porous LnCPs with desired properties by designing organic ligands is still difficult, due to the lack of systematic study on ligand modification for developing LnCPs. In particular, the influence of the slight change in the ligand structures on the porosity of LnCPs is unclear.

In this research, the design and synthesis of porous LnCPs were examined through the structural modifications of conventional ligand systems (Fig.1) : (i) the introduction of auxiliary phenoxy acetate (poa^-) ligand to disrupt dense framework (chapter 2), (ii) the insertion $-\text{NO}_2$ groups on the lengthy biphenyl-4,4'-dicarboxylate (BPDC^{2-}) ligand to enlarge the porosity (chapter 3), and (iii) the replacement of Rh^{III} centers in $[\text{Zn}_4\text{O}\{\text{Rh}(\text{L-cys})_3\}_4]^{6-}$ ($[\text{L}^{\text{Rh}}]^{6-}$) metalloligands by Ir^{III} ion to control the void through the modified hydrogen bonding interactions (chapter 4). In addition, the plausible applications of the resulting LnCPs were also explored. The several new series of porous LnCPs in this work were listed following;

Chapter 2: $[\text{Ln}(\text{poa})(2,5\text{-pydc})(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$ ($\mathbf{1}_{\text{Ln}}$) when $\text{Ln} = \text{Eu}^{\text{III}}, \text{Gd}^{\text{III}}, \text{Tb}^{\text{III}},$ and Sm^{III} , $2,5\text{-pydc}^{2-} = 2,5\text{-pyridine dicarboxylate}$, and $\text{poa}^- = \text{phenoxy acetate}$

Chapter 3: $[\text{Ln}_4(\text{di-nitro-BPDC})_4(\text{NO}_2)_3(\text{OH})(\text{H}_2\text{O})_5](\text{solvent})$ ($\mathbf{2}_{\text{Ln}}$) when $\text{di-nitro-BPDC}^{2-} = 2,2'\text{-dinitrobiphenyl-4,4'-dicarboxylate}$ and $\text{Ln} = \text{Pr}^{\text{III}}, \text{Nd}^{\text{III}}, \text{Sm}^{\text{III}}, \text{Eu}^{\text{III}},$ and Gd^{III}

Chapter 4: $\text{Ln}_2[\text{L}^{\text{Ir}}]\cdot n\text{H}_2\text{O}$ ($\mathbf{3}_{\text{Ln}}$) when $[\text{L}^{\text{Ir}}]^{6-} = [\text{Zn}_4\text{O}\{\text{Ir}(\text{L-cys})_3\}_4]^{6-}$, $\text{L-cys} = \text{L-cysteinate}$, $\text{Ln} = \text{Sc}^{\text{III}}, \text{La}^{\text{III}}, \text{Ce}^{\text{III}}, \text{Pr}^{\text{III}},$ and Nd^{III} and $\text{Ln}_{0.33}[\text{Ln}_4(\mu_3\text{-OH})_4(\mu_2\text{-OAc})_3(\text{H}_2\text{O})_7][\text{L}^{\text{Ir}}]\cdot n\text{H}_2\text{O}$ ($\mathbf{4}_{\text{Ln}}$) when $\text{Ln} = \text{Sm}^{\text{III}}, \text{Eu}^{\text{III}}, \text{Gd}^{\text{III}}, \text{Tb}^{\text{III}}, \text{Dy}^{\text{III}}, \text{Ho}^{\text{III}}, \text{Er}^{\text{III}}, \text{Tm}^{\text{III}}, \text{Yb}^{\text{III}}, \text{Lu}^{\text{III}},$ and Y^{III}

Chapter 2: Microporous Frameworks of Lanthanide-2,5-Pyridine-Dicarboxylate-Phenoxy Acetate and Selective Ammonia Sensing.

The use of mixed ligands of 2,5- H_2pydc and Hpoa for construction of LnCPs was reported in chapter 2. This combination of these two ligands led to one-dimensional porous LnCPs of $[\text{Ln}(\text{poa})(2,5\text{-pydc})(\text{H}_2\text{O})_2]\cdot 3\text{H}_2\text{O}$ ($\mathbf{1}_{\text{Ln}}$; $\text{Ln} = \text{Eu}^{\text{III}}, \text{Gd}^{\text{III}}, \text{Tb}^{\text{III}},$ and Sm^{III} , $2,5\text{-pydc}^{2-} = 2,5\text{-pyridine dicarboxylate}$, and $\text{poa}^- = \text{phenoxy acetate}$) with a window opening size of $5.5 \times 4.2 \text{ \AA}^2$ and 21% porosity. The presence of poa^- facilitates the extension of the void space in $\mathbf{1}_{\text{Ln}}$ through the reducing coordination of $2,5\text{-pydc}^{2-}$ to Ln^{III} centers. The one-dimensional channel was decorated by functional groups of the ligands, *i.e.* phenyl rings and free O atoms of poa^- as well as free O atoms from carboxylate groups of $2,5\text{-pydc}^{2-}$ ligands. Besides the expanded void space by the introduction of poa^- ligand, the functionalities of $\mathbf{1}_{\text{Ln}}$ were then promoted. The excellent photoluminescent properties of $\mathbf{1}_{\text{Eu}}$ and $\mathbf{1}_{\text{Tb}}$ were also investigated. Motivated by the specific pore size, available functional groups, and effective sensitization of the ligands to Ln^{III} , the potential application

of ammonia sensing of **1_{Bu}** was evaluated, showing significant selectivity and high sensitivity among several common volatile organic compounds (VOCs). For further practical use, the fabricated **1_{Bu}**/PVA film was then prepared for ammonia sensing with a working concentration range of 0.50 to 10.0 ppm, low detection limit (0.14 ppm), high sensitivity (4.04 %·ppm⁻¹), excellent recovery (103 to 111 %), narrow deviation (1.5 to 8.2 %RSD), and high repeatability (95 to 97 %).

Chapter 3: Nanoporous Frameworks of Lanthanide-2,2'-Dinitrophenyl-4,4'-Dicarboxylates as Multifunctional Materials.

In chapter 3, the -NO₂ insertion on the lengthy BPDC²⁻ ligand was studied to enlarge porosity. With the use of *di*-nitro-BPDC²⁻, the three-dimensional porous LnCPs structure of [Ln₄(*di*-nitro-BPDC)₄(NO₂)₃(OH)(H₂O)₅] (solvent) (**2_{Ln}**; *di*-nitro-BPDC²⁻ = 2,2'-dinitrophenyl-4,4'-dicarboxylate and Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, and Gd^{III}) was successfully synthesized. Within the framework, there are two types of one-dimensional channels running along the a and b directions with the window opening size ranging from 1.1 nm to 2 nm. The insertion of -NO₂ group plays an important role in enlarging the porosity, which may be due to the electronic repulsion and steric effect. The coordination of organic ligands to Ln^{III} centers was then reduced. Owing to the highly directional channel, accessible -NO₂ groups as well as the Lewis acidic sites in the frameworks, **2_{Ln}** showed very high performance of various potential applications, e.g. proton conductivity, selective CO₂ capture, and catalysis for CO₂ cycloaddition reaction with epoxides.

Chapter 4: Tunable Installation of Lanthanide Cubane Clusters in Porous Supramolecular Frameworks Based on Multicarboxylate Metalloligands.

The tunable porosity by replacement of metal centers in multicarboxylate metalloligand of [L^M]⁶⁻ was investigated in Chapter 4. The use of a heavier and more rigid Ir^{III} instead of Rh^{III} in [L^M]⁶⁻ could enlarge the porosity from 46 to 53% with the expansion of pore size from 4.7 × 11.5 Å² to 6.0 × 12.2 Å². In addition, the border of the installation of lanthanide hydroxide cubane clusters Ln₄(OH)₄, in those [L^M]⁶⁻ was differentiated. In the case of [L^{Ir}]⁶⁻, a series of porous LnCPs Ln_{0.33}[Ln₄(μ₃-OH)₄(μ₂-OAc)₃(H₂O)₇][L^{Ir}]⁶⁻·nH₂O (**4_{Ln}**; Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III}, Tm^{III}, Yb^{III}, Lu^{III}, and Y^{III}) were synthesized from Sm^{III} to Lu^{III}, and Y^{III}. For the smaller porosity of [L^{Rh}]⁶⁻, the Ln₄(OH)₄ cluster could be grown in the crystal lattice of [L^{Rh}]⁶⁻ from Gd^{III} to Lu^{III} leading to the LnCPs Lu_{0.33}[Ln₄(μ₃-OH)₄(μ₂-OAc)₃(H₂O)₇][L^{Rh}]⁶⁻·nH₂O (**6_{Ln}**). Furthermore, the photoluminescent properties in this class of LnCPs could also be improved by replacing the metal centers from Rh^{III} to Ir^{III} in K₆[L^M]⁶⁻·nH₂O.

Conclusions

This study proposed three practical approaches for designing and fabricating porous LnCPs through modifying conventional ligand systems. First, the use of divergent dicarboxylate ligands could provide a high dimensionality of the framework. While introducing a small molecule to fulfill the coordination requirement of Ln^{III} centers could avoid the formation of dense frameworks. Second, the pore size could enlarge by using the longer ligands and functionalized ligands with steric groups of electron-rich moieties, which could also disrupt dense frameworks. Third, using multicarboxylate metalloligands could provide exceptional possibilities to control the hydrogen-bonded framework by the metal substitution in the metalloligands. The achievements presented in this thesis would provide effective ways for further designing and synthesizing porous LnCPs with desired structures and functionalities.

論文審査の結果の要旨及び担当者

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論文審査の結果の要旨		
<p>Supaphorn Thammakan は、タイ国チェンマイ大学に在籍するとともに、部局間協定にもとづく Double Degree Program (DDP)により本部局の統合理学特別コースに在籍しており、コチュテルの合意にしたがって博士論文審査を進めた。提出された博士論文のタイトルは「Crystal Engineering of Porous Lanthanide Coordination Polymers with Multicarboxylate Ligands (多座カルボキシレート配位子をもつ多孔性希土類配位高分子の結晶工学)」で、内容は以下の通りである。</p> <p>第一のトピックは、分子間相互作用する配位子を持つランタノイド錯体の超分子構造が高い空隙率を持ち、構造骨格で増感された高い発光挙動を示すことであった。それは、ゲストであるアンモニア分子の吸着に応答して、発光挙動が変化するというセンサー材料として特異な挙動を示した。第二のトピックは、立体化学的な分子構造の捻じれとニトロ基を有する架橋配位子を用いて形成したランタノイド錯体が、高い空隙率を有する超分子構造を有し、ゲストとして吸着した水分子によりプロトン伝導性を示したほか、ゲストとして吸着した二酸化炭素の触媒的変換も行ったことである。第三のトピックは、金属錯体配位子を用いて空隙率や電荷の補償を高めた超分子構造が、内部に取り込むランタノイドイオンの種類の許容範囲を拡大し、さらに取り込まれたランタノイドイオンがクラスター化して、構造骨格で増感された興味深い発光特性を示すことであった。</p> <p>この論文に対して、それぞれの部局で予備審査を行い、双方ともに本審査を受けるに値するものと認めた。なお、本部局では、化学専攻Aコースの教授全員による内審査を2023年2月1日に行った。これを受けて、2023年2月15日にチェンマイ大学にて博士公聴会が開かれ、コチュテルに正式に記載された大阪大学の審査委員はオンライン形式で出席した。この公聴会の直後に、大阪大学とチェンマイ大学の合同審査委員会をオンライン形式で開催し、博士論文の内容および公聴会における発表内容と質疑応答に基づいて評価を行なった。その結果、本論文は学位論文として十分価値あり、双方の大学から博士号を授与するに値すると認められた。</p>		