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Osaka University

CRYSTAL ENGINEERING OF POROUS LANTHANIDE COORDINATION POLYMERS WITH MULTICARBOXYLATE LIGANDS

SUPAPHORN THAMMAKAN

DOCTOR OF PHILOSOPHY IN CHEMISTRY

GRADUATE SCHOOL CHIANG MAI UNIVERSITY

2023

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DOCTOR OF PHILOSOPHY IN SCIENCE

DEPARTMENT OF CHEMISTRY GRADUATE SCHOOL OF SCIECE OSAKA UNIVERSITY 2023

CRYSTAL ENGINEERING OF POROUS LANTHANIDE COORDINATION POLYMERS WITH MULTICARBOXYLATE LIGANDS

SUPAPHORN THAMMAKAN

A THESIS SUBMITTED TO CHIANG MAI UNIVERSITY AND OSAKA UNIVERSITY IN PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY

GRADUATE SCHOOL, CHIANG MAI UNIVERSITY AND GRADUATE SCHOOL, OSAKA UNIVERSITY

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SUPAPHORN THAMMAKAN

THIS THESIS HAS BEEN APPROVED TO BE A PARTIAL FULFILLMENT OF THE REQUIREMENTS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY IN CHEMISTRY

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Supaphorn Thammakan

หัวข้อดุษฎีนิพนธ์	วิศวกรรมผลึกของแลนทาไนด์ โคออร์ดิเนชันพอ โดยมัลติคาร์บอกซิเลตลิแกนด์	เลิเมอร์แบบมีรูพรุน
ผู้เขียน	นางสาวสุภาพร ธรรมขั้น	
ปริญญา	ปรัชญาคุษฎีบัณฑิต (เกมี)	
คณะกรรมการที่ปรึกษา	รองศาสตราจารย์ คร. อภินภัส รุจิวัตร์ Prof. Dr. Takumi Konno รองศาสตราจารย์ คร. ปียรัตน์ นิมมานพิภักดิ์ รองศาสตราจารย์ คร. อธิพงศ์ งามจารุ โรจน์	อาจารย์ที่ปรึกษาหลัก อาจารย์ที่ปรึกษาร่วม อาจารย์ที่ปรึกษาร่วม อาจารย์ที่ปรึกษาร่วม

บทคัดย่อ

แลนทาในด์โดออร์ดิเนชันพอลิเมอร์แบบมีรูพรุนได้รับความสนใจ ด้วยว่าเป็นวัสดุที่สามารถ ถูกปรับแต่งโครงสร้างได้ และมีคุณสมบัติเฉพาะเจาะจง อย่างไรก็ตามการวิจัยในส่วนนี้ยังคงมีความ ท้าทายอยู่มาก เนื่องมาจากความเป็นไปได้ของเลขโดออดินชันและรูปร่างเชิงเรขาคณิตของไอออน แลนทาไนด์มีความหลากหลายและแปรเปลี่ยนได้มาก ลิแกนด์ที่มักจะถูกใช้ในการออกแบบแลนทา ในด์โดออร์ดิเนชันพอลิเมอร์แบบมีรูพรุน คือ มัลติคาร์บอกซิเลตลิแกนด์ ซึ่งจะถูกปรับแต่งด้วยการ เติมแต่งหมู่ฟังก์ชันหลายชนิด แต่ถึงอย่างไร การคิดค้นแลนทาไนด์โดออร์ดิเนชันพอลิเมอร์แบบมีรู พรุนเพื่อให้มีคุณสมบัติตามที่ด้องการด้วยการออกแบบลิแกนด์อินทรีย์นั้นยังคงเป็นไปได้ยาก เนื่องจากขาดการศึกษาอย่างเป็นระบบในการปรับแต่งลิแกนด์ การศึกษาอิทธิพลของการเปลี่ยนแปลง โครงสร้างของลิแกนด์ที่ส่งผลต่อความเป็นรูพรุนของแลนทาไนด์โดออร์ดิเนชันพอลิเมอร์นั้น ปราศจากข้อสรูปที่ชัดเจน และยังคงต้องการการศึกษาอีกมาก

ในงานวิจัยนี้ได้ทำการออกแบบและสังเคราะห์แลนทาไนด์โคออร์ดิเนชันพอลิเมอร์แบบมีรู พรุนโดยการปรับแต่งโครงสร้างของลิแกนด์ (ภาพที่ 1) ดังนี้ (i) เพิ่มลิแกนด์ตัวช่วยฟีนอกซีอะซิเตท เพื่อช่วยขยายพื้นที่ที่สามารถใช้งานได้และพัฒนาความเป็นรูพรุนให้เพิ่มขึ้น (ii) เติมกลุ่มไนโตรบนลิ แกนด์ที่มีขนาดยาว อาทิเช่น ไบฟีนิล-4,4'-ไดคาร์บอกซิเลต เพื่อขยายขนาดและความเป็นรูพรุน (iii) แทนที่โรเดียมไอออนในสารประกอบเชิงซ้อนลิแกนด์โลหะของ [Zn4O{Rh(L-cys)34]⁶⁻ ด้วยเออริ เดียมไอออน เพื่อควบคุมความเป็นรูพรุนผ่านพันธะไฮโดรเจน ซึ่งทำให้สามารถสังเคราะห์ สารประกอบโคออร์ดิเนชันพอลิเมอร์อนุกรมต่าง ๆ ดังนี้

- [Ln(poa)(2,5-pydc)(H₂O)₂]·3H₂O (1_{Ln}) เมื่อ Ln = Eu^{III}, Gd^{III}, Tb^{III}, และ Sm^{III}, 2,5-pydc²⁻ = 2,5-ไพริดีนไดคาร์บอกซิเลต และ poa⁻ = ฟีนอกซีอะซิเตท (บทที่ 2) ที่แสดงความสามารถ ในการตรวจวัดแอมโมเนีย
- [Ln₄(*di*-nitro-BPDC)₄(NO₂)₃(OH)(H₂O)₅]·(solvent) (2_{Ln}) เมื่อ *di*-nitro-BPDC²⁻ = 2,2'-ใด ในโตรฟีนิล-4,4'-ใดคาร์บอกซิเลต และ Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, และ Gd^{III} (บทที่ 3) ที่ แสดงศักยภาพการนำไปใช้งานได้หลากหลาย (การนำโปรตรอน และการเป็นสารตรวจวัด ความชื้นและอุณหภูมิ)
- $\operatorname{Ln}_{2}[\mathbf{L}^{Ir}] \cdot \operatorname{nH}_{2}O(\mathbf{3}_{Ln}) \operatorname{In}^{II} \partial [\mathbf{L}^{Ir}]^{6-} = [\operatorname{Zn}_{4}O\{\operatorname{Ir}(\operatorname{L-cys})_{3}\}_{4}]^{6-}, \operatorname{L-cys} = \operatorname{L-\overline{v}} \partial \overline{\partial} \overline{\partial} \operatorname{Iu} \partial, \operatorname{Ln} = \operatorname{Sc}^{II}, \operatorname{La}^{III}, \operatorname{Ce}^{III}, \operatorname{Pr}^{III}, \operatorname{IIAz} \operatorname{Nd}^{III} \operatorname{IIAz} \operatorname{Ln}_{0.33}[\operatorname{Ln}_{4}(\mu_{3} \cdot \operatorname{OH})_{4}(\mu_{2} \cdot \operatorname{OAc})_{3}(\operatorname{H}_{2}O)_{7}][\mathbf{L}^{Ir}] \cdot \operatorname{nH}_{2}O(\mathbf{4}_{Ln}) \operatorname{In}^{II} \partial \operatorname{Ln} = \operatorname{Sm}^{III}, \operatorname{Eu}^{III}, \operatorname{Eu}^{III}, \operatorname{Cd}^{III}, \operatorname{Tb}^{III}, \operatorname{Dy}^{III}, \operatorname{Ho}^{III}, \operatorname{Er}^{III}, \operatorname{Tm}^{III}, \operatorname{Yb}^{III}, \operatorname{Lu}^{III}, \operatorname{IIAz} \operatorname{Y}^{III}(\mathbf{Unn}^{III} \mathbf{4})$

 $[Ln(poa)(2,5-pydc)(H_2O)_2]\cdot 3H_2O (1_{Ln}). การใช้ถิแกนผสมระหว่าง 2,5-H_2pydc และ Hpoa นำไปสู่ โครงสร้างหนึ่งมิดิของ [Ln(poa)(2,5-pydc)(H_2O)_2]\cdot 3H_2O (1_{Ln}; Ln = Eu^{III}, Gd^{III}, Tb^{III}, และ Sm^{III}) โดยมีขนาดช่องเปิดของรูพรุนเท่ากับ 5.5 × 4.2 Å² และมีคุณสมบัติความเป็นรูพรุนเท่ากับ 21% การมีอยู่ของ poa⁻ ทำให้เกิดการขยายของขนาดรูพรุนใน 1_{Ln} ผ่านการลดจำนวนโคออดิเนตของ 2,5-pydc²⁻ กับแลนทาในด์ไอออน ช่องเปิดหนึ่งมิติดังกล่าวถูกตกแต่งโดยหมู่ฟังก์ชันของลิแกนด์ ได้แก่ 2,5-pydc²⁻ กับแลนทาในด์ไอออน ช่องเปิดหนึ่งมิติดังกล่าวถูกตกแต่งโดยหมู่ฟังก์ชันของลิแกนด์ ได้แก่ วงฟีนีล และ อะตอมออกซิเจนอิสระของ poa⁻ รวมไปถึงอะตอมออกซิเจนจากหมู่คาร์บอกซิเลตของลิ แกนด์ 2,5-pydc²⁻ ในส่วนของฟังก์ชันการใช้งานของ 1_{Ln} พบว่า 1_{Eu} และ 1_{Tb} แสดงคุณสมบัติเชิงแสงที่ ดีเชี่ยม ทั้งนี้เนื่องมาจากขนาดรูพรุนที่จำเพาะ หมู่ฟังก์ชันที่สามารถใช้งานได้ และการส่งต่อพลังงาน อย่างมีประสิทธิภาพของลิแกนด์สู่แลนทาในด์ไอออน ทำให้ 1_{Eu} มีสักขภาพในการใช้งานสำหรับการ ตรวจจับแอม โมเนียโดยแสดงให้เห็นความจำเพาะเจาะลงอย่างมีนัยขะสำกัญและความไวในการ ดรวจจับที่สูง นอกจากนี้เพื่อพัฒนาวัสดุสำหรับการใช้งานได้ระหว่าง 0.50 ถึง 10.0 ppm สามารถตรวจจับ กวามเข้มข้นด่า่สุดที่ 0.14 ppm ด้วยความไวในการตรวจจับสูงถึง 4.04 % ppm⁻¹ กำร้อยละการกิดบัตน ในช่วง 103 ถึง 111 % ค่าความเบี่ยงเบน 1.5 ถึง 8.2 %$ *RSD*และความสามารถในการถูกใช้งานซ้ำสูง 95 ถึง 97 %

 $[Ln_4(di-nitro-BPDC)_4(NO_2)_3(OH)(H_2O)_5] \cdot (solvent) (2_{Ln}).$ การใช้ลิแกนด์ di-nitro-BPDC²⁻ ทำให้เกิด โครงสร้างสามมิติของแลนทาในด์โคออร์ดิเนชันพอลิเมอร์แบบมีรูพรุนของ $[Ln_4(di-nitro-BPDC)_4(NO_2)_3(OH)(H_2O)_5] \cdot (solvent) (Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, และ Gd^{III}) โดยภายในโครงข่ายมีรู$ พรุนแบบหนึ่งมิติที่แผ่งขายไปตามทิศทางของแกน *a* และ *b* ช่องเปิดของรูพรุนมีขนาดตั้งแต่ 1.1 nm ถึง 2 nm การเติมหมู่ในโตรมีบทบาทสำคัญในการขยายขนาดของรูพรุน อันเนื่องมาจากแรงผลักทาง ไฟฟ้าและผลจากความเกะกะของหมู่ในโตร ทำให้จำนวนของการโคออดิเนตของลิแกนด์กับแลนด์ทา ในด์ไอออนลดลง สารประกอบ 2_{Ln} แสดงประสิทธิภาพในการนำโปรตรอนที่ดีเยี่ยม และยังมี ความจำเพาะในการเลือกจับกับแก๊สการ์บอนไดออกไซด์ และเป็นตัวเร่งปฏิกิริยาไซโคลแอดดิชันของ การ์บอนไดออกไซด์ด้วยอีพอกไซด์ โดยศักยภาพการใช้งานดังกล่าวสืบเนื่องมากจากผลของการมี ช่องเปิดที่มีทิศทางแน่ชัด หมู่ในโตรที่สามารถเข้าถึงและใช้งานได้ รวมไปถึงบริเวณความเป็นกรด ของลิวอิสในโครงสร้าง 2_{Ln}

 $Ln_{2}[L^{Ir}] \cdot nH_{2}O(3_{Ln})$ และ $Ln_{0.33}[Ln_{4}(\mu_{3}-OH)_{4}(\mu_{2}-OAc)_{3}(H_{2}O)_{7}][L^{Ir}] \cdot nH_{2}O(4_{Ln})$. การ แทนที่โลหะอะตอมกลางในสารประกอบเชิงซ้อนลิแกนด์โลหะของ $[L^{M}]^{6-}$ จากโรเดียมไอออน (Rh^{III}) เป็นเออริเดียมไอออน (Ir^{III}) สามารถเพิ่มความมีรูพรุนของโครงข่ายจาก 46% เป็น 53% และขนาดรู พรุนจาก 4.7 × 11.5 Å² เป็น 6.0 × 12.2 Å² ในส่วนของการสังเคราะห์แลนทาไนด์คิวเบนคลัสเตอร์ $Ln_{4}(OH)_{4}$ ภายใน $[L^{M}]^{6-}$ สามารถจำแนกได้ดังนี้ ในกรณีของ $[L^{Ir}]^{6-}$ สามารถสังเคราะห์อนุกรมของ $Ln_{0.33}[Ln_{4}(\mu_{3}-OH)_{4}(\mu_{2}-OAc)_{3}(H_{2}O)_{7}]$ $[L^{Ir}] \cdot nH_{2}O(4_{Ln}; Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, Er^{III},$ $Tm^{III}, Yb^{III}, Lu^{III}, และ Y^{III})$ และสำหรับ $[L^{Rh}]^{6-}$ สามารถสังเคราะห์ $Ln_{0.33}[Ln_{4}(\mu_{3}-OH)_{4}(\mu_{2}-OAc)_{3}(H_{2}O)_{7}]$ $[L^{Rh}] \cdot nH_{2}O(6_{Ln}; Ln = Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, In = Sm^{III}, Tm^{III}, Yb^{III}, Lu^{III}, In = Lu^{III})$ ได้ นอกเหนือจากนี้ยังพบว่าสามารปรับปรุงกุณสมบัติเชิงแสงของ 4_{Ln} ได้โดยการแทนที่ไอออนอะตอม กลางจาก Rh^{IIII} เป็น Ir^{III} ใน $K_{6}[L^{M}] \cdot nH_{2}O$

โดยสรุป ในงานวิจัยนี้ได้เสนอแนวทางปฏิบัติสามรูปแบบสำหรับการออกแบบแลนทาไนด์ โดออร์ดิเนชันพอลิเมอร์แบบมีรูพรุนผ่านระบบการปรับแต่งลิแกนด์ ได้แก่ (i) การใช้ลิแกนด์ไดการ์ บอกซิเลตที่สามารถให้โครงสร้างที่มีมิติสูง ร่วมกับการเติมโมเลกุลขนาดเล็กเพื่อหลีกเลี่ยงการเกิด โครงสร้างแบบหนาแน่น (ii) การขยายรูพรุนในโครงข่ายโดยใช้ลิแกนด์ที่ยาวขึ้นและมีการปรับแต่ง หมู่ฟังก์ชันด้วยหมู่ที่มีความเกะกะมาก และ (iii) การใช้สารประกอบเชิงซ้อนลิแกนด์โดหะแบบมัลติ การ์บอกซิเลตสามารถนำไปสู่การปรับแต่งพันธะไฮโดรเจนในโครงสร้างได้ด้วยการเปลี่ยนไอออน อะตอมกลางในสารประกอบเชิงซ้อนลิแกนด์โลหะดังกล่าว

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	Polymers with Multicarboxylate Ligands	
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ABSTRACT

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 $-NO_2$ 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 [Zn₄O{Rh(Lcys)₃}₄]^{6–} ([**L**^{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: $[Ln(poa)(2,5-pydc)(H_2O)_2]\cdot 3H_2O(\mathbf{1}_{Ln})$ when $Ln = Eu^{III}$, Gd^{III} , Tb^{III} , and Sm^{III} , 2,5-pydc²⁻ = 2,5-pyridine dicarboxylate, and poa⁻ = phenoxy acetate

Chapter 3: $[Ln_4(di\text{-nitro-BPDC})_4(NO_2)_3(OH)(H_2O)_5] \cdot (\text{solvent}) (2_{Ln})$ when di- nitro-BPDC²⁻ = 2,2'-dinitrobiphenyl-4,4'-dicarboxylate and Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, and Gd^{III}

Chapter 4: $Ln_2[\mathbf{L}^{Ir}] \cdot nH_2O(\mathbf{3}_{Ln})$ when $[\mathbf{L}^{Ir}]^{6-} = [Zn_4O\{Ir(L-cys)_3\}_4]^{6-}$, L-cys = L-cysteinate, $Ln = Sc^{III}$, La^{III} , Ce^{III} , Pr^{III} , and Nd^{III} and $Ln_{0.33}[Ln_4(\mu_3-OH)_4(\mu_2-OAc)_3(H_2O)_7][\mathbf{L}^{Ir}] \cdot nH_2O(\mathbf{4}_{Ln})$ when $Ln = Sm^{III}$, Eu^{III} , Gd^{III} , Tb^{III} , Dy^{III} , Ho^{III} , Er^{III} , Tm^{III} , Yb^{III} , Lu^{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-H₂pydc and Hpoa for constrction of LnCPs was reported in chapter 2. This combination of these two ligands led to one-dimensional porous LnCPs of $[Ln(poa)(2,5-pydc)(H_2O)_2] \cdot 3H_2O$ (1Ln; Ln = Eu^{III}, Gd^{III}, Tb^{III}, and Sm^{III}, 2,5-pydc²⁻ = 2,5-pyridine dicarboxylate, and poa⁻ = phenoxy acetate) with a window opening size of 5.5 \times 4.2 Å² and 21% porosity. The presence of poa⁻ facilitates the extension of the void space in 1_{Ln} through the reducing coordination of 2,5-pydc²⁻ 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-pydc²⁻ ligands. Besides the expanded void space by the introduction of poa⁻ ligand, the functionalities of $\mathbf{1}_{Ln}$ were then promoted. The excellent photoluminescent properties of 1_{Eu} and 1_{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_{Eu} was evaluated, showing significant selectivity and high sensitivity among several common volatile organic compounds (VOCs). For further practical use, the fabricated 1_{Eu} /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'-Dinitrobiphenyl-4,4'-Dicarboxylates as Multifunctional Materials.

In chapter 3, the $-NO_2$ insertion on the lengthy BPDC^{2–} ligand was studied to enlarge porosity. With the use of *di*-nitro-BPDC^{2–}, the three-dimensional porous LnCPs structure of $[Ln_4(di\text{-nitro-BPDC})_4(NO_2)_3(OH)(H_2O)_5] \cdot (\text{solvent})$ (**2**_{Ln}; *di*-nitro-BPDC^{2–} = 2,2'-dinitrobiphenyl- 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 $-NO_2$ 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 $-NO_2$ 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 multicarboxyalte metalloligand of $[\mathbf{L}^{\mathbf{M}}]^{6-}$ was investigated in Chapter 4. The use of a heavier and more rigid Ir^{III} instead of Rh^{III} in $[\mathbf{L}^{\mathbf{M}}]^{6-}$ 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 $[\mathbf{L}^{\mathbf{M}}]^{6-}$ was differentiated. In the case of $[\mathbf{L}^{\mathbf{Ir}}]^{6-}$, a series of porous LnCPs Ln_{0.33}[Ln₄(µ₃-OH)₄(µ₂-OAc)₃(H₂O)₇][$\mathbf{L}^{\mathbf{Ir}}$]·nH₂O ($\mathbf{4_{Ln}}$; 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 $[\mathbf{L}^{\mathbf{Rh}}]^{6-}$, the Ln₄(OH)₄ cluster could be grown in the crystal lattice of $[\mathbf{L}^{\mathbf{Rh}}]^{6-}$ from Gd^{III} to Lu^{III} leading to the LnCPs Ln_{0.33}[Ln₄(µ₃-OH)₄(µ₂-OAc)₃(H₂O)₇][$\mathbf{L}^{\mathbf{Rh}}$]·nH₂O (**6**L_n).

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 $K_6[L^M] \cdot nH_2O$.

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.

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LIST OF ABBREVIATIONS AND SYMBOLS

%	Percent
RSD	Relative Standard Deviation
SD	Standard Deviation
h ⁻¹	Per hour
TON	Turnover number
TOF	Turnover frequency
CPs	Coordination polymers
<i>e.g.</i>	example gratia (for example)
i.e.	id est (that is)
Ln ^{III}	Lanthanide ions
LnCPs	Lanthanide Coordination Polymers
pН	pouvoir hydrogène
ca.	Approximately
S	Siemens
RH	Relative Humidity
AC	Alternating Current
Hz	Hertz
ν	stretching
δ	Chemical shift
Ω	Ohm
via	Through
$\chi_{ m m}$	Molar magnetic susceptibility
θ	theta

ข้อความแห่งการริเริ่ม

ง้ำพเจ้า นางสาวสุภาพร ธรรมขัน ขอยืนยันว่าเนื้อหาในคุษฎีนิพนธ์หัวข้อ "วิศวกรรมผลึกของแลนทาในค์โคออร์ดิเนชันพอลิเมอร์แบบมีรูพรุนด้วยมัลติคาร์บอกซิเลตลิแกนค์" เล่มนี้เป็นผลงานต้นฉบับของข้าพเจ้าภายใต้คำแนะนำและการชี้แนะจาก รศ.คร. อภินภัส รุจิวัตร์ และ Prof. Dr. Takashi Yoshimura (อาจารย์ที่ปรึกษาหลัก)

ง้าพเจ้าขอรับรองว่าคุษฎีนิพนธ์เล่มนี้เป็นผลงานของข้าพเจ้า รวมถึงฉบับแก้ไขสุดท้าย ซึ่งได้รับความเห็นชอบจากคณะกรรมการสอบวิทยานิพนธ์และบัณฑิตวิทยาลัย มหาวิทยาลัยเชียงใหม่แล้ว และคุษฎีนิพนธ์เล่มนี้ยังไม่เคยถูกใช้ยื่นสาหรับขอปริญญา หรือกุณวุฒิจากมหาวิทยาลัยหรือสถาบันใดมาก่อน

STATEMENTS OF ORIGINALITY

I, Supaphorn Thammakan, hereby declare that the material presented in my dissertation entitled "Crystal Engineering of Porous Lanthanide Coordination Polymers with Multicarboxylate Ligands" is an original work performed by me under the guidance and advice of my advisors, Assoc. Prof. Dr. Apinpus Rujiwatra and Prof. Dr. Takashi Yoshimura.

I declare that this is a true copy of my dissertation, including any final revisions, as approved by my thesis committee and the Graduate School, Chiang Mai University. To the best of my knowledge, this dissertation has not been previously submitted for a degree to any other university or institution.

CHAPTER 1

General Introduction

Porous frameworks, particularly in the class of coordination polymers (CPs), have emerged as a new platform for the development of multifunctional materials owing to their tunable functionality through pore surface and pore size engineering [1,2]. Motivated by the outstanding properties of lanthanide ions (Ln^{III}) arising from the presence of 4*f* electrons, *e.g.* unique magnetic, electronic, and optical properties [2-5], porous lanthanide coordination polymers (LnCPs) have gained an earnest interest recently. A wide range of applications, *e.g.* magnetism, luminescence, and catalysis [2-5], have been realized. However, the implementation of crystal engineering with porous LnCPs is challenging due to the flexible geometries and high coordination numbers of Ln^{III} as well as their exceptional susceptibilities to water and small solvent molecules [7,8]. Contrary to transition metal ions, the versatile and sentient coordination chemistry of Ln^{III} is directed mainly by organic ligands [7,8]. Choices of organic ligands are thus critical for designing structures with desired properties.

In accordance with the hard-soft acid-base principle [9], the carboxyl groups should promote strong Ln^{III}—O bonding and therefore robust frameworks. The commonly used ligands in the design of porous LnCPs are multicarboxylate ligands, which have been modified through the addition of various functional groups or the use of mixed ligands (Fig. 1.1). To yield porous LnCPs, the relative arrangement and number of donor atoms, length, rigidity and steric effect of the employed ligands must be considered with great care [10-12]. According to the literature, the divergent ligands processing two carboxylate groups are one of the important ligands promoting porous LnCPs. For example, monobenzene or pyridine-dicarboxylate could provide microporous LnCPs, *e.g.* [Ln(nitro-BDC)(L)_{0.5}(H₂O)]·3H₂O (Ln = Pr^{III}, Nd^{III}, Sm^{III} and Gd^{III}, and L = BDC^{2–} or BDC^{2–}/nitro-BDC^{2–}) [13], [Tb(L)_{1.5}(H₂O)]·3H₂O (L = 2-(2-Hydroxy-propionylamino)- terephthalate) [14], [Ce₂(2,5-pydc)₂(2,5-Hpydc)(H₂O)₂]Cl·nH₂O [15], [Nd(2,5-pydc)(OAc)(H2O)]_n·2nH₂O [16], [Ln₆(BDC)₉(DMF)₆(H₂O)₃]·3DMF (Ln = La^{III}, Ce^{III}, and Nd^{III}) [17], [Ce₆O₄(OH)₄(F-BDC)₆] [18], and Ln₄(μ_3 -OH)₄(NH₂-BDC)₃(H₂O)_{7.5} (μ_1 -OH)_{0.5}]·1.5Cl,10DMF and (Ln = Y^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Er^{III}, Ho^{III}, Tm^{III}, and Yb^{III}) [19]

To yield larger porosity of LnCPs, lengthy ligands have been employed rendering open frameworks with large windows, e.g. $[Gd_2L_3(DMF)_4] \cdot 4DMF$, $3H_2O$ (L = tetranitro-BPDC^{2–}) [20], [LnK(DSBPDC)(DMF)(H₂O)] \cdot x(solvent) (Ln = Pr^{III}, Sm^{III}, and Eu^{III}) [Ln4(µ3-OH)4(NH2-BPDC)4(DMF)3(H2O)]·8H2O,4.2DMF, [21]. $[Ln_4(\mu_3 -$ OH)₄(NH₂-TPDC)₄(DMF)(H₂O)₃] \cdot 16.6H₂O,15.2DMF (Ln = Y^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Yb^{III}) Er^{III}, Ho^Ⅲ. Tm^Ⅲ. and [19], and $[(CH_3)_2NH_2]_2[Tb_6(\mu_3 OH_{8}(DFBPDC)_{6}(H_{2}O)_{6}] \cdot x(solvent)$ [22]. Most of these ligands are notably decorated with pending groups, especially those of the electron-rich moieties such as -SO₃H, -NH₂, -F, and -NO₂. The effect of steric groups should be carefully considered as they can be useful in disrupting the dense frameworks and allowing a larger pore size.

Apart from judicious choices of ligands, the synthesis of porous framework depends also on the number of lanthanide centers [23]. High-nuclearity of lanthanide centers can lead to large porosity [18,19,22]. Based on the common synthetic approach of ligand-controlled hydrolysis, the synthesis of the lanthanide clusters is still challenging for chemists due to the highly flexible chemistry of Ln^{III} [23]. Multicarboxylate ligands, *e.g.* hexa-, octa-, and dodecacarboxylate ligands, are great candidates to provide high-nuclearity lanthanide clusters with high stability and dimensionality [24]. In addition, multicarboxylate ligands could also decorate the internal pore spaces of the frameworks with free carboxylate groups, which should promote the potential functions of the derived frameworks [25,26]. Furthermore, there can be free carboxylate groups available for the establishment of hydrogen-bonding interactions, which can improve porosity through supramolecular assembly [27]. However, the synthesis procedure and structural arrangement based on organic multicarboxylate ligands might limit the development of the synthesis of desired structures. Multicarboxylates provided by discrete metal complexes or metalloligands have become more attractive owing to their stabilities,

solubilities, tunable structures and functionalities [25]. Known examples of LnCPs derived through this strategy are nonetheless limited, *e.g.* {Ln₇(OH)₅[Ru(dcbpy)]₄·nH₂O} [28], [{Gd(OAc)(H₂O)}{Gd₄(OH)(OH)₄(H₂O)₁₁}{(*m*-L_{Ru})₄(HCOO)}] {SiW₁₂O₄₀}₂· xDMF·yH₂O [29], and [Ln{Ln₄(μ ₃-OH)₄(H₂O)₁₀}{(*m*-L_{Ru})₄(HCOO)₂}]{SiW₁₂O₄₀}₂ · xDMF·yH₂O (*m*-L_{Ru} = Ru^{II}(bpy)₂(4,4'-dcbpy), Ln = Dy^{III} and Er^{III}) [29].

In this thesis, the design and synthesis of porous LnCPs were examined through the use of multicarboxylate ligands with diverse rigidity, length, number of coordinating groups, and functional groups. All the ligands chosen herein are designed by slight structural modification of conventional ligand systems, *i.e* the introduction of small ligands, the addition of pendant groups, and the substitution of the metal center. The results and discussion are presented in three chapters classified in accordance with different crystal structures (Fig.1.2). Properties and potential functions of the derived frameworks are also included.

- **Chapter 2**: $[Ln(poa)(2,5-pydc)(H_2O)_2]\cdot 3H_2O$ (**1**_{Ln}) (Ln = Eu^{III}, Gd^{III}, Tb^{III}, and Sm^{III}, poa⁻ = phenoxy acetate, and 2,5-pydc²⁻ = 2,5-pyridine dicarboxylate)
- **Chapter3**: $[Ln_4(di\text{-nitro-BPDC})_4(NO_2)_3(OH)(H_2O)_5] \cdot (\text{solvent})$ (**2**_{Ln}) (*di*-nitro-BPDC²⁻ = 2,2'-dinitrobiphenyl-4,4'-dicarboxylate and Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, and Gd^{III})
- Chapter 4: $Ln_2[\mathbf{L}^{Ir}] \cdot nH_2O(\mathbf{3}_{Ln})([\mathbf{L}^{Ir}] = [Zn_4O\{Ir(L-cys)_3\}_4]^{6-}, L-cys = L-cysteinate,$ $Ln = Sc^{III}, La^{III}, Ce^{III}, Pr^{III}, and Nd^{III})$ and $Ln_{0.33}[Ln_4(\mu_3-OH)_4(\mu_2-OAc)_3(H_2O)_7][\mathbf{L}^{Ir}] \cdot nH_2O(\mathbf{4}_{Ln})(Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III},$ $Er^{III}, Tm^{III}, Yb^{III}, Lu^{III}, and Y^{III})$



 $\begin{array}{l} R = H \ (benzene \ dicarboxylic \ acid; \ H_2BDC) \\ = -NO_2 \ (nitro-benzene \ dicarboxylic \ acid; \ nitro-H_2BDC) \\ = -NH_2 \ (amino-benzene \ dicarboxylic \ acid; \ NH_2-H_2BDC) \\ = -NH(C=O)OH \ (2-(2-Hydroxy-propionylamino-benzene \ dicarboxylic \ acid) \\ \end{array}$



R= H (Biphenyl-dicarboxylic acid; H₂BPDC)

- = -F (difluoro-biphenyl-dicarboxylic acid; H₂DFBPDC)
- -HSO₃ (Disulfonyl-biphenyl-dicarboxylic acid; H₂DSBPDC)
- = -NH₂ (diamino-biphenyl-dicarboxylic acid; NH₂-H₂BPDC)





2,5-pyridine dicarboxylic acid (2,5-H₂pydc)



tetranitro-biphenyl-dicarboxylic acid (*tetra*-nitro-H₂BPDC)



Diamino-triphenyl-dicarboxylic acid (NH₂-H₂TPDC)



Tetrakis(4-carboxyphenyl)porphyrin (TCPP)



4,4',4"-tricarboxytriphenylamine (TCA)



 $[M(dcbpy)_3]^{4-}$ (M = Co^{II} and Ru^{II})



 $[Zn_4O{M(L-cys)_3}_4]^{6-}(M = Rh^{III} and Ir^{III})$

Fig. 1.1 Examples of ligands employed in the synthesis of porous LnCPs.



Fig. 1.2 Diagrams summarizing all reported LnCPs in this thesis.

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CHAPTER 2

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

2.1 Introduction

In this chapter, new series of porous $[Ln(poa)(2,5-pydc)(H_2O)_2]\cdot 3H_2O$ (1Ln) coordination polymers, where Ln = Eu^{III}, Gd^{III}, Tb^{III}, and Sm^{III}, were synthesized and characterized. 2,5-pyridine-dicarboxylic acid (2,5-H₂pydc) and phenoxy acetic acid (Hpoa) were chosen as organic building motifs. With respect to framework design, 2,5-H₂pydc containing two divergent carboxylates, was expected to provide infinite framework structures through various coordination modes, particularly $\mu_4-\eta_1:\eta_1:\eta_1:\eta_1:\eta_1$ (Fig. 2.1). However, both porous and dense frameworks are possible (Table 2.1). To disrupt dense framework formation, Hpoa with only one carboxylate was concurrently used. Regarding the promotion of the f-f emissions, both 2,5-H₂pydc and Hpoa are acknowledged as effective sensitizers according to the antenna model [1,2]. The existence of pyridine ring of 2,5-H₂pydc as well as the O atom and phenyl ring of Hpoa should additionally encourage sufficient interactions with some small molecules, especially ammonia, to induce perturbation in *f*-*f* emission profile through weak interactions, *e.g.* hydrogen bonding. Through these interactions with ammonia-responsive functional groups, the frameworks have been expected to exhibit sensing ability toward ammonia [3,4]. Single crystal structures, thermal stability and solid-state photoluminescent properties at room temperature of the synthesized frameworks were investigated. On the basis of room-temperature photoluminescent results, 1_{Eu} was chosen for the study of ammonia gas sensing. The results are described and discussed in relation to the deduced structures and spectroscopy. Encouraged by the efficient single crystal photoluminescence for further practical uses, the $1_{Eu}/PVA$ composite film was also fabricated via a facile drop-casting method providing exceptional performance as

selective, robust, and reusable ammonia gas sensors. The film can potentially be used for on-site monitoring due to its fast response and portability.



Fig. 2.1 Coordination modes of 2,5-pydc^{2–} found in LnCPs deposited to the Cambridge Structural Database [5] (frequency of appearance shown in brackets).

	Coordination modes	Number of structures in va	rious d	imensions of fra	amework
		1D	2D	3D Dense	3D Porous
μ_1		2	3	-	-
μ_2		2	-	-	-
μ_3			3	8	1
μ_4		ⁿ 1	7	13	4
μ ₅				7	-

Table 2.1 Coordination modes of 2,5-pydc^{2–} or 2,5Hpydc[–] and dimensionality of LnCPs deposited to the Cambridge Structural Database [5]

*1D = one-dimension, 2D = two-dimension, and 3D = three-dimension

2.2 Experimental

2.2.1 Synthesis of 1_{Ln} (Ln = Eu^{III}, Gd^{III}, Tb^{III}, and Sm^{III})

[Eu(poa)(2,5-pydc)(H₂O)₂]·3H₂O (1_{Eu}). First, EuCl₃·6H₂O (73.3 mg, 0.20 mmol), 2,5-H₂pydc (33.4 mg, 0.20 mmol), and Hpoa (91.3 mg, 0.6 mmol) were dissolved in a mixed solvent of EtOH (10.00 mL) and water (5.00 mL), which was adjusted pH of the solution to 6 using TEA The solution was then transferred into a 30 mL vial, which was sealed tightly and placed in an 80 °C oven. After 24 h, the vial was opened and heated at 60 °C for 72 h and then cooled down to room temperature. The colorless block-shaped crystals were then recovered through filtration (63% yield based on Eu^{III}).

 $[Gd(poa)(2,5-pydc)(H_2O)_2]\cdot 3H_2O$ (1_{Gd}). The colorless block-shaped crystals of 1_{Gd} were synthesized following the same procedure as 1_{Eu}, but with GdCl₃· 6H₂O (74.3 mg, 0.20 mmol; 67% yield based on Gd^{III}).

 $[Tb(poa)(2,5-pydc)(H_2O)_2]\cdot 3H_2O$ (1_{Tb}). The colorless block-shaped crystals of 1_{Tb} were synthesized following the same procedure as 1_{Eu}, but with TbCl₃· 6H₂O (74.7 mg, 0.20 mmol; 61% yield based on Tb^{III}).

 $[Sm(poa)(2,5-pydc)(H_2O)_2]\cdot 3H_2O$ (1sm). The colorless block-shaped crystals of 1sm were synthesized following the same procedure as 1_{Eu}, but with SmCl₃·6H₂O (73.0 mg, 0.20 mmol; 62% yield based on Sm^{III}).

2.2.2 X-ray crystallography

The single cystal data of of $\mathbf{1_{Ln}}$ (Ln = Eu^{III}, Gd^{III}, and Tb^{III}) were collected using a Rigaku-Oxford XtalLab Supernova diffractometer equipped with a micro-focus sealed X-ray tube of Mo K α radiation ($\lambda = 0.71073$ Å) and direct photon counting HyPix3000 detector at 293 K. The intensity data sets were carried out using the CrysAlisPro program [6]. SADABS program was applied for the empirical absorption corrections [7]. The crystal structures were solved using the SHELXT program [8] and refined on F^2 by the full-matrix least-squares technique using the SHELXL program [9] *via* the Olex² interface [10]. All hydrogen atoms were calculated using riding mode. Details on the crystallographic and refinement are summarized in Table 2.2. The hydrogen bond distances and angles of $\mathbf{1_{Eu}}$ were summarized in Table 2.3. The crystals of $\mathbf{1_{Sm}}$ were too small and not appropriate for full data collection. The structure of $\mathbf{1_{Sm}}$ is isostructure to $\mathbf{1_{Eu}}$, $\mathbf{1_{Gd}}$, and $\mathbf{1_{Tb}}$. Their purity was evaluated based on the PXRD experiment and elemental analysis (Table 2.4).

	1 _{Eu}	1 _{Gd}	1ть
CCDC NO.	2206221	2206226	2206229
Crystal formula	$EuC_{15}O_{12}NH_{20} \\$	$GdC_{15}O_{12}NH_{20}$	$TbC_{15}O_{12}NH_{20} \\$
Formula weight	554.25	559.54	561.21
Space group	Triclinic <i>P</i> –1	Triclinic <i>P</i> –1	Triclinic <i>P</i> –1
<i>a</i> (Å)	8.8731(1)	8.8712(2)	8.8591(3)
<i>b</i> (Å)	9.3731(4)	9.3698(10)	9.3380(3)
<i>c</i> (Å)	11.8367(6)	11.8432(2)	11.8545(4)
α(°)	99.632(4)	99.00(100	99.424(3)
β(°)	95.378(3)	95.258(2)	95.130(2)
$\lambda(^{\circ})$	92.476(7)	92.4960(10)	92.509(2)
$V(Å^3)$	964.55(7)	964.76(3)	961.86(6)
Ζ	2	2	2
$ ho/{ m g\cdot cm^{-3}}$	1.908	1.926	1.938
Radiation λ (Å)	Μο Κα (0.71073)	Μο Κα (0.71073)	Μο Κα (0.71073)
Temperature (K)	293(2)	293(2)	293(2)
Crystal size (mm ³)	0.1×0.1×0.2	0.2×0.1×0.05	0.1×0.1×0.05
F(000)	544	546	548
Data/parameters/	4119/296/12	4125/289/0	4111/283/0
restraints			
$R_1(I>2\sigma(I))^{\dagger}$	0.0289	0.0315	0.0353
wR_2 (all data) ^{† †}	0.0628	0.0672	0.0819

Table 2.2 Crystallographic and refinement data of $\mathbf{1}_{Eu},\,\mathbf{1}_{Gd},\,\text{and}\,\mathbf{1}_{Tb}$

 $^{\dagger}R_1 = \Sigma |(|Fo| - |Fc|)| / \Sigma (|Fo|). ^{\dagger \dagger}wR = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$

D—H····A	<i>d</i> (D—H)	<i>d</i> (H····A)	<i>d</i> (D····A)	\angle (D—H····A)
O9w—H9WA····O7 ⁱ	0.89	2.16	2.9002	140
O9w—H9WB····O10A ⁱⁱ	0.89	1.96	2.7559	148
O8w—H8WB·····O7 ⁱ	0.86	2.13	2.8845	145
O10A—H10A·····O6	0.85	2.50	3.3154	160
$C4 - H4 \cdots O8 W^{iv}$	0.93	2.47	3.3223	152
С6—Н6О3	0.93	2.44	2.7688	101
O8W ⁱⁱⁱ —H8WA ⁱⁱⁱ ····O1	0.86	1.85	2.7090	173
O8W ⁱⁱⁱⁱ —H8WB ⁱⁱⁱ ·····O1	0.86	2.90	2.7090	69
O8W ⁱⁱⁱ —H8WA ⁱⁱⁱ ····O2	0.86	2.63	3.1180	117
O8W ⁱⁱⁱ —H8WB ⁱⁱⁱ ····O2	0.86	2.68	3.1180	113
O8W ^{iv} —H8WA ^{iv} ·····O4	0.86	3.06	3.5560	118
O8w—H8WA····O1 ⁱⁱⁱ	0.86	1.85	2.7090	173
O8w—H8WA·····O2 ⁱⁱⁱ	0.86	2.63	3.1180	117
O8w—H8WA·····O4 ^{iv}	0.86	3.06	3.5540	118
O8w—H8WB·····O1 ⁱⁱⁱ	0.86	2.90	2.7090	69
O8w—H8WB·····O2 ⁱⁱⁱ	0.86	2.68	3.1180	113
$C4^{iv}$ — $H4^{iv}$ … $O8W$	0.93	2.47	3.3220	152
$C3^{iv}$ — $H3^{iv}$ ····O9W	0.93	2.83	3.4810	128
O10B ^{iv} —H10C ^{iv} …·O2	0.85	3.05	2.9056	72
O10B ^{iv} —H10D ^{iv} …O2	0.85	2.09	2.9056	162
O9w—H9WA····O10A	0.89	2.92	2.7565	71
O9w—H9WA····O10B	0.89	3.03	2.7218	62
O9w—H9WB····O10A	0.89	1.96	2.7565	148
O9w—H9WB…·O10B	0.89	2.05	2.7218	131
Symmetry: (i)1-x, 2-y, 1-z (ii) 1-x, 1-y, 1-z	z (iii) -x, 2-y, 1	-z (iv) -x, 1-y, 1-z	x (v) x, 1+y, Z

Table 2.3 Hydrogen bonding distance (d, Å) and angles (\angle, \circ) found in 1_{Eu}

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(vi) x, -1+y, z (vii) 1-x, 1-y, 2-z (viii) -x, 1-y, 2-z (ix) -1+x, y, z

D—H····A	<i>d</i> (D—H)	<i>d</i> (H····A)	$d(\mathbf{D}\cdots \mathbf{A})$	∠(D—H····A)
O10A—H10B…O9W	0.85	3.06	2.7565	62
O10B—H10C····O9W	0.85	2.60	2.7218	89
O10B—H10D…O9W	0.85	3.00	2.7218	49
O10A—H10A…O12	0.85	2.54	2.6945	91
O10A—H10B·····O12	0.85	2.58	2.6945	88
O10A—H10A····O6 ^{vi}	0.85	2.50	3.3150	160
O10A—H10A…O11A	0.85	3.10	2.7533	58
O10A—H10B·····O11A	0.85	1.99	2.7533	149
O10B—H10C····O11A	0.85	1.53	2.1167	123
O10B—H10D…O11A	0.85	2.08	2.1167	81
O10B—H10C·····O2 ^{iv}	0.85	3.05	2.9056	72
O10B—H10D·····O2 ^{iv}	0.85	2.09	2.9056	162
$C3^{iv}$ — $H3^{iv}$ …·O1B	0.93	2.86	2.6933	150
C12 ^{viii} —H12 ^{viii} ·····O11B	0.93	3.12	4.0364	170
011A02 ^{iv}	-	-	2.7730	-
O11B·····O2 ^{iv}	-	-	3.2390	-
011A012	-	-	3.9820	-
011A012 ^{vii}	-	-	2.6940	-
O11B····O12 ^{vii}	-	-	2.2530	-
O11B·····O11B ^{viii}	-	-	1.9670	-
O11BO12 ^{ix}	-	-	3.3550	-
012····011A ^{vii}	-	-	2.6970	-
012011B ^{vii}	-	-	2.2530	-

Table 2.3 Hydrogen bonding distance (d, Å) and angles (\angle, \circ) found in $\mathbf{1}_{Eu}$ (Cont.)

Symmetry: (i)1-x, 2-y, 1-z (ii) 1-x, 1-y, 1-z (iii) -x, 2-y, 1-z (iv) -x, 1-y, 1-z (v) x, 1+y, Z (vi) x, -1+y, z (vii) 1-x, 1-y, 2-z (viii) -x, 1-y, 2-z (ix) -1+x, y, z

2.2.3 Preparation of 1_{Eu}/PVA composite film using a drop-cast method

Composite films of $\mathbf{1}_{Eu}$ and PVA were prepared using a simple drop-casting method (Fig. 2.2). A suspension of finely ground $\mathbf{1}_{Eu}$ (20 mg, 0.036 mmol) in PVA solution (50 mg of PVA in 2.00 mL of hot water) was first prepared and dropped into a 2 × 2 cm² well excavated on a glass slide. It was then dried at 40 °C for 4 to 6 h. The yielded films were characterized by PXRD, scanning electron microscopy (SEM), and energy dispersive X-ray (EDX) spectroscopy.



Fig. 2.2 Schematic illustration of the setup for VOCs sensing experiments using (a) the finely ground **1**_{Eu} and (b) the **1**_{Eu}/**PVA** composite film.

2.2.4 Photoluminescent study and ammonia sensing experiments

Room-temperature emission spectra of the as-synthesized 1_{Eu} , 1_{Gd} , 1_{Tb} , and 1_{Sm} were first collected and analyzed, from which 1_{Eu} was selected for the study of ammonia gas sensing (Fig. 2.10). First, the study was carried out using the finely ground crystals of 1_{Eu} (10 mg) was added into a small glass cylinder (1 cm in diameter and 0.5 cm tall), which was then placed separately in a tightly closed glass chamber (volume of the

container = 844 (±1) mL). An ammonia solution was then injected into the chamber without touching the sample, using a 10.00 µL syringe. The volume of the introduced ammonia solution was varied from 0.95 to 38.00 µL in order to generate ammonia vapor concentrations of 0.25 to 10.0 ppm. To accelerate the vaporization of ammonia within the chamber, the vial was gently warmed at *ca*. 45 °C. After exposure to the vapor for a designed duration, photoluminescent spectrum of **1**_{Eu} was collected immediately using the excitation wavelength of 370 nm. The response (*R*) of **1**_{Eu} was evaluated based on the change in the integral area under the most intense ${}^{5}D_{0}\rightarrow{}^{7}F_{2}$ emission at 615 nm (*A*_{exp}) with respect to that of the pristine **1**_{Eu} (used as a reference, *A*₀). All the experiments were carried out in triplicate.

$$R(\%) = \left[\frac{A_{exp} - A_0}{A_0}\right] \times 100$$
 eq. (2.1)

The same procedure was adopted for the experiments using the composite films. The concentration of the ammonia vapor and contract time varied from 0.50 to 15.0 ppm, and 1 to 120 min contact time. Both the ground crystal and film experiments should be noted that all the measurements were carried out at room temperature and pressure. The value of A_0 was measured before every measurement of A_{exp} , which was proved to promote reliability of the acquired data.

The responses of the ground crystals of 1_{Eu} (*ca.* 10 mg) and the 1_{Eu} /PVA films to the other common volatile organic compounds, including chloroform (CHCl₃), dichloromethane (CH₂Cl₂), benzene, *n*-hexane (*n*-hex), tetrahydrofuran (THF), acetonitrile (MeCN), ethanol (EtOH), methanol (MeOH) and acetone, were also investigated, which evaluated selectivity of the sensing. All experiments were also performed at ambient temperature and pressure. The long contract time and high concentrations of these analysts were studied; 17h under 4000 ppm for ground crystals and 30 min under 15.0 ppm for 1_{Eu} /PVA films. The emission spectra were collected instantly after the exposure. It should be noted that all the ammonia vapor sensing experiments were carried out in triplicate.

To investigate the robustness and reusability of the 1_{Eu} /PVA film, the ammonia concentration of 3.50 and 7.50 ppm with 30 min contracting time were chosen. The used

film was left under an ambient atmosphere overnight to regenerate the 1_{Eu} /PVA films for the next cycles. The restoration of the emission spectra to approximately the original intensity was assured before every cycle.

2.3 Results and discussions

2.3.1 Crystal structure description of 1_{Ln}

The crystal structure of 1_{Eu} is described here as a representative of 1_{Gd} , 1_{Tb} , and 1_{sm} since they are all isostructural with the same crystal formula of $[Ln(poa)(2,5-pydc)(H_2O)_2] \cdot 3H_2O$ (Ln = Eu^{III}, Gd^{III}, Tb^{III}, and Sm^{III}). The structure of 1_{Eu} features a one-dimensional ladder-like framework (Fig. 2.4), which is constructed from a nine-fold tricapped trigonal prismatic Eu^{III} building motif, *i.e.* TPRS-{EuNO₈} (Fig. 2.3c). Each TPRS-{EuNO₈} motif is delineated by N and O atoms from 2,5-pydc²⁻, poa⁻, and water molecules. The neighboring TPRS-{EuNO₈} motifs are connected by two oxo-bridges of poa⁻ and two carboxylatebridges of 2,5-pydc²⁻ to form an edge-shared *TPRS*-{ $EuNO_8$ }₂ dimers. To establish the polymeric ladder-like structure, these dimers are further fastened by 2,5-pydc^{2–} in the direction of the b axis (Fig. 2.4a). Coordination modes of poa⁻ is μ_2 - η^2 : η^1 and 2,5-pydc²⁻ is μ_3 - η^0 : η^1 : η^1 : η^1 (Fig. 2.3b). Through these coordination modes, 2,5-pydc²⁻ plays an important role as a divergent linker in the construction of the framework whereas poa⁻ fulfills the coordination of Eu^{III} and limits dimensionality of the framework to be one-dimension. In the crystal structure, the established ladders are assembled into a three-dimensional supramolecular assembly via hydrogen bonding and $\pi - \pi$ interactions (Table 2.3). The assembly of these ladders leads to the establishment of the one-dimensional channels running along a axis (Fig. 2.4b), which account for ca. 21% of solvent accessible void calculated by PLATON [11]. The effective window opening to these channels is $ca. 4.2 \times 5.5 \text{ Å}^2$. Within the channels, the crystallizing water molecules are accommodated. They show site disordering, which is consistent with their involvement with the hydrogen bonding interactions. Noticeably, size of the opening should allow the entry of small molecules, e.g. ammonia (3.26 Å), carbon dioxide (3.33 Å), and hydrogen sulfide (3.60 Å) [12,13]. In addition, the internal surface of these channels is decorated by potential functional groups of the organic ligands, *i.e.* O atoms of both 2,5-pydc^{2–} and phenyl ring of poa[–]. These should be available for interactions with these molecules, especially ammonia.



Fig. 2.3 Crystallographic illustrations of 1_{Eu} : (a) asymmetric unit (drawn using 50% thermal ellipsoids), (b) modes of the coordination adopted by poa⁻ and 2,5-pydc²⁻, (c) the *TPRS*-{EuNO₈} structural building motif, (d) the coordination environment of Eu^{III} and (e) the formation of the edge-shared *TPRS*-{Eu₂N₂O₆} dimer.

Compared to the previous repoted LnCPs showing only 2,5-pydc^{2–} ligand of $[Ln_{1.375}(pydc)_2(H_2O)_4]$ (Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, and Er^{III}) [1], non-porous LnCPs was observed. This might be due to the crowned coordination, which might reduce the aviable space and led to be non-porosity. The introduction of auxiliary poa[–] ligand into the framework is thus an important role to disrupt dense framework as we expected. To yield porous LnCPs, the influence of small auxiliary ligands to fulfill the coordination sphere of Ln^{III} might be a potential approach for further development.



Fig. 2.4 Illustrations of (a) the *TPRS*-{ $EuNO_8$ }₂ dimer and a one-dimensional ladder in **1**_{Eu}, and their assembly viewed along (b) *a* axis.

2.3.2 Purity and thermal stability of 1_{Ln}

The isostructure $\mathbf{1}_{Ln}$ and their purity were confirmed by PXRD experiments, which showed the consistency of all the diffraction peaks (Fig. 2.5), and elemental analysis (Table 2.5). A slight discrepancy in the intensity of a few diffraction peaks at low 2θ range from the patterns simulated from the single crystal data is commonly observed after the grinding of the crystals. The presence of their expected functional groups was affirmed based on FT-IR spectroscopy. The band assignments are shown in Fig. 2.6 and Table 2.4.

Thermal stability of 1_{Eu} as a representative of 1_{Gd} , 1_{Tb} , and 1_{Sm} was evaluated by TG/DTA analysis (Fig. 2.7). Evidently, the framework was retained even after the endothermic liberation of the crystallizing water molecules, which occurred at *ca*. 90 °C. The retained framework structure of 1_{Eu} after heating up to 90 °C for 30 min was also confirmed by PXRD (Fig. 2.8). On the other hand, the loss of the coordinating water molecules at *ca*. 200 °C leaded to the disruption of the framework. The substantial weight drop commenced at *ca*. 400 °C should attribute to the decomposition of the organic molecules. Therefore, the stability of the framework and the application at room temperature up to *ca*. 90 °C is verified.



Fig. 2.5 PXRD patterns of 1_{Ln} compared with the patterns simulated from the corresponding single crystal data in the cases of 1_{Eu} , 1_{Gd} , and 1_{Tb} .



Fig. 2.6 FT-IR spectra of 1_{Ln} compared with those of H₂poa and 2,5-H₂pydc.

Band assignment	$1_{Eu} (cm^{-1})$	1 Ga (cm ⁻¹)	1ть (сm ⁻¹)	$1s_{m} (cm^{-1})$
ν(О-Н)	3520-3080	3519–2982	3519–2982	3520–2985
v(COO), phenyl ether	1660	1660	1660	1663
v(COO)	1593	1593	1593	1593
v(C=N), aromatic	1495	1495	1493	1500
v(C=C), aromatic	1473	1473	1473	1473
δ(C-H), alkyl	1422-1400	1422–1400	1422-1400	1422-1400
ν(C-O), COO ⁻	1350	1350	1350	1350
δ (C-H), aromatic	1288–1036	1285–1036	1285–1036	1288–1036
δ (C=C), mono-substituted	966	966	964	966
δ (C=C), di-substituted	891	891	891	891
δ (C-H), di-substituted	756	756	756	756
δ (C-H), mono-substituted	717	717	717	717
Ln ^{III} —O	513	511	511	514

Table 2.4 Band assignments of FT-IR spectra of 1_{Ln} compared with Hpoa and 2,5-H₂pydc

Table 2.5 CHN analyses of $1_{Ln} \label{eq:linear}$

		C (%)	H (%)	N (%)
1 _{Eu}	Anal. Calcd for EuC ₁₅ O ₁₂ NH ₂₀	32.37	3.61	2.51
	Found	32.27	3.40	2.56
1_{Gd}	Anal. Calcd for GdC ₁₅ O ₁₂ NH ₂₀	31.97	3.58	2.49
	Found	31.79	3.08	2.94
1ть	Anal. Calcd for TbC15O12NH20	31.87	3.57	2.78
	Found	31.71	3.11	2.86
1 _{Sm}	Anal. Calcd for SmC ₁₅ O ₁₂ NH ₂₀	32.36	3.62	2.52
	Found	32.51	3.39	2.67



Fig. 2.7 TG/DTA curves of 1_{Eu}.



Fig. 2.8 PXRD patterns of 1_{Eu} before and after the treatment at 90 and 200 °C for 30 min compared with the patterns simulated from the single crystal data.

2.3.3 UV-Vis and photoluminescent properties of 1Ln

The UV-Vis spectra of $\mathbf{1}_{Ln}$ are demonstrating the ligand centered $\pi \rightarrow \pi^*$ absorption at 219 nm and $n \rightarrow \pi^*$ absorption at 268, 274, and 281 nm (Fig. 2.9). Compared to the $\pi \rightarrow \pi^*$ absorption of Hpoa (217 nm) and 2,5-H₂pydc (222 nm), the $\pi \rightarrow \pi^*$ absorption of $\mathbf{1}_{Ln}$ is red shifted from Hpoa but blue shifted from 2,5-H₂pydc. Similar fashion was also observed in the $n \rightarrow \pi^*$ absorption of Hpoa (268 and 275 nm) and 2,5-H₂pydc (270 nm). This feature corresponds to the increased molecular rigidity of organic ligands upon the coordinating to Ln^{III} metal centers of both terminations of 2,5-pydc²⁻ and π - π stacking between neighbored pyridyl groups. In the poa⁻ ligand case, the contrarily enhanced disarray in poa⁻ molecular due to the influences of both the O—H····O and C—H····O hydrogen bonding at phenyl rings, leading to more flexibility and distortion in poa⁻ ligand. This is consistent with the shifting of the transition features and consistently manifested through the significantly larger thermal ellipsoids of O and C atoms of poa⁻.



Fig. 2.9 UV-Vis spectra of 1_{Ln} (solid line) compared to the Hpoa (dash line) and 2,5-H₂pydc (dash-dot line) ligands.

2.3.4 Room-temperature photoluminescent spectra of 1Ln

The room-temperature emission spectra of $\mathbf{1}_{Ln}$ were carried out under the excitation at 370 nm (Fig. 2.10), which revealed the effective sensitization of the characteristic f-femissions from $\mathbf{1}_{Eu}$ (${}^{5}D_{0} \rightarrow {}^{7}F_{J}$, J = 1 - 4), $\mathbf{1}_{Tb}$ (${}^{5}D_{4} \rightarrow {}^{7}F_{J}$, J = 6 - 3) and $\mathbf{1}_{Sm}$ (${}^{4}G_{5/2} \rightarrow {}^{6}H_{J}$, J = 5/2 - 11/2). Based on the emission spectra of 1_{Gd} , the triplet state energies of the sensitizers were estimated [14], which showed a broad energy range of ca. 15,000 -25,000 cm⁻¹. Compared with the emission spectra of 2,5-H₂pydc and Hpoa, this energy range encloses the combined range of the ligand-centered emissions, which could be taken as the range of triplet state energies of the co-existing sensitizers without considering the interactions between the triplet state energies of the two sensitizers [15]. According to the literatures [16,17], the energy gap between the sensitizer's triplet state energy and the Ln^{III} accepting level should be approximately $ca. 2500 - 3500 \text{ cm}^{-1}$, leading to the high efficiency of the sensitization of the *f*-*f* emissions. With respect to the common accepting energy levels of Eu^{III} (${}^{5}D_{0} = 17,270 \text{ cm}^{-1}, {}^{5}D_{1} = 19,030 \text{ cm}^{-1}$) and Tb^{III} $({}^{5}D_{4} = 20,470 \text{ cm}^{-1})$, the sensitization of 1_{Eu} and 1_{Tb} should be effective. This corresponds excellently with the absence of the ligand-centered emission in the spectra of 1_{Eu} and 1_{Tb} [14].

Regarding the emission spectra of 1_{Sm} , the intensity and broad emission in the emission range of 2,5-H₂pydc were decreased. While the intense and broad emission of Hpoa was still present. Based on our assumption on the non-interacting triplet states of the two co-existing sensitizers, the sensitization of Sm^{III} can be from only 2,5-pydc^{2–}. On the other hand, the poor emission profile may ascribe to the competitive non-radiative emissions caused by the excessive number of the low-lying energy multiplex of Sm^{III}, each of which is divided by small energy gaps [1,18].



Fig. 2.10 Room-temperature emission spectra (solid line) of (a) 1_{Eu} (b) 1_{Gd} (c) 1_{Tb} , and (d) 1_{Sm} .

2.3.5 Chemical robustness of 1_{Eu} and its selective sensing of ammonia gas

Inspired by its opened supramolecular structure, specific porosity, availability of potentially functional groups on the ligands, and the intense red emission of Eu^{III} , 1_{Eu} was chosen for further experiments on ammonia gas sensing. The robustness of 1_{Eu} upon exposure to different volatile organic compounds (VOCs) in gaseous state including ammonia, MeOH, EtOH, acetone, MeCN, THF, *n*-hex, benzene, CHCl₃, and CH₂Cl₂, was first examined. Regarding the PXRD results (Fig. 2.11), 1_{Eu} was substantially robust with respect to every experimented VOCs even after the prolonged contact. Following the confirmation of its stability, the photoluminescent responses of 1_{Eu} upon being exposed

to these VOCs were then explored. Intriguingly, only ammonia caused the significant and reliable quenching of the most intense $\text{Eu}^{\text{III}:5}D_0 \rightarrow {}^7\text{F}_2$ emission. It is therefore conclusive that the quenching of $\mathbf{1}_{\text{Eu}}$ by ammonia is selective (Fig. 2.12), which is not due to the collapse of the framework. This obvious selectivity corresponds well with the small molecular-sized window of the framework structure of $\mathbf{1}_{\text{Eu}}$, which prohibits the other VOCs possessing larger molecular structures from accessing into the framework. The extremely high vapor concentration of 4000 ppm and the lengthy exposure time of 17 h were decided for these experiments to ensure the selectivity to ammonia and the robustness of $\mathbf{1}_{\text{Eu}}$. It should be noted that the quenching of the $\text{Eu}^{\text{III}:5}D_0 \rightarrow {}^7\text{F}_2$ emission by ammonia gas at this concentration could be apparent within only a few minutes.

Considering the framework structure of 1_{Eu} , there are several functional groups showing potential to form hydrogen bonding interactions with ammonia gas, *i.e.* the uncoordinated O atom of carboxylate and the pyridine ring of 2,5-pydc²⁻ as well as the O atom and the phenyl ring of poa⁻ (Fig. 2.3). These functional groups notably aligned along the internal surface of the framework's one-dimensional channel and therefore should be susceptible to the incoming ammonia gas. This type of host-gest interactions may induce the change in molecular rigidity and consequently the energy levels involving with the sensitization process [19]. This assumption is well supported by the additional $\pi \rightarrow \pi^*$ transitions at 202 nm, the blue shift of the $n \rightarrow \pi *$ transitions from 268, 274, and 281 nm to 263, 269 and 276 nm, respectively, after being exposed to ammonia (Fig. 2.13). These changes agree well based on the assumption of the interactions with ammonia to be on the organic motifs in the framework structure of 1_{Eu} to a change in the triplet state energies [19]. This assumption has been evident through the DFT calculation, which suggests the formtion of hydrogen bonding interaction between the analyte and the framework (Fig. A-1 and Table A-1). Based on the calculation, the plausible active sites have been disclosed. Regarding the TG/DTA results, the crystallizing and coordinated water still occurred until ca. 90 °C and 200 °C, all those water molecules including coordination about Eu^{III} thus remained. Therefore, Eu^{III} should not be any direct interaction between ammonia.



Fig. 2.11 Simulated PXRD patterns of $\mathbf{1}_{Eu}$ (a) compared with the PXRD patterns after exposed to MeOH, EtOH, ammonia, acetone, MeCN, THF, *n*-hex, benzene, CHCl₃, and CH₂Cl₂ (b-k), respectively.

To study the triplet state energies of the poa⁻ and 2,5-pydc²⁻ sensitizers after contact with ammonia, photoluminescent spectrum of **1**Gd after being exposed to ammonia gas was collected to ensure the non-sensitization effect of Gd^{III} (Fig. 2.14). The change in the emission profile of **1**Gd was certain with a drastic drop in intensity of the emission in the 400 to 480 nm range, which indicated the inefficacy of poa⁻ as a sensitizer. The shift of the broad and intense band centering at *ca*. 550 nm (18,200 cm⁻¹), which clearly reflected the lowered energy range of 2,5-pydc²⁻. These altered features indicate the modulation of the triplet state energies of both sensitizers to be more prominent in the lowered energy range implying the shrinkage of the energy gap with respect to the accepting energy levels of Eu^{III} in the case of **1**Eu. It can therefore be assumed that the interactions between ammonia and **1**Eu disturb the energy gap between the triplet state energies of the guenching of the Eu^{III}.⁵D₀→⁷F₂ emission. It is worth noted that the emission profile of **1**Eu was restored after being left under ambient air or warmed at low temperatures. The

reversible interactions between 1_{Eu} and ammonia gas are certainly suggested as hydrogen bonding, which can be easily released from the framework. These features are essential to encourage the possibility in recovering of 1_{Eu} and its reusability in sensing.



Fig. 2.12 (a) Emission spectra of 1_{Eu} after being exposed to VOCs and (b) the corresponding *R* values.



Fig. 2.13 UV-Vis spectra of 1_{Eu} (solid-red line) and after being exposed to ammonia gas (solid-blank line) compared to the Hpoa (dash line) and 2,5-H₂pydc (dash-dot line) ligands.



Fig. 2.14 Emission spectrum of **1**_{Gd} before and after being exposed to ammonia compared with those of 2,5-H₂pydc and Hpoa.

2.3.6 Characterization of 1_{Eu}/PVA composite film and its photoluminescence

To fabricate film of $1_{Eu}/PVA$ was chosen as a matrix because of (i) its hydrophilic nature, which allows the incorporation of a variety of aqueous-based guest molecules; (ii) its ready formulation as a film, which naturally produced folds during drying and demolding; (iii) its inertness towards guest molecules [20]. A drop-cast method was employed due to its simple handling and inexpensive instrumentation [21]. After attempting various 1_{Eu} -to-PVA mole ratios, a film with a smooth and crack-free surface could be obtained only when it was fixed at 1:60 mole ratio (Fig. 2.15a). The thickness of the film was estimated from the SEM images and found to be ca. 100 µm. The mappings of the composing elements of both the surface and the cross-section area of the fabricated film displayed a good dispersion of 1_{Eu} in the casted film (Fig. 2.15). Despite the smooth surface, the cracking and the existence of holes were apparent inside which should own to the drying condition. These defects were apparently insignificant to the photoluminescent profile of 1_{Eu} (Fig. 2.16). The emission spectrum of the 1_{Eu} /PVA film was identical to 1_{Eu} displaying the characteristic emissions of ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1 – 4) of Eu^{III}. In addition, the remained structure of 1_{Eu} in the 1_{Eu} /PVA film was also confirmed by the PXRD result displaying well matching with the pristine 1_{Eu} .

To further evaluate the stability of the film after long storage, it was stored under ambient conditions for a month. The photoluminescent profile of the 1_{Eu} /PVA film after the long storage was also collected (Fig. 2.16), which showed the remained profile ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1 – 4) of Eu^{III} compared with the freshly prepared one. This feature should indicate excellent stability in long-term storage and promising application as ammonia sensor. In addition, the film did not show any physical deterioration.



Fig. 2.15 (a) PXRD pattern of 1_{Eu} /PVA film (with a photo of the film in the inset (b) SEM images with the corresponding elemental mappings showing (b) the top surface) and (c) the cross-sectional area of the film.



Fig. 2.16 Photoluminescent spectra of the freshly prepared 1_{Eu} /PVA film compared with that left at ambient condition for a month (photos of the films shown in insets).

2.3.7 Determination of ammonia gas concentration using 1_{Eu}/PVA film

The exposure of 1_{Eu} /PVA film to different VOCs provided almost identical responses to those of 1_{Eu} (Fig. 2.17). Selective quenching to ammonia gas in photoluminescence of 1_{Eu} /PVA film was clearly observed with substantially lower vapor concentration of 15.0 ppm and shorter exposure time of 30 min. Photoluminescent signals of the film have been demonstrated to be reliable with smaller values of standard deviation (*SD*) than the ground crystals sample on the basis of the triplicate data, especially on ammonia gas. The impregnation of 1_{Eu} within the PVA film apparently did not cause the deviation in responses of 1_{Eu} to ammonia and the other VOCs. Therefore, the fabrication of 1_{Eu} /PVA film could be successfully achieved without any adverse effect on the sensing.

To optimize the ammonia gas sensing by $\mathbf{1}_{Eu}$ /PVA film, exposure time, which is one of the important parameters in real practice, was studied using the ammonia gas concentration of 10.0 ppm (Fig. 2.18a and b). The quenching of the Eu^{III}: ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission was apparently rapid and could be observed since the first minute of contact. The substantial turn-off of *ca*. 50% could nonetheless be yielded at *ca*. 30 min, which was decided for further study on the sensing conditions. Stability of the photoluminescent signal reflected through the preserved emission profile of $\mathbf{1}_{Eu}$ /PVA film throughout the experiments even after 120 min of exposure time should be noted.



Fig. 2.17 Responses of 1_{Eu} /PVA film in terms of (a) emission spectra and (b) the corresponding *R* values after contact with different VOCs vapors (15.0 ppm and 30 min).

At the constant exposure time of 30 min, the gradual quenching in the intensity of the ${}^{5}D_{0} \rightarrow {}^{7}F_{J}$ (J = 1 – 4) of Eu^{III} was revealed with increased concentration of ammonia gas from 0.20bto 15.0 ppm, without any shift in position of every emission (Fig. 2.18c). Founded on the change of the ${}^{5}D_{0} \rightarrow {}^{7}F_{2}$ emission with the pristine 1_{Eu}/PVA film, the R values were calculated and plotted against the ammonia vapor concentration over the range of 0.50 to 10.0 ppm with excellent linear correlation (Fig. 2.18d). Based on the slope of the linear plot and the SD of the triplicate data of the reference (A_0) , the sensitivity and limit of detection (LOD) of 4.04 % and 0.14 ppm were calculated, respectively. Compared with the other photoluminescent sensing probes based CPs-films (Table 2.6), *e.g.* Tb-BTC inkjet printed patterns (LOD = 0.3 ppm, sensitivity = $0.0586 \,\% \,\text{ppm}^{-1}$) [22], Eu@UMOF-Eu-LA (LOD = 9 ppm, sensitivity = $0.016 \text{ }\%\text{ppm}^{-1}$) [23], Eu^{3+} @Ga(OH)bpydc (LOD = 2.4 ppm, sensitivity = 0.015 %·ppm⁻¹) [19], Phen-Eu-IM@BMOF (LOD = 12.750 ppm, sensitivity = $0.0006 \text{ }\%\text{ ppm}^{-1}$) [24], TMOF-6 (Cl) (LOD = 12 ppm, sensitivity = 0.045 % ppm⁻¹) [25], and 1-PVDF membranes (LOD = 22) ppm, sensitivity = 0.0243 % ppm⁻¹ [26], the 1_{Eu} /PVA film provided a remarkably low LOD and high sensitivity. It is worth noted that the yielded working range of concentration and precision provided by 1_{Eu} /PVA are comparable to those materials applied for breath ammonia sensors, which is a useful biomarker predicting chronic kidney disease (0.4 - 1.8 ppm) and lung diseases (0.8 - 14.7 ppm) [27,28], *e.g.* SnO¹⁺ (0.5 - 5 ppm) [29], Fc@ZIF-8 (0.4 - 20 ppm) [30]. With respect to the established linear calibration, the accuracy and precision of the three known ammonia vapor concentrations, *i.e.* 3.50, 6.50, and 7.50 ppm, were evaluated (Fig. 2.18d). The read-out concentrations from the calibration curve were closely similar to the expected values, which are summarized in Table 2.7. The corresponding statistical data are also listed in Table 2.7.



Fig. 2.18 (a, c) Emission spectra of 1_{Eu} /PVA film for time-dependence at 10 ppm of ammonia vapor concentration and concentration-dependence at 30 min contract time and (b, d) the consisted *R* values calculated from triplicate data.

Sensor	Concentration range (ppm)	Detection limit (ppm)	Contact time (min)	Sensitivity (% · ppm ⁻¹)	Repeatability	%Recovery	RSD (%)	Ref
Eu ^{III} @Ga(OH)bpydc	10-500	2.4	4	0.015	na	na	<4	[19]
Tb-BTC	5-80	0.3	2	0.0586	na	na	na	[22]
Eu@UMOF-Eu-LA	25-400	9	5	0.016	na	na	na	[23]
Phen-Eu-IM@BMOF	0-000	<i>ca.</i> 13	60	0.0006	na	na	па	[24]
TMOF-6 (Cl)	25-400	12	<i>ca.</i> 1.8	0.045	na	na	na	[25]
1-PVDF	0-3000	22	na	0.0243	na	na	na	[26]
MIL-124@Eu ^{III}	100-1350	26.2	5	0.0002	na	na	na	[31]
MR-MOF-RE	0-300	<i>ca.</i> 11	-	0.005	na	na	na	[32]
ZA-MPTMS-Eu-UiO-67	0-200	<i>ca.</i> 8.4	60	0.009	na	na	na	[33]
SNNU-88	3-100	na	>10	na	na	na	na	[34]
1eu/PVA	1.00-15.0	0.61	30	4.04	95% (at 3.50 ppm)	111 (at 3.50 ppm)	3.3 (at 3.50 ppm)	This work
					na	103 (at 6.50 ppm)	na	
					97% (at 8.50 ppm)	104 (at 8.50 ppm)	1.5 (at 8.50 ppm)	

Table 2.6 Performances of exemplified photoluminescent CP-films used for ammonia sensing

 ξ *na* = not available

Expected Conc. (ppm)	Read-out conc. (±SD) (ppm)	%recovery	%RSD
3.50	3.90 (±0.32)	111	8.2
6.50	6.73 (±0.33)	103	4.9
8.50	8.83 (±0.13)	104	1.5

 Table 2.7 The read-out ammonia concentrations and statistical data

2.2.8 Recyclability of 1_{Eu}/PVA film

Recyclability and robustness over several cycles of the measurements and restorations of the film are highly essential for practical sensing probes. This aspect of 1_{Eu} /PVA film was evaluated using two different ammonia gas concentrations of 3.50 and 8.50 ppm at 30 min of exposure time. To regenerate the used film, it was simply left under ambient pressure and temperature overnight. The emission spectra of the regenerated films were checked before the re-use to ensure complete restoration of all the Eu^{III}:⁵D₀ \rightarrow ⁷F_J (J = 1 - 4) emissions. Ten successive cycles of the measurements and regenerations were explored (Fig. 2.19 and 2.20), disclosing excellent repeatability of 95% and 97% and small value of the variation of 3.3 and 1.5 %*RSD* for the expected concentration of 3.50 ppm and 8.50 ppm, respectively. These values indicate the excellent reliability and reusability of the film. Among the ammonia sensors based on CPs-films, *e.g.* Eu^{III}@Ga(OH)(bpydc) (%*RSD* <4%) [19], the values obtained for the 1_{Eu} /PVA film are exceptional.

The SEM images with the corresponding mappings of the comprising elements of the **1**_{Eu}/PVA film after ten cycles were carried out (Fig. 2.21). The reused film appeared to remain approximately the same although a slight increase in surface roughness was apparent. The mappings of the comprising elements accordingly exhibited an insignificant change in the distribution of the elements on both the surface and the cross-section of the film. The emission profile of Eu^{III}:⁵D₀ \rightarrow ⁷F_J (*J* = 1 - 4) was apparently the same as those freshly prepared. It is therefore conclusive that the long storage of at least a month did not result in any deterioration of the film. Therefore, it should be concluded that the film is significantly stable and robust during several cycles of the measurement-and-regeneration process.

Cycle number	Read-out conc. (ppm)	Read-out conc. (ppm)
1	3.44	8.70
2	3.71	8.71
3	3.47	8.83
4	3.79	8.61
5	3.52	8.50
6	3.66	8.50
7	3.57	8.83
8	3.93	8.67
9	3.75	8.97
10	3.71	8.70

Table 2.8 Read-out concentration (ppm) from the calibration curve for tenth

 measurements compared with the expected concentration of 3.50 and 8.50 ppm



Fig. 2.19 (a) The *R* values of the 1_{Eu} /PVA films over ten cycles of the measurementand-regeneration and the (b) corresponding concentrations of ammonia vapor determined using the standard calibration method for the expected concentrations of 3.50 ppm.



Fig. 2.20 (a) R values of the 1_{Eu} /PVA films over ten cycles of the measurement-andregeneration and (b) the corresponding concentrations of ammonia vapor determined using the standard calibration method for the expected concentrations of 8.50 ppm.



Fig. 2.21 SEM images and the elemental mapping analysis of the 1_{Eu} /PVA-film after ten successive measurements of ammonia vapor sensing in (a, b) top-view and (c, d) cross-section for 3.50 ppm and 7.50 ppm, respectively.

2.4 Conclusions

Aiming at the design of porous LnCPs using dicarboxylate ligand, *i.e.* 2,5-pydc²⁻ as the linker to extend the framework and poa⁻ as the fulfilled ligand of the coordination sphere of Ln^{III} to avoid dense framework, a new series of isostructural [Ln(poa)(2,5 $pydc)(H_2O)_2$]·3H₂O (1_{Ln}), where Ln = Eu^{III}, Gd^{III}, Tb^{III} and Sm^{III}, were synthesized and characterized. The single crystal data revealed the open framework structure with ca. 21% void and 4.2×5.5 Å² opening. The efficient sensitization of the *f*-*f* emissions of Eu^{III} (**1**_{Eu}) and $Tb^{III}(\mathbf{1}_{Tb})$ by poa⁻ and 2,5-pydc²⁻ were disclosed. Found on the specific open window and photoluminescent property, the ammonia sensing probe of 1_{Eu} was evaluated with high selectivity among the common organic vapors. For practical use, the composite 1_{Eu}/PVA films were then successfully prepared without deteriorating the photoluminescent profile of 1_{Eu} using a simple drop-casting method. The robustness and selectivity of 1_{Eu} /PVA film toward different VOCs in gaseous state were also examined leading to the conclusions on their exceptional stability toward every experimented VOCs and obviously selective quenching to ammonia gas. Based on both experimental and calculated results, the selectivity quenching to ammonia is evidenced through the molecular sieve property of the framework and the change in triplet state energies of the sensitizers *via* the hydrogen bonding formation. The calculation findings are in line with experimentally perceived electronic transitions of the ligands in 1_{Eu} from the $n \rightarrow \pi *$ features and $\pi \rightarrow \pi *$ after being exposed to ammonia from the UV-Vis and photoluminescent measurement. Ammonia gas sensing performance of 1_{Eu} /PVA was then examined. With respect to the linear calibration established within 0.50 - 10.0 ppm range, the ammonia gas sensing by 1_{Eu} /PVA displayed excellent sensitivity (4.04 % ppm⁻¹) and detection limit (0.14 ppm). The determination of three ammonia gas concentrations, *i.e.* 3.50, 6.50, and 7.50 ppm, were calculated from the calibration providing excellent accuracy and precision manifested through the percentage recoveries of 103 - 111% and %*RSD* of 1.5 - 8.2%. Additionally, the regeneration of the used films was easily achieved by being exposed to ambient air and reusable for at least ten cycles (95 - 97% repeatability) without changes in the film structure and photoluminescent profile.

2.5 References

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CHAPTER 3

Nanoporous Frameworks of Lanthanide-2,2'-Dinitrobiphenyl-4,4'-Dicarboxylates as Multifunctional Materials

3.1 Introduction

Contrary to microporous LnCPs, the fabrication of nanoporous LnCPs is more complicated owing to the flexible coordination geometry and high coordination number of Ln^{III}, which tend to render the crowded coordination and therefore microporosity. To yield nanoporous LnCPs, number and relative arrangement of donor atoms, length, rigidity, and steric effect of ligands must be carefully considered [1-3]. According to literatures (Table 3.1), a linear and rigid biphenyl-4,4'-dicarboxylic acid (H₂BPDC) and its derivatives can lead to large porous frameworks. The steric effect introduced by additional functional groups, *e.g.* $-SO_3H$, $-NH_2$, -F, and $-NO_2$, on the backbone can hinder the formation of dense frameworks [4-6]. In this chapter, the synthesis and characterization of nanoporous [Ln₄(*di*-nitro-BPDC)₄(NO₂)₃(OH)(H₂O)₅] · (solvent) (**2**Ln) when *di*-nitro-H₂BPDC = 2,2'-dinitrobiphenyl-4,4'-dicarboxylic acid and Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, and Gd^{III} are reported. Their potential applications in superprotonic conductivities, humidity and temperature sensing, and catalysis of CO₂ capture and conversion are presented and discussed in relevant to the single crystal structures.

Organic linker	Chemical formula	Pore size (nm ²)	Surface area $(m^2 g^{-1})$	Ref
	[Gd ₂ L ₃ (DMF) ₄]·4DMF,3H ₂ O	0.33 × 0.86	NA	[4]
	$[Ln_4(\mu_3-OH)(L)_3(BPDAC)_{0.5}$ $(H_2O)_6]$ $(Ln = Gd^{III} and Tb^{III})$	0.30×0.70 and 0.45×0.55	NA	[7]
	$(DMA)_2[Ln_6(\mu_3-OH)_8$ $(L)_6] \cdot x(Solvent)$ $(Ln = Eu^{III} and Tb^{III})$	1.2×1.2 and 1.8×1.8	NA	[8]
	$\begin{split} & [Ln_4(\mu_3\text{-}OH)_4(L)_4(DMF)_3(H_2O)] \\ & \cdot 8H_2O, 4.2DMF \ (Ln = Sm^{III}, \\ & Eu^{III}, \ Gd^{III}, \ Tb^{III}, \ Dy^{III}, \ Ho^{III}, \\ & Er^{III}, \ Tm^{III}, \ and \ Yb^{III}) \end{split}$	0.90 × 1.1	NA	[9]
	$[Ln_2(L)_3 (DMF)_4] \cdot 3DMF, 2H_2O$ (Ln = Nd ^{III} , Eu ^{III} , and Gd ^{III})	0.80 × 1.2	NA	[10]
	$[LnK(L)(DMF)(H_2O)] \cdot x(solvent)$) $(Ln = Sm^{III}, Eu^{III}, and Pr^{III})$	1.3×1.3 and 2.8×2.8	738	[11]
	$[(CH_3)_2NH_2]_2[Tb_6(\mu_3-OH)_8(L)_6(H_2O)_6] \cdot x(solvent)$	1.2×1.2 and 1.6×1.6	1854	[12]
	$[(CH_3)_2NH_2]_2[Tb_6(\mu_3-OH)_8(L)_6(H_2O)_6] \cdot x(solvent)$	1.2×1.2 and 1.6×1.6	1940	[12]

Table 3.1 Selected examples of LnCPs of BPDC²⁻ and its derivatives possessing large pores

3.2. Experimental

3.2.2 Synthesis of *di*-nitro-H₂BPDC

The synthesis of *di*-nitro-H₂BPDC was modified following the reported procedure [13]. A suspension of 0.1200 g of biphenyl-4,4-dicarboxylic acid (H₂BPDC) in 12.50 mL of concentrated sulfuric acid was prepared and kept at temperatures below 50 °C using an ice bath. With continuous stirring, 3.00 mL of fuming nitric acid was added. The reaction mixture was refluxed at 80 °C for 4 h. The reaction was then subsequently cooled down using an ice bath after complete the consumption of H₂BPDC. The yellowish precipitate was collected by filtration. The precipitate was washed with a large amount of cold water and dried at 60 °C (84% yield). Thin-layer chromatography was used to follow up the reaction. The visualization was prompted under the UV light (254 nm). The crude product was dissolved in DMSO-*d*6 and then the ¹H NMR spectra were recorded at room temperature.

The yielded *di*-nitro-H₂BPDC was notably sufficient (over 90%) for further use without any purification (Fig. 3.1). The purity of the crude product was indicated as ¹H NMR (500 MHz, DMSO-*d6*): δ 8.68 (*d*, *J* = 1.6 Hz, 1H), 8.37 – 8.35 (*m*, 1H), 7.70 (*dd*, *J* = 21.7, 8.0 Hz, 1H).



Fig. 3.1 ¹H NMR spectrum of the as-synthesized *di*-nitro-H₂BPDC.

3.2.3 Synthesis 2_{Ln} (Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, and Gd^{III})

[Pr4(*di*-nitro-BPDC)4(NO₂)₃(OH)(H₂O)₅] · (solvent) (2_{Pr}). Pr(NO₃)₃· 6H₂O (0.20 mmol) and *di*-nitro-H₂BPDC (0.50 mmol) were dissolved in 12.5 mL of a mixed solvent of dimethylformamide/water (4/1). The mixture was then transferred into a 25 mL Teflon-lined hydrothermal, closed and placed under autogenous pressure generated at 140 °C for 12 h (84% yield). Based on the TGA data, 6 molecules of methanol solvent, which occupied in the void space, were calculated after soaking the crystals in MeOH for overnight.

 $[Nd_4(di-nitro-BPDC)_4(NO_2)_3(OH)(H_2O)_5] \cdot (solvent) (2_{Nd})$. Following the same synthesis procedure as 2_{Pr} , 2_{Nd} was synthesized using $Nd(NO_3)_3 \cdot 6H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$ and the reaction duration of 24 h (78% yield). Based on the TGA data, 4 molecules of methanol solvent, which occupied in the void space, were calculated after soaking the crystals in MeOH for overnight.

 $[Sm_4(di-nitro-BPDC)_4(NO_2)_3(OH)(H_2O)_5] \cdot (solvent) (2_{Sm})$. Following the same synthesis procedure as 2_{Pr} r, 2_{Sm} was synthesized using $Sm(NO_3)_3 \cdot 6H_2O$ instead of $Pr(NO_3)_3 \cdot 6H_2O$ and the reaction duration of 48 h (81% yield). Based on the TGA data, 4 molecules of methanol solvent, which occupied in the void space, were calculated.

[Eu4(*di*-nitro-BPDC)4(NO₂)₃(OH)(H₂O)₅] · (solvent) (2_{Eu} Following the same synthesis procedure as 2_{Pr}, 2_{Eu} was synthesized using Eu(NO₃)₃·6H₂O instead of Pr(NO₃)₃·6H₂O and the reaction duration of 72 h (84% yield). Based on the TGA data, 5 molecules of methanol solvent, which occupied in the void space, were calculated after soaking the crystals in MeOH for overnight.

[Gd4(*di*-nitro-BPDC)4(NO₂)₃(OH)(H₂O)₅] · (solvent) (2_{Gd}). Following the same synthesis procedure as 2_{Pr} , 2_{Gd} was synthesized using Gd(NO₃)₃·6H₂O instead of Pr(NO₃)₃·6H₂O and the reaction duration of 72 h (70% yield). Based on the TGA data, 4 molecules of methanol solvent, which occupied in the void space, were calculated after soaking the crystals in MeOH for overnight. The bimetallic frameworks of Pr^{III}/Gd^{III} (2Pr/Gd) and Pr^{III}/Eu^{III} (2Pr/Eu) were synthesized following the same synthesis procedure as the monometallic $2L_n$ ($Ln = Pr^{III}$, Nd^{III}, Sm^{III}, Eu^{III}, and Gd^{III}) but using an equimolar ratio of the corresponding $Ln(NO_3)_3 \cdot 6H_2O$; $Pr(NO_3)_3 \cdot 6H_2O$ (0.10 mmol) and $Gd(NO_3)_3 \cdot 6H_2O$ (0.10 mmol) for 2Pr/Gd with 76% yield, and $Pr(NO_3)_3 \cdot 6H_2O$ (0.10 mmol) and $Eu(NO_3)_3 \cdot 6H_2O$ (0.10 mmol) for 2Pr/Eu with 80% yield. Contents of Ln^{III} in the bimetallic 2Pr/Gd and 2Pr/Eu were indicated by an energy dispersive X-ray (EDX) spectroscopy provided on a scanning electron microscope (SEM).

3.2.4 X-ray crystallography

The single cystal data of 2_{Gd} were collected using a Rigaku-Oxford XtalLab Supernova diffractometer equipped with a micro-focus sealed X-ray tube of Mo K α radiation ($\lambda = 0.71073$ Å) and direct photon counting HyPix3000 detector at 293 K. The intensity data set were carried out using the CrysAlisPro program [14]. SADABS program was applied for the empirical absorption corrections [15]. The crystal structure was solved using the SHELXS program [16] and refined on F^2 by the full-matrix least-squares technique using the SHELXL program [17] *via* the Olex² interface [18]. The data set were treated using the SQUEEZE routine [19] because of the problem with diffusing guest species in the void, which could not be identified with precision by the X-ray diffraction technique. A number of diffused electrons could be determined *ca*. 13,464 per unit cell. Details on the crystallographic and refinement are summarized in Table 3.2. The crystal qualities of others 2_{Ln} (Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, Pr^{III}/Gd^{III}, and Pr^{III}/Eu^{III}) were not appropriate to collect full data. Their purities were evaluated based on the PXRD experiment and elemental analysis (Table 3.3).

CCDC No.	1919470
Crystal formula	$Gd_4C_{56}N_{11}O_{44}$
Formula weight	2183.86
Space group	Tetragonal $I\bar{4}_2d$
<i>a</i> (Å)	25.2376(2)
<i>c</i> (Å)	46.3754(4)
$V(Å^3)$	29,538.4(5)
Ζ	8
$ ho (\text{g} \cdot \text{cm}^{-3})$	0.982
Radiation λ (Å)	Μο Κα (0.71073)
Temperature (K)	293(2)
Crystal size (mm ³)	0.5 imes 0.4 imes 0.3
F(000)	13505
Data/ parameters/restraints	10640/536/16
$R_1 (I > 2\sigma(I))^{\dagger}$	0.0633
wR_2 (all data) [†] [†]	0.2035
$^{\dagger}P_{c} = \Sigma \langle F_{0} F_{0} \rangle \langle \Sigma (F_{0}) ^{\dagger} \downarrow \cup P = [\Sigma w (F_{0})^{2}]$	$E_{2}^{2}^{2}/\Sigma_{W}(E_{2}^{2})^{2}/1/2$

Table 3.2 Crystallographic and refinement data of 2_{Gd}

 $^{\dagger}R_1 = \Sigma |(|Fo| - |Fc|)| / \Sigma (|Fo|). ^{\dagger \dagger} wR = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$

		C (%)	H (%)	N (%)
2 _{Pr}	Anal. Calcd for Pr ₄ C ₆₂ H ₅₉ N ₁₁ O ₅₀	32.07	2.56	6.64
	Found	36.45	2.33	6.25
2_{Nd}	Anal. Calcd for $Nd_4C_{60}H_{51}N_{11}O_{48}$	31.73	2.26	6.78
	Found	35.82	2.28	6.21
$2s_m$	Anal. Calcd for $Sm_4C_{60}H_{51}N_{11}O_{48}$	31.39	2.24	6.71
	Found	36.39	2.28	6.64
2_{Eu}	Anal. Calcd for Eu ₄ C ₆₁ H ₅₅ N ₁₁ O ₄₉	31.39	2.38	6.60
	Found	36.91	2.35	6.61
2_{Gd}	Anal. Calcd for Gd ₄ C ₆₀ H ₅₁ N ₁₁ O ₄₈	31.02	2.21	6.63
	Found	36.06	2.28	6.36

Table 3.3 Elemental analysis of 2Ln

3.2.5 Proton conductivity measurements

Proton conductivity experiments were measured using single crystal samples under the customized chamber (Fig. 3.2). A TH2827 precision LCR meter with frequency operation from 1000 Hz to 1 MHz and an amplitude of 1 V AC voltage was used as impedance analyzer. The humidity, which was generated by vapor generator with seting target values as 55 to 99 RH%, was measured using a digital Thermo-Hygrometer O-271BK. A THORLabs TED3 temperature controller was used to control temperature, which was varied from 25 to 55 °C. To ensure the contact with electrodes, th crystals were painted with a conductive silver paint on the trigonal faces.

The proton conductivities (σ , S·cm⁻¹) could be calculated based on the impedance data following equations:

$$\sigma = \frac{1}{\rho} \qquad \qquad \text{eq. (3.1)}$$

$$\rho = \frac{ZS}{d} \qquad \text{eq. (3.2)}$$

$$\sigma = \frac{d}{ZS} \qquad \qquad \text{eq. (3.3)}$$

where *d* is the thickness (cm) of the single crystal, *S* is cross-sectional area (cm²) of the single crystal, and *Z* is the total resistance of the sample (Ω), which was yielded from the fit of the semicircle of the Nyquist plots (using ZView software). Dimensions of the single crystals were measured using the scale equipped with the optical microscope. Values of the thickness (*d*) and the surface area (*S*) of the single crystal samples used for all the measurements were listed in Table 3.4.

From the data collected at 99 RH% and 25 to 55 °C, an Arrhenius plot was established between $\ln(\sigma/S \cdot cm^{-1})$ and 1000/T from which the activation energy of the proton conduction (*E_a*) was calculated;

$$\sigma_{\rm T} = \sigma_0 \left[e^{(-Ea/RT)} \right] \qquad \text{eq. (3.4)}$$

$$\ln(\sigma_T) = \ln\sigma_0 - \frac{Ea}{RT} \qquad \text{eq. (3.5)}$$

$$\ln(\sigma_T) = \ln \sigma_0 - \frac{1000Ea}{1000RT}$$
 eq. (3.6)

where $\sigma =$ proton conductivity of the sample; $E_a =$ activation energy, R = ideal gas constant, and T = temperature in Kelvin (K). And from the plot between $\ln(\sigma_T)$ versus $\frac{1000}{T}$, the value of E_a can be calculated from slope of the plot.

Table 3.4 Thickness (d/cm) and surface areas (S/cm²) of 2_{Gd} used in proton conductivity experiments

Single Crystal Experiments	d	S
Humidity- and temperature-dependence	0.077	0.0020
Ten successive measurements between 55 and 99 RH%	0.077	0.0020
Ten successive measurements between 25 and 40 $^{\circ}\mathrm{C}$	0.059	0.0015
Humidity sensing	0.095	0.0079
Temperature sensing	0.061	0.0016
Pellet of Grinding Crystal Experiments		
Temperature dependence of proton conductivity (25 and 55 °C)	0.055	0.7663



Fig. 3.2 Diagram showing the experimental setting and the measurement chamber used in proton conductivity experiments.

3.2.6 Gas adsorption experiments

A BELSORP-mini II instrument was used to for gas adsorption/desorption experiments, which were performed in a range of 0 - 1 bar pressures with ultra-pure grade N_2 , H_2 , O_2 , and CO_2 . Before the measurements, the samples were immersed in methanol for overnight and then heated at 80 °C for 4 h under vacuum. The experiments were carried out at 77 K for N_2 and H_2 , 195 K for CO_2 , N_2 and O_2 , and 298 K for CO_2 and N_2 . Water sorption/desorption measurement was conducted using a BELSORP-max volumetric adsorption instrument at 298 K.

The enthalpy of CO_2 adsorption (Q_{st}) onto the framework was calculated using the Clausius-Clapeyron equation at near-zero CO_2 coverage [20].

$$\frac{\mathrm{dln}(P)}{\mathrm{d}(1/T)} = \frac{Q_{\mathrm{st}}}{R} \qquad \text{eq. (3.7)}$$
$$\ln\left(\frac{P_1}{P_2}\right) = Q_{\mathrm{st}} \frac{T_1 - T_2}{R \times T_1 \times T_2} \qquad \text{eq. (3.8)}$$

where P_i = pressure for isotherm *i*; T_i = temperature in Kelvin for isotherm I (K), R = ideal gas constant (8.315 J·mol⁻¹·K⁻¹) and Q_{st} = enthalpy of CO₂ adsorption.

3.2.7 Catalytic activities for CO₂ cycloaddition reactions with epoxides

The ground samples were soaked in MeOH for overnight and then was dried at 80 °C for 4 h under the N₂ flow to allow the vacant coordination sites. Tetrabutylammonium bromide (*n*-Bu₄NBr) and epoxyhydrin (ECH) were subsequently added into the pretreated sample in a 10 mL round bottom flask, which was then equipped with a CO₂ balloon. The experiments were performed under ambient CO₂ pressure and solvent-free conditions. The reaction was then cooled to room temperature. The reactions were progressed by using ¹H NMR spectroscopy. The performance of catalysts was indicated based on percentage conversion, selectivity, turnover number (TON), and turnover frequency (TOF), which were calculated following these equations when integral areas of a single proton derived from the epoxide substrate (I_{ep}) and the products (I_p)

%conversion =
$$\frac{I_p}{I_{ep}} \times 100$$
 eq. (3.9)

%selectivity =
$$\frac{I_c}{I_p} \times 100$$
 eq. (3.10)

$$TON = \left(\frac{\% conversion}{100} \times \frac{\% selectivity}{100}\right) \times \frac{mmol \ of \ epoxides}{mmol \ of \ cat.} \quad eq. (3.11)$$
$$TOF = \frac{TON}{reaction \ time} \quad eq. (3.12)$$

when I_{ep} is integral areas of a single proton derived from the epoxide substrate, I_c is the integral area of the desired product (cyclic carbonate).

To make certain that the negligible diversity in structural subtleties effect, which might obtaine from different batches of the syntheses, triplicate data were produced for every experiment. Influences of type of catalysts, (2Pr, 2Nd, 2sm, 2Eu, 2Gd, 2Pr/Gd, and 2Pr/Eu), mole percentage of the catalysts, type of co-catalysts (tetraethylammonium bromide or Et₄NBr, tetrapropylammonium bromide or *n*-Pr₄NBr, and *n*-Bu₄NBr), reaction temperature, and reaction time were studied. A scope of other epoxides was also attempted. To study recyclibilities, the catalysts were filtrated, washed with CHCl₃ several times, and then dried under ambient temperature for using in the next cycle. The retaining of the framework structures was affimed by PXRD after the recycling experiments.

3.3 Results and discussions

3.3.1 Crystal structure description of 2_{Gd}

 2_{Gd} crystallized in the tetragonal space group $I\overline{4}2d$ with the refined unit cell parameters a = 25.0247(3) Å, c = 46.3377(5) Å, V = 29.018.32(76) Å³ (Table 3.2). The framework features a nanoporous framework with high disorder. Its structure consists of three unique Gd^{III} ions (Gd1, Gd2, and Gd3) and three independent *di*-nitro-BPDC²⁻. One of di-nitro-BPDC²⁻ is presented with fully occupied crystallographic sites. The other two di-nitro-BPDC²⁻ exhibit however 50% possibility of site occupancy due to the substitutional disorder (Fig. 3.3a). Nitrites were generated in situ under the highly acidic solvothermal condition [5,21]. Atoms O8, O9, O13, and O19 can attribute to both carboxylates of O8-C27-O19 and O9-C3-O13 in the same *di*-nitro-BPDC²⁻ and two crystallographically unique nitrites of O8-N2-O19 and O9-N1-O13. The other disordering di-nitro-BPDC²⁻ exhibits similar substitutional disorder with coordinating water instead nitrites at O10, O25, O28, and O34 atoms, which can form to be both carboxylates in the same di-nitro-BPDC²⁻ of O25-C28-O28 and O10-C41-O34 and four independent coordinating water. Noticeably, there also is one of the -NO₂ group of the fully occupied di-nitro-BPDC²⁻ showing the disorder between two crystallographic sites with site occupying ratio of 50%, *i.e.* O1–N10–O2 and O5–N9–O6. Due to the relatively shorter Gd^{III}—O28 distance of 2.292(17) Å compared to the other Gd^{III}—O distance and the statistical data from the Cambridge Structural Database [22]. it was identified as hydroxide rather than water molecule resulting in the charge neutralization of the framework.



Fig. 3.3 Depictions of (a) an asymmetric unit of 2_{Gd} drawn using 50% thermal ellipsoid and (b,c) coordination modes adopted by *di*-nitro-BPDC^{2–} and nitrite anions. Symmetry codes: (i) 1-x, 1-y, z; (ii) -0.5+x, -y, 0.75-z; (iii) -0.5+x, 1+y, 0.25+z; (iv) 1-x, -y, z; (v) 0.5-x, 0.5+y, 0.5-z; (vi) 0.5+x, 1.5-y, 0.5-z; (vii) 0.5-x, y, 0.75-z; (viii) 0.5-x, 1-y, 0.25+z).

Owning to the substitutional disorder accompanying the coordinating ligands, it leads to significant variation in the coordination environment of all three unique Gd^{III} ions in the asymmetric unit of **2**_{Gd}. Although they are eight-fold coordinated alike, the number of the coordinating *di*-nitro-BPDC²⁻ ligand around the Gd^{III} ions ranges from eight to two (Fig. 3.4-3.6). The *di*-nitro-BPDC²⁻ ligands exhibit two different coordination modes, *i.e.* μ_4 - η^2 : η^1 : η^1 : η^1 : η^1 for the fully occupied *di*-nitro-BPDC²⁻ μ_4 - η^1 : η^1 : η^1 : η^1 : η^1 for the substitutional disordering *di*-nitro-BPDC²⁻ (Fig. 3.3b). The commonly found bridging μ_2 - η^1 : η^1 (N1, N2) and μ_3 - η^2 : η^2 (N3) coordination modes of the nitrite ligand are adopted (Fig. 3.3c). Based on the coordination modes of *di*-nitro-BPDC²⁻ and nitrite linkers, the Gd^{III} ions were bridged to form one-dimensional chains extending along the *a* and *b* axises (Fig. 3.7a and b). The derived chains feature a zigzag pattern performed by the μ_4 - η^2 : η^1 : η^1 : η^1 : η^1 *di*-nitro-BPDC²⁻ and the μ_3 - η^2 : η^2 nitrite coordinating to the Gd2 position.

The three-dimensional framework of 2_{Gd} can be regarded as being built up of these Gd^{III} zigzag chains (Fig. 3.7) containing two disconnected channels aligning also along the *a* and *b* directions. Due to the disordering of *di*-nitro-BPDC^{2–} and nitrate ligands, the effective window opening size could be varied in the range from 2.0×1.1 nm² to 1.5×1.1 nm² which

can be accounted for *ca.* 45% void or 0.46 cm³·g⁻¹ (Fig. 3.8). If there is no *di*-nitro-BPDC^{2–} involving in the window opening site, the window opening size of $2.0 \times 1.1 \text{ nm}^2$ should be observed. But if *di*-nitro-BPDC^{2–} ligands appear in the window opening site, then the smallest window opening size of $1.5 \times 1.1 \text{ nm}^2$ should be responsible. These values are in good agreement with the BET active surface area, the void volume, and the average pore size of 770.84 m²·g⁻¹, 0.49 cm³·g⁻¹, and 1.7 nm, respectively. They are also consistent with those nanoporous frameworks fabricated using H₂BPDC and its derivatives (Table 3.1).

With reference to the Cambridge Structural Database [22], the nanoporous LnCPs frameworks based on BPDC^{2–} and their derivatives linkers are limited, and noticeably they all contain secondary linkers and functional groups on the organic linkers. In the case of **2**_{Gd}, the nitrite functions as the secondary linker and fulfilled the Ln^{III} coordination sphere introducing the zigzag character to the Gd^{III}-carboxylate chains. To confirm the effect of the electron-withdrawing $-NO_2$ pendants on the organic linkers, the same synthesis condition was controlled resulting in $[Tb(BPDC)_2] \cdot (CH_3)2NH_2]$ with a smaller opening size of 5.6 × 8.3 Å² [23]. This smaller porosity might be due to the more crowded environment around Ln^{III} center, which could reduce the pore spaces in the framework. The decorated $-NO_2$ moieties of BPDC^{2–} are the important steric groups to disrupt the shrinkage porosity and then provide the larger pore size to be nanoporous frameworks as expected.



Fig. 3.4 Variation in coordination environment of Gd1 due to substitutional disorder dinitro-BPDC²⁻ with nitrites and water molecules in 2_{Gd} .



Fig. 3.5 Variation in coordination environment of Gd2 due to substitutional disorder dinitro-BPDC²⁻ with nitrites and water molecules in 2_{Gd} .



Fig. 3.6 Variation in coordination environment of Gd3 due to substitutional disorder dinitro-BPDC^{2–} with nitrites and water molecules in 2_{Gd} .



Fig 3.7 (a, b) the arrangement of the three unique Gd^{III} in the zigzag chains along a and b directions within (c) the three-dimensional framework.



Fig. 3.8 Views of different possibilities of window openings arose from the crystallographic disorder. (a) with nitrite (N1 and N2) and water (O10, O25, O28, and O34), but not di-nitro-BPDC^{2–}, (b) with a di-nitro-BPDC^{2–} and water, but not nitrite (N1 and N2) (c) with nitrite (N1 and N2) and a di-nitro-BPDC^{2–}, and (d) with di-nitro-BPDC^{2–}, but not water and nitrite. Symmetry operation: (i) 0.5-x, y, 0.75-z, (ii) 2-x, 1-y, z, (iii) 1-x, 1-y, z.

3.3.2 Phase and purity of 2Ln

Based on the PXRD results (Fig. 3.9a), pure phases of 2_{Ln} , which are isostructural, were successfully synthesized. The FT-IR spectra of 2_{Ln} showed also similar profiles (Fig. 3.9b). The phase and purity of 2_{Ln} could be confirmed based on PXRD diffraction patterns, which were well matched with simulated patterns gerating from the single crystal data of 2_{Gd} . Due to the grinding effect, the intensity of a few diffraction peaks in the low 2θ range were different. Elecmetal mapping analysis confirms the regular distribution of the corresponding elements (Fig. 3.10). Based on the EDX spectroscopic results, the equimolar ratio of the composing Ln^{III} in the bimetallic $2_{Pr/Gd}$ and $2_{Pr/Eu}$ frameworks can be ensured. On the basis of these characterization, phase and purity of 2_{Ln} could be certain.



Fig. 3.9 (a) PXRD patterns of 2_{Ln} compared with the simulated pattern generating from single crystal data of 2_{Gd} , and (b) FT-IR spectra of 2_{Ln} with corresponding band assignments.

3.3.3 Thermogravimetric behavior and stability

The occluded solvents are readily lost even at room temperature under the flow of N_2 gas, suggesting the remarkably weak intermolecular interactions, which are consistent with their diffusing character in the single crystal data. They can be substituted with methanol through a simple immersion overnight. After being soaked, the thermogravimetric behaviors of 2_{Ln} were carried out under the N_2 flow, which exhibited the same fashion (Fig. 3.11). The difference in type of Ln^{III} in 2_{Ln} did not cause any significant variation in their thermogravimetric profiles, which could ensure their isostructures.



Fig. 3.10 Element mappings of 2_{Ln} crystals with corresponding elemental mappings.

Based on the TGA curves, the methanol was also readily liberated under the N₂ gas flow due to showing endothermic behavior even at room temperature. The continual weight loss due to the desolvation was then observed until *ca*. 100 °C. The multiple endothermic behaviors during the loss (up to *ca*. 250 °C) imply disparity in intermolecular interactions involving these guest species. A partial disruption of the framework would be displayed after heating at 250 °C. It migh be due to the decomposition of the organic moieties, which was affirmed by the loss of a long-range order in PXRD patterns of 2_{Ga} (Fig. 3.12e). The collapse of the framework leading to the additional 64% weight loss was evident after heating higher than 250 °C, which provided a white powder of Gd₂O₃ as a product (Fig. 3.12f). The generation of vacant coordination sites on Ln^{III} could be, therefore, expected at temperatures lower than *ca*. 100 °C, which sould be appropricated for the pretreatment for further pretreatment of other experiments was considered.

To study the water stability, the diffraction patterns of 2_{Gd} after being immersed in the water at room temperature for a week and 80 °C for 72 h were collected (Fig. 3.12c and e). The maintained structures were affirmed through the unchanged diffraction patterns compared with the as-synthesized sample. Due to the strong Ln^{III}—O bond in the frameworks, it may lead to robustness with excellent water stability.



Fig. 3.11 TGA profiles of 2_{Ln} under heating from room temperature to 1000 °C under N₂ flow with a list of the initial weight losses.



Fig. 3.12 PXRD of (a) simulated pattern from single crystal data of 2_{Gd} compared with (b) as-synthesized 2_{Gd} , (c) immersed in water at room temperature for a week, (d) immersed in hot water (80 °C) for 72 h, (e) heated at 250 °C for 3 h, and (f) heated at 1000 °C for 3 h.

3.3.4 Proton conductivity of 2_{Gd}

3.3.4.1 Superprotonic conductivity

Inspired by the specific direction of the one-dimensional channels in the nanoporous framework structure of 2_{Gd} , the introduction of mobile proton carriers into the large void and the transportation promoters into the framework could be enhanced [24-26]. Additionally, introducing the electron-withdrawing $-NO_2$ groups can also improve the ability of proton carriers in the framework structures through the enhancing the hydrogen bonding interactions and increasing the hydrophilicity along the surface channel [6]. To avoid the effects of the grain boundary and nondirectional proton conduction, the proton conductivities of 2_{Gd} based on single crystal data are revealed to be substantial using applied AC voltage of 0.1V and 1V. Both voltages provided a similar

fashion of the dependence conductivity on humidity temperature (Fig. 3.13 and 3.14). Based on the impedance data, the lower applied voltage however resulted in slightly lower proton conductivity values under the same conditions. With increasing humidity from 55 RH% to 99 RH% (fixed 25 °C), the conductivities were enhanced from 7.28×10^{-5} S·cm⁻¹ to 1.18×10^{-2} S·cm⁻¹ at 0.1V and 9.08×10^{-5} S·cm⁻¹ to 1.42×10^{-2} S·cm⁻¹ at 1V. While the temperature-dependence conductivities from 25 °C to 55 °C (fixed 99 RH%) results also could improve values as high as 5.76×10^{-2} S·cm⁻¹ at 0.1V applied voltage and 55 °C and 6.17×10^{-2} S·cm⁻¹ at 1V applied voltage and 55 °C.

According to the literature (Table 3.5), the proton conductivities with both maximum values of $5.76 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1} (0.1 \text{ V})$ and $6.17 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1} (1 \text{ V})$ under 99 RH% and 55 °C are very high value among those reported for the single crystals. The room temperature conductivity of $2_{\text{Gd}} (1.42 \times 10^{-2} \text{ S} \cdot \text{cm}^{-1}; 99 \text{ RH}\%$ and 25 °C) is also leading high value among proton-conducting CPs. These results could be clarified as superprotonic conducting LnCPs, which could be rationalized by the large content of diffused mobile proton carriers and the existence of the pending $-\text{NO}_2$ moieties of BPDC^{2–} along the channels [27]. To verify the assumption, the conductivities of the polycrystalline sample were investigated (Fig. 3.15). The proton conductivities of the pellet samples were 4.64×10^{-7} and $7.40 \times 10^{-7} \text{ S} \cdot \text{cm}^{-1}$ under 99 RH% at 25 and 55 °C, respectively. The disconnection of the channels could therefore disrupt the proton conduction. The water sorption ability of 2_{Gd} was therefore evident (Fig. 3.18d), providing a maximum value of 6.66 mmol·g⁻¹ at 1 bar and 298 K.

Regarding the temperature-dependence conductivities at the highest humidity (99 RH%), the activation energy (E_a) of the single crystal sample was calculated as 0.43 eV (Fig. 3.16), which could estimate the proton conducting mechanism pathway. This calculated E_a value is in the borderline between the proton-carrier pathway (> 0.4 eV) and the proton-hopping pathway (< 0.4 eV) suggesting the possibility of both pathways to be responsible for the superprotonic conduction in $2G_d$ [39]. Both transportation pathways in $2G_d$ could be attributed due to the interaction between proton and polar groups on the internal surface of the channel in the framework and only the interaction of the water carrier, which is further away from the surface into the large void in the channel. This

phenomenon is not unexpected for nanoporous frameworks, *e.g.* MFM-500(Ni) (average pore size = 1.2 nm, $E_a = 0.43 \text{ eV}$) [40] and (H₃O)[Y₂(H₅btp)(H₄btp)]·H₂O (average pore size = 1.07 nm, $E_a = 0.40 \text{ eV}$) [41].



Fig. 3.13 (a, c) The humidity-dependent Nyquist plots and (b, d) the corresponding conductivities of 2_{Gd} at 0.1 and 1V applied voltages, respectively.



Fig. 3.14 (a, c) The temperature-dependent Nyquist plots and (b, d) the corresponding conductivities of 2_{Gd} at 0.1 and 1 V applied voltages, respectively.



Fig. 3.15 The Nyquist plots of the pelletized polycrystalline sample of 2_{Gd} prepared from ground crystals 1 V applied voltages.



Fig. 3.16 Arrhenius plot of the proton conductivity of 2_{Gd} (25 to 55 °C and 99 RH%).

3.3.4.2 Humidity- and temperature-dependent proton conductivities

As the proton conductivities of 2_{Gd} in terms of $\log \sigma$ (S·cm⁻¹) exhibit excellent linear correlation for both humidity and temperature with $R^2 > 0.99$ for 55-99 RH% at 25 °C and $R^2 > 0.99$ for 25 to 55 °C at 99 RH% at 1V applied voltage (Fig. 3.17 and 3.18). With reference to the calibration curve, excellent accuracy and precision have been revealed for the humidity measurements; 64 ± 1 , 74 ± 1 , and 95 ± 1 RH% for the expected values of 65, 75, and 95 RH%, respectively. This is comparable to the commercialized humidity sensors. The temperature sensing performance of 2_{Gd} was also studied for the 25 to 40 °C at 99 RH% and 1V applied voltage, *i.e.* 27.61±0.19, 32.04±0.64, and 36.98±0.73 °C for the expected value of 28.00, 32.00, and 36.50 °C, respectively. Regarding these temperature and humidity sensing ranges, 2_{Gd} is a significant candidate to use in a wide range of industries applications, *e.g.* storage and logistics of agricultural products as well as electronic devices.

Founded on ten successive measurements (Fig. 3.19), the excellent δ (RH) (*ca.* 1 % at both 55 and 99 RH%, R > 97%) and δ T (0.42 °C at 25 and 40 °C, R > 97%) were investigated. Note that R is the repeatability of the measurements and δ is the standard deviations of the read-outs values. Based on the R values of the measurements provided

by 2_{Gd} , the highest among the sensing materials based on conducting CPs [42,43] could be reported, which could be essentially comparable to those of conducting ceramics, *e.g.* SnO₂ nanowires (R < 90%) [44] and graphite oxide (R = 90%) [45]. The robustness of 2_{Gd} is notable through ten successive measurements for both humidity and temperature experiments. The high stability of 2_{Gd} is also evident *via* the remained PXRD patterns after immersion in water at both room temperature and 80 °C (Fig. 3.12c and d).

Samplas	σ (Secom ⁻¹)	Temp.	Humidity	E_a	Ref
Samples	σ (S·cm ⁻)	(°C)	(RH%)	(eV)	
UiO-66-SO ₃ H ^{††}	1.64×10^{-1}	80	95	0.107	[28]
BUT-8(Cr)A ^{††}	1.27×10^{-1}	80	100	0.11	[27]
PCMOF2 ^{1/2} (Tz) ^{††}	1.17×10^{-1}	85	100	0.22	[29]
PCMOF2 ^{1/2} (Pz) ^{††}	1.1×10^{-1}	85	90	0.16	[29]
UiO-66-(SO ₃ H) ₂ ^{††}	8.4×10^{-2}	80	90	0.32	[30]
$\{H[(N(CH_3)_4)_2][Gd_3(NIPA)_6]\}$.	7.17×10^{-2}	75	98	0.12	[6]
$3H_2O^{\dagger}$	/.1/×10	75		0.15	
2_{Gd} This work [†]	6.17×10 ⁻²	55	99	0.43	
Fe-CAT-5 ^{††}	5×10^{-2}	25	98	0.24	[31]
$[(Me_2NH_2)_3(SO_4)]_2[Zn_2(ox)_3]^{\dagger\dagger}$	4.2×10^{-2}	25	98	0.13	[32]
$PCC-72^{\dagger}$	3.4×10^{-3}	25	99	0.23	[33]
CFA-17	2.1×10^{-3}	22	95	0.3	[34]
$[Cu_2(Htzehp)_2(4,4-$	1 42, 10-3	20	95	0.49	[35]
bipy)]·3H ₂ O [†]	1.45×10	80		0.48	
PCMOF-17 [†]	1.25×10^{-3}	25	40	0.31	[36]
$(Me_2NH_2)[Eu(L)]^{\dagger}$	1.25×10^{-3}	150	0	0.21	[37]
CoLa-II [†]	3.1×10 ⁻⁴	25	95	0.34	[38]

Table 3.5 Proton conductivities and activation energies of 2_{Gd} compared with previously reported superprotonic conducting CPs and single crystal samples

[†]The values were from single crystal samples.

^{††}The values were from pellet samples.



Fig. 3.17 Calibration curves (red dashed-line) and the read-out data points (black) of humidity dependence with the expected values shown in brackets.



Fig. 3.18 Calibration curves (red dashed-line) and the read-out data points (black) of temperature dependence with the expected values shown in brackets.



Fig. 3.19 Ten successive measurements of (a) relative humidity (55 and 99 RH%, 25 °C) and (b) temperature (25 to 40 °C, 99 RH%) at 1V applied voltage.

3.3.5 Gas adsorption and selectivity

As we expected that the larger pore may promote the gas adsorption capacity and the decorated polar $-NO_2$ groups may enhance the selectivity. The gas adsorption behaviors of 2_{Gd} were evaluated for several gases, *i.e.* H₂, N₂, O₂, and CO₂ at different temperatures of 77 K, 195 K, and 298 K. The typical type I adsorption isotherm was observed for all the tested gases, exhibiting sudden uptake at the initial experiments before approaching the saturation plateau (Fig. 3.20). The intriguing characteristic of 2_{Gd} is its temperature-dependent adsorption selectivity (Table 3.6).

At 77 K (Fig. 3.20a), the adsorption of the H₂ was significantly poorer than the N₂ gas, which showed a sudden uptake to the saturation of 7.33 mmol·g⁻¹ (164.22 cm³·g⁻¹) at 1 bar. On the other hand, H₂ gas showed a gradual uptake with the rising pressure and reached 2.95 mmol·g⁻¹ (66.06 cm³·g⁻¹) at 1 bar. At 195 K (Fig. 3.20b), the highly selective adsorption of CO₂ was significantly evident compared with N₂ and O₂ gases. Whilst the adsorption of the two gases was extremely poor, the CO₂ uptake capacity of **2**_{Gd} was 4.87 mmol·g⁻¹ (109.1 cm³·g⁻¹) at 1 bar. At 298 K (Fig. 3.20c), the CO₂ uptake capacity at 1 bar fell drastically to 0.80 mmol·g⁻¹ (18 cm³·g⁻¹), whereas the N₂ gas was negligible. The abrupt adsorption was not observed at this temperature. Intriguingly, the uptake capacities

of CO_2 for all temperatures are much higher than N_2 and O_2 , indicating significant gas selectivity behavior for CO_2 .

To study the adsorption selectivity for CO₂ over O₂ and N₂, the initial uptake capacity ratios at 0.1 bar were determined. The selectivity of 2_{Gd} toward CO₂ over O₂ and N₂ were investigated, i.e. 39:1 for CO₂/O₂ at 195 K, 46:1 for CO₂/N₂ at 195 K and 21:1 CO₂/N₂ 298 K, respectively. The values of selectivity are relatively high which are comparable to those previous reported MOFs under similar conditions. The high CO₂ adsorption properties and outstanding selectivity of 2_{Gd} could be due to the interactions between the polar –NO₂ groups on the *di*-nitro-BPDC^{2–}. The interaction between CO₂ and the frameworks could be also evident *via* the isosteric adsorption enthalpies (Q_{st}) using the Clausius-Clapeyron equation [46,47]. Based on the adsorption isotherms at 195 K and 298 K, the Q_{st} for CO₂ was calculated to be the average value of *ca* 20.7±4 kJ·mol⁻¹ (Fig. 3.20e) suggesting the strong physical interactions between the CO₂ molecules and the framework, *e.g.* open metal site and polar –NO₂ functional group.

In comparison to the CO₂ uptake capacity for those 2_{Ln} (Ln = Pr^{III}, Nd^{III}, Sm^{III}, and Eu^{III}), the adsorption/desorption behaviors were measured at 195 K (Fig. 3.20f). The sudden rise in CO₂ adsorption could confirm the presence of vacant coordination sites on Ln^{III}. The CO₂ adsorption capacity of those 2_{Ln} (Ln = Pr^{III}, Nd^{III}, Sm^{III}, and Eu^{III}) was 1.81 mmol·g⁻¹ (40.5 cm³·g⁻¹) for 2_{Pr} , 2.00 mmol·g⁻¹ (44.8 cm³·g⁻¹) for 2_{Nd} , 2.98 mmol·g⁻¹ (66.6 cm³·g⁻¹) for 2_{Sm} , and 5.97 mmol·g⁻¹ (133.8 cm³·g⁻¹) for 2_{Eu} , respectively. The corresponding surface areas and average pore sizes of the framework were also determined as 107 m²·g⁻¹ and 1.90 nm for 2_{Pr} , 120 m²·g⁻¹ and 1.87 nm for 2_{Nd} , 194 m²·g⁻¹ and 1.72 nm for 2_{Sm} , 408 m²·g⁻¹ and 1.65 nm for 2_{Eu} , and 407 m²·g⁻¹ and 1.35 nm for 2_{Gd} , respectively. These values consist of the effect of lanthanide contraction resulting in different interactions between CO₂ and Ln^{III} vacant coordination sites as well as the other active sites within the frameworks. On the other hand, the slightly smaller CO₂ capacity of 2_{Gd} than 2_{Eu} was observed due to the substantial shrinkage of the opening of framework 2_{Gd} , which might limit the entering of CO₂.

Temperature	perature Sample Gas Gas uptake cap			pacities at 1 bar	
(K)			$V(\mathrm{cm}^3\cdot\mathrm{g}^{-1})$	$mmol \cdot g^{-1}$	
77	2 _{Gd}	N_2	164.2	7.33	
	2_{Gd}	H_2	66.06	2.95	
195	2 _{Pr}	CO_2	40.51	1.81	
	$2_{\rm Nd}$	CO_2	44.75	2.00	
	2 _{Sm}	CO_2	66.56	2.98	
	2 _{Eu}	CO_2	133.79	5.97	
	2 _{Gd}	CO_2	109.07	4.87	
	2_{Gd}	N_2	15.34	0.68	
	2_{Gd}	O_2	14.25	0.64	
298	2 _{Gd}	CO_2	17.82	0.80	
	2_{Gd}	N_2	1.33	0.059	
	2_{Gd}	H ₂ O	149.16	6.66	

Table 3.6 The gas uptake capacities at 1 atm for 77 K, 195 K, and 298 K



Fig. 3.20 Gas adsorption/desorption isotherms of 2_{Gd} for CO₂, N₂, H₂, and O₂ (a) at 77 K, (b) at 195 K, (c) at 298 K, (d) water adsorption/desorption isotherms of 2_{Gd} at 298 K, (e) the isosteric adsorption enthalpy of CO₂ for 2_{Gd} , and (f) comparison of CO₂ adsorption/desorption of 2_{Ln} at 298 K.

3.3.6 Acidity and basicity of 2Pr, 2Eu, and 2Gd

To study content of acidic and basic sites and acidic and basic strength in the frameworks, the NH₃-TPD and the CO₂-TPD profiles of the supposedly weakest Lewis acidic Pr^{III} (2_{Pr}) and the two strongest Lewis acidic Eu^{III} (2_{Eu}) and Gd^{III} (2_{Gd}) were evaluated (Fig. 3.21). According to the NH₃ desorptions, a range of acidic sites possessing different strengths from weak to medium can be assumed, occurring in the 90 to 170 °C temperature range and at temperatures >200 °C. Based on the integral area at the lower temperature range of 2_{Pr} was obviously larger than both 2_{Eu} and 2_{Gd} , which required the higher temperature. The presence of weaker acidic sites in 2_{Pr} can therefore be presumed. On the other hand, the profile of 2_{Eu} exhibited a tendency of large integral area at high temperature. This might suggest the strong interaction with NH_3 in the framework resulting in stronger acidic strength. The profile of 2_{Gd} presented a small peak at low temperature, which was unexpectedly poorer than 2_{Eu} . Since the major desorption of 2_{Gd} was still required at the higher temperature, a large amount of strong acidic sites could, however, be assumed. Regarding the results, the increasing acidity from 2_{Pr} to 2_{Eu} and 2_{Gd} could be concluded, corresponding to the lanthanide contraction effect. Concerning the CO_2 -TPD profiles, the desorption of CO_2 was observed with similar profiles of NH_3 . In the case of 2_{Pr} , the desorption peak was clearly observed at the temperature range of 70 to 190 °C with a rising trend at higher temperatures. In contrast, the predominant desorption profile of 2_{Eu} and 2_{Gd} required temperatures >180 °C. The stronger attractions of CO_2 in 2_{Eu} and 2_{Gd} than 2_{Pr} were therefore conclusive.

It should be noted nonetheless that all of the present functional groups in the frameworks such as the electron withdrawing $-NO_2$, the electron rich phenyl rings, the lone-paired electron of O atoms of carboxylates on the organic ligand, and the vacant coordination sites on Ln^{III} can interact with both NH₃ and CO₂ through different strength of interactions. As 2_{Pr} , 2_{Eu} , and 2_{Gd} are isostructural and contain the same functional groups, dissimilarities in strength and content of both acidity and basicity the frameworks are clearly attributable to type of Ln^{III} , *i.e.* $Pr^{III}(2_{Pr})$, $Eu^{III}(2_{Eu})$, and $Gd^{III}(2_{Gd})$. The smaller Gd^{III} should in principle interact with both NH₃ and CO₂ with better strength than the larger Pr^{III} .



Fig. 3.21 (a) NH₃-TPD and (b) CO₂-TPD profiles of 2_{Pr} (solid lines), 2_{Eu} (dotted lines), and 2_{Gd} (dashed lines).

3.3.7 Catalytic activities

3.3.7.1 CO₂ cycloaddition reactions with epoxides

Inspired by the highest CO₂ sorption capacity, 2_{Eu} was selected as a representative of others 2_{Ln} to evaluate the catalytic performance based on the CO₂ cycloaddition reaction with ECH as a catalytic model. The reaction was carried out with ECH in the presence of *n*-Bu₄NBr co-catalyst and optimized out under solven-free and ambient CO₂ pressure conditions (Table 3.7). The percentage conversion, selectivity, TON, and TOF were calculated based on the ¹H NMR spectra. These parameters reflect only the performance of the catalyst and not the other processing factors. The common by-product of 1-chloro-3-bromo-2-propanol was also slightly observed in ¹H NMR spectra (Fig 3.22). The selectivity of the reaction was thus additionally included for accuracy of the evaluation. The catalyzed reactions with only either *n*-Bu₄NBr or 2_{Eu} were also conducted (Table 3.7; entry 1 and 2) to illustrate the essence of the co-catalyst and its synergy with 2_{Eu}. Intriguingly, this synergistic effect was pronounced through the percentage conversion.



Fig. 3.22 Exemplary ¹H NMR spectrum of the CO_2 cycloaddition reaction with ECH catalyzed by 2_{Eu} .

The influences of reaction temperature and time were investigated from 80 to 60 °C (Table 3.7; entry 3-6) and 4 to 2 h (Table 3.7; entry 3, 7, and 8), respectively under controlled other catalytic conditions (20 mmol of ECH, 2.5 mol% of *n*-Bu₄NBr and 0.25 mol% of **2**_{Eu}). At low reaction temperature and short reaction time revealed low conversion due to the restriction of transportation and accessibility to the catalytic sites in the framework [48]. Based on these results, the reaction temperature of 80 °C and reaction time of 4 h were chosen for the other experiments with the fixed 20 mmol of ECH. With an increasing amount of *n*-Bu₄NBr from 2.5 mol% to 5.0 mol% (Table 3.7; entry 3 and 9) under the specified condition, the conversion of ECH did not improve. In contrast, the selectivity of the reaction was reduced by approximately 10%. This suggests that the large amount of *n*-Bu₄NBr apparently favors the formation of by-product, which can occur in the presence of any acid [49-51]. In addition, the influences of different co-catalyst were also investigated.

Cl $(Cl$ (Cl) $(Cl$								
Ent	Co-catalyst	IV	Temp	Time	%Conversion	% selectivity	TON	TOF
ry	(mol%)	(mol%)	(°C)	(h)	$(\pm SD)$	$(\pm SD)$	*	\$
1	<i>n</i> -Bu ₄ NBr	-	80	4	58^{\dagger}	85^{\dagger}	20	5
	(2.5)							
2	-	0.25	80	4	19^{\dagger}	58^{\dagger}	44	11
3	<i>n</i> -Bu ₄ NBr	0.25	80	4	98(±2)	91(±1)	356	89
	(2.5)							
4	<i>n</i> -Bu ₄ NBr	0.25	75	4	94(±2)	93(±1)	351	88
	(2.5)							
5	<i>n</i> -Bu ₄ NBr	0.25	70	4	88(±10)	86(±4)	303	76
	(2.5)							
6	<i>n</i> -Bu ₄ NBr	0.25	60	4	68(±12)	90(±1)	244	61
_	(2.5)							
7	$n-\mathrm{Bu}_4\mathrm{NBr}$	0.25	80	3	95(±5)	92(±1)	349	116
0	(2.5)	0.05	00	2		06(11)	254	107
8	n-Bu ₄ NBr	0.25	80	2	/4(±6)	86(±1)	254	127
0	(2.5)	0.25	80	4	00(+1)	82(12)	210	70
7	(5.0)	0.23	80	4	98(±1)	82(±2)	516	13
10	(J.0) <i>n</i> -Bu ₄ NBr	0.12	80	4	80(+1)	87(+1)	623	156
10	(2.5)	0.12	00	-	0)(±1)	07(±1)	023	150
11	$n-Bu_4NBr$	0.062	80	4	79(±4)	87(±1)	1106	276
	(2.5)							
12	<i>n</i> -Pr ₄ NBr	0.25	80	4	99(±2)	91(±1)	360	90
	(2.5)					~ /		
13	Et ₄ NBr	0.25	80	4	91(±3)	91(±1)	330	83
	(2.5)					· · ·		

Table 3.7 Catalytic activities of 2_{Eu} in CO₂ cycloaddition reactions with ECH under solvent-free and ambient CO₂ pressure conditions

[†]Data from one experiment [‡]Determined from average conversion and selectivity

Compared with the other co-catalysts showing different hydrocarbon chain lengths *i.e. n*-Pr₄NBr and Et₄NBr (Table 3.7; entry 12 and 13), the comparable performances to *n*-Bu₄NBr suggested the flexibility in choices of the co-catalysts in this reaction. Moreover, the attempt to decrease amount of the catalyst (Table 3.7; entry 3, 10, and 11) from 0.25 to 0.12 and 0.062 mol% brought down the conversion from $98(\pm 2)\%$ to $89(\pm 1)$
and 79(±4)%, respectively under controlling the other catalytic conditions. Nonetheless, the selectivity was slightly dropped from 91(±1)% to 87(±1)%. TON and TOF factors were also evaluated to indicate the performance of different catalysts. Under the maximum values of conversion and selectivity of 98(±2)% and 91(±1)%, respectively (Table 3.7; entry 3), the satisfying values of TON of 356 and TOF of 89 h⁻¹ were displayed. These values are comparable to those previous reported transition metal- and Ln^{III}- based CPs under the ambient CO₂ pressure (Table 3.10). The TON and TOF values of **2**_{Eu} could be raised to 1,106 and 276 h⁻¹ under diminished catalyst to 0.062 mol% with satisfiable conversions and selectivity of of \geq 79(±4)% and 87(±1)%, respectively. Compared with the other nanoporous MOFs catalysts (Table 3.10), these catalytic conditions of **2**_{Eu} are considerably milder with notable TON and TOF values, especially for the ambient CO₂ pressure.

One of the significant features of 2_{Eu} is its robustness, which illustrated through the recyclability and the retaining framework even after eight successive measurements (Fig. 3.23b). The conversions were approxilately unchanged from the first to the last cycle, varying between 91 and 100% (Fig. 3.23a). However, the selectivity slightly dropped from 91% in the first cycle to 76% in the eighth cycle. This may be due to the framework blockage and the resticted transportation within the framework. The constant catalytic conversion throughout the measurement could be meant the completely abstracted of ECH substrate in the reaction and capted within the framework. Therefore, the selectivity should be poisoned as the formation of the by-product, which could be occurred outside the framework. To prove the assumption, the FT-IR and the EDX results of 2_{Eu} after the eighth measurements were conducted (Fig. 3.23c and d). There were characteristics of v(C-Cl) and remaining of Br and Cl elements, which were evident in the elemental mappings. The remaining ECH substrate, by-product (1-chloro-3-bromo-2-propanol), and chloropropene carbonate product in 2_{Eu} were considered. The traping of these molecules within the framework could be resulted in the diminished selectivity values of the reaction, affirming the assumption. Therefore, the occlusion of these molecules in the framework is a critical issue for the droped performance of the re-used catalyst, which may need more attention.

To extend the scope of epoxides in this reaction, 2_{Eu} and *n*-Bu₄NBr were used as the representative catalyst and co-catalyst (Table 3.8). The smaller size of substrates, *i.e.* propylene oxide (1a) and 1,2-epoxybutane (1b), could exhibit exceptional conversion to cyclic carbonates, but the selectivity was apparently low. On the other hand, the longer and the bulky substrates obviously showed ineffective performance with very low conversion. Therefore, nanoporous framework 2_{Eu} can provide potential molecular sieve properties for the diffusion of bulky epoxides.



Fig. 3.23 (a) Percentage conversion (dark gray) and selectivity (light gray) for the recycling experiments of 2_{Eu} , (b) the observed PXRD, (c) FT-IR spectra, and (d) SEM image with elemental mappings of 2_{Eu} (selected element only Eu, Cl, and Br) after the eighth successive measurements.

	$\mathbb{R}_{20 \text{ mmol}}^{O} + C$	$O_2 = \frac{\frac{0.25 \text{ mol}\% 2_{EI}}{2.5 \text{ mol}\% n - Bu_4}}{80 \text{ °C}, 4 \text{ h}}$	$\xrightarrow{a^+}_{R} \xrightarrow{(2)}$)	
	Substrate	% conversion (SD)	% selectivity (SD)	TON	TOF
1a		100^{\dagger}	NA ^{††}	$\mathrm{NA}^{\dagger\dagger}$	$NA^{\dagger\dagger}$
1b	\checkmark	99(±2)	58(±14)	214	54
1c		75(±3)	100	300	75
1d		72(±14)	100	288	72
1e		40(±8)	100	160	40
1f		39(±5)	100	155	39

Table 3.8 Catalytic activities of 2_{Eu} in CO2 cycloaddition reactions with several epoxidesunder solvent-free and ambient CO2 pressure conditions

[†]Data from one experiment

^{††}Unidentified by-product

3.3.7.2 Influence of lanthanide contraction on the catalytic performance

To investigate the effect of diverse Lewis acidic strength introduced by the diminishing in ionic radii of Ln^{III} through the lanthanide contraction, the catalysis performances of 2_{Ln} ($Ln = Pr^{III}$, Nd^{III} , Sm^{III} , Eu^{III} , and Gd^{III}) were evaluated (Table 3.9). The increasing conversion, TON, and TOF values from 2_{Pr} to 2_{Gd} was observed (Table 3.9; entry 1-5). Through the effect of lanthanide contraction with the gradual diminishing in ionic radii from Pr^{III} to Gd^{III} , the enhanced catalysis tendency should be ascribed to the improved acidic strength of Ln^{III} . The highest performance catalyst of 2_{Gd} provided the

TON and TOF of 695 and 174 h^{-1} , respectively. On the basis of these results, the significance of Lewis acidic Ln^{III} in the catalysis by the nanoporous 2_{Pr} to 2_{Gd} has nonetheless been emphasized. Interestingly, the selectivity of difference in Lewis acidity strength of the reactions was not as vividly modulated as the conversion suggesting the formation of the by-product outside the framework.

Table 3.9 Catalytic activities of 2_{Ln} in CO₂ cycloaddition reactions with ECH under solvent-free and ambient CO₂ pressure conditions

$Cl \underbrace{\bigcirc}_{20 \text{ mmol}}^{O} + CO_2 \underbrace{\xrightarrow{0.12 \text{ mol}\% \text{ catalyst } + \\ \frac{2.5 \text{ mol}\% \text{ n-Bu}_4 \text{NBr}}{80 \text{ °C 4 h}}}_{80 \text{ °C 4 h}} Cl \underbrace{\bigcirc}_{O}$							
Entry	2_{Ln} catalyst	%Conversion (SD)	% selectivity (SD)	TON [‡]	TOF [‡]		
1	2 _{Pr}	77 (±1)	82 (±4)	504	125		
2	2_{Nd}	84 (±5)	86 (±4)	580	145		
3	2_{Sm}	86 (±3)	88 (±2)	604	150		
4	2 _{Eu}	89 (±1)	87 (±1)	623	156		
5	2_{Gd}	98 (±1)	89 (±4)	695	174		
6	2 _{Pr/Gd}	94 (±4)	86 (±6)	692	173		
7	2 _{Pr/Eu}	95 (±1)	87 (±5)	698	174		

[‡]Calculated from the average conversion and selectivity

Compared to the homometallic framework, the dilution of the stronger Lewis acidic Ln^{III} (Eu^{III} and Gd^{III}) in the framework by weaker acidic Pr^{III}, *i.e.* **2**_{Pr/Gd} (Table 3.9; entry 6) and $2_{Pr/Eu}$ (Table 3.9; entry 7), significantly promoted the conversion about *ca*.17% and 18%, respectively. The synergistic effect of the fluctuation in Lewis acidic strength within the framework could be thus essential to the catalyst. With mixing different Ln^{III} within the coordination framework, the creation of framework defects should also be considered. It could be concluded that introducing different Ln^{III} into the same coordination framework without the disruption of the structure may be benificial for their coordination chemistry and can be an additional route to regard in designing new catalysts.

Referring to the mechanism of the CO₂ cycloaddition reactions with epoxides as depicted in Fig. 3.24, the ring-opening process the determining step to indicate the performance of the catalysts [52,53]. Therefore, the strong interaction between catalyst and substrate should provide high catalytic performance. In addition, the accessibility of the substrate and available Lewis acidic sites are also critical. These factors might depend on the number of vacant coordination sites on Ln^{III}. To affirm this assumption, the computational calcuculation were supported [54], which suggested the less crowded environments of Ln^{III} centers as effective catalytic sites.



Fig. 3.24 Diagram showing a possible mechanism of the CO₂ cycloaddition reactions with epoxides (ECH as a model epoxide).

Catalyst	Catalyst	Co-Cat.	Temp.	Time	Р	Conversion	Selectivity	TON	TOF	Pore Size	Ref.
	(mol%)	(mol%)	(°C)	(h)	(atm)	(%)	(%)		(h^{-1})	(nm)	
Ce ₂ NDC ₃	2.4	1.8	RT	8	1	92	NA	372	47	1.3	[55]
PCN-900(Eu)-CoTCPP-	0.12	4.32	50	12	1	74	NA	617	31	1.3	[56]
CoBPYDC											
1.Gd	7.5	2.5	60	12	1	97	NA	13	1	1	[57]
$[TbL(H_2O)_2] \cdot H_2O\}_n$	3.5	3.5	70	12	1	>99	NA	29	2	0.78×1.21	[58]
NUC-25	2.5	5	75	8	1	99	NA	40	5	0.54 - 1.04	[59]
[Me ₂ NH ₂][Cd(dtztp) _{0.5}	0.2	2	80	4	1	97	NA	485	121	1 - 1.59	[60]
$(HCOO)] \cdot 1.5DMF \cdot H_2O$											
$Mn_4(L)_2(H_2O)_4]_n \cdot 4DMF \cdot H_2O$	0.5	10	80	8	1	99	NA	198	25	1.13×0.88	[61]
										1.07×0.87	
${[Co(TCPB)_{0.5}(H_2O)] \cdot DMF}_n$	0.10	2.5	80	9	1	99	NA	990	110	1.14	[62]
NUC-7	0.2	5	80	24	1	98	98	632	23	1.18 & 1.26	[63]
(I ⁻)Meim-UiO-66	0.52	-	120	24	1	100	93	179	7.5	0.6, 1.1, 3.4	[64]
Zn(Bmic)(AT)	0.54	1.45	80	6	5	98	98	180	30	0.59,0.73,1.18	[65]
$[Zn_3(L)_3(H_2L)\cdot 2DMF\cdot H_2O]$	0.27	0.9	80	5	10	97	98	360	72	0.98×1.1	[66]
Zn-MOF	0.2	2	80	4	20	97	NA	485	121	0.6 & 1.2	[67]
Cr-MIL-101-[BuPh ₃ P]Br	0.045	-	120	2	20	98.3	99.3	2184	1092	2.4	[68]
gea-MOF-1	0.15	0.15	120	6	20	89	NA	593	99	1.12×0.56	[69]
										2.48×1.46	
										2.24×2.24	

Table 3.10 Conversion, selectivity (if available), and the corresponding TON and TOF values reported for nanoporous CPs catalysts employed in the CO_2 cycloaddition with ECH under various conditions

3.4 Conclusion

To enlarge porosity of LnCPs, di-nitro-BPDC^{2–} was used to fabricate a new series of [Ln₄(di-nitro-BPDC)₄(NO₂)₃(OH)(H₂O)₅]·(solvent) (**2**_{Ln}; Ln = Pr^{III}, Nd^{III}, Sm^{III}, Eu^{III}, and Gd^{III}). The effective one-dimensional window openings varying in sizes from 2.0 × 1.1 nm² to 1.5 × 1.1 nm² have been achieved. Owning to the large porosity and the accessible –NO₂ groups, the framework exhibited capacity in proton conduction, temperature and humidity sensing, CO₂ gas adsorption and selectivity, and catalytic properties.

Regarding the proton conductivity, 2_{Gd} exhibited superprotonic conduction with a maximum value of 6.17×10^{-2} S·cm⁻¹ at 1V applied voltage, 55 °C, and 99 RH%. Based on proton conduction, the sensing of humidity and temperature were shown to be excellent within a working range of 55 to 99 RH% at fixed 25°C and 25 to 40 °C at fixed 99 RH%, respectively. Its outstanding reusability was indicated with 97% repeatability and the standard deviations of 1 RH% and 0.42 °C. The fabricated LnCPs also showed excellent selectivity with CO₂ over other gases (N₂, O₂, and H₂), which could motivate the study of catalytic activities with CO₂, *i.e.* CO₂ cycloaddition reaction with epoxides. The excellent performances with high selectivity under ambient CO₂ pressure and 80 °C manifested through the maximum TON of 1,106 and TOF of 276 h⁻¹ for **2**_{Eu}. The effect of lanthanide contraction was also investigated providing the increased performance with the gradual diminishing in ionic radii from Pr^{III} to Gd^{III}. These could suggest a further design to achieve effective catalysts.

3.5 References

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CHAPTER 4

Tunable Installation of Lanthanide Cubane Clusters in Porous Supramolecular Frameworks Based on Multicarboxylate Metalloligands

4.1 Introduction

In recent years, the high-nuclearity lanthanide clusters in LnCPs becomes the most interesting research frontier because of their unique properties and fantastic architectures. In some cases, the combination of lanthanide clusters with bridging ligands provides porous LnCPs [1,2]. Among a variety of lanthanide clusters, lanthanide clusters with bridging hydroxide groups, *i.e.* $Ln_x(OH)_y$, have attracted much attention in various fields owing to their intriguing chemical, physical, and magnetic properties as well as their potential applications [3-5]. A variety of $Ln_x(OH)_y$ clusters with different compositions have been rationalized by a ligand-controlled hydrolytic approach. Using suitable ligands can limit and control the degree of hydrolysis of Ln^{III} ions leading to the formation $Ln_x(OH)_y$ clusters ability [6-9]. The available literature indicated that carboxylate ligands, amino acids, Schiff base ligands, and other polydentate ligands are reasonable options for supporting the $Ln_x(OH)_y$ clusters formation [9].

Regarding the ligand-control approach for constructing tetranuclear clusters, *i.e.* $Ln_4(OH)_4$ cubanes, the contributions of the ligands, *e.g.* their identity, charge, polarity, polarizability, and binding ability, are critical [10]. Known examples of the ligands are limited, *e.g.* amino acid; L-aspartic acid, L-glutamic acid, DL-cysteine, L-valine, proline, [6,11-13], Schiff-base complexes [14,15], and aromatic carboxylic acid; nicotinic acid (Hnic) [16], isonicotinic acid (HIN) [7], 4-(4-carboxyphenyl)-1,2,4-triazole ligand (Hcpt) [17], and 4,4',4''-tricarboxytriphenylamine (H₃TCA) [18]. However, the synthetic approach for controlling the number of lanthanide ions in the clusters is still challenging

due to the large pH dependency of lanthanides and their exceptional flexibility of coordination spheres and geometries.

The study on the template effects, *e.g.* anions and pores, to control the generating Ln₄(OH)₄ cubane clusters would be an alternative pathway for overcoming the limitations of conventional methods [19,20]. Concerning pore as a template, the discrete metallosupramolecular complexes could be regarded as an effective candidate to control the Ln₄(OH)₄ cubane formation through the tunable porosity by modification of weak interactions, *e.g.* hydrogen bonding [21]. Literature examples of such pores as a template in discrete metallosupramolecular systems are, however, quite rare. To the best of our knowledge, there is only one example published by Konno's group, *i.e.* Ln_{0.33}[Ln₄(μ_3 -OH)₄(μ_2 -OAc)₃(H₂O)₇][**L**^{**Rh**}]·**n**H₂O (**6**L**n**) when [**L**^{**Rh**}]⁶⁻ = [Zn₄O{Rh(L-cys)₃}₄]⁶⁻, Ln = Gd^{III}, Tb^{III}, Dy^{III}, Er^{III}, Ho^{III}, Tm^{III}, Yb^{III}, and Lu^{III} [22]. In this system, the lanthanide cubane clusters are formed in specific spaces surrounded by free carboxylate groups belonging to the metalloligand K₆[Zn₄O{Rh(L-cys)₃}₄]·**n**H₂O (K₆[**L**^{**Rh**}]·**n**H₂O). Nevertheless, lanthanide cubane clusters were formed only for the late lanthanide ions. While cluster formation was not observed for the early lanthanide ions, *i.e.* La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, and Eu^{III}, which had formula as Ln₂[**L**^{**Rh**}]·**n**H₂O (**5**_{Ln}).

To expand the range of the cubane cluster formation in the lanthanide series, in this chapter, a new discrete anionic metalloligand $K_6[Zn_4O\{Ir(L-cys)_3\}_4]\cdot 48H_2O$ ($K_6[L^{Ir}]\cdot 48H_2O$) (Fig. 4.3a) was designed. The heavier Ir^{III} centers would differently direct the interactions for the packing structure, particularly hydrogen bonding, allowing a different porosity. Moreover, the higher energy of the *d*-*d* excited state of Ir^{III} compared to Rh^{III} may diminish the emission quenching due to the energy transfer to the *d*-*d* excited state [23]. The enhancement of photoluminescent properties in $K_6[L^{Ir}]\cdot 48H_2O$ and the lanthanide cubane clusters in the frameworks was thus investigated. The study of the interaction between Ln^{III} in the cubane clusters was also presented through magnetic measurements.

4.2 Experimental

4.2.1 Synthesis (Δ_{LLL})₄-K₆[Zn₄O{Ir(L-cys)₃}₄]·48H₂O (K₆[L^{Ir}]·48H₂O)

A suspension of 0.25 g (0.44 mmol) of Δ_{LLL} -H₃[Ir(L-cys)₃], which was synthesized following the literature [24], in 10 mL of DI. water was prepared at room temperature. With continuous stirring, 0.38 g (4.6 mmol) of ZnO and 0.23 g (1.0 mmol) of ZnBr₂ were added. The pH of the mixture was adjusted to *ca*. 8 to 9 using 0.5 M of KOH aqueous solution. The mixture was stirred at room temperature for 2 h and then filtered to remove insoluble ZnO. The colorless filtrate was concentrated to a small volume with a rotary evaporator, followed by adding a large amount of ethanol to precipitate the product. The resulting pale-white-yellow solid was filtrated and dried at room temperature (65% yield). The crude product was dissolved in 0.1 M of KOAc aqueous solution and then recrystallized *via* diffusing ethanol vapor for 3 days. ¹H NMR (500 MHz, D₂O): δ (ppm) 2.62 – 2.65 (*dd*, 1H) and 2.77 – 2.82 (*t*, 1H) (methylene signals) and 3.26 – 3.29 (*dd*, 1H) (methine signal). Anal. Calcd for K₆[L^{Ir}]·48H₂O = K₆C₃₆Zn₄Ir₄O₇₃H₁₅₆S₁₂N₁₂: C, 12.09; H, 4.23; N, 4.71. Found: C, 12.09; H, 4.40; N, 4.70.

4.2.2 Synthesis of Ln₂[L^{Ir}]·nH₂O (3_{Ln}; Ln = Sc^{III}, La^{III}, Ce^{III}, Pr^{III}, and Nd^{III}) and Ln_{0.33}[Ln₄(OH)₄(OAc)₃(H₂O)₇][L^{Ir}]·nH₂O (4_{Ln}; Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Er^{III}, Ho^{III}, Tm^{III}, Yb^{III}, Lu^{III}, and Y^{III})

50 mg (14.0 μ mol) of freshly prepared single crystals of K₆[L^{Ir}]·48H₂O were immersed in 10 mL of a 0.02 M of Ln(OAc)₃ in ethanol:water (3:1) solution in a sealed glass vessel and allowed to stand at room temperature for a week. The solution was then changed to 5 mL of a 0.1 M Ln(OAc)₃ aqueous solution while keeping the crystals in the vessel for 2 days to complete the reaction. The resulting block crystals of **3**_{Ln} or **4**_{Ln} were then collected by filtration and then washed with DI. water.

Anal. Calcd for $Sc_2[L^{Ir}] \cdot 23H_2O$ (**3**_{Sc}) = $C_{36}H_{106}Sc_2N_{12}O_{48}Ir_4S_{12}Zn_4$: C, 14.51; H, 3.58; N, 5.63%. Found: C, 14.53; H, 3.41; N, 5.30%.

Anal. Calcd for La₂[L^{Ir}]·30H₂O (**3**_{La}) = C₃₆H₁₂₀La₂N₁₂O₅₅Ir₄S₁₂Zn₄: C, 13.12; H, 3.67; N, 5.10%. Found: C, 13.09; H, 3.57; N, 4.98%.

Anal. Calcd for Ce₂[L^{Ir}]·29H₂O (**3**ce) = C₃₆H₁₁₈Ce₂N₁₂O₅₄Ir₄S₁₂Zn₄: C, 13.18; H, 3.63; N, 5.13%. Found: C, 13.05; H, 3.52; N, 5.00%.

Anal. Calcd for $Pr_2[\mathbf{L}^{Ir}] \cdot 26H_2O(\mathbf{3}_{Pr}) = C_{36}H_{112}Pr_2N_{12}O_{51}Ir_4S_{12}Zn_4$: C,13.42; H, 3.49; N, 5.20%. Found: C, 13.44; H, 3.39; N, 4.97%.

Anal. Calcd for $Nd_2[L^{Ir}] \cdot 35H_2O(3_{Nd}) = C_{36}H_{130}Nd_2N_{12}O_{60}Ir_4S_{12}Zn_4$: C, 12.73; H, 3.85; N, 4.95%. Found: C, 12.66; H, 3.67; N, 4.79%.

Anal. Calcd for $Sm_{0.33}[Sm_4(OH)_4(OAc)_3][L^{Ir}] \cdot 22H_2O(4_{Sm}) = C_{42}H_{117}Sm_{4.33}N_{12}O_{57}$ Ir₄S₁₂Zn₄: C, 13.39; H, 3.13; N, 4.46%. Found: C, 13.43; H, 3.27; N, 4.43%.

Anal. Calcd for $Eu_{0.33}[Eu_4(OH)_4(OAc)_3][L^{Ir}] \cdot 21H_2O$ (4_{Eu}) = $C_{42}H_{115}Eu_{4.33}N_{12}O_{56}$ Ir₄S₁₂Zn₄: C, 13.42; H, 3.03; N, 4.47%. Found: C, 13.58; H, 3.18; N, 4.46%.

Anal. Calcd for $Gd_{0.33}[Gd_4(OH)_4(OAc)_3][L^{Ir}] \cdot 28H_2O$ (4_{Gd}) = $C_{42}H_{129}Gd_{4.33}N_{12}O_{63}$ Ir₄S₁₂Zn₄: C, 12.91; H, 3.33; N, 4.30%. Found: C, 12.94; H, 3.35; N, 4.27%.

Anal. Calcd for $Tb_{0.33}[Tb_4(OH)_4(OAc)_3][L^{Ir}] \cdot 32H_2O$ (**4**_{Tb}) = $C_{42}H_{137}Tb_{4.33}N_{12}O_{67}$ Ir₄S₁₂Zn₄: C, 12.66; H, 3.46; N, 4.22%. Found: C, 12.59; H, 3.33; N, 4.32%.

Anal. Calcd for $Dy_{0.33}[Dy_4(OH)_4(OAc)_3][L^{Ir}] \cdot 21H_2O(4_{Dy}) = C_{42}H_{115}Dy_{4.33}N_{12}O_{56}$ Ir₄S₁₂Zn₄: C, 13.26; H, 3.05; N, 4.42%. Found: C, 13.26; H, 3.11; N, 4.44%.

Anal. Calcd for Ho_{0.33}[Ho₄(OH)₄(OAc)₃][**L**^{Ir}]·23H₂O (**4**_{H₀}) = C₄₂H₁₁₉Ho_{4.33}N₁₂O₅₈ Ir₄S₁₂Zn₄: C, 13.10; H, 3.12; N, 4.37%. Found: C, 13.03; H, 3.10; N, 4.44%.

Anal. Calcd for $\text{Er}_{0.33}[\text{Er}_4(\text{OH})_4(\text{OAc})_3][\mathbf{L}^{Ir}] \cdot 29\text{H}_2\text{O}$ (**4**_{Er}) = C₄₂H₁₃1Er_{4.33}N₁₂O₆₄ Ir₄S₁₂Zn₄: C, 12.71; H, 3.33; N, 4.24%. Found: C, 12.59; H, 3.24; N, 4.38%.

Anal. Calcd for $Tm_{0.33}[Tm_4(OH)_4(OAc)_3][L^{Ir}]\cdot 25H_2O$ (4_{Tm}) = $C_{42}H_{123}Tm_{4.33}N_{12}O_{60}$ Ir₄S₁₂Zn₄: C, 12.92; H, 3.18; N, 4.31%. Found: C, 12.96; H, 3.21; N, 4.49%.

Anal. Calcd for $Yb_{0.33}[Yb_4(OH)_4(OAc)_3][L^{Ir}] \cdot 25H_2O$ (4_{Yb}) = $C_{42}H_{123}Yb_{4.33}N_{12}O_{60}$ Ir₄S₁₂Zn₄: C, 12.86; H, 3.16; N, 4.29%. Found: C, 12.79; H, 3.16; N, 4.50%. Anal. Calcd for $Lu_{0.33}[Lu_4(OH)_4(OAc)_3][L^{Ir}] \cdot 24H_2O$ (4Lu) = $C_{42}H_{121}Lu_{4.33}N_{12}O_{59}$ Ir₄S₁₂Zn₄: C, 12.90; H, 3.12; N, 4.30%. Found: C, 12.80; H, 3.10; N, 4.39%.

Anal. Calcd for $Y_{0.33}[Y_4(OH)_4(OAc)_3][L^{Ir}] \cdot 28H_2O$ (**4**_Y) = $C_{42}H_{129}Y_{4.33}N_{12}O_{63}$ Ir₄S₁₂Zn₄: C, 13.97; H, 3.60; N, 4.66%. Found: C, 13.81; H, 3.43; N, 4.73%.

4.2.3 X-ray crystallography

Crystallographic data sets of $K_6[L^{Ir}]$ ·48H₂O, 3_{Ln} and 4_{Ln} were collected at 100(2) K using a Rigaku XtaLAB Synergy Custom X-ray Diffractometer equipped with a Hypix-6000HE hybrid pixel array detector ($\lambda = 0.71075$ Å) excepting 4_{Sm}, 4_{Dy}, and 4_{Er}, which were collected using a synchrotron X-ray source at the BL02B1 beamline in SPring-8 (Japan) ($\lambda = 0.7005$ Å). Data collection and reduction of K₆[L^{Ir}]·48H₂O, 3_{Ln} and 4_{Ln} were performed using CrysAlisPro 1.171.40.60a [25]. Empirical absorption corrections were applied using the SADABS program [26]. For 4_{Sm} , 4_{Dy} , and 4_{Er} , the absorption correction was applied using the Mulabs program [27]. All structures were solved by the intrinsic phasing method within the SHELXT program [28] and refined on F^2 by the full-matrix least-squares technique using the SHELXL program [29] via the Olex² interface [30]. Hydrogen atoms, except those of water molecules and hydroxides, were calculated and placed using riding models. Due to the high disordering at Sm3A and Sm3B in 4sm, three OAc⁻ molecules in the cubane cluster could not be assigned. However, the present OAc⁻ moieties in 4sm were confirmed by elemental analysis. The crystallographic and refinement data for $K_6[L^{Ir}]$ ·48H₂O, 3_{Ln} , and 4_{Ln} are summarized in Table 4.1, Table 4.2, and Table 4.3, respectively.

Crystal formula	$C_{36}H_{60}Ir_4K_6N_{12}O_{50}S_{12}Zn_4$
Formula weight	3110.59
Crystal System	Cubic
Space group	<i>P</i> 2 ₁ 3
<i>a</i> (Å)	23.4451(5)
$V(Å^3)$	12887.1(8)
Ζ	4
$\rho/\text{g·cm}^{-3}$	1.603
Radiation λ (Å)	0.71073
Temperature (K)	100(2)
Crystal size (mm ³)	0.15×0.15×0.15
F(000)	5976.0
Data/ restraints/parameters	10633/16/295
Flack parameter	0.006(6)
R _{int}	0.0455
$R_1 (I > 2\sigma(I))^{\dagger}$	0.0641
wR_2 (all data) ^{† †}	0.1771

Table 4.1 Crystallographic and refinement data of $K_6[L^{Ir}]$ ·48H₂O

 $^{\dagger}R_1 = \Sigma |(|Fo| - |Fc|)| / \Sigma (|Fo|). ^{\dagger \dagger}wR = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$

	3 _{Sc}	3 _{La}	3 _{Ce}	3 _{Pr}	3 _{Nd}
Crystal formula	C ₃₆ H ₅₇ Ir ₄ N ₁₂ O ₃₉	$C_{36}H_{60}La_2Ir_4N_{12}$	$C_{36}H_{60}Ce_2Ir_4N_{12}$	$C_{36}H_{60}Pr_2Ir_4N_{12}$	$C_{36}H_{60}Nd_2Ir_4N_{12}$
	$S_{12}Sc_2Zn_4$	$O_{41}S_{12}Zn_4$	$O_{44}S_{12}Zn_4$	$O_{38}S_{12}Zn_4$	$O_{42}S_{12}Zn_4$
Formula weight	2786.85	3009.81	3060.20	2965.78	3036.44
Crystal System	Cubic	Cubic	Cubic	Cubic	Cubic
Space group	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3
<i>a</i> (Å)	23.2847(4)	23.4807(3)	23.3229(4)	23.4111(3)	23.6007(3)
$V(Å^3)$	12624.4(7)	12945.9(5)	12686.7(7)	12831.1(5)	13145.4(5)
Ζ	4	4	4	4	4
$ ho/\text{g}\cdot\text{cm}^{-3}$	1.466	1.544	1.602	1.535	1.534
Radiation λ (Å)	0.71073	0.71073	0.71073	0.71073	0.71073
Temperature (K)	100(2)	100(2)	100(2)	100(2)	100(2)
Crystal size (mm ³)	$0.04 \times 0.04 \times 0.04$	0.09×0.12×0.12	0.12×0.12×0.12	0.15×0.15×0.12	0.09×0.09×0.09
F(000)	5301.0	5400.0	5792.0	5608.0	5744.0
Data/ restraints/parameters	8926/20/207	10545/11/287	9771/3/292	10193/8/279	10519/12/299
Flack parameter	0.002(10)	0.009(5)	0.004(6)	0.007(6)	0.030(5)
R _{int}	0.0526	0.0267	0.032 5	0.0342	0.0307
$R_1 (I > 2\sigma(I))^{\dagger}$	0.0868	0.0689	0.0692	0.0721	0.0699
wR_2 (all data) ^{††}	0.2573	0.1972	0.2083	0.2217	0.1952

Table 4.2 Crystallographic and refinement data of 3_{Ln}

[†] $R_1 = \Sigma |(|Fo|-|Fc|)|/\Sigma (|Fo|)$. ^{††} $wR = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$

	4 _{Sm}	4 _{Eu}	4 _{Gd}	4 _{Tb}
Crystal formula	$\begin{array}{c} C_{36}H_{60}Sm_{4.33}Ir_{4}N_{12}O_{73}S_{12}\\ Zn_{4}\\ 2782,07\end{array}$	C ₄₂ H ₆₉ Eu _{4.33} Ir ₄ N ₁₂ O ₆₄ S ₁₂ Zn ₄	C ₄₂ H ₆₉ Gd _{4.33} Ir ₄ N ₁₂ O ₆₉ S ₁₂ Zn ₄	C ₄₂ H ₆₉ Tb _{4.33} Ir ₄ N ₁₂ O ₇₃ S ₁₂ Zn ₄
Formula weight	3782.97	3839.07	3941.98	4013.21
Crystal System	Cubic	Cubic	Cubic	Cubic
Space group	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3
<i>a</i> (Å)	23.748(3)	23.7101(2)	23.7624(2)	23.7712(2)
$V(Å^3)$	13392(5)	13329.1(3)	13417.5(3)	13432.4(3)
Ζ	4	4	4	4
$\rho/\text{g·cm}^{-3}$	1.876	1.910	1.951	1.984
Radiation λ (Å)	0.7005	0.71073	0.71073	0.71073
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal size (mm ³)	0.02×0.03×0.04	0.06×0.06×0.09	0.12×0.12×0.09	0.09×0.06×0.09
F(000)	7106.0	7239.0	7416.0	7514.0
Data/ restraints/parameters	10268/8/333	11149/18/327	10548/11/364	11079/17/369
Flack parameter	0.056(12)	0.012(6)	-0.006(5)	-0.005(5)
$R_{\rm int}$	0.1194	0.0465	0.0305	0.0452
$R_1 (I > 2\sigma(I))^{\dagger}$	0.0848	0.0785	0.0642	0.0568
wR_2 (all data) [†] [†]	0.2539	0.2377	0.1880	0.1610

Table 4.3 Crystallographic and refinement data of 4_{Ln}

[†] $R_1 = \Sigma |(|Fo|-|Fc|)|/\Sigma (|Fo|)$. ^{††} $wR = [\Sigma w (Fo^2 - Fc^2)^2 / \Sigma w (Fo^2)^2]^{1/2}$

	4 _{Dy}	4 _{Ho}	4_{Er}	4 _{Tm}
Crystal formula	$C_{42}H_{60}Dy_{4.33}Ir_4N_{12}O_{57}S_1$	$C_{42}H_{68.67}Ho_{4.33}Ir_4N_{12}O_{73}S_1$	$C_{42}H_{69}Er_{4.33}Ir_4N_{12}O_{58}S_1$	$C_{42}H_{69}Tm_{4.33}Ir_{4}N_{12}O_{8}$
	$_2Zn_4$	$_2Zn_4$	$_2Zn_4$	$_{1}S_{12}Zn_{4}$
Formula weight	3811.62	4038.90	3809.32	4184.55
Crystal System	Cubic	Cubic	Cubic	Cubic
Space group	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3
<i>a</i> (Å)	23.6018(14)	23.798(3)	23.5792(11)	23.6918(4)
$V(\text{\AA}^3)$	13147(2)	13,478.2(5)	13109.5(18)	13298.2(7)
Ζ	4	4	4	4
$\rho/\text{g·cm}^{-3}$	1.926	1.990	1.930	2.090
Radiation λ (Å)	0.7005	0.71073	0.7005	0.71073
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Crystal size (mm ³)	0.08×0.08×0.06	0.09×0.09×0.09	0.1×0.09×0.06	0.09×0.12×0.12
F(000)	7127.0	7595.0	7134.0	7887.0
Data/ restraints/parameters	10078/24/303	10887/11/343	6303/15/328	10341/11/402
Flack parameter	0.019(9)	-0.009(5)	0.012(8)	-0.005(5)
$R_{ m int}$	0.0742	0.0315	0.0525	0.0354
$R_1 (I > 2\sigma(I))^{\dagger}$	0.0682	0.0525	0.0515	0.0504
wR_2 (all data) ^{† †}	0.1938	0.1455	0.1455	0.1312

Table 4.3 Crystallographic and refinement data of 4_{Ln} (cont.)

[†] $R_1 = \Sigma |(|Fo|-|Fc|)|/\Sigma (|Fo|)$. ^{††} $wR = [\Sigma w (Fo^2 - Fc^2)^2/\Sigma w (Fo^2)^2]^{1/2}$

	4 _{Yb}	4 _{Lu}	4 _Y
Crystal formula	$C_{42}H_{69}Yb_{4.33}Ir_4N_{12}O_{72}S_{12}Zn_4$	$C_{42}H_{69}Lu_{4.33}Ir_4N_{12}O_{78}S_{12}Zn_4$	$C_{42}H_{69}Y_{4.33}Ir_4N_{12}O_{73}S_{12}Zn_4$
Formula weight	4058.35	4163.15	3710.07
Crystal System	Cubic	Cubic	Cubic
Space group	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3	<i>P</i> 2 ₁ 3
<i>a</i> (Å)	23.5740(3)	23.7498(3)	23.7790(3)
$V(\text{\AA}^3)$	13100.9(5)	13396.1(5)	13445.6(5)
Ζ	4	4	4
$\rho/\text{g}\cdot\text{cm}^{-3}$	2.058	2.064	1.833
Radiation λ (Å)	0.71073	0.71073	0.71073
Temperature (K)	100(2)	100(2)	100(2)
Crystal size (mm ³)	0.1×0.1×0.08	0.06×0.06×0.04	0.09×0.09×0.06
F(000)	7616.0	7826.0	7111.0
Data/ restraints/parameters	10847/17/355	11266/2/405	10956/7/404
Flack parameter	0.009(5)	-0.001(5)	0.003(4)
R _{int}	0.0419	0.0381	0.0342
$R_1 (I > 2\sigma(I))^{\dagger}$	0.0613	0.0467	0.0457
wR_2 (all data) ^{† †}	0.1643	0.1245	0.1233

Table 4.3 Crystallographic and refinement data of 4_{Ln} (cont.)

4.3 Results and discussions

4.3.1 Synthesis, characterizations, and crystal structures of K₆[L^{Ir}]·48H₂O

The colorless block crystals of $K_6[\mathbf{L}^{Ir}]\cdot 48H_2O$ were yielded by the recrystallization process with ethanol vapor diffusion in a KOAc aqueous solution. The phase purity of the product could be affirmed by H-NMR spectra (Fig. 4.1). To confirm the presence of the ligands in $K_6[\mathbf{L}^{Ir}]\cdot 48H_2O$, the IR spectrum of $K_6[\mathbf{L}^{Ir}]\cdot 48H_2O$ was shown in Fig. 4.2. The characteristic C=O stretching band at 1610 cm⁻¹ indicated fully deprotonated carboxylate groups on the L-cys ligand.

The single crystal X-ray analysis revealed that the complex crystallizes in the cubic $P2_13$ space group. The structure contained four Δ_{LLL} -[Ir(L-cys)₃]³⁻ units binding with tetrahedral {Zn₄O}⁶⁺ core (Fig. 4.3a). Each Zn^{II} ion was coordinated with three S atoms from three different units of Δ_{LLL} -[Ir(L-cys)₃]³⁻ and one central O atom resulting in [L^{Ir}]⁶⁻ anionic complex with a diameter size of *ca*. 15.32 Å similar to that of [L^{Ir}]⁶⁻ anionic complex (*ca*. 15.34 Å) [31]. Through hydrogen bonding N—H····O_{COO} (average N····O distance of 2.90 Å) with six adjacent [L^{Ir}]⁶⁻ units (Fig. 4.3b), the three-dimensional supramolecular framework of [L^{Ir}]⁶⁻ was built up (Fig. 4.3c). The framework showed the effective window opening with the approximate window opening size of *ca*. 6.0 × 12.2 Å² and 53 % porosity. The pore`s surface was decorated by free carboxylate groups from five [L^{Ir}]⁶⁻ units (Fig. 4.3d).

To balance the charge of the framework, six disordered K^+ ions, *i.e.* K1, K2, K3, K4, K5, and K6, were located in different spaces. Site A was occupied by the K1 ion, which was surrounded by three positional disordered K2 ions (Fig. 4.4a). The disordered K3 ion was located at site B and was also surrounded by three positional disordered K4 ions as shown in Fig. 4.4b. Other K5 and K6 ions were coordinated with carboxylate groups as shown in Fig. 4.4a and 4.4c. Due to the high disordering of the water solvent molecules in the framework, the number of water solvents was affirmed by elemental analysis.



Fig. 4.1 ¹H NMR spectrum of the as-synthesized $K_6[L^{Ir}]$ ·48H₂O in D₂O.



Fig. 4.2 FT-IR spectrum of $K_6[L^{Ir}]$ ·48H₂O.



Fig. 4.3 Crystal structures of $K_6[L^{Ir}]$ ·48H₂O. (a) $[L^{Ir}]^{6-}$ metalloligand, (b) surrounded by six adjacent $[L^{Ir}]^{6-}$ through N—H····O hydrogen bonds (black dash line), (c) the packing framework through hydrogen bonding, (d) window opening decorated with COO⁻ functional groups from five $[L^{Ir}]^{6-}$ metalloligands, and (e) O····O distance at pore space (site A) for available creating lanthanide cubanes; H atoms were omitted for clarity. Ir (brown), Zn (olive-green), S (yellow), N (blue), C (light grey), O (red), and $[L^{Ir}]^{6-}$ (light blue).



Fig. 4.4 Perspective views of disordered (a) K1, K2 occupied at site A and K6, (b) K3 and K4 occupied at site B, and (d) K5 coordinated with carboxylate groups in $K_6[L^{Ir}]$ ·48H₂O. H atoms were omitted for clarity. Ir (brown), Zn (olive-green), S (yellow), N (blue), C (light grey), and O (red).

A shorter averaged N····O distance of 2.86 Å was observed in the relating $[\mathbf{L}^{\mathbf{Rh}}]^{6-}$ framework, leading to the stronger N—H····O_{COO} hydrogen bonding in the packing structure. The stronger interaction in the $[\mathbf{L}^{\mathbf{Rh}}]^{6-}$ framework resulted in a smaller porosity of *ca*. 46 % and a smaller opening window of *ca*. 4.7 × 11.5 Å². The heavier metal center of the Ir^{III} ion might stabilize the Ir^{III}—N bond rather than the Rh^{III} center [32,33], which is supported by the shorter Ir^{III}—N distance *ca*. 2.101 to 2.112 Å in the $[\mathbf{L}^{\mathbf{Ir}}]^{6-}$ compared to the $[\mathbf{L}^{\mathbf{Rh}}]^{6-}$ (Rh^{III}—N = 2.107 to 2.113 Å in). Therefore, it is assumed that the hydrogen

bond donor ability of the NH₂ groups on the Ir^{III} center might be reduced leading to the weaker and longer N—H····O_{COO} interactions in the crystal packing of K₆[**L**^{Ir}]·48H₂O having the larger interstitial space *ca*. 4.69 Å (Fig. 4.3e). The available space might be significant for further developing the construction of lanthanide cubane clusters in a confined space.

4.3.2 Synthesis, crystal structures, and characterizations of 3Ln

Freshly prepared crystals of $K_6[L^{Ir}]$ ·48H₂O were soaked in 0.02 M Ln(OAc)₃ solutions in ethanol/H₂O 3:1 for a week (Ln = Sc^{III}, La^{III} – Nd^{III}). To complete the reaction, the mixture was then changed to 0.1 M aqueous solutions of Ln(OAc)₃. The retained shape of the crystals was shown after the treatment. The same profiles of FT-IR spectra suggested the unchanged structure and functional groups on the ligand (Fig. 4.5).

The crystal structure of 3_{La} is descript as a representative of those 3_{Ln} since they are all isostructural with the same crystal formula of Ln₂[L^{Ir}]·nH₂O. Based on the single crystal X-ray diffraction analysis, 3_{La} revealed the cubic $P2_13$ space groups featuring a high disorder at La^{III} centers in the framework. The structure of 3_{La} contains two La^{III} ions, which disorder between four crystallographic sites of La1A, La1B, La2A, and La2B, and one $[L^{Ir}]^{6-}$ metalloligand. As shown in Fig. 4.6a, the three disordered La1A ions were coordinated with three COO⁻ groups from three $[L^{Ir}]^{6-}$ metalloligands at the space site A surrounded by one disordered La1B ion. The space site B was occupied by three La2A ions coordinated with three [L^{Ir}]⁶⁻ metalloligands. Whilst the La2B was only coordinated with other COO⁻ groups (Fig. 4.6b). Therefore, the disordered La^{III} ions only played a role to balance the charge of the anionic crystal framework. The framework structure of 3_{La} could thus form a three-dimensional supramolecular framework (Fig. 4.6c), which was similar to the pristine framework of $K_6[L^{Ir}]$ ·48H₂O. The framework structures of other 3_{Ln} were shown in Fig. 4.7. Quite similar PXRD profile of 3_{Ln} compared with the pristine framework was also verified (Fig. 4.11). The diffraction peaks in the PXRD patterns of 3_{Ln} could be indexed based on the generated patterns from their single crystal data. The number of Ln^{III} in 3_{Ln} was affirmed via XRF results, which indicate the ratio of 2 to 1 for Zn to Ln (Table 4.4). The coordinating water and crystallizing water in the void were affirmed based on the elemental analysis.

Samples	Ratio Zn to Ln from XFA data	Ratio Zn to Ln from crystal structures
3 _{Sc}	4:1.6	4:2
3 _{La}	4:1.0	4:2
3Ce	4:1.5	4:2
3 _{Pr}	4:1.4	4:2
3 _{Nd}	4:1.9	4:2
4_{Sm}	4:2.5	4:4.33
$4_{\rm Eu}$	4:2.7	4:4.33
4_{Gd}	4:3.4	4:4.33
4 _{Tb}	4:3.3	4:4.33
4_{Dy}	4:3.2	4:4.33
4 _{Ho}	4:3.5	4:4.33
4 _{Er}	4:3.9	4:4.33
4_{Tm}	4:3.8	4:4.33
4_{Yb}	4:4.3	4:4.33
4_{Lu}	4:3.6	4:4.33
$4_{\rm Y}$	4:4.2	4 : 4.33

Table 4.4 Comparisons of ratio Zn to Ln in XFA data and crystal structure data of 3_{Ln} and 4_{Ln}



Fig. 4.5 FT-IR spectra of 3_{Ln} (red line) and 4_{Ln} (black line).



Fig. 4.6 Perspective views of the disordered La1A, La1B, La2A, and La2B ions occupied at the (a) pore site A and (b) pore site B in 3_{La} , and (c) packing framework of 3_{La} with Ln^{III} ions occupied (space-filling) at the sites A and B; H atoms were omitted for clarity. La (dark blue), Ir (brown), Zn (olive-green), S (yellow), N (blue), C (light grey), O (red), and [L^{Ir}]^{6–} (light blue); symmetry code (i) 0.5+x, 1.5-y, 1-z, (ii) 1-x, -0.5+y, 1.5-z, (iii) 0.5+x, 0.5-y, 1-z, (iv) 0.5-x, 1-y, -0.5+z.



Fig. 4.7 Perspective views of the Ln^{III} ions occupied (space-filling) at the sites A and B in (a) 3_{Sc} , (b) 3_{Ce} , (c) 3_{Pr} , and (d) 3_{Nd} ; Sc (orange), Ce (pink), Pr (green), Nd (purple), and H atoms of $[L^{Ir}]^{6-}$ (light blue) were omitted for clarity.

4.3.3 Synthesis, crystal structures, and characterizations of 4Ln

The same treatment procedures as $\mathbf{3}_{Ln}$ were followed for $\mathbf{4}_{Ln}$ (Ln = Sm^{III} – Lu^{III}, Y^{III}). Their crystal shape remained intact after the reaction. The high stabilities in water were also observed indicating the formation of the exceptionally strong Ln^{III}—O bond. The same profiles of FT-IR spectra as those of $\mathbf{3}_{Ln}$ and $K_6[\mathbf{L}^{Ir}]\cdot 48H_2O$ were treasured (Fig. 4.5).

Based on the single crystal X-ray diffraction, the same cubic $P2_13$ space group of 4_{Ln} was provided. However, cubane structures of Ln^{III} ions in a three-dimensional

framework were observed in 4_{Ln} , which is markedly different from the disordered Ln^{III} ions in 3_{Ln} . From PXRD profiles of 4_{Ln} , the intensity at (111) and (200) indices were however different from those 3_{Ln} indicating the different packing structures. The crystal structure of 4_{Lu} is selected to descript as a representative of those 4_{Ln} . The structure of 4_{Lu} features a three-dimensional framework, which was constructed from the formation of $[Lu_4(OH)_4(OAc)_3(H_2O)_7]^{5+}$ cluster in the interstices of the host framework of $[L^{Ir}]^{6-}$. In each tetranuclear cubane cluster, four molecules of bridging μ_3 -OH⁻ were coordinated to form the $[Lu_4(OH)_4]^{8+}$ cubane structure showing the average Lu^{III} —O bond length of 2.26 Å and Lu…Lu distance of 3.67 Å. Based on the bond length of Lu^{III}—OH and in the Cambridge structural database [34] for tetranuclear Lu₄(OH)₄ cubanes compounds with hydroxide-bridging, the bridging species of each cubane in 4_{Lu} should be assigned as OH^- rather than O^{2-} and H_2O . In each cubane cluster, three OAc^- molecules were bridged three pairs of Ln1 to form the [Lu₄(OH)₄(OAc)₃]⁵⁺ structure. To fulfill the coordination sphere of Lu^{III} centers, seventh molecules of coordinating water were coordinated around the cluster resulting in [Lu₄(OH)₄(OAc)₃(H₂O)₇]⁵⁺ formula (Fig. 4.8a). The derived cluster was transfixed by three coordinating carboxylate groups from three $[\mathbf{L}^{\mathbf{Ir}}]^{6-}$ anions showing averaged Lu^{III}—O_{COO} bond length of 2.28 Å (Fig. 4.8b).

As shown in Fig. 4.8e, the $[Lu_4(OH)_4(OAc)_3(H_2O)_7]^{5+}$ could function as a building block to construct a three-dimensional porous framework through the forming coordination bond with bridging COO⁻ groups in the $[\mathbf{L}^{Ir}]^{6-}$ motif. The calculated 34% porosity and pore size $ca. 5.6 \times 9.9 \text{ Å}^2$ of 4_{Lu} could be also estimated. The N—H····O_{COO} hydrogen bond in **4**_{Lu} was calculated *ca*. 2.96 Å. The average N—H····O_{COO} hydrogen bonds of other 4_{Ln} were summarized in Table 4.6. Due to the highly disordered water solvents occupied in the void, the number of those water molecules was confirmed via elemental analysis. Another disordered Lu3 ion was occupied in other voids (Fig. 4.8d) with total occupying ratio of 33% leading to a formula of a $Lu_{0.33}[Lu_4(OH)_4(OAc)_3(H_2O)_7][L^{Ir}] \cdot nH_2O$. This formula corresponded well with elemental analysis data. Other 4_{Ln} frameworks were shown in Fig. 4.9.

Concerning the space for creating the cubane cluster, which was surrounded by three $[\mathbf{L}^{\mathbf{Ir}}]^{6-}$ metalloligands as shown in Fig. 4.3e, the pore size might play an important

role to limit the border for tuning the lanthanide-hydroxide cluster formation. The averaged Ln^{III}—O_{COO} bond lengths and Ln····Ln distances in the [Ln₄(OH)₄]⁸⁺ of those **4**_{Ln} (Fig. 4.10) were summarized in Table 4.5. The tendency of distances decreased in the order from **4**sm to **4**_{Lu} corresponding with the decreasing of the ionic radii of Ln^{III}, *i.e.* 0.96 Å (Sm^{III}), 0.95 Å (Eu^{III}), 0.94 Å (Gd^{III}), 0.92 Å (Tb^{III}), 0.91 Å (Dy^{III}), 0.90 Å (Ho^{III}), 0.89 Å (Er^{III}), 0.88 Å (Tm^{III}), 0.87 Å (Yb^{III}), and 0.86 Å (Lu^{III}) as well as 0.90 Å for Y^{III} [35]. The available space is, therefore, a critical factor to limit the size of lanthanide ions for tuning [Ln₄(OH)₄]⁸⁺ cubane formation. In the case of Sc^{III} ions, the ionic radii of 0.74 Å might be too small and not favor to form the cubane cluster in this confined space. To verify our assumption, the similar complex of K₆[L^{Rh}]·nH₂O processing smaller unit cell of a = 22.99 Å was compared. The bordering lanthanide cubane formation in the [L^{Rh}]^{6–} framework was limited only between Eu^{III} and Gd^{III} ions. The forming [Ln₄(OH)₄]⁸⁺ cubane clusters for La^{III}, Ce^{III}, Pr^{III}, Nd^{III}, Sm^{III}, and Eu^{III} ions could thus not be observed.

Comparison of Ln...Ln in the $[Ln_4(OH)_4]^{8+}$ and Ln^{III} —O_{COO} bonds between both 4_{Ln} and 6_{Ln} , the average Ln....Ln in 4_{Ln} were slightly shorter, but the Ln^{III}—O_{COO} bond lengths were significantly longer These differences could be due to the larger pore size of $[L^{Ir}]^{6-}$, which was estimated from O····O distance between COO⁻ groups (Fig. 4.3e), were expanded from 4.05 Å to 4.69 Å for $[\mathbf{L}^{\mathbf{Rh}}]^{6-}$ and $[\mathbf{L}^{\mathbf{Ir}}]^{6-}$, respectively. This larger cavity size could be due to the weaker and longer N-H--OCOO hydrogen bonds, i.e. average ca. 2.91 Å and 2.86 Å for $[\mathbf{L}^{Ir}]^{6-}$ and $[\mathbf{L}^{Rh}]^{6-}$, respectively, resulting in the expanded cavities in the packing structures. In addition, the N-H---OCOO hydrogen bonds in 3_{Ln} and 4_{Ln} were also compared and summarized in Table 4.6, which supported our assumptions. By using the larger pore size of the $K_6[L^{Ir}]\cdot 48H_2O$, the bordering lanthanide cubane formation was shifted to larger ionic radii between Nd^{III} and Sm^{III} as we expected. To further design and tune the formation of lanthanide cubane clusters in other platforms, the pore space is critical. The tunable porosity through the controlling hydrogen bonding interaction by replacement of M^{III} centers in metalloligands is an effective approach for further developing and controlling the border of lanthanide cubane installation rather than the conventional method.

The phase purity of those 4_{Ln} was confirmed *via* the PXRD patterns (Fig. 4.12), which showed the consistency of all the diffraction peaks with their single crystal data. To evident the number of Ln^{III} in the cubane clusters of 4_{Ln} , XRF analysis was also investigated. The results revealed the 1:1 ratio of Ln:Zn except for 4_{Sm} and 4_{Eu} , which were lower than expected. It might be due to the overlapped profiles of Sm and Eu with other elements. However, the formation of cubane in 4_{Sm} and 4_{Eu} , which were isostructural with those 4_{Ln} , was affirmed *via* PXRD profiles. Therefore, the four lanthanide ions in the cubane cluster of 4_{Ln} were verified.



Fig. 4.8 Perspective views of (a) $[Lu_4(OH)_4(OAc)_3(H_2O)_7]^{5+}$ cluster, (b) three $[L^{Ir}]^{6-}$ coordinated with the cluster, (c) the connectivity of three adjacent cubanes through $[L^{Ir}]^{6-}$ (d) disordered Lu3 ion occupied at pore site B, and (e) packing framework showing the pore size *ca*. $5.6 \times 9.9 \text{ Å}^2$ in 4_{Lu} ; H atoms were omitted for clarity. Lu (orange), Ir (brown), Zn (olive-green), S (yellow), N (light blue), C (light grey), and O (red); symmetry code (i) x, y, z.



Fig. 4.9 Packing structures of (a) 4_{Sm} , (b) 4_{Gd} , (c) 4_{Tb} , (d) 4_{Dy} , (e) 4_{Ho} , (f) 4_{Er} , (g) 4_{Tm} , (h) 4_{Yb} , and (j) 4_{Y} ; H atoms were omitted for clarity. [L^{Ir}]⁶-(light gray).



Fig. 4.10 Perspective views of the $[Ln_4(OH)_4(OAc)_3(H_2O)_7]^{5+}$ clusters in (a) $4s_m$, (b) 4_{Eu} , (c) 4_{Gd} , (d) 4_{Tb} , (e) 4_{Dy} , (f) 4_{Ho} , (g) 4_{Er} , (h) 4_{Tm} , (i) 4_{Yb} , and (j) 4_Y .


Fig. 4.11 Simulated (red solid line) and observed (black solid line) PXRD patterns of 3_{Ln} ($\lambda = 0.8$ Å).



Fig. 4.12 Simulated (red solid line) and observed (black solid line) PXRD patterns of 4_{Ln} ($\lambda = 0.8$ Å).

Samples	Ln ^{III} —Ocoo	Ln ^{III} —Ocoo	Ln…Ln	Ln…Ln
	$(\text{\AA})^a$	$(\text{\AA})^b$	$(\text{\AA})^a$	$(\text{\AA})^b$
4_{Sm}	2.43	na	3.94	na
$4_{\rm Eu}$	2.42	na	3.83	na
4 _{Gd} or 6 _{Gd}	2.42	2.35	3.80	3.81
4ть or 6ть	2.41	2.35	3.80	3.79
4 _{Dy} or 6 _{Dy}	2.37	2.40 ^c	3.75	3.77
4 _{но} or 6 _{но}	2.31	2.31	3.74	3.75
4 _{Er} or 6 _{Er}	2.33	2.30	3.72	3.73
4 _{Tm} or 6 _{Tm}	2.30	2.31^{c}	3.70	3.73
4yb or 6yb	2.28	2.29 ^c	3.68	3.69
4 _{Lu} or 6 _{Lu}	2.28	2.26	3.67	3.68
4 Y	2.33	na	3.73	na

Table 4.5 The averaged distance of Ln^{III}—O_{COO} and Ln…Ln in the cubanes of 4_{Ln} compared to 6_{Ln}

^{*a*}Calculated from **4**_{Ln}

^bCalculated from 6Ln

^cPositional disordering at Ln^{III} centers may lead to a large deviation in the distances

Samples	N—H····O _{COO} (Å) ^a	N—H····O _{COO} (Å) ^b
3sc	2.93	na
3 _{La} or 5 _{La}	2.89	2.88
3Ce or 5Ce	2.97	2.88
3pr or 5pr	2.86	2.88
3_{Nd} or 5_{Nd}	2.95	2.87
4_{Sm} or 5_{Sm}	2.97	2.87
4 _{Eu} or 5 _{Eu}	2.92	2.84
4_{Gd} or 6_{Gd}	2.97	2.93
4ть or 6ть	2.94	2.94
4_{Dy} or 6_{Dy}	2.94	2.93
4 _{но} or 6 _{но}	2.93	2.91
4er or 6er	2.91	2.91
4 _{Tm} or 6 _{Tm}	2.93	2.90
4yb or 6yb	2.85	2.70
4Lu or 6Lu	2.96	2.88
4 _Y	2.90	na

Table 4.6 The averaged N—H····O_{COO} hydrogen bond distances in 3_{Ln} and 4_{Ln} compared to 5_{Ln} and 6_{Ln}

^{*a*}Calculated from 3_{Ln} and 4_{Ln}

^bCalculated from 5_{Ln} and 6_{Ln}

4.3.4 Photoluminescent properties of K6[L^{Ir}]·48H2O, 4Eu and 4Tb

In addition to the tuning border of lanthanide cubane formation in the supramolecular frameworks, the solid-state photoluminescent properties of K₆[L^{Ir}]·48H₂O and 4_{Ln}, *i.e.* 4_{Eu} and 4_{Tb}, were enhanced by changing the Rh^{III} to Ir^{III} centers in the metalloligands. The emission spectra of the pristine framework $K_6[L^{Ir}]$ ·48H₂O could not be observed at room temperature due to the high thermal vibration at a high temperature. At 77 K, a broad emission band with a maximum peak at 620 nm of $K_6[L^{Ir}]$ ·48H₂O was then shown (Fig. 4.13). This emission spectrum is tentatively assigned to the emission from the Zn_4O core structure (O_{2p} to Zn_{4s}), which shows a similar profile with the emission spectra of ZnO with a maximum peak at 515 nm but a large difference in intensity and slightly shifting peak. The photoluminescence efficiency may be promoted by increasing energy transfer populations through the bonding with S atoms from L-cys ligand of $[Ir(L-cys)_3]^{3-}$ moieties (S_{3p} to Zn_{4s}) [36-38], resulting in the 4.4 % quantum yield at 77 K of K₆[L^{Ir}]·48H₂O. A slightly red-shifted excitation band from 360 to 370 nm for ZnO and $K_6[L^{Ir}]$ 48H₂O, respectively, could be also contributed by the bonding with S atoms of L-cys ligands, which may reduce the band gap energy by mixing between S_{3p} and Zn_{4s} orbitals [36,37]. In addition, the shifted emission spectrum at 620 nm of $K_6[L^{Ir}]$ 48H₂O from 515 nm of ZnO might be due to a much larger of vibrational perturbation of the discrete supramolecular framework, leading to a larger stokes shifts compared to the bulk ZnO structure [39].

For non-emissive character of $K_6[L^{Rh}]\cdot nH_2O$ even at low temperature, the *d-d* transition band with maximum bands at 324 and 370 nm (Fig 4.14), which overlapped with the charge transfer band of the Zn₄O core structure. Therefore, the irradiation of excitation light at the ZnO charge transfer band promotes unfavorable energy transfer to the non-emissive *d-d* excited state of Rh^{III}, rather than the photoluminescence from radiative ZnO excited state. This led to the silent of photoluminescence in K₆[L^{Rh}]·nH₂O. Whereas, the K₆[L^{Ir}]·48H₂O does not possess any absorption bands over 400 nm due to the higher energy of the *d-d* excited state of Ir^{III}. This could account for the enhancement of photoluminescence in K₆[L^{Ir}]·48H₂O [23]. In addition, the heaver Ir^{III} centers may also

help to improve the emission efficiency by promoting the intersystem crossing (ISC) from singlet state to triplet state charge transfer rather than Rh^{III} centers [40,41].

The room temperature emission was observed under the excitation at 395 and 370 nm for 4_{Eu} and 4_{Tb} , respectively. Their emission spectra revealed the characteristic f-ftransitions of 4_{Eu} (${}^{5}D_{0} \rightarrow {}^{7}F_{J}$, J = 1 - 4), 4_{Tb} (${}^{5}D_{4} \rightarrow {}^{7}F_{J}$, J = 6 - 3) with calculated quantum yields of 0.22 and 0.21% for 4_{Eu} and 4_{Tb}, respectively (Fig. 4.15a and 4.15b). At 77 K, the broad emission band from the metalloligand $[L^{Ir}]^{6-}$ overlapped with the *f-f* emissions of Eu^{III} and Tb^{III} with 3.57 and 3.96 % quantum yield for 4_{Eu} and 4_{Tb} , respectively (Fig. 4.15c and 4.15d). To clarify the interaction between both $[\mathbf{L}^{Ir}]^{6-}$ and Ln^{III} , the diffused reflectance spectra of 4_{Eu} and 4_{Tb} compared with $K_6[L^{Ir}]$ ·48H₂O were investigated. The broad absorption band tails covering 200 to 400 nm with a maximum peak at 240 nm were observed (Fig. 4.16), indicating the absorption band of $K_6[L^{Ir}]$.48H₂O, *i.e.* charge transfer and d-d transition in Ir^{III} centers. The similar profiles of 4_{Eu} and 4_{Tb} were confirmed with a slightly red shifting of the maximum peak from 240 to 250 nm, which contributed to the changes in rigidity due to coordinating to Ln^{III} centers. These adsorptions only slightly overlapped with the excitation and emission spectra of 4_{Eu} and 4_{Tb} , resulting in the independent emission of both emissions of $[L^{\text{Ir}}]^{6-}$ metalloligand and *f*-*f* emissions of Eu^{III} and Tb^{III} in 4_{Eu} and 4_{Tb} . In other words, the energy transfer from the metalloligand to Ln^{III} is negligible. However, to further enhance the photoluminescent properties of 4_{Eu} and 4_{Tb}, the modified coordination sphere on Ln^{III} centers for introducing other antenna ligands should be proposed. Compared to the previous system of $[\mathbf{L}^{\mathbf{Rh}}]^{6-}$ metalloligand, *i.e.* **5**_{Eu} and **6**_{Tb}, the characteristic *f*-*f* emissions could not be allowed due to the overlapping between its adsorption processing peaks at ca. 324 and 370 nm (Fig. 4.14) and excitation wavelength of *f*-*f* emissions Eu^{III} (λ_{ex} 395 nm) and Tb^{III} (λ_{ex} 370 nm). Thus, insufficient excitation to Ln^{III} centers had occurred for **5**_{Eu} and **6**_{Tb}. Whereas, the $[L^{Ir}]^{6-}$ metalloligand showed negligible absorption at those wavelengths. Therefore, the characteristic f-f emissions of Eu^{III} and Tb^{III} in $[L^{Ir}]^{6-}$ metalloligand could be enhanced.



Fig. 4.13 Excitation (λ_{em} 620 nm; black dot line) and emission (λ_{ex} 370 nm) (black solid line) spectra of K₆[**L**^{Ir}]·48H₂O at 77 K compared to the excitation (λ_{em} 515 nm; red dot line) and emission (λ_{ex} 360 nm; red dot line) spectra of ZnO.



Fig. 4.14 Absorption spectra in water of $K_6[\mathbf{L}^{\mathbf{Rh}}] \cdot nH_2O$ (black line) and $K_6[\mathbf{L}^{\mathbf{Ir}}] \cdot 48H_2O$ (red line).



Fig. 4.15 Solid-state excitation (black line) and emission spectra of (a) 4_{Eu} at room temperature, (b) 4_{Tb} at room temperature, (c) 4_{Eu} at 77 K, and (d) 4_{Tb} at 77 K.



Fig. 4.16 Diffused reflectance spectra of $K_6[L^{Ir}]$ ·48H₂O (black line), 4_{Eu} (solid red), and 4_{Tb} (solid green).

4.3.5 Magnetic properties of 3Ln and 4Ln

The temperature-dependent magnetic susceptibilities of 3_{Ln} and 4_{Ln} complexes were performed in the temperature range 2 – 300 K at 1000 Oe applied magnetic field. As shown in Fig. 4.17, the $\chi_m T$ values at 300 K of 3_{Ln} were 1.49 (3_{Ce}), 3.49 (3_{Pr}), and 4.00 (3_{Nd}) cm³K·mol⁻¹ consisting of the expected values as 1.60, 3.20, and 3.28 cm³K·mol⁻¹ [35], respectively. A similar fashion of 4_{Ln} was also observed. At 300 K, the $\chi_m T$ values were 1.05, 32.30, 42.10, 53.50, 53.60, 43.50, 24.30, and 9.63 cm³K·mol⁻¹ for 4_{Sm} , 4_{Gd} , 4_{Tb} , 4_{Dy} , 4_{Ho} , 4_{Er} , 4_{Tm} , and 4_{Yb} , respectively. To study the interaction between each Ln^{III} in the cubane clusters, the typical $\chi_m T$ profiles and calculated $\chi_m T$ values from isolated Ln^{III} ions were considered. The calculated $\chi_m T$ values of those 4_{Ln} with isolated ions are following, *i.e.* 0.39 (Sm^{III}), 34.12 (Gd^{III}), 51.18 (Tb^{III}), 61.36 (Dy^{III}), 60.92 (Ho^{III}), 49.71 (Er^{III}), 30.96 (Tm^{III}), and 11.13 (Yb^{III}) cm³K·mol⁻¹. As the result of these considerations, the interaction between each Ln^{III} center in the cubane clusters was found to be therefore almost silent, probably due to the cubic arrangement of the Ln^{III} ions. The absence of magnetic interactions among the Ln^{III} centers is beneficial to the future application for the magnetic cooling materials.

As an exception, the magnetic properties of 4_{Sm} largely differ from the prediction. These contributions to the very low spin-orbit coupling make the lower gap between the ground state and the excited state, which allowed the thermal accessibility to other low-lying paramagnetic levels with higher magnetic moment than the ${}^{6}H_{5/2}$ ground state, *e.g.* ${}^{6}H_{7/2}$ state [35].



Fig. 4.17 The $\chi_m T$ vs *T* plots for 3_{Ln} and 4_{Ln} .

4.4 Conclusions

In this chapter, fine-tuning of the crystal porosity of the metallosupramolecular framework of $K_6[L^M] \cdot nH_2O$ was achieved through the metal substitution of the metalloligand from Rh^{III} to Ir^{III}. By using the heavier Ir^{III} center, the Ir^{III}—N bonds were more stabilized rather than Rh^{III}—N bonds, leading to the longer N—H····O_{COO} hydrogen bonding in $K_6[L^{Ir}] \cdot 48H_2O$. The enlarged pore size of 6.0×12.2 Å² with larger porosity of 53% was achieved in $K_6[L^{Ir}] \cdot 48H_2O$. The extension of the space resulted in the expansion of the available space for the lanthanide cubane clusters formation. As a result,

a series of clusters $[Ln_4(\mu_3-OH)_4(\mu_2-OAc)_3(H_2O)_7]^{5+}$ in $[\mathbf{L}^{\mathbf{Ir}}]^{6-}$ framework was obtained after the border between Nd^{III} and Sm^{III} ions, whilst the cubane formation in $[\mathbf{L}^{\mathbf{Rh}}]^{6-}$ framework could be synthesized after the border between Eu^{III} and Gd^{III} [22]. In the conventional approach, *i.e.* ligand-controlled hydrolysis, the creation of the lanthanidehydroxide cubane clusters are achieved by (i) reducing the number of coordinating water or solvent on Ln^{III} coordination sphere by occupying organic ligands and (ii) controlling pH by using suitable ligands such as amino acids. On the other hand, in our system, the control of the cubane cluster formation was readily achieved through the tuning porosity by replacing only M^{III} centers of K₆[$\mathbf{L}^{\mathbf{M}}$]·nH₂O metalloligand. This concept is exceptionally beneficial for further design and synthesis of the lanthanide hydroxide clusters in other platforms.

Furthermore, the Ir^{III} could improve the photoluminescent properties by avoiding the quenching effect due to the *d*-*d* transition. The photoluminescence of 4_{Eu} and 4_{Tb} was also enhanced. For the development of photoluminescent properties of 4_{Eu} and 4_{Tb} , the modified coordination sphere of Ln^{III} would be a potential approach for further work. The magnetic properties of 3_{Ln} and 4_{Ln} indicated almost silent interaction between Ln^{III} ions in the cubane structures, which would be significantly essential for the magnetic cooling application.

4.5 References

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CHAPTER 5

Concluding Remarks

In this research, several porous lanthanide coordination polymers (LnCPs) with enhanced solid-state functionalities were newly synthesized through the structural modifications of conventional ligand systems as shown in Fig. 5.1: (i) the introduction of auxiliary poa⁻ ligand to disrupt dense framework (Chapter 2), (ii) the insertion $-NO_2$ groups on the lengthy BPDC²⁻ ligand to enlarge the porosity (Chapter 3), and (iii) the replacement of Rh^{III} centers by Ir^{III} ion in [Zn₄O{Rh(L-cys)₃}]⁶⁻ ([**L**^{Rh}]⁶⁻) metalloligands to control the void through the modified hydrogen bonding interactions (Chapter 4). These ligands are different in their rigidity, length, the number of coordinating groups, and functional groups providing different pore sizes, dimensions of the framework structures, and different functionalities of LnCPs. The plausible applications of the resulting LnCPs were also explored.

In chapter 2, the combination of two ligands, dicarboxylate 2,5-pydc²⁻ and monocarboxylate poa⁻ was proposed to synthesize microporous LnCPs. Under the appropriate synthesis condition, a new series of robust porous LnCPs [Ln(poa)(2,5-pydc)(H₂O)₂]-3H₂O (**1**_{Ln}; Ln = Eu^{III}, Gd^{III}, Tb^{III}, and Sm^{III}) were obtained. In the crystal structure, the one-dimensional coordination polymer structure of **1**_{Ln} was further assembled into three-dimensional supramolecular structures *via* hydrogen bonding and π - π interactions. The supramolecular structure provided the one-dimensional channel with an effective opening size of 4.2 × 5.5 Å². It should be mentioned that the opening channels in **1**_{Ln} are quite larger than those of our previous LnCPs having only 2,5-pydc²⁻ ligand, *i.e.* [Ln_{1.375}(pydc)₂(H₂O)₄] (Ln = Sm^{III}, Eu^{III}, Gd^{III}, Tb^{III}, Dy^{III}, Ho^{III}, and Er^{III}), which are non-porous. This result indicated that the poa⁻ ligand act as a fulfilled ligand in coordination with Ln^{III} centers, which expanded the pore space in the framework. Motivated by specific pore size, it is suitable to act as a molecular sieve for ammonia. The decorated channel by the functional groups of the ligand, *i.e.* phenyl and free O atom

from poa⁻ as well as O atoms from the carboxylate groups on 2,5-pydc²⁻ was also indicated as possible interaction sites for ammonia adsorption. Encouraged by the excellent photoluminescent properties of these complexes, which are enhanced by effective sensitization of those ligands to Ln^{III} , and high selective interaction with ammonia, the sensing application was investigated. For further practical use, the fabricating film of 1_{Eu} /PVA was then established. The ammonia sensing of 1_{Eu} /PVA showed a working range of 0.50 – 10.0 ppm with an excellent sensitivity of 4.04 %·ppm⁻¹ and a detection limit of 0.14 ppm. The accuracy and precision of this sensing manifested through the percentage recoveries of 103 - 111% and %*RSD* of 1.5 - 8.2%. The proposed interacting sites were supported by the DFT calculation and spectroscopic data. The reusable 1_{Eu} /PVA film for ammonia sensing could be achieved in at least ten cycles with 95 - 97% repeatability.

In chapter 3, the use of a longer divergent dicarboxylate ligand di-nitro-BPDC²⁻ was adopted to achieve the nanoporous LnCPs with expanded pore size. As a result, a new series of $[Ln_4(di-nitro-BPDC)_4(NO_2)_3(OH)(H_2O)_5] \cdot (solvent)_n (2_{Ln}; Ln = Pr^{III}, Nd^{III}, Nd^{III})$ Sm^{III}, Eu^{III}, and Gd^{III}) were successfully synthesized and characterized. The threedimensional frameworks with the effective one-dimensional window opening size of 2.0 \times 1.1 nm² to 1.5 \times 1.1 nm² were observed. The channel surface was decorated by NO₂ LnCPs BPDC^{2–}. with non-functionalized groups. In previous e.g. $[Tb(BPDC)_2] \cdot (CH_3)_2NH_2$, the pore size was small (*ca.* 5.6 × 8.3 Å²). The small opening channels and low porosity in [Tb(BPDC)₂]·(CH₃)₂NH₂ might be due to the crowded environment around Ln^{III} center. On the other hand, in this system the introduction of electron-rich -NO₂ functional groups on the *di*-nitro-BPDC²⁻ ligand, prevented the crowned coordination sphere around Ln^{III} centers through the electronic repulsion, resulting in the large pore size. Prompted by their large porosity and available -NO2 groups along the channel, several potential functionalities were surveyed, proton conductions, temperature and humidity sensing, CO₂ gas adsorption and selectivity, and catalytic properties. On the proton conductivities results, 2_{Gd} exhibited a maximum value of 6.17×10^{-2} S·cm⁻¹ (1 V applied voltage, 55 °C, and 99 RH%), which could be accounted for a superprotonic conducting material. The compound 2_{Gd} was also applicable as the humidity and temperature sensor with a working range of 55 – 99 RH%

at 25 °C and 25 – 40 °C at 99 RH%, respectively. The reusable abilities of 2_{Gd} for both humidity and temperature sensing manifested through the repeatability of 97% with the standard deviations of 1 RH% and 0.42 °C. Moreover, these complexes showed excellent selectivity with CO₂ over other gases (N₂, O₂, and H₂). This exceptional selectivity could be encouraged for further catalytic activities with CO₂. In this work, the CO₂ cycloaddition reaction with epoxides was selected as a model reaction to study the catalytic performance of these complexes. The excellent performances with high selectivity under ambient CO₂ pressure and 80 °C manifested through the maximum TON of 1,106 and TOF of 276 h⁻¹ for **2**_{Eu}. The effect of lanthanide contraction was also investigated providing the increased performance with the gradual diminishing in ionic radii from Pr^{III} to Gd^{III}. Due to the high disordering in the framework, DFT calculation was performed on the evaluation of the possible catalytic sites, which suggested the effective catalytic sites at larger available space around Ln^{III} centers. These would be very helpful for the further development of a catalyst for this reaction.

In chapter 4, the tuning of the porosity in the supramolecular frameworks based on multicarboxylate metalloligands $K_6[L^{Rh}] \cdot nH_2O$ was examined. The use of a heavier Ir^{III} instead of Rh^{III} led to the highly stabilized Ir^{III}-N bonds resulting in the weaker interaction of N—H····O_{COO} hydrogen bonding in the $[L^{Ir}]^{6-}$ framework. The metal substitution caused the enhancement of the porosity from 46% to 53% and the pore size from 4.7 × 11.5 Å² to 6.0 × 12.2 Å². As in the case of K₆[L^{Rh}]·nH₂O, lanthanide cubane clusters were grown inside the crystal lattice of $K_6[L^{Ir}]$ ·nH₂O, leading to a series of LnCPs clusters, with the lanthanide hydroxide cubane $Ln_{0.33}$ [Ln₄(µ₃-OH)₄(µ₂- $OAc_{3}(H_{2}O_{7})[L^{Ir}] \cdot nH_{2}O (4_{Ln}, [L^{Ir}]^{6-} = [Zn_{4}O\{Ir(L-cys)_{3}\}_{4}]^{6-}, Ln = Sm^{III} to Lu^{III}, and$ Y^{III}). However, due to the improvement of the porosity in the $[\mathbf{L}^{Ir}]^{6-}$ framework, the border of the cubane clusters installation had been successfully modified from Eu^{III}/Gd^{III} to Nd^{III}/Sm^{III}. By replacing the metal centers from Rh^{III} to Ir^{III}, the photoluminescence properties of this class of LnCPs could also be improved.

To sum up the present study, three practical approaches for the design and fabrication of porous LnCPs were proposed. 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, the use of multicarboxylate metalloligands could provide exceptional possibilities to control the hydrogen-bonded framework by the metal substitution in the metalloligands.



Fig. 5.1 Diagrams summarizing all reported LnCPs in this thesis.

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