

ห้องสมุดงานวิจัย สำนักงานคณะกรรมการวิจัยแห่งชาติ



E41063



DESIGN OF METAL ORGANIC FRAMEWORKS (MOFs) AND  
THEIR FUNCTIONS TOWARDS CATALYSIS AND  
ANION-EXCHANGE

MR.PONGTHIPUN PHUENGPхай

A THESIS FOR THE DEGREE OF DOCTOR OF PHILOSOPHY  
KHON KAEN UNIVERSITY

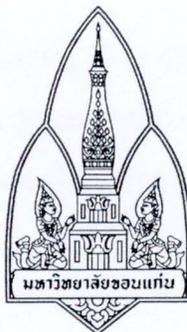
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**MR. PONGTHIPUN PHUENGPхай**

**A THESIS SUBMITTED IN PARTIAL FULFILLMENT OF THE REQUIREMENTS  
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**Thesis Title:** Design of Metal Organic Frameworks (MOFs) and Their Functions  
Towards Catalysis and Anion-exchange

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### บทคัดย่อ

**E41063**

งานวิจัยนี้มีวัตถุประสงค์เพื่อความเข้าใจเชิงลึกเกี่ยวกับหลักการของการออกแบบและการสังเคราะห์โครงข่ายโลหะอินทรีย์ (MOFs) ที่เกิดจากการรวมกันของลิแกนด์ 4,4'-ไบไพรีดีนและหมู่บังคับโมโนคาร์บอกซิเลต ที่ทำหน้าที่เป็นสะพานร่วมกับโลหะแทรนซิชัน และศึกษาถึงอิทธิพลของลิแกนด์คาร์บอกซิเลตที่ส่งผลต่อโครงสร้างโดยรวมของโคออร์ดิเนชันพอลิเมอร์พร้อมศึกษาถึงหน้าที่ของผลิตภัณฑ์ที่สังเคราะห์ได้

จากการรวมกันของหน่วยโคออร์ดิเนชันซิงค์(II)-4,4'-ไบไพรีดีน และคอปเปอร์(II)-4,4'-ไบไพรีดีนกับลิแกนด์สะพานฟอร์มेट อะซิเตต และโพรพิโอเนต ทำให้เกิดผลิตภัณฑ์ใหม่ของโครงข่ายโลหะอินทรีย์ทั้งสองระบบ ผลการศึกษาพบว่าสามารถสังเคราะห์โคออร์ดิเนชันพอลิเมอร์ของซิงค์(II)-4,4'-ไบไพรีดีน-คาร์บอกซิเลต ที่มีโครงสร้างหลากหลายได้ 11 ตัวอย่าง ได้แก่ โครงข่าย 3 มิติ  $\{[Zn_3(4,4'-bpy)_3(\mu-OOCH)_4(H_2O)_2](X)_2\}_n$  เมื่อ X คือ  $ClO_4^- \cdot H_2O$  (1),  $PF_6^-$  (2),  $BF_4^- \cdot H_2O$  (3), ชั้น 2 มิติ  $\{[Zn(4,4'-bpy)(\mu-OOCH)(H_2O)_2](CF_3SO_3)(H_2O)\}_n$  (4) ชั้น 2 มิติแบบสลับ  $\{[Zn_4(4,4'-bpy)_4(\mu-OOCH)_5(H_2O)_5](NO_3)_3(4,4'-bpy)_2(H_2O)_3\}_n$  (5), สายโซ่แบบบันไดสามขา  $\{[Zn_3(4,4'-bpy)_3(\mu-OOCCH_3)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$  (6), ชั้น 2 มิติ  $\{[Zn_3(4,4'-bpy)_4(\mu-OOCCH_2CH_3)_4](ClO_4)_2(4,4'-bpy)_2(H_2O)_4\}_n$  (7), สายโซ่สลับแบบเกลียวคู่  $\{[Zn_3(4,4'-bpy)_4(\mu-OOCC_2H_5)_4(H_2O)_2](PF_6)_2(H_2O)_2\}_n$  (8), ชั้น 2 มิติ  $\{[Zn_2(4,4'-bpy)_2(\mu-OOCC_2H_5)_2(OH)(H_2O)](BF_4)(H_2O)_2\}_n$  (9), สายโซ่แบบบันไดคู่  $\{[Zn_2(4,4'-bpy)_2(\mu-OOCC_2H_5)_2(H_2O)_2](CF_3SO_3)_2\}_n$  (10) และสายโซ่สลับแบบเกลียวคู่  $\{[Zn_3(4,4'-bpy)_4(\mu-OOCC_2H_5)_4(H_2O)_2](NO_3)_2(H_2O)_3\}_n$  (11) รวมทั้งโคออร์ดิเนชันพอลิเมอร์ของคอปเปอร์(II)-4,4'-ไบไพรีดีน-คาร์บอกซิเลต อีก 9 ตัวอย่าง ได้แก่ ชั้น 2 มิติแบบเกลียวสามแขน  $\{[Cu_3(4,4'-bpy)_2(\mu-OOCH)_4(H_2O)_2](X)_2(H_2O)_6\}_n$  เมื่อ X คือ  $ClO_4^-$  (12),  $PF_6^-$  (13),  $BF_4^-$  (14),  $CF_3SO_3^-$  (15), ชั้น 2 มิติแบบสลับ  $\{[Cu(4,4'-bpy)(\mu-OOCH)(NO_3)]\}_n$  (16) และ ชั้น 2 มิติแบบเกลียวสี่แขน  $\{[Cu_2(4,4'-bpy)_2(\mu-OOCCH_3)_3](X)(H_2O)\}_n$  เมื่อ X คือ  $ClO_4^-$  (17),  $PF_6^-$  (18),  $BF_4^-$  (19),  $CF_3SO_3^-$  (20) การศึกษานี้ได้แสดงให้เห็นว่าการเปลี่ยนแปลงหมู่คาร์บอก

**E41063**

ซีเลตจากลิแกนด์ฟอร์เมโต เป็นอะซิเตโตและโพรพิโอเนโตนั้น มีผลต่อการเกิดโครงข่ายโลหะอินทรีย์ที่แตกต่างกันอย่างชัดเจน ทั้งนี้เป็นผลเนื่องมาจากปัจจัยทางสเตอริกของหมู่คาร์บอกซีเลต การศึกษาสมบัติเชิงความร้อนและเชิงแสง การแลกเปลี่ยนแอนไอออน และสมบัติการเร่งปฏิกิริยารวมถึงพฤติกรรม การเปลี่ยนแปลงทางโครงสร้าง พบว่าสาร 6-9 และ 11 แสดงพฤติกรรม การเปลี่ยนแปลงทางโครงสร้างจากสถานะผลึกสู่สถานะผลึก หลังการไล่และใส่กลับโมเลกุลน้ำที่เป็นเกสต์ สารประกอบซิงค์(II) และคอปเปอร์(II) แสดงสมบัติการแลกเปลี่ยนแอนไอออนและมีสมบัติการคัดสรรชนิดของแอนไอออน ขณะที่พบว่าเฉพาะสาร 1 แสดงสมบัติการแลกเปลี่ยนแอนไอออนแบบย้อนกลับอย่างสมดุลในสารละลายได้ นอกจากนี้พบว่าสารประกอบซิงค์(II) ยังแสดงสมบัติการเป็นตัวเร่งปฏิกิริยาแบบวิวิธพันธ์ของปฏิกิริยาไฮยาโนซิลิเลชันที่ดี โดยแสดงค่าเปอร์เซ็นต์คอนเวอร์ชันที่สูงสำหรับสารตั้งต้นอะเซทัลดีไฮด์ในสารละลายไดคลอโรมีเทน พร้อมทั้งแสดงสมบัติการคัดสรรขนาดของสารตั้งต้นอีกด้วย ในทางตรงกันข้ามสารประกอบคอปเปอร์(II) แสดงสมบัติเป็นตัวเร่งปฏิกิริยาและการคัดสรรขนาดของสารตั้งต้นได้น้อย สำหรับสารตั้งต้นอะเซทัลดีไฮด์ในปฏิกิริยาไฮยาโนซิลิเลชัน

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**Thesis Advisors:** Assoc. Prof. Dr. Sujittra Youngme, Prof. Dr. Jan Reedijk

## ABSTRACT

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The aim of this research was to gain more insight into the design and synthesis of metal organic frameworks assembled from the combination of **4,4'-bpy** and monocarboxylate-regulator as a bridge and transition metal ions and to investigate the influence of the monocarboxylate ligands on the overall solid-state structure of coordination polymers. Their functional properties have been investigated in details.

The combination of framework-builder coordination moiety (zinc(II)-**4,4'-bpy** and copper(II)-**4,4'-bpy**) with respectively formate, acetate and propionate ligands provides two series of novel metal organic frameworks. Eleven zinc(II)-**4,4'-bpy**-carboxylate coordination polymers, *i.e.* the 3D frameworks  $\{[\text{Zn}_3(\mathbf{4,4'-bpy})_{3.5}(\mu\text{-OOCH})_4(\text{H}_2\text{O})_2](\text{X})_2\}_n$  when  $\text{X} = \text{ClO}_4^- \cdot \text{H}_2\text{O}$  (**1**),  $\text{PF}_6^-$  (**2**),  $\text{BF}_4^- \cdot \text{H}_2\text{O}$  (**3**), the 2D layer  $\{[\text{Zn}(\mathbf{4,4'-bpy})(\mu\text{-OOCH})(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)(\text{H}_2\text{O})\}_n$  (**4**), the 2D zig zag layer  $\{[\text{Zn}_4(\mathbf{4,4'-bpy})_4(\mu\text{-OOCH})_5(\text{H}_2\text{O})_5](\text{NO}_3)_3(\mathbf{4,4'-bpy})_2(\text{H}_2\text{O})_3\}_n$  (**5**), the 1D three-leg ladder  $\{[\text{Zn}_3(\mathbf{4,4'-bpy})_3(\mu\text{-OOCCH}_3)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$  (**6**), the 2D layer  $\{[\text{Zn}_3(\mathbf{4,4'-bpy})_4(\mu\text{-OOCCH}_2\text{CH}_3)_4](\text{ClO}_4)_2(\mathbf{4,4'-bpy})_2(\text{H}_2\text{O})_4\}_n$  (**7**), the double-stranded zig zag chain  $\{[\text{Zn}_3(\mathbf{4,4'-bpy})_4(\mu\text{-OOCCH}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{PF}_6)_2(\text{H}_2\text{O})_2\}_n$  (**8**), the 2D layer  $\{[\text{Zn}_2(\mathbf{4,4'-bpy})_2(\mu\text{-OOCCH}_2\text{H}_5)_2(\text{OH})(\text{H}_2\text{O})](\text{BF}_4)(\text{H}_2\text{O})_2\}_n$  (**9**), the double ladders chain  $\{[\text{Zn}_2(\mathbf{4,4'-bpy})_2(\mu\text{-OOCCH}_2\text{H}_5)_2(\text{H}_2\text{O})_2](\text{CF}_3\text{SO}_3)_2\}_n$  (**10**) the double-stranded zig zag chain  $\{[\text{Zn}_3(\mathbf{4,4'-bpy})_4(\mu\text{-OOCCH}_2\text{H}_5)_4(\text{H}_2\text{O})_2](\text{NO}_3)_2(\text{H}_2\text{O})_3\}_n$  (**11**) and nine copper(II)-**4,4'-bpy**-carboxylate coordination polymers, the triple-stranded layers  $\{[\text{Cu}_3(\mathbf{4,4'-bpy})_2(\mu\text{-OOCH})_4(\text{H}_2\text{O})_2](\text{X})_2(\text{H}_2\text{O})_6\}_n$  when  $\text{X} = \text{ClO}_4^-$  (**12**),  $\text{PF}_6^-$  (**13**),  $\text{BF}_4^-$  (**14**),  $\text{CF}_3\text{SO}_3^-$  (**15**), the zig zag 2D layer  $\{[\text{Cu}(\mathbf{4,4'-bpy})(\mu\text{-OOCH})(\text{NO}_3)]\}_n$  (**16**), the quadruple-stranded layers  $\{[\text{Cu}_2(\mathbf{4,4'-bpy})_2(\mu\text{-OOCCH}_3)_3](\text{X})(\text{H}_2\text{O})\}_n$  when  $\text{X} = \text{ClO}_4^-$  (**17**),  $\text{PF}_6^-$  (**18**),  $\text{BF}_4^-$  (**19**),  $\text{CF}_3\text{SO}_3^-$  (**20**) are obtained and have been crystallographically characterized. This study shows that the change from a

formato ligand to an acetato and a propionato ligand gives rise to the formation of drastically distinct metal organic frameworks, as the result of the different steric bulk of the carboxylato unit involved. **E41063**

The thermal and optical properties, ion-exchange with structure retention and catalytic reactivity, as well as dynamic structural transformation have been investigated. Compounds **6-9** and **11** show a crystalline-to-crystalline structural transformation up on removal/reintroduction of water guest molecules. The anion exchange among zinc(II) and copper(II) compounds is found to be highly selective while anion-sensing properties in an aqueous solution is found only in **1**. Interestingly, these zinc(II) compounds are effective heterogeneous catalysts for the high-yielding cyanosilylation of acetaldehyde in dichloromethane with size-selective. Contradictory, all copper(II) compounds are less active and less selective catalysts for cyanosilylation of aldehydes.

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**The good aspects of the present thesis are dedicated to my parents and entire teaching staffs.**

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Pongthipun Phuengphai

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## LIST OF ABBREVIATIONS

|       |                                      |                   |  |
|-------|--------------------------------------|-------------------|--|
| azpy  | 4,4'-azopyridine                     | <i>g</i>          | Landé multiplet splitting factor (2.0023)              |
| bdc   | benzenedicarboxylate                 | kK                | kiloKayser ( $10^3 \text{ cm}^{-1}$ )                  |
| ben   | benzene                              | im                | imidazole  |
| bpp   | 1,3-bis(4-pyridyl)propane            | in                | isonicotinate  |
| bpy   | bipyridine                           | Oct               | distorted octahedral                                   |
| btc   | benzenetricarboxylate                | paH               | phenylacetic acid                                      |
| BTT   | 1,3,5-benzenetristetrazol-5-yl       | phz               | phenazine  |
| ca    | chloranilate                         | ptmtc             | tris(2,3,5,6-tetrachloro-4-carboxyphenyl)methylradical |
| DMIC  | 3,5-dimethylisoxazole-4-carboxylate  | py                | pyridine   |
| dmf   | dimethylformamide                    | Py <sub>2</sub> O | oxybispyridine   |
| dmpyz | 2,5-dimethylpyrazine                 | pyz               | pyrazine   |
| dmsO  | dimethylsulfoxide                    | pzdc              | pyrazine-2,3-dicarboxylate                             |
| dpe   | 1,2-di(4-pyridyl)ethylene            | salphdc           | N,N'-phenylenebis(salicylideneiminedicarboxylate)      |
| dpyg  | 1,2-di(4-pyridyl)glycol              | SUBs              | secondary building units                               |
| edtpn | ethylendiamine<br>tetrapropionitrile | suc               | succinate  |
| EPR   | Electron paramagnetic resonance      | tpt               | 2,4,6-tri(4-pyridyl)-1,3,5-triazine                    |
|       |                                      | TBP               | distorted trigonal bipyramidal                         |