DESIGN AND SYNTHESIS OF METAL ORGANIC FRAMEWORKS FOR
CO₂ SEPARATION AND CATALYSIS

by

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And approved by

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ABSTRACT OF THE DISSERTATION

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JINGMING ZHANG

Dissertation Director: Professor Jing Li

Energy demand is currently a prevalent global issue that we are facing due to the dramatic increase in both population and industrial processes around the world. Presently, over 80% of the world's energy consumption is supplied by the burning of non-renewable fossil fuels. The CO₂ gas emitted from this process has proven to contribute to global warming. One possible strategy in addressing this problem is the development of materials that can selectively capture CO₂ from flue gas mixtures. A new flexible microporous metal-organic framework (MMOF), [Zn₂(bpdc)₂(bpe)]·2DMF (bpdc = 4,4'-biphenyldicarboxylate, bpe = 1,2-bis(4-pyridyl)-ethane, DMF = N,N-dimethylformamide), was synthesized and found to selectively capture CO₂ over other small gasses (N₂, CH₄, O₂ and CO), which makes it good candidate for CO₂ separation.
Another possible method to solve the energy crisis is to find an alternative, clean and renewable energy source/carrier, such as hydrogen, to replace traditional fossil fuels. Recently, scientists have proposed that producing hydrogen from the water splitting process is an efficient and reliable way to create this clean burning fuel due to the high abundance of water sources on earth. Water oxidation is considered to be the bottleneck of the whole reaction due to the thermodynamic and kinetic limitations, hence development of materials that can catalyze water oxidation is then highly desired. A previously reported Mn based MOF, \([\text{Mn}_4(\mu_3\text{-O})(\text{nic})_4]\) (nic = isonicotinate), was synthesized and was found to form birnessite-type MnO_2 nanoparticles during the photochemical water oxidation reaction, which is known to be an efficient heterogeneous water oxidation catalyst.

In addition to water oxidation, MOFs can also be used as heterogeneous catalysts for other organic transformations, with the active sites either integrated at metal nodes or located on the backbones of the frameworks. A new layered MOF structure, \([\text{Co(Hoba)}_2(\text{H}_2\text{O})_2]\) (Hoba = 4,4'-oxydibenzoic acid), was synthesized and, after removal of the terminal water molecules, was found to be a highly active heterogeneous catalyst for olefin epoxidation with both high conversion and selectivity to form epoxide products.

Finally, synthesis, characterization, PL properties and preliminary results of gas adsorption studies of a new MOF are described.
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Dedicated to

My Parents

and

My Love, Luwei Zhang
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<table>
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<th>Description</th>
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<tbody>
<tr>
<td>BET</td>
<td>Brunauer-Emmett-Teller</td>
</tr>
<tr>
<td>CUS</td>
<td>Coordinatively Unsaturated Site</td>
</tr>
<tr>
<td>bpdc</td>
<td>biphenyl dicarboxylate,</td>
</tr>
<tr>
<td>bpe</td>
<td>1,2-bis(4-pyridyl)ethane</td>
</tr>
<tr>
<td>DHCDC</td>
<td>2,5-dihydroxy-1,4-benzenedicarboxylic acid</td>
</tr>
<tr>
<td>DMA</td>
<td>$N,N$-dimethylacetamide</td>
</tr>
<tr>
<td>DMF</td>
<td>$N,N$-dimethylformamide</td>
</tr>
<tr>
<td>DMSO</td>
<td>$N,N$-dimethylsulfoxide</td>
</tr>
<tr>
<td>EPR</td>
<td>Electron Paramagnetic Resonance</td>
</tr>
<tr>
<td>ICP</td>
<td>Inductively Coupled Plasma</td>
</tr>
<tr>
<td>MOF</td>
<td>Metal-Organic Framework</td>
</tr>
<tr>
<td>MMOF</td>
<td>Microporous Metal-Organic Framework</td>
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<tr>
<td>nic</td>
<td>nicotinate</td>
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<tr>
<td>oba</td>
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<td>PXRD</td>
<td>Powder X-ray Diffraction</td>
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<tr>
<td>RPM</td>
<td>Recyclable Rutgers Porous Material</td>
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xx
SBU  Secondary Building Unit
TBHP  tert-butyl hydroperoxide
TEA  triethylamine
TOF  Turn-Over Frequency
TGA  Thermogravimetric Analysis
ZIF  Zeolitic Imidazole Framework
CHAPTER 1

INTRODUCTION

1.1 Introduction

Metal-organic frameworks (MOFs) are crystalline materials synthesized via self-assembly process by using metal ions or metal ion clusters serving as nodes, respectively known as primary building units (PBUs) or secondary building units (SBUs), and polytopic organic ligands serving as linkers to form infinite network structures through coordination bonds. The collection of compounds has also been variously named as coordination polymers (CPs) or organic zeolite analogues (ZIFs) depending on the type of framework and the researchers who constructed them. Based on different synthetic conditions, MOFs with one dimensional (1D), two dimensional (2D), or three dimensional (3D) structures can be formed. The pores, or void space, can be generated in-situ in many of the 3D MOFs. Recently, microporous metal-organic frameworks (MMOFs) with pore sizes less than 20 Å have emerged as a promising new family of materials for applications in catalysis and small gas storage and separation; high porosity and surface area, uniform and tunable pore size, high metal content, low density, and thermal and chemical stability are the features that highlight these materials as candidates for these applications. The pores of the as-synthesized MMOFs are usually occupied by solvent molecules, which we generally call "guest molecules", that must be removed for most applications. Structure collapse may occur during the process of removing the guest molecules and generally, the larger the pore, the more likely the
collapse. In this sense MMOFs are usually more desirable than their mesoporous analogues, whose frameworks typically collapse upon solvent removal, while most of the MMOF structures will remain intact, hence permanent porosity can be achieved. Construction of MMOFs with specific geometries is highly desired and facilitated by the reticular approach, the recognition of explicit geometric building blocks which have predictable outcomes. Such an approach might have a chance to finally achieve real "design" by obtaining compounds with expected structures and properties.26-28

1.2 Design and synthesis of MMOFs

In the construction of MMOFs, multidentate organic ligands are chosen as the linkers while metal clusters, or SBUs, serve as connecting nodes.26,29 It should be noted that the concept of SBUs originally came from zeolites and are used to facilitate structural analysis and predict the final topology in MMOFs.30 In addition to metal clusters, branched organic moieties with greater than two coordinating functionalities can also be treated as preformed SBUs.31 Some examples of different types of SBUs (metal cluster or organic linker) are shown in Figure 1.31 Generally SBUs are not prepared prior to the MOF synthesis, but are rather formed in-situ under a specific set synthetic conditions.31 The real design element of MMOFs is the judicious selection of SBUs and organic linkers, and as a result, not only can different types of topologies and structures be formed,1,32 but the pore size of the framework can be systematically tuned by simply using organic linkers with different lengths.33-35 To illustrate this concept, Yaghi and his coworkers have done wonderful work, by synthesizing a series of sixteen isoreticular
MOFs (IRMOFs) using the same SBU (tetranuclear octahedron \( \text{Zn}_4\text{OCOO}_6 \)) but different organic linkers.\(^{34}\) For example, by changing the linear dicarboxylate organic linker from benzene-1,4-dicarboxylate (bdc) to terphenyl-4,4''-dicarboxylate (tpdc) (Figure 2), the pore size of the framework could be tuned from 18.5 Å to 28.8 Å.\(^{34}\) Other than reticular synthesis, which forms MMOFs with the same SBUs but different organic linkers, constructing MMOFs using the same organic linker and similar SBUs but with different metal ions has also been realized. Yaghi and his coworkers demonstrated this idea by synthesizing the MOF-74 series using 2,5-dihydroxy-1,4-benzenedicarboxylic acid (DHBDC) as the organic linker.\(^{29}\) The result shows that reacting DHBDC with different metal ions (\( \text{Zn}^{2+}, \text{Mg}^{2+}, \text{Co}^{2+} \) and \( \text{Ni}^{2+} \)) will generate isostructural MMOFs with the same topology; this phenomena can be partially explained by the similarities of these transition metal ions, both in coordination modes and oxidation states. Recently, a new "linker-pillar" strategy has been applied for generating 3D MMOFs (Figure 3).\(^{7}\) The SBUs (e.g. paddlewheel dinuclear metal centers) will first connect to the "linker" organic ligands (eg. dicarboxylate ligand) to form a 2D layer. These layers are then further joined by a "pillar" ligand (eg. 4,4'-bipyridine) to construct a 3D network. The pore size of these MMOFs can be tuned simply by changing the lengths of the linker or pillar ligands, and since two different kinds of organic ligands are employed, more structures are expected to be generated. In general, the success of an SBU in the design of MMOFs depends on both its rigidity and directionality of bonding, which must be reliably maintained during the assembly process.\(^{31}\)
Figure 1.1. Selected inorganic secondary building units (SBUs): (a) paddlewheel dinuclear; (b) tetranuclear octahedron; (c) trinuclear prism. Examples of organic SBUs: (d) square tetrakis(4-carboxyphenyl)porphyrin; (e) tetrahedral adamantane-1,3,5,7-tetracarboxylic acid; and (f) trigonal 1,3,5-tris(4-carboxyphenyl)benzene. Metals are shown as blue, carbon as black, oxygen as red, nitrogen as green. Reproduced with permission from Ref 31. Copyright © 2004 Elsevier Inc.
Figure 1.2. Selected IRMOFs (IRMOF-1, 8, 10, 16) showing the tunable pore size by adjusting the length of the organic linker from benzene-1,4 dicarboxylate (IRMOF-1) to terphenyl-4,4"-dicarboxylate (IRMOF-16). Reproduced with permission from Ref 31. Copyright © 2004 Elsevier Inc.

Figure 1.3. "linker-pillar" strategy of generating 3D MMOFs from 2D layers to 3D frameworks. (Paddlewheel dinuclear SBUs are selected as example, P = pillar ligand, L = linker ligand).
Typically, the most important aspect in the synthesis of new MOFs is to obtain high quality single crystals for structural determination and analysis. The different solubilities between organic ligands and polar inorganic components, and the inverse relationship between metal-organic bond strength and reversible formation are generally the main obstacles for synthesis.\(^{36}\) Fortunately a new method, solvothermal synthesis, was employed and found to be an effective approach which largely replaced the older, often time-consuming, methods. A typical solvothermal synthesis involves loading a transition metal salt, organic linker ligand, and solvent into a reaction vessel, such as a Teflon-lined stainless steel bomb or glass tube, which is then sealed and heated to elevated temperatures (above 150 °C) to generate autogenous pressure. The construction of MOF structure is simply a Lewis acid-base reaction where the metal ions act as Lewis acids while the deprotonated organic ligands serve as Lewis bases.\(^{37}\) However, even a subtle change in the reaction conditions can lead to poorer quality crystals, reduced yields, or the formation of entirely different phases. The synthetic conditions depend on many parameters, including but not limited to: 1) concentration of the starting materials, 2) the polarity of solvent, 3) the pH value of the reaction mixture, 4) temperature of the reaction, and 5) reaction time. The selection of appropriate solvent plays a critical role in synthesis since it can determine whether or not the rate of ligand deprotonation matches that of the coordination bond formation. Mixed solvent systems can be employed to fine-tune the solution's polarity and the kinetics of solvent-ligand exchange. Solvents such as dimethylformamide (DMF), diethylformamide (DEF), and dimethylacetamide (DMA) undergo hydrolysis at relatively high temperatures (60 – 85 °C), releasing amine groups
which can deprotonate the carboxylic acid organic ligands and facilitate the reaction. Dimethyl sulfoxide (DMSO) can be used without hydrolysis at higher temperature (>100 °C) to help overcome the energy barrier and form products with novel geometry. In addition to solvothermal synthesis, several other methodologies have also been developed, including the mixture of non-miscible solvents, electrochemical techniques, and the high-throughput approach. Two of the most promising methods are microwave assisted and ultrasonic reactions, which allows for the widening of the reaction temperature range and the shortening the crystallization time, while controlling phase morphology and particle size distributions. Many nano-sized MOFs have been synthesized by this method; by decreasing the size of the MOF particles, larger surface area is achieved which is desirable in both adsorption and heterogeneous catalysis applications.

1.3 Characterization of MOF materials

There are several techniques developed for the characterization of MOF materials. The crystal structure of MOF materials can be solved by single crystal X-ray diffraction if good quality single crystals can be obtained from the synthesis. Powder X-ray Diffraction (PXRD) measurements are usually used to identify and examine the purity of crystalline products formed after a reaction. By comparing the pattern of the as-synthesized sample with a simulated pattern, which is generated from the single crystal data, one can confirm whether a pure phase of a given material is formed. The thermal stability of MOF materials are often tested by Thermogravimetric Analysis (TGA). The weight loss during the heating process is generally attributed to the removal of guest
molecules trapped in the pores and the eventual decomposition of the framework itself. In order to prove that a given MMOF has permanent porosity, gas adsorption studies are applied. The MMOF materials are typically activated through solvent-exchange, followed by evacuation of the solvents via heating under dynamic vacuum to remove all of the solvent molecules residing in the pores or channels before the gas adsorption measurement is taken. Finally, the adsorption-desorption isotherms of selected gasses will be performed on the activated samples. Usually, nitrogen adsorption measurements are carried out at 77 K to obtain surface area, pore volume and pore size distribution; alternatively, they can also be obtained by argon adsorption at 87 K or CO₂ adsorption at 195 K. Based on IUPAC classification, there are a total of six different types of adsorption isotherms that can reflect the interaction between adsorbent and adsorbate (Figure 1.4). Most MMOFs exhibit type-I adsorption behavior, although recently there have been reports of a few cases with type-IV behavior in some mesoporous MOFs. Generally, the surface area (both Brunauer-Emmett-Teller (BET) and langmuir), pore volume and pore size distribution can be automatically calculated by the software accompanying the sorption apparatus. To further confirm the permanent porosity of an MMOF, PXRD and TGA measurements should be taken after the adsorption-desorption study. The PXRD pattern verifies the integrity of the framework and phase purity of the sample after evacuation, while the TGA verifies that there is negligible weight loss from solvent guest molecules while also providing the thermal stability of the evacuated framework. For MOFs with specific functional groups (-OH, -NH₂, etc.), infrared spectroscopy (IR) can be employed to identify whether the functionalized organic ligands are in fact incorporated into the framework.
1.4 Using Microporous Metal Organic Frameworks (MMOFs) for storage and separation of CO$_2$

Energy demand is currently a prevalent global issue that we are facing due to the dramatic increase in both population and industrial processes around the world. Presently, over 80% of the energy consumption is supplied by the burning of fossil fuels (coal, petroleum, and natural gas)$^{47}$ As a result, the annual global emission of CO$_2$ increased by 80% between 1970 and 2004,$^{48}$ and in 2004 the CO$_2$ emitted from combustion of fossil fuels was responsible for more than half of the total greenhouse gas emission (Figure 1.5).$^{49}$ The increasing concentration of CO$_2$ in the atmosphere has been proven to be the main contributor to global warming.$^{50,51}$ In order to solve this problem, the US Department of Energy (DOE) issued the Carbon Capture and Sequestration (CCS)
program in 2009. This program aims to have 90% of the CO$_2$ produced by fossil fuel combustion to be captured by 2020, with a cost of no more than a 35% increase of electricity use for the post-combustion process.$^{50}$ CCS will require the separation of CO$_2$ from N$_2$ in flue gas since: 1) the flue gas emission from power plants is responsible for over 30% of the total CO$_2$ emission,$^{52}$ and 2) the major component in flue gas is N$_2$ (>70%) while the major impurity is CO$_2$ (10-15%).$^{53}$

Another important energy-related separation is sequestering CO$_2$ from natural gas. Burning natural gas produces less CO$_2$ than other fossil fuels making it an environmentally cleaner process. The main component of natural gas is methane (80-95%), with CO$_2$, N$_2$, and some heavier hydrocarbons present as impurities.$^{54}$ The methane produced from industrial landfills is currently a growing source of natural gas, but it often contains unacceptable amounts of CO$_2$ (40-60%). So separating CO$_2$ from methane is essential for both increasing the quality of natural gas, and the treatment of landfill gas to improve purity and reduce pipeline corrosion induced by acidic CO$_2$ gas.$^{54}$ A number of techniques have been developed for selective capture of CO$_2,$ including conventional methods such as using aqueous ammonia$^{55}$ or amine functionalized solids$^{56,57}$ and using solid porous materials, such as activated carbon, carbon molecular sieves, or zeolites.$^{58,59}$ Both of these approaches have shortfalls: high energy consumption for the former, and low capacities or difficult regeneration processes for the latter.$^{50}$ A possible solution lies within using MMOFs, as they have been well developed and have shown advantages in such separation applications due to their unique structural properties, including high surface area, high porosity, low crystal density, and high thermal and chemical stability.
1.4.1 The mechanisms of using MMOFs for selective capture of CO₂

Using MMOFs for the selective capture of CO₂ requires the material to have a high selectivity for CO₂ over other components in the gas mixture. There are mainly three mechanisms applied to the separation process, the molecular sieving mechanism, the kinetic separation mechanism and the thermodynamic separation mechanism. In the molecular sieving mechanism, an MMOF can separate the gasses based on their sizes. Table 1 summarizes the kinetic diameters of CO₂, CH₄ and N₂. If the pore size of the MMOF is between the kinetic diameters of two gasses (CO₂ and CH₄), it will separate the two gasses by a molecular sieving effect. If the pore size of an MMOF is only slightly larger than both of the gasses to be separated (CO₂ and CH₄), the difference in their diffusion rates may play an important role in their separation (the larger molecule CH₄ diffuses slower than the smaller molecule CO₂ and CO₂ will be selectively captured).
which is known as kinetic separation mechanism. The thermodynamic separation mechanism applies to MMOFs that have sufficiently large pores where diffusion of gases is fast. In such a case, separation is achieved based on different affinities between various components in the gas mixture and the pore surface of MMOFs. The separation can be realized by gas molecules having different physical properties such as the polarizability or the quadrupole moment (also summarized in Table 1), resulting in a higher enthalpy of adsorption of a certain gas over others. For example, with a higher polarizability and quadrupole moment of CO₂ over N₂ (Table 1), there will be a higher affinity between CO₂ and the surface of the pores than N₂, resulting in selective capture of CO₂ over N₂.

<table>
<thead>
<tr>
<th>Molecules</th>
<th>Kinetic diameter (Å)</th>
<th>Polarizability (10⁻²⁵ cm⁻³)</th>
<th>Quadrupole moment (10⁻²⁷ esu⁻¹cm⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>CO₂</td>
<td>3.3</td>
<td>29</td>
<td>43</td>
</tr>
<tr>
<td>N₂</td>
<td>3.6</td>
<td>17</td>
<td>15</td>
</tr>
<tr>
<td>CH₄</td>
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<td>26</td>
<td>0</td>
</tr>
<tr>
<td>O₂</td>
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<td>3.8</td>
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<td>25</td>
</tr>
<tr>
<td>H₂</td>
<td>2.9</td>
<td>8</td>
<td>6</td>
</tr>
</tbody>
</table>

1.4.2 CO₂ adsorption on MMOFs

The high porosity and surface area of MMOFs define their intrinsic potential for large CO₂ adsorption capacities due to the close approach and efficient packing of the guest molecules on the pore surface. The adsorptive capacity can be evaluated by two
factors: gravimetric CO₂ uptake and volumetric CO₂ uptake. The former is calculated by how much CO₂ can be adsorbed within a unit mass of MMOF material, which measures the storage capacity of a MMOF in weight. The latter refers to how densely the CO₂ can be stored in MMOF material. This is an equally important parameter as it can significantly influence the volume of the adsorbent. Both factors play an important role in evaluating the heating efficiency of the MMOFs, which is directly related to the energy penalty imposed for desorption of the adsorbed CO₂ and material regeneration.⁴⁹

Among the highest values reported to date for CO₂ uptake are 147 wt% (298 K, 35 bar) in MOF-177⁶² and 176 wt% (303 K, 50 bar) in MIL-101C,⁶³ which are much higher than the conventional materials used, zeolite 13X and MAXSORB⁶². It should be noted that the volumetric CO₂ uptake of MOF-177 is 320 cm³(STP)/cm³, which is almost nine times higher than the quantity stored at this pressure in a container without it⁴¹. Other than high-pressure CO₂ adsorption, which can give a high CO₂ capacity in MMOFs, lower-pressure (<1.2 bar) CO₂ uptake capacity at ambient temperatures (293-313 K) and 273K is more desirable since it is closer to the real conditions of CO₂ adsorption from industrial flue gas. Recently, Zhao et. al. reported that the adsorption capacity of CO₂ on IRMOF-1 was 9.2 wt% (1 bar, 296 K) which is much higher than the conventional adsorbents such as zeolites and activated carbon under the same conditions.⁶⁴ Another good example is the new family of MMOFs named zeolitic imidazole frameworks (ZIFs), which have high chemical and thermal stability, reported by Chen and Yaghi et al.⁶⁵ Among the ZIF compounds, the highest CO₂ adsorption performance belongs to ZIF-78 with about 20 wt% adsorption of CO₂ at 1 bar and 273 K, which, under the same
conditions, is three times higher than the CO$_2$ adsorbed on the commonly used industrial adsorbant, BPL carbon.

1.4.3 CO$_2$ separation using MMOFs

MMOFs can be categorized into two classes, rigid frameworks and flexible/dynamic frameworks. Rigid MMOFs usually have relatively stable and robust frameworks, similar to zeolites. Flexible MMOFs have dynamic, “soft” frameworks that are sensitive to external stimuli such as pressure, temperature, and especially guest molecules. In other words, dynamic MMOFs respond to gas molecules depending on their physical properties. Compared to the other gases, CO$_2$ has a higher quadrupole moment and greater polarizability which results in a higher heat of adsorption and thus is able to selectively capture CO$_2$. MMOFs with pore sizes that are within the range of the kinetic diameters of the adsorbates (3.3Å for CO$_2$, Table 1) can separate CO$_2$ using the kinetic separation mechanism, but the small pores will also limit the diffusion of gases throughout the material and significantly decrease the CO$_2$ uptake capacity of the material.$^{49}$ In order to achieve both high capacity and selectivity of CO$_2$, MMOFs with flexible frameworks have been developed and the adsorption properties and mechanisms have been well studied. The MIL-53 series are good examples of dynamic MMOFs with a "breathing" (phase transformation) phenomena during the process of CO$_2$ adsorption and desorption.$^{66-68}$ The phase transformation of MIL-53(Cr)$^{69}$ was monitored by gas-sorption-coupled X-ray diffraction and it was found that the geometric parameters of the pores changed upon CO$_2$ adsorption from large, square (8.5Å × 8.5Å) pores to narrow,
trapezoidal (2.6Å × 13.6Å) pores, and resulting in a 40% decrease of the cell volume. As the loading of the CO₂ increases, the structure can convert back from the narrow pores to large pores. This material showed good adsorption selectivity of CO₂ over CH₄, demonstrated by break-through studies.

Another good example is the flexible 3D MMOF, [Zn₂(bpdc)₂(bpe)]·2DMF (bpdc = 4,4'-biphenyldicarboxylate, bpe = 1,2-bis(4-pyridyl)-ethane, DMF = N,N'-dimethylformamide), which was recently developed by our group. The structural changes of this material during the CO₂ adsorption process was tracked by in-situ X-ray diffraction. The adsorption studies suggest that this MMOF is a good candidate for selective CO₂ capture, the details of which will be discussed in Chapter II.

1.5 Using MOF materials for heterogeneous catalysis

The development of practical catalysts for efficient synthesis is one of the most important keys to chemical industry.⁷⁰ Although homogeneous catalysts always show some advantages due to their high reaction activity and selectivity in various synthetic reactions,⁷¹ their practical applications are still limited by their instability and difficulty in catalyst/product separation. Immobilization of homogeneous catalysts on external supports such as inorganic materials or organic polymers⁷² was introduced as a solution to not only maintain the activity of the homogeneous catalysts, but also to achieve recyclability of the catalysts. However, there are still drawbacks to this type of catalyst such as reduced catalytic activity and/or selectivity because of the poor accessibility, random anchoring, or disturbed geometry of the active sites in the solid matrix.⁷³
Recently, using metal-organic frameworks (MOFs) as heterogeneous catalysts has become a hot research area. With "built-in" active sites either integrated at metal nodes or located on the backbones of the frameworks, and insolubility in conventional reaction media, MOFs can be treated as immobilized homogeneous catalysts without external supports. For this reason, these materials are also sometimes referred to as "self-supported" catalysts. Several strategies for using MOFs as "self-supported" catalysts have been developed. Some of these strategies include generating coordinatively unsaturated sites on metal ions or clusters, heterogenization of well-defined homogeneous catalysts, coupling of catalysis to chemical separations, post-synthesis incorporation of catalytic metalsites, etc.

1.5.1 Choosing chemical stable MOFs for heterogeneous catalysis

One of the most important factors in evaluating a MOF material as a potential heterogeneous catalyst is its chemical stability with regards to the reaction's conditions. The stability of many MOFs in certain solvents after heating for long periods of time can be somewhat limited; MOFs are generally more stable in hydrocarbon and non-polar solvents, although sometimes water and alcohols can also be used. The stability of MOFs can be tested by comparing their PXRD patterns before and after a reaction. A change in the PXRD patterns, especially in the case of decreasing intensity of the peaks, can sometimes be attributed to organic species occupying the internal void space of the framework, rather than actual framework collapse. This can be verified by pore characterization of MOFs after a reaction by doing gas adsorption measurements.
A number of MOF structures used in catalysis studies are thermally stable until at least 573K, which can be verified by TGA measurements. This temperature is sufficiently high to ensure the thermal stability of the material in many liquid phase reactions, which are generally performed below 473K. It should be noted that the TGA data has to be used cautiously; some structures are stable at specific temperatures only for a limited amount of time and may undergo extensive structural collapse when heated at lower temperatures for relatively longer times. Leaching of the metal species from the solid MOF materials to the solution can happen during a reaction and as such, the reaction should be monitored by performing chemical analyses (e.g. Inductively Coupled Plasma-ICP) on the reaction solution since even minute amounts of the leached metal species could be responsible for the catalytic performance. In this case, MOFs act as a precursor for the real catalyst by transferring a certain amount of metal into the solution. In general, leaching is an undesired process in heterogeneous catalysis because it involves the structural decomposition of the catalyst and produces a decrease of the catalytic activity of the material in the long term.

1.5.2 Designing MOFs containing Coordinatively Unsaturated Sites (CUS) for heterogeneous catalysis

In order to design MOFs with coordinatively unsaturated sites (CUS), labile ligands (terminal ligands) are introduced to the metal centers that are easy to remove during the activation stage prior to use in catalytic reactions. In most cases the labile ligands are solvent molecules and when they are removed, an open coordination position
is created on the metal centers which can be treated as Lewis acid catalytic sites. Plenty of MOFs containing CUS are have been synthesized, and their remarkable catalytic performances in different reactions are well studied. The catalytic activity of MIL-101 (\([\text{Cr}_3\text{F(H}_2\text{O)}_2\text{O(bdc)}_3]\), bdc = benzene-1,4 dicarboxylate) was studied by Kaskel and his co-workers.\(^6\) The coordinated water molecules can be easily removed by heating, leaving the Cr(III) sites unoccupied, which are a strong Lewis acid. The activated material was used for cyanosilylation of aldehydes and gave a very high (98.5%) yield. Our group recently synthesized a 2D MOF, \([\text{Co(Hoba)}_2(\text{H}_2\text{O})_2]\) (H\(_2\)oba = 4,4'-oxydibenzoic acid), which has Co(II) Lewis acid catalytic sites that can be generated by simply heating to remove the coordinated water molecules. The activated sample was used for an olefin epoxidation reaction which produced a high conversion (96%) and a high selectivity of epoxide products (96%), the details of which are discussed in Chapter III.

### 1.5.3 Building the homogeneous catalyst moieties into MOF structures for heterogeneous catalysis

In this strategy, the homogeneous catalyst will be modified to suit acting as the building blocks in the MOF structures either as the metal cluster SBU or organic ligand. Ideally, not only will the catalytic activity of the homogeneous catalyst be maintained, but it will also be "immobilized" in the structure of the formed MOF, in other words, this can be seen as a heterogenization process of a well-defined homogeneous catalyst. If the homogeneous catalyst is built into the organic ligands, sometimes modification will be
needed to generate the functional groups which will construct the MOF structures through coordination to the metal centers. Hupp and co-workers successfully incorporated a chiral salen Manganese strut, \(((R,R)-(2)-1,2\text{-cyclohexanedi amino-N,N'}\text{-bis}(3\text{-tert-butyl-5-(4-pyridyl)salicylidene})\text{Mn}^{\text{III}}\text{Cl})\), which is a highly effective catalyst for an asymmetric olefin epoxidation reaction into a Zinc based MOF structure by using the pyridyl groups as pillar ligands. Another biphenyl-4,4′-dicarboxylate ligand was used as the linker ligand to generate a 3D structure.\(^76\) The Zn-MOF shows an outstanding catalytic activity in asymmetric epoxidation of 2,2-dimethyl-2H-chromene with a 71% yield and 82% ee selectivity. Another good example is by Lin and co-workers who incorporated three Ir based molecular water oxidation catalysts into a highly water stable MOF, UiO-67, by replacing small amounts of biphenyl-4,4′-dicarboxylate linker ligands (the linker ligands in UiO-67) with a carboxylate group functionalized molecularIr catalyst.\(^81\) They demonstrated that these MOFs are active heterogeneous photocatalysts for the water oxidation reaction with a turn over frequency (TOF) of 0.0013 S\(^{-1}\). So far this is the first and only example of using MOFs as a heterogeneous catalyst for water oxidation.

1.5.4 Functionalizing MOFs by a postsynthesis treatment for heterogeneous catalysis

Postsynthetic modification has recently become a highly versatile tool to tailor MOFs for catalysis applications. Chemical functionalization of the framework can be achieved by either introducing a covalent attachment to the organic linker or grafting of
organic molecules at coordinatively unsaturated sites that are created after solvent removal. The first strategy has recently attracted great interest and has been well reviewed by Cohen and his co-workers. To demonstrate the approach, they successfully introduced Lewis acid sites (Cu$^{2+}$ and Fe$^{3+}$), which have catalytic functionality, onto UMCM-1-NH$_2$ MOF, whose formula is Zn$_4$O(NH$_2$-bdc)(btb)$_{3/4}$ (NH$_2$-bdc = 2-amino-1,4-benzenedicarboxylic acid, btb = 4,4’’,4’’’-benzene-1,3,5-triyl-tribenzoate), by reacting the free amino groups in the MOF structure with either 3-hydroxyphthalic anhydride or 2,3-pyrazinedicarboxylic anhydride to generate new chelating sites for Cu$^{2+}$ and Fe$^{3+}$ catalytic metal centers. The Fe$^{3+}$ modified MOF was used as a catalyst for the Mukaiyama-aldol reaction with a 58% conversion. The second strategy was established by Ferey and his coworkers by grafting an amine pendant group to the Lewis acidic Cr(III) sites in MIL-101 using ethylenediamine, followed by the other free amino group binding to another catalytic metal site (Pd$^{2+}$ in this case). Finally the Pd$^{2+}$ will be reduced by NaBH$_4$ to generate Pd nanoparticles inside the pores of MIL-101. The Pd loaded MIL-101 was found to be a highly active catalyst for the Heck coupling reaction at 393 K.

Inspired by the work described above, in the following chapters the author will introduce and discuss the topics of his own research on developing new MOFs for: 1) Selective capture of CO$_2$ over other small gases; and 2) heterogeneous catalysis applications (olefin epoxidation and water oxidation reactions).
CHAPTER 2

A NEW FLEXIBLE MICROPOROUS METAL ORGANIC FRAMEWORK (MMOF) EXHIBITING HIGH SELECTIVITY FOR CO₂ OVER N₂, CH₄ AND OTHER SMALL GASES

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2.1 Introduction

Effective capture of carbon dioxide from industrial flue gases has become one of the most pressing issues concerning environmental conservation and protection because CO₂ is the predominant greenhouse gas causing global warming. Conventional technology to remove carbon dioxide from the flue gases includes chemical absorption, but the solvents used, such as aqueous alkanolamines, usually requires high energy and often leads to environmental issues due to solvent loss and degradation. Physical adsorption of CO₂ on activated carbon or zeolites have also been explored, but the high cost of their regeneration remains a major drawback. Adsorption-based separation methods such as pressure swing adsorption (PSA) have the advantages of easy control and low energy demand. However, a proper absorbent with low cost, high selectivity and adsorption capacity of CO₂, especially at relatively low pressure (e.g. ~0.1–0.2 atm, the partial pressure of CO₂ in flue gases), is essential for making the process practical. During the past several years, the microporous metal-organic framework (MMOF)
materials have emerged as a promising new family of adsorbents for applications in gas separation and storage, catalysis and sensing\textsuperscript{94-97} due to their extremely high surface areas, low densities, and thermal and chemical stability. In addition, MOFs are chemically tunable and crystal and pore structures can be systematically controlled.\textsuperscript{98,99} A large number of porous MOFs have been developed and valuated for their CO\(_2\) storage and separation capacity by different research groups.\textsuperscript{86,94-118} Among the highest values reported to date for CO\(_2\) uptake are 147 wt\% (298 K, 35 bar) in MOF-177\textsuperscript{62} and 176 wt\% (303 K, 50 bar) in MIL-101C.\textsuperscript{63} However, these MOFs also take up a significant amount of other small gases under similar conditions, for example 62 and 51 wt\% of CH\(_4\) for MOF-177 (298 K and 35 bar)\textsuperscript{117} and MIL-101C (303 K and 50 bar),\textsuperscript{113} respectively.

Several parameters are important in achieving selective adsorption of CO\(_2\) vs. N\(_2\) and CH\(_4\). One of them is the relatively small kinetic diameter of CO\(_2\) (3.3 Å) compared to those of N\(_2\) (3.64 Å) and CH\(_4\) (3.8 Å).\textsuperscript{86} Another is the high quadrupole moment of CO\(_2\) (4.3 x 10\(^{-26}\) esu\(^{-1}\)cm\(^{-1}\)) in comparison with those of CH\(_4\) (0)\textsuperscript{119} and N\(_2\) (1.52 x 10\(^{-26}\) esu\(^{-1}\)cm\(^{-1}\)).\textsuperscript{120} Previous studies have shown flexible and dynamic porous MOFs exhibiting stepwise, hysteretic, pressure-dependent adsorption–desorption isotherms\textsuperscript{86,104} which could be particularly effective for selectively capturing CO\(_2\). In this chapter, we synthesize a new microporous MOF material built on two ligands serving as "linker" and "pillar", respectively. The relatively rigid linker molecule connects the metals to form a robust two-dimensional (2D) net, while the relatively flexible pillar molecule brings in a high level of structural flexibility\textsuperscript{121}. The resultant [Zn\(_2\)(bpdc)(bpe)]\textsubscript{2}DMF (bpdc = 4,4'-biphenyldicarboxylate, bpe = 1,2-bis(4-pyridyl)-ethane, DMF=N,N-dimethylformamide) or RPM4-Zn (1) is with a highly flexible three-dimensional (3D) framework and one-
dimensional (1D) open channels. RPM4-Zn demonstrates a very high adsorption selectivity of CO₂ over N₂, CH₄, CO and O₂ under conditions mimicking those of industrial flue gases.

2.2 Experimental

All chemicals were purchased from Aldrich, Acros or VWR and used as received without further purification unless stated otherwise.

2.2.1 Synthesis of [Zn₂(bpdc)₂(bpe)]·2DMF (1)

A mixture of zinc (II) nitrate hexahydrate (0.2975g 1.0 mmol), 1,2-bis(4-pyridyl)-ethane-bpe (0.1842g, 1.0 mmol) and 4,4’-biphenyldicarboxylic acid or H₂bpdc (0.2422g, 1 mmol) in DMF (15 mL) and toluene (0.8 mL) was heated in a programmable oven at 170 °C for 72 hours before it was cooled to room temperature at a rate of 0.1°C /min. The yellow block-shaped crystals of 1 were filtered, rinsed with DMF (10 mL) and dried under vacuum oven for 10 mins (85% yield based on zinc nitrate).

2.2.2 Powder X-ray diffraction and Thermogravimetric Analysis

Powder X-ray diffraction (PXRD) patterns of all the samples tested were performed on a Rigaku D/M-2200T automated diffractometer (Ultima+) using Cu Kα
radiation ($\lambda = 1.5406 \text{ Å}$). Graphite monochromator was used and the generator power settings were at 40 kV and 40 mA. Data were collected between a $2\theta$ of 3-50° with a step size of 0.02° at a scanning speed of 2.0 deg/min. Thermogravimetric data were collected on a TA Q50 Analyzer with a temperature ramping rate of 10 °C/min from room temperature to 600 °C under nitrogen gas flow.

2.2.3 Small gases adsorptions experiments

All gas sorption experiments were performed on a volumetric gas sorption analyzer (Autosorb-1 MP, Quantachrome Instruments). Liquid nitrogen and liquid argon were used as coolant to achieve cryogenic temperatures (77 and 87K). Ultra high purity N$_2$, CO, CO$_2$, O$_2$ and CH$_4$ (99.999%) were used. The initial outgassing process for each sample was carried out at 433K overnight (under vacuum). Outgassed samples in the amount of ~85-90mg were used for gas sorption measurements and the weight of each sample was recorded before and after outgassing to confirm the removal of guest molecules. The outgassing procedure was repeated on the same sample between experiments for 0.5~1 hour. Pore properties (e.g. pore volume, pore size, and surface area) were analyzed using Autosorb v1.50 software.

2.2.4 In-situ PXRD measurement on guest-free sample with different CO$_2$ loadings
The in-situ PXRD measurements were carried out as a function of CO$_2$ pressure using a specially designed sample holder for the PXRD unit. A guest-free sample was loaded in the sample holder and vacuum was applied to remove any gas residue. Full data set was then collected after the sample holder was refilled with CO$_2$ gas to a certain pressure and equilibrium was reached.

2.2.5 Stability test of sample 1 under water vapor

The stability of compound 1 in water vapor was examined at both room temperature and 60 °C. About 25 mg of sample 1 was loaded in an open vial suspended on the top of a closed glass jar containing water. The vial had no contact with water surface. The PXRD patterns were collected after 2 hrs and 6 hrs, respectively. The water was then heated to 60 °C and the same procedure was repeated again.

2.3 Results and Discussion

2.3.1 Characterization of compound 1

Crystals of 1 were grown by a reaction of Zn(NO$_3$)$_2$·6H$_2$O, bpe and H$_2$bpdc (in 1:1:1 molar ratio) in DMF at 170 °C for three days. The colorless plate-like crystals were collected and characterized by single X-Ray diffraction methods (Table 2.1). Compound 1 crystallizes in monoclinic crystal system, space group C2/c. All Zn atoms in 1 are
tetrahedrally coordinated to three O from three bpdc and one N from a bpe ligand with approximately tetrahedral geometry. The second building unit (SBU) is an eight-member ring, $\text{Zn}_2(\text{COO})_2^{2+}$ (Figure 2.1a) that is formed by inversion symmetry related pairs of Zn(II) atoms and bidentate carboxylate group from bpdc ligands. A monodentate carboxylate group from another bpdc ligand completes the SBU coordination. Each SBU is further connected to four neighboring SBU to form a $4^4$ brick-like net (Figure 2.1b). Two such identical nets interpenetrate to generate a 2D layer.

Adjacent 2D layers are connected by the bpe ligands via Zn-N bonds to complete the tetrahedral coordination of Zn(II) metal centers and to give rise to an overall 3D structure with 1D open channels extending along the crystallographic b-axis. These channels have a parallelogram-shaped cross section ($5 \times 7$ Å, excluding Van der Waals radius of the carbon atom, 1.7 Å) and the DMF guest molecules reside in the channel (Figure 2.1c). The $4^4$ net of 1 is a sql type, and the overall single 3D framework is a new self-catenated 6-coordinated uninodal net with the Point symbol of $\{4^4.6^{10}.8\}$ and Vertex symbol of $[4.4.4.4.6_2.6_2.6_5.6_5.6_5.6_5.6_5.6_5.6_5.10_{120}]$. The structure of 1 is distinctively different from Cd(bpdc)(bpe)(H$_2$O)$_{122}$ and [Ag$_2$(bpdc)(bpe)$_2$·H$_2$O]$_{123}$ the two other MOF structures also made of bpdc and bpe. Both structures are nonporous and the metals (Cd and Ag) are six- and three- coordinated, respectively. The DMF molecules can be removed by heating 1 under vacuum at 160 °C for 12 hours. The TG analysis of 1 (Figure 2.2) gave a weight loss of 15.13 wt% that matches very well with the calculated value (15.5 wt%) based on the crystal data. Upon removal of guest DMF, the guest-free compound (1') underwent a minor structure change but remained highly crystalline, as confirmed by PXRD analysis (Figure 2.3). The original structure was fully restored by
heating 1’ in DMF at 80 °C for 6 hours (Figure 2.3). The water vapor stability of 1 was also tested under both room temperature and 60 °C. The PXRD patterns of 1 after exposed to water vapor (Figure 2.4) clearly show that the samples remained intact and highly crystalline in both cases. The solvent accessible volume of 1’ was calculated to be 1041.8Å³ (25.1% of the unit cell volume) using program PLATON/SQUEEZE.124

Table 2.2 Crystal data and structure refinement for 1.

<table>
<thead>
<tr>
<th>Identification code</th>
<th>jz1-53b</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C23 H21 N2 O5 Zn</td>
</tr>
<tr>
<td>Formula weight</td>
<td>470.79</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Monoclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>C2/c</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 26.4310(18) Å, ( \alpha = 90^\circ ), b = 6.6400(5) Å, ( \beta = 108.464(1)^\circ ), c = 24.9341(17) Å, ( \gamma = 90^\circ ).</td>
</tr>
<tr>
<td>Volume</td>
<td>4150.7(5) Å³</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
</tr>
<tr>
<td>Density (calculated)</td>
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<tr>
<td>F(000)</td>
<td>1944</td>
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<tr>
<td>Crystal size</td>
<td>0.35 x 0.09 x 0.03 mm³</td>
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</tr>
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<tr>
<td>Independent reflections</td>
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</tr>
<tr>
<td>Completeness to theta = 30.53°</td>
<td>99.8 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
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</tr>
<tr>
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<td>Full-matrix least-squares on F2</td>
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<td>----------------------------------</td>
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<tr>
<td>Data / restraints / parameters</td>
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<tr>
<td>Goodness-of-fit on F2</td>
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</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0530, wR2 = 0.1166</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0775, wR2 = 0.1271</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>1.213 and -1.095 eÅ⁻³</td>
</tr>
</tbody>
</table>

(a)
Figure 2.1. Views of the crystal structure of 1. (a) the SBU and the coordination around the Zn(II)$_2$ pair; (b) the single $4^4$ brick-like net; (c) perspective view of 1 showing the 1D
channels along the b-axis (DMF molecules are removed for clarity). Zinc cyan, Carbon gray, Oxygen red, Nitrogen blue.

Figure 2.2. Thermogravimetric analysis of a freshly prepared sample of 1, showing a good agreement between the observed weight loss of DMF (15.13 wt%) and the calculated value (15.5 wt%).
Figure 2.3. PXRD patterns of as-synthesized sample of 1 (red), guest-free 1’ (blue), and 1’ after being heated in DMF at 80 °C for 6 hours (dark-green). The pattern in black (bottom) is calculated from the single crystal structure of 1.
Figure 2.4. PXRD patterns of 1 taken after exposure to water vapor at room temperature and 60 °C. (a) simulated; (b) before exposure; (c) after 2 hrs at RT; (d) after 6 hrs at RT; (e) after 2 hours at 60 °C; and (f) after 6 hours at 60 °C.

2.3.2 Pore characterization of the guest-free sample 1′

The activated samples (1′) were prepared by heating 1 under vacuum at 160 °C overnight. The pore volume and surface area were obtained from the CO₂ isotherm at 273 K. The surface area was estimated to be 88.4 m²/g (BET) and 137.8 m²/g (Langmuir) in the pressure range P/P₀ = 0.05-0.25 (Table 2.2). The total pore volume was estimated to be 0.08 cc/g, substantially smaller than the value calculated based on the crystal structure of 1 (0.2 cc/g, Table 2.2). This is consistent with the observation of structure change/distortion upon guest removal (Figure 2.3, red and blue patterns), and confirms that the pores in 1′ are significantly shrunk with respect to the original structure of 1. These data show that 1′ is a porous framework with relatively small surface area and pore size.
Table 2.3 Pore characteristics of \([\text{Zn}_2(\text{bpdc})_2(\text{bpe})]\cdot 2\text{DMF (1)}\).

<table>
<thead>
<tr>
<th>BET Surface Area (P/P₀=0.05-0.25) (m²/g)</th>
<th>Langmuir Surface Area (P/P₀=0.05-0.25) (m²/g)</th>
</tr>
</thead>
<tbody>
<tr>
<td>88.4</td>
<td>137.8</td>
</tr>
</tbody>
</table>

Total Pore Volume (cc/g)

<table>
<thead>
<tr>
<th>Experimental</th>
<th>Calculated</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.08 (P/P₀ = 0.99)</td>
<td>0.2*</td>
</tr>
</tbody>
</table>

*Calculated by Platon from single crystal data of 1.

2.3.3 CO₂ adsorption study on guest-free sample 1’

The adsorption isotherms for CO₂ at 273, 288 and 298K are plotted in Figure 2.5. The isotherms show a three-step adsorption profile. At 298K, about 0.55 wt% of CO₂ (2.8 cc/g at STP) is adsorbed in the first step (up to 0.08 atm). In the second step, 1’ takes up ~3.5 wt% CO₂ (18.0 cc/g) in the pressure range of 0.08-0.6 atm. In the final step, the CO₂ uploading reaches 5.4 wt% (27.76 cc/g) at 1 atm. The isotherms at 273 and 288 K show a similar trend. Such observations are well documented for a number of previously reported flexible MMOFs where pressure-dependent structure changes occur during adsorption-desorption processes. The structure change as a function of CO₂ pressure in each of the three steps was monitored and confirmed by an in-situ powder X-ray diffraction experiment, (Figure 2.6). As shown in Figure 2.5, the inflection becomes more pronounced as temperature decreases, and the on-set pressure of each inflection point
also decreases as temperature is lowered, which is similar to several other cases and modeled by grand canonical Monte Carlo (GCMC) simulations.\textsuperscript{98,125}

Figure 2.5. The CO\textsubscript{2} adsorption-desorption isotherms measured at 273, 288 and 298K.
Figure 2.6. Room temperature PXRD patterns at low angles ($2\theta = 7-10^\circ$) for guest-free sample 1’ (black), 1’ after refilling CO$_2$ at 0.08 atm (red, first step), 1’ after refilling CO$_2$ at 0.2 atm (blue, second step), 1’ after refilling CO$_2$ at 0.6 atm (green) and 1’ after refilling CO$_2$ at 1 atm (pink, third step).

2.3.4 Heats of adsorption of CO$_2$ on guest-free sample 1’

The heats of CO$_2$ adsorption were calculated based on the adsorption isotherms obtained at 273, 288 and 298K using the virial coefficient (VC) method$^{126-129}$ and are plotted in Figure 2.7. The highest value is obtained for the first step, namely ~37.6 kJ/mol at a very low loading of 0.064 cc/g. For the second and third steps, the values are 29.2-32.9 and 28.5-29.2 kJ/mol, for a loading range of 2.93-17.86 and 18.11-28.06 cc/g, respectively. These values are comparable with other reported flexible structures having similar porosity, for example, MIL-53(Cr) (32 kJ/mol) and MIL-53(Al) (35 kJ/mol), at similar temperatures.$^{104}$
2.3.5 Selective capture of CO₂ over other small gasses (N₂, CH₄, CO and O₂)

To evaluate the adsorption selectivity and capacity of 1’, the adsorption-desorption isotherms of other small gases such as CH₄, N₂, O₂ and CO were also measured at room temperature. Figure 2.8 shows the N₂ and CH₄ isotherms compared with that of CO₂. And Figure 2.9 shows the CO and O₂ isotherms compared with that of CO₂. Clearly 1’ adsorbed essentially N₂ and very little CH₄ in the pressure range given (Figure 2.8). The single-component CO₂/N₂ separation ratios of 1’ at 0.09, 0.5 and 1 atm are 98:1 (v/v), 169:1 (v/v) and 360:1 (v/v), respectively (Table 2.3). At ~0.16 atm (a pressure that is well within a typical CO₂ partial pressure range in flue gases), the number is 99:1 (v/v). All these CO₂/N₂ separation ratios are considerably higher than the best values reported to this date, namely, 6:1 and 49:1 for SNU-M10⁸⁷ and MOF74-Mg¹¹².
under 0.16 atm and 298K (Table 2.3). For CO₂/CH₄, the separation ratios are 73:1 (v/v), 53:1 (v/v), 25:1 (v/v) and 24:1 (v/v) at 0.09, 0.16, 0.5 and 1 atm which is decreasing (opposite to CO₂/N₂) as the pressure goes up. And this is because the uptake of CH₄ on I' is increased more apparently than N₂ (almost no change) as the pressure increases (0.082 cc/g at 0.09 atm, 0.16 cc/g at 0.16 atm, 0.63 at 0.5 atm and 1.15 at 1 atm). This might be due to the relatively bigger polarizability of CH₄ (2.6×10⁻²⁴ cm⁻³) than N₂ (1.7×10⁻²⁴ cm⁻³). From Figure 2.9, it is obvious that I' barely adsorbs any CO or O₂ compared to CO₂ which indicates the separation ratios of CO₂ over CO and O₂ should be much higher within the pressure range given. The separation ratios for CO₂/CO under 0.09, 0.16, 0.5 and 1 atm are 147:1 (v/v), 213:1 (v/v), 584:1 (v/v) and 351:1 (v/v) while for CO₂/O₂ the ratios are 111:1 (v/v), 124:1 (v/v), 376:1 (v/v) and 327:1 (v/v) under the same condition which adopts the same trend as CO₂/N₂ separation ratios. These results make I' a better material for CO₂/N₂, CO₂/CO and CO₂/O₂ separation material than CO₂/CH₄.

Figure 2.8 Room temperature adsorption isotherms of CO₂, N₂ and CH₄ on I'.
Figure 2.9. (a) Comparison of room temperature adsorption isotherms of CO\textsubscript{2} and CO on 1', (b) Comparison of room temperature adsorption isotherms of CO\textsubscript{2} and O\textsubscript{2} on 1'.

Table 2.4. Single-component separation ratios of CO\textsubscript{2}/N\textsubscript{2} at 25 °C.

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Separation Ratio (v/v)</th>
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<tbody>
<tr>
<td></td>
<td>1'</td>
</tr>
<tr>
<td>0.09</td>
<td>98</td>
</tr>
<tr>
<td>0.16</td>
<td>99</td>
</tr>
<tr>
<td>0.5</td>
<td>169</td>
</tr>
<tr>
<td>1</td>
<td>360</td>
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Table 2.5. Single-component gas uptake in 1' and separation ratios at 25 °C.

<table>
<thead>
<tr>
<th>Pressure (atm)</th>
<th>Gas</th>
<th>Gas Uptake (STP, cc/g)</th>
<th>wt%</th>
<th>CO\textsubscript{2}/Gas Ratio (v/v)</th>
</tr>
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<tbody>
<tr>
<td>0.09</td>
<td>CO\textsubscript{2}</td>
<td>6.02</td>
<td>1.18</td>
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<tr>
<td></td>
<td>N\textsubscript{2}</td>
<td>0.061</td>
<td>0.0076</td>
<td>98</td>
</tr>
<tr>
<td></td>
<td>CH\textsubscript{4}</td>
<td>0.082</td>
<td>0.0059</td>
<td>73</td>
</tr>
<tr>
<td></td>
<td>CO</td>
<td>0.041</td>
<td>0.0051</td>
<td>147</td>
</tr>
<tr>
<td></td>
<td>O\textsubscript{2}</td>
<td>0.054</td>
<td>0.0077</td>
<td>111</td>
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<tr>
<td>0.16</td>
<td>CO\textsubscript{2}</td>
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<tr>
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<td>N\textsubscript{2}</td>
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<td>0.011</td>
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<tr>
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<td>CH\textsubscript{4}</td>
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<td>0.012</td>
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### Table

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<tr>
<td></td>
<td>CO</td>
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<td>CH₄</td>
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<td>O₂</td>
<td>0.085</td>
<td>0.012</td>
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</table>

### 2.4 Conclusion

In conclusion, we have successfully synthesized and structurally characterized a highly flexible 3D MMOF material, [Zn₂(bpdc)₂(bpe)]·2DMF (1). Compound 1 exhibits a very high selectivity for CO₂ over several other small gases, including CH₄, N₂, O₂ and CO. This high selectivity makes 1 a promising candidate for the future development of adsorption based low-cost and energy-efficient method to selectively capture CO₂ from industrially important mixtures such as flue gas and natural gas.
CHAPTER 3

A NEW LAYERED METAL-ORGANIC FRAMEWORK AS A PROMISING CATALYST FOR OLEFIN EPOXIDATION REACTIONS


3.1 Introduction

Selective oxidation of hydrocarbons to higher-value chemical feedstocks are very important reactions; however, it remains a great challenge to achieve high performance of these reactions via chemical synthesis. In particular, the selective oxidation of olefins into epoxides (or olefin epoxidation) has attracted tremendous attention in the scientific community because epoxides are widely used as industrially important intermediate chemicals for making valuable products such as epoxy resins, paints and surfactants. Epoxides are also versatile precursors in various organic syntheses leading to a number of pharmaceutical synthesis. Over the past few decades, various homogeneous and heterogeneous catalysts have been developed and used to catalyze the epoxidation reactions of various olefins. Major research efforts have also included the development of effective heterogeneous catalysts that could be easily recovered, reused, and separated from reaction mixture at the end of reaction, making the procedures more cost effective.
In addition, solvent-free process has drawn particular attraction since it is greener and environmentally more friendly.

The dispersion and attachment of catalytic-active metallic nanoparticles or organometallic complexes onto polymeric or inorganic solid support materials via non-covalent or covalent interactions can generally produce effective heterogeneous catalysts for various reactions including olefin epoxidation.\textsuperscript{136,137} This approach has also been used for most commonly homogeneous epoxidation catalysts such as Co\textsuperscript{3+}, Fe\textsuperscript{3+}, Mn\textsuperscript{3+} and Mo\textsuperscript{6+} complexes. Such an immobilization process has successfully produced heterogeneous epoxidation catalysts that are as effective as their homogeneous counterparts.\textsuperscript{136,138,139} However, the syntheses of these catalysts are often costly. In addition, some of them have poor selectivity and possess randomly dispersed catalytic groups with geometries less conducive for the active sites in the solid matrix.\textsuperscript{73,135,140}

Very recently, promising heterogeneous catalytic activities of metal organic frameworks (MOFs) have been reported for a number of reactions. These reactions are catalyzed by: (1) build-in active sites (metal centers\textsuperscript{141,142} or functional organic linkers\textsuperscript{143,144}); and (2) grafted active sites (MOFs as solid support for grafting metal nanoparticles\textsuperscript{145,146} or post-synthesis method,\textsuperscript{78,83} which can generate metal binding sites). MOFs exhibit numerous advantages in heterogeneous catalysis including interesting regioselectivity\textsuperscript{147,148} or enantioselectivity,\textsuperscript{149} because of their large surface area, high metal content and coordination unsaturation, chirality, and systematically tunable structures and composition.\textsuperscript{74,84,149,150} These multifunctional properties make MOFs especially suitable as self-supported heterogeneous catalysts with build-in active metal centers that can readily be modified. MOFs containing unsaturated metal coordinate sites
are of particular interest and have been employed in numerous catalytic reactions because of their Lewis acidity and associated catalytic functionality, well-organized and well-maintained active sites during reaction.

To the best of our knowledge, only very few MOFs have been reported to date as self-supported catalysts for epoxidation of olefins. Spodine and co-workers obtained a 24% conversion of styrene and 71% selectivity to styrene oxide using a 2D MOF \([\text{Cu(H}_2\text{btec)(bipy)}]_\infty\) as catalyst. In another recent work by Koner and co-workers, 1D lanthanide MOF catalysts gave a 92% conversion of styrene with 41% yield of styrene oxide in 24 h. While these examples illustrate that MOFs are capable of catalyzing olefin epoxidation reactions, most of them are unable to simultaneously give both high conversion and high selectivity to epoxide product. Furthermore, all of these reactions are carried out in organic solvents. We have laid our focus on the development of Co(II) MOF catalyst not only because Co(II) cations are well known for their catalytic functions in the oxidation of olefins due to their excellent oxygen transferring ability, relatively high abundance and low cost, but also because very few Co(II) based MOF catalysts have been tested for olefin epoxidation. We have synthesized a new two-dimensional (2D) layered \([\text{Co(Hoba)}_2(\text{H}_2\text{O})_2]\) (H\(_2\)oba = 4,4'-oxydibenzoic acid) (2) and investigated its catalytic activity in solvent-free olefin epoxidation.

### 3.2 Experimental

**Reagents and materials:** Co(NO\(_3\))\(_2\)·6H\(_2\)O (Alfa Aesar, 99.7%), 4,4'-oxydibenzoic acid (H\(_2\)oba) (Sigma Aldrich, 99%), triethylamine (TEA) (Sigma Aldrich,
99.9%), acetonitrile (Sigma Aldrich, 99.8%), dimethyl sulfoxide (DMSO) (Alfa Aesar, 99.9%), methanol (Fisher Scientific, 99.9%), toluene (Acros, 99%), Styrene (Sigma Aldrich, 99%), 4-chlorostyrene (Sigma Aldrich, 99%), 4-tertbutylstyrene (Sigma Aldrich, 93%), ethyl cinnamate (Sigma Aldrich, 99%), trans-stilbene (Sigma Aldrich, 99%), tertbutyl hydroperoxide (TBHP) (Sigma Aldrich, 5.5M in decane) and chlorobenzene (Fisher Scientific, 99%). All chemicals were used as received without further purification unless stated otherwise.

3.2.1 Synthesis of \([\text{Co(Hoba)}_2 \cdot 2\text{H}_2\text{O}] (2)\) and \([\text{Co(Hoba)}] (2')\)

\([\text{Co(NO}_3)_2 \cdot 6\text{H}_2\text{O}] (0.4 \text{ mmol})\) and \([\text{H}_2\text{oba}] (0.8 \text{ mmol})\) were mixed in 10 mL of distilled water, and two drops of TEA was added in to the solution to adjust the pH value to ~7.00. The solution was then heated at 120 °C for 3 days, followed by cooling at a rate of 0.1 °C/min to room temperature. The pink plate-like crystals of 2 (0.1452 g, 0.24 mmol, 60 % yield based on cobalt) were collected. 2’ was obtained by heating 2 at 150 °C in vacuum oven for 2 hours, which resulted in a color change to the sample from pink to purple, indicating the transformation of 2 to 2’. 2 can be easily regenerated by immersing 2’ in water and stirring overnight at room temperature.

3.2.2 Powder X-ray Diffraction Analysis

Powder X-ray diffraction patterns of all the samples were recorded on a Rigaku Ultima IV X-Ray diffractometer using Cu Kα radiation (λ = 1.5406 Å). Graphite
monochromator was used and the generator power settings were at 40 kV and 44 mA. Data were collected between a 2θ of 3-50° with a step size of 0.02° at a scanning speed of 4.0 deg/min.

3.2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric profiles were collected on a TA Q50 Thermogravimetric Analyzer with a temperature ramp of 10 °C/min from room temperature to 600 °C under nitrogen gas flow.

3.2.4 Olefin epoxidation catalytic reaction monitored by Gas Chromatography (GC) and Gas Chromatography-Mass spectroscopy (GC-MS)

The catalytic reactions were probed by withdrawing reaction mixtures in selected intervals of time. The reaction analysis was performed by gas chromatography using an Agilent 6850 gas chromatograph (GC) equipped with an HP-1 column (1% dimethyl polysiloxane, 30 m length, 0.25 mm internal diameter, and 0.25 μm film thickness) and a flame ionization detector (FID).

The GC measurements were calibrated using chlorobenzene as an internal standard to obtain reactant conversion, product selectivity and reaction yield. The products were further confirmed by a HP gas chromatograph-mass spectrometer (GC-MS, HP-5972) containinga HP-5 MS 50 m × 0.200 mm × 0.33 μm capillary column.
3.2.5 Olefin epoxidation catalytic activity test of 2 and 2’

In 50 mL three-neck round flask, desired amount of reactant, oxidant, catalyst, internal standard (chlorobenzene) and solvent (if needed) were charged. The reaction mixture was then immersed in a preheated oil bath at the desired temperature (75 °C) and the reaction was initiated by stirring the reaction mixture by magnetic stirrer. The reaction was carried out under atmospheric air. The progress of the reaction was monitored by withdrawing aliquot samples at a selected time interval and analyzed by GC and GC-MS.

3.2.6 Recyclability test of 2’

The catalytic reaction was carried out under the reaction condition described in last section for 6 hours, then after each reaction cycle (6 hours), the catalyst was re-weighted, and the amount of styrene and TBHP was scaled appropriately based on the mole of the catalyst in order to make the relative concentration of substrate to catalyst ratio the same in each cycle. And the product of each cycle was injected to GC and GC-MS for analyzing.

The hot filtration experiment was also performed, in which the catalyst was removed from the reaction mixture by centrifugation after 2 hours and the reaction was allowed to run for 4 hours without catalyst, and then the product was injected to GC and GC-MS for analyzing.
3.2.7 Mechanism study of olefin epoxidation catalyzed by 2'

To determine if the reaction proceeds through radical intermediates, the presence of radicals in the reaction was checked. Typically, 20 mmol styrene, 40 mmol oxidant (TBHP-5.5M in decane) and 15 mmol internal standard (chlorobenzene) were charged to a 50 mL three-neck round flask and the solution was stirred with magnetic stirrer. The reaction was heated at 75 °C for 2h, and then 40 mmol of the radical scavenger butyl hydroxyl toluene (BHT) was added into the reaction and the reaction was continued for another 4h. For the control reaction, the reaction was performed under the same procedure, except addition of BHT. The reaction was monitored by withdrawing aliquot samples at selected interval of time and analyzed by GC. The products were confirmed by GC-MS. In addition, pure oxygen and argon protected catalytic reactions were carried out under the same conditions.

3.3 Results and Discussion

3.3.1 Characterization of [Co(Hoba)2·2H2O] (2)

The pure-phase crystals of 2 were grown under hydrothermal conditions from a reaction between Co(NO3)2·6H2O and H2oba in 1:2 molar ratio in 10 mL distilled water and in the presence of triethylamine (TEA). The latter was used to adjust the pH to ~7.00. The reaction at 120 °C for 3 days afforded plate-like pink crystals, which were
characterized by single crystal X-ray diffraction method (selected single crystal data in Table 3.1). Compound 2 crystalizes in triclinic crystal system, space group $P-\overline{1}$. The primary building unit (PBU) is shown in Figure 3.1a. All the cobalt atoms in 2 are octahedrally coordinated to four oxygen atoms from carboxylate groups in the equatorial positions and two oxygens from water molecules in the axial positions. Each cobalt atom is connected to the four neighboring cobalt atoms via the bidentate carboxylate groups from oba ligands to form a $4^4$ brick-like 2D layer (Figure 3.1b). Only one carboxylic acid of each oba ligand is deprotonated (Figure 3.1a). The unde protonated carboxylic groups point outward from both sides of the Co(Hoba)$_2$ layer and form hydrogen bonds between the adjacent layers (Figure 3.1c).

Table 3.1. Selected crystallographic data for 2.

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Empirical formula</td>
<td>C28 H22 Co O12</td>
</tr>
<tr>
<td>Formula weight</td>
<td>609.39</td>
</tr>
<tr>
<td>Temperature</td>
<td>100(2) K</td>
</tr>
<tr>
<td>Wavelength</td>
<td>0.71073 Å</td>
</tr>
<tr>
<td>Crystal system</td>
<td>Triclinic</td>
</tr>
<tr>
<td>Space group</td>
<td>$P-\overline{1}$</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td>a = 6.5938(6) Å $\alpha$ = 88.223(1)$^\circ$.</td>
</tr>
<tr>
<td></td>
<td>b = 7.3333(7) Å $\beta$ = 89.712(2)$^\circ$.</td>
</tr>
<tr>
<td></td>
<td>c = 25.306(2) Å $\gamma$ = 89.770(2)$^\circ$.</td>
</tr>
<tr>
<td>Volume</td>
<td>1223.1(2) Å$^3$</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
</tr>
<tr>
<td>-------</td>
<td>------------</td>
</tr>
<tr>
<td>Density (calculated)</td>
<td>1.655 Mg/m³</td>
</tr>
<tr>
<td>Absorption coefficient</td>
<td>0.774 mm⁻¹</td>
</tr>
<tr>
<td>F(000)</td>
<td>626</td>
</tr>
<tr>
<td>Crystal size</td>
<td>0.20 x 0.11 x 0.05 mm³</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>2.42 to 31.62°</td>
</tr>
<tr>
<td>Index ranges</td>
<td>-9≤h≤9, -10≤k≤10, -36≤l≤37</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>15498</td>
</tr>
<tr>
<td>Independent reflections</td>
<td>8044 [R(int) = 0.0288]</td>
</tr>
<tr>
<td>Completeness to theta = 31.62°</td>
<td>97.6 %</td>
</tr>
<tr>
<td>Absorption correction</td>
<td>Semi-empirical from equivalents</td>
</tr>
<tr>
<td>Max. and min. transmission</td>
<td>0.9623 and 0.8605</td>
</tr>
<tr>
<td>Refinement method</td>
<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>8044 / 0 / 391</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.033</td>
</tr>
<tr>
<td>Final R indices [I&gt;2sigma(I)]</td>
<td>R1 = 0.0662, wR2 = 0.1667</td>
</tr>
<tr>
<td>R indices (all data)</td>
<td>R1 = 0.0814, wR2 = 0.1785</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>3.418 and -0.592 e.Å⁻³</td>
</tr>
</tbody>
</table>
Figure 3.1. (a) The PBU and the coordination around Co(II); (b) the 4^4 brick-like 2D layer parallel to the ab plane (the light turquoise polyhedral represent the octahedral coordination around Co(II). Benzene rings of the oba ligands are deleted for clarity); (c) the layered structure packed along the c axis and the outlined area indicates the hydrogen bonding section between the two adjacent layers. Color scheme: Co turquoise; C gray; O red; H orange; and all the hydrogen atoms are deleted for clarity except those on the undeprotonated carboxylate groups).

Thermogravimetric (TG) analysis (Figure 3.2) shows a weight loss of 6.0 wt% for 2 in the range of 110 °C to 160 °C upon heating. The weight loss can be assigned to the coordinated water molecules in 2 and matches very well with the theoretically calculated amount (5.9 %) based on the crystal structure. The water-free sample (2') is thermally stable up to 300 °C, followed by decomposition at higher temperatures. 2' can also be
generated by heating the as-made sample at 150 °C under vacuum for 2 h. The PXRD patterns of as-made sample (2) and water-free sample (2') are shown in Figure 3.3 along with a simulated pattern from single crystal data. Compound 2 is highly crystalline and pure compared with the simulated pattern. As indicated by the sharp PXRD peaks, 2' remains highly crystalline with (001), (002), (003), (004) and (005) peaks shifted slightly to lower angles (Figure 3.4). These peaks all correlate to the c direction in the crystal structure and the shifts suggest a unit cell expansion in the c direction. This is most likely due to the hydrogen bond breaking upon removal of coordinated water molecules in 2 (Figure 3.5). Hence, the structure is maintained after removing coordinated water molecules and this is most likely due to the strong hydrogen bonding between carboxylic groups from the adjacent layers (Figure 3.1c) while the 2D layers are fairly flexible, making them readily accessible to the substrate molecules. A color change was observed from an as-made sample (2, pink) to water-free sample (2', purple), and the former can be readily regenerated from the latter by simply immersing the sample in water and stirring for 6h at room temperature. Thus, the conversion between the two can be confirmed by either the change in color or in the PXRD patterns (Figure 3.3).
Figure 3.2. Thermogravimetric analysis of a freshly prepared sample showing a good match of the observed weight loss due to water removal with the calculated value.

Figure 3.3. The PXRD patterns of the simulated (black), as-made (red), water-free (blue) and water-regenerated (green) samples.
Figure 3.4. PXRD patterns of simulated (black), as-made (2, red) and water-free (2', blue, after heating to remove all the water molecules) samples. The first five (00l) peaks of 2 are labeled.

Figure 3.5. Hydrogen bonds between water molecules and carboxylate groups in an as-made sample.
3.3.2 Olefin epoxidation reaction in acetonitrile using 2 and 2' as catalysts

The catalytic activity of both 2 and 2' were tested in the liquid-phase epoxidation reactions of styrene (Figure 3.6). The reactions were run in the presence of 2 or 2' in acetonitrile (as solvent) with anhydrous tert-butyl hydroperoxide (TBHP) as oxidant. A 69% and 51% conversion of styrene to styrene oxide was achieved for 2' and 2, respectively, in 6 h (see Table 3.2). In addition, a selectivity of 77% to styrene oxide was attained for both 2' and 2. The higher catalytic activity of the water-free sample 2' is presumably due to the presence of highly reactive open Co(II) Lewis acid sites.

![Chemical Reaction](image)

Figure 3.6. Epoxidation of olefins catalyzed by 2 or 2'.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a'</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>51</td>
<td>24</td>
</tr>
<tr>
<td>2</td>
<td>2'</td>
<td>69</td>
<td>22</td>
</tr>
</tbody>
</table>
Reaction condition: Styrene: 1 mmol; TBHP (5.5 M in decane): 2 mmol; catalyst (2’), 15 mg (2.5 mol %); internal standard (chlorobenzene): 15 mmol; Acetonitrile (10 mL); Temperature: 75ºC; and time: 6 h.  

3.3.3 Solvents effect in catalytic olefin epoxidation reaction using 2’ as catalyst

Solvents often play a crucial role in catalytic efficiency as well as selectivity. Thus, the effect of solvents in epoxidation reactions catalyzed by 2’ was investigated in detail (Table 3.3). A solvent free reaction by 2’ was also carried out as a control experiment. This reaction is said to be "solvent-free" to indicate that there is no additional solvent added into the reaction mixture other than decane in the TBHP solution. When a non-polar solvent such as toluene was used, no reaction was observed (Table 3.3, Entry 1). When a polar solvent such as MeOH and DMSO were used, a high conversion of 92% and 84% was obtained for methanol (MeOH) and dimethylsulfoxide (DMSO), respectively. Interestingly, however, the selectivity of the reaction products was remarkably different. Reaction in MeOH resulted in styrene oxide as the main product (74% selectivity), whereas the same reaction in DMSO produced 61% benzaldehyde as the major product (Table 3.3, Entries 2 and 3). While conversion rate and catalytic activity are both relatively high with these two solvents, 2’ dissolves in the reaction mixture, and cannot be recovered at the end of the reaction through centrifugation. This is not uncommon as numerous MOFs can be dissolved in solvents of high dielectric
constant and high polarity, including DMSO and MeOH. Furthermore, since Co(II) is a relatively hard Lewis acid, it is readily soluble in O-donor solvent such as DMSO and MeOH. On the other hand, when the catalytic reaction was performed in acetonitrile, the MOF catalyst can be fully recovered along with a good conversion of styrene (69%) and selectivity to epoxide (78%). Interestingly, the highest styrene conversion (96%) and selectivity (96% to epoxide) were achieved for \(2'\) under solvent-free conditions (Table 3.3, Entry 5). This may be due to the better interactions between the catalyst and substrates when the concentration of reactants is very high under such conditions. The catalytic olefin epoxidation reaction was also carried out using \(2\) as the catalyst under solvent-free condition, and a lower 70% styrene conversion and 90% selectivity to epoxide were obtained (Table 3.4). \(2'\) gives better performance than \(2\) because of the presence of highly reactive open Co(II) centers (Lewis acid sites) in \(2'\). As \(2'\) showed higher catalytic activity in both solvent and solvent-free conditions, it was used for all further studies as described below.
Table 3.3. MOF 2’ catalyzed epoxidation of styrene in various solvents\textsuperscript{i} or under solvent-free\textsuperscript{j} conditions.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Solvent</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
<th>A\textsuperscript{k}</th>
<th>B\textsuperscript{l}</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Toluene</td>
<td>0</td>
<td>0</td>
<td>0</td>
<td>0</td>
</tr>
<tr>
<td>2</td>
<td>Methanol</td>
<td>92</td>
<td>74</td>
<td>26</td>
<td></td>
</tr>
<tr>
<td>3</td>
<td>Dimethylsulfoxide</td>
<td>84</td>
<td>39</td>
<td>61</td>
<td></td>
</tr>
<tr>
<td>4</td>
<td>Acetonitrile</td>
<td>69</td>
<td>78</td>
<td>22</td>
<td></td>
</tr>
<tr>
<td>5</td>
<td>No solvent</td>
<td>96</td>
<td>96</td>
<td>4</td>
<td></td>
</tr>
</tbody>
</table>

Reaction conditions: \textsuperscript{i} Styrene: 1 mmol; TBHP (5.5 M in decane): 2 mmol; catalyst (2’): 15 mg (2.5 mol%); Chlorobenzene (internal standard): 15 mmol; Solvent (10 mL); Temperature: 75°C; and Reaction time: 6h. \textsuperscript{j} Styrene: 50 mmol; TBHP (5.5 M in decane): 100 mmol; catalyst (2’): 15 mg (0.5 mol%); Chlorobenzene (internal standard): 15 mmol; Temperature: 75°C; and Reaction time: 6h. \textsuperscript{k} a = Epoxide products. \textsuperscript{l} b = Aldehyde products. The selectivity is only based on the two major products a and b.

Table 3.4. Comparison of catalytic activities between 2 and 2’ under solvent-free condition\textsuperscript{i}

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a\textsuperscript{a}</td>
</tr>
<tr>
<td>1</td>
<td>2</td>
<td>70</td>
<td>90</td>
</tr>
<tr>
<td>2</td>
<td>2’</td>
<td>96</td>
<td>96</td>
</tr>
</tbody>
</table>
3.3.4 Substituents effect on catalytic epoxidation reaction using 2' as catalyst under solvent-free condition

In order to further explore the versatility of the 2D MOF as a selective epoxidation catalyst and the effect of substituents on the epoxidation reaction, different types of olefins were used as substrates under "solvent-free" conditions. The results are compiled in Table 3.5. When an electron-withdrawing group, chloride, was used as a substituent at the para-position on styrene (4-chlorostyrene), similar conversion as styrene, but lower selectivity to the epoxide product, was obtained. On the other hand, when an electron-donating group, tert-butyl, was used as a substituent on styrene at the para-position (4-tert-butylstyrene), the reaction produced lower % conversion than styrene, but similar selectivity (Table 3.5, Entries 2 and 3). When ethyl cinnamate was used as a substrate, lower conversion (69%) compared to styrene but high selectivity (ca.100%) was obtained (Table 3.5, Entry 4). When trans-stilbene was used as substrate, the reaction gave the same selectivity (ca.100%) as ethyl cinnamate but higher conversion (86%) (Table 3.5, Entry 5). The difference in the conversion between Entries 1 and 3, as well as between Entries 4 and 5, may be attributed to the electronic and steric effects of the substituents at the double bond. The difference in % reactant
conversion for the reactions in Entry 4 and Entry 5 is most likely due to electronic and steric effects caused by the different substituent groups attached to ethene of the two substrates. As reported in various papers previously, the epoxidation of alkenes by various oxidants is unusually sensitive to steric factors around the alkene group as well as how electron rich or poor the alkene group is as the result of the substituent. Any substituent that makes the alkene more sterically hindered is generally expected to make the alkene react more slowly, although there have been also cases where higher number of substituents, especially less bulky ones, around the alkene favor the reaction to go faster. Specifically to our case, the electronic effects by the acetate group and its electron withdrawing effect via electronic resonance on the alkene group would make the double bond to react much less favorably than the one with phenyl substituent. This is probably the main reason for the difference in the % reactant conversion per unit time between the catalytic reactions in Entry 4 and 5 (where acetate and phenyl groups are the substituents, respectively). The selectivity of the epoxidation reactions of trans-substituted alkenes is almost always trans-substituted epoxides. Thus, our result in this regard is actually not unexpected. All the products were further confirmed by GC-MS method (shown in Figure 3.7).
Table 3.5. Epoxidation of various olefins under solvent-free condition by $2^*$.  

<table>
<thead>
<tr>
<th>Entry</th>
<th>Substrates</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>A$^i$</td>
</tr>
<tr>
<td>1</td>
<td><img src="image1.png" alt="Substrate 1" /></td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td><img src="image2.png" alt="Substrate 2" /></td>
<td>96</td>
<td>65</td>
</tr>
<tr>
<td>3</td>
<td><img src="image3.png" alt="Substrate 3" /></td>
<td>47</td>
<td>94</td>
</tr>
<tr>
<td>4</td>
<td><img src="image4.png" alt="Substrate 4" /></td>
<td>69</td>
<td>ca.100</td>
</tr>
<tr>
<td>5</td>
<td><img src="image5.png" alt="Substrate 5" /></td>
<td>86</td>
<td>ca.100</td>
</tr>
</tbody>
</table>

$^i$ Reaction conditions: Olefins: 50 mmol; TBHP (5.5 M in decane): 100 mmol; catalyst(1$^*$): 15 mg (0.5 mol%); Chlorobenzene (internal standard): 15 mmol; Temperature: 75 °C; and Reaction time: 6h.  $^j$ a = Epoxide products.  $^k$ b = Aldehyde products. The selectivity is only based on the two major products a and b.

---

![Abundance Graph](image6.png)

(a)
Scan 1090 (12.237 min): JZ-13F.D

Scan 1422 (15.966 min): JM57-F.D

Abundance

m/z→

(b)

(c)
Scan 1814 (20.33 min): JM39-6H.D

Scan 1814 (20.33 min): JM39-6H.D

Cl
CHO
Abundance

Scan 2078 (23.272 min): JM37-6H.D

(f)

Abundance

Scan 1996 (22.356 min): JM37-6H.D

(g)
Figure 3.7. GC-MS spectra of selected products from Co-MOF catalyzed epoxidation reactions: (A) Styrene oxide, (B) Benzaldehyde, (C) Benzoic acid, (D) 2-(4-chlorophenyl)oxirane, (E) 4-chlorobenzaldehyde, (F) 2-(4-tert-butylphenyl)oxirane, (G) 4-tert-butylbenzaldehyde, (H) 2,3-diphenyloxirane and (I) Ethyl 3-phenyl oxirane-2-carboxylate.
3.3.5 Recyclability test of using 2' as a heterogeneous catalyst for olefin epoxidation

In order to confirm the heterogeneous nature of catalyst 2', the recyclability of using 2' for olefin epoxidation reaction in both acetonitrile and solvent-free conditions were tested. The catalyst was recovered and reused four times, and the PXRD patterns of 2' before and after catalytic reactions in acetonitrile solvent and under solvent-free conditions are shown in Figures 3.8 and 3.9, respectively. Small structure changes of the framework are possible during the catalytic reactions since the oxidation state of Co may vary from Co(II) to Co(III) and then back to Co(II). However, the PXRD analysis shows that the structure remains nearly the same after multiple cycles of catalytic reactions (see Figures 3.8 and 3.9). The PXRD patterns also confirm that coordination unsaturated Co(II) metal sites remain open after the reactions (see Figure 3.10). This may simply suggest that the layered framework of 2' is sufficiently flexible so that it can be readily and rapidly restored from any possible changes occurred during the reactions. The conversion and selectivity of olefin epoxidation reaction for different cycles (both in acetonitrile and solvent-free conditions) are shown in Table 3.6 and 3.7. All repeated reactions gave similar % conversion, with only slightly lower selectivity. The small decrease in the selectivity is likely due to the reduced crystallinity of the MOF catalysts after repeated use (see Figures 3.8). Based on the result shown in Tables 3.6, the main changes in conversion and selectivity are between the first and the second cycle while both quantities remain almost constants in the subsequent cycles (2-4). This result is
generally consistent with the PXRD patterns shown in Figures 3.8 in which the peak intensity decreases significantly going from the first cycle to the second while the changes between cycle 3 and 4 are relatively small. This is also evident in the recyclability test of the MOF catalyst under solvent-free conditions (Table 3.7) in which there is almost no change in conversion or selectivity between first two cycles while a gradual decrease in both conversion and selectivity is observed after the 2nd cycle, consistent with the result shown in Figure 3.9.

Figure 3.8. PXRD patterns of $2'$ (blue), $2'$ after 1st (green), 2nd (pink), and 4th (orange) cycle of catalytic reaction in acetonitrile.
Figure 3.9. PXRD patterns of $2'$ (blue), $2'$ after 1$^{st}$ (green), 2$^{nd}$ (pink), and 4$^{th}$ (orange) cycle of catalytic reaction under solvent-free conditions.
Figure 3.10. PXRD patterns of 2 (black), 2’ (blue), 2’ after 1st (green) cycle of catalytic reaction under solvent-free conditions.

Table 3.6. Recyclability test of 2’ using acetonitrile as solvent.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion (%)</th>
<th>% Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a’</td>
</tr>
<tr>
<td>1</td>
<td>70</td>
<td>70</td>
</tr>
<tr>
<td>2</td>
<td>83</td>
<td>59</td>
</tr>
<tr>
<td>3</td>
<td>84</td>
<td>58</td>
</tr>
<tr>
<td>4</td>
<td>82</td>
<td>59</td>
</tr>
</tbody>
</table>

Styrene: 1 mmol; TBHP (5.5 M in decane), 2 mmol; catalyst (2’): 15 mg (2.5 mol%); Internal standard (chlorobenzene): 15 mmol; Solvent: acetonitrile (10 mL); Temperature: 75°C; and Reaction time: 6 h. a’ = Epoxide products. b’ = Aldehyde products. The selectivity is only based on the two major products a and b.

Table 3.7. Recyclability test of 2’ under solvent-free conditions.

<table>
<thead>
<tr>
<th>Cycle</th>
<th>Conversion (%)</th>
<th>% Selectivity</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>a’</td>
</tr>
<tr>
<td>1</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>95</td>
<td>95</td>
</tr>
<tr>
<td>3</td>
<td>93</td>
<td>88</td>
</tr>
<tr>
<td>4</td>
<td>93</td>
<td>81</td>
</tr>
</tbody>
</table>
Styrene: 50 mmol; TBHP (5.5 M in decane), 100 mmol; catalyst (2'):15 mg (0.05 mol%); Internal standard (chlorobenzene): 15 mmol; Temperature: 75 °C; and Reaction time: 6 h. \(a\) = Epoxide products. \(b\) = Aldehyde products. The selectivity is only based on the two major products a and b.

Metal leaching from a solid matrix\(^{164}\) is an unwanted phenomenon that is not uncommon in many heterogeneous catalytic systems. Thus, to confirm the heterogeneous behaviour of 2', a hot filtration experiment was conducted. As a result, a 55% conversion was obtained after 2 h of reaction and another 16% of conversion was observed after removing the catalyst and running the reaction solution for another 4h (see Figure 3.11). The latter is most likely due to non-catalytic thermal oxidation. In order to verify this, a blank reaction was carried out without adding any catalyst. After reaction for 4h, the conversion reached 18%, which matches very well with the additional amount of conversion after removal of the catalyst (16%). Likewise, the selectivity for the epoxide product in a blank reaction is ca. 80%, similar to the values obtained after the CoMOF was removed from the reaction.
Figure 3.11. Test of heterogeneous nature of catalyst 2'. (a) % conversion versus reaction time of epoxidation of styrene oxide catalyzed by 2'. After 2 h, the catalyst was filtered.
off and the reaction continued. This has resulted in a substantial decrease in the rate of the reaction, indicating that catalyst $2'$ is mainly responsible for the catalysis. (b) % selectivity versus reaction time epoxidation of styrene oxide catalyzed by $2'$ (blue: epoxide and, red: aldehyde).

Inductively coupled plasma optical emission spectroscopy (ICP-OES) performed on the filtrate after the 1st and the 4th reaction cycle gave a trace amount of 0.8 and 30 ppm of Co(II), respectively. The calculated weight percent as a result of possible leaching of the catalyst is ~2 wt% (after 4 cycles) and thus, may be considered negligible.\textsuperscript{83,165,166}

### 3.3.6 Mechanism study of catalytic olefin epoxidation using $2'$ as catalyst

Finally, the possible mechanism for the reaction was also investigated. Previous reports show that two types of mechanisms were most commonly found in metal-ion catalyzed epoxidation reactions: concerted addition of oxygen and radical epoxidation.\textsuperscript{167} To probe if radicals were involved in our reactions, a radical scavenger, butyl hydroxy toluene (BHT), was added at the beginning of the reaction, and the reaction progress was monitored. It was observed that the reaction stopped immediately upon addition of the radical scavenger (see Figure 3.12), which suggests that the process indeed proceeds via radical epoxidation.\textsuperscript{167-169} On the other hand, the same reaction in the presence of oxygen clearly indicated the formation of benzoic acid and aldehyde products as a result of oxygen involvement (see Table 3.8). Thus, the proposed reaction mechanism is shown in Figure 3.13. First, reaction between Co(II)-MOF and TBHP takes place to form a Co(III)-peroxy adduct. The Co(III)-peroxy adduct then releases a t-butoxy radical and
regenerates Co(II)-MOF. This is followed by a reaction between t-butoxy radical and olefin to form a t-butoxperoxy species that will further undergo migration of oxygen to form the epoxide product and t-BuOH byproduct. Furthermore, possible involvement of oxygen or t-butoxy radicals with the t-butoxperoxy species will result in some acid and aldehyde byproducts.

Figure 3.12. Conversion vs. time for comparison between reactions with radical scavenger (black) and control reaction without adding radical scavenger (red).
Table 3.8. Comparison of catalytic activity between pure oxygen environment and argon protected environment. 

<table>
<thead>
<tr>
<th>Entry</th>
<th>Environment</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a^i</td>
</tr>
<tr>
<td>1</td>
<td>Oxygen</td>
<td>100</td>
<td>33</td>
</tr>
<tr>
<td>2</td>
<td>Argon</td>
<td>56</td>
<td>96</td>
</tr>
</tbody>
</table>

Styrene: 25 mmol; TBHP (5.5 M in decane): 50 mmol; catalyst (2^*): 15 mg (0.05 mol%); internal standard (chlorobenzene), 15 mmol; temperature: 75 °C; and Reaction time: 6 h. ^i a = Epoxide products. ^k b = Aldehyde products. ^l c = acid products. The selectivity of the reaction is based only on the major products, a, b and c.

Figure 3.13. Proposed reaction mechanism of epoxidation catalyzed by 2^*.
3.4 Conclusion

In conclusion, we have successfully synthesized and characterized a new 2D MOF material, Co(Hoba)$_2$(H$_2$O)$_2$∞ (2). Removal of coordinated water molecules in 2 gives rise to 2' which is thermally stable to 300 °C. 2' shows excellent conversion and selectivity in epoxidation of olefins compared to other catalyst systems (Table 3.9), especially under solvent-free conditions, and is highly recyclable.

Table 3.9. Comparison of catalytic activity of 2' with respect to Au$_{25}$-HAP, Au/SBA$_{15}$ and Co(OOCC$_6$H$_5$)$_2$, previously reported catalysts for styrene epoxidation.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Catalyst</th>
<th>Conversion (%)</th>
<th>Selectivity (%)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>a$^k$</td>
</tr>
<tr>
<td>1</td>
<td>2'</td>
<td>96</td>
<td>96</td>
</tr>
<tr>
<td>2</td>
<td>Au$_{25}$-HAP</td>
<td>100</td>
<td>92</td>
</tr>
<tr>
<td>3</td>
<td>Au/SBA15'</td>
<td>98</td>
<td>96</td>
</tr>
<tr>
<td>4</td>
<td>Co(OOCC$_6$H$_5$)$_2$</td>
<td>60</td>
<td>8</td>
</tr>
</tbody>
</table>

$^j$ Styrene: 50 mmol; TBHP (5.5 M in decane), 100 mmol; Catalyst (Co(OOCC$_6$H$_5$)$_2$), 7.3 mg (0.05 mol%); Internal standard (chlorobenzene): 15 mmol; Temperature: 75 °C and Reaction time: 6 h. The selectivity is only based on the two major products a and b.

$^j$ The substrate they used is 4-chlorostyrene. $^k$ a = Epoxide products. $^l$ b = Aldehyde products. The selectivity is only based on the two major products a and b.
4.1 Introduction

As the world population and industrialization process continue to expand, the demand of energy is increasing explosively. Recent report shows that over 80% of the energy consumption is supplied by burning of fossil fuels (coal, petroleum, and natural gas). As a result, the annual global emission of CO₂ has been increased by 80% between 1970 and 2004. The increasing of the concentration of CO₂ in the atmosphere has been proved to be the main reason for the global warming effect. In order to solve this problem, the replacement of the conventional energy source by alternative renewable energies that are sustainable and environment-friendly is urgently needed. Hydrogen generated through photochemical water splitting process is considered a good candidate, not only because such a process makes use of water and solar power, abundant and renewable, but also because it can convert and store the solar radiation into a form of chemical energy. The water splitting reaction (eq 1) can be divided into two half reactions: the hydrogen evolution (eq 2) and water oxidation (eq 3), where the latter half generates protons and electrons for the former half.
$2\text{H}_2\text{O} \rightarrow 2\text{H}_2 + \text{O}_2 \quad (1)$

$2\text{H}_2\text{O} \rightarrow \text{O}_2 + 4\text{H}^+ + 4\text{e}^- \quad (2)$

$4\text{H}^+ + 4\text{e}^- \rightarrow 2\text{H}_2 \quad (3)$.

It is well recognized that due to the thermodynamic and kinetic limitations, water oxidation is the bottleneck of the overall process since it involves the transfer of four electrons and the combination of two oxygens coming from different water molecules.\textsuperscript{171-174} Among the solid-state heterogeneous water oxidation catalysts (WOCs), the bulk metal oxides such as IrO\textsubscript{2} and RuO\textsubscript{2} were found to be highly active (turnovers in the order of $10^3$),\textsuperscript{175-178} however, the low natural abundances and high cost make them unsuitable for large-scale water oxidation catalysis. Therefore, developing more abundant and low cost WOCs is an on-going joint effort by scientists in many disciplines.\textsuperscript{179-184}

In nature, the water oxidation with extraordinary high catalytic activity occurs in photosystem II (PSII), and it has been shown that the $\mu$-oxo bridged cubic tetranuclear Mn cluster (CaMn\textsubscript{4}O\textsubscript{x}) within the photosynthetic organisms is the catalyst for this reaction.\textsuperscript{185-187} Since manganese is an abundant and inexpensive element, developing Mn based WOCs that can mimic the function of the cubic Mn cluster is highly desired in order to achieve the artificial water oxidation process. The first research interest focused on synthesizing different polymorphs of manganese oxides for water oxidation catalysis.\textsuperscript{188-193} One of the challenges is the complexity of the chemical composition in the formed catalyst product based on different synthesis methods. Due to the poor characterization methods involved in some cases, it is difficult to claim which specific phase of manganese oxide is responsible for the water oxidation catalytic reactions.
Robinson and coworkers recently reported the synthesis and characterization of eight pure polymorphs of manganese oxides. Among them, only Mn_2O_3, Mn_3O_4 and \( \lambda \)-MnO_2 are active catalysts for water oxidation due to their longer average Mn-Mn bond distance in the MnO_6 octahedra building units. This is the first systematic study on evaluating water oxidation activity on pure manganese oxides polymorphs and the correlation between the activity and structure parameters.

Our group has recently attempted to design Metal-Organic Frameworks (MOFs) capable of water oxidation catalysis. One of the candidates is ([Mn_4(\mu_3-OMe)(nic)_4, nic = isonicotinate]) which contains a Mn_4O_4 cubical second building unit structurally similar to the CaMn_4O_x cubical catalytic center in PSII. Using a widely-adapted assay with [Ru(bpy)_3]^{2+} as a photosensitizer and S_2O_8^{2-} as a sacrificial electron acceptor, we find that O_2 is evolved catalytically from water, however, \textbf{1} is not responsible for this catalysis. Rather, the resulting catalytic activity of oxygen evolution in this system is attributed to in-situ formed birnessite-type MnO_2 nanoparticles due to the dissociation of the MOF structure in the photooxidation process. A recent study by Spiccia and coworkers showed that previously synthesized WOC [Mn_4O_4L_6]^+ (L = diarylphosphinate) in fact dissociated to form Mn(II) compounds in the Nafion polymer matrix followed by electro-oxidation to a disordered Mn(III/IV) oxide phase (similar to birnessite MnO_2) which is responsible for the water oxidation catalysis. And our case serves another good example of this dissociation triggered in-situ formed MnO_2 phenomena. Birnessite-type MnO_2 is a layered material with edge-sharing MnO_6 as the basic unit. They contain different cations (K^+, Na^+, Mn^{3+}) and water molecules in the interlayer. They are important materials for battery applications, supercapacitors and even visible light-
driven catalysis. However, studies of using birnessite-type MnO₂ for water oxidation catalysis are still limited due to either the difficulty in characterization caused by structural disorder resulting from cation vacancies, random sheet stacking, lack of long range order and complexity of starting material to synthesize it which gives the opportunity to form a mixture rather than a specific phase of MnO₂ polymorphs or reasonable activity only under specific condition (pH > 9). In this work, we characterized the MnO₂ catalyst formed from the MnMOF to be a specific phase - Na birnessite-type MnO₂ by Pair Distribution Function (PDF) analysis, Raman spectroscopy, X-Ray photoelectron spectroscopy (XPS), Powder X-Ray diffraction (PXRD), Thermogravimetric Analysis (TGA) and Transmition Electron Microscope (TEM) and evaluate its water oxidation catalysis activity using [Ru(bpy)₃]²⁺/S₂O₈²⁻ photo assay in a buffered pH 7.0 media by Clark-Type electrode and Gas Chromatography.

4.2 Experimental

Reagents and materials. All chemicals were purchased from Aldrich, Alfa-Aesar, Acros or VWR and used as received without further purification unless stated otherwise.

4.2.1 Synthesis of [Mn₄(µ₃-OMe)(nic)₄] (3)

3 was synthesized according to the literature method. Mn(ClO₄)₂·6H₂O (0.25 mmol) and isonicotinic acid (0.5 mmol) were placed in a mixed solvent of
CH$_3$CN/CH$_3$OH (7 mL, v/v = 4:3) and heated at 160 °C for two days followed by cooling slowly at a rate of 0.1 °C /min to room temperature. The brown prism crystals were collected, washed with methanol thoroughly and dried in air (70% yield based on Mn).

4.2.2 Light-driven in-situ transformation from 3 to birnessite-type MnO$_2$ nanoparticles

Here we provide a general method to prepare bulk Birnessite-Type MnO$_2$ nanoparticles (4) from the MnMOF precursor (3). The conversion of 3 to Birnessite-Type MnO$_2$ was first noted when 3 was attempted as catalyst for photochemical water oxidation reaction. After 4 was identified as the active catalyst in the observed water oxidation activity, we synthesized 4 directly via decomposition of 3. In a 20 mL glass vial, 10 mg of Ru(bpy)$_3$Cl$_2$·6H$_2$O, 9.4 mg of Na$_2$S$_2$O$_8$ and 10 mg of 3 was mixed in a 10 mL pH = 7 bicarbonate buffer (0.1 mM, adjusted with HNO$_3$). As soon as the solution was illuminated to four LED lamps which collectively provide the included light profile (Figure A1) under magnetic stir, a color change from light gray to dark brown was observed indicating the conversion from 3 to 4. This process might be triggered by dissociation of the MnMOF structure under the oxidation condition in water. After one hour, the in-situ formed birnessite-type MnO$_2$ nanoparticles (4) were centrifuged and washed with DI water for several times in order to remove any surface adsorbed impurities. The sample was then dried in air at room temperature.

4.2.3 Catalyst characterization
Pair-Distribution Function (PDF) data on 4 was collected at station 11-ID-B at the Advanced Photon Source (APS), Argonne National Laboratory, using monochromatic X-rays. Dry samples were loaded into a polyimide (Kapton) capillary. The scattered beam was collected on a Perkin-Elmer amorphous silicon detector. The data conversion from 2D to 1D was carried out using the program fit2D. PDF patterns were generated by Fourier transformation of the total structure function, \( S(Q) \), using the program PDFgetX2, corrected for background scattering, Compton scattering and oblique incidence.

The manganese to sodium elemental ratio on the surface, the oxidation state of manganese in 4 and Ru deposition on the surface of 4 were determined by X-Ray photoelectron spectroscopy (XPS K-Alpha, Thermo Scientific. Inc.) with a monochromated Al K\( \alpha \) X-ray source using Au4f\( _{7/2} \) as an energy reference.

The Raman measurements were collected using a Nicolet Almega XR Dispersive Raman spectrometer from ThermoFisher. A 532 nm solid state laser was used for excitation. The output power was reduced to 1% (0.117 mW) and the acquisition time varied from 5 to 10 min to avoid sample decomposition or phase transition induced by laser heating. The spectra were obtained from 50 to 2000 cm\(^{-1}\), and the spectrometer was equipped with a 50 objective microscope.

Powder X-ray diffraction patterns of 3 and 4 were recorded on a Rigaku Ultima IV X-Ray diffractometer using Cu K\( \alpha \) radiation (\( \lambda = 1.5406 \) Å). Graphite monochromator was used and the generator power settings were set to 40 kV and 44 mA. Data were collected between a 2\( \theta \) of 3-50\(^o\) with a step size of 0.02\(^o\) and a scanning speed of 3.0 deg/min. The morphologies of 4 was studied using TEM with a Topcon 002B
microscope operating at 200 kV. The samples for TEM were prepared by dispersing the powders of 4 in ethanol followed by sonication for 10 min. The suspension was then dropped on a carbon coated copper grid.

The amount of water molecules in the birnessite-type MnO2 nanoparticles (4) was determined by Thermogravimetric Analysis (TGA) collected on a TA Q5000 Thermogravimetric Analyzer with a temperature ramp of 10 °C/min from room temperature to 600 °C under nitrogen gas flow. The Brunauer–Emmett–Teller (BET) surface area of 4 was measured by N2 gas adsorption experiment under 77K on a volumetric gas sorption analyzer (Autosorb-1 MP, Quantachrome Instruments). All samples were activated at 120 °C overnight.

4.2.4 Photochemical Water Oxidation Test monitored by a Clark-Type Electrode

The photochemical water oxidation reactions were conducted in a 2 mL quarts reaction chamber capped with no headspace containing a widely adopted photo-oxidant assay to quantify water oxidation rates as O2 evolution: 0.76 mg of Ru(bpy)3Cl2·6H2O, 9.4 mg of Na2S2O8, various amount of catalyst (3 or 4) in 2 mL pH = 7 bicarbonate buffer (0.1 M, adjusted with HNO3). The reaction chamber was illuminated with four LED lights for about 3 mins, and the temperature in the chamber was kept at room temperature by the surrounded water bath. Dissolved O2 concentrations were measured with a Clark-type electrode (Hansatek Ltd), which was calibrated with both sodium dithionate and N2 purged solutions daily.
4.2.5 Photochemical Water Oxidation Test monitored by Gas Chromatography

In a 12 mL sealed glass vial, the same photo-oxidant assay (1.9 mg of Ru(bpy)$_3$Cl$_2$·6H$_2$O and 23 mg of Na$_2$S$_2$O$_8$) and different amount of 4 was added into 5 mL pH = 7 bicarbonate buffer (0.1 mM, adjusted with HNO$_3$). The solution was purged with N$_2$ for 30 mins with aluminum foil covered on in order to keep it from the light source followed by illumination to four LED lights for 1 hours under magnetic stir. After that, about 200 μL of gas sample from the headspace of the glass vial was drawn and injected to a GOW MAC Series 350 Gas Chromatography equipped with a packed molecular sieve column and Thermal Conductivity Detector (TCD).

4.2.6 Mn leaching test after water oxidation reaction

The Inductive Coupled Plasma (ICP) was used to detect the amount of Mn ions in the reaction solution. The water oxidation test was conducted in a 12 mL sealed vial containing 1.9 mg of Ru(bpy)$_3$Cl$_2$·6H$_2$O, 23 mg of Na$_2$S$_2$O$_8$, 3mg of 4 and 5 mL pH = 7 bicarbonate buffer (0.1 mM, adjusted with HNO$_3$). After illuminated for two hours, the catalyst was separated from the solution using centrifuge. The solution was diluted to 10 mL with DI water and injected into ICP to test the amount of Mn content leaching into the solution during the reaction.
4.3 Results and Discussion

4.3.1 Characterization of the in-situ formed birnessite-type MnO₂ nanoparticles (4)

The as-synthesized MnMOF (3) was characterized by powder X-ray diffraction (PXRD) and the powder pattern was compared with the simulated pattern from the single crystal data to confirm pure phase was obtained (Figure 4.1). The structure of 3 is composed of \{M₄(μ₃-OMe)₄\} cubanes and nic⁻ bridges (Figure 4.2). In each \{M₄(μ₃-OMe)₄\} cubane, the manganese atoms are located at the four alternative vertices of the cube, whereas the methoxide oxygen atoms occupy the rest of the four vertexes. Each \{M₄(μ₃-OMe)₄\} repeating unit in the structure is linked to its four neighbors by eight nic⁻ ligands to form a 3D framework. After the photochemical water oxidation test using 3 as the catalyst, a precipitate was recovered by centrifuging. The PXRD pattern of the recovered material revealed only three low intensity and broad peaks around 2θ = 12.5°, 25.5° and 37.2° indicating the low crystallinity and particle size decreasing of the sample (Figure 4.3). This pattern is also found in a previously reported birnessite-type MnO₂⁴ which implies there might be a light-driven transformation from the MnMOF (3) to the birnessite-type MnO₂ during the photochemical water oxidation reaction. Birnessite-type MnO₂ is a 2D layered structure formed by edge sharing MnO₆ octahedral (Figure 4.4). The MnO₂ layers are normally negatively charged due to the Mn⁴⁺ vacancies in their octahedral sites (Figure 4.4a) or substitution of Mn⁴⁺ by Mn³⁺ (Figure 4.4b).⁴ Different
kinds and amount of cations (e.g. K\(^+\), Na\(^+\), Mn\(^{3+}\)) will intercalate into the interlayers to balance the charge, which forms different phases of birnessite-type MnO\(_2\) including hexagonal birnessite, biogenic MnO\(_2\), acidic birnessite, \(\delta\)-MnO\(_2\) and polymeric MnO\(_2\).\(^{207}\) Since most of them are poorly-crystalline or nanocrystalline materials, PXRD technique is no longer suitable for their structure characterization.\(^{209}\) The atomic Pair Distribution Function (PDF) analysis is a total scattering technique that can probe both local structure and long-range order is a suitable method and was therefore used in our study.\(^{210}\) The powder diffraction experiment was conducted on the sample recovered after reaction at station 11-ID-B of Advanced Photon Source at Argonne National Laboratory and converted to PDF form. We compared the PDF pattern of the recovered sample with the PDF patterns of different phases of birnessite MnO\(_2\) (hexagonal birnessite, biogenic MnO\(_2\), acidic birnessite, \(\delta\)-MnO\(_2\) and polymeric MnO\(_2\)) reported previously.\(^{207}\) The sample pattern matches very well with that of hexagonal birnessite (Figure 4.5) confirming the hexagonal birnessite-type MnO\(_2\) was formed during the photochemical water oxidation reaction.
Figure 4.1. The PXRD patterns of the as-synthesized MnMOF (3, blue) and the simulated pattern from the single crystal data of 3 (red).

Figure 4.2. The Second Building Unit (SBU) of compound 3, the connectivity between the SBUs by nicotinic acids and the overview of 3D structure of compound 3. Color scheme: Mn purple, N green, C gray, O red, and the turquoise polyhedrons represent for the \{Co_4(\mu_3-OMe)_4\} cubane SBUs.
Figure 4.3. The PXRD patterns of compound 3 before (black) and after (red) photochemical water oxidation reaction.
Figure 4.4. (a) Single MnO₂ layer with a fraction of Mn⁴⁺ octahedral vacancies. (b) single MnO₂ layer with Mn³⁺ substitution of Mn⁴⁺. Color scheme: the teal octahedra represent the MnO₆ basic building units with Mn⁴⁺, and the orange octahedra represent MnO₆ with Mn³⁺.

Figure 4.5. PDF patterns of birnessite MnO₂ (black) formed in-situ and hexagonal birnessite (red). The inset shows a zoom-in feature for r = 1-10 Å.

The morphology of the recovered catalyst was studied using TEM technique showing in Figure 4.6. Figure 4.6a is a general view of the well distributed nanoparticles. During the photochemical water oxidation reaction, the MnMOF (3) was converted to birnessite-type MnO₂ nanoparticles (4) with the average size of ~50 nm in diameter. Figure 4.6b shows a zoom-in picture of three individual nanoparticles. Each particle is
composed of multiple thin layers with a thickness of less than 2 nm and all the thin layers intersect with each other to form a "flower-like" morphology. The BET surface of 4 was measured to be 216 m$^2$/g (Figure 4.7) which is more than 70 times increased compared with the MnMOF (only 3 m$^2$/g).

Figure 4.6. TEM images: (a) overview of well dispersed in-situ formed birnessite MnO$_2$ nanoparticles (4), (b) zoom-in picture of individual nanoparticles with "flower-like" morphology.
Figure 4.7. N₂ gas adsorption and desorption isotherms on compound 4 under 77 K.

Since the photochemical water oxidation test was carried out in pH = 7 sodium bicarbonate buffer, there might be sodium cations in the interlayer section of 4. The manganese to sodium elemental ratio on the surface and the oxidation states of manganese in 4 were determined by XPS. The XPS spectra for Mn 2p₃/₂, O 1s and Na 1s regions of 4 are shown in Figure 4.8. The fitted Mn 2p₃/₂ spectra shown in Figure 4.8a shows four peaks around 640.6 eV, 641.7 eV, 642.8 eV and 644.2 eV. The multiplet peaks around 641.7 eV, 642.8 eV and 644.2 eV are the evidence of the presence of Mn⁴⁺ in birnessite-type MnO₂ while the peak in low binding energy region (640.6 eV) represents for the Mn³⁺ in the sample of the MnO₂ layer or intercalating in the interlayer section.²¹¹ There are also other cations (in our case, it is Na⁺) existing between the MnO₂ layers to balance the total charge. The Na 1s XPS spectra shown in Figure 4.8b confirms
the presence of Na⁺ in the sample and the manganese to sodium elemental ratio on the surface is about 1/0.18. The fitted O 1s spectra in Figure 4.8c shows three peaks which represent for three different kinds of oxygen: 529.5 eV for the O²⁻ from MnO₂, 531.5 eV for the OH⁻ groups on the surface and 533.1 eV for the O²⁻ from chemisorbed and physisorbed water molecules in the sample. There is no Ru species (Ru²⁺, Ru³⁺ or Ru⁴⁺) detected by XPS indicating there is no Ru deposition on the surface of the catalyst 4. As a result, the Na⁺ intercalated birnessite-type MnO₂ nanoparticles were formed from the MnMOF (3) precursor. Thermogravimetric Analysis (TGA) was used to determine the amount of water molecules in 4 (Figure 4.9). Due to the large surface of the material, it is difficult to specify different types of water molecules only based on different temperature ranges. Generally, the 8% weight loss before 80°C is attributed to the physisorbed water molecules on the external surface while the 12% weight loss from 80 to 300 °C is for the structural water molecules in the interlayer, and there is averagely 0.65 structural water molecules per MnO₂ unit.
Figure 4.8. XPS spectra of sample 4 for the (a) Mn 2p$_{3/2}$ region, (b) Na 1s region and (c) O 1s regions (blue) with the fitted spectra inside (red).
4.3.2 In-situ transformation from 3 to 4 during photochemical water oxidation reaction

The photochemical water oxidation catalysis test of 3 and 4 was carried out in a 2 mL pH = 7 bicarbonate buffer solution containing 3 or 4, Ru(bpy)$_3^{2+}$ as photosensitizer and Na$_2$S$_2$O$_8$ as sacrificial electron acceptor under visible light illumination. A Clark-type electrode was used to detect the dissolved O$_2$ content in the solution. The in-situ light-driven transformation from 3 to 4 was proven by using 3 and 4 for the water oxidation test containing the same Mn concentration (Figure 4.10). Quantitatively both materials evolve the same amount of oxygen (about 0.11 μmol) after 210 s illumination. The kinetics of 3 and 4 are different with respect to the lag time between illumination and O$_2$
evolution, as expected. While $3$ has approximately a 40 s delay in the onset for water oxidation, $4$ has a delay roughly half as long. Combined, these observations prove that the in-situ formed birnessite $\text{MnO}_2$ nanoparticle ($4$) is the real catalyst which is responsible for the observed water oxidation catalytic activity. The transformation from $3$ to $4$ was also monitored by X-band Electron Paramagnetic Resonance (EPR) spectroscopy, which can discriminate between the two species. At 4 K, $3$ gives a sharp signal at 3000-3500 Gauss (ascribed to its exclusive $\text{Mn}^{2+}$ content), while $4$ gives no significant signal (Figure 4.11). When a sample of the photoassay after illumination but before the $\text{O}_2$ evolution was quickly frozen, the resulting EPR spectrum contained only a small $\text{Ru(bpy)}_3^{3+}$ signal (2500 Gauss). This observation strongly suggests that the dissociation of $3$ allows for formation of catalyst $4$. 

![Graph showing time vs. units of $\text{O}_2$](image)
Figure 4.10. Dissolved oxygen concentration measured by Clark-type electrode at room temperature and pH 7.0. Reaction condition: 0.5 mM of Ru(bpy)$_3^{2+}$, 20 mM of NaS$_2$O$_8$, 50 ppm of catalyst 4 (red), 100 ppm of 3 (black) in 2 mL pH 7.0 bicarbonate buffer. Illumination begins at time $t = 30$ s and stops at $t = 240$ s.

![Graph showing dissolved oxygen concentration over time](image)

Figure 4.11. X-band spectra of solid 3 (black), solid 4 (red), and the photoassay after illumination but before the O$_2$ evolution (blue). Spectrometer settings: Temperature = 4 K, X-band microwave power = 1.02 mW.

![X-band spectra graphs](image)

4.3.3 Photochemical water oxidation tests with 4 as the catalyst

The photochemical water oxidation catalytic activity using different concentration of 4 (synthesized from MnMOF 3) is shown in Figure 4.12. Figure 4.12a shows the
relation between catalyst concentration and initial rate of oxygen evolution, determined by calculating the slope of the linear region from 60 s to 120 s. As the concentration of 4 is increased proportionally from 50 ppm to 200 ppm, the initial rate is also increased proportionally from $5 \times 10^{-4}$ μmol/s to $2.4 \times 10^{-3}$ μmol/s which shows a first order reaction kinetic of catalyst concentration (Table 4.1). The catalyst turnover frequencies (TOF) were determined by normalizing the rate to the amount of catalyst in solution (Figure 4.12b). The highest TOF is $3.95 \times 10^{-4}$ S$^{-1}$ which was obtained using 100 ppm catalyst concentration (Table 4.1). Since not every Mn atom is accessible and active during the catalytic reaction, this TOF underestimates the real activity of the catalyst. As only the surface Mn atoms are involved in the catalytic reaction, the TOFs can also be normalized to surface area and the highest number is 0.033 μmol O$_2$ m$^{-2}$ S$^{-1}$ (Table 4.1, Figure 4.12c) using 100 ppm catalyst concentration. Previous research by Robinson et al showed complete results by using different polymorphs manganese oxide for photochemical water oxidation reaction. They synthesized the crystalline δ-MnO$_2$ (birnessite-type) and claimed no activity (Table 4.2) found in photochemical water oxidation reaction under similar reaction condition (0.5 mM Ru(bpy)$_3^{2+}$, 10 mM Na$_2$S$_2$O$_8$, 250 ppm catalyst in pH 7.0 bicarbonate buffer)$^{7c}$. The different observation may arise from different reasons: 1) the synthesized crystalline δ-MnO$_2$ particles are highly aggregated while in our case shown in Figure 4.6 the individual nanoparticles are better dispersed. This can be further confirmed by the big difference of surface area between the two samples (216 m$^2$/g for 4 vs 17.88 m$^2$/g for δ-MnO$_2$, Table 4.2). In the catalytic reaction, large surface area is desired to increase the accessibility between the active sites and substrates, and the zero activity observed in their case might be due to the small surface area limiting the number
of active sites exposed to the substrates; 2) The δ-MnO₂ prepared by direct synthesis is highly crystalline with well-organized layered structure and long range order. But our sample shows nanocrystalline behavior monitored by PDF analysis. The broad features in the diffraction PDF pattern are reminiscent of layered materials with significant stacking faults due to no strong directional bonding interactions between the layers and significant stacking disorder. This phenomena was also observed by Raman spectroscopy. The measurements were performed on sample 3, 4 and the synthesized crystalline δ-MnO₂ (Figure 4.14). The Raman spectra of sample 3 as shown in Figure 4.13a is dominated by the intense bands associated with the organic parts of 3. For instance, the bands at 1695 cm⁻¹ and 1040 cm⁻¹ are due to the ν(C=C) and β(C-H) of the ring modes. 1397 cm⁻¹ band is ascribed to ν₄(COO⁻) units coordinated to metal ions in MOF structure. Ring deformation modes δ₆a and δ₆b are observed at 848 cm⁻¹ and 614 cm⁻¹, mixed with δ(COO) vibration. After the photochemical water oxidation reaction, the MnMOF (3) transforms into birnessite-type MnO₂ (4) which is characterized by the several feature bands at 650-625, 585-575 and 510-500 cm⁻¹ (Figure 4.13b). The band at 650 cm⁻¹ is assigned to the symmetric stretching mode ν₂(Mn-O) perpendicular to the chain of octahedra MnO₆. The band appearing at 575 cm⁻¹ is usually attributed to stretching vibration ν₃(Mn-O) in the layer of octahedra MnO₆ units. Compared to the spectra of crystalline δ-MnO₂ (Figure 4.13c), ν₂(Mn-O) mode in sample 4 shifts to a higher wavenumber. According to the previous study, the ν₂(Mn-O) mode frequencies of birnessite-type MnO₂ can be correlated with the interaction between the layers. The increase of the Mn-O streching mode frequency observed in sample 4 compared to crystalline δ-MnO₂ indicates shorter Mn-O chemical bond along the direction perpendicular to the MnO₆ chains and weaker
interaction between the layers possibly induced by a local lattice distortion. This claim is also supported by the morphology of sample 4 (Figure 4.6b). Rather than well packed, the thin layers (less than 2 nm thickness) intersect with each other to form a "nano-flower" morphology. Similar to the defoliation process that can highly increase the surface area by separating the packed layers into randomly distributed individual ones, the dissociation triggered in-situ transformation from 3 to 4 and led to the formation of the MnO₂ nanoparticles with preferred morphology for catalytic reactions which cannot be achieved by direct synthesis method. Another good example of using birnessite-type MnO₂ for photochemical water oxidation reaction was done by Iyer et al.¹⁹² They synthesized an amorphous manganese oxide (AMO) that they claimed belong to the birnessite family characterized by PXRD, Raman spectroscopy and IR spectroscopy. This material is active in photochemical water oxidation reaction with a surface area of 184 m²/g and normalized to surface area TOF of 0.004 μmol O₂ m⁻² S⁻¹ (Table 4.2). The high surface area of this material is possibly due to the amorphous nature of the material. As discussed before, PXRD technique is not suitable to characterize material structures with low crystallinity (especially amorphous material) which makes the claim of belonging to birnessite family doubtful. The synthesis method they used (mainly reduction of KMnO₄) gives a possibility of forming a mixed valence of Mn species which might limit the catalytic performance and is difficult to identify which specific phase is responsible for the catalytic performance.
Figure 4.12. Dissolved oxygen concentration: (a) amount of oxygen evolved, (b) amount of oxygen evolved normalized to per manganese atom, (c) amount of oxygen evolved normalized to total surface area measured by Clark-type electrode at room temperature and pH 7.0. Reaction condition: 0.5 mM of Ru(bpy)$_3^{2+}$, 20 mM of Na$_2$S$_2$O$_8$, 50 ppm (black), 100 ppm (red), 200 ppm (blue) of catalyst 4, control experiment without any catalyst (green) in 2 mL pH 7.0 bicarbonate buffer. Illumination begins at time $t = 30s$ and stops at time $t = 240s$. 
Figure 4.13. Raman spectra of (a) as-synthesized MnMOF (3), (b) birnessite-type MnO$_2$ nanoparticle (4) formed in-situ, (c) crystalline $\delta$-MnO$_2$. 
Table 4.1. Photochemical water oxidation catalytic activities monitored by Clark-type electrode using different concentration of catalyst $4^i$.

<table>
<thead>
<tr>
<th>Concentration of catalyst (ppm)</th>
<th>TOF ($\times 10^{-4}$ S$^{-1}$)</th>
<th>$O_2$ evolution rate ($\times 10^{-4}$ μmol/s)</th>
<th>TOF (surface) ($\mu$mol O$_2$ m$^{-2}$ S$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>2.75</td>
<td>5</td>
<td>0.023</td>
</tr>
<tr>
<td>100</td>
<td>3.95</td>
<td>11</td>
<td>0.033</td>
</tr>
<tr>
<td>200</td>
<td>2.17</td>
<td>24</td>
<td>0.018</td>
</tr>
</tbody>
</table>

$^i$ 0.5 mM of Ru(bpy)$_3$$^{2+}$, 20 mM of NaS$_2$O$_8$, 50 ppm, 100 ppm, 200 ppm of catalyst 4 in 2 mL pH 7.0 bicarbonate buffer. Illumination begins at time $t = 30s$ and stops at time $t = 240s$.

Table 4.2. Comparison of the photochemical water oxidation catalytic activities monitored by Clark-type electrode between 4 and other birnessite-type MnO$_2$ catalysts.

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>BET (m$^2$/g)</th>
<th>TOF ($\times 10^{-4}$S$^{-1}$)</th>
<th>TOF (surface) ($\times 10^{-3}$μmol O$_2$ m$^{-2}$ S$^{-1}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>$2^i$</td>
<td>216</td>
<td>4</td>
<td>33</td>
</tr>
<tr>
<td>Crystalline birnessite MnO$_2$$^{/}$</td>
<td>18</td>
<td>N.A.</td>
<td>N.A.</td>
</tr>
<tr>
<td>AMO$^k$</td>
<td>184</td>
<td>0.63</td>
<td>4</td>
</tr>
</tbody>
</table>
0.5 mM of Ru(bpy)$_3^{2+}$, 20 mM of NaS$_2$O$_8$, 100 ppm of catalyst in 2 mL pH 7.0 bicarbonate buffer. 0.5 mM of Ru(bpy)$_3^{2+}$, 10 mM of NaS$_2$O$_8$, 250 ppm of catalyst in 2 mL pH 7.0 bicarbonate buffer. 1.5 mM of Ru(bpy)$_3^{2+}$, 13 mM of NaS$_2$O$_8$, 68 mM Na$_2$SO$_4$, 440 ppm of catalyst in 80 mL pH 5~6 Na$_2$SiF$_6$-NaHCO$_3$ buffer.

In the photochemical water oxidation catalytic reaction, the Ru(bpy)$_3^{2+}$ dye will adsorb photons and be exited to Ru(bpy)$_3^{2+*}$ followed with quenching to Ru(bpy)$_3^{3+}$ by S$_2$O$_8^{2-}$. The Ru(bpy)$_3^{3+}$ species act as the photooxidant in water oxidation reaction. In some cases, the initial amount of Ru(bpy)$_3^{2+}$ will affect the catalytic performance. As changing the Ru(bpy)$_3^{2+}$ concentration from 0.1 mM to 1 mM, there is almost no change in the rate of evolution of oxygen (Figure 4.14, Table 4.3) which suggests that the amount of Ru(bpy)$_3^{2+}$ used in our water oxidation reaction doesn't limit the catalytic activity.
Figure 4.14. Dissolved oxygen concentration measured by Clark-type electrode at room temperature and pH 7.0. Reaction condition: 0.1 mM (black), 0.2 mM (red), 0.5 mM (blue), 1 mM (green) of Ru(bpy)$_3$$^{2+}$, and control experiment without Ru(bpy)$_3$$^{2+}$ (pink), 20 mM of NaS$_2$O$_8$, 100 ppm of catalyst 4 in 2 mL pH 7.0 bicarbonate buffer. Illumination begins at time $t = 30$s and stops at $t = 240$s.
Table 4.3. Photochemical water oxidation catalytic activities monitored by Clark-type electrode using different concentration of Ru(bpy)$_3^{2+}$.

<table>
<thead>
<tr>
<th>Concentration of Ru(bpy)$_3^{2+}$ (mM)</th>
<th>O$_2$ evolution rate ($\times 10^{-4}$ μmol/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.1</td>
<td>11.4</td>
</tr>
<tr>
<td>0.2</td>
<td>11.3</td>
</tr>
<tr>
<td>0.5</td>
<td>11.4</td>
</tr>
<tr>
<td>1</td>
<td>10.2</td>
</tr>
</tbody>
</table>

'0.1 mM, 0.2 mM, 0.5 mM and 1 mM of Ru(bpy)$_3^{2+}$, 20 mM of NaS$_2$O$_8$, 100 ppm of catalyst 4 in 2 mL pH 7.0 bicarbonate buffer. Illumination begins at time $t = 30s$ and stops at time $t = 240s$.

The gas sample collected from the headspace of the reaction mixture was injected into GC and the evolution of oxygen after one hour reaction was confirmed (Figure A2). The amount of oxygen evolution was monitored when using different concentration of catalyst 4 (50 ppm, 100 ppm and 200 ppm, Table 4.4) and more oxygen was produced as higher concentration of catalyst 4 was used. The same phenomena was also observed on Clark-electrode (Figure 4.12a) suggesting the higher oxygen evolution rate will result in more oxygen produced in the catalytic reaction.
Table 4.4. Photochemical water oxidation catalytic activity monitored by GC using different concentration of catalyst 4i.

<table>
<thead>
<tr>
<th>Concentration (ppm)</th>
<th>O₂ produced (mmol)</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>0.0022</td>
</tr>
<tr>
<td>100</td>
<td>0.003</td>
</tr>
<tr>
<td>200</td>
<td>0.006</td>
</tr>
</tbody>
</table>

0.5 mM of Ru(bpy)₃²⁺, 20 mM of NaS₂O₈, 50 ppm, 100 ppm, 200 ppm of catalyst 4 in 5 mL pH 7.0 bicarbonate buffer. Illumination was performed for one hour.

### 4.3.4 Recyclability test of 4 as the heterogeneous water oxidation catalyst

The recyclability of catalyst 4 was also tested. 200 ppm catalyst concentration was used for this test. After the photochemical water oxidation reaction in 0.5 mM Ru(bpy)₃²⁺ and 20 mM Na₂S₂O₈ in pH 7.0 bicarbonate buffer, the catalyst was recovered by centrifuge followed by washed with DI water for several times to get rid of any surface absorbed impurities. The catalyst was then dried in a 60 °C oven for one hour and subjected to the second cycle of water oxidation reaction using fresh Ru(bpy)₃²⁺, Na₂S₂O₈ and buffer solution. This process was repeated for 6 cycles and the gas sample drawn from the headspace of the reaction mixture after cycles was tested by GC. The result gives an identical oxygen amount (0.0058 mmol) as the first cycle (0.006 mmol) indicating no decrease of catalytic activity after 6 reaction cycles. The ICP result on the reaction solution after first and sixth cycle also shows negligible amount of Mn (< 0.02 ppm and < 0.03 ppm) indicating no Mn leaching to the solution during the catalytic reaction.
4.4 Conclusion

In conclusion, the birnessite-type MnO₂ nanoparticles (4) formed in-situ from the decomposition of MnMOF (3) precursor during photocatalytic water oxidation reactions was well characterized by PDF analysis, Raman spectroscopy, XPS, TEM and TGA. The dissociation triggered in-situ transformation from 3 to 4 was confirmed by both Clark-type electrode experiment and in-situ EPR study. 4 is actually responsible for the observed water oxidation activity and proved as an active heterogeneous catalyst monitored by both Clark-electrode and GC method. Since the birnessite-type MnO₂ formed from other direct synthetic routes either gives no activity (δ-MnO₂ in Robinson's paper) or relatively lower activity in photochemical water oxidation reaction and are lack of evidence to prove the formation of pure birnessite-type MnO₂ (AMO in Iyer's paper), the synthetic procedure to generate pure active birnessite-type MnO₂ with the "nano-flower" morphology from MnMOF (3) precursor is considered to be a unique way. The authors believe that this study also provides insight for future investigations of using MOF as precursor or direct catalyst for water oxidation catalysis.
CHAPTER 5
DESIGN AND SYNTHESIS OF A NEW MESOPOROUS METAL ORGANIC FRAMEWORK

5.1 Introduction

In recent years, many efforts have been made to develop MOFs with large surface area and pore size (≥ 2nm) for possible applications in gas storage and catalysis. The ordered framework, composed of metal-carboxylate coordination building blocks and tunable organic linkers, often have open channels or cavities ranging from micropore (pore size < 2nm) to mesopore (2nm < pore diameter < 50nm). Most of the MOFs reported to date feature micropores, which limit fast molecular diffusion and mass transfer. The micropores are also seldom accessible for the large molecule substrates that are often present in catalytic reactions, which limits their application in fine chemical transformations. The presence of mesopores in MOFs broadens their use as hosts to accommodate larger, bulkier molecules, allowing their reaction or transformation without diffusion limitations in a confined space. As previously described, the pore sizes of MOFs can be tuned by changing the length of the organic linkers whereby using longer organic linkers should result in forming MOFs with larger pore sizes and surface areas. In this chapter a new organic linker, tetra(4-pyridylphenyl)ethylene (tppe), was synthesized and used to generate a new mesoporous MOF structure, [Zn₃(bpdc)₃(tppe)]ₓDMA (5). Due to the large size of the tppe ligand, this new MOF has a high surface area of 1287 m²/g with 2D channels built in the structure. The preliminary gas adsorption results of 5
are presented in this chapter. Since tppe ligand is also a highly conjugated molecule, the photoluminescence properties of 5 were also studied.

5.2 Experimental

Reagents and materials. All chemicals were purchased from Aldrich, Alfa-Aesar, Acros or VWR and used as received without further purification unless stated otherwise.

5.2.1 Synthesis of \([\text{Zn}_3(\text{bpdc})_3(\text{tppe})]\cdot x\text{DMA} \ (5)\)

Compound 5 was prepared by mixing Zn(NO$_3$)$_2$·6H$_2$O (0.0149 g, 0.05 mmol), 4,4’-biphenyldicarbpxylic acid or H$_2$bpdc (0.0121 g, 0.05 mmol), and tetra(4-pyridylphenyl)ethylene or tppe (0.012 g, 0.02 mmol) in 8 mL of dimethylacetamide (DMA), 2 mL of dimethylsulfoxide (DMSO), and 2 mL of 2-propanol and then heating to 150°C for 12 hours before being cooled to room temperature. The colorless plate-like crystals of 1 were filtered, rinsed with DMA (10 mL) and dried in air for 30 mins (30% yield based on zinc nitrate). Tetra(4-pyridylphenyl)ethylene (tppe) was synthesized based on a previous reported method.$^{221}$

5.2.2 Powder X-ray Diffraction Analysis
Powder X-ray diffraction patterns of all the samples were recorded on a Rigaku Ultima IV X-Ray diffractometer using Cu Kα radiation (λ = 1.5406 Å). Graphite monochromator was used and the generator power settings were at 40 kV and 44 mA. Data were collected between a 2θ of 3-50° with a step size of 0.02° at a scanning speed of 3.0 deg/min.

5.2.3 Thermogravimetric Analysis (TGA)

Thermogravimetric profiles were collected on a TA Q5000 Thermogravimetric Analyzer with a temperature ramp of 10 °C/min from room temperature to 600 °C under nitrogen gas flow.

5.2.4 Solvent exchange experiment on sample 5

200 mg sample 5 was immersed into 15 mL of methylene chloride for 2 hours, then the supernatant was decanted followed by another fresh 15 mL of methylene chloride filling into the glass vial. This process was repeated for 6 times to complete the solvent exchange. The final product was collected and named as sample 6.

5.2.5 Sample preparation for photoluminescence (PL) study
In order to make a thin layer of the sample, a glass slide of dimension (16 mm x 60 mm) was rinsed with ethanol and double-sided tape was then applied to the lower half of the slide. The ground powder of the as-made (or outgassed) sample is then spread evenly onto the taped surface of the slide. The excess particles are then removed by gently tapping the side of the slide while it is being held aloft. Using this process creates a very thin, continuous layer of sample on the tape’s surface. This slide was then used for the PL studies collected on the Varian Cary Eclipse fluorescence spectrophotometer.

5.2.6 Gas adsorption study

All gas sorption experiments were performed on a volumetric gas sorption analyzer (Autosorb-1 MP, Quantachrome Instruments). Liquid nitrogen was used as coolant to achieve cryogenic temperature (77 K). Ultra high purity N₂, CO₂ and H₂ (99.999%) were used. The initial outgassing process for each sample was carried out at 358K overnight (under vacuum). Outgassed samples in the amount of ~65-70 mg were used for gas sorption measurements and the weight of each sample was recorded before and after outgassing to confirm the removal of guest molecules. The outgassing procedure was repeated on the same sample between experiments for 0.5~1 hour. Pore properties (e.g. pore volume, pore size, and surface area) were analyzed using Autosorb v1.50 software.
5.3 Results and Discussion

5.3.1 Characterization of compound 5

Due to strong disorder of solvent molecules in compound 5 SQUEEZE function in PLATON software was used to omit the unresolved disorder. Crystals of 5 were grown by a reaction of Zn(NO$_3$)$_2$$\cdot$6H$_2$O, tppe and H$_2$bpdc (in 2:2:1 molar ratio) in DMA, DMSO and 2-propanol mixed solvent at 150 °C for 12 hours. The colorless plate-like crystals were collected and characterized by single crystal X-Ray diffraction methods. Compound 5 crystallizes in the monoclinic crystal system, space group C2. The primary building unit (PBU) is shown in Figure 5.1. There are two kinds of Zn atoms with different coordination environments in compound 5. Zn1 (Figure 5.1a) is six coordinated to four oxygen atoms from carboxylate groups and two nitrogen atoms from tppe, while Zn2 (Figure 5.1b) is five coordinated with three oxygen atoms from carboxylate groups and two nitrogen atoms from tppe. As a result, one of the carboxylate groups coordinating to Zn2 remains monodentate mode while all others exhibit a chelating mode. Each PBU is further connected by bpdc and tppe to generate the 3D network (Figure 5.2a), and three of the identical networks interpenetrate to form the overall framework of 5 (Figure 5.2b) with 2D open channels extending along the crystallographic b-axis (Figure 5.2c) and c-axis (Figure 5.2b). The channels along the c-axis have a triangle-shaped cross section with a ~2 nm opening (excluding Van der Waals radius of the carbon atom, 1.7 Å) while the channels along the b-axis have a square-shaped cross section with a ~8.5 Å opening (excluding Van der Waals radius of the carbon atom, 1.7 Å). All guest molecules (DMA, DMSO and 2-propanol) reside in the
channels. In addition, Large "cages" (Figure 5.3) are also observed with a 2 nm opening (excluding Van der Waals radius of the carbon atom, 1.7 Å ) along the c direction.

Figure 5.1. The coordination environment of (a) Zn1 and (b) Zn2. Color scheme: Zn turquoise, O red, N blue, C gray.
Figure 5.2. The overall structure of compound 5: (a) single 3D network along the c-axis, (b) 3-fold interpenetrated 3D network along the c-axis (each color represents for one identical 3D network), (c) 3-fold interpenetrated 3D network along the b-axis (each color represents one of the three identical 3D networks). Color scheme: Zn turquoise, O red, N blue, C gray.
Figure 5.3. View of a "cage" along the c-axis. Color scheme: Zn turquoise, O red, N blue, C gray, the yellow ball represents for the void space in the cage.

The guest molecules can be removed by heating \(5\) under vacuum at 120 °C for 12 hours. The TG analysis of \(5\) (Figure 5.4) shows a weight loss of 40 wt% that is attributed to the guest molecules in the channels. The outgassed sample \(5'\) is thermally stable up to 400 °C followed by decomposition of the framework. The PXRD patterns of the as-made sample \(5\) and outgassed sample \(5'\) are shown in Figure 5.5 along with simulated pattern from single crystal data. Indicated by the PXRD pattern of sample \(5'\), the structure can be retained after removal of guest molecules. The solvent exchange process was performed on sample \(5\) to prepare the sample for gas adsorption studies. The guest molecules in the channels of \(5\) can be easily exchanged with methylene chloride to form
sample 6. After the exchange, the PXRD pattern of 6 was collected to confirm that no structural changes took place during the exchange process (Figure 5.6). The TGA of sample 6 shows only 2% weight loss (Figure 5.4). This is probably due to the fact that most of methylene chloride has been evolved from the pores because of its low boiling point. For all of the gas adsorption studies, sample 6 was used after activating it at 60 °C under vacuum overnight.

Figure 5.4. Thermogravimetric analysis of sample 5 (blue) and sample 6 (red).
Figure 5.5. The PXRD patterns of the simulated (black), as-made (red), and outgassed (blue) samples.
Figure 5.6. The PXRD patterns of the simulated (black), outgassed (red), and solvent exchanged (blue) samples.

5.3.2 Photoluminescence property of sample 5 and 5'

The solid-state optical absorption spectrum of the sample 5 was obtained from diffuse reflectance data collected on Shimadzu UV-Vis-NIR spectrophotometer (Figure 5.7). The diffuse reflectance measured was converted to Kubelka-Munk Function. The optical band gap was estimated to be ~2.7 eV.
Figure 5.7. The optical absorption spectrum obtained from diffuse reflectance data of sample 5.

The photoluminescence spectra of sample 5 and 5' were shown in Figure 5.8 using an excitation wavelength of 350 nm. Both of the samples are highly luminescent in the solid-state at room temperature. The maximum intensity of the emission peak appears at around 470 nm for sample 5, while that of sample 5' is around 530 nm with a red shift of 60 nm. These interesting behavior will be investigated further for possible PL related sensing applications.
Figure 5.8. Emission spectra of sample 5 (black) and 5' (red) exited at 350 nm.

5.3.3 Preliminary gas adsorption results on compound 5.

The 77K N\textsubscript{2} adsorption-desorption isotherms are shown in Figure 5.9, and the BET surface area for compound 5 is 1287 m\textsuperscript{2}/g. The adsorption-desorption isotherms for CO\textsubscript{2} at low pressure and 298K are plotted in Figure 5.10. At 298K, about 3.6 wt\% of CO\textsubscript{2} is adsorbed at 1 atm. The adsorption curve shows a nearly linear profile which is not uncommon for MOFs with large pore sizes such as compound 5, due to weak interactions between the framework and CO\textsubscript{2} molecules. The low pressure hydrogen isotherm data was also collected to examine the hydrogen storage capability of 5 (Figure 5.11). The hydrogen uptake at 77K is 1.1 wt\% at 1 atm.
Figure 5.9. N\textsubscript{2} 77K adsorption (black)-desorption (red) isotherms of compound 5.
Figure 5.10. CO$_2$ 298K adsorption (black)-desorption (red) isotherms of compound 5.
Figure 5.11. $\text{H}_2$ adsorption (black) and desorption (red) isotherms of compound 5 collected at 77K.

5.4 Conclusion

A new meso-porous MOF with a large surface area (1287 m$^2$/g) was synthesized using a new organic linker ligand (tppe) and was characterized by single crystal diffraction. The TG analysis shows the framework is stable up to 400 °C. The PL study on the as-made and outgassed samples shows that both samples are highly luminescent and exhibit interesting emission behavior.
Figure A-1. Light profile for the LED lamps.
Figure A-2. Gas Chromatograms showing oxygen and nitrogen present in the headspace before (red) and after (blue) 1 hour of illumination in the ruthenium photosensitizer assay. The small peak in blue curve corresponds to oxygen and the big peaks in both red and blue curves for nitrogen.
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