Abstract

Metal-organic frameworks (MOFs) have attracted significant attention during the past decade due to their high porosity, tunable structures, and controllable surface functionalities. Therefore many applications have been proposed for MOFs. All of them however are still in their infancy stage and have not yet been brought into the market place.

In this thesis, the background of the MOF area is first briefly introduced. The main components and the motifs of designing MOFs are summarized, followed by their synthesis and postsynthetic modification methods. Several promising application areas of MOFs including gas storage and separation, catalysis and sensing are reviewed. The current status of commercialization of MOFs as new chemical products is also summarized.

Examples of the design and synthesis of two new MOF structures Eu(4,4′,4″,4‴-(porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid))·2H2O·xDMF and Zn4O(azobenzene-4,4″-dicarboxylic acid)3·xNMP are described. The first one contains free-base porphyrin centers and the second one has azobenzene components. Although the structures were synthesized as designed, unfortunately they did not possess the expected properties.

The research idea to use MOFs as template materials to synthesize porous polymers is introduced. Several methods are discussed to grow PMMA into IRMOF-1 (Zn6O(benzene-1,4-dicarboxylate)3, IR stands for isoreticular) structure. High concentration of the monomers resulted in PMMA shell after MOF digestion while with low concentration of monomers no PMMA was left after digestion due to the small
molecular weight. During the study of this chapter, Kitagawa and co-workers published several papers on the same topic, so this part of the research was terminated thereafter.

Many MOFs are reported to be unstable in air due to the water molecules in air which greatly limited their applications. By incorporating a number of water repelling functional groups such as trifluoromethoxy group and methyl groups in the frameworks, the water stability of MOFs are shown to be significantly enhanced. Several MOFs including Banasorb-22 \((\text{Zn}_4\text{O}(2\text{-trifluoromethoxybenzene-1,4-dicarboxylate})_3)\), Banasorb-24 \((\text{Zn}_4\text{O}(2, 5\text{-dimethylbenzene-1,4-dicarboxylate})_3)\) and Banasorb-30 \((\text{Zn}_4\text{O}(2\text{-methylbenzene-1,4-dicarboxylate})_3)\) were synthesized and proved to have isostructures with IRMOF-1. Banasorb-22 was stable in boiling water steam for one week and Banasorb-30’s shelf life was over 10 months under ambient condition. For comparison, IRMOF-1’s structure collapses in air after a few hours to several days.

Although MOF is a very popular research area nowadays, only a few studies have been reported on the mechanical properties of MOFs. Many of MOF’s applications involve high pressure conditions, so it is important to understand the behavior of MOFs under elevated pressures. The mechanical properties of IRMOF-1 and a new MOF structure \(\text{Eu}_2(\text{C}_{12}\text{N}_2\text{O}_4\text{H}_6)\text{H}_3(\text{DEF})_{0.87}(\text{H}_2\text{O})_{2.13}\) were studied using diamond anvil cells at Advanced Photon Source. IRMOF-1 experienced an irreversible phase transition to a nonporous phase followed by amorphization under high pressure. \(\text{Eu}_2(\text{C}_{12}\text{N}_2\text{O}_4\text{H}_6)\text{H}_3(\text{DEF})_{0.87}(\text{H}_2\text{O})_{2.13}\) showed reversible compression under pressure up to 9.08GPa.
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Chapter 1: Introduction to Metal-Organic Frameworks and Their Applications

Metal-organic frameworks (MOFs) or porous coordination polymers are a new type of porous materials that has attracted significant attention during the past decade. They have the same two major components as coordination polymers, the inorganic connectors and the organic linkers. One main character that distinguishes MOFs and other types of coordination polymers is that MOFs are crystalline while others are usually amorphous compounds. Moreover, the crystallinity of most MOFs is remained after complete solvent removal, leaving MOFs as empty pore structures. From the crystalline structures of MOFs, we can get to know the positions of each atom and the connections between atoms, and further study the correlation between the experimental properties and the structures, which guides the design of new MOF structures with desired properties. Compared with other porous materials such as zeolites and carbon-based materials, MOFs have not only the crystalline structures, but also mild synthesis conditions, higher surface areas, uniformed small pores from one to tens of nanometers depending on different linker lengths. Besides, most importantly the chemistry of MOFs’ internal surfaces can be easily tuned to reach desired properties. In this chapter, the background of MOFs is briefly introduced. First, the main components and how to design MOFs is summarized, followed by several synthesis methods. Next, some promising application areas of MOFs such as adsorption, catalysis and sensing are reviewed. At last is the current status of commercialization of MOFs as new chemical products.
1.1 Design and Synthesis of Metal-Organic Frameworks (MOFs)

As suggested by the name, there are two components in the backbones of MOFs, the metal centers and the organic linkers. Transition metals, both ions and clusters, are often employed in the construction of MOF structures. Most transition metals’ coordination numbers range from 2 to 10, which allow them to act as nodes in the structure and connect multi ligands together. In addition, the coordination geometry decides the direction of each ligand, thus further affects the crystal structure of MOFs. Both the metal centers and the organic linkers are called secondary building blocks (SBUs) in the construction of MOFs. SBUs are simplified geometric schemes of MOF components that can help us to visualize the MOF structures. Figure 1(a) shows schemes of metal ions or clusters as connectors and ligands as linkers in the design of MOF structures. Metal connectors can form many possible geometry centers such as linear, angled, triangle, square planar, tetrahedral, square pyramidal, octahedral centers depending on different coordination numbers and environment.

There are several types of ligands including inorganic ligands, neutral, anionic and cationic organic ligands as in Figure 1(b). There are several common characters of different types of ligands. First, they are rigid so that after removing the guest molecules in the pores, the ligands can still sustain the open pore structure. As for this reason, organic ligands with phenyl rings are widely used, while flexible long-chain molecules such as alkanes are rarely employed. Moreover, the ligands are multi-dental so that they are able to connect more than two metal centers to form extended networks. Small inorganic ligands like halides usually form 1D networks because of their limited coordination numbers and small sizes. Neutral organic ligands such as 4, 4’-bipyridyl
Figure 1.1 (a) Schemes of metal centers and organic linkers as secondary building blocks.

(b) Examples of different types of ligands used in MOF construction.²

and anionic organic ligands like benzene-1,4-dicarboxylic acid can build a variety of MOF structures. Because that the carboxylates have the ability to aggregate metal into M-O-C clusters and result in more stable structures than others, they are widely used in MOF construction.³ Cationic ligands are not often employed due to their low affinity to metal cations.
There are several types of interactions to form MOFs. Coordination bonds form usually between metal centers and ligands. Hydrogen bonds and other interactions such as metal-metal bonds and π-π interactions can also be found in the structures. Since coordination bond is the strongest among all of the interactions in MOFs, structures with more coordination bonds are more stable; on the other hand, structures with more hydrogen bonds or other interactions often lack structural stability.

The last component may present in MOF structures is guest molecules or template molecules, which can be removed later to leave open pore MOF structures. Since the nature does not tend to form big void structures, MOFs are usually filled with guest molecules when synthesized. So it is possible to add template molecules with specific sizes to modulate the pore size of MOFs. For example, organic amines can help to arrange the metal centers and ligands at appropriate distance to form MOF structures, similar with their functions in zeolite synthesis.4

MOF synthesis needs only mild conditions, which is a great advantage compared with zeolites or carbon based porous materials. It is important to control the nucleation and growth rate to obtain well crystallized MOFs. One of the most prevalent methods is the solvothermal technique. Metal salt and organic ligands are dissolved in polar solvent, then the temperature is gradually raised and kept at 50°C to 150°C. It takes a few hours to several days to form MOF crystals using the solvothermal method. Because this method is easy to process and needs no expensive instruments, it is widely employed in MOF synthesis. Elevated temperature can help the bond formation; meanwhile, room temperature synthesis is also possible for MOFs. For example, vapor of volatile amines can be slowly diffused into a solution of metal salt and carboxylate ligand, and gradually
deprotonate the carboxylate group.\textsuperscript{5} It is of the similar effect as slowly releasing reactants into the reaction environment. Layering one solvent containing metal salt over another solvent with ligands, or vice versa can also slow the mixing rate of the two reactants.

In addition to the conventional solvothermal method, microwave-assisted solvothermal method is a fast and high yield synthesis method for MOFs. Microwave not only creates hot spots in polar solvents, which greatly help the nucleation, it also enhances the movement of the solvent molecules and the reactant molecules, as a result greatly accelerates the growth MOF crystal. It takes one to several minutes to produce MOFs using microwave assisted method, while the conventional solvothermal method usually takes several days.\textsuperscript{6} However, it is hard to growth big crystals with the microwave assisted solvothermal synthesis, and the crystal size achieved is usually below 100\(\mu\)m. Besides, sonochemical synthesis can also greatly reduce the reaction time of the conventional solvothermal method. The acoustic cavitation creates extremely high local temperatures and pressures, which enhance the nucleation and growth.\textsuperscript{7}

Although most synthesis needs polar solvents to first dissolve metal salt and ligands, solvent-free synthesis method was also developed for MOFs. Metal acetates and organic ligands are placed in a ball-mill system or grind manually, and after grinding for a few minutes, MOFs are obtained with high yield. Grinding can enhance the mass transfer, reduce the particle size, create defects on reactants and locally heat and melt the reactants, which greatly accelerate the reaction.\textsuperscript{8}

With many kinds of metal centers, ligands and synthesis methods, a large number of MOF structures can be produced. Yaghi \textit{et al.} demonstrated the systematical design and synthesis of the IRMOF series (IR stands for isoreticular). By reacting dicarboxylate
type ligands of different lengths and functional groups with zinc nitrate, they successfully synthesized a series of isostructures with different pore sizes and functionalities.\textsuperscript{9} Ferey group used aluminium nitrate or chromium nitrate and 1,4-benzenedicarboxylic acid to obtain the same MIL-53 structure (MIL = Matériaux de l'Institut Lavoisier).\textsuperscript{10} Besides the carboxylate ligand MOF series, new series of imidazolate ligand MOFs, ZIFs (zeolitic imidazolate frameworks) were also developed.\textsuperscript{11}

The diversity of choices of metal salt and ligands enables MOF structures to contain more than one type of metal ions or ligands. Mixed metals or ligands MOFs were also realized. For example, Suslick \textit{et al.} showed that in one step synthesis, mixed valence Co(II) and Co(III) both appeared in the porphyrin MOF structure PIZA-1 network (PIZA= porphyrinic Illinois zeolite analogue).\textsuperscript{12} With multiple steps, one metal can be first incorporate into the ligand, then further react with another type of metal in later steps, as demonstrated by Maverick group in the Cu-Cd mixed MOF structure.\textsuperscript{13}

Two different types of ligands are used some time in the design of MOF structures to achieve desired structures. Choe \textit{et al.} used 4, 4'-bipyridine as pillars to assemble 2D metal-porphyrin MOFs into 3D structures. Mixed ligands MOFs are not confined to only two types of ligands. Recently, MOFs containing three to four different types of ligands were also obtained, called multivariate MOFs (MTV MOFs). In MTV MOFs, pores have different functionalities, so that different desired adsorption properties can be realized in one MOF.\textsuperscript{14}
1.2 Postsynthetic Modifications of MOFs

One advantage of MOF is that the functionality of the pores can be controlled. As a result, the interactions between the pore surface and guest species can be tuned so that the adsorption is selective. Since there are numerous choices of ligands with different functionalities, MOFs with several different functional groups have been achieved.

However, there are times that the desired functionalities cannot be realized before or during the MOF synthesis. For example, if the functional groups interfere with the MOF synthesis, the desired MOF structures cannot be formed from those ligands directly. In addition, it is also possible that the ligands are too bulky in size or cannot survive the synthesis conditions. It is very challenging to obtain MOFs with these functionalities. So there is a great need to develop a method to functionalize MOFs after they are synthesized.

Postsynthetic modification provides another way to tune MOF’s functionality meanwhile solves the problems encountered by using ligands with desired functionalities. As shown in Figure 1.2, metal centers and starting ligands with functional groups that are able to be modified react at common MOF synthesis conditions to form MOFs with desired crystal structures and pore sizes. Then the functional groups on the ligands can react with postsynthetic reagents to obtain the final desired functionalities.

![Figure 1.2 Scheme illustrating the concept of postsynthetic modification](image)

**Figure 1.2** Scheme illustrating the concept of postsynthetic modification
There are several advantages of postsynthetic modification strategy over using different ligands in one step synthesis. First, ligands with different functionalities may result in different crystal structures during synthesis. However, using postsynthetic modification, once the desired structure is achieved, the crystal structure is identical after postsynthetic modification and the possibility of obtaining different structures is ruled out. Second, even the synthesis condition has been studied before, if changing ligand to the one with extra functional groups, it is very possible that the condition needs to be re-optimized. With postsynthetic modification, efforts on synthesis condition optimization can be saved. Last but not the least, postsynthetic provides a way to modify one MOF to different ones that have different functionalities or even multiple functionalities integrated into one MOF.

Postsynthetic modifications of MOFs can be realized by many interactions, among which covalent bonds and coordination bonds are the two major ones. For most of the postsynthetic modifications, one character in common among the MOFs that can be modified is that they have the further modified functional groups pre-designed in the structure backbones. In other words, when designing the MOFs, reactive yet non-coordinating functional groups are usually parts of the ligands. There are two reasons for this: first, it is hard to modify the ligands without reactive functional groups under the chemical conditions that MOFs can survive; second, if the functional groups are already in place, which means that the modification positions are decided, it is less possible that the modified structure will be affected.
IRMOF-3 is an isostructural MOF with IRMOF-1, comprised of zinc oxide centers and 2-aminobenzene dicarboxylate ligands. The non-coordinating amino groups make IRMOF-3 ideal candidates for postsynthetic modifications via covalent bonds.

Cohen et al. first demonstrated the modification of IRMOF-3 by acetylation of the amino groups with acetic anhydride, as the second reaction in Figure 1.3. They showed that by soaking IRMOF-3 crystals in diluted acetic anhydride CDCl₃ solutions at ambient conditions, over 85% of the amino groups were acetylated. Meanwhile the structural integrity of IRMOF-3 was remained after the modification.

Figure 1.3 Postsynthetic modification of different MOFs with amino groups

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With the same method, they also successfully modified two other MOFs with different structures and multi-ligands. The two MOFs contain both 2-aminobenzenedicarboxylate and 1, 4-diazabicyclo[2.2.2]octane or 4,4’,4’’-benzene-1,3,5-triyl-tribenzoate ligands respectively as shown in Figure 1.3. The experiments showed that the acetylation of amino groups in MOFs was not affected by either different structures or other ligands and it could be applied as a general postsynthetic modification method in amino MOFs. They also found that MOFs with higher surface areas have higher conversion rate.

![Figure 1.4 Various terminal groups were realized in IRMOF-3 by acetylation](image)
In addition, they further systematically studied the method using a series of linear alkyl anhydrides and cyclic anhydrides$^{18-20}$ As shown in Figure 1.4, various functional groups including amine, carboxylate and chiral groups were achieved in IRMOF-3 by acetylation of amino groups. They also obtained MOFs containing up to five different functional groups by sequential modification steps.

Another method to modify MOFs postsynthetically is by coordination interactions, which requires potential coordinative sites in the structure. However, the coordinative sites of ligands usually either get occupied by metal ions during MOF synthesis or interfere with the synthesis to cause failure in obtaining MOFs. Nevertheless, these potential coordinative sites can be introduced into MOFs by covalent postsynthetic modification, so that they are not causing any interference with the synthesis, yet still available for later coordination modification. For example, Rosseinsky et al. used imine condensation to modify IRMOF-3 by reacting salicylaldehyde with amino groups in IRMOF-3. Then V(O)acac$_2$ was loaded into the framework to coordinate with salicylidene groups.$^{21}$ The conversion of the first step was only 13%, despite the second step was almost quantitative. They also investigated the catalysis capability of the modified MOF on the oxidation of cyclohexene with tBuOOH, but got a low conversion of the reaction. Although the result was not as expected, it demonstrated a new approach to modify MOFs by first covalent modification followed by coordination modification. It also showed an example to make new MOFs for catalysis with existing MOFs by postsynthetic modification.
In summary, MOFs can be modified by both covalent bonds and coordination bonds, and various reactions have been demonstrated in postsynthetic modifications so far. Multiple modification steps can be performed to introduce either single or multiple functionalities into MOFs. By postsynthetic modification, one MOF can be modified into many new MOFs with desired functionalities, which significantly diversifies the choices of MOFs for different applications.

1.3 Metal-Organic Frameworks for Gas Storage and Separation

MOFs have extraordinarily high surface areas, tunable pore structures, and controllable surface functionalities, all of which make MOFs ideal materials for gas adsorption, especially in applications such as gas storage and separation.

For example, MOFs are proposed to be promising in hydrogen storage. People have been trying to find new energy sources to replace the fossil fuels for a long time due to both sustainability and environment issues. Hydrogen is expected to be one of the most possible substitutes for fossil fuels and become the next generation energy source. However, as a gas at ambient conditions, it is hard to carry large volume of hydrogen to supply the energy consumption. Although hydrogen gas can be compressed or liquefied, the density is still below the desired 81g/L and 9.0wt% in 2015 by the United States
Department of Energy.\textsuperscript{22} So it is necessary to develop an efficient hydrogen storage system to achieve a density higher than liquid hydrogen.

Rosi \textit{et al.} first measured hydrogen adsorption on MOFs and obtained promising results.\textsuperscript{23} Figure 1.6 shows the hydrogen adsorption isotherms at 78K and 298K. They found that at 78K, saturation appeared at low pressure followed by a pseudoplateau. The maximum hydrogen uptake achieved at 78K was 4.5wt\%. At ambient temperature, in the pressure range from ambient pressure up to 20bar, the hydrogen isotherms was linear,

\textbf{Figure 1.6} Hydrogen gas adsorption isotherm of IRMOF-1 at (A) 78K (B) 298K.\textsuperscript{23}

and saturation was not reached until 20bar. At 20bar, the hydrogen uptake was 1.0\%. Further inelastic neutron scattering results showed that there were two hydrogen binding sites in IRMOF-1 associated with the zinc centers and the linkers respectively. As the loading of hydrogen increased, more hydrogen bound to the linker sites, which suggested that higher hydrogen sorption capacity might be achieved in MOFs with larger linkers. So they tested the hydrogen sorption behavior on IRMOF-6 with cyclobutylbenzene linker and IRMOF-8 with naphthalene, both of which had isostructures as IRMOF-1 (shown in
The hydrogen uptake of IRMOF-1 at ambient pressure and 10 bar was doubled and quadrupled in IRMOF-6 and IRMOF-8. The result verified their prediction from the neutron scattering experiment. The adsorption of hydrogen on IRMOFs also showed reversibility in their experiments.

![Image](image.png)

**Figure 1.7** Structures of (A) IRMOF-1 (B) IRMOF-6 (C) IRMOF-8.23

Molecular simulations on a series of IRMOFs by Snurr et al. show that there are three pressure regimes for hydrogen adsorption, as in Figure 1.8.24 In the low pressure regime, hydrogen first binds to the metal centers, and heat of adsorption decides the amount of hydrogen adsorbed (Figure 1.8(a)). In the second regime with middle pressure, hydrogen starts to adsorb onto the pore surface, so surface area becomes the key factor for the amount of hydrogen adsorbed (Figure 1.8(b)). At high pressure, hydrogen starts to fill the pores and free volume is dominant (Figure 1.8(c)). Their simulations correlate very well with the experimental results by other groups.
Besides IRMOFs, many other MOFs also possess high capacity of hydrogen adsorption. For example, HKUST-1 has been reported to have similar hydrogen capacity as IRMOF-1. However, the adsorption behavior is not exactly the same. This can be explained that after removing the water molecules coordinated to Cu(II) centers in HKUST-1 by drying procedures, Cu(II) became unsaturated centers, thus was able to interaction with hydrogen and formed dihydrogen complex.

The amount of hydrogen adsorption on MOFs so far already makes it promising storage materials. Furthermore, the adsorption amount of dissociated hydrogen in MOFs is even higher. Supported catalyst such as Pt can dissociate hydrogen into hydrogen atoms and adsorb them onto the catalyst surface. Then the hydrogen atoms can migrate onto the supporting materials surface, which is called spillover. Li et al. showed that by mixing active carbon supported Pt catalyst and MOFs, the hydrogen uptake of IRMOF-1 and IRMOF-8 can be enhanced by 3.3 and 3.1 times respectively (shown in Figure 1.9). The desorption of hydrogen was also measured, followed by evacuation of the sample and another cycle of adsorption and desorption to test the reversibility. Despite the slight
discrepancy of the adsorption and desorption curve in Figure 1.9, the result indicated almost fully reversibility of the dissociated hydrogen adsorption, which was also confirmed by the second cycle of adsorption and desorption. Their research developed a new method to achieve higher hydrogen adsorption with MOFs.

![Figure 1.9 Enhancement of hydrogen storage in MOF-5 via spillover.](image)

**Figure 1.9** Enhancement of hydrogen storage in MOF-5 via spillover.\textsuperscript{26}

In addition to hydrogen, MOFs are also ideal materials for the storage of other gases, such as carbon dioxide. Because of the global warming, reducing CO\textsubscript{2} emission has become an urgent issue. Thus, developing CO\textsubscript{2} capturing materials is of great significance. Although the traditional aqueous monoethanolamine (MEA) method is widely used in industry, the degradation and regeneration procedures make it less desirable.\textsuperscript{27} So there is a need for stable and reusable materials for CO\textsubscript{2} capture. The robust structure, high thermal and chemical stability and high pore volume of MOFs make them candidate materials for CO\textsubscript{2} capture.
CO₂ uptake from ambient pressure to 42bar at room temperature in different MOFs has been measured by Millward et al. (Figure 1.10).²⁸ The result shows that MOF-177 has an extraordinarily high capacity of CO₂ of 33.5mmol/g or 147wt%, which is the highest CO₂ uptake among all of the known CO₂ capture materials. In other words, one tank filled with MOF-177 can take as much as nine tanks of compressed CO₂. The high CO₂ capacity is explained as condensation in the pores of MOFs by molecular simulations.²⁹ Besides MOFs, zeolitic imidazolate frameworks (ZIFs) are also reported to have exceptional high capacity of CO₂.¹¹

![Figure 1.10 CO₂ capacities of different MOFs at room temperature.²⁸](image)
MOFs can be good storage materials for many gas molecules as discussed above. Meanwhile, because of the controllable pore structure and surface functionalities, selective adsorption of gas molecules from mixtures and gas separation can also be achieved in MOFs. There are several possible mechanisms of gas separation such as molecular sieving effect, thermodynamic equilibrium effect, kinetic effect and quantum sieving effect.\textsuperscript{30}

Dybtsev \textit{et al.} showed the selective adsorption of H\textsubscript{2} and CO\textsubscript{2} in a Mn(II) formate MOF structure. Other gases such as N\textsubscript{2}, Ar and CH\textsubscript{4} cannot be absorbed by the MOF.\textsuperscript{31} The selectivity was because of the molecular sieving effect of the 1D channel. The channel diameter allowed only H\textsubscript{2} and CO\textsubscript{2} molecules to enter. In addition to the separation of small gas molecules, hydrocarbon separation was also achieved in MOFs via size exclusion effect. It has been reported that a MOF with large chambers and narrow necks in the 1D channels can selectively absorb C\textsubscript{2}, C\textsubscript{3} and n-C\textsubscript{4} alkanes and olefins, but not higher carbon number alkanes or olefins.\textsuperscript{32}

Equilibrium based separation can be realized in MOFs due to their tunable surface functionalities. For example, CO\textsubscript{2} was selectively absorbed from a mixture of CO\textsubscript{2}/CH\textsubscript{4} in a mixed ligand MOF.\textsuperscript{33} The selectivity of CO\textsubscript{2} over CH\textsubscript{4} was 30 times, which was one of the highest selectivity so far. The selectivity was because of the different polarity. CO\textsubscript{2} had a high quadrupole moment while CH\textsubscript{4} was nonpolar in the mixture. CO\textsubscript{2}/CO separation can also get separated because of the same mechanism.\textsuperscript{11}

Besides single crystalline MOFs, interpenetrated MOFs are also widely employed in gas separation. Under different pressure and temperature, the pore size of interpenetrated MOFs may change, and different separations can be achieved in the same
MOF. Interpenetrated MOF-508 was demonstrated to be used in gas chromatography columns for the separation of alkanes. It could separate n-alkanes with different lengths by different van der Waals interactions. The 1D channels of MOF-508 was also able to discriminate linear alkanes from branched alkanes. Figure 1.11 shows the separation of n-alkanes and alkane isomers using MOF-508 packed GC columns.

**Figure 1.11** Separations of alkane mixtures by MOF-508 packed GC column. (a) *n*-pentane and *n*-hexane (b) 2-methylbutane and *n*-pentane, (c) 2,2-dimethylbutane, 2-methylpentane, and *n*-hexane (d) (1) 2-methylbutane, (2) *n*-pentane, (3) 2,2-dimethylbutane, (4) 2-methylpentane, (5) *n*-hexane.

In summary, MOFs have become potential adsorbents for many small molecules. Due to the high adsorption capacity, they are promising storage materials for many single
component molecules. In addition, gas mixtures can be separated in MOFs due to size effect or other interactions, MOFs are can be effective separation materials in the future.

1.4 Luminescent MOFs As Detection Materials

The two components of MOFs, metal ions and organic ligands are both possible to have luminosity. Not surprisingly, many MOFs are found to be luminescent as a result. However, the luminescence in MOF structures is much more complex than in either just metal ions or organic ligands. The luminescence of MOFs can be originated from both metal centers and organic ligands, followed by further interactions among the components or sometimes guest molecules to present unexpected results.

For MOFs with luminescence from ligands, examples of both unaffected ligands emission and emission after ligand-to-metal charge transfer have been reported. For example, it has been reported that in IRMOF-1 the emission wavelength was at $\lambda_{\text{emis}} = 518$ nm with excitation wavelength $\lambda_{\text{ex}} = 350$ nm.\textsuperscript{36} For comparison, the linker-based emission from terephthalic acid was at $\lambda_{\text{emis}} = 418$ nm with $\lambda_{\text{ex}} = 335$ nm, and the metal-based emission from zinc oxide was at $\lambda_{\text{emis}} = 560$ nm with $\lambda_{\text{ex}} = 380$ nm. The emission from IRMOF-1 was different from the ones from either the ligand or the metal center. Further Raman spectroscopy explained this as a result of the ligand-to-metal charge transfer (LMCT). Later study showed that replacing the Zn ions in IRMOF-1 with other metal ions by doping did not change the band gap in the structure, which also supported the explanation of the LMCT mechanism in IRMOF-1.

Allendorf et al. studied luminescence of MOFs with similar topologies with IRMOF-1 and found that in MOFs with greater $\pi$-conjugation ligands, the emission
spectra were very similar to the ligands alone, and zinc oxide centers had little influence on the ligands.$^{36}$ Figure 1.12 shows the emission spectra of IRMOF-11, IRMOF-13 and stilbene MOF on the left and the explanation of less influence of metals on larger conjugated ligands on the right. The increased conjugation can increase the energy level of linkers’ LUMO and decrease HOMO. As a result, the charge transfer from ligands to metals were greatly weakened or disappeared, so the emission from the ligands was not influenced.

![Emission Spectra](image)

**Figure 1.12 Left:** emission spectra of MOFs consisting of ZnO$_4$ and dicarboxylates of stilbene, tetrahydropyrene and pyrene. **Right:** Depiction of energy levels in MOFs.$^{36}$

Linker-based luminescence can also be influenced by metals in other ways. For example, Lu et al. reported their study on MOFs containing the same ligands but different metal ions.$^{37}$ The emission from the Cd(II) MOF was enhanced more than three times compared with the emission from the ligands alone. On the other hand, the emission from the Mn(II) MOF was much weaker than the ligands, and the Co(II) and Ni(II) MOFs
were not luminescent. The emission enhancement was because of a mixed effect of LLCT and MLCT, while the weakening and disappearing of the emission was explained as the quenching effect of the metals.

Besides linker-based luminescence, incorporating lanthanoid ions into MOFs is a popular strategy to generate metal-based luminescent frameworks. Lanthanoid ions are known to have narrow emission but weak intensity due to their forbidden electronic transition. The antenna effect can help to overcome the weak intensity when mixing lanthanoid ions with strongly absorbing ligands.\textsuperscript{38} As shown in Figure 1.13, the ligands can first absorb energy and get excited to the excited states. Then the energy transfer from the excited states of the ligands to the lanthanoid emitting state can be realized by vibronic coupling. Thus, the forbidden pathway of electron transfer in lanthanoid ions is circumvented.

\begin{figure}
\centering
\includegraphics[width=0.5\textwidth]{antenna_effect.png}
\caption{Scheme of antenna effect.\textsuperscript{38}}
\end{figure}
The $^5D_0 \rightarrow ^7F_2$ transition of Eu(III) is very sensitive to the coordination environment due to its strong electric dipole, so MOFs containing Eu(III) have been demonstrated as sensing materials. Chen et al. synthesized a Eu(III) MOF with Lewis basic pyridyl sites for metal ion sensing. As shown in Figure 1.14, they found that different metal ions including Na$^+$, K$^+$, Mg$^{2+}$, Ca$^{2+}$, Mn$^{2+}$, Co$^{2+}$, Cu$^{2+}$, Zn$^{2+}$, and Cd$^{2+}$ presented different quenching capabilities on the luminescent Eu(III) MOF. In particular, the quenching effect of Cu$^{2+}$ was correlated to the ion concentration. 10mM of Cu$^{2+}$ in DMF was able to quench the emission intensity to only half of the original one. The explanation of the quenching effect of the guest metal ions was because that the Lewis basic pyridyl sites bound to the Lewis acidic metal ions, which greatly reduced the antenna effect, so the electronic transition of Eu(III) was again forbidden without antenna effect of the ligand.

![Figure 1.14](image)

**Figure 1.14** Quenching effects of (a) different concentrations of Cu$^{2+}$ (b) different metal ions. 40
The quenching effect was also used in the detection of explosives by luminescent MOFs. The MOF containing zinc centers and mixed ligands of 4,4’-biphenyldicarboxylate and 1,2-bipyridylethene was presented to be luminescent and able to detect explosive molecules such as DNT and DMNB reversibly.\textsuperscript{41} The $\pi$-conjugated ligands acted as both luminescent centers and binding sites. The emission of the MOF was significantly quenched by both DNT and DMNB, as shown in Figure 1.15. The detection of explosive molecules was very fast and the luminescent emission was quenched by 84% when the MOF was exposed to DMNB for only 10 seconds.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure1.png}
\caption{Time-dependent fluorescence quenching by (a) DNT (b) DMNB. The insets showed the intensity change before and after exposing MOFs to explosive molecules for 10 seconds for the first three cycles.\textsuperscript{41}}
\end{figure}

MOFs have large surface areas that allow more molecules to interact with the pore surface, so the emission of luminescent MOFs can be greatly influenced by guest molecules and presents different response to not only different molecules but different
concentrations as well. All of the features above make MOFs candidate materials for small molecule sensing.

1.5 Heterogeneous Catalysis in MOFs

It has been long known that metal and metal ions can catalyze a variety of reactions. Since MOFs contain metal centers and organic ligands, they are proposed to be catalytic materials. Not only the metal centers in MOFs can act as catalysts, many examples showed that the ligands could play the same role. Besides, due to the large surface area and uniform pore size of MOFs, it is expected that the catalysis efficiency in MOFs is higher and the selectivity is better.\textsuperscript{42} Besides, not only MOFs themselves can play the role of catalysts, the guest molecules incorporated in MOFs sometimes have the catalysis capability as well, so MOFs can also become supporting materials for other catalysts.

Fujita and co-workers first discovered the size and shape selective clathration effect in the 2D Cd(II) and bipyridine MOF.\textsuperscript{43} The MOF can clathrate \textit{o}-dibromobenzen and \textit{o}-dichlorobenzen, however, the meta and para isomers were excluded due to their bigger size (as in Figure 1.16). They also observed the same clathration effect on the cyanosilylation of aldehydes in the 2D MOF. After removing the coordination water molecules, Cd(II) became the catalytic centers for the reaction. In their study, the conversion of 2-tolualdehyde and \textit{α}- and \textit{β}-naphthaldehyed was much higher than 3-tolualdehyde and 9-althaldehyde respectively. The results showed that the reactants must first enter the pores to start reaction, and the pore size greatly limited the size of the reactants and the clathration effect presented.
As mentioned above, coordinatively unsaturated metal centers can become Lewis acidic catalysis centers. Horike \textit{et al.} has demonstrated very high conversion yield of cyanosilylation of aldehydes and ketones in the microporous MOF Mn$_3$[(Mn$_4$Cl)$_3$BTT$_8$(CH$_3$OH)$_{10}$]$_2$ (I, H$_3$BTT = 1,3,5-benzenetristetrazol-5-yl).\textsuperscript{44} There were two types of Mn(II) in the structure, among which type II Mn(II) was only two-coordinated and could serve as catalysis centers (Figure 1.17). The conversion of benzaldehyde and 1-naphthaldehyde was as high as 98\% and 90\% respectively. Besides, the MOF was also able to catalyze Mukaiyama–aldol reaction which required very reactive Lewis acidic sites.
Figure 1.17 Scheme of two types of Mn(II) sites (left) and reactions catalyzed in the presence of the Mn(II) MOF (right).\textsuperscript{44}

Besides the metal centers in MOFs, the ligands can also become catalysis sites. Usually the catalytic ligands contain some metal ions; however, metal ions here are not serving as the nodes in MOF structure but part of the ligands instead. This can be achieved both by using metallated ligands in MOF synthesis, or by postsynthetic modification of ligands with free coordinative sites. For example, metalloporphyrin can catalyze many oxidation reactions, thus is usually used as building blocks in MOF construction for catalysis application. Suslick and co-workers have synthesized a series of porous metalloporphyrin MOFs called PIZA (porphyrinic Illinois zeolite analogue), among which PIZA-3 containing Mn(III) and tetra(p-carboxyphenyl) porphyrins was able to catalyze the hydroxylation of a wide range of alkanes and cyclic alkanes and epoxydation of cyclic alkenes.\textsuperscript{45} The catalysis yield was similar to maganese porphyrin in other heterogeneous systems. Schiff-base ligands are also employed as catalysis sites in
MOF structures. Morris et al. synthesized a MOF comprised of Zn(II) porphyrin and (salen) Mn(II). The MOF was reported to be able to catalyze the olefin epoxydation.  

By postsynthetic modification, catalysis centers can also be realized on the ligands in MOFs. Wu and co-workers showed the postsynthetic modification of a new MOF and the enantioselective catalysis in the MOF. As in Figure 1.18, they employed \((R)-6,6'-\text{dichloro}-2,2'-\text{dihydroxy}-1,1'-\text{binaphthyl}-4,4'-\text{bipyridine}\) as the ligand. The MOF contains the chiral bipyridyl as the primary functional group for MOF construction and 2, 2'-dihydroxy group as the secondary functional group for postsynthetic modification. After the ligand formed the MOF structure with Cd(II) centers, Ti(O′Pr)₄ was added to further react with the chiral dihydroxy group to become catalysis sites. The Ti(IV) catalysis site was enantioselective to the ZnEt₂ additions to aromatic aldehydes and the enantiomeric excess was up to 93%.

![Figure 1.18](image)

**Figure 1.18** (a) MOF with chiral dihydroxy groups (b) postsynthetic modification with Ti(O′Pr)₄ (c) scheme of the ligand.
Since MOFs are porous materials, besides being catalysts themselves, they can also serve as supporting substrates for other catalysts. For example, Macksimchuck and co-workers successfully encapsulated titanium- and cobalt-monosubstituted Keggin heteropolyanions $[\text{PW}_{11}\text{CoO}_{39}]^{5-}$ and $[\text{PW}_{11}\text{TiO}_{40}]^{5-}$ into MOF MIL-101 structure (composed of Cr(II) and terephthalic acid) by electrostatic interaction (Figure 1.19).\textsuperscript{48} Catalytic performance of the composite material was tested on the oxidation of three $\alpha$-pinene, caryophyllene, and cyclohexene and showed both good catalytic activity and selectivity on $\alpha$-pinene allylic oxidation and cyclohexene epoxidation. Furthermore, they found that the composite catalyst was stable under the mild reaction condition and can be recycled with no catalytic capability loss. However, it was not stable in the presence of higher concentration $\text{H}_2\text{O}_2$, since MIL-101 was destroyed.

Figure 1.19 Scheme of $[\text{PW}_{11}\text{CoO}_{39}]^{5-}$ or $[\text{PW}_{11}\text{TiO}_{40}]^{5-}$ encapsulated in MOF MIL-101.\textsuperscript{48}
In summary, many components of MOFs can act as catalytic sites, which can be achieved either during MOF synthesis or postsynthetic modification. Besides, encapsulated catalyst MOF composites demonstrate the possibility to use MOFs as supporting materials. The catalytic capability of the active sites in MOFs is as good as in dispersed systems. The pore sizes and crystal structures of MOFs further help to enhance the reaction selectivity, which is of great significance especially in enantioselective reactions. Although using MOFs as catalysts is still in its infancy, there are already many exciting results so far which indicate that more research needs to be done in this promising field.

1.6 Industrial Production of MOFs

As summarized above, MOFs are an emerging class of porous materials. They are proposed to be useful in many application areas thus attracting more and more attentions. However, none of the applications has been brought into the market place yet. But several MOFs have been mass produced in industry and mostly sold to research institutions.

MOF synthesis has been scaled up from lab scale to industrial level. Most of the production is following the solvothermal method and the flow chart is depicted in Figure 1.20(a). The metal salt and organic ligands are dissolved in solvent separately. Then the two solutions are mixed and kept at 200°C for a few hours to form MOF crystals as precipitate. After filtration and drying procedures, MOFs are further processed into shaped bodies. Besides the conventional solvothermal method, BASF has developed an electrochemical method to avoid the use of large amount of salt and the safety issues accompanied. Sacrificial anodes are used to replace metal salts in the new method. The
method involves the oxidation of the metal anodes in the ligand solution in an electrochemical cell (Figure 1.20(b)). Later procedures are the same as the solvothermal method.

**Figure 1.20** Flow charts of industrial production of (a) Mg-MOF (b) Cu-MOF (c) shaped MOFs.\(^9\)

Now the largest MOF manufacturing company is BASF. Their pilot plant in Ludwigshafen, Germany can produce MOFs in kilograms in one batch using the solvothermal method. The MOFs manufactured by BASF called Basolites are sold through Sigma-Aldrich, and there are four MOFs being commercialized so far, as shown in Table 1.1.
Table 1.1 Basolites sold by Sigma-Aldrich

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<tr>
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<td>1100-2100 m²/g</td>
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<td>1300-1800 m²/g</td>
<td>100°C</td>
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<tr>
<td>F300</td>
<td>Hydrophilic Ferric MOF</td>
<td>1300-1600 m²/g</td>
<td>200°C</td>
</tr>
</tbody>
</table>

Although the industrial produced MOFs are mainly sold to research institutions, with the rapid development of MOF field and the potential applications, it is expected that large quantity of MOFs will be needed, and procedures for more types of MOFs need to be further developed to satisfy the increasing demand of MOF materials.
References


53. Jacoby, M., Heading to market with MOFS. *Chemical & Engineering News* **2008**, *86* (34), 13-16.
Chapter 2: Design and Synthesis of New MOF Structures

In this chapter, examples of the design and synthesis of two new MOF structures are described, one containing free-base porphyrin centers, the other one containing azobenzene ligands. The background and motifs of the structure are first introduced, followed by the synthesis procedures and various characterizations of the two new MOFs. Although the MOF structures were obtained as designed, unfortunately they did not possess the expected properties. Further study is needed to explore application areas for the two MOFs.

2.1 Introduction

Porphyrin MOFs

Porphyrin chemistry is of great interest due to the widespread applications of metalloporphyrins in catalysis. Metalloporphyrin is the parent molecule of many enzymatic catalytic centers, for example hemes, chlorophylls and vitamin B12. It can catalyze a variety of redox reactions.

![Figure 2.1 Tetra(4-carboxylphenyl)porphyrin (TCPP)](image)

Figure 2.1 Tetra(4-carboxylphenyl)porphyrin (TCPP)
It has been proposed to assemble metalloporphyrins into porous supramolecular structures to achieve well arranged and concentrated catalytic centers; meanwhile, the confined reaction space in the pores is expected to be able to enhance the reaction selectivity.

Tetraphenylporphyrin derivatives are rigid multifunctional molecules suitable for building supramolecular structures. The functional groups on the phenyl rings enable the molecule to further react with other components without affecting the porphyrin center. Besides, the porphyrin ring with four phenyl groups is rigid enough to support a porous structure. Thus they played an important role in the design of supramolecular structures as building blocks within the past decade.\(^1,2\) Since multi carboxylate groups ligands are widely used in MOF construction, tetra(4-carboxylphenyl)porphyrin (TCPP) as shown in Figure 2.1 has become a popular ligand in MOF design.

Many efforts have been made to assemble porphyrins into 2D and 3D frameworks using TCPP. Molecular crystal structures of 2D hydrogen bonded TCPP and core metallated TCPP have been reported.\(^3,4\) George and co-workers assembled free base porphyrins into 2D frameworks and the structure was sustained by the hydrogen bonds

![Figure 2.2 2D framework of free-base TCPP (left) and Mn(III)-TCPP (right).\(^3\)]
between cyclic dimeric carboxylate groups. In the assembly of the metallated Mn(III)-
TCPP 3D frameworks, the counter ion PO₄³⁻ acted as nodes and formed catermeric bonds
with Mn(III)-TCPP ligands.

By reacting with transition metal cations 2D and 3D coordination frameworks of
TCPP have also been obtained. For example, Choi and co-workers demonstrated the
assembly of Zn(II) and TCPP into a 2D paddle wheel structure PPF-1, as shown in Figure
2.3. The MOF showed a high surface area and good thermal stability.⁵ Suslick et al.
successfully synthesized a series of 3D TCPP MOFs with transition metal ions such as
Co(III) in PIZA-1 and Zn(II) in PIZA-4.⁶, ⁷ Both PIZA-1 and PIZA-4 showed high
surface areas and good thermal stabilities. Metal cations bound to both carboxylate
groups and porphyrin centers in both structures. In PIZA-1, the cobalt ions showed mixed
valence. Cobalt ions in TCPP center were Co(III), while the ones coordinated with
carboxylates were Co(II) clusters. PIZA-1 showed size-, shape-, and functional group

![Figure 2.3 MOF structures from TCPP and zinc (left) and cobalt (right) ions.⁵, ⁶](image)
selectivity on adsorption of alcohols, amines and common organic solvents. PIZA-4 showed different selectivity on common organic solvents than PIZA-1.

Although many TCPP MOFs have been developed, most of them have the metal at both the structure nodes and TCPP centers. However, sometimes metal ions may only be able to act as catalytic centers in TCPP but not structure nodes. There are two ways to overcome this problem. First, we can metallate the porphyrin centers then assemble them into frameworks. Some examples of this method have been described earlier. However, due to the repelling interaction between metalloporphyrins with the same type of charges, the desired structures cannot be obtained sometimes. The other method is to build a structure with free base porphyrins and incorporate metal ions into the framework by post synthetic modifications.

To leave the porphyrin centers free, metal ions used to construct MOF structures need to be carefully chosen. Lanthanide ions are good candidates for this purpose. Because of their big size, they cannot fit into the porphyrin centers, leaving the final structure with free base porphyrin centers. In addition, they have large coordination numbers that are suitable to coordinate with multiple ligands to form MOF structures.

With the aid of lanthanide ions, free base TCPP and metallated TCPP structures have been achieved by Goldberg group. They tried to use both TCPP and metallated TCPP to react with lanthanide ions and obtained a series of 2D MOF structures by solvothermal synthesis method (Figure 2.4). The MOFs were stable up to 200°C during TGA test. Although the crystal structure showed open pore structures, they did not obtain experimental surface area data on the MOFs. Their research showed promising results to
achieve free base porphyrin MOFs, but the limited porosity greatly hindered the applications of these MOFs.

![Figure 2.4 TCPP (left) and metallated TCPP (right) MOF structures with the aid of lanthanide ions.](image)

Here we report a fast room temperature synthetic route to assemble free base TCPP into a structure between molecular porphyrin crystals and 3D coordination frameworks. Eu(III) was chosen for its big size, high coordination numbers and affinity to carboxylates. The thermal stability of the MOF was fair, but high surface areas were achieved in the new structure.

**Azobenzene MOFs**

It has been long known about the isomerization of azobenzene and its derivatives. Azobenzene and its derivatives can transform from the stable trans- configuration to cis-
form upon exposure to specific wavelength by photoisomerization. The cis-to-trans isomerization can be realized either thermally or photochemically. In other words, the trans-isomer is thermally favored, while the cis-isomer is photochemically favored. The energy needed for the trans-to-cis isomerization is 50kJ/mol. As shown in Figure 2.5, the isomerization can be realized by either the rotation of one phenyl ring along the N=N axis or the in plane inversion of the phenyl ring, and azobenzene at different excitation states takes different pathways during the isomerization.\textsuperscript{10,11} Upon isomerization, the distance between the para carbon atoms in azobenzene changes from 9.0Å in trans-isomer to 5.5Å in cis-isomer.\textsuperscript{12}

\textbf{Figure 2.5} The inversion and rotation mechanism of trans- to cis- isomerization of azobenzene.\textsuperscript{11}

The easy procedures and high yield of isomerization have made azobenzene and its derivatives popular components in the synthesis of photochemically active polymers
for long. For example, in early study azobenzene fragments have been incorporated into polyamides backbone by polymerizing azodibenzoic acid or azodianiline. The isomerization of azobenzene fragments in the polymer backbone in both dilute solution and entangled polymer were very similar with azobenzene monomers, which indicated that the isomerization was not affected by incorporating azobenzenes into the polymer backbones. As a building component, azobenzene derivatives can also be attached to the sided chains of polymers. It was found that in solution, the isomerization was not affected much; however, in the glassy state of the polymers the trans-cis isomerization was much slower. It indicated that in solid state the photoisomerization could get substantially hindered.

Examples of using azobenzene derivatives as building blocks in MOF synthesis have been reported. 4,4'-Azobenzenedicarboxylate and 3,5-dicarboxyl-(3',5'-dicarboxylazophenyl)benzene were employed with Cu(II) and Zn(II) to build various new structures. However, in all of the structures, only the thermal stable trans- form of azobenzene presented, and azobenzene ligands were used as common building blocks. There was no report on the photo or heat isomerization of azobenzene derivatives in MOF structures.

Photochemical reactions among the building blocks in MOF structures have been demonstrated. 1D coordination polymers can be converted into 2D MOF structures by photochemical reactions. For example, Toh and co-workers successfully achieved single-crystal to single-crystal transformation within the 1D Zn–(4,4'-bipyridylethylene) coordination polymer by [2+2] photochemical cycloaddition across the rails (Figure 2.6 left). The coordination polymer transformed from the 1D chain to a ladder-like structure.
The conversion yield was up to 100%. Michaelides et al. reported the similar [2+2] photochemical cycloaddition in 2D planar rectangular framework containing Cd(II) and fumaric acid (Figure 2.6 right). Upon irradiation, color changes and volume contraction were observed in their study.

Examples above showed possibilities of structure transformation by photochemical reactions in crystal structures. Our research idea is to build a 3D MOF containing azobenzene fragments for controlled release application. By photoisomerization, we expect to achieve a structure transformation from big pore size to small pore size or a structure collapse due to the abrupt volume contraction. Then we can use the MOF to first adsorb desired molecules. Later when shedding light with specific wavelength on the MOF, the molecules will be released due to the volume change.

Figure 2.6 [2+2] Photochemical cycloaddition in 1D coordination polymers (left) and 2D planar rectangular framework. 

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44
2.2  Eu(4,4′,4″,4‴-(Porphine-5,10,15,20-tetrayl)tetrakis(benzoic acid))-2H$_2$O·xDMF MOF

Experiments

**MOF Synthesis**

All starting reagents, tetra(4-carboxylphenyl)porphyrin (TCPP) (Aldrich), europium(III) nitrate pentahydrate (Aldrich), N,N-dimethylformamide (DMF) (Fischer) were used as purchased without further purification.

Tetra(4-carboxylphenyl)porphyrin (TCPP) (10.7mg, 0.025mmol) was first dissolved in water (1.25mL), and europium(III) nitrate pentahydrate (9.9mg, 0.0125mmol) was dissolved in N,N-dimethylformamide (DMF) (3.75mL) separately. Then the TCPP solution was slowly added to the Eu(III) solution in a 20mL capped glass vial. The solution was left at room temperature for 30min. Then purple hexagonal or elongated hexagonal platy crystals formed in solution. The crystal size was about 50µm. Longer growing time up to several days resulted in larger crystal sizes up to 100 µm.

**Crystallography**

Single-crystal X-ray diffraction data were collected on National Synchrotron Light Source beamline x29 at Brookhaven National Laboratory. A focused monochromatic x-ray beam with a wavelength of 0.82660 Å was used with an ADSC Q315r detector in the experiments. The structure was solved using direct methods, SHELXS (Sheldrick, G. M. *SHELXS-97*, 97-2; University of Göttingen, Germany: 1997), and refined with the full-matrix least-squares SHELXL (Sheldrick, G. M. *SHELXL-97*, 97-2; University of Göttingen, Germany: 1997) program. The location of the remaining
guest molecules were poorly defined so their contributions were removed from the
diffraction data using the SQUEEZE bypass procedure in PLATON (Spek, A. L. and van
in modeling the framework and coordinated ligands.

**Powder X-ray Diffraction (PXRD)**

Powder XRD data were collected on a Bruker General Area Detector Diffraction
System (GADDS) equipped with a P4 four-circle diffractometer and HiStar multiwire
area detector. A Bruker M18XHF rotating anode generator operating at 50kV and
60mA supplied the Cu Kα (1.54056 Å) graphite monochromatized incident beam.

**Brunauer - Emmett – Teller (BET) Surface Area Tests**

3 point BET surface area tests were performed on QuantachromeNova 2200e gas
adsorption surface area apparatus. Before the tests, the crystals were isolated from the
mother solvent and dried in vacuum oven at room temperature for one day. Then the
samples were transferred into a calibrated BET tube, and degassed on
QuantachromeNova 2200e station over night. Next the 3 point BET (partial pressure 0.1,
0.2 and 0.3) were performed at liquid Nitrogen temperature using Nitrogen as adsorbate.

**Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis (TGA) was performed on Cahn Thermax 500
Thermogravimetric Analyzer. Before the tests, the crystals were isolated from the mother
solvent and dried in vacuum oven at room temperature for one day.
Results and Discussion

The light microscopy pictures of the as synthesized crystals are shown in Figure 2.7. After growing for 30 minutes at room temperature in the mother solution, purple hexagonal or elongated hexagonal platy crystals formed, and the size was about 30µm to 50µm. If longer growing time was allowed, the crystal could grow up to 100 µm.

Figure 2.7 Light microscopy pictures of Eu(TCPP)·2H₂O·xDMF after growing for 30 minutes and 1 week.

Figure 2.8 IR spectrum of Eu(TCPP)·2H₂O·xDMF
Table 2.1 Crystal Data and Structure Refinement

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<td>Full-matrix least-squares on F²</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>22106 / 834 / 1291</td>
</tr>
<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 = 0.0639, wR2 = 0.1731</td>
</tr>
<tr>
<td>R indices (all data)</td>
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</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>0.822 and -1.388 e.Å⁻³</td>
</tr>
</tbody>
</table>

IR spectrum of Eu(TCPP)·2H₂O·xDMF is shown in Figure 2.8. The yield of Eu(TCPP)·2H₂O·xDMF after one week growing time was 68%. Elemental analysis (CHN and ICP) showed the percentage of each component as Eu 10.66% (theoretical 16.69%), C 48.79% (theoretical 63.3%), H 3.52% (theoretical 3.32%), N 7.66%
(theoretical 6.15%). The inconsistency between the experiment value and the theoretical value may be due to the instability of the crystal structure upon environmental change which will be shown later in this chapter. The elemental analysis indicated that the sample contained 67% \( \text{Eu(TCPP)} \cdot x\text{DMF} \) (\( x \) was about 3.5 in the test) and the rest of the sample was 23% inert material which was possible to be \( \text{SiO}_2 \) leached from glass vials.

The crystallographic data of the as synthesized crystal is given in Table 2.1. The crystal was monoclinic in space group \( P 2_1/c \), with an empirical formula \( \text{Eu(TCPP)} \cdot 2\text{H}_2\text{O} \). Since the free solvent molecules of DMF were squeezed out in the crystal structure determination, they were not shown in the formula solved from the crystal structure. Combined with the formula from the elemental analysis, the sample will be denoted as \( \text{Eu(TCPP)} \cdot 2\text{H}_2\text{O} \cdot x\text{DMF} \) hereafter. Due to the thin platy crystal shape, single crystal X-ray diffraction data could not be obtained with \( \text{Cu} \ K\alpha \) radiation. So the data were collected at the Brookhaven National Laboratory beamline at a similar fashion to a protein collection. However, the direction cosine of the individual reflections was not calculated due to the different data collection fashion, so absorption corrections could not be performed. As a result, fitting parameters were higher. In addition, beamline data collections also introduced instrument error into the intensities measured because of the inability of the detector phosphor to convert hard X-rays to light, which may also contribute to higher fitting parameters.

The coordination structure of \( \text{Eu(TCPP)} \cdot 2\text{H}_2\text{O} \cdot x\text{DMF} \) is depicted schematically in Figure 2.9. A pair of Eu(III) cations are connected by the carboxylate arms of four different TCPP building units via Eu(III)-O-C-O-Eu(III) bridges. Besides, oxygen atoms of two other TCPP units’ carboxylate groups and two water molecules coordinate to each
Eu(III) cation, making the total coordination number of Eu(III) eight. TCPP units act as bident ligands in the structure, since only two carboxylate groups on the para position bind to metal centers. As a result, there are two unbound carboxylate groups on each TCPP. For each TCPP unit, all of the four benzoic acid groups are twisted from the porphyrin plane. One of the carboxylate arms acts as the bridge between two Eu(III) cations, while on the para position, only one oxygen of the carboxylate group binds to another Eu(III).

![Eu³⁺ centers](image1)

**Figure 2.9** Coordination schemes of Eu(III) centers and TCPP ligand. (Eu, O, C,N atoms are shown in cyan, red, grey and blue colors respectively)

The coordination between Eu(III) centers and TCPP units yields a 2D network as shown in Figure 2.10(a). The size of the rhombic pore is about 13.2Å by 6.0Å. Porphyrin planes are perpendicular to the 2D network. On the third dimension, unbound carboxylate groups interlock with each other by steric hindrance and form a zipper structure between layers (Figure 2.10(b)). There are 2.2 x10⁶ pairs of carboxylate groups per square µm.
Free base porphyrin centers are aligned along the c axis (Figure 2.10(c)). The size of the large pores along c axis is 15.0Å by 10.7Å.

![Crystal structure of Eu(TCPP)·2H₂O·xDMF](image)

**Figure 2.10** Crystal structure of Eu(TCPP)·2H₂O·xDMF looking down (a) a axis (b) b axis (c) c axis.

The BET surface area of Eu(TCPP)·2H₂O·xDMF was 698m²/g. From single crystal calculation, the density is 1.519g/cm³ with a pore volume of 0.658cm³/g. The unit cell volume is 15925Å³ and the pore volume is 9303 Å³. So Eu(TCPP)·2H₂O·xDMF has 58.4% void percent, which indicates high porosity in the structure.
From Figure 2.11 we can see that the PXRD pattern of the wet powder of Eu(TCPP)·2H₂O·xDMF matched well with the calculated one from the single crystal structure. However, after the solvent removal, there was an obvious change of the PXRD in the dry powder, which indicated a structure collapse upon solvent removal. Although the structure collapse may greatly reduce the porosity, the collapsed structure still achieved a surface area of 698 m²/g.

**Figure 2.11** Powder X-ray diffraction of calculated, wet powder and dry powder of Eu(TCPP)·2H₂O·xDMF.

TGA test of Eu(TCPP)·2H₂O·xDMF is shown in Figure 2.12. The weight loss below 100°C was due to the solvent removal. Then from 100°C to 130°C, the weight remained the same, so the structure was stable up to only 130°C. At temperature above 130°C, the structure started a gradual decomposition.
Both the solvent and thermal instability of Eu(TCPP)·2H₂O·xDMF may be due to the weak interdigitation interaction between the layers. So the application environment of Eu(TCPP)·2H₂O·xDMF is limited by the instability.

The single crystal structure proved that the porphyrin centers are free of metal ions. Eu(III) only bound to carboxylate groups. Further solvent exchange experiment also confirmed the accessibility of porphyrin centers in the structure. The purple color of the as synthesized crystal is from the deprotonated TCPP ligands. When the mother solvent was exchanged with water, the crystal color changed from purple to green gradually as the water diffused into inner crystal layers, but the crystal morphology was intact (shown in Figure 2.13). Using diluted HCl and NaOH to control the pH of the water solvent, at pH=5-7 the crystals were in green color and at pH= 7-10, the crystals were in purple
color. When the pH was below 5 or over 9, the crystals were dissolved in the solvent and formed green and purple solution respectively. Protonation and deprotonation can largely change the resonance structure of the porphyrin ligand, thus change the crystal color. The color change from purple to green is due to the protonation of porphyrin centers. The experiment above indicates that porphyrin centers in the framework are accessible to small molecules such as water.

Further attempts to metallate the free base porphyrin centers with Fe$^{3+}$ Co$^{3+}$ and Mg$^{2+}$ were not successful. Only very limited outer layers can be metallated, and the charge repelling interaction between two adjacent metallated porphyrins often resulted in structure collapse.
2.3 Zn₄O(Azobenzene-4,4′-dicarboxylic acid)₃·ₓNMP MOF

Experiments

**MOF Synthesis**

All starting reagents, azobenzene-4, 4′-dicarboxylic acid (ABDC) (Aldrich), zinc(II) nitrate hexahydrate (Aldrich) and 1-methyl-2-pyrrolidinone (Aldrich) were used as purchased without further purification.

Azobenzene-4,4′-dicarboxylic acid (ABDC) (10.7mg, 0.025mmol) and Zinc(II) nitrate hexahydrate (9.9mg, 0.0125mmol)) were dissolved in 10mL 1-methyl-2-pyrrolidinone (NMP) in a 20mL capped glass vial and left in an oven at 100°C for one week to form orange colored crystals.

**Crystallography**

Single-crystal X-ray diffraction data were collected on National Synchrotron Light Source beamline x29 at Brookhaven National Laboratory. A focused monochromatic x-ray beam with a wavelength of 0.82660Å was used with an ADSC Q315r detector in the experiments. The structure was solved using direct methods, SHELXS (Sheldrick, G. M. SHELXS-97, 97-2; University of Göttingen, Germany: 1997), and refined with the full-matrix least-squares SHELXL (Sheldrick, G. M. SHELXL-97, 97-2; University of Göttingen, Germany: 1997) program. The location of the remaining guest molecules were poorly defined so their contributions were removed from the diffraction data using the SQUEEZE bypass procedure in PLATON (Spek, A. L. and van der Sluis, P. (1990). Acta Cryst. A46, 194-201). Additional restraints were added to aid in modeling the framework and coordinated ligands.
**Powder X-ray Diffraction (PXRD)**

Powder XRD data were collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a P4 four-circle diffractometer and HiStar multiwire area detector. A Bruker M18XHF\textsuperscript{22} rotating anode generator operating at 50kV and 60mA supplied the Cu Kα (1.54056 Å) graphite monochromatized incident beam.

**Brunauer - Emmett – Teller (BET) Surface Area Tests**

3 point BET surface area tests were performed on QuantachromeNova 2200e gas adsorption surface area apparatus. Before the tests, the crystals were isolated from the mother solvent and dried in vacuum oven at room temperature for one day. Then the samples were transferred into a calibrated BET tube, and degassed on QuantachromeNova 2200e station over night. Next the 3 point BET (partial pressure 0.1, 0.2 and 0.3) were performed at liquid Nitrogen temperature using Nitrogen as adsorbate.

**Scanning Electron Microscopy**

SEM pictures were obtained on Hitachi S-4700 High Resolution SEM. Before the tests, the crystals were isolated from the mother solvent and dried in vacuum oven at room temperature for one day. Before the tests, the crystals were soaked in chloroform for three days, and fresh solvent was exchanged each day. To completely remove the solvent, the crystals were dried in vacuum oven at 150°C for one day. Then the crystals were sputtered with Pd-Au for 30 seconds to achieve good resolution under SEM.
Results and Discussion

The crystal structure data of the as synthesized crystals are shown in Table 2.2. The formula of the crystal structure is Zn₄O(ABDC)₃. It is in space group P-3 and the crystal system is trigonal. The unit cell volume is 6553.9 Å³ and the calculated void space is 4952 Å³, which is 75.6% void percent.

![IR spectrum of Zn₄O(ABDC)₃·xNMP](image)

**Figure 2.14** IR spectrum of Zn₄O(ABDC)₃·xNMP

IR spectrum of Zn₄O(ABDC)₃·xNMP is shown in Figure 2.14. The yield of Zn₄O(ABDC)₃·xNMP after one week growing time was 67.2%. Elemental analysis (CHN and ICP) showed the percentage of each component as Zn 24.17% (theoretical 18.64%), C 46.74% (theoretical 46.61%), H 2.24% (theoretical 2.59%), N 7.77% (theoretical
7.59%). The inconsistency between the experiment value and the theoretical value may be due to

**Table 2.2 Crystal Data and Structure Refinement of Zn₄O(ABDC)₃**

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<thead>
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<th>Property</th>
<th>Value</th>
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</tr>
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<tr>
<td></td>
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<td></td>
<td>β = 90°</td>
</tr>
<tr>
<td></td>
<td>γ = 120°</td>
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<tr>
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<td>Refinement method</td>
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<td>R indices (all data)</td>
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<tr>
<td>Largest diff. peak and hole</td>
<td>0.456 and -0.905 e.Å⁻³</td>
</tr>
</tbody>
</table>

the instability of the crystal structure upon environment change which will be discussed later. The elemental analysis indicated that the sample contained 91%
\(\text{Zn}_4\text{O(ABDC)}_3\cdot x\text{NMP}(x \text{ was about } 2 \text{ in the test})\) and the rest of the sample was 9% inert material which was possible to be \(\text{SiO}_2\) leached from glass vials.

The crystallographic data of the as synthesized crystal is given in Table 2.2. The crystal was monoclinic in space group \(P -3\), with an empirical formula \(\text{Zn}_4\text{O(ABDC)}_3\). Since the free solvent molecules of NMP were squeezed out in the crystal structure determination, they were not shown in the formula solved from the crystal structure. Combined with the formula from the elemental analysis, the sample will be denoted as \(\text{Zn}_4\text{O(ABDC)}_3\cdot x\text{NMP}\) hereafter. Due to the small crystal size crystal shape, single crystal X-ray diffraction data could not be obtained with \(\text{Cu K}\alpha\) radiation. So the data were collect at the Brookhaven National Lab beamline at a similar fashion to a protein collection. However, the direction cosine of the individual reflections was not calculated due to the different data collection fashion, so absorption corrections could not be performed. As a result, fitting parameters were higher. In addition, beamline data collections also introduced instrument error into the intensities measured because of the inability of the detector phosphor to convert hard X-rays to light, which may also contribute to higher fitting parameters.

Figure 2.15 shows the coordination scheme of \(\text{Zn}_4\text{O(ABDC)}_3\cdot x\text{NMP}\). Four Zn(II) and one O compose \(\text{Zn}_4\text{O}\) tetrahedron centers. Each edge of the tetrahedron is further bridged by one carboxylate of ABDC to form a Zn-O-C-O-Zn bridge. Each Zn(II) is coordinated by four oxygens, one from the \(\text{Zn}_4\text{O}\) center, three other ones from different carboxylate groups. Each ABDC connects two different \(\text{Zn}_4\text{O}\) clusters to extend the structure and there are two ABDC between a pair of \(\text{Zn}_4\text{O}\) clusters.

One thing worth to note in the structure is that the C-N=N-C bond angle is quite different from both the cis- and the trans- configurations, lying between the two. In each
ABDC, the bond angle of the two C-N=N bonds are 119.03° and 117.37° respectively, very different from the 120° in both cis- and trans- ABDC. Moreover, the torsion angle of the two C-N bonds is 78.06°. The configuration of ABDC in Zn₄O(ABDC)₃·xNMP lies between cis- and trans- ABDC which is not stable under ambient conditions. The lattice energy balanced the instability of the configuration, and made the special configuration possible in Zn₄O(ABDC)₃·xNMP.

![Figure 2.15](image_url) Coordination scheme of Zn₄O(ABDC)₃·xNMP. Zn, O, C and N atoms are shown in pink, red, grey and blue colors respectively.

The extended structure of Zn₄O(ABDC)₃·xNMP looking along a or b and c axis is depicted in Figure 2.16. Along a or b axis, zinc oxide clusters are connected by ABDC ligands to form 2D layers. The layers are held together by interlocked bended ABDC ligands between layers. The space is taken up by the bended ABDC ligands, leaving very limited pore space. However, along c axis six Zn₄O clusters are connected by pairs of ABDC ligands to form a ring structure. There are large channels at the centers of the rings. As calculated the void percent is 75.6%. The six membered ring structure here is
very stable, so that the instability of the special configuration of ABDC can be balanced. On the other hand, a pair of ABDC between two Zn₄O clusters reinforced the stability of the six membered ring.

**Figure 2.16** Crystal structure of Zn₄O(ABDC)₃∙xNMP looking down (a) a or b axis (b) c axis.

Figure 2.17 is the SEM picture of Zn₄O(ABDC)₃∙xNMP. Not all of the crystals were in good shapes, especially after the solvent exchange and drying procedures. The BET surface area tests confirmed the porosity of the structure. Zn₄O(ABDC)₃∙xNMP’s surface area was 351m²/g. Fast drying may cause quick evaporation of the solvent and
result in cracking or breaking down of the crystals to some extent. Furthermore, since the layers are held together by the weak interdigitation reaction between the bended ABDC ligands, the structure is not stable and may fall apart upon solvent exchange and drying procedures.

![SEM picture of Zn₄O(ABDC)₃·xNMP.](image)

**Figure 2.17** SEM picture of Zn₄O(ABDC)₃·xNMP.

To test the possibility of photoisomerization of ABDC in Zn₄O(ABDC)₃·xNMP, 254nm UV light was shed on Zn₄O(ABDC)₃·xNMP crystals and PXRD are compared before and after the test, as shown in Figure 2.18. After one day, PXRD remained the same and no obvious change was detected. Other wavelengths from a continuous light source also failed to excite the isomerization. For azobenzene derivatives, the wavelength needed for the photoisomerization ranges from 250nm to 350nm. However, in Zn₄O(ABDC)₃·xNMP, two ends of the ABDC are fixed by Zn₄O clusters. As a result, the
rotation and inversion of the azobenzene bonds, which is a significant step in the isomerization mechanism, is greatly hindered. Besides, the stable six membered ring structure further stabled the special configuration. So it is very possible that isomerization of ABDC requires very high energy which means not only lower wavelength but higher beam intensity. Furthermore, the energy of the 254nm light is $7.8 \times 10^{-19}$J and the energy barrier for the trans-cis photoisomerization of azobenzene is about 200KJ/mole, which is $3.3 \times 10^{-19}$J per molecule. The energy from the light can only provide the energy for two azobenzene to initiate the isomerization. Even the energy level of the bended ABDC in

![Figure 2.18 PXRD of Zn₄O(ABDC)₃⁻xNMP before and after shedding 254nm UV light.](image)

the structure is higher than the trans-ABDC, and the barrier is smaller, the energy provided by the light is not enough to photoisomerize the bulk crystal of Zn₄O(ABDC)₃⁻xNMP. It is possible that only the outer a few layers can be
photoisomerized, leaving the bulk crystals unchanged. Considering all of the factors above, photoisomerization in the Zn₄O(ABDC)₃·xNMP MOF may not be feasible.

2.4 Conclusions

We have developed a fast room temperature synthetic route to self assemble free base porphyins and Eu(III) cations into a 2D framework further hold together by the interdigitation interactions among unbound carboxylate groups between layers to form an open pore structure Eu(TCPP)·2H₂O·xDMF. The structure was sensitive to both solvent removal and thermal heating, due to the weak interdigitation interaction between layers. Porphyrin centers in the framework were shown to be accessible to small molecules such as water. However, further attempts to metallate the free base centers were not successful.

A new MOF structure containing azobenzene derivative ligands was synthesized with a formula of Zn₄O(ABDC)₃·xNMP. There were channel voids along c axis in the structure, and the porosity was further confirmed by BET surface area tests. The configuration of ABDC in Zn₄O(ABDC)₃·xNMP lies between the cis- and trans- ABDC, which is not stable under ambient conditions. The lattice energy and the six member Zn₄O clusters ring structure greatly stabilized the special configuration. However, due to the stabilization of the crystal structure, the hindrance of the rotation, and insufficient energy from the light source, photoisomerization was not achieved under the conditions investigated.
References


16. Bauer, C. A.; Timofeeva, T. V.; Settersten, T. B.; Patterson, B. D.; Liu, V. H.; Simmons, B. A.; Allendorf, M. D., Influence of connectivity and porosity on


Chapter 3: MOFs as Template Materials

In this chapter, the study on using MOFs as template materials is described. The research goal is to synthesize a type of materials inside the interconnected pores of MOFs first, when the MOFs are removed, new porous materials with complementary structure are obtained. Methyl methacrylate is first diffused into MOFs. Then in the presence of initiator, the monomers are expected to polymerize in the pores. Next MOFs can be completely dissolved under mild condition, leaving only the polymers. However, during the study of this chapter, Kitagawa and co-workers in Japan published several papers on the same topic, which will be reviewed at last in this chapter. So this part of the research was terminated.

3.1 Introduction

Metal-organic frameworks are best known for their extraordinary high surface areas. Properties like uniformed porosity and easy to be removed make them ideal templates for other porous materials synthesis. The pore sizes of MOFs range from one to tens of nanometers.\(^1\) It has been reported that large organic molecules or metal precursors

![Figure 3.1 Inclusion of (a) C\(_{60}\) and (b) dye molecules into MOF-177.\(^2\)](image-url)
could diffuse into pores of MOFs, and the uptakes were considerable. For example, Chae and co-workers successfully included C$_{60}$ and dye molecules into the MOF-177 structure by soaking the MOFs in solutions containing desired molecules, as shown in Figure 3.1.$^2$

Fischer et al. demonstrated the incorporation of several metal ions or clusters into the pores of MOFs by CVD method. Metal precursors were first diffused into MOFs followed by further steps to convert metal precursors to metal ions or clusters.$^3,^4$

Only very recently, one publication reported using MOFs as a template to synthesize porous carbon which showed a high surface area and good electrochemistry performance, but the porosity had a wide range of distribution.$^5$ As in Figure 3.2, carbon precursor furfuryl alcohol vapor was first diffused into MOF-5. Then carbonization was performed at 1000°C with Ar flow. Under such a high temperature, MOF-5 was dissociated into ZnO and organic parts followed by the vaporization of both. The resulting porous carbon displayed a high surface area and hydrogen storage capacity as well as good electrochemical property.

**Figure 3.2** Scheme of porous carbon templated by MOF-5.$^5$
Porous polymers have wide applications such as separation media, ion exchange resin, artificial antibodies and sensor materials.\textsuperscript{6,7} Surface characters of porous polymers can be achieved by choosing monomers with different side chains. In other words, the surface of porous polymers is already functionalized and the character of active sites on porous polymers surface is controllable.

There are two ways to achieve porous polymers. One is to design special oligomers to support the cavities\textsuperscript{8,9}. Mechanically stable monomers usually containing large resonance structures are employed to support the pore volume. However, this method needs a lot of effort in the design and synthesis of monomers.

The other way is to create the pores by template materials when growing normal polymers. Gas, solvents and surfactants which can create emulsions are used as soft templates\textsuperscript{10,11}. Shown in Figure 3.3, polymerization in different phases of emulsion can result in colloids, porous polymers and composite materials. In porous polymer synthesis,

\textbf{Figure 3.3} Emulsion as template for polymerization.\textsuperscript{11}
the emulsion phase can create small pores and easily get removed later, however, the pore size has a wide distribution, and it is hard to achieve uniformed interconnected pores.

On the other hand, mechanically stable small particles or porous materials can be employed as hard templates. For example, Weber and co-workers demonstrated using silica nanoparticles as templates to obtain porous poly( benzimidazole).

However, the pores created by nanoparticles are often not interconnected. Zeolites such as aluminosilicate MCM-41 is commonly used to template the synthesis of a variety of polymers in their mesoporous channels, including PMMA and polyaniline. In addition, other porous materials like fumed silica are also employed to create pores in polymers synthesis. It has been reported that fumed silica templated melamine-formaldehyde resin had a largely enhanced capacity of CO\textsubscript{2} adsorption. For zeolites, removal of templates needs HF which is very dangerous. And only meso pores are generated by the templating methods above.

**Figure 3.4** Hard templates for porous polymer synthesis: (a) nanoparticles as templates to obtain mesoporous polymer (b) structure of MCM-41.

Metal-organic frameworks are well known for their high surface areas and controllable pore sizes. They are thermally stable over 400°C, which is enough for polymers synthesis. In addition, the removal of MOFs only needs common acid like HCl.
with some organic solvent, for example DMSO\textsuperscript{16}, which is much safer than HF. So if MOFs can be used as a template for polymers synthesis, we may get nanoporous long-range ordered polymers structures.

The research idea is to first develop a general method to grow polymers using MOFs as a template, then remove MOFs leaving only porous polymers. After the method is developed and optimized, a variety of polymers can be synthesized into a porous structure with similar methods.

3.2 Templating Poly(methyl methacrylate) (PMMA) in MOF

Experiments

\textit{Microwave Synthesis of IRMOF-1}

All starting reagents, zinc nitrate hexahydrate (Aldrich), 1, 4-benzenedicarboxylate acid (Aldrich), and N,N-diethylformamide (DEF) (TCI America) were used as purchased without further purification.

Zinc nitrate hexahydrate (0.200 g, 0.67 mmol) and 1,4-benzenedicarboxylate acid (0.083 g, 0.50 mmol) were dissolved in 10 mL N,N-diethylformamide (DEF). The solution was then sealed in a reaction tube and heated by CEM Discover Labmate Microwave Synthesizer at 150W for a reaction time of 90 seconds. Small clear cubic shape crystals formed in the tube after reaction.

\textit{Growing PMMA in IRMOF-1(Method 1)}
Methyl methacrylate (MMA) (Aldrich) and ethylene glycol dimethacrylate (EGDMA) were distilled before using. Azobisisobutyronitrile (AIBN) (Aldrich) was used without further purification.

The mother solvent of IRMOF-1 was decanted and IRMOF-1 was washed with fresh DEF three times. A solution of 0.5% AIBN dissolved in MMA (containing 10%v EGDMA for method 1 with EGDMA) was added to IRMOF-1, followed by three times of freeze-to-thaw cycles (liquid nitrogen temperature to room temperature) by a Schlenk line system to remove any gas in the solution. Then IRMOF-1 was soaked in MMA with AIBN (and EGDMA) at 0 °C for one day. The soaking solution was exchanged everyday with fresh MMA and AIBN twice by filtrating IRMOF-1, adding fresh solvent and three freeze-to-thaw cycles to have the pores of IRMOF-1 filled with MMA. Next, IRMOF-1 was again isolated and transferred into a flask. The flask was flushed with argon to remove excess MMA on IRMOF-1 surface, followed by polymerization at 100 °C for two hours.

Growing PMMA in IRMOF-1 (Method 2)

Methyl methacrylate (MMA) (Aldrich) and was distilled followed by three times of freeze-to-thaw cycles (liquid nitrogen temperature to room temperature) by a Schlenk line system to remove any gas in the solution before using. Azobisisobutyronitrile (AIBN) (Aldrich) was used without further purification.

IRMOF-1 was soaked in chloroform for three days, and fresh solvent was exchanged each day. To completely remove the solvent, the crystals were dried in a vacuum oven at 150°C for one day. Then IRMOF-1 was transferred into a flask, kept in
vacuum for one day at 120°C and cooled to room temperature with vacuum on. Boiling MMA vapor was introduced into the vacuumed IRMOF-1 flask continuously for one day. Next, 0.01g AIBN was dissolved in chloroform and added into IRMOF-1 flask. The reaction was kept at 100 °C for two hours for polymerization.

**IRMOF-1 Digestion**

To remove the IRMOF-1 template, digestion solution containing 35% HCl and DMSO was used. The samples were soaked in digestion solution for 10 minutes. Pure IRMOF-1 completely dissolved in the digestion solution immediately and formed a clear solution.

**Powder X-ray Diffraction (PXRD)**

Powder XRD data were collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a P4 four-circle diffractometer and HiStar multiwire area detector. A Bruker M18XHF22 rotating anode generator operating at 50kV and 60mA supplied the Cu Kα (1.54056 Å) graphite monochromatized incident beam.

**Infrared Spectroscopy**

IR spectra were obtained on a Mattson Galaxy Series FTIR 3000 spectrometer. Before the tests, IRMOF-1 was soaked in chloroform for three days, and fresh solvent was exchanged each day. To completely remove the solvent, the crystals were dried in vacuum oven at 150°C for one day, and 50°C for PMMA. Then the samples were pressed into pellets with KBr for IR tests.
**Brunauer - Emmett – Teller (BET) Surface Area Tests**

3 point BET surface area tests were performed on QuantachromeNova 2200e gas adsorption surface area apparatus. Before the tests, the samples were isolated from the solvent and dried in vacuum oven at 150°C for MOFs and 50°C for PMMA for one day. Then the samples were transferred into a calibrated BET tube, and degassed on QuantachromeNova 2200e station over night. Next, the 3 point BET tests (partial pressure 0.1, 0.2 and 0.3) were performed at liquid Nitrogen temperature using Nitrogen as adsorbate.

**Scanning Electron Microscopy and Energy-Dispersive X-ray Spectroscopy**

SEM pictures and EDX data were obtained on Hitachi S-4700 High Resolution SEM. Before the tests, IRMOF-1 was soaked in chloroform for three days, and fresh solvent was exchanged each day. To completely remove the solvent, the crystals were dried in vacuum oven at 150°C for one day, and 50°C for PMMA. Then the samples were sputtered with Pd-Au for 30 seconds to achieve good resolution under SEM.

**Results and Discussion**

The reason to choose MMA as monomers and AIBN as the initiator for this study is because that the system is simple which only involves two components, and both of the components are small enough to get into the pores of MOFs. IRMOF-1 is a well studied MOF with high porosity and easy to prepare in large amount using microwave assisted solvothermal method.
Method 1

The IR spectra of IRMOF-1, IRMOF-1 with PMMA and PMMA after IRMOF-1 digestion are shown in Figure 3.5. IRMOF-1’s characteristic peaks are at 1385 and 1580 cm\(^{-1}\). After polymerizing PMMA in IRMOF-1, characteristic peaks of PMMA at 1451, 1735 and 2950 cm\(^{-1}\) appeared indicating that PMMA was successfully synthesized in the composite material. After IRMOF-1 digestion, only PMMA peaks remained, while IRMOF-1 peaks disappeared, suggesting that IRMOF-1 was removed, and the remaining material was PMMA.

Figure 3.5 IR spectra of IRMOF-1, IRMOF-1 with PMMA and PMMA after IRMOF-1 digestion.
To further identify the component removed by the IRMOF-1 digestion step, the IR absorbance of PMMA after digestion was subtracted from the IRMOF-1 with PMMA, and compared with the original IRMOF-1 spectrum, as shown in Figure 3.6. We can see that the spectra difference matched the IRMOF-1 spectrum very well. So the component removed by the digestion step was confirmed to be IRMOF-1.

Figure 3.6 Comparison of the difference of the IR spectrum before and after digestion and IRMOF-1.

Figure 3.7 shows the comparison of PXRD of IRMOF-1, IRMOF-1 with PMMA and PMMA after digestion. Most of the peaks of IRMOF-1 with PMMA match IRMOF-1 very well, except the one at 12.5°, which is due to sample exposure to air. So IRMOF-1 remained the structure during the polymerization. After IRMOF-1 digestion, no sharp peaks were left in PXRD, only huge bumps presenting the appearance of amorphous
phase. It indicated that the remaining PMMA was amorphous, and IRMOF-1 was completely removed by digestion.

![Figure 3.7 PXRD of IRMOF-1, IRMOF-1 with PMMA and PMMA after digestion.](image)

All the test results indicated that PMMA was grown with IRMOF-1 and by digestion IRMOF-1 was completely removed leaving only PMMA. However, SEM pictures in Figure 3.8 indicated that PMMA may be only in the outer layers of pores of IRMOF-1 or it formed a shell over IRMOF-1 cubes. The SEM pictures of IRMOF-1 with PMMA before and after EDX test in Figure 3.8 (a) and (b) showed that IRMOF-1 with PMMA was quite stable to EDX. After EDX, no morphology change was observed on
the sample. IRMOF-1 with PMMA sample remained the cubic shape and there was no obvious damage on the surface. On the contrary, for PMMA after digestion, after the EDX test, the cubic shaped sample collapsed towards the center, and the surface was melted by the EDX beam. Since PMMA is a polymer sensitive to high temperature, high EDX beam can cause the glass transformation of PMMA. However, from SEM picture, the cube collapsed towards the center indicating that the center was void. So it was very possible that IRMOF-1 took up the center space during PMMA growth, and PMMA only got into the outer a few layers of IRMOF-1, not the center pores, to form a core-shell

**Figure 3.8** SEM pictures of IRMOF-1 with PMMA (a) before and (b) after EDX, and PMMA after digestion (c) before and (d) after EDX.
structure. So after IRMOF-1 digestion, only the PMMA shell was left. In Figure 3.8(d), we can see that the thickness of the PMMA shell was about 1µm.

![Figure 3.9 EDX results of (a) IRMOF-1 with PMMA and (b) PMMA after digestion.](image)

From the EDX results in Figure 3.9(a), we can see that in the sample IRMOF-1 with PMMA, Zn still presented in the sample, indicating that IRMOF-1 was in the composite material. After IRMOF-1 digestion, EDX again proved that IRMOF-1 was completely removed since there was no Zn left in Figure 3.9(b). The sulfur in EDX was from the remaining DMSO which was in the digestion solution. The analysis depth of EDX was about 1-2µm. From the SEM pictures in figure 3.8(d), we knew that the thickness of the PMMA shell was approximately 1µm, so the EDX beam was able to penetrate the PMMA shell to reach the IRMOF-1 shell in the IRMOF-1 with PMMA
sample. After IRMOF-1 was removed, only the PMMA shell was analyzed, showing no Zn peak.

3 point BET surface area tests showed that the surface area of IRMOF-1 was 968.3 m$^2$/g. After PMMA was grown into IRMOF-1, the surface area was dramatically reduced to 10.98 m$^2$/g. After IRMOF-1 was removed, the surface area slightly recovered to 33.04 m$^2$/g. The significant drop in surface area indicated that the open pores of IRMOF-1 were filled by PMMA, so that nitrogen could not enter the pores. As a result, the surface area dropped dramatically. The result also showed that the remaining PMMA was porous, which was in line with the fact that the digestion solution can penetrate the PMMA layer and digest IRMOF-1, and the dissolved components of IRMOF-1 could diffuse outside of the PMMA layer so that EDX detected no Zn left.

The experiment results above indicated that PMMA and IRMOF-1 formed a core-shell material after polymerization, and after IRMOF-1 was removed, the remaining PMMA had a moderate surface area. However, we could not confirm whether PMMA formed a loose shell structure over the cubic IRMOF-1 or it entered the outer layers of IRMOF-1. In other words, we wanted to make sure whether the surface area was from the loose structure of PMMA shell or the IRMOF-1 templated PMMA. Besides, the remaining PMMA was not very mechanically stable. It got melted by the EDX beam. Another concern was that even PMMA entered the outer layers of IRMOF1, if it did not have high enough molecular weight, the porous structures of the templated PMMA could not be maintained. So to improve the mechanical property of the remaining PMMA and maintain the templated structure if it was indeed achieved, EDGMA crosslinkers was added in method 1.
Method 1 with EGDMA Crosslinkers

To enhance the molecular weight and mechanical property of PMMA and help to maintain the templated structure, 10%v EGDMA crosslinkers were added to the MMA and AIBN solution in method 1, with no other steps was changed.

Figure 3.10 IR spectra of IRMOF-1, IRMOF-1 with PMMA, PMMA after digestion and the difference of the latter two.
The IR spectra showed very similar results as method 1 in Figure 3.10. It confirms that PMMA was in the composite material, and after the digestion step, IRMOF-1 was removed.

Figure 3.11 shows the SEM pictures of IRMOF-1 with PMMA and crosslinked PMMA after digestion after EDX tests. Similar with uncrosslinked PMMA, the crosslinked PMMA also collapsed into the center after EDX tests. However, the affected area was much smaller in the crosslinked PMMA. Only the center part collapsed. From Figure 3.11(b) we can also see that instead of the melted PMMA, there were many cracks in the affected area in the crosslinked sample. We can infer that the mechanical property of the crosslinked PMMA was greatly enhanced. However, from the SEM pictures, we can still see the void space of the PMMA after digestion, which indicated that the crosslinked PMMA formed a similar core-shell structure with the uncrosslinked PMMA in method 1.

**Figure 3.11** SEM pictures of (a) IRMOF-1 with PMMA and (b) PMMA after digestion after EDX tests.
EDX results in Figure 3.12 demonstrated that although after IRMOF-1 digestion, the content of Zn was lower than IRMOF-1 with PMMA, Zn still presented in the PMMA after sample digestion. It means that IRMOF-1 was not completely removed or the Zn(II) in dissociated IRMOF-1 could not diffuse through the crosslinked PMMA shell. We think that the uncrosslinked PMMA shell has a loose structure, so that the dissociated IRMOF-1 can diffuse through it. But in the crosslinked PMMA, the shell is much denser than the uncrosslinked PMMA, so the diffusion is slower and within the same digestion time, not all of the dissociated IRMOF-1 diffused outside the shell. That is why we observed the reducing of the Zn content but still some remaining Zn in the sample after digestion.

Figure 3.12 EDX results of (a) IRMOF-1 with PMMA and (b) PMMA after digestion.
The BET surface area of the crosslinked PMMA was 82.93 m$^2$/g, higher than the uncrosslinked PMMA’s 33.04 m$^2$/g. But since there was Zn left in the sample after digestion, it was hard to prove whether the higher surface area was because the remaining IRMOF-1 or the crosslinker stabilized the templated porous PMMA.

Although the EGDMA crosslinker enhanced the mechanical stability of the PMMA shell, the dense structure hindered the diffusion of the dissociated IRMOF-1. Besides, it still formed the core-shell structure with IRMOF-1, not into inner layers of IRMOF-1. We think it is because that after isolating the IRMOF-1 from the MMA-AIBN solution and air flush, there was still a thin layer of MMA solution on the outside of IRMOF-1. When starting the polymerization, there are more AIBN in the MMA solution layer outside of IRMOF-1 than in the pores. Besides, it is easier for AIBN to diffuse in the solution than inside the pores of IRMOF-1. So the polymerization was first initiated on the interface of IRMOF-1 and the solution and the chain growth was from the interface into the pores of IRMOF-1. Due to the diffusion limitation in the small pores of IRMOF-1, PMMA was grown only a few layers into the pores.

**Method 2**

Besides the liquid MMA in method 1, vapor MMA was also tried in method 2. Since method 2 involved no liquid MMA, we expected that no shell PMMA would present in the sample after digestion.

Figure 3.13 are the IR spectra of IRMOF-1 and IRMOF-1 with PMMA. There was a very small peak at 1736 cm$^{-1}$ representing the appearance of PMMA, but a very low content in IRMOF-1. As expected, after adding the digestion solution to IRMOF-1 with
PMMA polymerized using method 2, all of the samples dissolved to form a clear solution. No solid PMMA was left.

![Figure 3.13 IR spectra of IRMOF-1 and IRMOF-1 with PMMA in method 2.](image)

The low content of PMMA in IRMOF-1 was due to the lower molecular concentration of MMA in the vapor phase compared with in liquid phase. So even IRMOF-1 was saturated with MMA vapor, the pores were not fully occupied by MMA molecules. During the polymerization, since the diffusion among the small pores of IRMOF-1 was slow, polymer chain growth was hindered, especially when there were not enough monomers around. As a result, small molecular weight PMMA formed in the pores after polymerization, which could be dissolved in the digestion solution.
3.3 Conclusions

In our study of using MOFs as templates to synthesize porous polymers, both liquid and vapor phase MMA was employed. The vapor phase MMA resulted in no PMMA left after digestion, probably due to the low molecular weight of the PMMA. Meanwhile the liquid MMA method formed a core-shell structure with IRMOF-1 and after removing the IRMOF-1, the remaining PMMA shell had a moderated surface area.

Although more studies could have been performed on this research topic, to the date of our study above, Kitagawa and co-workers published several papers on the same topic. They systematically investigated radical polymerization reactions in MOFs. However, in their research, they did not obtain the desired porous polymers due to the low molecular weight and mechanical stability of polymers, like our result with method 2. Instead, they reported using MOFs to control the molecular weight and stereoregularity.\textsuperscript{17} Other research on using MOFs to promote polymerization reactions was summarized in their recent review paper.\textsuperscript{18}

Despite this part of the research was incomplete, I would still like to include it in my thesis here since much effort was made on it. Meanwhile, I was very pleased to see the completion of this research topic by Kitagawa and co-workers, and moved on to my next research topic in later chapters.
References


Chapter 4: Improving the Water Stability of MOFs

Many MOFs have been reported to be unstable upon exposure in air due to the water molecules in air. However, many of the proposed application areas of MOFs involve the humid condition. So the water instability greatly limits MOFs’ applications. Experiments and theoretical calculations on this topic are first introduced in this chapter. Then, the design and synthesis of several MOFs isostructural to IRMOF-1 but with water repelling functional groups such as trifluoromethoxy group and methyl groups are described. The water stability of these MOFs was shown to be significantly enhanced. One of the MOFs was stable in boiling water steam for one week. The shelf life of another MOF was more than 10 months at ambient condition. For comparison, IRMOF-1 will collapse in air after a few hours to several days.

4.1 Introduction

The nanoporous metal-organic frameworks (MOFs) synthesized by copolymerization of organic ligands with metal ions have received widespread attention in recent years. Their unique sorption capabilities have been proposed for many important industrial applications, such as fuel storage, catalysis and sensing.¹⁻⁵ Unfortunately, none of potential applications have been brought into the market place.⁶ One of the major drawbacks of many MOFs is that they show a dramatic drop in surface area when exposed to air. The drop in surface area has been attributed to an effect of the water in the air.
MOFs are unstable under some vapor conditions due to the weak bonds between metal ions and ligands. Small molecules in vapor can attack the metal-organic bond and substitute the ligand. After the substitution, ligands cannot link to metal centers, as a result, framework structures collapse to some extent, and dramatical decrease of surface areas will be observed. This is especially true for most MOFs containing carboxylate ligands in water vapor.

Huang and co-workers studied the effect of water and acid on MOF synthesis and properties. As in Figure 4.1, they found that IRMOF-1 (MOCP-L in their study) experienced a structure collapse when treated with water or acid. After 5 minutes water treatment, the surface area of IRMOF-1 dramatically dropped from 666 m$^2$/g to 45 m$^2$/g. The mechanism they proposed was that the oxygen atom in water could substitute the oxygen in carboxylates. After the substitution, metal centers were not connected by the

**Figure 4.1** a) IRMOF-1(a) structure change after 5 min water treatment (b) and 30 min acid treatment (c); b) scheme of IRMOF-1 structure change mechanism; c) reversible hydrolysis reaction.
linkers, thus resulted in the structure collapse. They further summarized the mechanism to the reaction in Figure 4.1(c). Adding base into the mixture of metal ions and organic acid helps to obtain MOFs; on the other hand, adding acid into the system can reverse the reaction. Water can be considered a week acid compared with carboxylates.

IRMOF-1 is also predicted to be water unstable theoretically. The molecular dynamics simulations by Greathouse et al. showed that IRMOF-1 was stable only when the water content was lower than 4%. At water content higher than 4%, the structure would collapse. Similar with Huang’s study, they also proposed the mechanism to be the substitution of the oxygen atom in carboxylates by the oxygen atom in water molecules (Figure 4.2). Their simulations were validated by the comparison with experimental IRMOF-1 X-ray diffraction results.

**Figure 4.2** Simulated lattice parameter as a function of water content (left) and simulated disrupted IRMOF-1 structure at 2.3% water content (right).
Kaye *et al.* studied the impact of preparation and handling on the hydrogen storage capacity of IRMOF-1.\(^9\) Again, they confirmed the structure collapse of IRMOF-1 caused by water molecules in air. Furthermore, from PXRD they identified the collapsed IRMOF-1 phase to be MOF-69c that had been reported by Rosi and co-workers.\(^10\) So they developed improved synthesis and handling procedures to minimize the exposure of IRMOF-1 to water and air and achieved high nitrogen and hydrogen capacity with their method.

However, the special handling procedures involved extra efforts and made the procedures more complicated. Besides, it did not solve the problem of the water instability of IRMOF-1 which greatly hinged the applications of MOFs. So the objective of this chapter is to improve MOFs’ water stability by incorporating a number of water repelling functional groups in the frameworks. When water molecules approach the metal-organic bonds, they will be repelled away by the hydrophobic functional groups. As a result, the MOF structures can be protected from the water molecule attack.

Noticing that organic linkers of MOFs have the potential to bring a variety of functional groups into the frameworks, we proposed that ligands containing one or more water repelling groups may be possible to obstruct the water intrusion into the framework structures. By using this synthetic strategy, we have synthesized a new class of MOFs with the cubic topology similar to Yaghi’s IRMOF-1 structure as shown in Figure 4.3. They are constructed from zinc nitrate and terephthalic linkers attached with water repelling groups \(R_1\) or \(R_2\). Specifically, \(R_1=\) trifluoromethoxy in Banasorb\(^{\text{TM}}\)-22 (CAS#1138238-16-0); \(R_1=\)methyl, \(R_2=\)methyl in Banasorb\(^{\text{TM}}\)-24 (CAS#1138238-18-2); \(R_1=\)methyl in Banasorb\(^{\text{TM}}\)-30 (CAS#1138238-15-9). We expect that the hydrophobic
Figure 4.3 Scheme of Bansorb-n (left) (Banasorb-22: R₁= OCF₃, R₂= H; Banasorb-24: R₁= CH₃, R₂= CH₃; Banasorb-30: R₁= CH₃, R₂= H) and the mechanism of the water stability enhancement.

groups on the linkers will repel the water molecules away from approaching the metal-organic bonds, thus protect the frameworks (Figure 4.3).

4.2 Synthesis and Water Stability of Banasorb-22

Experiments

All starting reagents, zinc nitrate hexahydrate (Aldrich), 2-trifluoromethoxy terephthalic acid and N, N-diethylformamide (DEF) (TCI America) were used without further purification.

Microwave Assisted Solvothermal Synthesis of Banasorb-22

Zinc nitrate hexahydrate (0.15 g, 0.504 mmol) and 2-trifluoromethoxy terephthalic acid (0.0946 g, 0.378 mmol) were dissolved in 10 mL N, N-diethylformamide (DEF). The solution was then sealed in a reaction tube and heated in
CEM Discover Labmate Microwave Synthesizer at 150W for a reaction time of 80 seconds. The crystals are yellow in cubic shape, with size ranging from 4 to 7 microns.

**Solvothermal Synthesis of Banasorb-22**

For the synthesis of Banasorb-22, zinc nitrate hexahydrate, Zn(NO$_3$)$_2$.6H$_2$O, (0.1500 g, 0.504 mmol) and 2-trifluoromethoxy terephthalic acid, (2-CF$_3$O-BDCH$_2$) (0.0946 g, 0.378 mmol), were dissolved in 10 mL N, N-diethylformamide. The solution was then sealed with a Pyrex sample vial and heated to 110 °C. Transparent cubic crystals were collected after one week.

**Crystallography**

Single-crystal X-ray diffraction data were collected with the use of monochromatized Cu Kα radiation (λ = 1.5418Å) at 150 K on a Rigaku Saturn944+ CCD diffractometer (Rigaku (2010). Saturn944+. Rigaku Americas Corporation, The Woodlands, Texas, USA). Combinations of φ and ω scans were used to collect the data. The collection, cell refinement, integration of intensity data, and absorption correction were carried out with the CrystalClear-SM Expert suite of software (Rigaku (2010). CrystalClear-SM Expert 2.0 r5. Rigaku Americas Corporation, The Woodlands, Texas, USA). The structure was solved using direct methods, SHELXS (Sheldrick, G. M. SHELXS-97, 97-2; University of Göttingen, Germany: 1997), and refined with the full-matrix least-squares SHELXL (Sheldrick, G. M. SHELXL-97, 97-2; University of Göttingen, Germany: 1997) program. The location of the remaining guest molecules were poorly defined so their contributions were removed from the diffraction data using

**Powder X-ray Diffraction (PXRD)**

Powder XRD data were collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a P4 four-circle diffractometer and HiStar multiwire area detector. A Bruker M18XHF rotating anode generator operating at 50kV and 60mA supplied the Cu Kα (1.54056 Å) graphite monochromatized incident beam.

**Scanning Electron Microscopy**

SEM pictures and EDX data were obtained on Hitachi S-4700 High Resolution SEM. Before the tests, MOFs were soaked in chloroform for three days, and fresh solvent was exchanged each day. To completely remove the solvent, the crystals were dried in vacuum oven at 150°C for one day. Then the samples were sputtered with Pd-Au for 30 seconds to achieve good resolution under SEM.

**Brunauer - Emmett – Teller (BET) Surface Area Tests**

3 point BET surface area tests were performed on QuantachromeNova 2200e gas adsorption surface area apparatus. Before the tests, MOFs were soaked in chloroform for three days, and fresh solvent was exchanged each day. To completely remove the solvent, the crystals were dried in vacuum oven at 150°C for one day. Then the samples were transferred into a calibrated BET tube, and degassed on QuantachromeNova 2200e
station over night. Next the 3 point BET tests (partial pressure 0.1, 0.2 and 0.3) were performed at liquid Nitrogen temperature using Nitrogen as adsorbate.

**Water Stability Tests**

Before the tests, MOFs were soaked in chloroform for three days, and fresh solvent was exchanged each day. To completely remove the solvent, the crystals were dried in a vacuum oven at 150°C for one day. Then boiling water vapor was passed through dry MOFs for 1 day or 1 week. After the tests, the MOFs were dried in vacuum oven at 150°C for one day to remove the remaining water molecules in the pores.

**Thermogravimetric Analysis (TGA)**

Thermogravimetric analysis (TGA) was performed on Cahn Thermax 500 Thermogravimetric Analyzer. Before the sorption test, MOF samples were activated by soaking in CHCl₃ for two days to exchange with mother liquor in framework, and were then heated at 150 °C under vacuum to completely remove the solvate. About 5 mg dried sample was added into a clean Pyrex tube. Tested vapor was carried by 15 sccm air flow through a saturator and then passed through the sample at 25 °C. After 10 µL of solvent loss was observed from saturator, saturated samples were them collected for desorption study by TGA.

**Results and Discussions**

The samples used in our tests were synthesized by microwave-assisted solvothermal synthesis. The as synthesized crystals were in the form of micro-sized cubic
powder within 25-60 seconds by using our previously reported microwave-assisted synthesis. This convenient microwave synthesis allows us to easily scale the MOFs production up to a few hundred grams a day. However, the size of the crystals synthesized by the method was usually below 50 µm, too small for structure determination. For example, in the SEM picture shown in Figure 4.4, the crystal size of Banasorb-22 MOFs synthesized by the microwave assisted method was only 5-10 µm. So the conventional solvothermal method was employed to obtain large crystals (over 100 µm) for single X-ray diffraction and structure determination. The yield of Banasorb-22 using microwave assisted method was 71.4%. Elemental analysis (CHN, halides and ICP) showed the percentage of each component as Zn 21.46% (theoretical 25.60%), C 32.80% (theoretical 31.73%), H 1.47% (theoretical 0.89%), N 0.80% (theoretical 0%), F 10.82% (theoretical 16.73%). The presence of N in Banasorb-22 showed incomplete removal of the mother solvent DEF.

![Microwave synthesized Banasorb-22.](image)

**Figure 4.4** Microwave synthesized Banasorb-22.

As in Table 4.1, single-crystal X-ray diffraction shows that Banasorb-22 crystallized in space group *Fm-3m*. The R functional groups are disordered in all the four
Figure 4.5 Coordination structure of Banasorb-22 (left) and unit cell of Banasorb-22 (right).

Table 4.1 Crystallographic data of Banasorb-22.

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possible positions on phenyl ring. Banasorb-22 has the same cubic open pore structures as IRMOF-1 (see Figure 4.5), with thermal stability up to 350°C.

The XRPD comparison in Figure 4.6 revealed that Banasorb-22 synthesized by microwave method and conventional solvothermal method have the same crystallographic structure and the PXRD matched very well. So we confirmed that the Banasorb-22 we used in our tests had the structure described above which was isostructural to IRMOF-1.

![Graph](image)

**Figure 4.6** Comparison of single crystal XRD calculated and PXRD of microwave synthesized Banasorb-22

Trifluoromethoxy group is known for its strong water repelling effect in polymer chemistry. Therefore, we tested the water stability of Banasorb-22 by exposing it to boiling water steam for one week. As in Figure 4.7, peak positions of Banasorb-22
remained the same in the PXRD compared with the one collected before the test. However, intensity changes were observed for peaks at 6.78º and 9.60º. BET measurements showed that the surface area of Banasorb-22 was reduced from 1113m²/g to 210 m²/g after 1 week exposure to water steam. The PXRD intensity change and dropped surface area may attribute to the water molecules remained in the structure of the framework after water vapor test and activation procedures.¹²

![Figure 4.7 XRPD comparison of Banasorb-22 before (black curve) and after water vapour exposure (red curve).](image)

By comparison under the same condition, IRMOF-1’s PXRD showed the crystal structure collapsed after water vapor exposure for only 2 hours (Figure 4.8). The surface area of IRMOF-1 dramatically dropped from 2365m²/g to 50m²/g in just a few minutes.
Figure 4.8 XRPD comparison of IRMOF-1 before (black curve) and after water vapor exposure (red curve).

No obvious changes were observed for elemental analyses of both of the MOFs before and after water vapor test (Table 4.2). There was no obvious structural change of Banasorb-22 after the water stability test; the elemental analysis result was in line with the PXRD. However, for IRMOF-1, it collapsed into a low surface area structure after 2 hours exposure to water steam, but the elemental analysis showed similar results for IRMOF-1 before and after the water stability test. So we think that very small amount of water in the MOF structures can result in the structure collapse of IRMOF-1. After the
collapse, the components of IRMOF-1 remained the same, but the way that the building blocks connected were changed.

Table 4.2 Elemental Analyses of IRMOF-1 and Banasorb-22 before and after water vapor exposure.

<table>
<thead>
<tr>
<th></th>
<th>IRMOF-1</th>
<th></th>
<th>Banasorb-22</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>Element</td>
<td>Calculated</td>
<td>Found before (±0.4%)</td>
<td>Found after (±0.4%)</td>
<td>Calculated</td>
</tr>
<tr>
<td>Zn</td>
<td>33.97%</td>
<td>31.12%</td>
<td>30.07%</td>
<td>25.60%</td>
</tr>
<tr>
<td>C</td>
<td>37.44%</td>
<td>33.38%</td>
<td>33.30%</td>
<td>31.73%</td>
</tr>
<tr>
<td>H</td>
<td>1.57%</td>
<td>1.57%</td>
<td>1.75%</td>
<td>0.89%</td>
</tr>
<tr>
<td>N</td>
<td>0.00%</td>
<td>0.23%</td>
<td>0.19%</td>
<td>0.00%</td>
</tr>
<tr>
<td>F</td>
<td>16.73%</td>
<td>10.82%</td>
<td>11.11%</td>
<td>16.73%</td>
</tr>
</tbody>
</table>

Figure 4.9 shows the SEM pictures of Banasorb-22 and IRMOF-1 before and after water stability tests. Banasorb-22 maintained the cubic crystal morphology very well after the test and no damage was observed from the SEM picture. In comparison, after the drying procedures in air, some IRMOF-1 crystals were already damaged on the surface. After the water stability test, IRMOF-1 collapsed into small pieces from the surface to the
center. BET surface area test demonstrated that the collapsed phase above had a low surface area as mentioned earlier.

![Figure 4.9 SEM pictures of MOFs before and after water vapor exposure: (a) Banasorb-22 before; (b) Banasorb-22 after; (c) IRMOF-1 before; (d) IRMOF-1 after.](image)

To further investigate the binding sites of water molecules in MOFs, both IRMOF-1 and Banasorb-22 were first saturated by water vapor at ambient temperature then tested by TGA. Thermal water desorption curves and normalized differential curves of IRMOF-1 and Banasorb-22 are shown in Figure 4.10. TGA analyses showed a capacity of 0.11g H₂O/g for decomposed IRMOF-1 and 0.08g H₂O/g for Banasorb-22, as shown in Figure 4.10(a). Furthermore, the differential plots of TGA curves revealed that
Figure 4.10 (a) Water thermal desorption curves and (b) normalized differential curves of IRMOF-1 and Banasorb-22.
water vapor in decomposed IRMOF-1 exhibited three binding sites at around 65 °C, 110 °C and 200°C respectively. Meanwhile, only one binding site was found in Banasorb-22 at about 60°C. (See Figure 4.10(b)) We consider the binding sites below 70 °C in both frameworks are caused by the weak physical adsorption of water molecule inside MOF pores. Trifluoromethoxy groups in Banasorb-22 should play an important role to prevent water molecule from attacking (Zn₄O) cores, therefore making the framework more resistible to the moisture in air. To verify the assumption above, both MOFs were further saturated by water vapors at 70°C. The following TGA analyses showed that Banasorb-22 adsorbed nearly no water vapor, while decomposed IRMOF-1 still showed a considerable capacity of a 0.05 g H₂O/g as shown in Table 4.3.

<table>
<thead>
<tr>
<th></th>
<th>Sorption capacity comparison between IRMOF1 and Banasorb22.</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Banasorb-22</td>
</tr>
<tr>
<td>Toluene</td>
<td>0.03</td>
</tr>
<tr>
<td>DMMP</td>
<td>0.18</td>
</tr>
<tr>
<td>Nitrobenzene</td>
<td>0.18</td>
</tr>
<tr>
<td>Water at 25 °C</td>
<td>0.08</td>
</tr>
<tr>
<td>Water at 70 °C</td>
<td>0</td>
</tr>
</tbody>
</table>

The results above indicate that Banasorb-22 could have a substantial advantage in the application for gas-phase adsorption from the air, where water molecule always presents as a common interference. To evaluate Banasorbs’ sorption capacities with
common volatile organic vapors, we selected toluene, dimethylmethylphosphonate (DMMP) and nitrobenzene for the study. Table 4.3 shows that Banasorb-22 exhibits relatively smaller capacities than that of IRMOF-1 as we expected because of the partially occupancy of R group in the pores. Previously, we have demonstrated a severely high preconcentration gain of DMMP in IRMOF-1. Banasorb-22 would be more appropriate for air sensing applications given its high stability in moisture environment.

4.3 Synthesis and Water Stability of Banasorb-24 and Banasorb-30

Experiments

All starting reagents, Zinc nitrate hexahydrate (Aldrich), 2,5-dimethylterephthalic acid, N,N-Diethylformamide (TCI America), and 2-methylterephthalic acid (ECA International) were used without further purification.

Microwave Assisted Solvothermal Synthesis of Banasorb-24 and Banasorb-30

Zinc nitrate hexahydrate (0.1 g, 0.336 mmol) and 2,5-dimethylterephthalic acid (0.0490 g, 0.252 mmol) or 2-methylterephthalic acid (0.0454 g, 0.252 mmol), were dissolved in about 10 mL N,N-diethylether (DEF). The solution was then sealed in a reaction tube and heated in CEM Discover Labmate Microwave Synthesizer at 150W for a reaction time of 30 seconds. The crystals were in cubic shape with light yellow color, size ranging from 1 μm to 3 μm.

Breakthrough Volume Tests

Breakthrough volume was test by inverse-gas chromatography (IGC) studies. Dry MOF powder was packed into an approximately 7 cm length of 0.53 mm ID guard
column. The gas chromatograph was set up using UHP helium as a carrier gas. For activation, the inlet of the gas chromatograph was pressurized to 20 psi and the oven temperature is slowly ramped (1 °C/min) to 200 °C where the temperature was held for 10 h before being slowly returned to room temperature. This step was done to remove any residual guest molecules in the MOF and to increase the available porosity for IGC measurements. The packed column was then disassembled and reweighed to account for any mass changes due to removal of residual solvent in the MOF. The packed column was then reassembled and the effluent at the end of the column was connected to a flow meter (Omega, FMA-A2300) and the flow rates were recorded for all combinations of temperature and pressure investigated. The flow meter readings were converted to helium by multiplication by a conversion factor. After measuring and recording the flow rates for each set of temperature and pressure, the outlet of the column was connected to a flame ionization detector (FID) and pulse injections of analytes were performed. Breakthrough volume was calculated from the carrier gas flow rate and retention time.

**Results and Discussions**

With the same idea of introducing water repelling groups into MOF structures, we have also synthesized similar MOFs including Banasorb™-24 (R₁=methyl, R₂=methyl, CAS#1138238-18-2) and Banasorb™-30 (R₁= methyl, R₂=H, CAS#1138238-15-9). Similar with Banasorb-22, they are also isostructural to IRMOF-1. However, their water stability was not as good as Banasorb-22’s.
Figure 4.11 XRPD comparison of (a) Banasorb-24 (R1= CH3, R2= CH3) and (b) Banasorb-30 (R1= CH3, R2= H) before (blue curve) and after one week boiling water vapor exposure (pink curve).

Figure 4.11 shows the PXRD comparison of Banasorb-24 (R1= CH3, R2= CH3) and Banasorb-30 (R1= CH3, R2= H) before and after 1 week water steam exposure.
Unfortunately, structure collapse was observed in both of the MOFs in PXRD comparison. The result indicates that the water repelling capability of methyl groups is weaker than trifluoromethoxy groups as in Banasorb-22, so Banasorb-24 and Banasorb-30 did not survive the harsh water stability test condition in which Banasorb-22 survived.

However, the boiling water steam condition we employed in our early tests is a severe condition involving both the high concentration of water molecules and heat. High water concentration means high probability of substitution of the carboxylate groups of the ligands by water molecules. In addition, the heat can help the diffusion of water molecules into the pores as well as enhance the substitution reaction. In real applications of MOFs, usually the condition is milder than the boiling water steam. So if the MOFs can survive the severe condition of boiling water steam, they are stable under the mild conditions. However, even some of the MOFs are not stable under the severe condition as Banasorb-22, their water stability was still improved a lot compared with IRMOF-1 under milder conditions.

For example, the shelf-life of Banasorb-30 was demonstrated to be over 10 months compared with a few hours to several days of IRMOF-1 in ambient air. A batch of Banasorb-30 was synthesized in July 2009 and the breakthrough volumes of n-decane and 1,2,3,4-tetrahydronaphthalene were tested in July 2009 and April 2010, shown in Figure 4.12. The sample was stored in ambient air condition and no special treatment was performed between the two sets of breakthrough volume tests. The breakthrough volumes of both of the analytes remained almost the same after 10 months. So Banasorb-30 was stable in air for at least 10 months.
Compared with IRMOF-1 whose shelf-life is only a few hours to several days, by incorporating one methyl group into the structure, the shelf-life was greatly elongated. Noticing that Banasorb-30 did not survive the severe condition of one week exposure to...
boiling water steam but Banasorb-22 did, Banasorb-22’s shelf-life is expected to be longer than 10 months.

4.4 Conclusions

In summary, we have demonstrated that it is possible to build water-resistant MOF structures by introducing the water repelling functional groups into the framework. Followed by this synthesis strategy, we have built a new MOF Banasorb-22 with trifluoromethoxy group on the ligand that was stable up to one week in boiling water steam. Although Banasorb-24 and Banasorb-30 with methyl group on the ligand did not survive the severe condition in water stability test due to the weaker water repelling capability of methyl group than trifluoromethoxy group, Banasorb-30 demonstrated a shelf-life of more than 10 months, much longer than IRMOF-1. It is expected that Banasorb-22’s shelf-life to be longer than 10 months due to better water stability. In addition to the improved water stability, Banasorb-22 exhibited good sorption capacities of vapors such as DMMP. It may become a suitable material for air sensing.
References


Chapter 5: Mechanical Property Studies of MOFs

Although MOF is a very popular research area nowadays, only a few studies have been reported on the mechanical properties of MOFs. Many of MOF’s applications involve high pressure conditions, so it is important to understand the behavior of MOFs under elevated pressures. Examples of mechanical studies on MOFs using post-pressurized method and diamond anvil cells are first introduced in this chapter. Then, the mechanical properties of IRMOF-1 and a new MOF structure Eu$_2$(C$_{12}$N$_2$O$_4$H$_6$)$_3$(DEF)$_{0.87}$(H$_2$O)$_{2.13}$ are described using diamond anvil cells with synchrotron beam from Advance Photon Source. IRMOF-1 shows an irreversible phase transition to a nonporous phase followed by amorphization under high pressure. Eu$_2$(C$_{12}$N$_2$O$_4$H$_6$)$_3$(DEF)$_{0.87}$(H$_2$O)$_{2.13}$ shows reversible compression under pressure up to 9.08GPa.

5.1 Introduction

Metal-organic frameworks (MOFs) have attracted increasing attention as a new class of porous materials during the past decade. They have extraordinarily high surface areas, well defined crystalline structures and controllable surface functionalities. They have been proposed as promising materials in many application areas such as gas storage,$^{1,2}$ gas separation,$^{3,4}$ sensing$^5$ and heterogeneous catalysis.$^6$ All of these potential applications may involve exposing MOFs to extreme conditions like high pressure, high temperature, and radiation contamination environment etc. Thus it is fundamentally important to understand the structural stability of MOFs under such conditions.
However, only very limited amount of studies on this topic have been reported so far. Theoretical calculations by Kuc, Mattesini and Samantha using density functional based tight-binding method showed that IRMOFs’ bulk moduli ranged from 0.5 to 24GPa and MOFs with shorter linkers had higher moduli.\textsuperscript{7–9} Neutron inelastic scattering measurements by Zhou and co-workers showed that IRMOF-1’s shear modulus was 1.16GPa and they predicted that under high pressure IRMOF-1 would yield new phases.\textsuperscript{10} By using nanoindentation techniques, Bahr and co-workers reported that the average single-crystal Young’s modulus (E) of IRMOF-1 was 2.7 ± 1.0 GPa, with a large discrepancy from the theoretical one.\textsuperscript{11}

Chapman and co-workers first reported the mechanical study on MOFs using diamond anvil cells.\textsuperscript{12} Cu-btc MOF with different guest molecules including Fluorinert (FC-70, perfluorotri-N-pentylamine), iso-propanol and methanol-ethanol-water (MEW), 16:3:1 by volume) as pressure media were reported to have different compressibility

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{figure5.1.png}
\caption{Pressure induced lattice volume changes in Cu-btc MOF with different guest molecules.\textsuperscript{12}}
\end{figure}
shown in Figure 5.1. The compressibility of MOFs can be modulated in a wide range by using different guest molecules using their method.

Later, they reported the pressure-induced amorphization in ZIF-8 using the same method. They pressurized ZIF-8 both with and without pressure media to reveal the intrinsic mechanical property of ZIF-8 and eliminate the effect of guest molecules. ZIF-8 was stable below pressure of 0.34GPa. Beyond this pressure point, ZIF-8 became amorphous irreversibly in both cases, as shown in Figure 5.2. In their study, they also found that the surface area of the pressure-treated ZIF-8 was greatly reduced.

![Figure 5.2](image)

**Figure 5.2** Pressure induced amorphization in ZIF-8.¹³

Besides amorphization, Spencer and co-workers demonstrated cooperative bond rearrangement caused by pressure in a zinc-imidazolate framework ZnIm.¹⁴ The ZnIm MOF underwent a phase transition from α-phase to β-phase in the pressure range of
0.543 GPa to 0.874 GPa, shown in Figure 5.3. The tetragonal crystal system was conserved but with space group and lattice parameter changes.

IRMOF-1 is the prototype of the most widely studied IRMOF series that demonstrate the systematic design of MOFs.\textsuperscript{15} Hu et al. reported the irreversible amorphization of the post-pressurized IRMOF-1 at pressure of only 3.5 MPa, shown in Figure 5.4.\textsuperscript{16} They used the post-pressurized method in their study by first compressing MOFs with a pressure machine, and the following tests were performed after releasing the pressure. The Raman spectra indicated that the irreversible amorphization was due to the destroying of carboxylate groups. The surface area dropped from 3450 m\textsuperscript{2}/g to only 6 m\textsuperscript{2}/g after treated with pressure.
Here we report the first in situ high pressure study of the structural stability of IRMOF-1 up to 7.4GPa, and the results showed a different structural change pathway comparing to the post-pressurized method. Using the same method, we also tested a new MOF structure Eu$_2$(C$_{12}$N$_2$O$_4$H$_6$)$_3$(DEF)$_{0.87}$(H$_2$O)$_{2.13}$, in which the compression was reversible at pressure up to 9.08GPa, much higher than any reported MOFs so far.

5.2 IRMOF-1 Under High Pressure

Experiments

All starting reagents, zinc nitrate hexahydrate (Aldrich), terephthalic acid (Aldrich) and N, N-diethylformamide (TCI America) were used without further purification
**Solvothermal Synthesis of IRMOF-1**

IRMOF-1 crystals were synthesized by the solvothermal method. 100.0mg zinc nitrate hexahydrate and 41.9 mg 1, 4-benzenedicarboxylic acid were dissolved in 10 ml N,N-diethylformamide (DEF) in a Teflon lined glass vessel. The vessel was kept at 90ºC for three days to obtain cubic crystals. Then solvent exchange was performed by soaking the crystals in fresh chloroform solvent for one day three times. Next, the chloroform was decanted and the crystals were dried in an oven at 120ºC for one day to remove the remaining chloroform in the pores. IRMOF-1 crystals were then crushed to fine powder for later experiment.

**Ambient Pressure Powder X-ray Diffraction (PXRD)**

To check the crystal quality and sensitivity to air, the fresh IRMOF-1 sample was subjected to powder diffraction at ambient condition. Then the sample was kept in air for a day, and subjected to lab x-ray diffraction again. Powder X-ray data were collected on a Bruker General Area Detector Diffraction System (GADDS) equipped with a P4 four-circle diffractometer and HiStar multiwire area detector. A Bruker M18XHF rotating anode generator operating at 50kV and 60mA supplied the Cu Kα (1.54056Å) graphite monochromatized incident beam.

**High Pressure Experiments (PXRD)**

A Mao-bell type diamond anvil cell was used for in-situ high pressure x-ray diffraction studies. Diamond anvils with 800 μm culet size were used for this experiment. A stainless steel gasket was preindented to 90 μm in thickness, and a 250 μm
diameter hole was drilled in the center as a sample chamber. The IRMORF-1 powder and one ruby ball were loaded into the gasket hole together. Pressures were determined by measuring the ruby fluorescence shifting.\textsuperscript{19} To obtain the intrinsic property of IRMOF-1, no pressure medium was employed in this experiment.

**High Pressure Powder X-ray Diffraction (PXRD)**

*In-situ* angle dispersive X-ray diffraction experiments were performed at HPCAT, beamline 16-BMD at the Advanced Photon Source (APS), Argonne National Laboratory (ANL). A focused monochromatic x-ray beam with a wavelength of 0.4134Å was used for the experiments. The XRD patterns were collected with a MAR345 Imaging Plate area detector, and the experimental geometry was calibrated with the NIST standard CeO\textsubscript{2} powder sample.

**Results and Discussions**

It is known that IRMOF-1 decomposes once exposed in air because of the H\textsubscript{2}O in the air.\textsuperscript{20-22} To clarify whether IRMOF-1 is stable during the sample loading and high pressure experiment, powder X-ray diffraction of IRMOF-1 samples were collected at ambient pressure before and after one day exposed in air. As shown in Figure 5.5, the PXRD patterns of fresh IRMOF-1 and the IRMOF-1 exposed in the air for one day match very well and both coincide with the diffraction pattern calculated from the published single crystal structure. Thus the concern that the sample may decompose during experiment time is eliminated. On basis of the data above, the decomposition effect can
be completely excluded and any change of IRMOF-1 should be caused by the applied pressure.

Figure 5.5 Comparison of PXRD of calculated IRMOF-1 structure, fresh IRMOF-1 and IRMOF-1 exposed in air for one day. Inset picture shows the unit cell of IRMOF-1.

Figure 5.6 shows the calculated powder pattern from the known structure and the integrated patterns collected at the measured pressures.\textsuperscript{15} We can see that at the first pressure point 0.21GPa, most peaks of the sample matched the calculated ones except a new peak at $2\theta = 2.37^\circ$. The emergence of the new peak suggested that a new phase appeared and IRMOF-1 underwent a phase transition at this pressure point. Upon increasing the pressure to 1.25GPa, another new peak appeared at $2\theta = 4.26^\circ$. The
intensities of the new peaks gradually grew stronger and the first three strong peaks (200),
(220) and (400) of the ambient pressure phase (denoted as AP phase hereafter) became
weaker, indicating that the fraction of the new phase was growing as pressure increasing.
Since only three peaks were obtained in our measurements, we are not able to determine
the structure of this new phase. Here we call the new phase as high pressure phase
(denoted as HP phase hereafter). We found that the AP-HP phase transition was sluggish,
and the AP phase completely transformed to HP at 5.17 GPa.

The new peak of the HP phase around 2.38° under different pressures matches the
nonporous IRMOF-1 phase reported by Kaye et al. They explained that the appearance
of their new phase was due to the decomposition of IRMOF-1. They observed the
complete transition from IRMOF-1 to the new phase after one day exposing IRMOF-1 in
a humid air environment, and the new phase was found nonporous by surface area test.
The peak stands for their new phase was at 8.9° in their study, which matches the HP
phase peak at 2.38° very well after wavelength conversion. Two additional peaks at 15.8°
and 17.8° from Kaye et al. matches our HP peaks at 4.23° and 4.76° very well, respectively.
From the ambient pressure PXRD data, we confirmed that our sample did
not undergo the same decomposition in the dry air environment during the sample
loading time, comparing to exposure to humid air condition as reported by Kaye et al. As
a result, we believe that the pressure induced the phase transition from the porous AP
phase to the nonporous HP phase by collapsing the pores in the structure. Unfortunately,
due to the small sample capacity of the diamond anvil cell, there was not enough
recovered sample for surface area test to further validate the low porosity of the HP phase.
Figure 5.6 PXRD of IRMOF-1 collected at different pressures showing a phase transition from ambient pressure phase to high pressure phase.

The relative changes in intensities of the first three strong peaks (200), (220) and (400) of AP phase and the strong peak of HP phase in Figure 5.6 were plotted in Figure 5.7. To discuss the features in Figure 5.6 and 5.7 in detail, we divided the diagram of pressure dependent intensity changes of AP phase and HP phase into three regions. At pressure below about 0.4GPa (region I) with the same exposure time of 500 seconds, the intensities of both the AP phase and the HP phase grew stronger. Then the AP phase intensities dramatically decreased with increasing pressure. Meanwhile, the HP phase intensity increased drastically. Upon compression up to 1.25GPa (region II), both the
decrease of the AP phase and the increase of the HP phase slowed down, and then the AP phase peaks disappeared completely at 5.17GPa.

At pressure below about 0.4GPa, both the AP phase and the HP phase peaks were enhanced, as indicated in Figure 5.7 range I, which were due to the pressure induced preorientation of the crystals, proved by the powdery X-ray diffraction pattern shown in Figure 5.8. In range II, the discrepancy of the AP phase and the HP phase showed the percentage of the HP phase increased while the percentage of the AP phase decreased with increasing pressure. Meanwhile, the decreasing of the (200) peak and the (220) peak indicated the disruption of the long-range symmetry and the collapse of the pore

**Figure 5.7** Variation of normalized peak intensity of ambient pressure and high pressure phase with pressure up to 5.17 GPa. Inset picture shows the scheme of (200) and (220) planes in green and purple respectively.
structures, as shown in the inset. Therefore, pressure enhanced the phase transition from the porous AP phase to the nonporous HP phase. We also noted that in range III both the increasing and decreasing of the HP phase and AP phase slowed down, suggesting that the high pressure phase became dominant and the competition between the two phases became weaker.

![Figure 5.8](image)

**Figure 5.8** Powder diffraction patterns of IRMOF-1 in pressure range I.

With further increasing pressure up to 7.43GPa, the HP phase peak at $2\theta = 2.37^\circ$ gradually shifted to higher angle, representing the compression of unit cell of the HP phase. Upon decompression from the highest pressure, the HP phase peak recovered partially as shown in Figure 5.9. The HP phase d-spacing of the first sharp peak was plotted in Figure 5.10 for both compression and decompression cycle.

One interesting feature needs to be pointed out: as pressure increases, there is an increasing broad background near the first HP peak at $Q$ (defined as $4\pi\sin(\theta)/\lambda$) around 0.66 Å$^{-1}$. This is the typical first sharp diffraction peak for amorphous structure, which represents the medium-range order (MRO) at length scale around 9.5Å.$^{23}$ As
disappearing of the AP phase, IRMOF-1 transformed to HP phase, while with further increased pressure, part of the materials turned amorphous and gave rise to the broad amorphous peak. At even highest pressure 7.43GPa, we still observed the strong HP phase peak with the broad amorphous background.

![Figure 5.9 PXRD of IRMOF-1 upon further pressure loading and unloading](image)

**Figure 5.9** PXRD of IRMOF-1 upon further pressure loading and unloading

Further examining the high pressure peak in Figure 5.7 and 5.9, we found that with increased pressure, the HP phase peak gradually shifted from $2\theta = 2.372^\circ$ at 0.21GPa to $2.405^\circ$ at 7.43GPa, which was a 1.35% change of d-spacing. When unloading the pressure, $2\theta$ partially recovered from $2.405^\circ$ at 7.43GPa to $2.381^\circ$ at 0.17GPa, which was 71% recovery of the total d-spacing change, as shown in Figure 5.10. The structural change of IRMOF-1 under pressure is summarized in Figure 5.11.
In our *in-situ* observation, IRMOF-1 exhibited more complicated structural transition comparing to the post-pressurized method by Hu et al. IRMOF-1 did not become amorphous completely even at the highest pressure 7.43 GPa investigated in this study, instead a HP phase was observed from the first pressure point at 0.21GPa. With increasing pressure, the irreversible AP-HP phase transition appeared, followed by amorphization at higher pressure. Upon decompression, the HP phase’s lattice parameter partially recovered, however, neither the pressure induced AP-HP phase transition nor the amorphization was reversible.

**Figure 5.10** d-spacing change (%) vs pressure
5.3 Eu$_2$(C$_{12}$N$_2$O$_4$H$_6$)$_3$(DEF)$_{0.87}$(H$_2$O)$_{2.13}$ Under High Pressure

Experiments

All starting reagents, europium nitrate pentahydrate (Aldrich) 2, 2’-bipyridine-5, 5’-dicarboxylic acid (BPDC) (Aldrich) and N,N-diethylformamide (TCI America) were used without further purification.

Solvothermal Synthesis of Eu-BPDC MOF

Eu(NO$_3$)$_3$·5H$_2$O (0.017 g, 0.04 mmol), and 2,2’-bipyridine-5,5’-dicarboxylic acid (0.015 g, 0.06 mmol) were mixed and dispersed in DEF (5 ml). The resulting white slurry solution was then put in an oven and heated to 100 °C for three days to afford light-yellow needle crystals.

Results and Discussions

The as synthesized Eu-BPDC MOF has the formula of Eu$_2$(C$_{12}$N$_2$O$_4$H$_6$)$_3$(DEF)$_{0.87}$(H$_2$O)$_{2.13}$ (denoted as Eu-BPDC MOF hereafter). Figure 5.12 shows the coordination scheme and the crystal structure along c axis. There are two
crystallographically independent Eu(III) ions in the structure, both of which are eight coordinated. The Eu(III) are bridged by the carboxylates of the BPDC to form a three-dimensional coordination framework. The two nitrogen atoms on the backbone of BPDC do not bind to anything, but the two pyridine rings twist from each other. As shown in Figure 5.12, there are large rhombus channels along the c axis. After solvent removal Eu-BPDC MOF had a BET surface area of 630m²/g.

**Figure 5.12** Coordination scheme (left) and rhombus channels (right) of Eu-BPDC MOF

Figure 5.13 shows the comparison of Eu-BPDC MOF’s PXRD at the first data point 0.15GPa and the one calculated from single crystal structure. All of the peaks shifted to lower angle compared with the calculated PXRD, which was because that the single crystal X-ray diffraction was performed at liquid nitrogen temperature but the high pressure experiments were performed at room temperature. At low temperature, the crystal compression would cause the peaks shifting to higher angles. Besides the peaks shifting, there was also intensity change for many peaks, indicating that structural change already started at the first pressure point. However, besides the primary (110) peak at
θ=1.76°, it was hard to assign other peaks by comparison with the calculated PXRD. In our analysis, we will focus on the change of the primary peak, two peaks around θ=1.86° (denoted as peak 2 and peak 3 hereafter), and two peaks around 3.40° (denoted as peak 4 and peak 5 hereafter).

Figure 5.13 PXRD of Eu-BPDC MOF at 0.15GPa and calculated from single crystal structure.

For the high pressure experiments, the pressure was gradually increased to 9.08GPa using the first pair of diamond anvil cell and the PXRD was recorded, shown in Figure 5.14. All of the peaks (primary peak, peak 2 to 5) shifted to higher angles upon increasing the pressure. However, the relative intensity of peak 2 and peak 3, and peak 4 and peak 5 changed when the pressure increased.
Figure 5.14 PXRD of Eu-BPDC MOF at pressures up to 9.08GPa.
Upon releasing the pressure, all of the peaks fully recovered from the shifting caused by pressure.

During the experiment with the first diamond anvil cell, no structure change was observed when the pressure was increased to the upper limit of the cell, so another pair of diamond anvil cell was used to achieve higher pressure up to 40GPa. Figure 5.15 shows the results of Eu-BPDC MOF under pressures up to 37.5 GPa. At pressure below 10.37GPa, the peaks shifted to higher angles as in earlier experiment. However, when the pressure was over 10.37GPa, the peaks became broader and peak 2 and peak 3, and peak 4 and peak 5 merged together respectively. Peak 2 and peak 3 disappeared with furthering increased pressure. All of the changes above indicated a structure change of Eu-BPDC MOF at pressures above 10.37GPa. Upon releasing the pressure, peak 2 to 5 did not recover, so the structure change was not reversible this time.

Figure 5.15 PXRD of Eu-BPDC MOF at pressures up to 37.5GPa.
To further understand the effect of pressure on the Eu-BPDC MOF structure, d-spacings calculated from the $2\theta$ are plotted vs different pressures for the primary peak (Figure 5.16), peak 2 and peak 3 (Figure 5.17) and peak 4 and peak 5 (Figure 5.18). Since the peak 2 to 5 became broad and even disappeared at pressures above 10.75GPa, it was hard to determine the peak positions. Only the primary peak’s data at higher pressure using the second diamond anvil cell were plotted.

From Figure 5.16 we can see that in the first experiment d spacing of the primary peak gradually decreased from 13.47Å to 13.03Å upon pressure increased to 9.08GPa. That was a 3.3% change of the d spacing. When releasing the pressure, the d spacing fully recovered at ambient pressure. Besides, the trend of d spacing change during the pressure increase and decrease matched very well. In the second experiment with the higher pressure diamond anvil cell, at pressures below 10.34GPa, the d spacing dropped from 13.47Å to 13.12Å, with a similar rate with the one in the first experiment. However, at pressures higher than 10.34GPa, the d spacing started to increase. At the highest pressure point in the second experiment 37.5GPa, the d spacing was 13.68Å, which was even higher than 13.47Å at the starting pressure point. After releasing the pressure to ambient pressure, the d spacing did not recover this time. Instead, it further increased to 14.11Å. From the primary peak change, we knew that Eu-BPDC MOF’s (110) plane was stable upon pressure change up to 9.08 GPa. The structure experienced reversible compression in this pressure range. But at pressure higher than 10.34GPa, structure change more than just compression happened, and the d spacing further increased. The structure change beyond 10.34GPa was irreversible after releasing the pressure.
Figure 5.16 d spacing change vs pressure for the primary peak

Figure 5.17 d spacing change vs pressure for peak 2 and peak 3.
Figure 5.17 and Figure 5.18 present the d spacing change for peak 2 to 5. Peak 2’s d spacing changed from 11.39Å to 10.24Å at 9.08GPa, a 10% change; peak 3’s d-spacing changed from 10.77Å to 9.52Å, an 11.6% change. For peak 4 and 5, the two d spacing changed from 7.23Å to 6.59Å and 6.78Å to 6.56Å, which are 8.9% and 3.3% change in d spacing. All of the changes of the peak 2 to 5 fully recovered when the pressure was released. The recovery peak 2 to 5 also supported the conclusion from the primary peak that Eu-BPDC MOF experienced compression and full recovery at pressure below 9.08GPa and no structure collapse or transformation happened.
The d spacing change for three strong peaks are compared in Figure 5.19. The primary (110) peak’s d changed more drastic than the other two, but the percentage change for the three d spacing shown here were 3.3%, 11.6% and 3.3%. So the lattice change in different directions was anisotropic in the structure. Figure 5.20 is the scheme of the (110) plan in Eu-BPDC MOF structure. (110) plane is the wall of the rhombus channel. Now we can explain that reversibility of the structure change of Eu-BPDC MOF under pressure was due to the flexibility of the rhombus channels. When the pressure was applied, the rhombus channel became thinner and wider, so that only deformation of the channel happened instead of structural change. When the pressure was released, the rhombus channel recovered from the deformation and resulted in the reversibility of the structure change.
5.4 Conclusions

The structure stability of IRMOF-1 was investigated under pressure up to 7.43GPa by in-situ high pressure X-ray diffraction method with synchrotron radiation source in a diamond anvil cell. We found that pressure first induced the phase transition from the porous AP phase to the nonporous HP phase by collapsing the pores, and the phase transition was almost complete at 5.17GPa. With further increased pressure, the nonporous HP phase displayed plasticity and could only partially recover when releasing the pressure. Furthermore, the AP phase to HP phase transition was irreversible upon unloading from the highest pressure down to ambient pressure. Partial amorphization occurred along with and after the transition from AP to HP, which was also irreversible.

The structure of Eu-BPDC MOF was stable under pressure up to 9.08GPa. At pressure below 9.08GPa, only deformation of the rhombus channel presented in the structure which was fully reversible after releasing the pressure. At pressures higher than
10.34GPa, the structure of Eu-BPDC MOF was damaged by the applied pressure, and the structure change was not reversible any more.
References


14. Spencer, E. C.; Angel, R. J.; Ross, N. L.; Hanson, B. E.; Howard, J. A. K., Pressure-Induced Cooperative Bond Rearrangement in a Zinc Imidazolate


Appendix A: Microwave Assisted Solvothermal Synthesis

The microwave assisted solvothermal synthesis MOFs is performed on CEM Discover Labmate Microwave Synthesizer.

Sample Preparation
1. Metal salt and ligand are weighed and completely dissolved in the mother solvent (usually polar solvent for microwave synthesis) to form a clear solution.
2. The solution above is transferred into a 10mL glass microwave reaction tube.
3. Put on the reaction tube cap and make sure the septum is in place so that no vapor will come out of the tube during reaction.

Microwave Synthesizer Operation
1. Turn on the microwave and place the reaction tube on the tube holder.
2. Press folder button and select new method.
3. Select mode as standard (keeping the reaction temperature constant by automatically adjusting the microwave power) or powertime (keeping the microwave power constant).
4. Set microwave power (maximum value in standard mode, constant value in powertime mode)
5. Set reaction temperature (constant value in standard mode, maximum value in powertime mode)
6. Set run time.
7. Set stirring speed if a stirrer is used.

8. Select cooling on to prevent overheating and help to control the temperature in the desired range.

9. Set maximum pressure in power time mode. The synthesis will be terminated once the maximum pressure is reached to prevent explosion.

10. Continue to edit next stage if needed.

11. Enter method name to save the method edited above.

Microwave synthesis

1. Place the pressure sensor on top of the reaction tube and make sure the clamps of the pressure sensor are in place.

2. Start the reaction by pressing start button.

3. Turn on the cooling gas to control the temperature in powertime mode or to get the temperature in the desired range in standard mode.

4. When synthesis is over, leave the cooling air on to help cool down the reaction tube.

5. After the reaction tube is cooled down to 50°C, the pressure sensor will release the reaction tube.

6. Take out the reaction tube with caution. Pressure is accumulated in the reaction tube during microwave synthesis. Do not open the tube until the septum becomes flat.
Appendix B: High Pressure Experiments Using Diamond Anvil Cells

1. A pair of diamonds are accurately aligned in a diamond anvil cell and fixed on the cylinder and piston respectively by adhesive, as shown in Figure B.1.

![Figure B.1 Picture of the cylinder and piston of a diamond anvil cell.](image)

2. A gasket preindented by the same diamond anvil cell with a hole drilled at the center of the indentation is placed on the diamond in the piston with the indentation facing down. Examine the edges of the gasket are aligned with the edges of the diamond under microscope.

3. Place the powder sample in the hole of the gasket then add one ruby ball in the center of the hole.
4. Insert the piston into the cylinder and carefully close the diamond anvil cell with
   the four screws.

5. Place the diamond anvil cell on to the holder for the beam radiation.

6. Apply pressure by tightening the four screws on the diamond anvil cell little by
   little.

7. Measure the fluorescence of the ruby. The pressure can be calculated from the
   peak shifting by the software.

8. If the desired pressure is not reached, repeat step 6 and 7.

9. Turn on the beam and start X-ray diffraction data collection.

10. Gradually increase the pressure by repeating step 6 to 9 until the maximum
    pressure of the diamond anvil cell is approached.

11. Release the pressure by loosening the four screws on the diamond anvil cell very
    slowly.
Author’s Biography

Tianjiao Wu was born in Shenyang, China in 1983, and grew up in Beijing, China. She received B.S. in Chemistry from Peking University in China in 2006. Her undergraduate research was on growth and Raman spectroscopy of carbon nanotubes in Prof. Zhongfan Liu and Prof. Jin Zhang’s research group at Center for Nanoscale Science and Technology at Peking University. In 2006, Tianjiao entered graduate school at University of Illinois at Urbana-Champaign and joined Prof. Richard I. Masel’s research group. She worked on several projects during her graduate study, including developing new metal-organic frameworks (MOFs), synthesis of porous polymers and covalent organic frameworks, improving the water stability of MOFs and adsorption and mechanical properties studies of MOFs.

Publications

4. Luebbers, M. T.; Wu, T.; Shen, L.; Masel, R. I., Trends in the adsorption of
volatile organic compounds in a large pore metal-organic framework, IRMOF-1. 

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