

Synthesis and Characterization of Boronic-acid-Containing Metal Organic
Frameworks

by

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ABSTRACT

We report the synthesis of novel boronic acid-containing metal-organic frameworks (MOFs), which was synthesized via solvothermal synthesis of cobalt nitride with 3,5-Dicarboxyphenylboronic acid (3,5-DCPBC). Powder X-ray diffraction and BET surface area analysis have been used to verify the successful synthesis of this microporous material.

We have also made the attempts of using zinc nitride and copper nitride as metal sources to synthesize the boronic acid-containing MOFs. However, the attempts were not successful. The possible reason is the existence of copper and zinc ions catalyzed the decomposition of 3,5-Dicarboxyphenylboronic acid, forming isophthalic acid. The ended product has been proved to be isophthalic acid crystals by the single crystal X-ray diffraction. The effects of solvents, reaction temperature, and added bases were investigated. The addition of triethylamine has been shown to tremendously improve the sample crystallinity by facilitating ligand deprotonation.

DEDICATION

I want to dedicate this thesis first of all for my parents, Guoyi and Ailing. Thank you so much dad and mom for all your love, for raising me to be the person that I am today. And your words, behaviors and thoughts affect me to chase my dreams. Without your supports, I can't study in America to improve myself like today.

This thesis goes to my grandfather next. I would not finish this thesis on time if it were not for you. Thank you so much for encouraging me to be a better me. I remember your words forever and I will always miss you. You are the best grandfather in the world.

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CHAPTER 1

INTRODUCTION

1.1 History of MOFs

Metal Organic Frameworks, abbreviated as MOFs, are a burgeoning class of crystalline material constructed by metal ions or clusters and organic linkers. The structures of MOFs can be zero-dimensional (0D), one-dimensional (1D), two-dimensional (2D) or three-dimensional (3D) architecture.

The term coordination polymer was firstly introduced in 1916 (Shibata, 1916). However, because of restrict of knowledge and technology of people at that time, people cannot know well about them without characterization method like single-crystal-XRD.

In the year of 1996, the first “MOF”, called as MOF-5, was synthesized by the Yaghi et al (1999). As shown in the Fig. 1.1.1, MOF-5 consists of Zn_4O clusters and the clusters were connected by 1,4-benzenedicarboxylate organic linkers. In the following decades till now, after MOF-5 came out, thousands of research workers synthesized many kinds of MOFs with different chemical and physical properties which leads to many special applications of MOFs.

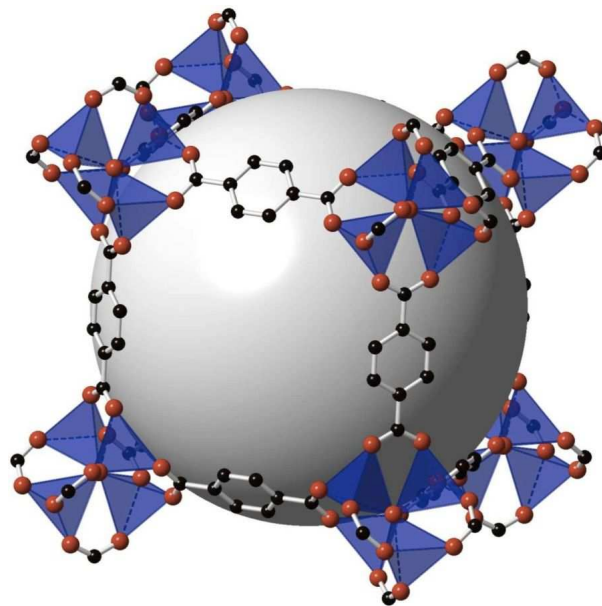


Figure 1.1 Ball-and stick representation of framework of MOF-5

With the development of MOFs, many derived acronyms are introduced: CP (Coordination Polymers), IRMOF (IsoReticular Metal Organic Framework), ZIF (Zeolitic Imidazole Framework) and more.

1.2 Introduction of several classical MOFs

1.2.1 IRMOFs

One of the most famous series of MOFs is the Isoreticular Metal-Organic Framework (abbreviated as IRMOF) by Yaghi et al (2002). The MOFs are composed of

second building units, $[Zn_4O]_{6+}$ and a series of aromatic carboxylic acid ligands. IRMOF-1 is the simplest MOF in the series. IRMOF-1 is cubic crystal. It has the features like high surface area, regular pore structure, high structure volume and the ability of hydrogen storage to some extent. By change the functional groups on the ligands, the team got a series of IRMOF-n ($n=1\sim 16$) with the same topological structure. By using longer ligands, the pore size of IRMOFs can be as high as 28.8\AA ; the percent of void can be extended from 55.8% to 91.1%, which is much larger than zeolites. The properties are really rarely to be found in inorganic porous materials.

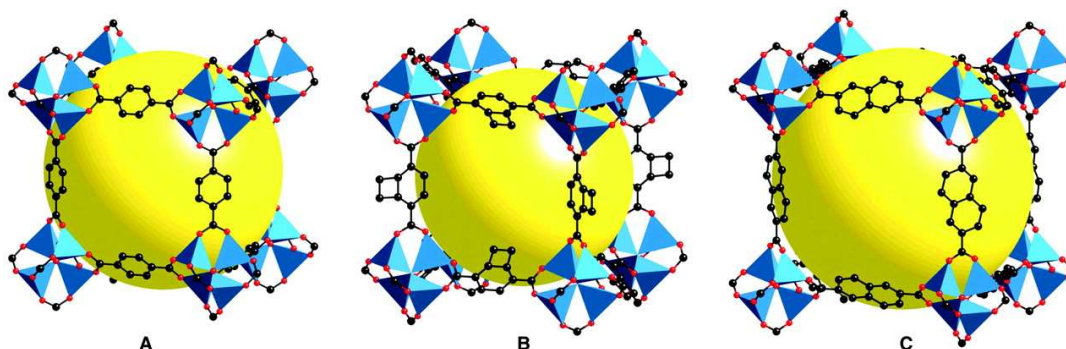


Figure 1.2.1 Ball-and stick representation of framework of IRMOF-1 (A), IRMOF-6 (B) and IRMOF-8 (C) (Rosi et al., 2003).

1.2.2 MOFs with pocket-channel structure.

Among the vast MOFs invented already, another representative material is the $[Cu_3(TMA)_2(H_2O)_3]_n$ (also called HKUST-1 and Cu-BTC), which is synthesized by Williams et al (1999). The synthesis is made by putting $Cu(NO_3)_2 \cdot xH_2O$ and trimesic acid into the solvent of ethylene glycol/H₂O then heating for 12 hours under the

temperature of 180 °C, the pore size of the pocket-channel in the MOF is 9.5Å×9.5Å, the BET (Brunauer-Emmett-Teller) surface area is 692.2 m²/g. In this series of MOFs, each metal cluster connects with four organic ligands and each ligand connects with three metal clusters. The pocket-channel structure made the MOFs become the crystals with hollow space inside. Each pocket is connected with four channels and the size of channel can be changed by using different ligands.

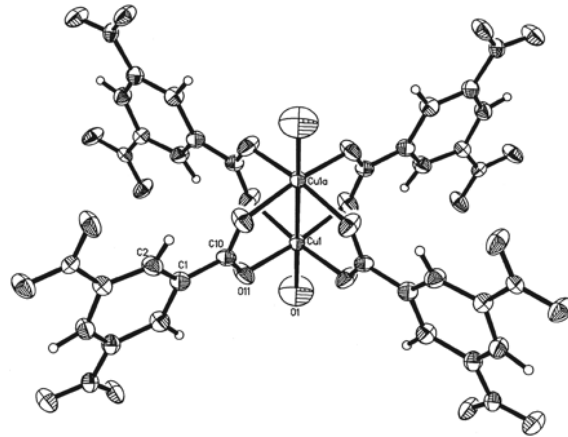


Figure 1.2.2 Single crystal structure of Cu-BTC (Williams et al., 1999).

1.2.3 MIL-MOFs

The Materials of Institute Lavoisier (abbreviated as MIL) is also a famous series of MOF materials. The most famous one is the MIL-53(Cr) synthesized by Ferey et al (2002). The MOF is synthesized by using solvothermal synthesis method to heat Cr(NO₃)₃•4H₂O, terephthalic acid (TPA), hydrofluoric acid and H₂O with the mole ratio of 1:1:1:280. A series of MIL-MOFs are also synthesized by changing the metal salts and ligands (Ferey et al.,2003; Barthelet et al.,2003; Barthelet et al.,2023). The structure of the crystal is flexible; the framework can change with the change of the environment

like temperature and pressure. This effect is called breath effect and the breath effect has become an important research area.

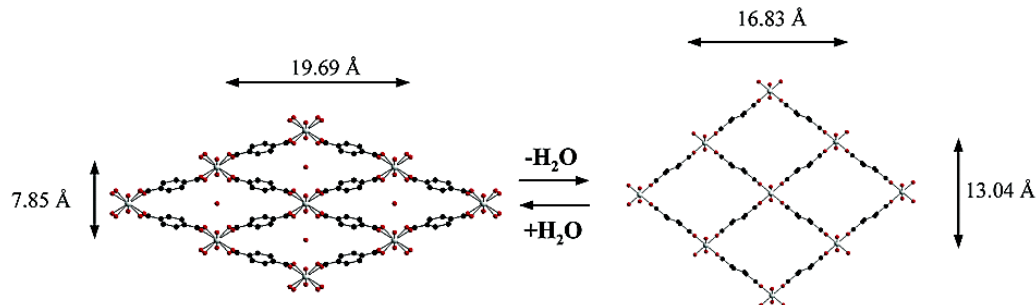


Figure 1.2.3 Schematic representation of the reversible hydration-dehydration of MIL-53t and MIL-53ht (Ferey et al., 2002)

1.2.4 ZIFs

Recently, The group of Yaghi synthesized a new series of MOFs, zeolitic imidazolate framework (ZIF). It is constructed by Zn(II) or Co(II) metal salts and imidazole ligands. The structure of ZIFs is similar to zeolites. In the aluminosilicate molecular sieve, aluminum or silicon atoms are substituted by transition metal and the oxygen atoms are substituted by imidazole ligands. Among ZIFs, they can be classified by several classical topological structures. Like ZIF-5, it's a MOF which contains Zn(II) and In(III) metal ions and imidazole ligands with the gar topology. The mostly studied ZIF is ZIF-8 and ZIF-11 on the aspect of gas adsorption and thermal and chemical stability. The research results show that ZIF have the high surface area around $1810\text{m}^2/\text{g}$, high thermal stability as high as 550°C and very good chemical stability that it can keep stable in boiling alkaline aqueous solution and organic solvent. In addition, the imidazole

in ZIFs makes the crystal have high selectivity for absorbing CO₂ in stack gas and vehicle exhaust.

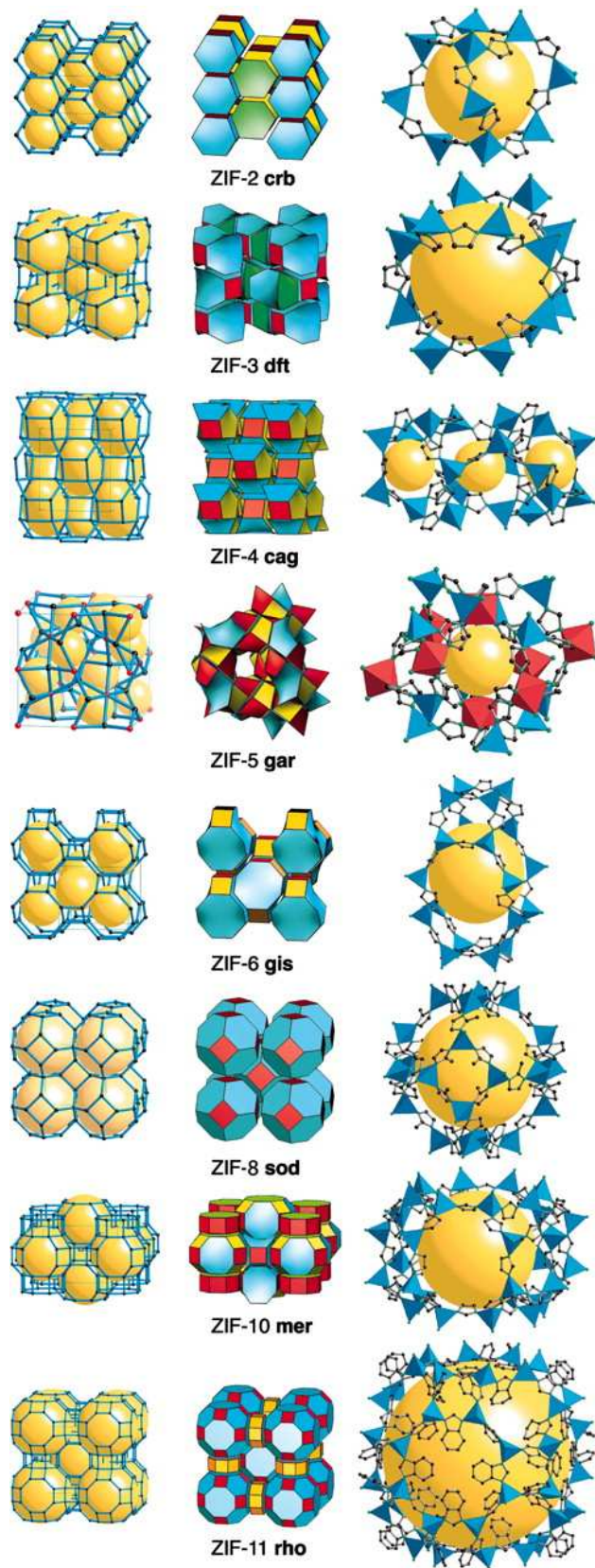


Figure 1.2.4 the single crystal structures of ZIFs shown as a stick diagram (left)

and as a tiling (center) and the largest cage in each ZIF (right) (Park et al., 2006)

1.2.5 UiO-MOFs

UiO (University of Oslo) MOFs are a series of zirconium (Zr) based MOFs that attract wide concerns. (Kavka, 2008) UiO-66 is the most classical MOF among UiO-MOFs. It has high selectivity in CO₂/CH₄ separation and is reusable. The structure of UiO-66 made its thermal stability higher than 500°C. The structure of UiO-66 is stable in many organic solvents. It's the most stable MOF that has been reported so far. The high stability makes the materials suitable for separation. Recent research shows that introducing -SO₃H and -CO₂H can highly improve UiO-66 the effects of CO₂ capture (Yang, 2011).

1.3 Synthesis methods of MOFs

1.3.1 Hydrothermal/ solvothermal synthesis method

Hydrothermal synthesis method is a staple way to synthesize inorganic materials and it's widely used in the area of nanomaterial, biomaterial and geological material. The method is mainly to use water as solvent and make the reactants to be solutions and put them into a hydrothermal synthesis reactor. Then heat the reactor to a certain temperature (normally 100~200°C). The hydrothermal synthesis reactor makes the system in a self-generating pressure range. Normally under this situation a lot of nanomaterial with excellent properties can be made. In the year of 1999, Kitagawa et al (1999) put aqueous

solution of Na_2pzdc in to the aqueous solution of $\text{Cu}(\text{ClO}_4)_2 \cdot 6\text{H}_2\text{O}$ and pyrazine slowly and stir under room temperature. Then blue tiny crystal CPL-1 can be made after filtration. After that, the group of Ferey used hydrothermal methods to make the MIL-MOFs serious materials.



Figure 1.3.1 Teflon-lined stainless steel reactor usually used in hydrothermal/solvothermal synthesis of MOFs.

Solvothermal synthesis method has the same principle as hydrothermal synthesis method, but the solvent is not only limited to water. Solvothermal method is one of most important and frequently used methods. Normally hydrothermal thesis is to mix reactants with organic solvents like organic amine, methanol, ethanol and so on. Then put the mixture in to some closed containers like Teflon-lined stainless steel reactor or glass tubes and then hate the reactors under the temperature normally around $100\sim 200^\circ\text{C}$. The reaction will happen under the self-generating pressure and with the temperature increase

the reactant will dissolve gradually. The method decreases the reaction time and solves the problem that the reactants can't dissolve in ambient temperature. The organic solvents used in the reactions usually have different functional groups, especially different properties like polarity, specific inductive capacity (SIC), boiling point, viscosity and so on, which made the reaction environments and the structure of resultants more flexible and various. The advantages of solvothermal synthesis technology like low cost, simple equipment and well-grown crystals made the methods one of the most often used methods chose by researchers. For example, the famous MOF serious like IRMOFs, ZIFs and UiO-MOFs are synthesized by using solvothermal synthesis method. In the year of 2002, Yaghi et al (2002) mix 12 different organic ligands with $Zn(NO_3)_2 \cdot 4H_2O$ separately and then put into N,N-Diethylformamide (DEF) solvent. After the reaction, a serious of IRMOFs with different pore sizes is obtained. The group of Stock (Ahnfeldt, 2009) mixed $AlCl_3 \cdot 6H_2O$ with H_2N-H_2BDC and then put in to methanol solution. After the reaction, Al-based MOF, CAU-1, was obtained.

1.3.2 Microwave synthesis

The major differences between microwave synthesis method and the traditional hydrothermal/ solvothermal synthesis method is the way to heat. Direct current (DC) supplies the power to the permatron in the microwave oscillator and the microwave oscillator will produce alternative electric filed. The macromolecules in the alternative electric filed will absorb the electromagnetic wave and start to rotate and collide fiercely. So the polar molecules will move with the alternative electric filed and produce heat to increase the temperature of reactant fast in a short time. So the character of microwave synthesis is its short reaction time. It can decrease the reaction time from several days to

several hours even several minutes. Additionally, using microwave synthesis method can control the size of produced MOFs more easily.



Figure 1.3.2 Microwave synthesizer produced by CEM Corporation.

Ni and Richard (2006) firstly introduced the solvothermal synthesis methods assisted by microwave to the area of MOF synthesis. He synthesized the crystallites with the size around $4\mu\text{m}$ of IRMOF-1, IRMOF-2 and IRMOF-3. So far, microwave synthesis is the most widely used synthesis method except hydrothermal/ solvothermal synthesis in the area of MOF synthesis. For example, Jing et al (2007) use microwave synthesis method to successfully produced MIL-101 (Cr), and reduced the reaction time to less than 1 hour. The BET surface area of sample produced is $3900\text{m}^2/\text{g}$ and the adsorption ability is also studied. Recently, Khan et al (2011) decreased the reaction time to 15min and Bromberg et al (2012) successfully synthesized MIL-101 (Cr) by using microwave synthesis method without adding HF and studied its catalytical properties after loaded with many

kinds of oxometallates. Compared with the original synthesis methods, the synthesis avoided using the poisonous and highly corrosive HF and for this reason it decreased the pollution to the environment effectively.

1.3.3 Ultrasonic synthesis

Ultrasonic synthesis can continuously produce bubbles. The growing and bursting bubbles form acoustic cavitation. Acoustic cavitation can lead to very high partial temperature (about 5000K) and partial pressure (about 1000atm). For this reason, using Ultrasonic synthesis to produce MOFs can increase the activity of reactants. Size of produced MOFs will be more uniform and reaction time will be highly decreased. The method is good for produce MOF samples with small crystal size.



Figure 1.3.3 Q500-Sonicator produced by Qsonica, LLC

Son et al (2008) used ultrasonic synthesis method to high quality MOF-5 with the particle size from 5~25 μm and the reaction time is decreased to 30min. Jung et al (2010) found the ultrasonic power and reaction time can affect the surface area of the MOFs when synthesizing MIL-177. Additionally, using ultrasonic synthesis method with the other methods together can improve the effect of synthesis. Sabouni et al (2010) use ultrasonic and microwave synthesis methods to study how the react condition affect the synthesis of IRMOF-1. After optimization, they made the sample with surface area of 1874 m^2/g . The compare with the sample got from traditional synthesis method by using scanning electronic microscope (SEM) showed that the sample has more perfect crystal.

CHAPTER 2

SYNTHESIS AND CHARACTERIZATION OF BORIC ACID CONTAINING MOF

2.1 Introduction

The design and synthesis of the burgeoning porous material, metal-organic frameworks (MOFs) are widely concerned and has become a popular research area because of their unique structure and properties and their potential in gas adsorption, separation, drug delivery and catalysis. The large majority of unique properties of MOFs have been found and the properties lead to the various applications of MOFs (Yaghi et al., 1999; Sabouni et al., 2010). Borax is an ore that easily accessible on and near the surface of the earth. In the past centuries, many applications of borax has been explored like metallurgy, glass, ceramics, medicine, detergents, insecticides, lubricants, oil exploitation and catalysis (Schubert, 2003). With the development of the study of borax, B-based compounds have been studied a lot and the study of boric acid accounts for a large proportion. In the past decades, the interests of study of boronic acid in medical application were increased a lot. For example, bortezomib, the dipeptide-boronic acid has been tried to use as proteasome inhibitor for treating relapsed multiple myeloma and mantle cell lymphoma as artificial sensors of sugars (Gupta, 2003). The function of boric acid as sugar sensors has a huge potential to be used in the area of industry, biology, and medical treatment because of the non-poisonous and environment friendly properties. Some other techniques of boric-acid including fluorescence, pH depression, colorimetry, electrochemistry and magnetic resonance imaging (MRI) were reported (Merbach, 2013).

To produce MOFs, the ligand must have at least two carboxylic groups on it to react with the metal salts. The ligands, 3,5-Dicarboxyphenylboronic acid (3,5, DCPBC) and 3,5-Dicarboxyphenylboronic acid, pinacol ester (3,5, DCPBC, PE) were found and chosen. 3,5, DCPBC, PE was considered to use to protect the boronic acid groups during the process of synthesis.

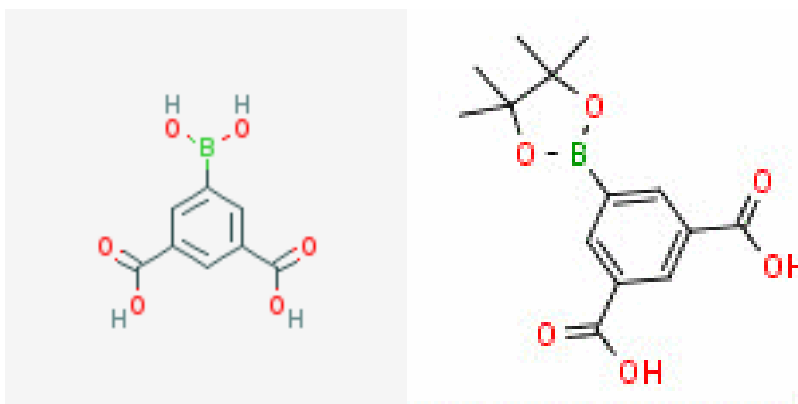


Figure 2.1-1 Molecular structure of 3,5-Dicarboxyphenylboronic acid (left) and 3,5-Dicarboxyphenylboronic acid, pinacol ester (right).

Many groups focused on synthesis of MOFs used zinc nitrate as one of the first several metal salts to try to synthesis new MOFs (Yaghi et al., 2002; Park et al., 2006) because it's easy to bind with organic ligands. So we chose $Zn(NO_3)_2 \cdot 6H_2O$ as one metal salt to try to synthesize the new MOF we want. Normally, perfect MOF samples have the appearance of crystals and can be seen by human eyes or under the microscope or very tiny microcrystals but looks pretty good. Like the Cu-BTC sample synthesized by our Lab, it obviously has the appearance of blue crystals.

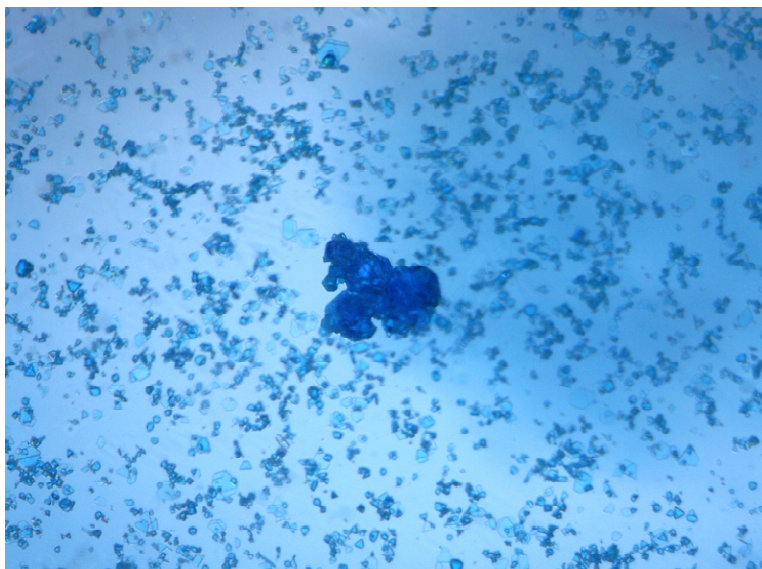


Figure 2.1-2 Microscope image of Cu-BTC.

However, when the synthesis process is finished, many impurities like the unreacted reactants or some other resultant will exist with MOFs. Especially for the initial period of trying to synthesize a new MOF, sometime there will be more impurities than MOF crystals in the sample. And if the MOF and impurities looks similar, it will be very hard to tell if the MOF is synthesized. For this reason, colored metal salts are preferred because they will make the synthesized MOF has color that is easy to be found in the impurities. And concerned about the properties of the metal ions, copper nitrate and cobalt nitrate were chosen because of their unique color. Normally Cu-based MOF will have a blue or green color and Co-based MOF will have a rose or purple color. The color will change with the valence state of the metal atoms.

Concerned about the economic factors and the universality of the synthesis methods, hydrothermal/ solvothermal methods were used for trying to synthesis the boron-containing MOF. 45mL Teflon-lined stainless steel hydrothermal reactors, which can

generate high-pressure environment when heated, were used and a heating furnace is used to heat the reactor.

By using the hydrothermal/solvothermal method, the react conditions can be controlled were the temperature, heating time and the solvent decided to use in the reaction. Because MOF is a really big and complex area of study, there are no universal experiences of setting the react conditions of MOF synthesis. The react condition of synthesizing each kind of MOF is unique. So different reaction conditions need to be tested and then the range of reaction condition values will be narrowed by testing the qualities of samples. However, trying different reaction conditions blindly will be very low efficient and it's not a scientific way to find the right way to synthesize new MOFs. The methods to produce the MOFs containing same metal salts and Ligands with similar structure were used references (Yaghi et al, 2002; Adhikari and Lin, 2014). The efficiency to approach our final goal was highly improved.

2.2 Methodology

2.2.1 Materials

All chemicals are commercially available and were used as received without further purification. Zinc nitrate hexahydrate (Sigma-Aldrich), cupper nitrate hydrate (Sigma-Aldrich), cobalt nitrate hexahydrate (Sigma-Aldrich), 3,5-Dicarboxyphenylboronic acid (Combi-Blocks, 98%) and 3,5-Dicarboxyphenylboronic acid, pinacol ester (Combi-Blocks, 96%), N,N-dimethylformamide, DMF (Sigma-Aldrich), N,N-Diethylformamide, DEF (TCI, > 99.0%), ethanol (Sigma-Aldrich, 92%),

Deionized water (Sigma-Aldrich), triethylamine (Sigma-Aldrich) were used to synthesize the MOFs.

2.2.2 Synthesis of Zn-, Cu- and Co-based 3,5 DCPBC MOF

To test the influence of the metal salts and solvents to synthesis of the MOFs, the three kinds of metal salts, 0.5 mmol of zinc nitrate hexahydrate ($\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) and Copper (II) nitrate hydrate ($\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$) and cobalt nitrate hexahydrate ($\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$) were fully dissolved into different solvents like DMF, DEF, ethanol and deionized water. Then added the Ligands, 3,5, DCPBC and 3,5, DCPBC, PE into the mixture. After that the resulting mixtures were transferred into 45mL Teflon-lined stainless steel reactors and heated under the temperatures of 100°C, 120°C and 150 for 72 hours. After cooling down to room temperature, the generated solids are filtered and dried. Triethylamine was also added after ligands were dissolved in DMF to test the effects of alkaline in increasing the deprotonation of ligands (Manos, 2012).

Sample #	Metal salts/0.5mmol	Ligands/0.5mmol	Solvent/30mL	Temperature	TEA
1	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DMF	100°C	-
2	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DMF	100°C	-
3	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DEF	100°C	-
4	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DEF	100°C	-
5	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	ethanol	100°C	-
6	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	ethanol	100°C	-
7	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	water	100°C	-
8	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	water	100°C	-
9	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC	DMF	100°C	-
10	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC,PE	DMF	100°C	-
11	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC	DEF	100°C	-
12	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC,PE	DEF	100°C	-
13	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC	ethanol	100°C	-

14	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC,PE	ethanol	100□	-
15	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC	water	100□	-
16	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC,PE	water	100□	-
17	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DMF	100□	-
18	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DMF	100□	-
19	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DEF	100□	-
20	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DEF	100□	-
21	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	ethanol	100□	-
22	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	ethanol	100□	-
23	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	water	100□	-
24	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	water	100□	-
25	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DMF	120□	-
26	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DMF	120□	-
27	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DEF	120□	-
28	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DEF	120□	-
29	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	ethanol	120□	-
30	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	ethanol	120□	-
31	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	water	120□	-
32	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	water	120□	-
33	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC	DMF	120□	-
34	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC,PE	DMF	120□	-
35	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC	DEF	120□	-
36	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC,PE	DEF	120□	-
37	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC	ethanol	120□	-
38	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC,PE	ethanol	120□	-
39	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC	water	120□	-
40	$\text{Cu}(\text{NO}_3)_2 \cdot x\text{H}_2\text{O}$	35DCPBC,PE	water	120□	-
41	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DMF	120□	-
42	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DMF	120□	-
43	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DEF	120□	-
44	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DEF	120□	-
45	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	ethanol	120□	-
46	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	ethanol	120□	-
47	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	water	120□	-
48	$\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	water	120□	-
49	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC	DMF	120□	-
50	$\text{Zn}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$	35DCPBC,PE	DMF	150□	-

51	Zn(NO ₃) ₂ •6H ₂ O	35DCPBC	DEF	150□	-
52	Zn(NO ₃) ₂ •6H ₂ O	35DCPBC,PE	DEF	150□	-
53	Zn(NO ₃) ₂ •6H ₂ O	35DCPBC	ethanol	150□	-
54	Zn(NO ₃) ₂ •6H ₂ O	35DCPBC,PE	ethanol	150□	-
55	Zn(NO ₃) ₂ •6H ₂ O	35DCPBC	water	150□	-
56	Zn(NO ₃) ₂ •6H ₂ O	35DCPBC,PE	water	150□	-
57	Cu(NO ₃) ₂ •xH ₂ O	35DCPBC	DMF	150□	-
58	Cu(NO ₃) ₂ •xH ₂ O	35DCPBC,PE	DMF	150□	-
59	Cu(NO ₃) ₂ •xH ₂ O	35DCPBC	DEF	150□	-
60	Cu(NO ₃) ₂ •xH ₂ O	35DCPBC,PE	DEF	150□	-
61	Cu(NO ₃) ₂ •xH ₂ O	35DCPBC	ethanol	150□	-
62	Cu(NO ₃) ₂ •xH ₂ O	35DCPBC,PE	ethanol	150□	-
63	Cu(NO ₃) ₂ •xH ₂ O	35DCPBC	water	150□	-
64	Cu(NO ₃) ₂ •xH ₂ O	35DCPBC,PE	water	150□	-
65	Co(NO ₃) ₂ •6H ₂ O	35DCPBC	DMF	150□	-
66	Co(NO ₃) ₂ •6H ₂ O	35DCPBC,PE	DMF	150□	-
67	Co(NO ₃) ₂ •6H ₂ O	35DCPBC	DEF	150□	-
68	Co(NO ₃) ₂ •6H ₂ O	35DCPBC,PE	DEF	150□	-
69	Co(NO ₃) ₂ •6H ₂ O	35DCPBC	ethanol	150□	-
70	Co(NO ₃) ₂ •6H ₂ O	35DCPBC,PE	ethanol	150□	-
71	Co(NO ₃) ₂ •6H ₂ O	35DCPBC	water	150□	-
72	Co(NO ₃) ₂ •6H ₂ O	35DCPBC,PE	water	150□	-
73	Co(NO ₃) ₂ •6H ₂ O	35DCPBC	DMF	150□	50μ L
74	Co(NO ₃) ₂ •6H ₂ O	35DCPBC	DMF	150□	100μ L
75	Co(NO ₃) ₂ •6H ₂ O	35DCPBC	DMF	150□	150μ L

Table 2.2.2 Selected MOF react conditions

2.2.3 Characterization

Powder X-ray diffraction analyses of all the samples were performed to characterize the crystalline phases by using (Panalytical X' Pert Pro) with Pixcel detector using Ni-K α radiation ($\lambda=1.5406 \text{ \AA}$). Textural properties of the samples were characterized. The BET specific surface area and cumulative pore volume were measured by TriStar II 3020

analyzer (Micromeritics) BET using Barret-Joyner-Halenda (BJH) model while the average pore diameter for the samples were calculated by density functional theory (DFT) method using the ASAP 2020 analyzer's built-in software. Before the measurement, the samples were soaked in acetone and new acetone was exchanged every 24 hours for 3 times and then the sample activation was carried out under evacuation at 150°C for 12 hours.

2.3 Results and discussion

From sample #75, purple crystals in colorless solution which was synthesized from adding $\text{Co}(\text{NO}_3)_2 \cdot 6\text{H}_2\text{O}$ and 3,5, DCPBC and triethylamine in DMF were obtained.

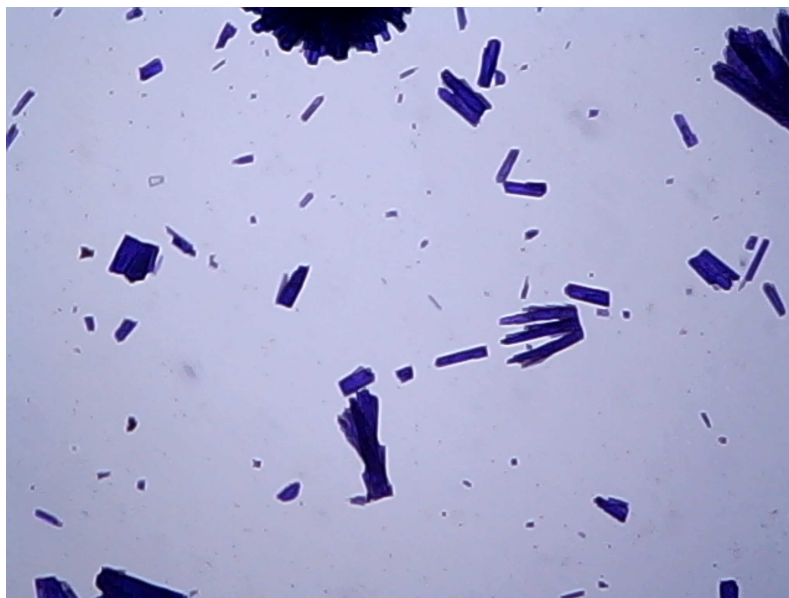


Figure 2.3-1: Optical microscope image of sample #73

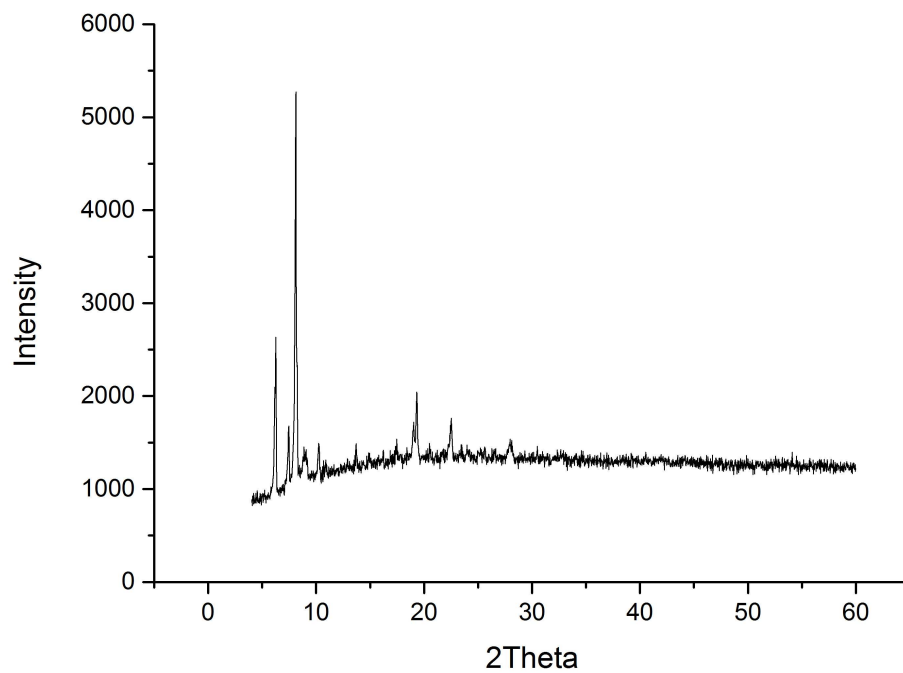


Figure 2.3-2 powder XRD patterns of Co-based crystals sample #73 as synthesized.

The powder XRD characterization shows that the crystals structures exist in the sample, but the background value indicate the exist of impurities.

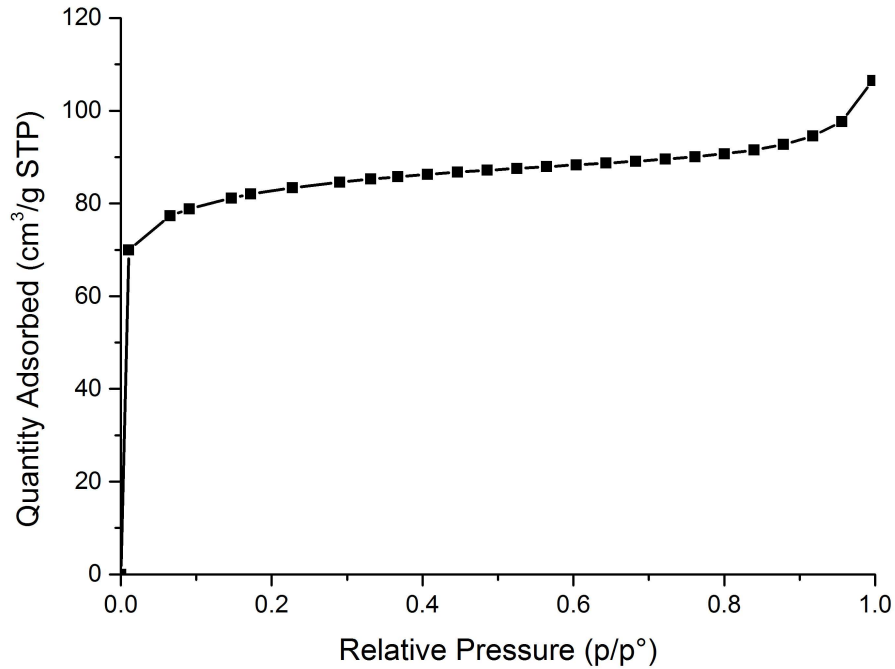


Figure 2.3-3 N₂ adsorption isotherms of sample #73.

From the N₂ adsorption isotherms curve it can be know the crystal is microporous material. The BET surface area of the sample is 313.9m²/g; the Langmuir surface area is 393.16m²/g; the pore volume is 0.0452cm³/g and the average pore size is 27.593Å. The result shows the sample has the characters of porous materials.

Large amounts of needle-shaped crystals were obtained in sample #55 and #63 were also obtained.

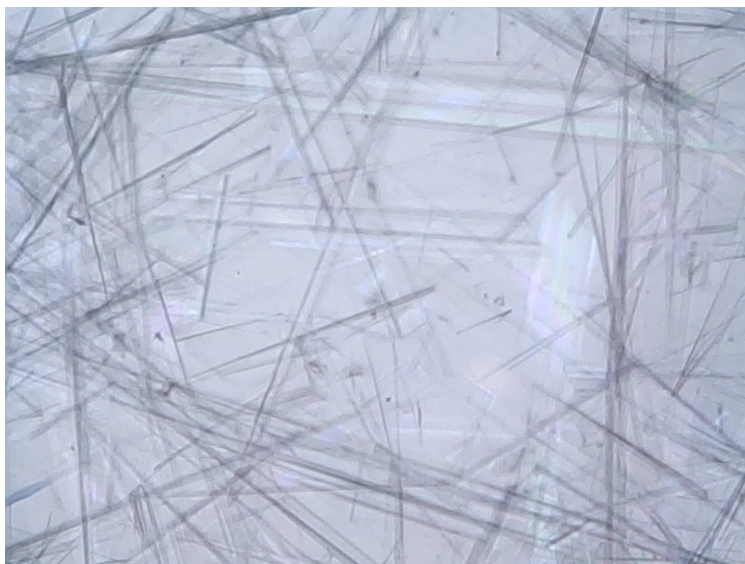


Figure 2.3-4 Optical microscope image of sample #55.

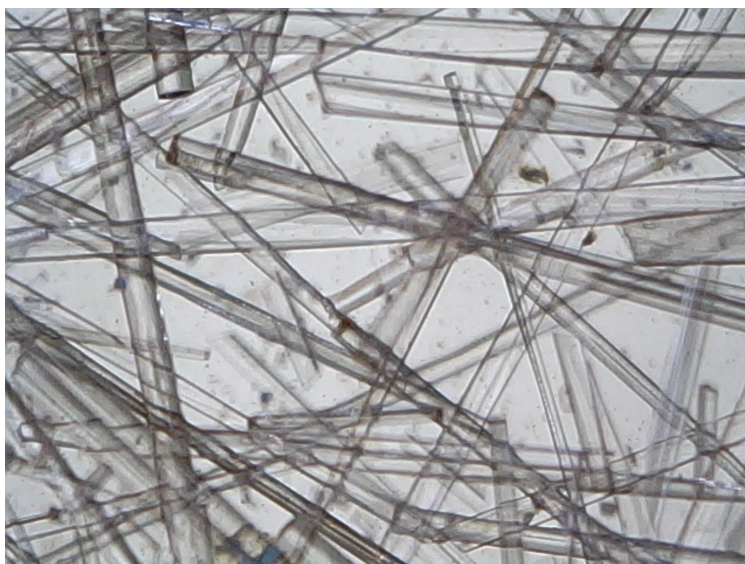


Figure 2.3-5 Optical microscope image of sample #63.

For the needle-shaped crystal obtained from synthesis of sample #55 and #63. The Figure2.4-1 shows the crystals are same and the samples are highly pure crystals.

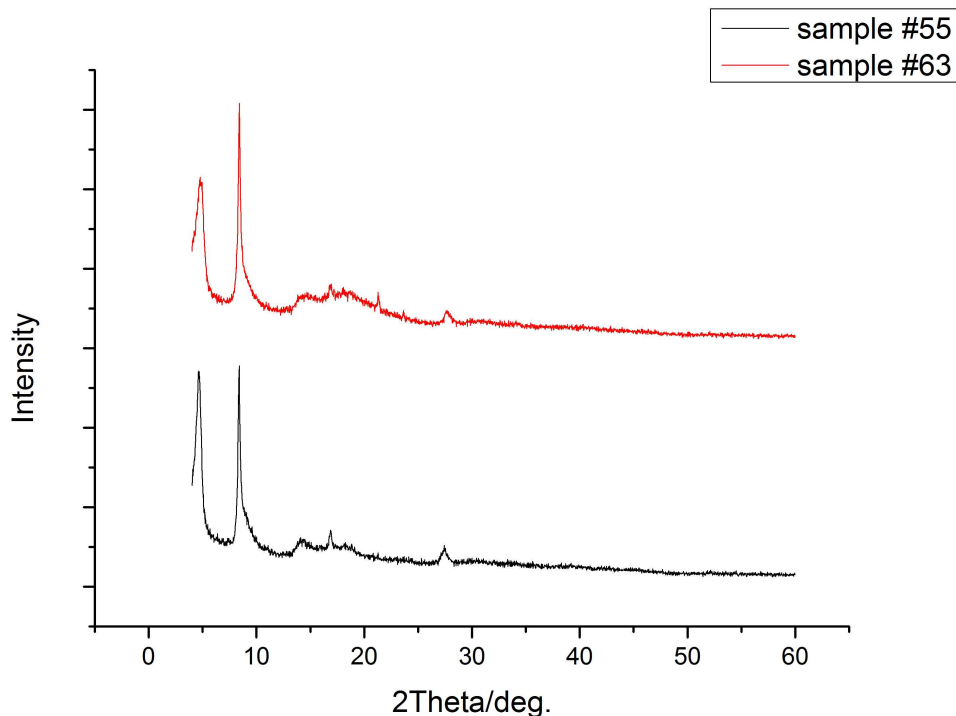


Figure 2.3-6 powder XRD patterns of sample #55 and #63 needle-shaped crystals

Single-crystal-XRD characterizations of the samples were carried out. The results of the characterization sent back showed that the crystal was not MOF but the crystal of isophthalic acid (IPA) because the unit cell size was too small. From the result it can be concluded that the benzoic-acid functional groups would fall off from 3,5, DCPBC when heated in deionized water as solvent with the possibility that the Zn can Cu ions catalyzed the process of decomposition of the ligands.

Compared sample #73 with sample #65, the reason that the crystals were obtained it's possible the triethylamine accelerated the deprotonation process of the ligands before they react with the metal salts.

For the synthesis under the other react conditions we tried, no samples has the appearance of crystals and rest of the samples are amorphous solids and the samples are not crystals tested by powder x-ray diffraction (powder XRD) characterization. The influence of temperature to the MOFs in the range of 100~150°C is not obvious. There are no obvious differences between the samples synthesized from using 3,5, DCPBC and 3,5, DCPBC, PE under the same situation.

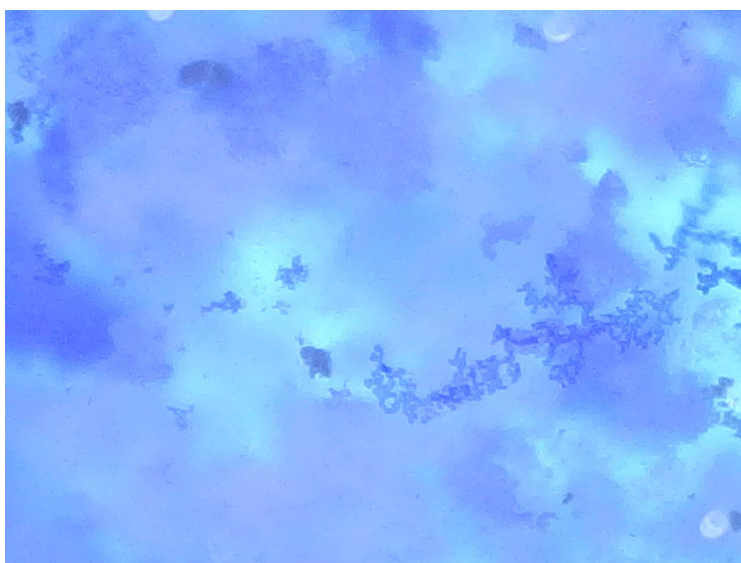


Figure 2.3-7 Optical microscope image of sample #65.

CHAPTER 3

CONCLUSION AND FUTURE WORK

The microporous Co-based 3,5, DCPBC MOF crystals were obtained through solvothermal route. From the characterizations of the Co-based MOF, we can know the sample contained impurities. The synthesis conditions will be tuned to get the MOFs with higher crystallinity. The activation will be optimized to improve the surface area of the MOF. The strategy of adding triethylamine to accelerate the process of deprotonation will be used to try to synthesis MOFs based on 3,5, DCPBC,PE and other metal salts.

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