Layered Metal-Organic Frameworks for Carbon Dioxide Capture Applications

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1.0 ABSTRACT

As the culprit of global warming, the emission of carbon dioxide has gradually become one of the most severe and environmental concerns haunting the human beings for several decades. These emissions are mainly generated from the combustion of fossil fuels - the main energy resources for our daily life, economic growth and industrial development (Chen, Kim, & Ahn, 2012). In order to prevent global warming deteriorating, it is urgent for all humankind to seek effective and feasible methods to capture and store carbon dioxide. Undoubtedly, Porous solid materials such as metal-organic frameworks (MOFs) are very promising candidates for this application due to their extraordinary capability of capturing Carbon dioxide and excellent regenerative ability as compared to other materials. The study is to explore the feasibility of method to synthesize layered MOFs by introducing new organic linkers into amorphous state precursors.

Recently, metal-organic frameworks (MOFs) composed of metal ions and organic linkers to form various dimensional structure, emerge as the cost-effective materials for carbon dioxide capture and separation. Due to the desirable pore property like high surface area, excellent uniformity and tunable pore size, the MOFs attract a great deal of researchers fixating on solving carbon dioxide issue. On the one hand, by replacing the original organic linkers with the specific organic linkers, the MOFs’ properties can be modified to make the particular application in the certain field. On the other hand, the
selection of multiple metal ions such as some transition metals also make the configurations of MOFs diverse.

The purpose of study is to search for feasible and cost-reducing process to form new metal-organic frameworks (MOFs) by hypothetically introducing new organic linkers such as BPBDC (Biphely-4,4’-Dibenzoic acid), BDC (Terephthalic acid), DABCO (1,4-diazabicyclo[2.2.2]octane) into the amorphous state of original metal-organic frameworks. Meanwhile, by altering the reaction conditions (reaction time, reaction temperature, polarity of solvent, sample preservation state, air condition, the amount of organic linkers), the crystallinity and morphology of new layered MOFs can be optimized in the study.
2.0 INTRODUCTION

Since the time of the industrial revolution, the atmospheric CO$_2$ concentration has risen by nearly 35% to its current level of 383 ppm (Wang, Zhang, & Zhou, 2011). It is widely accepted that the rising CO$_2$ Concentration is one of the significant triggers of the global warming. To prevent the issue from getting worse, research needs to be done to reduce the anthropogenic CO$_2$ emissions. As the main emission point sources, fossil-fuel-based power generation facilities are making attempts to decrease the emission of CO$_2$ effectively. In order to feasibly capture and store carbon dioxide, there is a need for human beings to seek the promising materials with extraordinary properties such as fast adsorption and desorption kinetics, satisfying adsorption capacity, infinite regenerability and stability.

Typically speaking, the amine scrubbing such as the alkanolamines DEA (Diethanolamine), MEA (Ethanolamine), and MDEA (Methyl diethanolamine) (Shi et al., 2014) is predominantly utilized to capture carbon dioxide in industry because of the economic expense and commercial availability (Veltman, Singh, & Hertwich, 2010). Nevertheless, when it comes to the future direction of reducing carbon dioxide, the drawbacks of amine should be taken into consideration such as high energy consumption and environmental problems. For example, the toxicity of MEA increased 10-fold as the scrubber on fresh water system than before being used as the scrubber (Liang, Fu, Idem, & Tontiwichwuthikul, 2016).

Therefore, solid carbon dioxide adsorbents, including zeolites, activated carbons, calcium oxides, hydrotalcites, organic–inorganic hybrids, and metal-organic frameworks come into researchers’ view. Especially, during this decade, tons of studies specializing
in metal-organic frameworks (MOFs) propel metal-organic frameworks (MOFs) to become the most promising candidate to capture carbon dioxide. The study fixates on characterization and synthesis of new layered metal-organic frameworks (MOFs), which new organic linkers get introduced into by the hypothetical method - heating up the precursors and then introducing the organic linkers into amorphous state precursors. At the same time, countless attempts are made to optimize the crystallinity and morphology of the new layered MOFs.
3.0 CRITICAL LITERATURE REVIEW

3.1 Current CO₂ Capture Method

With the global warming issue deteriorating, the exploration of the feasible and effective way to capture carbon dioxide is gradually becoming a hot topic. As is known to all, Monoethanol amine (MEA) - a primary amine, has been mainly utilized since the 1960s in the coal- or natural gas - fired power plant. It is tipped as a state-of-the-art process (Conway et al., 2015). However, lots of drawbacks of amine are apparent in capturing carbon dioxide. First and foremost, the reclaiming of absorbents is a critical part of determining their value in the actual application. Obviously, although it has rapid reaction kinetics with CO₂, more energy is required to break the strong bond of N-C to regenerate it. In other words, the high reclaiming cost makes it imperative to find better absorbents to replace Monoethanol amine (MEA) (Iida & Sato, 2012). Also, due to the presence of CO₂, SOₓ and NOₓ species in the post-combustion gas, the degradation of MEA is inevitable and results in the amine loss (Biswas et al., 2016). On the other hand, Monoethanol amine (MEA) after capturing CO₂ will degrade into other acids which will be responsible for iron corrosion (it is why we can’t use the pure amine to capture carbon dioxide), and oxidation degradation of MEA will enhance the maintenance fees of the total carbon dioxide capturing system as well (Chi & Rochelle, 2002). Accordingly, Porous solid adsorbents can be the promising materials to replace amine solvent to capture carbon dioxide.

Due to the degradation and corrosion issues, solids loaded with amines and polyamines supports have been regarded as an alternative to aqueous solutions (Goff & Rochelle, 2004). Current research about it focuses on dry adsorption systems using dry
adsorbents. A wide range of solid physical adsorbents have been taken into consideration for CO₂ capture including microporous and mesoporous materials (carbon-based sorbents such as activated carbon and carbon molecular sieves, zeolites, metal oxides and Metal-organic frameworks) (Goeppert et al., 2011). However, despite the fact that low production cost and large micropores/mesopores make the zeolite excel in certain regards (Alessandro, Smit, & Long, 2010), the poor performance of CO₂ adsorption in water renders it mediocre on account of the instability in humid condition. At the same time, Activated carbon with better adsorption capability under moisture condition, obtains several doubts due to the limitation of surface chemistry (Ramasubramanian, Severance, Dutta, & Ho, 2015). When it comes to Metal oxides-based adsorbents, the stark comparison between them and MOFs make them pale in the aspect of regeneration cost (Shafeeyan, Mohd, Wan, Houshmand, & Shamiri, 2010). Thereby, the extraordinary properties of metal-organic frameworks turn them into the hot topic in the world.

3.2 Metal-Organic Frameworks

Metal–organic frameworks (MOFs) are a new class of microporous and mesoporous materials that catch plenty of researchers’ eyeballs because of their extremely large surface areas, good CO₂ capture capacity and adjustable chemical functionality (Article & Article, 2011). These materials are synthesized by the self-assembly of metal nodes and organic linkers. In contrast to more common adsorbents, such as activated carbon or zeolites, the structure tunability of MOFs makes applications versatile (Sumida et al., 2012). Especially, on account of the extraordinary properties, zinc – based MOFs are widely investigated. Porous metal–organic frameworks (MOFs), also known as porous coordination polymers, have been one of the fastest developing
fields in the industry during the past decade (Lismont, Dreesen, & Wuttke, 2017). Figure 1 is typical structure of MOFs.

Figure 1. The Structure of Metal-Organic Frameworks (Red Balls are Metal Ions and Blue Bars are Organic Linkers)

As the designer of the metal-organic frameworks, Yaghi took the lead in synthesizing first MOF, called MOF-5, which consists of tetranuclear super-tetrahedral clusters linked by BDC (Terephthalic acid) into an octahedral arrangement. In the MOF-5 structure, the DMF guest molecules replace the original CH$_2$Cl$_2$ molecules to form MOF-5 structure. Subsequently, by selecting a variety of metal ions and ligand linkers, a series of metal organic linkers are synthesized under hydrothermal and solvothermal condition. Generally speaking, metal-organic frameworks (MOFs) consist of metal ions and clusters coordinated to organic ligands to form one-, two-, three- dimension structure (Ma & Zhou, 2010).
Figure 2. The Mechanism of Introduction Organic Linkers into Amorphous State Precursors to Form New Layered MOFs (Blue Balls are Metal Ions, Black Bars are Remaining Organic Linkers, Red Bars are Removed Organic Linkers, Green Bars are New Organic Linkers)

High porosity, large surface areas, high pore diffusion rate, good thermal stability and diverse structure tunability propel MOFs to be promising materials to capture carbon dioxide. The measured Brunauer-Emmett-Taylor (BET) surface areas of metal-organic frameworks (MOFs) range from 10 to 3000 m²/g (Choi, Drese, & Jones, 2009). However, the current method of synthesizing metal-organic frameworks (MOFs) is mainly confined to direct synthesis and can’t cater to the requirement of low cost and high rate of synthesis. Furthermore, some metal-organic frameworks (MOFs) with excellent properties can not be synthesized directly, which is the reason why our group fixates on the method of introduction of new organic linker to form the new layered metal-organic frameworks (MOFs).

The reaction temperature, solvent composition, reagent concentrations and ratios, reaction time, and agitation conditions make lots of impacts on the process of forming metal-organic frameworks (MOFs). Similarly, these factors will influence the forming of the new layered metal-organic frameworks. What’s more, some by-products and impurity should be taken into consideration. For example, the reaction temperature will greatly influence crystal nucleation and coordination of metal sites. The reaction rate will play a critical role in determining placement of the ligands in the structure. The air condition will be essential to successfully introduce the new organic linkers rather than other things into the amorphous layers. The acidity or basicity of the selected metal will influence the interaction between Metal ion and ligand, and further affect the final structure of the new layered metal-organic frameworks (MOFs) (Meek, Greathouse, & Allendorf, 2011).
This new layered metal-organic frameworks (MOFs) makes it possible to modify the drawbacks of original metal-organic frameworks (MOFs), and the method of synthesizing the new layered metal-organic frameworks (MOFs) can be effective way to form some metal-organic frameworks (MOFs) which can’t be generated directly. In addition, by impregnating the amine into MOFs in the future, the ability of the new layered metal-organic frameworks (MOFs) to capture CO$_2$ can increases dramatically (Li, Chung, & Snurr, 2016).
4.0 EXPERIMENTAL

4.1 Synthesis of Metal–Organic Framework Precursor

The solvothermal synthesis of metal-organic framework precursor $[\text{Mg}_3(\text{bdc})_3(\text{DMF})_4]_n$ is on the basis of previously reported procedures, which are modified accordingly (Koteswara Rao, Zeller, & Lovelace-Cameron, 2012).

Mg(NO$_3$)$_2$.6H$_2$O (0.557g, 0.00187mol, Fisher Scientific) and Terephthalic acid (0.363g, 0.00218mol, Fisher Scientific) are added to big glass vessel (250ml). Then, all the reagents were dissolved in dimethylformamide (DMF) (44 mL, Fisher Scientific) with stirring bars. The solution was allowed to stir for half an hour to ensure complete mixing at room temperature in the air. Afterward, the reactor was placed in the oven with the controlled temperature at 110°C for one day. After the reaction was complete, the glass reactor was removed from the oven and allowed to cool it down to room temperature for the sake of safety. Finally, the vial will be utilized to preserve the samples in DMF.

4.2 Conditions of Synthesizing Amorphous State

The method to synthesize the amorphous state Mg(bdc) is based on the previously reported procedures modified accordingly (Davies, Less, Lickiss, & White, 2007). First and foremost, the $[\text{Mg}_3(\text{bdc})_3(\text{DMF})_4]_n$ got poured into the conical flask. Then by utilizing the self-assembled apparatus with the constant flow of nitrogen, the impurity factors contaminating the amorphous state Mg(bdc) in the air was eliminated, which is why the nitrogen condition was created. After checking gas tightness, the sample was divided into several parts which will be separately heated up for various time at 200°C to figure out the best heating time. Then under this optimal heating time, the original sample
[Mg₃(bdc)₃(DMF)₄]ₙ got rid of the DMF (boiling point at 152 to 154 °C) between multiple layers and turned into the amorphous state. This was confirmed by Powder X-ray diffraction analysis.

4.3 Procedures of New Organic Linkers Introduction

4.3.1 Various Organic Linkers

The metal-organic framework precursor [Mg₃(bdc)₃(DMF)₄]ₙ which is composed of countless 2D layers stacking up, was obtained as a product of the solvothermal reaction (Koteswara Rao et al., 2012). The asymmetric unit consists of three Mg cations, three terephthalate anions, and four coordinating DMF molecules. One of the four DMF molecules is refined as disordered over two mutually exclusive positions. The three Mg cations possess distorted octahedral coordination geometries that form linear Mg trimers. Among the three Mg cations, the central Mg is octahedrally coordinated by six different carboxylate O atoms. The terminal Mg cations are bonded to four O atoms of three bdc linkers and form the electrostatic interaction with DMF molecules. Accordingly, several organic linkers were taken into consideration for successfully introducing them into amorphous state Mg(bdc). BPBDC(Biphely-4,4’-Dibenoic acid), BDC(Terephthalic acid) and DABCO(1,4-diazabicyclo[2.2.2]octane) stand out of all candidates with their excellent properties to form the similar structure. The oxygens on the carboxyl group of BPBDC and BPBDC or the nitrogen of DABCO share a lone pair with terminal Mg of Mg(bdc) to form covalent bonds thus favouring the formation of highly-ordered, thermodynamically driven MOF structures. Hopefully, in the process of introducing new organic linkers, two terminate Mg will form same structure as the center Mg, which means they will be bonded to 6 different oxygen atoms of terephalic acid.
4.3.2 Reaction Time

In order to figure out the impact of reaction time on the process of introduction of new organic linkers, a series of experiments were conducted with various reaction times under same other reaction conditions in the flask. Shortly after finishing the heating part, the amorphous state Mg(bdc) were separated into 2 parts in 2 same flasks. Then same amount of organic linkers dissolved into solvent were separately added into the 2 flasks. To figure out the optimal reaction time, the reaction time for the first sample was set for 1 day, and the second one was set for 2 days. After finishing synthesizing the new layered MOFs, vials were respectively filtered with a Buchner funnel while samples were rinsed by solvent for dissolving organic linkers. Finally, the samples were left to dry in the air with aluminum foil covering.

4.3.3 Reaction Temperature

Regarding the previous literature for introducing the organic linker into the layers, Immediate soaking Mg(bdc) in the solvent with organic linkers will result in the generation of new layered metal-organic frameworks (MOFs), because amorphous state Mg(bdc) is highly hygroscopic and quickly forms \([\text{Mg(bdc)(H}_2\text{O)}_2]_n\) on exposure to moist air. However, there is no way to find details about temperature the author set for synthesizing the desired sample. Accordingly, the exploring for the optimal temperature of the introduction process is indispensable in order to get the best crystallinity and micro-structure of the desired new layered metal-organic frameworks (MOFs). A series of experiments were conducted to figure out the appropriate temperature to synthesize the new layered metal-organic frameworks (MOFs). In the experiments, the four amorphous state Mg(bdc) were prepared by following the same procedures as above in four vials.
Then room temperature, 60°C, 110°C and 200°C were set as the reaction temperature for the four amorphous state Mg(bdc), which were mixed with organic linkers in solvent. After finishing synthesizing the new layered MOFs, vials were respectively filtered with a Buchner funnel and flask while samples were rinsed by solvent for dissolving organic linkers. Finally, the samples were left to dry in the air with aluminum foil covering.

4.3.4 Diverse Solvent

Because the essence of the whole introduction process is the solubility of a new organic linker in the solvent, there is a need to figure out the effect of polarity of solvent on organic linkers introduction, because the non-polar solvent should be a better solvent for non-polar chemicals. Accordingly. Toluene with non-polarity and DMF with polarity stand out of other candidates. On the other hand, one way to figure out the effect of solvent is to conduct parallel experiments to make a comparison between the resulted samples with different solvents after procuring their XRD graphs. Initially, shortly after getting amorphous state Mg(bdc), Organic linkers dissolving into DMF were poured into the vessels where amorphous state Mg(bdc) was. Under nitrogen condition at room temperature, the whole process took optimal reaction time to complete. Afterward, the vials were respectively filtered with a Buchner funnel and flask while samples were rinsed by correspondent solvent. Finally, the sample was left to dry in the air with aluminum foil covering in order to do XRD scanning for them later. Then, by following same steps and replacing DMF with Toluene to finish the parallel experiment under identical reaction condition, the influence of polarity of solvent on the introduction process was figured out after obtaining the XRD graphs of resulted samples in different solvent.
4.3.5 Diverse Amount of Organic Linkers

As is known to all, the reaction rate will play a critical role in determining placement of the ligands in the structure. So various amount of organic linkers are considered to synthesize the desired new layered MOFs. For example, 0.1 g, 0.5g and 1g BPBDC in certain solvent were separately added into three amorphous state Mg(bdc) in three flasks to form \([\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n\). After certain reaction time at the optimal reaction temperature, samples with various amount of organic linkers were collected by following the same steps as before. Ultimately, the influence of amount of organic linkers was found out by comparing their XRD patterns with each other. As for \([\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n\), the similar steps were taken to synthesize it to figure out the impact of amount of organic linkers on the synthesis of \([\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n\).

4.4 Characterization

4.4.1 X-ray Diffraction

X-ray Diffraction is a well-known analytical technique that utilizes samples’ atomic arrangement to investigate the crystal structure of samples by scanning samples in different angles. The material in the study is struck by x-rays, then the other wave will shot out on the other side. The incoming beam prompts each scatters to re-radiate a small portion of its intensity as a spherical wave at pre-set angle. On account of the extra length the second wave traverses, constructive and destructive interferences will appear in the graphs. If the crest of first wave meets the second wave’s crest at same point, the constructive phase will appear. This is the reason why high-intensity peaks show up in the XRD patterns. On the other hand, if the rays of the same wavelength are in different phases, the destructive phase will occur, and the flat regions will appear on the XRD patterns as well. By utilizing
Bragg’s law (Eqn. 1), the distance between two parallel planes can be known, which can be used to probe the crystallinity of samples (Dutrow, 1912).

\[ n\lambda = 2d_{hk\ell}\sin\theta \]  \hspace{1cm} \text{(Eqn. 1)}

Where:
- \( n \) = number of reflections
- \( d_{hk\ell} \) = distance between two parallel planes

In this study, the instrument was a Rigaku Ultima IV X-RAY diffractometer using Cu Kα radiation. The data were collected over the range of 5-45° with a step size of 0.1 degree per second.

In this study, the analysis is conducted at Northeastern University.

4.4.2 Brunauer-Emmett-Teller (BET) Surface Area Analysis and Barrett-Joyner-Halenda (BJH) Pore Size and Volume Analysis

BET analysis is an effective technique to evaluate surface area of materials by nitrogen monolayer adsorption measured as a function of relative pressure. The technique includes external area and pore area evaluations to measure the total specific surface area in m\(^2\)/g.

BJH analysis is the other way to figure out pore area and specific pore volume by using Nitrogen multilayer adsorption and desorption curve.

The pores’ shape is imagined as cylinder, so the total pore volume is \( 1/4\pi d^2 l \), where \( d \) is the mean pore diameter and \( l \) is the total length of the pores. If BET surface area \( S(\text{BET}) = \pi d l \). From the two equations, \( l \) can be eliminated and the average diameter \( d \) can thus be calculated. It’s the way the certain pore size is calculated.

In this study, the analysis is conducted at Northeastern University.
5.0 RESULTS AND DISCUSSION

5.1 Synthesis of Metal-Organic Framework

It has been reported in literature that the \([\text{Mg}_3\text{(bdc)}_3\text{(DMF)}_4]_n\) can be hydrothermally synthesized at 110°C for one day. The XRD graphs of \([\text{Mg}_3\text{(bdc)}_3\text{(DMF)}_4]_n\) as precursors were collected in contrast to the XRD graphs of \([\text{Mg}_3\text{(bdc)}_3\text{(DMF)}_4]_n\) in literature to ensure the precision and feasibility of the whole instruction process.

As is shown in Figure 3, all the four selected \([\text{Mg}_3\text{(bdc)}_3\text{(DMF)}_4]_n\) synthesized as precursors displayed distinctive peaks and crystallinity at 2-theta degrees of 5, 10, 15, 23 and 30, which matches the XRD patterns of \([\text{Mg}_3\text{(bdc)}_3\text{(DMF)}_4]_n\) obtained in the literature in spite of the noise peaks appearing. On the other hand, due to XRD scanning for the four selected samples conducted in the order of number, the obvious increase in intensity
of distinctive peaks and the new peak appearing around 2-theta degrees of 30 indicate that the $[\text{Mg}_3(bdc)_3(DMF)_4]_n$ is quite easy to change into water form Mg(bdc). Therefore, preservation of sample in the solvent is necessary.

Table 1. BET Analysis and BJH Analysis of $[\text{Mg}_3(bdc)_3(DMF)_4]_n$

<table>
<thead>
<tr>
<th></th>
<th>Surface area</th>
<th>Pore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Mg}_3(bdc)_3(DMF)_4]_n$</td>
<td>3.370 m²/g</td>
<td>6.070e-02 cc/g</td>
</tr>
</tbody>
</table>

Figure 4. Pore Distribution Graph of $[\text{Mg}_3(bdc)_3(DMF)_4]_n$

In accordance with Table 1 and Figure 4, the surface area, total pore volume and the pore distribution of $[\text{Mg}_3(bdc)_3(DMF)_4]_n$ are collected to figure out the structure change occurring in the transition from the precursors to new layered metal-organic frameworks.

5.2 Synthesis of Amorphous State Layers

To create the amorphous state Mg(bdc) layers and introduce the new organic linkers into them, the DMF (boiling point - 153°C) between layers of
[Mg₃(bdc)₃(DMF)₄]ₙ should be removed by heating the precursors at a certain temperature. At the same time, two heating time were utilized to optimize the method of synthesis of the amorphous state Mg(bdc).

![XRD Patterns](image)

**Figure 5.** XRD Patterns of [Mg(bdc)(H₂O)₂]ₙ, Mg(bdc) Exposed to Air, [Mg₃(bdc)₃(DMF)₄]ₙ Heated at 200°C for 1D, [Mg₃(bdc)₃(DMF)₄]ₙ Heated at 200°C for 2H, [Mg₃(bdc)₃(DMF)₄]ₙ

It is shown in Figure 5, due to the boiling point of DMF (153°C), 200°C is viewed as the optimal temperature to heat the precursors without damaging the structure of layers. Based on the disappearance of certain angles at 2-theta degrees of 6, 15 and 23, it indicates that the DMF has been removed between layers. By comparing precursors which heated up for 2 hours and 24 hours with each other respectively, it is apparent that 24 hours is the perfect time for precursors to get rid of DMF because of the relatively low intensity of distinctive peaks in Figure 5. What’s more, after exposing amorphous state Mg(bdc) to the air for 1 day, the trend of amorphous state Mg(bdc) layers turning into water form Mg(bdc) is obvious on account of the existence of angles at 2-theta degrees of 10, 15, 25, 30. Which indicates the method was successful in removing DMF as well.
5.3 Selection of New Organic Linkers

On the basis of the literature germane to the structure of \([\text{Mg}_3(\text{bdc})_3(\text{DMF})_4]_n\), the potential candidates should own the carboxyl to form coordinate covalent bond with the Magnesium. Therefore, the potential linkers get narrowed down to three organic linkers- BPBDC (Biphely-4,4’-Dibenzoic acid), BDC (Terephthalic acid), DABCO (1,4-diazabicyclo[2.2.2]octane), which can be obtained easily in our Lab. At the same time, the size of new organic linkers will determine the surface area and selective molecular sieving of new layer MOFs, which is also the reason why BPBDC, DABCO and BDC were selected as the organic linkers.

![molecule structures of BPBDC, BDC, and DABCO]

**Figure 6. Various Organic Linkers Used to Synthesize the New Layered MOFs**

In accordance with Figure 6, the molecule structure of BPBDC is similar to the molecule structure of BDC, and both of them own a pair of electrons on the carboxyl groups at both ends of the benzene rings, which propels them to form coordinate covalent bond with the Magnesium ions of the original precursors. When it comes to DABCO, the
mechanism of it bonding to terminal magnesium ion resembles to BPBDC and BDC because of the pair of electrons on the nitrogen atom.

![Figure 7](image)

**Figure 7. XRD Patterns of BPBDC, BDC and DABCO in Literature**

Based on Figure 7, by comparing the original XRD patterns of BPBDC, BDC and DABCO with new layered MOFs synthesized later on, it is a shortcut to eliminate some side-products which will influence the consequence of the whole introduction process. What’s more, it will help figure out how to preserve the original layers.

**Table 2. Physical Properties of Various Organic Linkers Used in the Introduction Process**

<table>
<thead>
<tr>
<th>Linker</th>
<th>Molecular Weight (g/mol)</th>
<th>Melting Point (°C)</th>
<th>Boiling Point (°C)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BPBDC (Biphely-4,4’-Dibenzoic acid)</td>
<td>242.23</td>
<td>300</td>
<td>482.5</td>
</tr>
</tbody>
</table>
Boiling points of each compound is listed in Table 2. As the molecules’ weights grow bigger, the boiling points gradually increase. Due to intermolecular interaction and bonding, the new organic linkers within the new layered metal–organic frameworks (MOFs) will not reserve the same boiling point as the pure compounds, but boiling points listed above are still relatively precise value to predict the boiling points of new organic linkers within the new layered metal–organic frameworks (MOFs). In addition, in the process of creating the porous MOFs, the suitable temperature to degass is critical. Most importantly, as an essential part of characterizing the surface areas and pore volume, BET and BEJ analysis will require targeted products to be further activated at a certain temperature. Accordingly, the temperature should be picked cautiously and below the organic linkers’ boiling point.

5.4 Crystal Growth and the Effect of Different Variable

5.4.1 BPBDC (Biphely-4,4’-Dibenzoic acid) as the Organic Linker

The synthesis time of new layered metal–organic frameworks (MOFs) is quite vital to determine crystallinity and micro-structure of the new layered metal–organic frameworks (MOFs). One theory is widely accepted that the crystallization process can be divided into three stages. The first stage is nucleation, the second stage is continued crystal growth, and the last stage is termination due to depletion of resources. Accordingly,
by controlling the reaction time, the optimization of crystallinity and micro-structure of the new layered metal–organic frameworks (MOFs) can be reached.

In terms of Figure 8, it is apparent that the new layered MOFs synthesized for 1D, 2D are both \([\text{Mg(bdc)}(\text{H}_2\text{O})_2]_n\). Based on the distinctive peaks at 2-theta degrees of 10, 15, 25 and 30, it is safe to say the XRD graphs of the new layered MOFs for 1D, 2D are same as the XRD graph of \([\text{Mg(bdc)}(\text{H}_2\text{O})_2]_n\). Accordingly, reaction time seems not to determine whether or not the method can be successful, and there is a possibility that reaction temperature is not suitable for synthesizing the new layered MOFs.

In terms of the reported temperature to synthesize \([\text{Mg}_3\text{(bdc)}_3(\text{DMF})_4]_n\) in the literature, the temperature to synthesize \([\text{Mg}_3\text{(bdc)}_3(\text{BPBDC})_2]_n\) for 1D and Pure BPBDC is set around 110 °C. As is known to all, the whole structure will be jeopardized if the reaction temperature is set too high due to the evaporation of composites. However, the reaction temperature can be set too low to synthesize the satisfactory products. Accordingly, to explore the suitable
temperature, room temperature, 110°C and 200°C were separately selected to be as reaction temperature to synthesize $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$.

![XRD patterns](image)

**Figure 9.** XRD patterns of Pure BPBDC, $[\text{Mg(bdc)}(\text{H}_2\text{O})_2]_n$, $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ at room temperature, $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ at 110°C, $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ at 200°C

In accordance with Figure 9, all the XRD patterns of $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ synthesized at room temperature, 110°C and 200°C resembled the XRD pattern of $[\text{Mg(bdc)}(\text{H}_2\text{O})_2]_n$, which further demonstrates that the water is way easier to enter the amorphous state Mg(bdc) than BPBDC. Thereby the concentration of the introduction method shifts to how to avoid the formation of $[\text{Mg(bdc)}(\text{H}_2\text{O})_2]_n$.

To successfully introduce BPBDC into the amorphous state Mg(bdc), the circumstance should be controlled without any water getting involved in, and the polarity of solvent should be taken into consideration. By utilizing self-designed apparatus (Figure 10), the condition without water can be created, and the reaction system got filled with Nitrogen. In addition, the solubility of BPBDC in DMF is doubtful on account of polarity of DMF. It is scientifically proved that the non-polar solvent is paramount.
solvent for non-polar Chemicals, so Toluene was chosen as solvent for the next trial and replaced the original solvent – DMF.

Figure 10. The Display of Self-assembled Apparatus

![Figure 10](image)

Figure 11. XRD Patterns of \([\text{Mg(bdc)}(\text{H}_2\text{O})_2]_n\), Pure BPBDC, \([\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n\) in Toluene under Nitrogen Condition

In accordance with Figure 11, the XRD graph of \([\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n\) in Toluene under Nitrogen condition is similar to Pure BPBDC’s XRD graph. It is doubtful that the amount of BPBDC added to Amorphous state Mg(bdc) is suitable. So there is a need to adjust the amount of BPBDC as the organic linkers. By changing the amount of
organic linkers added to amorphous state Mg(bdc), the experiment was expected to be successful.

Due to the fact that the amount of BPBDC as organic linkers seem to make difference on the process, three introduction synthesis experiments are conducted simultaneously with various amount of organic linkers – 1g, 0.5 g and 0.1g. On basis of the XRD patterns above all, the excessive BPBDC can make it impossible to obtain the real XRD pattern of \([Mg_3(bdc)_3(BPBDC)_2]_n\).

![XRD Patterns](image)

**Figure 12.** XRD Patterns of \([Mg(bdc)(H_2O)_2]_n\), Pure BPBDC, \([Mg_3(bdc)_3(BPBDC)_2]_n\) with 0.1g BPBDC, \([Mg_3(bdc)_3(BPBDC)_2]_n\) with 0.5g BPBDC, \([Mg_3(bdc)_3(BPBDC)_2]_n\) with 1g BPBDC

In Figure 12, it is apparent that the amount of BPBDC change seemed not to influence the crystallization of \([Mg_3(bdc)_3(BPBDC)_2]_n\). As for \([Mg_3(bdc)_3(BPBDC)_2]_n\) with BPBDC 0.1g in Toluene and BPBDC 0.5g in Toluene, actual products are both water form Mg(bdc). When it comes to \([Mg_3(bdc)_3(BPBDC)_2]_n\) with BPBDC 1g, the amount of BPBDC added to the amorphous state is so excessive that the XRD graph of it
is similar to Pure BPBDC. The change of amount of BPBDC as the organic linkers didn’t contribute to the successful synthesis of $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$.

**Table 3. BET Analysis of $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with 0.1g BPBDC and $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with 1g BPBDC**

<table>
<thead>
<tr>
<th></th>
<th>Surface area</th>
<th>Pore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>$[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with BPBDC 0.1g in Toluene</td>
<td>4.578 m²/g</td>
<td>1.347e-01 cc/g</td>
</tr>
<tr>
<td>$[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with BPBDC 1g in Toluene</td>
<td>7.804 m²/g</td>
<td>7.298e-02 cc/g</td>
</tr>
</tbody>
</table>

**Figure 13. Pore Distribution Graphs of $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with 0.1g BPBDC and $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with 1g BPBDC**

In terms of Figure 13, the pore distribution graph of $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with BPBDC 0.1g can reflect that the pores are mainly mesopores, of which diameters are approximately 4.4 nm. Compared with the pore distribution graph of $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with BPBDC 0.1g, the graph of the pore distribution of $[\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n$ with BPBDC 1g is a little bit different due to that it’s main pores’ diameter is 14nm though: all of the them are mesopores. However, they can be same
products because they both have three same size pores - 4.4, 10, 15 nm. On the other hand, the surface area and pore volume of both of them are almost identical, which confirms that they are the same type of products - \([\text{Mg(bdc)(H}_2\text{O)}]_n\).

5.4.2 BDC (Terephthalic acid) as the Organic Linker

Based on the structure of BPBDC (Biphely-4,4’-Dibenkoic acid)) and BDC (Terephthalic acid), only difference between them is that BPBDC (Biphely-4,4’-Dibenkoic acid) has one more benzene ring than BDC (Terephthalic acid). Accordingly, since the investigation about time, the amount of organic linkers, temperature and solvent have been done for BPBDC as organic linkers. The next step of an experiment is to figure out where water was from. Because XRD graphs of \([\text{Mg}_3(\text{bdc})_3(\text{BPBDC})_2]_n\) as the organic linkers patterns indeed resemble XRD graph of \([\text{Mg(bdc)}(\text{H}_2\text{O})]_n\), there is a need to figure out whether or not \([\text{Mg(bdc)}(\text{H}_2\text{O})]_n\) formed during the transition of product from wet form to dry form.

![Figure 14. XRD Patterns of Pure BDC, \([\text{Mg(bdc)}(\text{H}_2\text{O})]_n\), Dry \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\), Slurry \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\)](image)
As can be seen in Figure 14, there is no obvious peaks in the XRD pattern of Slurry \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\). This means Slurry \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\) is intermediate state and BDC was not successful in being introduced into layers. On the other hand, according to XRD pattern of Dry \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\), there are apparent peaks at 2-theta degrees of 5, 10, 15, 20 and 25, which means that the process of introducing organic linkers seemed successful. At the same time, the XRD graph of it is totally different from BDC’s XRD pattern. However, after comparing the XRD pattern of Dry \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\) with \([\text{Mg}(\text{bdc})(\text{H}_2\text{O})_2]_n\’s \) XRD pattern, it is clear that their XRD patterns are identical. So it can be concluded that water is more likely to be introduced into the amorphous state than BDC. In other words, the concentration of the introduction method will be put on how to overcome the problem of the presence of water. In spite of fact that there are two distinctive peaks showing up in Figure 14, their intensity are extremely low compare to the typical peaks showing up in the XRD graph of crystal. Both of them seem to identify the crystallinity of the actual product, which is the intermediate state product. In order to figure out the pores’ properties, there is a need to do the BET and BJH Analysis of \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\) with 0.1g BDC and \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\) with 1g BDC to figure out what happened.

**Table 4. BET Analysis of \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\) with 0.1g BDC and \([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n\) with 1g BDC**

<table>
<thead>
<tr>
<th></th>
<th>Surface area</th>
<th>Pore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n) with 0.1g BDC in Toluene</td>
<td>8.713 m²/g</td>
<td>7.942e-02 cc/g</td>
</tr>
<tr>
<td>([\text{Mg}_3(\text{bdc})_3(\text{BDC})_2]_n) with 1g BDC in Toluene</td>
<td>0.527 m²/g</td>
<td>9.353e-03 cc/g</td>
</tr>
</tbody>
</table>
Figure 15. Pore Distribution Graphs of $[\text{Mg}_3(bdc)_3(BDC)_2]_n$ with 0.1g BDC and $[\text{Mg}_3(bdc)_3(BDC)_2]_n$ with 1g BDC

In Figure 15, it shows the pores of $[\text{Mg}_3(bdc)_3(BDC)_2]_n$ with 0.1g BDC are predominantly mesopores with diameters about 14nm. Also, the pores of $[\text{Mg}_3(bdc)_3(BDC)_2]_n$ with 1g BDC are around 4nm in diameter which is close to the diameter standard of micropores. Furthermore, based on Table 4, with the amount of BDC increasing from 0.1g to 1g, the surface area and pore volume seem to decrease dramatically. As is known to all, the more organic linkers are added between the layers of the original precursors, the more surface areas and bigger pore volume the new layered MOFs should get. Accordingly, it indicates the condition of introduction is far from satisfactory. In addition, the original structure Mg(bdc) seemed to be destroyed during the process of introducing the new organic linkers into layers.

5.4.3 DABCO (1,4-diazabicyclo[2.2.2]octane) as the Organic Linker

Regarding all factors listed above, there is a need to figure out why $[\text{Mg}(bdc)(H_2O)_2]_n$ becomes the dominant products rather than the targeted new layered metal-organic frameworks (MOFs). Except for the factors – reaction time, reaction temperature, solvent and form of products, it is possible that the temperature seemed to
be set so high that the structure of Mg(bdc) was destroyed. The next step is to know about the suitable temperature to heat up the precursors - \([\text{Mg}_3\text{(bdc)}_3\text{(DMF)}_4]\)_n, and the temperature should be higher than 153°C to evaporate DMF. Therefore, the revised heating temperature to synthesize amorphous state was initially set at 90°C for 12 hours, then increased to 190°C for 12 hours. Hopefully, under this temperature, the original structure of precursors can be maintained while the DMF between layers can be removed effectively, and the mechanism of introducing organic linkers between layers will work for DABCO.

![Figure 16. XRD Patterns of Pure DABCO, [Mg(bdc)(H2O)2]n, [Mg3(bdc)3(DMF)4]n Heated at 200°C to Synthesize [Mg3(bdc)3(DABCO)4]n, [Mg3(bdc)3(DMF)4]n Heated at 90°C and 190°C to Synthesize [Mg3(bdc)3(DABCO)4]n](image)

As is shown in Figure 16, based on the distinctive peaks in the XRD patterns of \([\text{Mg}_3\text{(bdc)}_3\text{(DABCO)}_4]\)_n - heating temperature at 200 °C and \([\text{Mg}_3\text{(bdc)}_3\text{(DABCO)}_4]\)_n - heating temperature at 90°C and 190°C, it can be seen that their XRD patterns are same as each other, and they are all amorphous state Mg(bdc). The only difference between
them is intensity, and both of them showed the tendency to turn into water form Mg(bdc) after adjusting the heating temperature to synthesize the amorphous state Mg(bdc). Accordingly, the heating temperature should be eliminated as the factor which influences the synthesis method.

Furthermore, the reaction time seems to be another factor in determining what is synthesized under the condition. To further investigate that potential effect of reaction temperature, two different reaction temperatures were chosen to figure out the influence of reaction temperature.

The first reaction temperature should be room temperature, and the other one was at 110°C to synthesize the new layered metal-organic frameworks (MOFs). Furthermore, on account of the fact that the melting point of DABCO is around 160°C, the reaction temperature should be set below it in case the structure of new layered metal-organic frameworks (MOFs) is broken during the process.

![Figure 17. XRD Patterns of Pure DABCO, [Mg(bdc)(H2O)2]n, [Mg3(bdc)3(DABCO)4]n at 110°C and [Mg3(bdc)3(DABCO)4]n at Room Temperature](image)

As can be seen in Figure 17, it is apparent that actual products of introduction reaction at 110°C is the water form Mg(bdc) because of the characteristic peaks appearing at 2-theta degrees of 10, 15, 20, 25 and 30. Even though several peaks at 2-theta degrees of 17 and 23, they are considered as the noise peaks rather than the sign to show the successful synthesis of $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$. In addition, the room temperature is also not suitable temperature because actual product of DABCO introduction reaction at room temperature is water form Mg(bdc).

To make sure that reaction time doesn’t contribute to the successful synthesis of $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$. Various reaction times were picked separately to synthesize $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$. From the previous literature reviewed, the appropriate reaction time is usually one day or two days, which is the reason why one day and two days were chosen as the reaction time.

![XRD Patterns of Pure DABCO, [Mg(bdc)(H2O)2]n, [Mg3(bdc)3(DABCO)4]n for 1D and [Mg3(bdc)3(DABCO)4]n for 2D](image)

**Figure 18. XRD Patterns of Pure DABCO, [Mg(bdc)(H2O)2]n, [Mg3(bdc)3(DABCO)4]n for 1D and [Mg3(bdc)3(DABCO)4]n for 2D**
Based on Figure 18, there are distinctive peaks matching distinctive peaks of water form Mg(bdc) emerging in the XRD patterns of \([\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n\) synthesized for one day and \([\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n\) synthesized for two days, which means the BPBDC is not successfully introduced into the amorphous state sample. Accordingly, the reaction time doesn’t contribute to the successful synthesis of the \([\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n\).

As was discussed before, the solubility of Organic linkers in solvent probably make a great impact on the introduction process. It is scientifically proved that the Non-polar solvent like Toluene is paramount solvent for Non-polar Chemicals. Accordingly, Toluene is an optimal alternative for DMF as the solvent to introduce DABCO into amorphous state Mg(bdc).

Figure 19. XRD Patterns of Pure DABCO, \([\text{Mg}(\text{bdc})(\text{H}_2\text{O})_2]_n\), \([\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n\) in DMF, \([\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n\) in Toluene

In Figure 19, concerning \([\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n\) in Toluene, there is a clear peak at 2-theta degrees of 10, which is likely to demonstrate the successful synthesis of
new layered MOF. Nevertheless, the intensity of peak is extremely low, and only one peak emerges in the XRD graph of $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$ in Toluene. Therefore, it can indicate that the $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$ in Toluene might be an amorphous state product, and the DABCO fails to be introduced into the amorphous state Mg(bdc). And it seems that polarity of solvent won’t determine the successful synthesis of $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$.

When it comes to the final possible factor to influence the synthesis of $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$, the amount of DABCO as organic linkers should be taken into consideration. Two experiments with different amounts of DABCO as organic linkers, were conducted at the same time. For the first experiment, the amount of DABCO was 0.1g as the organic linkers to be added to the amorphous state Mg(BDC). For the second experiment, 1g BPBDC was mixed with Mg(BDC) to synthesize the $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$, which means 1g BPBDC was added to Mg(bdc) layers to synthesize $[\text{Mg}_3(\text{bdc})_3(\text{DABCO})_4]_n$. 

![Graph showing XRD data](image)
According to Figure 20, it is obvious that \([\text{Mg}_3\text{(bdc)}_3(\text{DABCO})_4]_n\) with 0.1g DABCO is an amorphous state because there are no peaks in the XRD pattern except for one peak at 2-theta degrees of 10. The possible reason why the targeted new layered MOFs is an amorphous state is that the amount of DABCO is not enough. However, as for the synthesized sample with 1g DABCO, it is clear that the XRD pattern of \([\text{Mg}_3\text{(bdc)}_3(\text{DABCO})_4]_n\) with 1g DABCO is similar to \([\text{Mg(bdc)}(\text{H}_2\text{O})_2]_n\)’s XRD pattern.

Table 5. BET Analysis of \([\text{Mg}_3\text{(bdc)}_3(\text{DABCO})_4]_n\) with 0.1g DABCO and \([\text{Mg}_3\text{(bdc)}_3(\text{DABCO})_4]_n\) with 1g DABCO

<table>
<thead>
<tr>
<th></th>
<th>Surface area</th>
<th>Pore volume</th>
</tr>
</thead>
<tbody>
<tr>
<td>([\text{Mg}_3\text{(bdc)}_3(\text{DABCO})_4]_n) with 0.1g DABCO in Toluene</td>
<td>5.986 m²/g</td>
<td>9.725E-02 cc/g</td>
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<tr>
<td>([\text{Mg}_3\text{(bdc)}_3(\text{DABCO})_4]_n) with 1g DABCO in Toluene</td>
<td>10.475 m²/g</td>
<td>6.748E-02 cc/g</td>
</tr>
</tbody>
</table>

In terms of Figure 21, the pore size distribution of \([\text{Mg}_3\text{(bdc)}_3(\text{DABCO})_4]_n\) with 0.1g DABCO and \([\text{Mg}_3\text{(bdc)}_3(\text{DABCO})_4]_n\) with 1g DABCO are almost identical to what
Figure 10 and Figure 13 showed above. This suggests that all six samples can be 
[Mg(bdc)(H₂O)₂]ₙ. The main pores size of [Mg₃(bdc)₃(DABCO)₄]ₙ with 0.1g DABCO are around 14nm, and the main pores size of [Mg₃(bdc)₃(DABCO)₄]ₙ with 1g DABCO are about 3.6nm. In addition, according to Table 5, the data of surface area and pore volume also confirm the information acquired from Figure 21. It can be seen that the surface areas of [Mg₃(bdc)₃(DABCO)₄]ₙ with 1g DABCO with mesopores is almost same as [Mg₃(bdc)₃(DABCO)₄]ₙ with 0.1g DABCO with mesopores. And the pore volume of former one is almost same as the later one. So they are same products.
6.0 CONCLUSION

In this study, countless attempts were made to introduce multiple organic linkers into the amorphous state Mg(bdc) due to the special covalent bond possibly formed between Magnesium ion and atom with a lone pair of organic linkers. Initially, to fully remove DMF between layers of $[\text{Mg}_3(\text{bdc})_3(\text{DMF})_4]_n$, various factors like reaction time and heating temperature were meticulously examined under controlled condition. Obviously, the method to create the amorphous state Mg(bdc) is quite successful, because Mg(bdc) exposed to air for several days changed into water form Mg(bdc).

On the other hand, concerning the process of seeking the potential organic linkers as new pillars introduced into the original structure, it seems that the experimental method is far from mature to introduce the organic linkers as the substitution for the original linkers. Despite the fact that many factors including reaction temperature, reaction time, air condition, solvent, the state of samples and the amount of organic linkers have been considered, the introduction of new linkers still failed because of the presence of the water. It is the top priority to seek for the appropriate conditions to introduce new organic linkers into the Mg(bdc) layers.
7.0 RECOMMENDATIONS

One of the future steps is to optimize the synthesis of amorphous state Mg(bdc). On account of the difficulty of introducing new organic linkers into layers, it is imperative to search for the most effective and feasible methods to remove all DMF between layers to introduce the new organic linkers into layers. At the same time, to maintain the original layers’ structure of Mg(bdc), more attention should be paid to perfect the method without destroying them.

On the other hand, to eliminate the interference of water, it is necessary to seek the better condition for introducing new organic linkers into layers rather than water as pillars. According to the organic linkers utilized in the reviewed literature, there is a possibility to employ Propanol and N,N-Dimethylpropanamide to replace the solids organic linkers utilized in the future study. Hopefully, the change will make a total difference, and prove the feasibility of method.

Most importantly, after successfully synthesizing the new layered MOFs, it is fairly vital to characterize the new layered metal-organic frameworks (MOFs), like analyzing the surface area and pore volume/radius of samples via BET and BJH method. If the surface area and pore volume of new layered MOFs are satisfactory, it can be promising material to capture Carbon dioxide.

All in all, by probing the physical and chemical properties of new layered metal-organic frameworks (MOFs), the applications in different fields can be achieved accordingly. On the other hand, the method might be a ground-breaking way to synthesize some other MOFs which can’t be prepared directly if it does work.
8.0 REFERENCES

https://doi.org/10.1002/anie.201000431

https://doi.org/10.1039/c1ee01116b


https://doi.org/10.1016/j.fuel.2011.10.072


https://doi.org/10.1002/cssc.200900036


Iida, K., & Sato, H. (2012). Proton Transfer Step in the Carbon Dioxide Capture by Monoethanol Amine: A Theoretical Study at the Molecular Level, 2248(3).


